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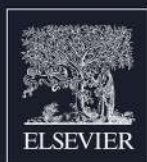
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Water in Textiles and Fashion

*Consumption, Footprint,
and Life Cycle Assessment*

Edited by Subramanian Senthilkannan Muthu



Water in Textiles and Fashion

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Consumption, Footprint,
and Life Cycle Assessment

Edited by

Subramanian Senthilkannan Muthu



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Dr. Subramanian Senthilkannan Muthu holds a PhD in textiles sustainability and has written around 65 books and 80 research publications. He is well known for his contributions in the field and has extensive academic and industrial experience. He currently heads the department of sustainability for SgT and API and is based in Hong Kong. He earned his diploma, bachelor's, and master's in textile technology from premier institutes of India. He was awarded his doctorate from The Institute of Textiles and Clothing of The Hong Kong Polytechnic University. He has a decade of working experience in the arena of sustainability in textiles and clothing. He has worked with hundreds of factories in Asia and Europe on various aspects of sustainability. He was an outstanding student throughout his studies and earned numerous awards and medals, including many gold medals during his study. He is editor, editorial board member, and reviewer for many international peer-reviewed journals on textiles and environmental science disciplines. He is one of the directors of the Textile and Bioengineering Informatics Society (TBIS), a charitable organization created to foster, develop, and promote all aspects of science and technology in the bioengineering of materials, fibers, and textiles. He is the editor-in-chief of Springer's Textiles and Clothing Sustainability Journal.

Environmental Footprints and Eco-design
of Products and Processes

Subramanian Senthilkannan Muthu
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The lotus feet of my beloved Lord
Pazhaniandavar
My beloved late Father
My beloved Mother
My beloved Wife Karpagam and
Daughters—Anu and Karthika
My beloved Brother
Everyone working in the food sector to make
it ENVIRONMENTALLY SUSTAINABLE*

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Environmental Footprints of Water— Concepts, Tools, Importance and Challenges



P. Senthil Kumar and K. Grace Pavithra

Abstract The worldwide demand for clean water makes water a vital importance in supply and efficiency in usage for the sustainable future. Rapid industrialization and economy, increases water demand mainly in the field of agriculture and industrial sector. There is vulnerability for the available quality of water due to the climate variability and raising demand. In order to predict the demand of water, footprint assessment techniques and tools are introduced in monitoring greenhouse gases and water flow across the world in last decades. This chapter provides a detail sketch of green, blue, grey water, virtual water and its global trends. The detailed review of water management in energy sectors such as, integration of waste water with water management planning, improvement in cooling systems, development and integration of decision-support tool with weather models and climate, their importance as well as future challenges are explained in detail.

Keywords Demand • Industrialization • Vulnerability • Water
Wastewater integration • Assessment tool • Footprint assessment techniques

1 Introduction

The overall fresh water availability is 2.5% and among 2.5%, 68.1% are in the form of ice, 30.1% are in the form of 30.1 and 1.2% of surface water. The fresh water availability in domestic sector is 11%, 19% in industry and finally in agriculture 70% (Bhat 2014). With reference to time and space precipitation is found to be renewable and the pathways are considered as green and blue water flows. The distribution of freshwater across the world is uneven and it is found to be essential element for humans and ecosystems. The fresh water availability for human consumption is under vulnerability due to climate, water supply and water demand and competition of freshwater resources are seen in past decades due to increase in

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population, economic growth, demand for agricultural products, industrialization and energy production. The surface water supply is associated with uncertainties with droughts and distribution of rainfall. In 2017, UN World Water Development Reported on wastewater that, the demand of water as well as the volume of wastewater produced increasing continuously. Around 80% of world's wastewater 95% are found in some developed countries which are released without treatment. The water once produced either diluted into river, lake, streams or transported to downstream. With referred to time and space precipitation is found to be renewable and the pathways are considered as green and blue water flows (Schneider 2013). Green water is considered as purest form of water and seen in the form of soil moisture, used by plants via transpiration. Surface and ground water which are stored in lakes, stream groundwater, in the form of glaciers and snow are considered as blue water (Rodrigues et al. 2014). Grey water (a product water of domestic activities and not in contact with fecal matter) and black water (sewage water flushed in the toilets) are the transformation of blue water which is in polluted form. The quantity of water utilized in food and in other products are referred as virtual water. Due to change in climate, limited water supply and demand, fresh water availability for human consumption is under threat. The uncertainty followed in spatio-temporal distribution of rainfall as well as multi-year droughts makes complications in the surface water supply. In future, due to impact of socioeconomic and drought there will be complexity in freshwater availability. There is continuation in the demand for water due to population growth, industrialization, agriculture, domestic use etc. (Vorosmarty et al. 2010; Srinivasan et al. 2013). It is expected that by 2025 around 1.8 billion people will witness water scarcity (WWAP 2012; WWDR 2015) and the percentage of water consumption for energy and agriculture production will increase by 2035 (IEA 2011). In order to attain sustainable management, water availability and its vulnerability in a changing environment are to be quantified.

This chapter provides detailed discussion about the water footprint and its components with its usage in primary sectors. Water footprint in terms of environmental sustainability were discussed. The water footprint general process steps in various primary sectors like, agriculture and forestry, wastewater treatment plants, some of the manufacturing industries like, textile, paper, food and beverages were included and finally the chapter has been concluded with establishment of WF benchmarks and challenges faced with the incorporation of water footprint in primary sectors.

Water Footprint-Introduction

The water footprint is a measure of humanity's abduction of fresh water in volumes either consumed or polluted. In other terms it can be represented as the amount of water utilized for each services and goods we use. From single process like growing of rice, multi-national company to a particular country from an aquifer or river basin. Water footprints answers the questions for companies, governments and individuals regarding water dependence in company's operation, water resources regular protection, security of food or energy supplies etc. (McKinsey 2009).

The Water Footprint Concept

Freshwater is one of the most valuable assets and it is becoming progressively rare. There is a need to evaluate how much of freshwater is accessible what's more, its human appointment over a specific period. The water footprint communicates the human assignment of freshwater in volume. The comparison of human's water footprint with freshwater availability is considered to be part of water footprint sustainability assessment. Today, one out of 10 individuals on the earth not have clean water for accessing and one in each three individuals don't have access to water for sanitary purposes. Water table level is diminishing at a speedier rate than it can be renewed (Strauss 2016). The water resources are over exploited due to human activities. In environmental agendas of nations, companies, decision makers and the public as well as across the media, the water scarcity has become an important issue. There is a need to conserve our water resources and protect our ecosystem by reducing water footprints (Ercin et al. 2012). The concept of water footprint was introduced in 2002 by Arjen Y. Hoekstra for measuring the used water. A water footprint refers to the amount of freshwater used directly as well as indirectly by an individual, community or country for a period of time can be represented in scientific term as water footprint. It is a product of fresh water volume used to produce a product, which is measured throughout the supply chain. It is referred as multidimensional indicator, showing water consumption volume and polluted water volume by source and type of pollution. (WATER FOOT PRINT 2). In 2011 Hoekstra stated four-step approach for fresh water appropriation, which is shown in Fig. 1.1.

Water Footprint Components (Water 2017)

Three components of water footprint namely, green water footprint, blue water footprint and grey water footprint. The first two account for total consumption and the last one determines the amount of fresh water polluted. The quantity of water used is calculated in terms of water footprint. It indicates amount of water consumed and contaminated during industrial processes. Figure 1.2 shows the components of water footprint.

Green water footprint—Rainwater is referred as green water footprint which does not run off or recharge the groundwater but stored in soil or stays on stop of soil. It refers to the rain water volume consumed for the production of various agricultural and forest products. It is a summation of water lost in evapotranspiration and precipitation and the amount of water locked in harvest.

Blue water footprint—It refers to the amount of groundwater or surface water consumed along the supply chain of a product or service. Domestic water use, industry and irrigated agriculture water usage comes under blue water footprint.

Grey water footprint—Grey water footprint is an indicator of amount of pollution in freshwater with the production of a product over its full supply chain. It is calculated based on the volume of water requires to dilute pollutants to an extent to meet water quality standards.

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The lotus feet of my beloved
Lord Pazhaniandavar
My beloved late Father
My beloved Mother
My beloved Wife Karpagam and
Daughters—Anu and Karthika
My beloved Brother
Everyone working in the Agricultural
and Consumer Products sectors to make it
ENVIRONMENTALLY SUSTAINABLE*

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Water Footprint of Agricultural Products



P. Senthil Kumar and G. Janet Joshiba

Abstract Water is a greatest gift of nature and it is an essential necessity of all living organism to survive in earth. Due to the over exposure of industrialization and urbanization the quantity and the quality of the water sources are getting depleted, thus it is necessary to measure the volume of the water consumed to create each of the merchandise and enterprises we utilize. The water foot printing helps people, organizations and nations by disclosing the amount of water utilized by all sectors from an individual level to national level. They also help in highlighting the volume of water utilized as a part of the considerable number of procedures engaged with assembling and delivering our products. They likewise represent the measure of water defiled amid assembling and generation. Agriculture is one of the major consumers of water and it fully depends on water for growth and production of agricultural products. It is directly and indirectly linked with the water scarcity, Furthermore it is also one of the major sources affecting the quality of water by overloading the fresh water with excess amount of nutrients. Food production is directly linked with the water scarcity and so to increase the food production it is essential to measure the water utility in agricultural process. Water footprint of agricultural products aims in developing new strategies to overcome the water scarcity in agricultural sector and it helps in administering many effective rules for empowering a more proficient governance of water sources under climatic changes, industrial pollution and various other factors affecting the quality of water. This review narrates the various features of the water footprint in the agricultural products.

Keywords Water footprint · Water scarcity · Food production · Agriculture

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1 Introduction

Water is one of the greatest gifts of Mother Nature. Life without water is unimaginable in earth. Water is an essential source for energy and every living being in earth depends on water for energy. Nowadays, due to high population growth, advancement in economy, industrial growth, changing climatic conditions, etc., causes depletion of fresh water sources (Hogeboom et al. 2018). With the explosion of population outgrowth combined with changing eating regimen inclinations, water withdrawals are relied upon to keep on increasing in the coming decades universally, the water scarcity has expanded about seven fold in the previous century. Even after the implementation of wastewater treatment in the industries, the used water cannot be regained for other purpose because of the unpredictable global warming, ozone depletion and climatic changes which are causing evaporation of water sources. Furthermore, around 85% of global water is utilized for farming purposes (Mekonnen and Hoekstra 2011). The developing assemblage of research on water utilize, shortage and contamination in connection to utilization, generation and exchange has prompted the development of the field of Water Footprint (Hoekstra 2017). The water footprinting of items is generally used by the private organisations to perform chance evaluation and it is used as an instrument to distinguish hotspots in their supply affixes or to couple it with instruments like LCA techniques keeping in mind the end goal to perform benchmarking of items. In the second case, it is used to provide the fundamental data of the occupants of a particular nation who are consuming the water sources and it is used by the scholarly community, Non-Governmental Organisations and private sectors (UNEP 2011). Agriculture is the largest global consumer of fresh water sources. The risk of depletion of global fresh water sources increases due to the outgrowth of inevitable environmental issues causing depletion of water sources globally leading to deficiency of fresh water sources for agricultural consumption. The water utilization for crop production is getting elevated every year by 0.7% and the requirement of water for crop production will increase from a level of 6400 Gm³/yr to 9060 Gm³/yr by the year 2050 to nourish around 9.2 billion of the global population (Mekonnen and Hoekstra 2013). Ground water is a best source of fresh water which meets the requirements of billions of people and it plays an extraordinary role in the agriculture which remains as the basic food production source of human beings. The ground water level is evaluated by many governmental and non-governmental organizations to know about the rate of depletion of ground water due to some environmental issues (Gleeson et al. 2012). Water acts as an outstanding resource of nature and it place a phenomenal role in the development of merchandise and enterprises, furthermore, the water utilized as a part of the manufacturing sector is known as the virtual water. For manufacturing 1 kg of grain we need approximately 1000–2000 kg of water. For delivering 1 kg of meat we require in normal 16000 kg of water, whereas for producing 1 kg of cheddar we require about 5000–5500 kg of water. Every item manufactured in an industrial sector compulsorily needs water as a main raw material (Hoekstra 2003). Various water consuming activities followed globally are depicted in the (Fig. 1). The developing freshwater shortage is as of now

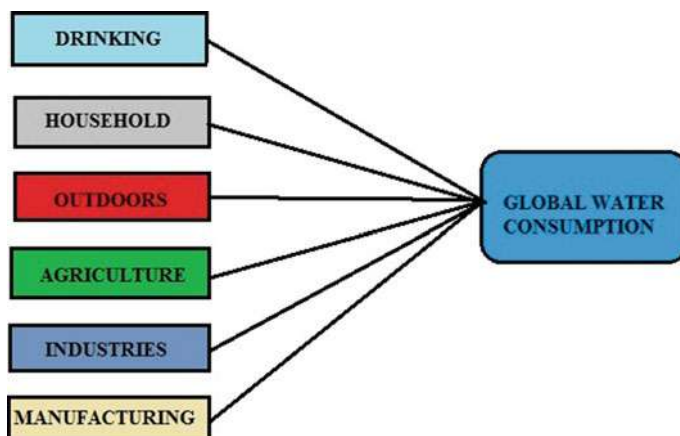


Fig. 1 Various water consuming activities

apparent in numerous parts of the world. Raising water scarcity increases the risk for deficiency of fresh water sources for agricultural utilization which leads to depletion in food production. The water footprint offers a quantifiable marker to quantify the volume of water utilization per unit of harvest, and in addition the volume of water contamination (Mekonnen and Hoekstra 2013). This article elucidate the impact of agriculture on the global water sources and it gives an clear description of the water footprinting concepts, its methodology, data collection method and it also explains the importance of water footprinting on the agricultural products and its impact on developing the global fresh water sources.

2 Global Demand for Water

2.1 Water Footprint Concept

The water footprint concept was enunciated in an international expert meeting on virtual water trade in the year 2002, December. Hoekstra and Hung have enunciated the idea of the water footprinting to know about this overall amount of virtual water substance of all merchandise and enterprises devoured by one individual or by the people of one nation. When compared with the other resources such as land, air and energy, only little research has been done in the water and its impact on its utilization by industries for manufacturing goods and services (Hoekstra 2003). The water footprinting measures the quantity of water used in manufacturing a product into every one of the merchandise and enterprises globally and it also likewise reveals about the amount of water being devoured by every nation globally (Water footprinting network). They presented the water footprint as a marker for utilization of water



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Introduction and the concept of circular economy

1

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1.1 Introduction

Matter and energy cannot be created or destroyed. Matter and energy also tend to disperse. These are two major laws of thermodynamics referring to infinity, on the one hand, and entropy, on the other. Infinity, because—as we will elaborate on throughout this chapter—matter is constantly changing and offers a wide range of possibilities. It has always existed and it will always exist, which leads us to the concept of entropy. Entropy refers to a measure of disorder within a system, which causes matter to change and evolve. Both concepts—infinity and entropy—are inherent to any element of nature. Every entity existing in the universe has these qualities and answers to these laws of physics. **These laws were mentioned by Ray Anderson—Founder of Interface and pioneer in the application of the circular economy as a business model—(1998) in his book “Mid-Course Correction,” and they are the pillars of the sustainability paradigm.** And, of course, as sustainability is systemic, we cannot talk about sustainability without referring to the circular economy. The circular economy is based on the natural operation of the universe. It leads us to a comprehensive understanding of our context, and reappraises the resources we use to conduct an undertaking. It guides us to a more frugal, less fictitious way of living, considering every circumstance within its context and becoming aware of the impact of every action we take. Therefore, a change of paradigm is impending, perhaps not to “save the planet” or to “save humanity,” but just to learn about the care and respect that every living being deserves.

The operation of the current economic system is evidenced in most industries, like the textile industry, and more frequently, in the fashion system. Over the past decades, leading industry brands have increasingly sped up the season cycles they offer and promote, and at present lack of transparency prevails. In order to meet increasingly tight deadlines, most fashion brands decide to manufacture their clothes outside the country of origin, choosing Eastern countries for this process, where production costs are much lower because labor rights are less respected as well. In these countries the working conditions are unhealthy. However, such working conditions are not restricted to manufacturing in Eastern countries, as neither is forced or child labor exclusive to the tailoring process, but go as far as every step of the production process. For

^a The author appreciates the contribution of **Victoria Celeste Zaccari** to develop this chapter.

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Miguel Angel Gardetti
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Preface

The purpose of this book is to make a contribution to the discussion with various specialists on whether organic cotton is sustainable or not. This is not about drawing conclusions but rather providing data to cast light into this discussion.

The book begins with a paper by Ali Serkan Soydan, Arzu Yavas, Gizem Karakan Günaydin, Sema Palamutcu, Ozan Avinc, M. Niyazi Kıvılcım, and Mehmet Demirtaş titled “[Colorimetric and Hydrophilicity Properties of White and Naturally Colored Organic Cotton Fibers Before and After Pretreatment Processes](#)”. This chapter researches colorimetric (CIE L^* , a^* , b^* , C^* , h° , K/S, whiteness properties, etc.) and hydrophilicity properties of two white (Nazilli 84 S and Aydın 110) and three naturally colored (Emirel, Akdemir, Nazilli DT-15) organic cotton fiber types under review, before and after scouring (with NaOH), conventional bleaching (with H_2O_2), and the combined application of scouring and bleaching (scouring + bleaching) processes in comparison with their greige (untreated) counterparts.

The next chapter, “[Physical Properties of Different Turkish Organic Cotton Fiber Types Depending on the Cultivation Area](#)” was written by Sema Palamutcu, Ali Serkan Soydan, Ozan Avinc, Gizem Karakan Günaydin, Arzu Yavas, M. Niyazi Kıvılcım, and Mehmet Demirtaş. The measured and recorded data are analyzed with the Least Squares Fit model statistical evaluation method to accomplish Analysis of Variance and Effect Tests. Statistical evaluation has been designed to evaluate the influence of dependent variables of fiber type, location, and year in the independent fiber properties of length, strength, and fineness (micronaire).

Following “[Sustainability Goes Far Beyond “Organic Cotton.” Analysis of Six Signature Clothing Brands](#)” was developed by Maria Lourdes Delgado Luque and Miguel Angel Gardetti. This chapter analyzes five Spanish signature fashion brands based on the sustainability criteria defined by the authors. For such purpose, all the public information referred to by the brands: websites, newsletters, articles, references from organizations, and case studies, if any, is studied. Each of the designers or owners of these microenterprises are also interviewed. All of this is compared to a model developed by the authors that addresses the meaning of being sustainable in the textile and fashion world.

Moving on, Gizem Karakan Günaydin, Ozan Avinc, Sema Palamutcu, Arzu Yavas and Ali Serkan Soydan developed “[Naturally Colored Organic Cotton and Naturally Colored Cotton Fiber Production](#)”. White cotton fiber is one of the most chemically intensive crops cultivated. Though grown on 3–5% of the world’s farmland, it is liable for the usage of 25% of the world’s pesticides. For these aforementioned reasons, organically grown naturally colored cotton fiber has attracted a massive attention over the past few years. This chapter describes in detail a comprehensive review of naturally colored organic cotton fibers, naturally colored cotton fiber types, their properties, their production and their recent developments from a broad perspective and from many different angles.

The chapter called “[Organic Cotton and Cotton Fiber Production in Turkey, Recent Developments](#)” was written by Gizem Karakan Günaydin, Arzu Yavas, Ozan Avinc, Ali Serkan Soydan, Sema Palamutcu, M. Koray Şimşek, Halil Dünder, Mehmet Demirtaş, Nazife Özkan, and M. Niyazi Kıvılcım. This chapter deals with organic and conventionally grown cotton fibers with a broad perspective in terms of cotton fiber cultivation and recent development about these fiber types in Turkey. First, details are provided about organic cotton and organic cotton fiber cultivation in Turkey, organic cotton growing regions in Turkey, limitations for the organic cotton markets, lack of information on cost of production, marketing and future trends. Moreover, information about general cultivation in lands and cotton fiber yield in Turkey is given in detail, as well as information about the diseases and pests encountered during the cotton fiber cultivation.

In turn, in their paper “[Organic Cotton and Its Environmental Impacts](#)” P. Senthil Kumar and P. R. Yaashikaa investigate that the organic production is not really any more or any less ecologically well disposed than current ordinary cotton generation. For the textile procurer, there is no contrast between routinely developed cotton and organically developed cotton as to pesticide build-ups. Developing natural cotton is more demanding and costly than developing cotton routinely. Organic generation can be a challenge if bug weights are high; however, with work and experience, it could give premium value to cultivators willing to address these difficulties.

The next chapter, “[Organic Cotton Versus Recycled Cotton Versus Sustainable Cotton](#)” was developed by P. Senthil Kumar, and A. Saravanan. Organic cotton is cotton that has been developed without manures and pesticides, with advance biodiversity, organic cycles, and soil health. In contrast, natural cotton makes cotton development “cleaner,” giving both natural and ordinary cotton experience a similar assembling process, which is water and vitality concentrated. Recycled cotton is repurposed, post-modern or post-shopper cotton that would somehow or another be considered straight up: squander for the landfill. The pieces of such cut and sew jobs are post-mechanical cotton “squander” with the ability of being reused. Contingent upon how reused cotton is utilized, it can possibly extraordinarily decrease water and vitality utilization in reasonable design and attire, and diminish landfill waste and space. Cotton development is related to various social, financial, and natural shortcomings that weaken the piece sustainability.

Completing the book, Seyda Eyupoglu prepared a chapter titled “[Organic Cotton and Environmental Impacts](#)”. This chapter investigates organic agriculture, organic cotton agriculture, comparison of conventional cotton agriculture with organic cotton agriculture, environmental impacts of organic cotton agriculture, and use of organic cotton products. And the final chapter contains conclusions and recommendations.

It is important to highlight that all of these diverse contributions represent a great step forward in expanding the insights in this field. It is certainly the most comprehensive collection of writings on this subject area to date. Note that this initiative has received a wide international response, and it is expected to continue stimulating further debate.

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Colorimetric and Hydrophilicity Properties of White and Naturally Colored Organic Cotton Fibers Before and After Pretreatment Processes



Ali Serkan Soydan, Arzu Yavas, Gizem Karakan Günaydin,
Sema Palamutcu, Ozan Avinc, M. Niyazi Kivılcım and Mehmet Demirtaş

Abstract It is widely known that conventionally grown cotton fiber/fabrics/apparel has chemical residues on the cotton which may cause cancer and some other health related troubles. It is also certain that organic cotton production does not consume most synthetically compounded chemicals (fertilizers, insecticides, herbicides, growth regulators and defoliants) which are suggested for only conventional cotton production. Therefore, organic cotton production lead to much more environmentally cotton fiber production in comparison to conventional cotton fiber growing. So, in this chapter, colorimetric (CIE L^* , a^* , b^* , C^* , h° , K/S, and whiteness properties etc.) and hydrophilicity properties of studied two white (Nazilli 84 S and Aydın 110) and three naturally colored (Emirel, Akdemir, Nazilli DT-15) organic cotton fiber types was investigated before and after scouring (with NaOH), conventional bleaching (with H_2O_2) and the combination application of scouring and bleaching (scouring + bleaching) processes in comparison with their greige (un-treated) counterparts. Greige (un-treated) Akdemir naturally colored organic cotton fiber displayed the reddest (with the highest a^* value), the yellowest (with the highest b^* value) appearance, the highest chroma (the most saturated), the lowest lightness (the darkest) and the highest color strength (the strongest color yield) and therefore the strongest color shade amongst the studied greige (un-treated) naturally colored organic cotton fibers. After scouring process, all three naturally colored organic cotton fibers congruously exhibited darker [with the lower lightness (L^*) values and higher color strength (K/S) values], slightly redder (slightly higher a^* values) and slightly less yellow (slightly lower b^* values) appearance in comparison to their greige (un-treated) counterparts. Overall, it can be concluded that solely bleaching

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process (without any prior scouring process) and combination sequential usage of scouring and bleaching processes (scouring then bleaching = scouring + bleaching) generally did not significantly affect the color properties of studied naturally colored organic cotton fibers leading to similar close colorimetric performance with their greige (un-treated) counterparts. So, after the bleaching process, scoured naturally colored organic cotton fibers which darkened due to the scouring process roughly turned back to their original colorimetric levels of greige (un-treated) versions. In this case, if the naturally colored organic cotton fibers are blended with the normal white and off-white organic cotton fibers or other cellulosic fibers, applied bleaching process does not cause a significant color change in the naturally colored organic cotton fibers and this indicates that they will approximately remain at the same color property levels as their greige (un-treated) counterparts. Moreover, the bleaching process following the scouring process slightly increases the hydrophilicity values of both white and naturally colored organic cotton fibers leading to more hydrophilic fibers.

Keywords Organic cotton · Naturally colored cotton · Color · Whiteness
Hydrophilicity · Pretreatment · Scouring · Bleaching

1 Introduction

Organic cotton fiber production does not consume most synthetically compounded chemicals (fertilizers, insecticides, herbicides, growth regulators and defoliants) which are suggested for only conventional cotton production leading to more sustainable and ecological way of production. In Turkey, not only the white and off-white but also naturally colored organic cotton fibers are produced. Naturally colored cotton has a long history and the cultivation history of naturally colored cotton dates back approximately 5000 years [1–3]. For example, it is known that naturally colored cottons were cultivated and utilized in South and Central America around 2300 B.C. [4]. Even though naturally colored cotton exhibit a long cultivation history, the cultivation of the naturally colored cotton plant nearly ceased for a long period of time. Since, naturally colored cotton fibers are generally regarded as inferior to common white cotton owing to their lower yield, their shorter, and weaker fiber types and problems regarding the repeatability and shade variability of their color [4]. Indeed, it was stated that brown and green naturally colored cotton fiber display approximately 33.6 and 41.9% lower yields than common white cotton fibers, respectively [5, 6]. It is also reported that naturally colored cottons possess lower boll numbers, lower boll mass and also lower lint yield. What is more, up to 17.4% fiber length reduction, lower micronaire index and lower strength but higher elongation was measured in the case of colored cotton in comparison to common white cotton [5, 6]. Naturally colored cotton fibers could be too short and weak to be spun into finer yarn counts and moreover there is a constraint of non-existence of petitive different colors and shades [7].

Environmental Footprints and Eco-design
of Products and Processes

Subramanian Senthilkannan Muthu
Editor

Energy Footprints of the Food and Textile Sectors

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Environmental Footprints and Eco-design of Products and Processes

Series editor

Subramanian Senthilkannan Muthu, SgT Group and API,
Hong Kong, Hong Kong

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Lord Pazhaniandavar
My beloved late Father
My beloved Mother
My beloved Wife Karpagam and
Daughters—Anu and Karthika
My beloved Brother
Everyone working in the food and Textiles
sectors to make it ENVIRONMENTALLY
SUSTAINABLE*

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Energy Footprints of Food Products



P. Senthil Kumar and A. Saravanan

Abstract In numerous regions, ecological issues that are both local (for instance, high rates of urbanization, mechanical exercises, arrive utilize changes, or rural practices,) and worldwide (for instance, desertification, or deforestation) have significantly lessened the capacity of land to ingest CO₂. A few endeavors have been made to orchestrate rules for natural footprints of food. The energy footprint, similar to the environmental footprint, is a marker of advance that can be utilized as methods for activating activity at the neighborhood level. It is an effectively comprehended idea as it scales the message down to the level of a person. It additionally legitimizes associations and cooperation among various partners to discover new, economical and less harming arrangements. The data exhibit that the impressions are critical, both locally, national and comprehensive and have comes about for overall sustenance security and condition prosperity and effectiveness. The writing about concurs that worldwide sustenance creation framework produces impressive natural impressions and the circumstance would likely get troubling.

Keywords Food waste · Green house emission · Sustainability
Natural footprints

1 Introduction

Energy utilize is relied upon to increment every year, the current pattern toward growing more residential vitality sources is driven to some degree by political shakiness in some oil-rich countries and to a limited extent by the want to keep up vitality security (Yergin 2006). Mechanical headways, for example, level boring in conjunction with pressure driven cracking have made extraction of shale assets financially reasonable,

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advancing a quick increment in unpredictable vitality creation throughout the most recent span (Kerr 2010). Simultaneously, acknowledgment of the impending communal and natural implications of environmental revolution is lashing the drive to direct emanations by extending carbon impartial wellsprings of vitality, for example, sun oriented and airstream control (Pimentel et al. 2002).

Real changes in farming innovation, foundation, and cultivating administration rehearses are required at this point. Through deteriorating speculations and prevailing tasks, the plan for worldwide supportability in sustenance generation frameworks appear to be overwhelming. This session distils modules from antiquity and from prevailing examinations to pick the correct ventures, arrangements, and official buildings to guarantee that water and vitality assets are utilized carefully in the testing a long time ahead (Khan and Hanjra 2009). Environmental change and populace development may have huge ramifications for rural creation and its ecological impression, particularly for inundated farming which gives around 40% of worldwide sustenance creation from only 18% of cropland. Rainfed sustenance creation frameworks will likewise go under extreme weight because of movements in climate designs also, changes in precipitation occasions and hydrological administrations and more noteworthy reliance ashore and water assets, bringing on additional assets corruption and dissolving efficiency.

Every footprint imagines the stream of vitality (as fuel, power, or steam) to significant end utilizes as a part of assembling, including boilers, control generators, process warmers, process coolers, machine-driven hardware, office warming, ventilation, and aerating and cooling, and lighting. The impressions exhibit information at two levels of detail. The principal page gives an abnormal state perspective of essential vitality (offsite and on location), while the second page indicates subtle elements of how vitality is circulated to nearby end employments. Note that vitality expended as a feedstock (i.e., nonfuel vitality supply that is changed over to made item and not utilized for warmth, power, or power age) is excluded in the vitality esteems exhibited in impressions.

Total information gave in every one of the divisions incorporates:

- Power and steam created offsite and exchanged to the office, and in addition power and steam produced nearby
- Fuel, power, and steam devoured by significant end utilizes as a part of an assembling office
- Offsite and on location vitality misfortunes because of the age, transmission and dissemination, and end utilize utilization of vitality (a few misfortunes are unrecoverable)
- Ozone depleting substance outflows discharged amid the burning of fuel.

1.1 Energy Footprint

The significance of the vitality impression free of the biological impression in vitality situation investigation by utilizing an input—yield examination (IOA) based casing work (Ferngs 2002). It was previously displayed as a sub-pointer of the organic impression, addressing the measure of timberland zone that is being prerequisite to hold CO₂ outflows from oil subordinate consuming and power age utilizing sequestration regards for a world-ordinary forest (Wackernagel and Rees 1996). Contingent upon refreshed information acquired from the Diplomatic Panelon Weather amendment, the estimation of the vitality impression has been reconsidered with a small amount of around 30% of the aggregate anthropogenic discharges for sea take-up (Borucke et al. 2013).

1.1.1 Segments and Units

The vitality impression can be arranged into solid segments, for example, the petroleum product impression, the water power impression, and the atomic impression (Browne et al. 2009), which are all communicated as the region of backwoods that is important to make up for human-incited carbon dioxide (Van Den Bergh and Verbruggen 1999). The unit of estimation can be nearby acreage with a particular decarbonization evaluate. Fundamental normal for the energy footprints was shown in Table 1. Rundown of methodologies connected to the investigations of vitality impressions from the writing was shown in Table 2.

Table 1 Fundamental normal for the energy footprints

S. No	Item	Energy footprint
1	Reasonable roots	Ecological footprint
2	Research stressors	Forest for absorbing—Energy-related green house gases outflows
3	Impression components	Fossil fuel, hydroelectricity, atomic, etc.
4	Metric units	Area-based (gha, ha, etc.)
5	Count methods	NFA, NFA-PLUM, IOA, base-up, top-down
6	Information availability	Medium
7	Methodological standardization	Low
8	Weighting accuracy	Not applicable
9	Resultant interpretation	High
10	Geographical specification	Medium
11	Worldwide comparability	High
12	General applicability	Low

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Social Life Cycle Assessment of Agricultural Products: Experiences on Rice, Sugarcane and Cassava in Thailand



Jittima Prasara-A and Shabbir H. Gheewala

Abstract This chapter presents social performances of major agricultural products in Thailand, i.e. rice, sugarcane and cassava. The social performances are social conditions associated with the products under study and are the results of Social Life Cycle Assessment (SLCA). It discusses the social performances of these crops individually, as well as compares the performance between crops. In addition, it presents social performances of these crops under conventional and area based practices. Moreover, it discusses the applicability of the social performance assessment method used in this study. The results suggest that the performances on working conditions for workers in cultivation of all crops are not much different. The workers gain higher wage on occasion that is competitive to hire workers. Despite relative high number of employment in sugarcane cultivation, its social performance on the local community is relatively low due to the problem of cane trash burning. Compared to all stakeholders, the farm owners for all crops have the lowest social performance. This is because they often face the problem of price fluctuation. Contract farming benefits sugarcane farm owners in all indicators examined. Contract farming provides technology development assistance and access to loan from the sugar factory. Moreover, the area based policy can help to significantly increase social performances of the farm owners for all crops in all aspects studied. In addition, the proposed Social Life Cycle Impact Assessment (SLCIA) method used is found to be applicable to all crops studied although modifications are needed to provide more comprehensive results.

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Keywords Social life cycle assessment • SLCA • Agricultural products • Rice
Sugarcane • Cassava

1 Introduction

Agriculture is one of the key economic sectors of Thailand. Moreover, the nation is one of the world's largest exporters of major agricultural based products such as rice, sugar and cassava starch. In 2017, rice made the largest value of total export among all exporting agricultural products at 175,160 million baht (1 USD $\equiv$ 33 baht). This was followed by products from cassava, the export of which was valued at 95,545 million baht while sugar products from sugarcane had a value of total export of 93,240 million baht (Ministry of Commerce 2017).

This implies that abundant amounts of rice, sugarcane and cassava are produced in the country. Like other nations, Thailand has a commitment towards achieving the sustainable development goals. Within these goals, sustainable agriculture is emphasized. The main goal is to help sustain food security and increase farmers' well-being. Social Life Cycle Assessment (SLCA) is a technique used to assess the social and socio-economic performances, both positive and negative, along the life cycle of products. This technique can be used to identify social hotspots for improvement (UNEP/SETAC 2009). It is a useful approach to help moving forward social sustainability of agricultural products.

There have been several SLCA studies on agricultural products globally—both food and non-food based products. For example, SLCA studies of agri-food products include roses (Ecuador and Netherlands) (Franze and Ciroth 2011), strawberry yogurt (USA) (Benoit-Norris et al. 2012), wine (Italy) (Arcese et al. 2017), tomato (Italy) (Petti et al. 2018), dairy farm (Ireland) (Chen and Holden 2017), citrus (Italy) (Iofrida et al. 2018), honey (Italy) (D'Eusanio et al. 2018) and soy bean (Brazil) (Zortea et al. 2018). There have also been SLCA studies on non-food agricultural products such as sugarcane for bio-refinery (Brazil) (Souza et al. 2018), bamboo for bicycle frame (Ghana) (Agyekum et al. 2017), oil palm for biodiesel (Indonesia) (Manik et al. 2013) and wood based products (Germany) (Siebert et al. 2018). The previous SLCA studies adopted a variety of their own developed SLCIA methods following the guidelines of UNEP/SETAC (2009). As to date there has not been a standardized SLCIA method to be used among all the studies; the previous SLCA studies on agricultural products have contributed to the methodology development.

In Thailand, there have also been some SLCA studies for both food and non-food based agricultural products including the previous study of the authors themselves. For example, SLCA studies of sugarcane for food and biofuel (Prasara-A and Gheewala 2018a; Sawaengsak and Gheewala 2017) and cassava for ethanol (Papong et al. 2017). The previous studies used different reference units; therefore, the comparison is not possible. In addition, they only considered conventional cultivation practices; alternative cultivation practices have not yet been examined.

This chapter discusses experiences on conducting SLCA case studies of the major agricultural products in Thailand, i.e. rice, sugarcane and cassava. The results presented here are mainly based on recent work, using cases in the northeastern region of Thailand which hosts the largest planting areas of these crops (Phantha et al. 2018; Prasara-A and Gheewala 2018b; Thuayjan et al. 2018). This chapter discusses results in the context of different crops. In addition, it compares results of different crops. Moreover, it discusses applicability of the social performance assessment method proposed for all selected crops.

Section 2 describes methodology adopted in this chapter. Sections 3–5 present the social performances of rice, sugarcane and cassava products respectively. Section 6 compares the social performances of all selected crops studied. Section 7 presents the social effects of area based agriculture policy on rice, sugarcane and cassava products. The applicability of the proposed SLCIA method used in this study is discussed in Sect. 8 and concluding remarks are presented in Sect. 9.

2 Materials and Methods

2.1 Goal and Scope Definition

The SLCA studies presented follow the framework as outlined in the guidelines of UNEP/SETAC (2009). The reference unit is 1 rai (a standard Thai area unit; equals to 0.16 ha) of plantation area. This reference unit was set to make the results comparable across different product systems. System boundary of this study is cradle to mill gate as shown in Fig. 1.

2.1.1 Site Selection

The sites selected are in the northeastern region of Thailand as it is the largest producer of rice, sugarcane and cassava (Office of Agricultural Economics 2017).

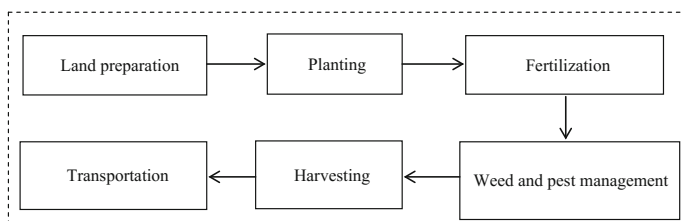


Fig. 1 System boundary

Table 1 Descriptions of sites selected for different crops

Crop	Description of site
Rice	Det Udom district, Ubon Ratchathani province. Distance from farm to rice mill is about 24 km. Plantation area is non-irrigated
Cassava	Khon Buri district, Nakhon Ratchasima province. Distance from farm to cassava starch factory is about 12 km. Plantation area is non-irrigated
Sugarcane	Ban Phue district, Udon Thani province. Distance from farm to sugar factory is about 14 km. Plantation area is non-irrigated

The sites selected are those areas with the largest plantation areas of each crop under study. Descriptions of the sites selected for each crop are shown in Table 1.

2.1.2 Stakeholder Identification

Stakeholders groups examined include workers, local community, and value chain actors (farm owners and machine contractors). The key stakeholder groups included are based on the suggestions in UNEP/SETAC (2009). The previous study on SLCA of sugarcane (Prasara-A and Gheewala 2018a) suggests that more than eighty percent of social effects of agricultural product occur in the plantation stage. This means that social performance in the cultivation stage plays an important role in the overall results. Therefore, the studies presented in this chapter emphasizes on cultivation stage of agricultural products. Consumers are excluded in these studies due to difficulty in data collection. The agricultural products are sold within the country and are also exported. Value chain actors included are based on expert consultation. It is noted that agro-chemical suppliers are not included in this study.

Results from previous study on SLCA of sugarcane (Prasara-A and Gheewala 2018a) show that workers are those stakeholders who are socially affected the most. Therefore, it is essential to include this stakeholder group in this study. Workers in the areas studied are mostly locals. They are not contracted workers and are seasonal workers. A single worker is free to work on any number of sites, including plantation of different crops. Some workers also have their own small sized plantation.

Local community is included as the plantation is part of the local community. The agricultural cultivation will have social effect on the local community. Most people who live in the studied areas work in agriculture for a living. There are also other minor jobs such as construction work. However, these jobs may need higher skills. Jobs in agriculture do not need high skills.

Farm owners in the areas examined are mostly small sized farmers. One farmer normally grows more than one crop. Farm owners included in this study for each crop are those who mainly grow each particular crop studied. Therefore, sites selected for each crop are those areas hosting the largest plantation areas for different crops.

Machine contractors are normally the farm owners themselves. They use their own machines in their farms and also rent out to other farm owners within their

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The lotus feet of my beloved

Lord Pazhaniandavar

My beloved late Father

My beloved Mother

My beloved Wife Karpagam and

Daughters—Anu and Karthika

My beloved Brother

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Social Performance of Electricity Generation in a Solar Power Plant in Spain—A Life Cycle Perspective



Blanca Corona and Guillermo San Miguel

Abstract This publication demonstrates the practical application of Social Life Cycle Assessment (S-LCA) methodology in the analysis of a 50 MW_e Concentrating Solar Power (CSP) plant located in Spain. The assessment makes use of two complementary analytical approaches: (1) a generic social hotspot analysis based on the social risks related to financial flows generated by the provision of goods and services taking place during the life cycle of the power generation system, and then (2) a site-specific analysis focussing on the social performance of the construction/energy company involved in the construction and operation of the power plant. The site-specific analysis followed the procedures proposed by UNEP/SETAC but included a new classification/characterization model suited to the particularities of the project and the energy sector. The analysis considered four stakeholder categories (workers; local community; society; and value chain actors) and used the number of worker hours as activity variable for the quantification of social risks. Worker hours attributable to each of the stages of the life cycle of the CSP system were calculated using input-output (IO) analysis. The impact assessment phase of the S-LCA was carried out using a Social Performance Indicator (SPI), which required the estimation of performance reference points for a series of indicators/subcategories proposed by the UNEP/SETAC Guidelines. The SPI calculated for the CSP plant (+0.388 for a ± 2 range) suggested that the use of solar power results in an increase of social welfare in Spain, primarily with regards to socioeconomic sustainability and fairness of relationships. The inventory data used in the social hotspot analysis were monetary flows attributable to each of the processes considered in the life cycle of the power system. These flows were assigned to the corresponding sector of the producer country. The Social Hotspot

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Database (SHDB) was used to link these demand values to social risks and opportunities. The results showed that the life cycle phase contributing the most to the social risk of the solar power system was operation and management. This is due primarily (over 75% of the weighed risk) to the social risks associated with the supply chain of the natural gas used as auxiliary fuel. For Spain, the main social risks associated with the solar power plant were related to gender inequality and corruption, and to a lesser extent to injuries and immigrants. Some of these risks were confirmed in the site-specific assessment. The paper ends with a discussion about the application of Multi-Criteria Decision Making (MCDM) for evaluating the results obtained in this Social-LCA in combination with environmental and economic oriented LCA.

Keywords S-LCA · Electricity · Social performance · Spain · Social risks Stakeholders

1 Introduction

The UN World Commission on Environment and Development (WCED), also known as the Brundtland Commission, developed between 1983 and 1987 the grounds for the modern interpretation of sustainability. In its final report “*Our Common Future*”, the Brundtland Commission produced a definition of Sustainable Development that is still widely accepted today: “*the development that meets the needs of the present without compromising the ability of future generations to meet their own needs*” (WCED 1987). That report also stated that the concept of sustainability rests on three elements: economic growth, environmental protection and social equality.

At present, the Sustainable Development Goals (issued by the United Nations in 2015, and a continuation of the Millennium Development Goals) (Biermann et al. 2017) are in the front line of international, national and local agendas. Public administrations and customers are exerting pressure on companies to ensure that the principles of sustainable development are incorporated into the goods and services that they supply to the market. The practical application of this ambition necessarily entails the use of a systematic methodology capable of quantifying the sustainability of specific goods and services in an objective manner.

A holistic methodology referred to as life cycle sustainability assessment (LCSA) is currently under development with the purpose of integrating the three pillars of sustainability under a coherent life cycle approach. UNEP/SETAC Life Cycle Initiative states in its report “Towards a Life Cycle Sustainability Assessment” that LCSA may be seen as the summation of three analysis tools: Environmental Life Cycle Analysis (E-LCA), Life Cycle Costing (LCC) and Social Life Cycle Analysis (S-LCA) (UNEP/SETAC 2011). This concept is illustrated in equation $SLCA = E-LCA + LCC + S-LCA$.

A more advanced and flexible approach to LCSA was developed under the Coordination Action for innovation in Life Cycle Analysis for Sustainability (CALCAS) (2006–2009) project (Heijungs et al. 2009). This new conceptual framework relies on expansion of the scope of conventional E-LCA to incorporate the economic and the societal dimensions of the system under consideration. The CALCAS project approach provides the practitioners with more flexibility in the selection of the analytical tools employed to evaluate different aspects of the system and provides an integrated framework where the results may be evaluated as a whole (Guinée et al. 2011).

The ultimate purpose of S-LCA is to assess the effect of a given product on human wellbeing. As the name suggests, the analysis applies a life cycle approach that takes into consideration social and socio-economic effects associated with the extraction and processing of raw materials required for the fabrication of the product, manufacturing activities, transportation and distribution, utilization and any end-of-life actions that may be associated with the product (reuse, recycling and final disposal). These effects considered in S-LCA are primarily those generated by the companies participating in the different stages of the life cycle of the product under consideration.¹ This performance has an effect (positive or negative) on the wellbeing of a series of stakeholders, which typically include Consumers, Workers, Local Community, Value Chain Actors and Society.

S-LCA may be used on its own or, as described above, it may be part of a broader Life Cycle Sustainability Assessment (LCSA) (Guinée et al. 2011; UNEP/SETAC 2011). The scientific community recognizes E-LCA and LCC as mature methodologies, while S-LCA is usually regarded as being at an early stage of development in terms of methodological harmonization and acceptance (Cinelli et al. 2013).

1.1 Key Methodological Issues in S-LCA

Since its inception in 2002, the *UNEP-SETAC Life Cycle Initiative* has distinguished itself as a key promoter and developer of S-LCA methodology. The *Guidelines for Social Life Cycle Assessment of Products* (from now on the S-LCA Guidelines) have become a landmark and a key reference in the field (UNEP/SETAC 2009). This methodology operates on the principles of ISO 14040 and 14044, with the typical four interrelated phases: (i) identification of goal and scope, (ii) inventory analysis, (iii) impact assessment and (iv) interpretation. The practical application of these guidelines is facilitated with the Methodological Sheets for Sub-Categories in Social Life Cycle Assessment (S-LCA) (UNEP/SETAC 2013).

In the identification of goal and scope phase, the S-LCA practitioner needs to set up the basis of the investigation including identifying the objectives of the

¹In addition, the ultimate utility of the product may also be considered in the analysis

Patterned 2D Thin Films Topological Insulators for Potential Plasmonic Applications

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Abstract

Topological insulators are electronics materials that have bulk bandgap like ordinary insulator. But they have secured conducting states on their edge or surface that behaves like a conducting metal. These surfaces have unique plasmonic properties of Topological Insulators (TI) and have many promising application using the plasmons – quantized electron density oscillations resulting from the interaction of light with metals. The high oscillating frequency and the high sensitivity to the metallic surface characteristics made plasmons for various applications like biosensors, high speed data transfer and surface bound to exploit spin based oscillations by controlling the collective spin excitations (spin plasmons) were useful for spintronics applications. Spins produced by the plasmons have very small amplitude that was not suitable for today's plasmonic materials. To overcome this issue, Dirac materials and Topological Insulators were used. In Dirac materials, the momentum is formed when passing the light and there has been mismatch between photons and plasmons during the excitation process. To overcome this problem, 2D based patterned thin film grafting it with correct size that could make up the differences in momenta. The aim of this chapter is to provide adequate subject matter on 2dimensional thin film topological insulators for plasmonics applications like sensors, energy harnessing, information transformation, plasmon enhanced effects on surface of the 2D materials and regulative measures/effective hierarchies about these 2D topological insulators based nanomaterials were also taken into consideration for various applications.

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Keywords: Topological Insulators, 2-dimensional thin films, plasmons, plasmonics, dirac materials, patterned thin films, nanomaterials

10.1 Introduction

Condensed matter of physics with enormous aspects emerges with concerned understanding on simple constituents like ions, magnetic moments or electrons interact with each other. To describe the topological insulator, metallic boundary behaves as insulator under vacuum. During the insulating behavior, topological invariants are formed at the metallic boundaries. In general, Topology is a branch of mathematics that studies the properties of objects that are invariant under smooth deformations, a classic example being a doughnut transforming into a coffee cup [1]. The idea of topological insulators grew out in 2D systems with quantum Hall Effect in the presence of magnetic field. More recently, the effect based on spin and orbital angular momentum degrees of free electrons are coupled with each other when moving through a spin dependent force under non magnetic systems. These spin-orbits do not have symmetry which is required to induce Hall Effect with simplified models that are developed in later 2003. In these models, electrons spin in opposite angle commonly called as spin up and spin down and depicted their behavior towards the better understanding on topological insulator. In 2005, Kane and Mele, expel quantum spin hall effect on computed topological invariant can survive for any 2D systems using basic physics and also predicted that, materials allow stable edge state for evaluating the characteristics of topological insulators. Later on, Bernevig, Hughes and Zhang made a theoretical prediction that 2D topological insulators such as mercury-cadmium telluride HgTe/CdTe quantum wells consists of 1D gapless conductive edge channels with a 2D area exhibiting an energy gap. The 2D layered version on topological insulator was bought out the theoretical prediction with weak 3D systems in 2006. Basically, Topological Insulators determines a novel quantum phase of matter, characterized by a bulk semiconducting materials and topologically protected surface states. This chapter describes the diversified applications of topological insulators using various materials and also focuses on 2D nanostructured thin films of topological insulators for different applications. All these fields of interest benefits from the exploitation of TI for both propagating and localized plasmonic modes are achieved in noble metals and graphene.

10.2 Fundamentals of Plasmons

A class of plasmon materials can possibly include new viewpoints for the frameworks incorporating 2-dimensional materials. A strong spin-orbit coupling at protected surface states give rise to spin-charge separation with collective excitations on dirac carriers. In TI, momentum spins are locked compared with graphene materials which are pointed out by hang and co-workers [2]. Their discussion based on collective modes of ‘helical metals’ focusing on density fluctuations that induce transverse spin fluctuations. A transverse spin wave can be generated by a transient spin grating consisting of two orthogonally polarized non-collinear incident beams [3] and charge density wave can be detected by measuring spatial modulation of reflectivity. These spin-plasmons were also discussed in terms of the plasmon wave function. Surface plasmons (or plasmon-polaritons) are collective charge oscillations which are usually confined to the surface of a metallic material. The interface of 2D metallic surface with topologically protected surface states (TSS) or a 2D depletion layer surrounded by two insulators: one is given by the topological bulk insulator and the other one is usually air.

10.2.1 Plasmons at Metals/insulator Interfaces

Surface plasmons with excitations are travelling along the interface between two materials (metals and insulators) have real and negative permittivity ϵ , while the other material has real and positive permittivity (e.g., vacuum). A typical example of a material with negative ϵ is an idealized metal described in terms of a gas of free electrons with surface plasmon frequency (Formula 1)

$$\omega_{sp} = \frac{\omega_p}{\sqrt{1 + \xi_2}}$$

10.2.1.1 Properties of Surface Plasmons

- The surface plasmons are set on a topologically nontrivial interface. These nontrivial interfaces supported between an insulator and metal.

From above equation 2, ϵ is real and positive for the insulator with the range of frequencies and they can be taken as real and negative for the metal. The polarization of the surface plasmon experiences a nontrivial

rotation due to the jump in θ across the interface: while for a standard metal/insulator interface the surface plasmon is entirely “transverse magnetically” (TM) polarized, with both $\mathbf{B}$ and $\mathbf{H}$ lying in the plane of the interface (as well as orthogonal to the direction of propagation of the surface wave), in the topologically nontrivial case the magnetic field is rotated out of the plane with interface by an angle $\nu_p \propto \alpha\theta$ [3].

The realization of topological interface is possible in 3D TI materials, such as $\text{Bi}_{1-x}\text{Sb}_x$ alloys Bi_2Se_3 , and Bi_2Te_3 has a nonvanishing bulk carrier density. The major obstacle for exploring low-energy based effects that it contains the topological $\theta\mathbf{E}\cdot\mathbf{B}$ term. For doped topological insulators (or “topological metals”) low-energy effective action can be described by standard quantized θ associated with the topological band structure together $\epsilon(\omega)$ (appropriate for a conductor). This effective field-based theory is limited to low frequencies and for hierarchy-based structures it can operate at defined range of frequencies that determines the novel surface phenomena. Further, effective field of theory describes the massless surface modes gapped by external T-breaking deformation. It is important to introduce the external magnetic field orthogonal to the interface due to the formation of deformation. So its very well understood surface plasmons are external magnetic fields.

10.2.2 Plasmons Based on Electromagnetic Fields

Surface plasmons caused by electromagnetic excitations called as polaritons which are induced by propagating between the dielectric and a conductor. These electromagnetic surface waves arise via the coupling of the electromagnetic fields to oscillate the conductor’s electron plasma. The behaviors of surface plasmon polaritons on both single, flat interfaces and in metal/dielectric multilayer structures were discussed in this session.

- For *planar elements*, bandgaps can be varied by monitoring the directions of surface plasmon polaritons between metal film and dielectric via scattering phenomenon. Their positions enable the generation of functional elements, which creates 2D planar photonic infrastructure for SPPs. These photonic infrastructure exhibits band gaps in desired frequency regions. The excitation of SPPs can be achieved by metallic film milled into slits are perpendicularly polarized and focused towards the center in metal film-based structures.

- SPPs interactions with *metal strips* with lateral confinement leading to the occurrence in coupled modes on insulator/metal/insulator multilayer system consisting of thin metal strips sandwiched between two thick dielectric cladding layers. Best example was metal nanowires, which forms the confinement in dielectric systems between the transverse components of the wave vector corresponding to transverse spatial coordinates. These metal nanowire waveguides form the leaky mode propagation of SPPs excited in prism -coupling geometries which was discussed in section.2.4.1.2. Based on the length of wire the reflections of SPPs may vary indenting to response in near infra intensity.
- For SPPs, in terms of *gaps and grooves* occurs with long ranging low field of localization. Due to the phase mismatch between the SPP modes propagating at the bottom without spreading laterally upwards. The investigations of metallic nanowires suggest that such structures allow a transverse mode area smaller than the diffraction limit. On both gaps and grooves offering sub-wavelength confinement are metal/insulator/metal waveguides, where the mode is confined to the dielectric core between the two interfaces.
- The metallic nanoparticles are responsible for guiding the electromagnetic waves between the closely coupled systems with transverse confinement. These coupling supported to one longitudinal and two transverse modes of propagating polarization waves. Further, the representation of nanoparticles as point-dipoles allowed computing quasi-static dispersion relation as solid curves. These quasi state approximations revealed the significant dispersion relation for the transverse mode near the light line. These metal nanoparticles forms vertical confinement with thin undercut silicon membrane and transverse confinement was achieved by lateral grading of nanoparticle size, thus in a sense creating a higher effective refractive index in the waveguide center. The behaviors of electromagnetic waves have unique features when interacted with different surfaces also size based interaction indicated the waves can propagate significant distractions.

The above mentioned behaviors can lead to the possible inherent attenuation losses (due to Ohmic heating) in metallic structures and can be

overcome by optical gain. For particles, optical gain results increases with magnitude polarization and decreases with line width in resonant mode. SPPs propagating at flat interfaces in the presence of gain media will result in an increase of the propagation length L . It is also shown that the localization of the fields metallic interface has to be increased [Avrutsky, 2004], contrary to the trade-off confinement with increase in gain.

10.2.3 Plasmons at Planar Interfaces

For planar interface, SPPs propagating between a conductor and a dielectric are essentially two-dimensional electromagnetic waves. These geometries with heterostructures forms weakly confined SPPs which are amenable to end-fire coupling, relying on spatial mode -matching rather than phase-matching. On exciting the planar interface with charged particles, using typical optical techniques with highly focused beams and their behavior for phase matching are presented in this discussion.

10.2.3.1 Behaviors of Plasmons at Planar Surfaces

- In diffraction metal films traditionally employ longitudinal volume plasmons which will undergo a low-lying energy loss. This energy loss $\hbar\omega_p/\sqrt{2}$ [4] is turned out to be due to the surface excitation subsequently theoretical investigations shows the sustenance of plasmons.
- In prism, Surface plasmon polaritons on a flat metal/dielectric interface cannot be excited directly by light beams since phase matching cannot achieved due to the SPP dispersion lies outside the prism light cone.
- The mismatch can overcome by patterning the metal surface with a shallow grating of grooves or holes with lattice constant 'a'. The grating can be milled directly into metal surface with depth of nanometers that can propagated towards the SPPs.

For SPPs with larger confinement, coupling with immediate vicinity of wave guide forms a phase-matched version with high efficiency.

10.2.4 Plasmons at Surface Imaging

There four prominent approaches influence the surface plasmons such as Surface near field optical microscopy, imaging based on either fluorescence

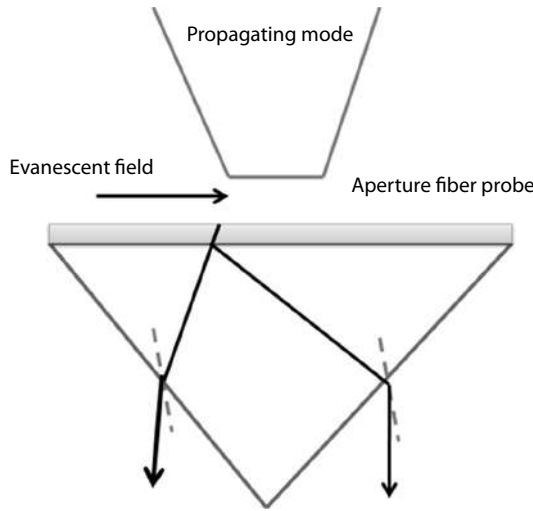


Figure 10.1 A typical setup for near-field optical imaging of SPP fields at a metal/air interface.

or leakage radiation detection and scattered light imaging. Of these four techniques, only near-field optical microscopy provides the sub-wavelength resolution required for the accurate determination of the loss/confinement ratio for spatially highly localized SPPs excited near ω_{sp} or in appropriate multilayer structures which was discussed as follows.

10.2.4.1 Principles Behind the Microscopic Techniques

10.2.4.1.1 Near Infrared Microscopy (NIM)

The metal film with collection mode uses sub-wavelength resolution called as photon scanning tunnelling microscopy and its working principle similar to the scanning tunnelling microscopy (STM). In both cases, sharp tip is brought into the immediate vicinity of the surface under study as shown in Figure 10.1 [5]. Surface plasmons for metal nanoparticles or nanostructures are studied by using Near-field optical microscopy. In case of STM, the measurement of electron between the surface and an atomically sharp metal tip were evaluated. On the other hand, photon scanning tunneling microscope (PSTM) that collects the photons by coupling with evanescent near field above the surface by propagating inside a tapered optical fiber. The near-field optical tip (also called the probe) is usually fabricated by pulling or etching an optical fiber taper with metal wrapper at the end in order to suppress the diffracted light fields. The resolution of this technique

is limited by the size of the tip's aperture, which can reach dimensions of only 50 nm or even less using etching (or more recently also microfabrication) techniques. In addition to metal-coated probes, uncoated probes are also frequently used, which have higher collection efficiency with different components of the electromagnetic field around nanostructures than probes coated with a conductive layer [Dereux *et al.*, 2001]. The fiber probe effectively acts as a local dipolar source for the excitation of surface plasmons using illumination mode [5].

In order to study the confinement and propagation of SPPs using this scheme, the tip has to be brought within a sufficiently close distance to the flat metal surface so that it is immersed in the evanescent tail of the SPP field, i.e., within a distance $\sim z$.

In this detection scheme, SPPs usually undergoes optical excitation either in prism coupling or tightly packed oil immersion in which high numerical aperture on the bottom side of the substrate is used to excite the SPPs with possible propagation constants β , but everything is inferred within the leaky modes. The very first studies of the physical properties of SPPs using near-field optical microscopy investigated the mode confinement at the interface of a thin silver film with air [5]. The excitation of electromagnetic energy is away from the spot in silver coated prism.

In this case, the propagation length of the silver/air SPP was determined to be 13.2 μm , in good agreement with theoretical modelling [5]. With evaluated experiments, to enable the direct determination of SPP with propagation length L to fit the exponential tail to the starting point of SPPs.

The initial investigations on collection mode in near field optical microscopy studied their SPP propagation based on metal strips and assessed the scattering losses on structural metal surfaces [5]. It has to be noted that the presence of probing tip can influence the dispersion with negligible dielectric effect [Passian *et al.*, 2005]. In these experiments, the light path is usually reversed: By illuminating the metal structure under study via light emanating through the sub-wavelength aperture of a fiber tip with localized modes. In addition, imaging of the spatial field distribution with illumination mode the fiber probe effectively acts as a local dipolar source for the excitation of surface plasmons. The transmitted and reflected light collected in far field on structure can be extracted using SPPs. Apart from photon collection in the far field, the investigated metal film structure can also be directly mounted on the photodiode itself, as shown by Dragnea and co-workers, which used geometric study for SPP propagation in sub-wavelength slits on a flat metal film [Dragnea *et al.*, 2003].

10.2.4.1.2 Fluorescence Imaging

Here, aperture fibre tip is responsible for emitting fluorescence molecules directly into evanescent tail placed in SPP field. The propagating frequency of SPPs lies within the broad spectral band. The intensity of the emitted fluorescence radiation is proportional to the intensity of the local field at the position of the emitters. Therefore, SPP propagation on a metal/air interface can be mapped by coating the surface with a dielectric film doped with emitters. During the operation of fluorescent molecule with their enhanced fluorescence yield which emits non-radiative quenching effect. To overcome this effect, few nanometers between the metal film sustaining the SPPs and the fluorescent molecules to inhibit non-radiative energy transfer and images can be obtained using CCD camera via dichroic mirror.

While designing Plasmon waveguides on metal strips, there is consideration of leakage radiation which laterally confined SPP propagation with prism-coupling excitation for investigating the modes in the leaky region. The light beam is targeted towards random roughness surface for direct visualization of SPP via *Leakage radiation imaging* for phase – matching which was demonstrated by Giannattasio and Barnes [Giannattasio and Barnes, 2005]. They explained the leaky radiation imaging for various substrates using silica and flat film substrates with the help of CCD camera were investigated using leakage radiation [5]. For determining more complex structured metal surface in convenient way, this scheme can be used.

10.2.4.1.3 Scattered Light Imaging

The propagation of SPPs on scattering light in metal films is imaged by collecting the random surface protrusions. Scattering at these localized bumps allows SPPs with wave vector $\beta > k_0$ to acquire a momentum component Δk_x , which can lower β into the region within the air light cone leading to coupling to the radiation with the emission of photons [5]. In flat surfaces, with good quality scattering amount will be reduced and thus making the determined properties to propagate the SPPs in simplest way along with decreased scattering. In order to map out the dispersion on modulated surfaces, light scattering from random roughness can be taken into consideration. With simple experimental set up as shown in Figure 10.2, SPP is excited by focusing a laser beam under an angle θ to the surface normal onto the grating, and the scattered light is projected onto a screen parallel to the substrate.

The polarization conversions of incoming reflected light beam are mediated via SPPs in blazed grating as shown in Figure 10.2. The reciprocal of two-dimensional plot in plane component of β is obtained by recording the intensity of the specular reflection versus incidence angle θ and the

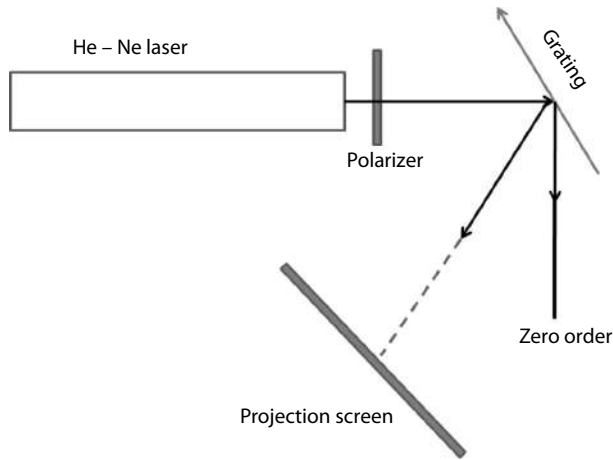


Figure 10.2 Experimental setup for diffuse scattering.

angle φ between β and the Bragg vector of the grating. For inherent surface roughness it was observed that diffuse background angular scanning (φ) is not necessary.

10.3 Plasmons at Structured Surfaces

Plasmons are collective oscillations of charge carriers in metals and semiconductors, which can propagate over extended surfaces or can be localized in engineered nanostructure, thus enabling subwavelength light confinement and a giant enhancement into specific nano-sized regions, called hotspots. This appealing property made the development of nano and microstructured devices whose plasmons are studied in the structured surfaces for various applications.

10.3.1 Graphene Based Structure

Graphene is the 2D material playing its active role in experimental and theoretical condensed matter of physics. Surface plasmons on graphene deliver its suitable alternative towards noble metals due to its atom confinement, electromagnetic fields, wavelength and tenability [6]. The interest towards the optical applications-based graphene materials produced strong electronic confinement and charge carriers' propagation lengths with possible electrostatic gate voltage. For layered structures when placed on top of each other forms the plasmonic spectrum in two fields. For real

part, it forms undamped plasmon dispersion with dielectric functions. But for imaginary part, structure forms ambiguous further investigations showed that energy loss is more for single and double layer structures based on dielectric function. For graphene on a typical dielectric substrate with relative dielectric constant $\epsilon \approx 3$ and covered by air, the plasmon dispersion is shifted to larger q -vectors, approximated by the compact formula,

$$\frac{q}{q_p} \approx \alpha \frac{E_F}{\hbar\omega}$$

Where $\omega = cq$ is the energy dispersion of the vacuum light cone, q_p is the wavenumber of the plasmon and E_F the Fermi energy of the doped graphene layer. For typical Fermi energies of $E_F = 0.3$ eV, strong reduction of the wavelength in the THz regime ($\hbar\omega \approx 4$ meV) and the Otto or Kretschmann configuration is not suitable to detect graphene's intrinsic plasmonic excitations. It was investigated by means of electron energy-loss spectroscopy (EELS) where the electronic beam was carrying the necessary momentum. These featured drawbacks can overcome by metal oxide based structures with prescribed length on substrates with its quantum charge carriers [7].

10.3.2 Metal Oxide-Based Structure

For metal oxide-based structures, plasmons response with prescribed channel length of substrates with quantum charge carriers. Carbon based materials renders susceptible to random dopant variations for deca-nanometer technology. For junction transistors doping variations in carbon materials employ insignificant diffusion of dopant atoms from junction into channel region especially for transistor applications. Therefore, for high contact resistance doping variations in carbon materials are still challenging. For metal oxide based materials with zero band gap energy ultimately no longer be an issue in contact resistance. Three dimensional (3D) topological insulators (TI) exhibits insulating energy band-gap in the bulk forms with quantum confinement which creates a energy on protected surfaces. With these fundamentals, topological insulators are exposed various applicable fields which will be discussed in upcoming sessions.

10.3.3 Dimensional Thin Films Based Topological Insulators

The material which carries the interior insulating property with movement of electrons on their surfaces falls under 2D plasmonic materials.

Materials like graphene and carbon-based materials forms topological surface states (TSS) with linear direct band – Dirac cone analogy. These materials forms timereversal symmetry for chiral protected from back scattering technology against nonmagnetic impurities. As a consequence of the timereversal symmetry, charge carriers from topologically protected surface states carry current with minimal dissipation with a subsequent reduction of the low-frequency electronic noise. For an application based on interconnects and optical data processing chips, these plasmons travelling on the surface forms a promising information carrier. The noble metals like silver and gold, considered as narrow class of materials for plasmons movements. The frequent considerable progress on plasmonic applications made in the search of infrared (IR) based plasmonic materials, most notably conductive oxides, nitrides and graphene. 2D based topological materials such as graphene, metal oxides and metamaterials with their enhanced plasmonic properties for the diverse applications will be discussed in this section.

10.3.3.1 Graphene Based Topological Insulators

10.3.3.1.1 Graphene – The Most Distinguished 2D TI

Graphene based TI's are most distinguished insulators due to their movement of electrons in gapless surface states protected by the time-reversal or crystalline symmetry. These gapless surface states helps in rectifying surface instability and chemical activity by using quasi relative dispersion described by massless Dirac Hamiltonian. These phenomenon carrying materials called as Dirac material [8].

10.3.3.2 Graphene in Spintronics Applications

The 2-Dimensional materials provide a discovery of new platform for science and technology i.e., spintronics applications. Graphene in honeycomb lattice used to study its unique electrical, thermal, and mechanical properties. For spintronic based applications, a specific property like spin relaxation time and diffusion length are considerable which particularly exist in room temperature. The challenge behind is producing spin-polarized currents at room temperature for practical spintronic applications. Spin in graphene was influenced by materials design or defects. Various approaches like atoms on surfaces, doping TM and introducing specific defects were applied for improving the device performances. The integration of 2D graphene into vertical van der Waals (vdW) with heterostructures forms 2D graphene based devices. These

devices yield novel physical properties like electron transfer and enhancing high potentials, these properties diverted to 2D electrode with ferromagnetic spin injection that provide proximity effects. Proximity occurrence by spin splitting with 2D tunable materials can provide dirac points and topological non-trivial band gap enabling a quantum anomalous Hall state along with fulfilling the emerging properties with well lattice matching, high spin polarization and strong exchange interaction. Recently, 2D materials - graphene/Cr₂C with heterostructures along with electronics properties were designed and computed using *ab initio* [9]. Since magnetic state perceived by Cr₂C can able to survive in room temperature based on molecular dynamics and it was also known to found that, hybridization interaction between Cr-3d and C-p_z states induces a large spin polarization (74%) of graphene π -bands and a large gap opening of 80 meV. The engineering of spin injection with proximity effects stands hallmark for future all-spin information processing technologies.

10.3.3.3 Graphene in Memory Based Applications

The 2-Dimensional layered materials like graphene received their significant research due to its flexibility, high electrical conductivity, high transparency, large surface area and high mechanical stability [10]. Moreover, its advantages of high density of states, high mobility, high work function, and low dimensionality compared with the conventional charge trap materials suggested that graphene could be used as the potential material in non volatile memory (NVM) devices. In order to retain the data in memory for real time applications, graphene quantum dots (GQDs) based fabricated devices were used for discrete charge trap materials that offer lateral charge movement owing to enhancing the retention of data for memory based applications. Reduced graphene oxide prepared using plasma treatments are used for NVM applications. rGO grown on ITO shows lower lattice quality due to high structural defects and topological defects after reduction. High quality and conductive rGO films grown on quartz substrates using plasma treatment will heal the lattice defects by addition of carbon atoms in clustering sp² domains. In that way, metal-insulator-metal (MIM) structure using silver nanowires/nanocomposite/rGO/ quartz were fabricated using solution deposition techniques and acted as p-type because of the interaction with the water molecules in the ambient attributed to the carbon atoms tend to share the electrons with the oxygen atoms, thus leaving hole in the carbon network [11]. On observation with optical properties, GO found to have enhanced reflection by decreasing the

transmittance and vice versa for rGO. Moreover, rGO films (MIM) has excellent electrical properties with improved carrier mobility was proven with Hall Effect measurement system. In evidence with I-V characteristics, MIM oriented developed device having a high current state even at opposite polarity indicating a write-once-read-many-times (WORM) memory device along with non-erasing capacity (dual role).

10.3.3.4 Graphene Based Topological Insulator for Thermoelectric Applications

The conversion of temperature into electric voltage and vice versa denoted the thermoelectric. Eventhough thermoelectric energy harvesting and cooling applications are envisioned, this usage is limited by poor efficiency. By increasing thermoelectric figure of merit, $ZT = S^2GT / (K_{el} + K_{ph})$ requires careful trade off between electrical conductance G , the seeback coefficient S , and the thermal conductance $K_{tot} = K_{el} + K_{ph}$. The total thermal conductance K_{tot} has contributions from both electrons K_{el} and phonons (i.e., lattice vibrations) K_{ph} . ZT quantifies the maximum efficiency of a thermoelectric cycle conversion in the linear-response regime where a small voltage $\Delta V = -S\Delta T$ exactly cancels the current induced by the small temperature difference $\Delta T = T_H - T_C$ at average operating temperature $T = (T_H + T_C)/2$. The values approaching $ZT \rightarrow \infty$ would ensure Carnot efficiency as the theoretical limit for a heat engine operating between a hot T_H and a cold T_C temperature. However, ZT of realistic devices is limited by irreversible energy losses via Joule heat and thermal conduction, so that a pragmatic goal is to achieve $ZT \gtrsim 3$ with low parasitic losses and stability over a broad temperature range. The very recent attempt was made using graphene based 2D TI nanoribbons. A simpler design using graphene with randomly distributed heavy adatoms has been conjectured using first principle studies [11]. Nanoribbons and nanopores with two end terminal set up locally enhance tiny intrinsic SOC coupling for increasing the bulk band gap. The adatoms provide sufficiently strong local SOC in some fraction of randomly chosen hexagons, so that such inhomogeneous SOC opens both the bulk band gap $EG \approx 17.3$ meV (for $nad \approx 19\%$ of hexagons covered) and generates topologically protected helical edge states. The electronic transmission through helical edge states in the form of the (approximately) boxcar function of width $\lesssim EG$ generates power factor S^2G per helical conducting channel, which turns out to be larger than the one obtained from the celebrated Mahan-Sofo model with delta-function-shaped electronic transmission function. This feature combined with 2 orders of magnitude reduction of phononic thermal conductance by

the nanopore array leads to thermoelectric figure of merit for this system $ZT \approx 3$ at low temperatures $T \approx 40$ K. Because the existing bulk thermoelectric materials are very inefficient at low operating temperatures $T \sim 10$ K (where they give $ZT \lesssim 0.01$), the TI-based high- ZT thermoelectrics at low temperatures designed by our study could be attractive for applications in radioisotope thermoelectric generators on spacecrafts or cooling of electronic satellite components.

10.3.3.5 Graphene in Sensing Applications Based Topological Line Defects

Carbon nanomaterials, such as graphene, fullerenes and nanotubes, host exciting physical and chemical phenomena and therefore are provoking a lot of scientific activity. The spatial confinement of the electronic states in such systems is key for their properties and also determines the interaction with other matter. In its ideal form, graphene consists of a two-dimensional honeycomb lattice of sp^2 hybridized C atoms. However, various structural imperfections can arise, for example line defects, for which the formation of pairs of pentagonal and octagonal rings allows the system to reduce the internal strain. This defect with fractional chirality was predicted previously for nanotubes and referring to the arrangement of the rings, is called 8-5-5-8 topological line defect [12]. It has been observed from the literature, as-grown graphene and can also be induced in a controlled fashion by electron irradiation. In general, the intentional introduction of defects into graphene is a topic that currently receives enormous attention, because it can lead to a multitude of applications. It was found that, graphene nanostructures (nanoribbons) offer high magnetoresistance which lead to enhance scattering and little control over the material properties. Moreover, growth on substrates, it introduces disorder and these disorder occurs with metal atoms further introduces spin polarization in graphene. The magnetic effect can be tuned by varying Fermi energy since adsorption and desorption on surfaces are largely controlled by surface defects. The interaction between graphene and metal atoms with magnetoresistance and spin polarization helps to magnetic sensor applications.

Another such line defects based topological insulator can be applied to gas sensing applications. It has shown that Schedin *et.al.*, [13] capability of detecting the single molecule adsorbed on graphene based sensor increases the device conductivity for acceptor molecules (e.g., H_2O and NO_2) and decreases in conductivity was monitored in case of electron donors (e.g., CO and NH_3). On the other hand, to increase the sensitivity

dopants or vacancies can be introduced in graphene based nanosensors. A good sensor possesses three basic features:

1. It should possess larger binding energy in which rendering the device non-responsive after the single use.
2. It should present significant sensitivity
3. Selectivity to different gases.

The line defects in graphene possess higher chemical reactivity that enhances the responses for sensing applications.

One-dimensional wires embedded in a pristine graphene sheet by applying a suitable part with appropriate gate voltage will enhance the chemical reactivity of atomic sites along the line defects, yields high promising system to act as a highly sensitive and selective gas sensor. Density functional theory (DFT) was performed for geometry relaxations and electronic structure calculations for generalized gradient approximations (GGA-PBE) using SIESTA code for correcting the vander waals interactions. Structural relaxations were carried out until residual force on each ion reaches lesser than $0.01 \text{ eV/\AA}$.

The development of DNA sequencing tools has advanced in strides over the past decades. Nonetheless the cost for sequencing a genome is yet too expensive for widespread use in personalized medicine. Nanopores have been heralded as a possible way of providing low-cost whole-genome sequencing by measuring either ionic currents as DNA translocates through a nanopore on a membrane or transverse electronic currents across the membrane itself. 2D materials represent the best possible surface to volume ratios - a key ingredient in detection - single molecule recognition remains challenging, especially if one is looking for all-electronic methods. Lower signal to noise ratio have not able to provide sensitivity but this property rendered its use in DNA sequencing. Indeed, reducing the dimensionality is a possible path towards improving sensitivity. An added advantage of this arrangement is that the overall stability of graphene is maintained while allowing for atomically precise edges. Use a combination of quantum mechanics/molecular mechanics (QM/MM) hybrid methods, and non-equilibrium Green's functions (NEGF) to investigate the electronic conductance modulation along extended line defects connecting a nanopore explicitly including the effects of the solvent.

By sampling over a large number of different orientations, distinction between four nucleobases was achieved. The change in electron movement across specific molecular states near the Fermi level and their respective coupling to the pore were configured [14].

10.3.4 Piezotronics Based Topological Insulators

Piezoelectric semiconductors have the coupling properties of piezoelectric and semiconductor, such as ZnO, GaN, InN and CdS. The emerging fields of piezotronic and piezophototronic have attracted much attention for flexible energy harvesting and sensor applications. A series of multifunctional electromechanical devices have been developed by nanostructure piezoelectric semiconductor, such as nanogenerator, piezoelectric field effect transistor, high-sensitivity strain sensor, piezo-phototronic photo-cell and LED. Piezotronic logic devices based on strain-gated transistors can convert mechanical stimulus to digital signal for logical computation. Taxel-addressable matrices and photon-strain sensor arrays have been fabricated for integrated chips. Furthermore, nanogenerator and piezotronic transistor have been developed by single-atomic-layer MoS_2 . For high sensitivity of piezotronic and piezophototronic devices plays a key role by controlling carrier generation, transport and recombination. By using the density functional theory, our previous theoretical studies used width carrying charge distribution for different combination with metal and semiconductors [15, 16]. For designing piezoelectric wavelength semiconductor based quantum devices were used such as ZnO nanowires, MoS_2 and CdTe quantum dot devices for various diversified applications.

The topological insulator piezotronic transistor based on HgTe/CdTe quantum well structure has been proposed [17] which consists of two layers carrying HgTe and CdTe were sandwiched each other forming a quantum well with inverted band. The quantum wells are responsible for electron transport modulated with induced stain. This type of Piezotronic transistor based on topological insulator can be used for high performance and ultra-low power consumption switch, logical unit and strain sensor applications.

The coupling of piezoelectric polarization with semiconducting properties resulted in both novel unprecedented device applications which give rise to piezotronics concept. The conceptual understanding behind it, that carries the stain induced polarization charges at interfaces can effectively modulate junction/contact with concentrated free carriers leading to semiconducting devices.

10.3.4.1 Fundamental Physics of Piezotronics and Its Applications

Metal Oxide based system forms the modular approach for studying the fundamental effects in piezotronics. Zinc oxide is used as the modular material system to elaborate the fundamental effect in piezotronics. It is

chosen not only because it is a representative piezoelectric semiconductor material, but also for its easy, low-cost and controlled synthesis at low temperature. Since immobilization of polarization charges in ZnO interfaces reduces inversion symmetry with modular doping in order not to diminish dielectric property unless it is not applied to other piezoelectric semiconductors (section 3.4). These interfacial ionic charges are capable of inducing considerable modulation to charge carrier distribution and the adjacent semiconductor/metal which forms junction/contact with ZnO.

M-S contact is a basic structure in semiconductor and optometric electronics. When metal and semiconductor come into contact, a significant redistribution of charge takes place. This is due to the overlap of wave functions from both the metal and semiconductor that leads to the formation of interface with electron movements (Fermi level) along with induced energy barrier. The induced energy barrier at the interface due to the alignment of Fermi levels results in a net charge transfer and an abrupt discontinuity, which is the Schottky barrier with barrier height of Φ_{Bn} . Schottky Barrier Height (SBH) is a measure of the mismatch of energy levels for majority carriers, which dictates the transport of charge carriers across M-S interface and is critical for operation of related semiconductor device. The semiconductor material is also piezoelectric material in which Schottky barrier formed between piezoelectric semiconductor and metal, the strain-induced negative piezoelectric polarization charges induced at the semiconductor side near the barrier interface can repel the electrons away from the interface, resulting in further depleted interface and increased local barrier heights while the positive piezoelectric polarization charges created at the semiconductor side can attract the electrons toward the interface, giving rise to less depleted/accumulated interface and hence decreased local barrier heights. The strain-induced polarization charges can hence directly affect the local contacts at the metal-semiconductor interfaces and the transport of charge carriers across the M-S contact by exerting substantial influences on the concentration/ distribution of free carriers in semiconductors and on modulation of electronic charge in interface states or metal, depending on the crystallographic orientation of the piezoelectric semiconductor material and the polarity of the applied strain. M-S based strain induced polarizations can be applied for various applications like Flexible strain sensors which are used for structural health monitoring and mechanical testing. Piezoelectric strain sensors carrying a metal semiconductor-metal interface are well-suited for the above mentioned applications due to their high sensitivity and fast response times [18–22].

10.3.5 Metamaterials Based Topological Insulators

Metamaterials(MM) are a manmade structure which provides exotic properties such as negative index of refraction that is not supported by natural materials. MM consists of an array of sub-wavelength resonators to provide electric(negative permittivity), magnetic(negative permeability) or electromagnetic response(negative refractive index) at the desired frequency. Generally, metals provide negative permittivity characteristics at the visible frequencies and some ferrite provides a magnetic response at lower frequencies. These characteristics could be achieved at any frequency by properly optimizing the structure of the resonators, the geometrical parameters and the material properties [23].

10.3.5.1 Operation Principle

The response to the incident EM wave for a material is characterized by two parameters namely permittivity and permeability. These properties are distinct for materials based on their atomic configurations. But metamaterials are manmade structures with their size less than the operating wavelength. These structures seem invisible to the incident EM wave and all the structures behave collectively and each structure act as a dipole in materials. By this means it achieves electric (negative permittivity) and magnetic response (negative permeability). Further, the index of refraction related with ϵ and μ as,

$$n = \sqrt{\epsilon\mu}$$

From the above equation, it is concluded that when both permittivity and permeability is positive, the refractive index is a real and positive value which allows wave propagation. If anyone of the two parameters is negative refractive index becomes imaginary which inhibits the wave propagation. When both these are negative, the refractive index is a real but negative value which allows the wave propagation in a reverse direction.

10.3.5.1.1 Classification of Materials

The material electromagnetic response is characterized by their permittivity and permeability and it is represented in Figure 10.3. It has been divided into four quadrants with respect to the sign of permittivity and permeability [24].

1. A medium with both permittivity and permeability are positive called double positive medium (DPM). This provides normal electromagnetic wave propagation.

2. A medium where the permittivity is negative and permeability is positive called ϵ -negative medium (ENG). No wave propagation is allowed through this medium.
3. A medium with both permittivity and permeability are negative called double negative medium (DNG). This provides backward electromagnetic wave propagation.
4. A medium where the permittivity is positive and permeability is negative called μ -negative medium (MNG). No wave propagation is allowed through this medium.

10.3.5.2 Mapping of MM with TI

Recently, MMs are being utilized in sensing of biological and other chemical samples, imaging and security applications, as modulators and so forth. One of the recent advancement in the field of the metamaterial is that it has certain similarities with the topological concepts. This makes MM as an emerging area to be looked into in the new direction, mapping of topological insulator and other topological phase transition concepts. The concept of magneto-electric coupling also referred as bianisotropy in metamaterial resembles spin-orbital coupling of electrons in the solid state [25, 26].

The topological insulators are characterized by the property 'spin-locked' which makes it insensitive to local defects, structural disorders etc. This exotic phenomena valued in electromagnetic where it is analogous to a state appears in magnetic photonic crystal and other bianisotropic metamaterials. Another interesting topological concept is an optical topological transition (OTT) which usually occurs in the hyperbolic metamaterial.

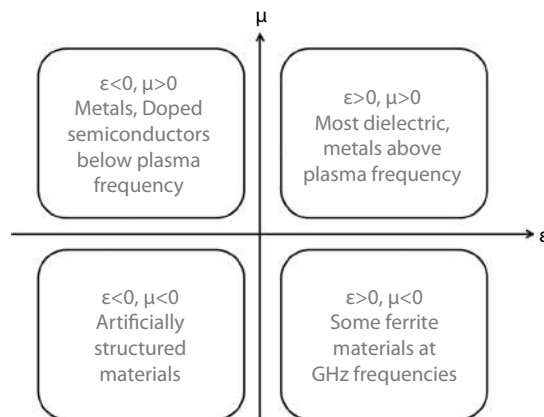


Figure 10.3 Classifications of Materials.

This structured metamaterial supports contour frequency regions which is a contrast to the elliptical contours found in conventional dielectrics. This also results in a sudden increase in the photonic density of states (PDOS) and further this is used to manipulate the light-matter interactions in a photonic environment [27].

The metamaterials consist of metal-dielectric structures. There are some major issues to be addressed in metamaterials are the fabrication method for creating the sub-wavelength features and losses associated with the metals. For fabrication, usually lithography techniques are preferred and sometimes imperfections in the created structure may occur. This imperfections further leads to local disorder and defects. In terms of electromagnetic performance, this results in broadening of resonance and back reflections also. The problem associated with the fabrication issue could be minimized by keeping the designs in a simple manner.

The presence of metals in the metamaterials provides certain lossy nature and leads to performances degradation. Recently, all dielectric metamaterials and MM based on transparent conducting oxides have received greater attention to overcome the issue of metallic losses. The phase mismatch occurs between the high-k states in the metamaterial and free space should also be minimized which affects OTT in the metamaterials. But nonmetallic plasmonic materials and advanced fabrication technique will definitely mitigate the above-mentioned issues. But still, the lossy metamaterials based OTT could find its place in high-quantum efficiency LEDs and in isolators also. Though these metamaterials have certain issues and impose challenges it provides a solution to two important issues in photonics. The first thing is, the topologically protected MM offers a solution and make less severe in disorder-induced scattering and the second thing is OTT to manipulate the light-matter interactions [28].

The topological description is used to understand and classify the atomic solids. Atomic solids with nontrivial topological are robust to transitions which could modify the symmetry of the atomic solids. Such examples are a topological insulator, integer quantum Hall effect (IQHE) and fractional quantum Hall effect (FQHE). In general, external magnetic fields are applied to create a topological band in two-dimensional metamaterials. But it is possible to develop a topological frequency band structure in the lattice of 2D electromagnetic metamaterial without applying external magnetic fields. This occurrence of topological band arises from a one-way guided modes concept in the MM. This concept is used to create a superconducting transmission lines based coupled-cavity lattice or developing cavity type QED components. Also, this is used to simulate a fractional quantum Hall effect (FQHE) [29].

The Dirac equations form the foundations of quantum mechanics which is extensively used in many applications include high energy physics and condensed matter such as Graphene and topological insulators. It actually predates the existence of an anti-particle of electron called positron. Also, it is used as a key to understand the phase transitions of insulators to superconductors and superfluids. Similarly, Maxwell's equations are basics of electrodynamics which is also used to describe the exotic phenomena occurrence in the metamaterials. With a great interest, the researchers have tried to link the relationship between chirality in metamaterials to the topological concepts in condensed matter. In literature, different lattice structures have been designed and obtained the Dirac point which describes the link between the topological insulators and the electromagnetic media. From the Dirac point, the topological invariant is calculated. The mapping of TI with metamaterials offers the flexibility of controlling the effective permittivity and permeability.

The first proof-of-principle of mapping topological concepts with left-handed chiral metamaterials have been done by Tan *et.al.*, This establishes the relation between the two independent groups namely topological concepts and electromagnetic. This is done by mapping Maxwell's equations to Dirac function. The main observation is, the metamaterial could be used to simulate the topological order in the condensed matter in a controlled environment. By using Dirac equation, the effective mass is calculated from the permittivity and permeability of the electromagnetic media. But the sign of mass relates with the topological order which further used to describe the photonic counterparts. The band inversion in Dirac function is due to the chirality change in the metamaterial. The band inversion of the Dirac equation is theoretically modelled and the corresponding results are obtained.

Further, the transmission lines are designed and fabricated on a copper clad RT5880 substrate. The numerical simulations are carried out using CST Microwave studio software. The fabricated structure is characterized for transmission and reflection properties using PNA network analyzer in the frequency range of 10–20 GHz. The density of states is also calculated. The electric field characteristics in the time domain are evaluated by applying a monochromatic wave to the transmission line. After applying the signal, the voltage value at different point is measured using high impedance probe. But at one point near shunt inductor, no LC resonance is observed. This shows a proof for mapping of topological transition concepts to the electromagnetic metamaterials. This also represents an explicit mapping of Dirac equations to Maxwell's equations. Thus by controlling the properties of metamaterials topological concept can be achieved [30].

A nontrivial topological concept in photonics has been demonstrated with the help of periodic photonic crystals. A new effective medium approach has been described to achieve protected topology photonic surface against local disorders and defects. This has been obtained using metamaterial based homogeneous medium where nontrivial arises from the concepts of transversality of electromagnetic waves. This acts as an intermediate between the classical optical phenomena and the topological concepts. In this, the topologically protected surface occurs between the chiral hyperbolic metamaterial and a vacuum. In 2D photonic crystals, the topologically protected surface relies mainly on the nonlocality and the band structure. The resultant phase obviously depends on the isolated fourfold degeneracies that occur within the permittivity and permeability. But in chiral hyperbolic MM, it originates from the concepts transversality in Maxwell's equations. Instead of using complex photonic crystal structure, simple material parameters based control on nontrivial topology happens in MM [31].

It is also possible to achieve metamaterial functionalities using thin film topological insulators. To prove this concept, a mechanism to control the helicity of Dirac fermions in thin film topological insulator is identified and demonstrated. The helicity determines the physical parameters of the particles. This provides the tunable nature of chiral metamaterial. Using first principles it is shown that helical splitting in the band structure occurs under an external magnetic field in a crystalline topological insulator $\text{SnTe} \langle 111 \rangle$. Based on this, many helicity based results such as electronic dichroism, negative refraction and birefractance have been demonstrated. The analogous to LH and RH property in MM, the helicity changed of Dirac fermions in thin film topological insulators is verified. Like spintronics and valleytronics, the helicity-based electronics will be dominating the future [32].

The hyperbolic metamaterials exhibit a topology transition from an ellipsoid to hyperboloid in a photon iso-frequency contour. This increases the photon density of states further which could affect the electronic and optical properties of the material. It has been proposed and demonstrates that high T_c superconductors can exhibit similar hyperbolic metamaterial behaviour in the far infrared and terahertz (THz) frequency range. It is noticed that hyperbolic metamaterial behaviour occurs only in the normal state whereas photon propagation is not allowed in the superconducting state. This indicates the occurrence of a topological transition in the superconductor at zero temperature with an external magnetic field. In this, Minkowski spacetime occurs in the mixed state of superconductor at some critical point of the external magnetic field. Then nucleation of Minkowski spacetime happens.

To understand the topological transition in a high- T_c superconductor, Bismuth strontium calcium copper oxide (BSCCO) has been identified and there are many reasons for selecting this particular material. This BSCCO exhibits the strongest anisotropy in all the ways; in high-quality crystal, the DC conductivity ratio of 10^4 has been noticed from in-plane to out of the plane, in-plane AC conductivity obeys Drude model while the AC conductivity perpendicular to copper oxide plane is insulating, anisotropy is also observed in the superconducting state. This anisotropy is the important component needed for exhibiting topological transitions. It is observed that at the frequencies of interest this material acts as a non-magnetic one because the permeability of BSCCO is equal to one at higher frequencies. From numerical simulation using COMSOL Multiphysics, it is verified that BSCCO when $\omega < 180 \text{ cm}^{-1}$ it deny the photon mode propagation in the superconducting state. And, hyperbolic appearance in the far infrared and THz range of $2400 \text{ cm}^{-1} < \omega < 4800 \text{ cm}^{-1}$ and another $200 \text{ cm}^{-1} < \omega < 1200 \text{ cm}^{-1}$ respectively. Using numerical simulation these concepts have been confirmed [33].

The topological insulators could also be used as a dielectric substrate in making metamaterial configuration to obtain the tunable optical properties. This optical tunability is achieved while some changes occur in the refractive index value. One common configuration of MM reported earlier is, use of bismuth selenide (Bi_2Se_3) as a dielectric layer between two gold metallic layers. It has been demonstrated that the designed structure (Au- Bi_2Se_3 -Au) achieved negative refractive index in the near infrared region (NIR). Bismuth selenide exists in two forms trigonal and orthorhombic phases respectively. The studies reveal that the bismuth selenide TI has a different optical dielectric constant for these two phases in the NIR region. The proposed structure consists of an array of elliptical nano-holes with a pitch value of 400 nm and the diameters are 240 nm, 120 nm in the x and y-axis respectively. The thickness of the gold and bismuth selenide is kept as 30 nm and 60 nm correspondingly.

A numerical simulation was done using finite difference time domain (FDTD) method. It uses periodic boundary conditions in the x-y plane and perfectly matched later absorbing condition (PML) in the z-direction with plane wave normal incidence. In modelling the gold layer is defined using Drude model. In NIR region, the dielectric constant of the bismuth selenide lies 29–34 for trigonal structure and 20–22 for the orthorhombic phase. The shift from trigonal to orthorhombic can be achieved by varying the pressure and temperature values. In this work, the transition is achieved by changing the pressure from 2 to 4.3 Pa at 500 °C. This way the tunability of dielectric properties in the NIR region has been achieved

which further changes the refractive index of the metamaterial. When this phase transition occurs, a shift 370 nm (2140nm to 1770nm) has been achieved in the NIR region. By this mean, it is easier to achieve the tunable MM. The designed blueshift tunable MM has potential applications as switches and modulators in the NIR region [34].

Plasmon resonance in topological insulators can be used to make tunable THz devices. All materials exhibit unique phonon resonant behaviour in the THz frequency range. Plasmon-phonon interaction will open up a new avenue for the researchers working in the THz community. To explain this further, a ring pattern has been fabricated using a thin film bismuth selenide TI by using electron beam lithography and chemical etching technique. The bismuth selenide exhibit phonon resonance at 2THz. Initially, a numerical modelling has been developed based on the THz conductivity of the material. The ring patterned developed on TI thin film supports plasmonic behaviour. The interaction between Plasmon-phonon in TI thin film is characterized using THz spectroscopy. By changing the diameter of the ring pattern, tunable devices can be easily made by exhibiting a bonding and anti-bonding Plasmon modes. This concept arises from the existence of Dirac electrons from the discovery of Graphene etc. Because this characteristic also exhibited by the topological insulator.

It is also possible to obtain topologically protected surface in metawaveguides. Consider an array of metallic cylinders which are supported by two metallic plates and one side attached to them. This kind of configuration supports reflection free waveguiding in the sharp corners which produce bianisotropy nature and act as a topologically protected band. This has proved the tunable spin-orbit interaction emulating Kane-Mele Hamiltonian. This structure works at terahertz frequencies and compared to other metamaterials, this can be easily scaled to work at other frequencies and no ohmic losses also occur. This kind bianisotropy metawaveguides has potential applications in optics and electromagnetic with a reflectionless transmission of electromagnetic energy.

An experimental demonstration of photonic topological insulator (PTI) based on gyro and star Meta atom in the metacrystal waveguide was done. The problem with permittivity/permeability matching based metamaterial for producing topologically protected surface is that the material is highly dispersive in nature. This dispersive nature causes narrowband response characteristics. To obtain a broadband resonance a combination of non-bianisotropic and nonresonant metacrystal cooperated into the waveguide is developed. This induces a topologically protected region. A numerical simulation of the proposed structure is done using COMSOL Multiphysics software. The fabrications of these structures are done using conventional

etching process. The nontrivial bandgap is confirmed by calculating the non-zero spin chern numbers and by obtaining experimental transmission spectrum. The underlying mechanism of this non-trivial topology is by coupling of transverse electric and transverse magnetic modes in the metacrystal waveguide. By this technique, ϵ/μ matching is done to obtain the broadband resonance characteristics. Thus experimentally broadband resonance based non-trivial topology is experimentally verified [35].

To avoid the ohmic losses in metallic-based waveguide and metamaterial, all-dielectric metamaterials, metacrystal could be alternatively used. This has been confirmed by creating 3D all-dielectric photonic topological insulator. In three dimensional systems, the same non-trivial topology occurs in 2D systems can be obtained. The first theoretical demonstration of three dimensional all-dielectric metamaterials is done. A classical toy based model is utilized to obtain the relativistic fermions behaviour. In this, the excitations of surface states in the system are due to Jackiw–Rebbi excitations. The concepts of using dielectric and semiconductor-based materials provide an opportunity for avoiding magnetic materials and necessity of external magnetic fields. This develops surface states along the 2D edges which are confirmed using first principle studies and also an electromagnetic duality exist between electric and magnetic fields [36].

Mechanical metamaterials provide exotic properties such as negative Poisson ratio, negative compressibilities and so forth. The main issues to be addressed in mechanical metamaterials are mechanical instability. Recently, tunable metamaterials with good mechanical stability have received many attentions these provide a negative Poisson ration, a tunable vibrational response, good elasticity behaviour etc. Though topological floppy modes have been developed from mechanical structures they are susceptible to global structural damage. To obtain the local flexibility and global stability a geared topological metamaterial is proposed. The structure consists of local solid link with a pair of gears mounted on it. This network avoids the gears sliding against each other in the same structure. This network also provides rotational and translational degrees of freedom which are essential for a tunable operation which is due to the absence of zero energy mode collapse. This concept can be utilized in colloidal and molecular assemblies system.

To obtain a tunable and dramatic change in the domain structure could be obtained by applying a soft strain to the system. It is easy to obtain tunable mechanical and acoustic properties for a reversibly deformable system with external soft strain. Though the applied strain is low value, the sound speed and edge stiffness will be changed in the order of magnitudes. The classification tunable topological metamaterials are based on soft

elastic deformation i.e. it requires a flexible hinge to connect the domain structures. These can be fabricated easily by conventional lithography or 3D printing technology [37, 38].

The applications of tunable topological metamaterials are as car components for absorbing the energy to reduce the load, gecko pads, nanotechnology-based therapy and so forth.

10.4 Nanostructured Thin Films and Its Applications

10.4.1 Plasmonic Applications

The fundamental approaches are recognizable with development of two-dimensional (2D) patterned nanostructures. These nanostructures have dependent properties based on the substrates and structure formation which made the intensive research in order to produce facile, inexpensive, efficient, and flexible nanolithography technique for preparing functional 2D patterned nanostructures with high reproducibility. Polystyrene (PS) formed the hexagonal self assembled spheres and applied to various fields like sensor, solar cells, photocatalysis, surface enhanced Raman scattering (SERS), light-emitting diodes (LED), antireflection layer, hydrophobia structures and so on. Nanocrystals with tunable localized surface plasmon resonance (LSPR) have significant applications towards medicine, sensing, electrocatalysts and microelectronics devices.

2D patterned VO_2 nanocrystals were studied earlier with different nanostructures. The periodicity of structure achieves down to 200 nm with sub-100 nm of nanoparticle size, while the area of samples can reach up to centimeter-scale. Their size-, media-, and temperature-dependent LSPR tunabilities in near infra-red (NIR) range are observed. LSPR red-shifts are observed with increase of the particle size and the media reflective index, respectively, while the relative LSPR intensity can be dynamically adjusted by varying temperature which has shown good performance in thermochromic smart window application [39].

10.4.2 Biomedical Applications

Early detection of viral diseases is a serious public health, homeland security and armed forces issue. Recently, Label-free biosensors have emerged as promising diagnostic tools for cancer and infectious diseases. These sensors circumvent the need for fluorescence/radioactive tagging or enzymatic detection, and enable compact, simple, inexpensive point-of-care

diagnostics. Various sensing platforms based on optical, electrical and mechanical signal transduction mechanisms have been offered for applications ranging from laboratory research to clinical diagnostics and drug development to combating bioterrorism. Among these sensing platforms, optical detection methods are particularly promising. Optical biosensors allow remote transduction of the bio molecular binding signal from the sensing volume without any physical connection between the excitation source and the detection channel. However, a drawback of optical biosensors is that they require precise alignments of light coupling to the bio-detection volume.

Nanoplasmonic biosensors are distinctive among photonic sensors as they allow direct coupling of the perpendicularly incident light and constitute a robust sensing platform thereby minimizing the alignment requirements for light coupling. Also, this property opens up opportunities for multiplexed detection. In addition, the extraordinary transmission (EOT) signals in nanoplasmonic biosensors create an excellent detection window enabling spectral measurements with minimal background noise and high signal-to-noise ratios. Recently, optofluidic nanoplasmonic sensors enable direct detection of intact viruses from biologically relevant media in a label-free fashion with the quantity of sample preparation (little to no sample preparations). Their main focus is in detection and recognition of small, enveloped RNA viruses [23, 24].

Similarly, surface plasmon resonance (SPR)-based assay is used for label-free, high-throughput exosome protein analyses. This system uses optical transmission through periodic nanoholes rather than total internal reflection. Significantly, new SPR chip, namely nano-plasmonic exosome (nPLEX) sensor, comprises arrays of periodic nanoholes patterned in a metal film [40]. Each array is functionalized with affinity ligands for different exosomal protein markers. With target-specific exosome binding, the nPLEX sensor displays spectral shifts or intensity changes proportional to target marker protein levels. Compared to conventional methods, the nPLEX technology offers highly sensitive and label-free exosome analyses and enables continuous and real-time monitoring of molecular binding.

Thus, 2D patterned nanostructures were applied to various fields like medical, sensing, imaging and photovoltaics.

10.5 Summary

Two – Dimensional patterned thin films based Topological Insulators are beginning to make significant impact towards plasmonic applications.

Basic fundamentals from the past on topological insulators created the adaptive techniques towards various materials. The nanotechnological applications talked about in this part are just a little subset of an immense scope of advances that are occurring, at a fast pace. The applications based on spintronics, thermoelectric and sensing using graphene were discussed in this chapter which is a multilayered excellent topological insulator. Piezotronic applications using piezoelectric materials and its applications directed to sensor for mechanical testing and energy harvesting were discussed. Piezoelectric based materials are the fundamental representatives for topological insulators.

Metamaterials based topological insulators used to develop THz devices for antenna, sensing applications which are discussed in this chapter. However, new developments based 2D thin films keep on making their effect felt towards nanostructures for different applications. This is obviously an essential research requirement for the future.

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Abstract	Vitamins are substances that are required by the human body for enhanced growth and development. Altogether thirteen types of vitamins are essential for the normal functioning of the body. The vitamins are broadly classified as water-soluble and fat-soluble vitamins which are further distinguished as vitamin A, B, C, E and K. The water-soluble and fat-soluble vitamins are separated and purified using various techniques such as capillary electrophoresis, HPLC and chromatography. Ion-exchange chromatography is being the most popular. It plays a major role in various environmental applications such as ecological remediation, water softening, catalysis, hydrometallurgy, wastewater treatment and biomolecular partitions. Various synthetic resins and several other resins have been used for the separation and purification of the vitamins. An overview of the different methodologies involved in the process of ion-exchange chromatography used in the separation and purification of vitamins B1, B2, B6, C and K1 is presented in this chapter.	
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Chapter 9

Separation and Purification of Vitamins: Vitamins B1, B2, B6, C and K1



P. Senthil Kumar and G. Janet Joshiba

Abstract Vitamins are substances that are required by the human body for enhanced growth and development. Altogether thirteen types of vitamins are essential for the normal functioning of the body. The vitamins are broadly classified as water-soluble and fat-soluble vitamins which are further distinguished as vitamin A, B, C, E and K. The water-soluble and fat-soluble vitamins are separated and purified using various techniques such as capillary electrophoresis, HPLC and chromatography. Ion-exchange chromatography is being the most popular. It plays a major role in various environmental applications such as ecological remediation, water softening, catalysis, hydrometallurgy, wastewater treatment and biomolecular partitions. Various synthetic resins and several other resins have been used for the separation and purification of the vitamins. An overview of the different methodologies involved in the process of ion-exchange chromatography used in the separation and purification of vitamins B1, B2, B6, C and K1 is presented in this chapter.

AQ1

9.1 Introduction

Vitamins are one of the major fundamental compounds required by the human body to carry out every enzymatic and chemical reaction. Vitamin molecules cannot be integrated directly by human beings and therefore must be derived from the dietary compounds [1]. Vitamins are important nutrients providing components which cannot be produced naturally by the human body. In any case, not all fundamental natural supplements are grouped as vitamins, for example, fundamental unsaturated fats and basic amino acids. The vitamins are subdivided as fat-soluble and water-soluble. Water-soluble vitamins, after retention from dietary foodstuffs, are disposed of significantly more rapidly than fat-soluble vitamins, which can be held in greasy tissues [2]. Vitamins are highly essential for the development and metabolism of the human body. The food from the animal sources such as meat, milk and eggs occupies the

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top position in the food chain, and it remains as the best sources of these vitamins [3].

9.2 Significance of Vitamins

Vitamins are very much essential on a daily basis for the proper functioning and metabolism of our human body. The inadequacy of vitamins in the eating regimen prompts many serious and deadly disorders. Many researchers have proved that the percentage of diabetes, tumour, heart and metabolic disorders has increased with the lacking supplement of vitamins amid adolescence and adulthood. Vitamins can be mainly derived through the balanced diet, other than that the vitamins cannot be synthesized by the human body. In recent decades, most of the creatures have lost the capacity to synthesize and integrate vitamins due to our evolution and development. Even though the Homo sapiens lose the capacity to orchestrate the vitamin compounds that are highly required for the survival and growth of the human beings, vitamins have been in pervasive also, copious supply inside the natural way of life [3].

9.3 Classification of Vitamins

The thirteen known vitamins are isolated into two classes in the light of their relative dissolvability in water and fat. Vitamins are broadly classified into two groups such as (a) water-emulsifiable vitamins and (b) fat-emulsifiable vitamins. The B-group vitamins and vitamin C come under the category of water-emulsifiable vitamins, whereas the vitamins such as A, D, E and K belong to the category called fat-emulsifiable vitamins [4].

9.3.1 Water-Soluble Vitamins

These vitamins are soluble in water, and they are excreted out from the human body through urine. The fluctuation in the fat absorption does not alter the function of the vitamin and its water absorption capacity. These vitamins function as coenzymes in several chemical reactions, and these also aid in improving the energy metabolism. The B-group vitamins and vitamin C are water-soluble. Among these, the thiamine, riboflavin and vitamin C are highly sensitive to heat and alkalinity. The water-soluble vitamins are easily degradable and difficult to store properly. Water-soluble vitamins are washed off and destroyed easily, and proper storage is very crucial. The B-group vitamins are distinguished as B1, B2, B3, B6 and B12. The water-soluble vitamins



are difficult to separate and purify due to the complex structure and highly unstable nature [5].

9.3.2 *Fat-Soluble Vitamins*

The fat-soluble vitamins are readily soluble in fat-dissolving substances but insoluble in water. Fat-dissolvable vitamins, including vitamins A, D and E, are required for a wide assortment of various physiological related activities. These vitamins require the fatty substances for their transfer and metabolism, and hence found in substances associated with high lipids. The adequate amount of bile flow and micelle formation enhance the absorption of fat-soluble vitamins and easily absorbed through the dietary fats. The fat-soluble vitamins are stored in the liver and cause serious threat when consumed in a higher amount, and also the excretion of these vitamins generally proceeds at a slower rate. Chylomicrons help in the transport of the fat-soluble vitamins from the lymph nodes to the liver. The vitamins A, D, E and K are the various types of fat-soluble vitamins. In the course of recent decades, insufficiencies of these vitamins have been related to expanded danger of a tumour, type II diabetes mellitus and various invulnerable framework issues.

9.4 Sources of Vitamins

Vitamins are derived from various food sources and are the fundamental needs of every human being for their growth and development. Some of the sources of certain vitamins are explained below:

9.4.1 *B Vitamins*

The B-group vitamins (B1, B2, B3, B6 and B12) help in digestion, cell repair, boosting metabolism and immune system. Some of the best food sources containing B-group vitamins are bananas, dates, broccoli, spinach, potatoes, asparagus, seeds, pulses, figs, nuts and dairy products.

9.4.2 *Vitamin C*

Vitamin C plays an immense role in boosting the immune system and growth of the individual. It helps in reducing the risk of high blood pressure, cholesterol, anaemia and several other diseases. Mostly, citrus fruits are the major source of vitamin C,



and some of the other food sources which are abundant in vitamin C are broccoli, spinach, green pepper, peas, potatoes, lemons, strawberries, pears, lime, chicken, seafood and pork.

9.4.3 Vitamin K

Vitamin K plays an important role in the blood clotting process in the body and helps to maintain strong bones. Some of the food sources containing vitamin K are meat, liver, egg yolk, whole grain, vegetables, Brussels sprouts, celery, parsley, iceberg lettuce, peas, asparagus, cabbage, cucumbers, broccoli and soya bean.

9.5 Vitamin Deficiency Disorders

Vitamins in nourishment are fundamental for the typical improvement of body capacities; thus, the nonappearance of vitamins can cause genuine physiological issues [6]. The insufficient amount of vitamins in the human body weakens the system, and it leads to some of the serious health complications. The vitamin deficiency disorders are distinguished into three main categories such as avitaminosis, hypovitaminosis and hypervitaminosis. The avitaminosis is a disorder caused due to the deficiency of one or other vitamin. The overloading of any one of the least water-soluble vitamin in the human body leads to the disorder called as hypervitaminosis, whereas the deficiency of any one of the vitamins leads to hypovitaminosis [4]. The multivitamin tablets are frequently utilized to improve the strength of the human body and are used in various therapeutic applications [5]. The insufficient amount of some fat-soluble vitamins causes some of the pathetic disorders. The vitamin A deficiency causes a bone disorder known as osteomalacia and night blindness. The shortage of vitamin E and vitamin K causes threatening disorders such as oxidative cell stress and haemorrhage [7]. Regardless of the significance of vitamins for our bodies, however, additional supplement of vitamins will prompt high stockpiling of vitamins in our bodies which will cause some harmful effects to our system known as hypervitaminosis. The hypervitaminosis is mainly caused due to the administration of a heavy dosage of the vitamin from pharmaceutical sources and improper monitoring of the dosage level of the vitamin to patients. The hypervitaminosis is diagnosed with some symptoms such as amenorrhea, weariness, bone and joint torment, gastrointestinal issues, weight reduction and severe pain in bone and joint [8].

9.6 B Vitamins

The B-group vitamins are composed of various emulsifiable vitamins such as B1, B2, B3, B6, B8, B9 and B12. These vitamins are mostly synthesized using the micro-organisms [4]. B-vitamins remain as an excellent coenzyme to a significant extent of the enzymatic procedures that support each part of the physiological working cell. As a coenzyme, the organically dynamic type of the vitamin ties inside a protein “apoenzyme” making a “holoenzyme”, in this manner expanding the resultant protein’s ability as far as the assorted variety of responses that it can catalyse. The B-complex vitamins are mostly derived from plants, particularly from the cytosol, chloroplast, mitochondria and other parts of the plant cell based on the plant’s fluctuating necessities.

9.6.1 Vitamin B1

Vitamin B1 as known as thiamine is the first primary B-vitamin. Vitamin B1 is a water-dissolvable vitamin, and its chemical name is 3-[(4-amino-2-methyl-5-pyrimidinyl)methyl]-5-(2-hydroxyethyl)-4-methylthiazolium [1]. This water-soluble vitamin is composed of heterocyclic rings made up of nitrogen and sulphur [9]. This vitamin B1 molecule is composed of two compounds (pyrimidine and a thiazole), and both pyrimidine and thiazole rings are connected to each other with the help of a methylene bond. The thiamine occurs in various phosphorylated forms such as thiamine monophosphate, thiamine diphosphate and thiamine triphosphate. Thiamine pyrophosphate is a well-known form of vitamin B1 which aids as a cofactor in various enzymatic digestions. The thiamine molecules act as the cofactor for several enzymatic reactions and assist as an important component in the vitality digestion. The inadequacy of thiamine causes some of the disorders such as cardiomyopathy, dry beri-beri, Wernicke–Korsakoff and retrograde amnesia. The insufficient consumption of nutrients causes thiamine deficiency in the human body [1]. Thiamine plays a crucial role in the pentose phosphate pathway, which is an essential process during the production of steroids, nucleic acids, fatty acids, etc. It also remains as an important cofactor in various metabolic processes enhancing the growth and function of cellular membranes [3].

9.6.2 Vitamin B2

Vitamin B2 is also known as riboflavin and chemically is 7,8-dimethyl-10-(-d-ribo-2,3,4,5-tetrahydroxypentyl) isoalloxazine. This is water-soluble and has high sensitivity towards light and alkalinity. This riboflavin being a thermally stable vitamin is used in many enzymatic and metabolic reactions. The two major flavoproteins



(flavin mononucleotide and flavin adenine dinucleotide) derived from the vitamin B2 are the major compounds limiting the reaction rate of a various enzymatic process involving cell. The vitamin B2 possesses more antioxidant properties. The food from animal sources such as meat, dairy products, milk, fish and poultry are the major sources of vitamin B2, and also the food sources from plants such as vegetables, cereals and bread provide a good source of riboflavin ([9]. Riboflavin plays an important role in various chemical processes such as oxidative phosphorylation, fatty acid beta-oxidation, lipid metabolism, vitamin metabolism, amino acid metabolism, amine metabolism, heme metabolism and nucleotide metabolism of the cellular compounds [9].

9.6.3 Vitamin B6

Vitamin B6 is commonly found in edible products as pyridoxal, pyridoxol and pyridoxamine [3]. It is known as niacin and is water-soluble vitamin composed of nicotinic acid amine, nicotinamide and niacinamide. Niacin remains as a forerunner of Nicotinamide adenine dinucleotide and Nicotinamide adenine dinucleotide phosphate which are required for the metabolism of various chemical reactions. The food sources such as seeds, dairy, meat, legumes, fish, poultry, vegetables and coffee are some of the main sources of the vitamin B6 [9]. The vitamin B6 plays a most crucial role in amino acid metabolism, and it remains as a rate-limiting factor in the production of serotonin, dopamine or melatonin, etc. It is a potential factor in regulating the brain glucose level, and it enhances the immune system [3].

9.7 Vitamin C

Vitamin C is a water-soluble essential nutrient, and its chemical form is called hexuronic lactone l-ascorbic acid. Vitamin C is an almost essential vitamin required in various physiological activities and metabolic activities of the human body. It occurs in three various redox states such as ascorbate, semidehydroascorbate and dehydro-I-ascorbic acids. Vitamin C is required for strengthening of gums, tissues, arteries and bones. It is a potential antioxidant providing defence against crucial diseases such as cancer and heart-related problems. Citrus fruits are the major sources of C vitamin, but extended refrigeration and overcooking damage the vitamin C in the food items. Vitamin C plays an important role in various processes such as amino acids metabolism, iron metabolism, DNA modification and sulphur transfer in the human body [9].



9.8 Vitamin K1

Vitamin K is composed of a 2-methylnaphthalene-1,4-dione ring, and it remains as a compound which possesses higher antihemorrhagic properties [9]. Vitamin K is most essential for the coagulation of blood, and it is required for the amalgamation of prothrombin and other coagulation factors [2]. Vitamin K is composed of vitamin K1 and vitamin K2. The vitamin K1 is also known as phyloquinone or phytylmenaquinone, which are majorly produced by plants. The other vitamin K2 is known as menaquinones which are produced by micro-organisms such as bacteria and algae [4]. The intestinal micro-organisms are one of the best sources for the production of vitamin K under ideal conditions. Kale, cooked spinach and green vegetables are some of the strongest sources of this vitamin. The vitamin K is easily absorbed by the human body with the support of fatty substance. The vitamin K plays a vital role in certain processes such as bone mineralization, regulation of tissue mineralization, glucose homeostasis, signalling, fertility, regulation of tissue mineralization and prostaglandin metabolism [9].

9.9 Separation and Purification of Vitamin

Many physical, chemical and biological methods have been followed for the separation of vitamins in the past decades. Ion-exchange chromatography can be used effectively for the quantitative investigation of analgesics, vitamins and pesticides; also it helps in enhancing the effectiveness of the instrument and provides precise results [10]. The investigations on water-dissolvable and fat-solvent vitamins have been performed by high-performance liquid chromatography, but the HPLC was not found to be an effective technique in the determination of vitamins due to the disturbance for the final peak and the absence of clarity in the final resolution of the peak [11]. Traditional filtration techniques required the underlying extraction of tissue on account of the simple low vitamin content and the method used for separation and purification of vitamins should have the following characteristics such as:

- It must be a less time-consuming method
- Should be rapid
- It should be capable of taking care of even a very small concentration of the sample
- It should tolerate the heat, UV and wellsprings of oxidation
- The final product should possess a satisfying purity level.

The ion-exchange chromatography, satisfying all the above characteristics, is the best method for the separation and purification of vitamin compounds [12]. All water-dissolvable vitamins are suitable for framing ionized states in the arrangement. Some variations of the ion-exchange chromatography give convergence of the example on a scientific segment amid the investigative technique. By legitimately choosing the pH of the eluent, it is conceivable to accomplish acceptable detachment of the mixes of intrigue even in multicomponent arrangements [11].



9.10 Ion-Exchange Chromatography

Ion-exchange chromatography is a special type of chromatography used in various separation and purification processes of biomolecules. The separation and purification using the ion-exchange chromatography include the reversible exchange of particles between a functionalized insoluble pitch and an ionisable substance in the arrangement. In 1850, Thomson was the first researcher to work with the ion-exchange chromatography, and he utilized normally happening muds and ion-exchange resins for recovering the desired product in the fermentation and biochemical sectors [13]. Ion-exchange chromatography is based on the binding of an ion between the stationary phase and mobile phase. The stationary phase in the ion exchange is made of the solid cross-linked polymer network, and the mobile phase is comprised of solvents containing ions [14]. It is specifically used to separate the ion molecules, and the separation is based on the charges of the molecules. The attraction and binding between the oppositely charged locales on a finely isolated, insoluble substance is the basic principle of the ion-exchange chromatography. It is composed of two different types of resins such as cation-exchange resin and anion-exchange resin. Basically, the cation-exchange resins possess negative charges, and the anion-exchange resins possess positively charged sites. Ion-exchange chromatography remains as one of the best techniques for separating and purifying the biomolecules such as proteins, nucleotides and vitamins. The ion-exchange chromatography is highly preferred for the detachment and decontamination of proteins, nucleic acids, polypeptides, vitamins, other charged particles.

9.11 Mechanism of Ion-Exchange Chromatography

The process involved in ion-exchange chromatography is divided into five different stages such as equilibration, sorption, desorption, elution and regeneration.

Resins are the important component of ion-exchange chromatography, and the processes involved in ion change chromatography are demineralization, conversion, purification and concentration.

9.12 Separation and Purification of Vitamins B1, B2 and B6

Ion-exchange chromatography is mainly preferred in the separation and purification of the water-soluble vitamins due to their ionic nature. Vitamin B1 is commonly known as thiamine and is one of the difficult compounds to elute. Thiamine is a quaternary amine, and it is made of a complex structure which is firmly held and cannot be effortlessly eluted from a cation-exchange column. The thiamine can be eluted only under the conditions of high ionic strength and pH. The vitamins with



amine group have been eluted using a cation-exchange column, whereas the vitamins with carboxylic or phosphate groups have been separated and purified using anion-exchange column [10]. The vitamin B2 has been separated and purified using a cation-exchange column in which the mobile phases were maintained at two different pH values. The vitamin B2 has been eluted in a strong cationic exchange column maintained at either acidic or neutral pH value. At pH lower than 2, the vitamin B2 is more strongly retained by ion-exchanger. B2 has been also separated using the anionic exchange chromatography column [10]. The vitamin B6 is divided into three different compounds such as pyridoxine, pyridoxal and pyridoxamine. The pyridoxine is the most preferred form of vitamin B6 which is mostly utilized in the pharmaceutical products as a source of nourishment. These three vitamin B6 compounds have been eluted from the Zipax SCX anionic exchanger column maintained at pH 4 [10]. The vitamins B2 and B6 have been separated using a cationic exchange column (Zipax SCX) maintained at pH 4.4 with phosphate buffer [15]. The vitamins have been effectively separated and purified using the zeolite resins, whereas alumina resins were not satisfactory for the separation of vitamins. The thiamine and riboflavin were successfully separated using the resin known as Amberlite IR-100. Initially, the thiamine compound was checked for adsorption with an acid-sensitive resinous exchanger known as Amberlite IR-4. The adsorption of thiamine with Amberlite IR-4 was not as effective as expected. In the separation of vitamins, the vitamins bound strongly to the resins containing active groups rather than zeolite compounds [16]. Hilker and Clifford utilized a 5-mm NH Microlab AX5 column for determination of the thiamine from the cereals and urine samples; this column was used along with the phosphate buffer of pH of about 2.85 [17].

9.13 Separation and Purification of Vitamin C

Vitamin C is commonly known as ascorbic acid and prevalently found in all types of citric fruits. It is always utilized in the fruit juices produced artificially to boost up the vitamin C concentration in the human body. Basically, the vitamin C compound has been separated using the Zipax SAX anionic exchange column maintained at acidic or neutral pH. As the vitamin C consists of ionic modifiers, it causes oxidation of the components in the solvent phase [10]. Vitamin C is highly sensitive to the oxidation, and after oxidation, it promptly changes to dehydroascorbic acid which can further segregate into more inactive species. For the separation of vitamin C, the chromatography column should be maintained in a lower pH condition and ionic strength [12]. In the determination of vitamin C, three various packings of ion exchange have been used such as Zipax SCX, Zipax SAX and Permaphase AAX. The Zipax SCX composed of sulphonated fluorocarbon resin acts as the stationary phase up to 50 °C in the aqueous solvents maintained at a pH range of 1–9, whereas it cannot be used in organic solvents. The Zipax SAX resin comprising of quaternary amines bound to the Zipax resin is a strong anionic exchange resin. The Zipax SAX resin can be easily used in aqueous solvents, whereas it cannot be utilized in organic solvents as well



as elevated temperatures. The Permaphase AAX column can be utilized at higher temperatures above 50 °C in both organic and aqueous solvents. It attains maximum stability in the pH range of 3–9 [10].

9.14 Ion-Exchange Separation and Purification of Vitamin K1

Vitamin K1 commonly known as phyloquinone is a highly required nutrient present in the green leafy vegetables of the plants. In natural form, vitamin K1 occurs in the transform, whereas, when the vitamin K1 is produced synthetically, it occurs in the cis form. The vitamin K in the transform is highly active, whereas the vitamin K in the transform is inactive. It is highly desirable to separate the trans- and the cis-vitamin K1 isomers to truly evaluate the nutritional value of the supplement ingredient. Vitamin K1 is one of the highly required cofactors in liver cells for the formation of endoplasmic reticulum enzyme. The vitamin K1-dependent blood clotting factors are converted into the zymogens with the help of the vitamin K1-dependent carboxylase [18].

9.15 Conclusion

Vitamins are the most essential components required for the growth and development of the human body. There are nearly thirteen types of vitamins required for the human body. The water-soluble and the fat-soluble vitamins are the major classifications of vitamins. The water-soluble vitamins are the B and C vitamins which are further classified into vitamin B1, B2, B3, B6, B12 and C. Primitively, many separation techniques have been used for the separation and purification of vitamins. Ion exchange is one of the widely utilized techniques in the separation and purification of all types of biomolecules including vitamins. The cationic and anionic exchange resins have been used in the ion-exchange chromatographic separation of vitamins.

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Abstract	The examination of a whole arrangement of constituents of biological significance, the nucleic acids, nucleotides, and related substances, has been blocked extensively by the absence of particular strategies for the separation and characterization of their nitrogenous constituents. The strategies accessible for the separation and purification of nucleotides and nucleic acids have been connected to an assortment of materials. Despite the fact that refinement of the nucleotides was endeavored by different systems, for example, precipitation of the nucleotides as insoluble salts and ion-exchange procedures, an appropriate general strategy is still to be developed. The detachment into singular nucleotides by ion-exchange chromatography has been the main dependable method for assessing the nucleotide content. Combination of purines, pyrimidines, amino acids, and different nitrogenous substances was observed to be isolated by ion chromatography on a solitary column of the cation-exchange resin and Dowex 50. The mixture components were eluted with hydrochloric acid and controlled by either their response with ninhydrin or UV adsorption. Ion exchange has turned out to be one of the real techniques for fractionation of organic substances.	
Keywords (separated by '-')	Ion-exchange chromatography - Nucleotides - Nucleosides - Purines and pyrimidines - Purification - Applications	

Chapter 8

Separation and Purification of Nucleotides, Nucleosides, Purine and Pyrimidine Bases by Ion Exchange



P. Senthil Kumar and P. R. Yaashikaa

Abstract The examination of a whole arrangement of constituents of biological significance, the nucleic acids, nucleotides, and related substances, has been blocked extensively by the absence of particular strategies for the separation and characterization of their nitrogenous constituents. The strategies accessible for the separation and purification of nucleotides and nucleic acids have been connected to an assortment of materials. Despite the fact that refinement of the nucleotides was endeavored by different systems, for example, precipitation of the nucleotides as insoluble salts and ion-exchange procedures, an appropriate general strategy is still to be developed. The detachment into singular nucleotides by ion-exchange chromatography has been the main dependable method for assessing the nucleotide content. Combination of purines, pyrimidines, amino acids, and different nitrogenous substances was observed to be isolated by ion chromatography on a solitary column of the cation-exchange resin and Dowex 50. The mixture components were eluted with hydrochloric acid and controlled by either their response with ninhydrin or UV adsorption. Ion exchange has turned out to be one of the real techniques for fractionation of organic substances.

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8.1 Introduction

Authentic and productive techniques for the isolation of nucleic acids are essential for their examination using molecular strategies. Methods, for example, restriction fragment length polymorphism (RFLP), polymerase chain reaction (PCR), real-time polymerase chain reaction (RT-PCR), library development, and numerous other downstream applications, rely on isolation of purified DNA or RNA, since remaining debasements in the nucleic acid can hinder enzymatic responses, electrophoresis, and evaluation. Techniques for the isolation of nucleic acids from complex materials, similar to plant and animal tissues, more often include a lysis phase, to discharge the cell substance, accompanied by the partition of the nucleic acid from other cell segments. Natural extraction methodologies enable a bigger number of tests to be handled at a

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time; however, they are additionally extremely difficult and include harmful chemicals. The pipetting steps important to isolate the fluid from the organic stage may bring about the loss of the sample material. To eradicate issues related to ordinary nucleic acid isolation from complex materials, techniques have been created which guarantee effective lysis of the sample followed by selective binding of the nucleic acids to a strong support. Nucleic acids that are immobilized on a solid-phase support can be purified by expelling every single-cell impurity with basic washing steps. Once washing is completed, purified DNA or RNA can be eluted from the matrix [1]. This way to deal with the isolation of nucleic acid has few advantages. It is quick and straightforward, does not require extraordinary research laboratory equipment and considers the separation of profoundly pure nucleic acids from an assortment of test samples. The utilization of toxic reagents is likewise wiped out or lessened to a base. Because of its effortlessness, it is appropriate for high-throughput applications. The current advancement of high-pressure liquid chromatographic instruments and the accessibility of little and consistently estimated resins have improved the part of column chromatography for the fast measure of nucleic acid constituents [2]. Chromatography alludes to a group of partition procedures that include an impediment of particles for the solvent that advances through the material. An important progression in the separation and purification has been because of the current illustration that the ion exclusion is more or similarly viable than the ion exchange as a partition rule for the determination of purine and pyrimidine bases, nucleosides, deoxynucleosides, and nucleotides. The separation of nucleic acid constituents on polystyrene gums column, which bears either cationic (sulfite) or anionic (quaternary mine) functional groups, depends on two primary contradicting standards: ion exchange and ion exclusion [3].

- (a) The anion exchange happens between an anion and a resin with anionic functional groups and a resin with cationic functional groups. Additionally, the cation exchange happens between the analyte and the resin with the cationic functional group.
- (b) The ion exclusion isolates ionized from non-ionized substances by eliminating the charged species because of repulsion rather than an attraction as in ion exchange. Ionic repulsions, as opposed to attraction, are intentionally looked for. In this way, “cation exchanger” can be used for anion-exclusion chromatography and an “anion exchanger” for cation-exclusion chromatography.

Despite the fact that ion exchange and ion exclusion are two contradicting standards, both may happen in the meantime in the separation of a combination of nucleic acid constituents. Other than these two ionic standards, non-ionic interactions are likewise critical. For example, purine bases are more strongly hindered on polystyrene exchangers than the similarly charged pyrimidine mixes. Hydrophobic interactions and partition chromatography play an essential and autonomous part in deciding the distribution coefficient of natural constituents on polystyrene networks. Suppose if there exists an attraction of an organic particle to an organic solvent, it ought to be conceivable to exhibit a “salting out” impact. The qualitative and quantitative evaluations of nucleotides and nucleosides are essential for inves-



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71 titating in nucleic acids in bioscience. Polynucleotides can be separated according
72 to their sizes. The desired nucleobases can be obtained in pure form by separation
73 [4]. The requirement for isolating and measuring nucleic acids and free nucleotides
74 has impelled the improvement of high-pressure liquid chromatography (HPLC) for
75 this application [5]. The most generally utilized partition methods engaged for the
76 examination of nucleosides and nucleotides are reversed-phase, ion-pair, and ion-
77 exchange chromatography. The commonly used ion-exchange technique suits more
78 for determination of nucleotides [6].

79 8.2 Ion-Exchange Chromatography

80 Ion-exchange chromatography (IEC) is a segment of ion chromatography which is
81 an essential investigative procedure for the separating and determining ionic mixes,
82 together with ion-partition and ion-exclusion chromatography. Separation by ion
83 chromatography depends on ionic or electrostatic communications among ionic
84 and polar analytes, ions introduced in the eluent, and functional groups settled on
85 the chromatographic support. Two well-defined mechanisms include ion exchange
86 because of aggressive ionic binding attraction and ion exclusion because of repulsion
87 between homogenous charged analyte ions and the ions settled on the chromato-
88 graphic support. This chromatography is a standout among the most vital adsorption
89 procedures utilized as a part of the separation of peptides, proteins, nucleic acids,
90 and related biopolymers which are charged atoms in various molecular sizes. The
91 detachment depends on the arrangement of ionic bonds between the charged groups
92 of biomolecules and an ion-exchange gel conveying the opposite charge [7].

93 8.2.1 Mechanism of Ion Exchange

94 Ion-exchange chromatography which is particularly suitable for the detachment of
95 diversely charged or ionisable mixes constitutes from stationary and mobile phases
96 that are similar to different types of column liquid chromatography strategies. Mobile
97 phase comprises a fluid support framework into which the solution to be settled.
98 The stationary phase commonly delivered utilizing inert characteristic cross-section
99 artificially auxiliary with ionisable functional groups which pass on displaceable
100 oppositely charged particles. Particles which exist in a state between the stationary
101 and mobile stages offer associations with anion and cation exchanges are referred to
102 as counter particles. Cations are isolated on cation-exchange resin column and anions
103 on an anion-exchange resin column. Detachment depends on the analyte binding to
104 positively or negatively charged groups which are settled on a stationary stage and are
105 in balance with free counter ions in the mobile stage as indicated by the distinction
106 in their net surface charges. Complex blends of anions or cations can normally be
107 isolated and quantitatively measured in a moderately short time by ion-exchange



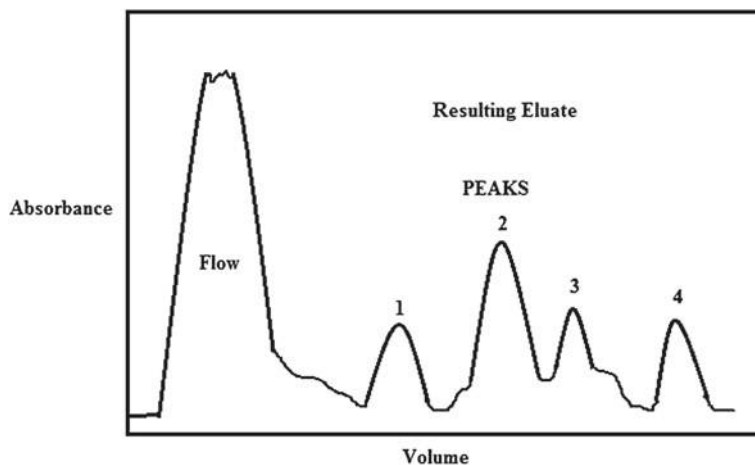


Fig. 8.1 A chromatogram

chromatography. In established ion-exchange chromatography, detachments have been performed in the open-column mode. Column is stuffed with stationary stage as little particles made of 1–2 cm diameter of glass. The mobile stage which is the eluent contains the contending ion, is passed persistently into the column, and permeates through it under gravity. Sample solution is connected to the highest point of the column and permitted to go into the bed of ion-exchange material. Eluent flow is then continued, and portions of eluent are collected at general intervals from the column outlet. This system has been utilized for the examination of anions and cations, including mono- and oligosaccharides, aminoglycosides, amino acids and peptides, natural acids, amines, alcohols, phenols, nucleotides, and nucleosides as well as other polar atoms [8]. The results of ion-exchange chromatography are obtained in the form of chromatogram which is defined as the outcome of the chromatographic run. The peaks in the chromatogram show the elution of compounds at different time intervals. Figure 8.1 depicts a chromatogram model.

Ion-exchange chromatography, which is otherwise called adsorption chromatography, is a valuable and prevalent strategy because of its high limit, high settling power, mild separating conditions, versatility and vast applications, tendency to focus the sample, and relatively minimal effort.

8.2.2 Components of Ion-Exchange Chromatography

- A high-pressure pump with pointers focusing on pressure and flow, to convey the eluent

- An injector for bringing the sample solution into the eluent flow and onto the column
- A column, to isolate the sample mixture into the individual parts
- A detector, to gauge the analyte peaks as eluent comes out from the column
- A data framework for collecting and sorting out the chromatograms and information.

8.3 Nucleotides

Nucleotides are negatively charged ionic atoms comprising of a nitrogenous base, a 5-carbon pentose sugar, and phosphoric acid. Four of the bases (A, T, C, and G), substituted with 2-deoxy- α -D-ribose, polymerize to give deoxyribonucleic acid (DNA), and three of these in addition to uracil (A, U, C, and G), substituted with α -D-ribose, join to form RNA. The progressive nucleotides of both RNA and DNA are covalently connected to each other when a compound (RNA or DNA polymerase) catalyzes arrangement of a phosphodiester bond between the 3'-hydroxyl group of one pentose and the 5'-hydroxyl of the following pentose. The hydrolysis of phosphate bonds in the precursors—that is, the nucleotide triphosphates—drives the DNA and RNA polymerase responses. Nucleotides additionally assume a focal part in metabolism at the cell level. They convey loads of chemical energy in the form of nucleoside triphosphates ATP, GTP, CTP, and UTP all through the cell to the numerous cell capacities that require energy, which incorporate integrating amino acids, proteins and cell films and parts; moving the cell and cell organelles, both inside and intercellular; separating the cell, and so on. There are many commercially used chromatographic techniques for the separation and purification of nucleotides such as ion exchange, ion exclusion, HPLC, and reversed-phase HPLC [9]. Among these, ion exchange is the most commonly used owing to its vast applications.

8.4 Nucleosides

A nucleoside is a chemical mixture of a pentose sugar and a pyrimidine or a purine base. The connection of the two segments is a general drying out synthesis response in which a particle of water is expelled between the base and the sugar; however, a nucleoside is an *N*-glycoside in which the sugar part is ribose or deoxyribose and the glucon is a pyrimidine or purine base. Nucleosides containing ribose are called ribonucleosides. Those containing deoxyribose are called deoxyribonucleosides.



8.5 Purines and Pyrimidines

There are two classes of nitrogen-containing bases—purines and pyrimidines. Purines involve a six-membered and a five-membered nitrogen-containing ring that is combined. Pyrimidines are composed of a six-membered nitrogen-containing ring, monocyclic, while purines are bicyclic. These bases are all polyfunctional in nature. Purine bases are composed of a 9-membered double-ring structure with four nitrogens and five carbons, while pyrimidine bases consist a six-membered ring with two nitrogens and four carbons. Purines and pyrimidines are differentiated on the basis of their shape. The state of the pyrimidine ring is planar, though the state of the purine rings is about planar. Purine and pyrimidine molecules are hydrophobic in nature and have a moderately low dissolvability in the water close to neutral pH. Hence, at acidic or basic pH, the purines and pyrimidines get charged and their solvency increases. They are conjugated molecules and weakly basic. As a result of the fragrant ring structure and related resonance, pyrimidine and purine bases ingest bright light (UV light), with an assimilation maxima at a wavelength of 260 nm. The estimation of the convergence of DNA or RNA in a given example is in this way performed by estimating the UV absorbance at this wavelength. Purines and pyrimidines, being integral bases, can assist in the pairing of bases, based on particular shapes and hydrogen bond properties. Guanidine, being a supplement of cytosine, sets with cytosine through three hydrogen bonds. Adenine (An) is the supplement of thymine (T) in DNA and uracil (U) in RNA. Adenine base sets with thymine and uracil combine through two hydrogen bonds.

8.6 Column Preparation and Operation

The anion and cation exchangers are cleaned by washing with a few volumes of the soluble base, acid, ethanol, acetone and water. The treated resin is centrifuged at every stage to minimize reduction during separation. This treatment expels most UV-absorbing free material from ion-exchange resins. The cation exchanger ammonium and anion exchanger acetic acid derivatives are set up by treating the resins with 3 M ammonium formate and 3 M sodium acetic acid individually. Consistent temperature is kept up by utilizing a rotating water shower. The generation of air bubbles, particularly at high temperatures and with natural solvents in the eluent, must be avoided by allowing the eluent to pass through a narrow tube [10].

• Hydrolysis of nucleic acids

The nucleic acid study can be done at the free base, the nucleoside or the nucleotide level. The nucleoside level has risen as a most loved due to its opportunity from isomeric sets (as in soluble RNA hydrolyzate) and from solid chemicals (as in liberating the bases of pyrimidine nucleosides). Nucleosides can be acquired by gentle enzymatic treatment of DNA.



• DNA (Deoxyribonucleic acids)

DNase I, venom phosphodiesterase, and basic phosphatase are set up in ammonium carbonate mixture. These three segments are included in a microtube in the proportion 1:1:2. The hydrolysis is finished in approximately 90 min at 50 °C. The RNA hydrolysis to bases is deficient and unsuitable. The purine bases are expelled from DNA under gentle acidic conditions (pH 1.6 at 37 °C for 25 h or pH 2.8 at 100 °C for 1 h); however, intense conditions are required to free pyrimidine bases. Concentrated 90–100% formic acid at 175 °C for 2 h, 6 M hydrochloric corrosive at 120 °C for 2 h or 12 M perchloric corrosive at 100 °C for 1 h have been utilized for quantitative separation of purine and pyrimidine bases from DNAs. Since the hydrolysis must be completed in fixed tubes and some loss of bases because of high acidity happens, the strategy is complex and in this way, DNA estimation at nucleoside level is favored.

• RNA (Ribonucleic acids)

Under appropriate conditions, tRNA is hydrolyzed to nucleosides enzymatically. Hydrolysis of tRNA to nucleosides happens at a slower rate at first, and a total RNA hydrolysis is relied upon to be accomplished within 2 h. The adjusted nucleosides are discharged gradually.

8.7 Operation

In ion-exchange chromatography, the pH and the nature of buffer are the essential parameters that impact the impediment of charged solutes. The pH influences capacity ratio and selectivity of columns while buffer ion concentration influences column capacity ratios. The expanding substitution of ion-exchange columns for the partition of charged solutes is because of its simplicity of dealing with versatile stage parameters in reversed-phase chromatography. In spite of the fact that this substitution is advocated by divisions of all classes of components, ion-exchange columns can be significantly more important [11].

8.8 Impact of Separation Parameters

There are several factors which affect the process of separation during ion-exchange chromatography. These parameters have to be optimized or kept under optimum conditions for effective separation and purification [12]. The factors such as pH, the ionic strength of the medium, temperature, nature of stationary, and mobile phases, size of resins, and flow rate of the eluent influence separation process.



8.9 Separation of Nucleotides

For evaluation of cyclic nucleotides and related compound exercises, ion-exchange chromatography is the most generally utilized separation procedure. Cation-exchange and also anion-exchange resins can be utilized for cyclic nucleotide detachments. Dowex-50 column created with acidic solvents is particularly valuable if the solutions contain a lot of electrolytes since such examples can specifically be connected. Anion-exchange resins have additionally been utilized for cyclic nucleotide partitions. These materials have been utilized particularly in examining adenylate and guanylate cyclase and of cyclic nucleotide phosphodiesterase reactions. Their application to the filtration of cyclic nucleotides from tissue concentrates is difficult because these excess electrolytes must be expelled out before sample application in the column. For this reason, adsorption of the nucleotides to charcoal under acidic conditions and elution into a mixture containing ammonia and alcohol have been applied. A charcoal advance can be dodged with emphatically essential anion-exchange materials, for example, QAE-Sephadex, if tissue homogenization and nucleotide extraction are not performed in acid, but rather in a zinc acetic acid derivation liquor arrangement. The water utilized for recovery of the resins ought to be deionized. For the last stages of the resin recovery and for the development of the elution liquids, in any case, the water of glass-redistilled quality ought to be utilized. A QAE-Sephadex column can be utilized for a quick and successful detachment of the marked nucleoside from the remaining cyclic nucleotide [13].

8.9.1 Fractionation of Nucleotides

The elution of the nucleotides often requires 3–6 mL of eluent. Different nucleotides can be isolated from each other and from nucleosides, bases, and uric acid by stepwise elution with various eluents. Nucleosides (adenosine, inosine, guanosine, and xanthosine), bases (adenine, hypoxanthine, guanine, and xanthine), and uric acid have been for the most part eluted with 5 mM acetic acid. Over 95% of each compound was found in the acetic acid eluate. For an entire elution of nucleosides, bases, and uric acid, further elution with 10 mL of water is required. Cyclic nucleotides and related nucleotides were fractionated from each other by stepwise expanding centralizations of LiCl arrangements. The cyclic nucleotides, cAMP, cIMP, or cGMP, were eluted by 4–5 mL of 0.02 M LiCl. If that a partition of cAMP from cIMP is required, cAMP can be eluted with 5 mL of 50 mM acetic acid, and afterward, cIMP can be eluted with 4 mL 0.02 M LiCl [14].



8.9.2 Cation-Exchange Resin

The anionic nature of nucleotides at an acidic pH is because of variations in the cationic charge of the bases and the anionic charge of the phosphate group connected to the ribose moiety; however, variations in the net negative charges of nucleotides can be normal. The charge differences among nucleotides, in conjunction with their variable segments between mobile eluent and stationary resin matrix, are attributes for chromatographic differences.

8.9.3 Anion-Exchange Materials

The main divisions of nucleotides were acquired by anion-exchange chromatography. The technique has been in wide application and changed to suit divisions of bases and nucleosides in a similar examination. Hence, the anion-exchange chromatography with smaller and uniform beads was reinvestigated to create frameworks that can be utilized to isolate the real nucleotides in single eluent and to isolate most nucleosides, nucleotides, and different hydrolysis items in a single analysis [15].

8.10 Separation of Nucleosides

Nucleosides are regularly isolated using the reversed-phase chromatographic technique. The impact of dissolvable salts in the eluent is distinctive for nucleosides than for nucleotides, because of the absence of phosphate aggregation. The impact of salt fixation in the eluent for nucleosides is considerably lower than that for nucleotides that the particle trade partition system does not have any significant bearing. pH is a critical factor which impacts the maintenance of nucleosides due to the variety of net electron charge in the particles. Higher pH upgrades the maintenance of nucleosides, as is valid for nucleotides. The hydrophobic association is the dominating partition component [16].

8.10.1 Purification of Nucleosides

At higher pH, numerous negative charges on the nucleosides extremely intensify the attaching stationary phase in the column. As the pH is decreased, the nucleosides get protonated and elute as per the pK, of each site. The isolated and purified nucleoside-5'-diphosphates (NDP) were desalted by reverse osmosis and after that spray dried from the concentrated mixtures. Cytidine diphosphate (CDP) was likewise solidified by treating concentrated solution with acetone. UDP was solidified by treating the



concentrated solution with methanol. The concentrated arrangements and the majority of the strong NDPs were polymerized effectively with PNPase to shape either poly-I or poly-C/U. The NDPs are not very stable in acidic solution, but stable at higher pH. The NDPs have been successfully eluted at low pH, around 1.0 [17].

8.10.2 Cation-Exchange Chromatography

Adenosine and cytidine are in the form of cations at an acidic pH; thus, they exchange with a cation exchanger. In spite of the fact that both uridine and guanosine are uncharged and barred at about pH 4.6, guanosine appears after uridine mixtures because of its organic nature. Here, the uridine group of nucleosides are resolved poorly that need charge variations and low non-ionic differences. To upgrade desorption of the firmly bound minor nucleosides and bases, three alterations have been presented in this cation-exchange strategy:

- Increase in the ionic quality
- Change in pH and temperature
- Addition of ethanol to the eluent.

8.10.3 Anion-Exchange Chromatography

Uridine and guanosine mixes are anionized at basic pH esteems; thus, these can exchange on an anion-exchange column or can experience anion avoidance on a cation-exchange column.

Deoxynucleosides

The deoxynucleosides can be separated just like ribonucleosides on both anion- and cation-exchange resins by either ion-exchange or ion-exclusion techniques. Since deoxynucleosides vary from ribonucleosides with low pK values, their separations, for the most part, require minor adjustments of the ribonucleoside detachment conditions. Anion-exclusion happens at pH 9.5; however, the ribonucleosides require a marginally higher pH.

8.11 Separation of Purines and Pyrimidines

Separation of purine and pyrimidine by ion-exchange chromatography finds tremendous application in biochemical examinations for detachment of these mixes. Of the five normally happening purine and pyrimidine bases, three (cytosine, guanine, and adenine) exist as cations in the arrangement of pH < 4 and subsequently can consolidate with cation exchangers. Since their affinities for the cation exchanger contrast,

they might be eluted progressively with basic reagents. This system does not separate the non-ionized bases, thymine and uracil. Since these will not be experienced together, their separation is easy and in addition to the other three substances, by turning to anion exchangers and basic arrangements [18]. The nucleotides of yeast nucleic acid (uridylic, cytidylic, guanylic, and adenylic acids) show to some degree the fundamental properties of the purine or pyrimidine constituent; this is adjusted by both size and the negative phosphate groups with the outcome that the exchanger-to-ion bond is significantly weaker. Weak acids have been observed to be the most eluting medium [19].

8.11.1 Cation-Exchange Chromatography

At the point when pH is raised from 4.75 to 6.75, keeping up ionic quality and temperature consistent, cytosine and adenine elute early, however, the other two bases show up at similar positions. A normal investigation of the four bases can be done at pH 5.2 in around 25 min at a direct column pressure of 200 psi.

8.11.2 Anion-Exchange Chromatography

All bases of the nucleic acids, aside from cytosine subordinates, are anionized at alkaline pH. Consequently, pH esteem can be resolved where the distinction in their anionic character is greatest. Hence, different properties, for example, hydrophobic groups, ought to likewise be considered in predicted detachments based on the ionization.

8.12 Applications of Ion-Exchange Chromatography

Various charged molecules such as nucleobases, nucleic acids, proteins, antimicrobials, vitamins, and peptides can be effectively separated using ion-exchange chromatography technique. This method also helps to separate and purify compounds from various natural organic sources to engineered molecules that may be protonated bases (alkaloids) or deprotonated acids (unsaturated amino acids). This technique is generally relevant to the investigation of a large number of biomolecules. The method is effortlessly exchanged to the assembling scales with minimal effort. An elevated level of purification of the substances of physiological importance can be accomplished by ion-exchange process [20]. Thus, ion-exchange chromatography has been utilized for the analysis of ionic species since they can be utilized as a valuable strategy for segregation of natural products in current medication revelation, and it will keep on expanding with the improvement of new advances.



8.13 Conclusion

The utilization of ion exchange for separation and purification of purine and pyrimidine bases, nucleotides, and nucleosides has brought about quantitative separation methods for the constituents derived from nucleic acids. It is suggested to apply the procedure to the isolation of pure polynucleotides from enzymatic or synthetic condensations of nucleic acids. Anion-exchange chromatography in the past has been connected to determine nucleotides by utilizing distinctive separation conditions. Different arrangements of separation criteria have been investigated to isolate the basic nucleotides by single, weak suspensions. A technique including an anion exchanger of little consistently estimated resins and a direct elution slope is portrayed for the partition of complex solutions, similar to tRNA hydrolysates, containing nucleosides, major and minor nucleotides, and different results.

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Chapter 8

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Chapter 5

Product Lifecycle in the Pharmaceutical Industry

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ABSTRACT

The composite of the present pharmaceutical industry requires more effective medication improvement and generation. A product lifecycle (PLC) is the progression of stages from the product's production to the world until its last withdrawal from the market. Product lifecycle comprises various stages that a product must possess in its lifespan, for example, launching, growth, maturity, and decline stage. While each stage brings huge changes, a progression of procedures for the administration of product lifecycle is required. Product lifecycle management (PLM) is a precise, controlled idea for overseeing and creating products and product-related data. Enhanced patient consistency, income development, extended clinical advantages, and faster market dispatch are among the primary utilization of product lifecycle management. To create a viable and productive product lifecycle management program many qualities are viewed like promising start, vital arranging clear authority, supporting information and abilities, readiness for changing tenets of government and associations.

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INTRODUCTION

Product advancement basically defines the pharmaceutical industry. Research on the front line of science, the production of new learning bases, the innovation in the form of the new solutions and the change of existing medications constitute the fuel that drives the firms in this industry. The incidental success of making a novel treatment in a range with no earlier medications considers as a part of the pharmaceutical sectors' most defining trademarks. This is the main industry whose yield can have any kind of effect by influencing the particles we are made of. Current time drugs can impact the quality and the term of human life in ways that were never conceivable. Effective and constant new medication presentations constitute the wellspring of practical upper hand for the organizations in this industry (Phelps, 2011). A portion of the difficulties the pharmaceutical industry faces incorporate R&D (innovative work) disappointments, changes in administrative viewpoints, patent expiries, and remote cash developments. The legislatures over the world are endeavouring to check these medicinal services costs either by sedate value modifications, requesting higher rebates and refunds to the makers or by advancing nonspecific medications. In any case, with the dispatch of inventive medications, pharmaceutical organizations can get deals with development. The sector development is driven by particular functions, for example, invulnerable oncology. With expanding occurrence of disease, oncology drugs are relied upon to witness solid request. The life-sparing capacities of these medications get higher costs and more extensive edges (Zannou et al., 2009).

Even though creation and advancement is the backbone of any industry, the revelation and improvement of new drugs are joined by a large group of difficulties, ethical issues, moral suggestions, and social duties. One will be unable to think about another industry where fastidious research, thorough testing, and stringent product principles can have such a significant effect on human prosperity. The central part of the pharmaceutical industry in keeping up and upgrading human life is additionally reflected in the greatness of its R&D action. The production of new medications is not really a deliberate, unsurprising procedure. There are tremendous troubles related to the making of a protected and effective medication. Regardless of phenomenal late advances in science and innovation, good fortune and chance still assume a part in the revelation and combination of compelling mixes. There is essentially no chance to get of guaranteeing the extreme R&D endeavours and immense expenses will pay off liberally, at last, as the rates of achievement in sedate revelation remain consistently low. Imperatively, the execution vulnerability is intensified by the nearness of stringent directions and extraordinary examination over the whole improvement process. The basic choice to go to advertise is basically outside the control of the firm. The market endorsement for another drug at last rests with the American Food and Drug Administration (FDA), the administration

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Chapter 7

Production Process in the Pharmaceutical Industry

Senthil Kumar Ponnusamy
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ABSTRACT

The most important stress related to the industrialized societies are diseases and health issues caused by taking medicines that are in unfavorable condition. The health issues caused due to the medications mainly depend on the quality of drugs. This is the main test confronted by any pharmaceutical organization wishing to guarantee its survival. The benefit in the pharmaceutical industries is higher. But now, the cost of the medicines is reduced as per the estimation is given by the government. Hence, pharmaceutical organizations now confront a moment of challenge to diminish costs through upgrading and enhancing their production methods. Based on the production process following in the pharmaceutical industries, the product quality can be varied and improved. This chapter prescribes the detailed information regarding the production practices that are followed in the pharmaceutical industries for the production of high-quality products.

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INTRODUCTION

Pharmaceutical industries bring out the major changes in the developed countries as well as in developing countries. Pharmaceutical industries use chemical materials for the production of antibiotics through research and development investment, which was useful to both the animals and humans. They tend to produce a profit source for the next generation and less expensive drugs that increase the enterprise value (Lee & Choi, 2015). Pharmaceutical industries get involved in the production of pharmaceuticals that represses the contaminants and infections of the living creatures. The pharmaceutical enterprises grew new methodologies in advances, explore fields and framework. The drug produced by the pharmaceutical industries contains various toxicological properties and therapeutic activity. Advancement in the research and technology innovation prompts the discovery of new pharmaceuticals that aid in the diminishment of symptoms. The manufacturing techniques of pharmaceuticals include two major processing techniques namely primary processing and secondary processing. In the primary processing, active drug production takes place and in the secondary processing, the alteration of the drug takes place and converts them into a good product for administration. These drugs inhibit the infections and diseases of the living beings. The manufactured pharmaceutical groups include patented products like Proprietary ethical products or prescription only medicines (POM), general ethical products and over-the counter (OTC), or non-prescription products.

The entire pharmaceutical part is in need of creative technological solutions and basic scientific work which empowers in the generation of highly engineered drug materials. The product development process in the pharmaceutical industries includes logical and systematic process. The dosage form is created based on the successful outcome. Due to a deficiency in the control steps of product production, the above-mentioned developmental process becomes difficult. Based on the risk, regulatory demands are increasing rapidly in which the pharmaceutical industries are trying to change and match with the regulatory measures. The achievement of the pharmaceutical industry is due to the increase in population, high sale of drugs in the pharmaceutical industries and product innovation to treat various diseases. Research and development labs play out the work of medication discovery and improvement while fabricating plants create the final medications for purchasers. Most R&D research facilities are found independently from assembling plants, yet a few labs and generation plants are incorporated. In order to safeguard the characteristics of quality of the product regulatory conditions were developed which regulates the manufacturing process of products in the pharmaceutical and similar industries (Rantanen & Khinast, 2015). This chapter gives a short description of the production methods along with significance and limitations

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Chapter 8

Characteristics of Pharmaceutical Supply Chains

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ABSTRACT

The pharmaceutical supply chain is presently a noteworthy research topic in process operations and administration. A lot of research has been embraced on office area and configuration, stock and circulation arranging, limit and generation arranging, and point-by-point planning. Just a little extent of this work straightforwardly addresses the issues confronted in the pharmaceutical division. The pharmaceutical industry is facing extraordinary difficulties caused by a maturing population, the expanding expense of medicinal services, the priority given by the governments to bring down the cost of medications, boundaries to a passage in developing markets, and the more extensive reception of non-specific medications. These are quite recently a portion of the many difficulties making weight on the overall revenue of pharmaceutical firms. Expanded expenses of R&D and a diminished number of affirmed sedates additionally demonstrates that the lion's share of prescription, which is anything but difficult to find, has just been found.

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INTRODUCTION

The pharmaceutical business can be characterized as a complex of procedures, operations and associations engaged with the revelation, improvement and produce of medications and meds (Jarrett, 1998). The World Health Organization (WHO) characterizes a medication or pharmaceutical readiness as: any substance or blend of substances made, sold, offered available to be purchased or spoken to for use in the conclusion, treatment, moderation or avoidance of malady, strange physical state or the manifestations thereof in man or creature; reestablishing, redressing or adjusting natural capacities in man or creature (Burns, 2002).

Pharmaceuticals merit unprecedented thought in controlling stock, including the essential contrasts amongst medications and other customer items: they are produced, made, and distributed by meeting the strict administrative prerequisites; medications are regularly chosen by a physician for a particular patient and can be repaid in entire or to some degree by an outsider guarantor or the state. These particular attributes make the pharmaceutical business an intense power in its own right, representing 15.4% of aggregate well-being consumption.

Generally, pharma organizations have complex supply chains that are under-used and wasteful. More terrible still, they are badly prepared to adapt to the kind of items that are coming down the pipeline. By 2020, huge numbers of the meds the business makes will be master treatments that require entirely distinctive assembling and conveyance systems from those used to deliver little particles. The pharmaceutical supply chain needs a radical upgrade, and it will experience three key changes over the following decade:

1. It will piece, with various models for various item sorts and patient fragments,
2. It will end up being a method for advertising separation and wellspring of monetary esteem; and
3. It will end up being a two-route road, with data streaming upstream to drive the downstream stream of items and administrations (Booth, 1999).

This is a wide definition, and correspondingly, there is a number of key players in the pharmaceutical business, counting:

1. The huge, innovative work-based multinationals with a worldwide nearness in marked items, both moral/remedy and over-the-counter. They tend to have production destinations in numerous areas,
2. The extensive non-specific makers, who create out-of-patent items and over-the-counter items,

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Abstract	Date is an extremely rich-nutritious fruit that could develop in an exceptionally poor condition also. Date fruit is an imperative item on the planet and assumes a significant part in the monetary and political life in date developing districts. Date palm (<i>Phoenix dactylifera</i> L.) is a monocotyledon plant that experiences different stages amid aging. Despite the fact that more than three-fourths of the fruit comprises of sugars, the rest is extremely rich in vitamins, dietary strands, phenolic mixes or antioxidants, and minerals. An extremely profitable compound, for example, oleic acid could be removed from the seed with other unsaturated fats and utilized as food for humans and animals. The medical advantage of dates is another vital viewpoint. Date concentrate could shield human bodies from the harm of free radicals or responsive oxygen species and even weaken the impact of diarrheal movement and turned out to be compelling as neuroprotective against two-sided regular carotid artery impediment. Lately, a lot of research has been carried on the various medical advantages of dates including identification and evaluation of different classes of photochemical with an awesome potential uses in the developing sectors of important sustenance and nutraceuticals. The health benefits and the importance of date palm fruit for human wellbeing are discussed in this chapter.
Keywords (separated by ‘-’)	Date palm - Growth and development - Industrial uses - Medical applications - Healthy food - Nutritional constituents - Destruction

Chapter 1

Date Palm as a Healthy Food

P. Senthil Kumar and P. R. Yaashikaa

Abstract Date is an extremely rich-nutritious fruit that could develop in an exceptionally poor condition also. Date fruit is an imperative item on the planet and assumes a significant part in the monetary and political life in date developing districts. Date palm (*Phoenix dactylifera* L.) is a monocotyledon plant that experiences different stages amid aging. Despite the fact that more than three-fourths of the fruit comprises of sugars, the rest is extremely rich in vitamins, dietary strands, phenolic mixes or antioxidants, and minerals. An extremely profitable compound, for example, oleic acid could be removed from the seed with other unsaturated fats and utilized as food for humans and animals.

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Keywords Date palm · Growth and development · Industrial uses · Medical applications · Healthy food · Nutritional constituents · Destruction

1.1 Introduction

Plants serve as a major natural source of nutrients to humans and animals. A transcending date palm (*Phoenix dactylifera*) resembles somewhat like a coconut tree, yet its enormous groups of organic product offer something which is sweeter. Apart from their richness, caramel flavoured and delicate, chewy substance, it's

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nothing unexpected that dates which are weighing about 70% sugar are normally alluded to as “nature’s treat”(Farag 2016). Dates might be as sweet as confection; however they convey much more supplements – and potential medical advantages. The family Phoenix is composed of 17 palm species, for example, *canariensis*, *dactylifera*, *sabal*, *rupicola*, *reclinata*, and so forth. It is an individual from the palmae family (Arunachalam 2012). These palms are well known things in close ice free atmospheres around the globe. This palm is moderately developing when youthful, yet once the storage compartment achieves its full distance across the development rate increments and it grows completely in spring and summer. It is tolerant to very much depleted soils. The *Phoenix dactylifera* is a palm tree which is oftentimes planted for its elaborate characteristics. This palm is best utilized along lanes, on grounds and in parks. The developed *Phoenix dactylifera* dates are of red shading and contain a seed about 1 cm long. Fruits of date palm are not harmful but rather have a repulsive taste which renders them unfit for utilization yet when it is ripped totally this natural product is sweet (Ibrahim et al. 2001). The utilization of date pits as an animal feed in the customary way is still likely the most widely recognized practice. Date palms begin to hold up fruits at 4 years old to 5 years and achieve full development at 10 years old to 12 years contingent upon neighbourhood conditions influencing rate of development and improvement. Blossoms (flowers) are borne in strands on clusters at the highest point of the tree. The quantity of bundles per tree changes from 3 to 10 and each pack incorporates several strands and a huge number of individual dates. Contingent upon the flesh consistency and dampness content at gather when completely ready, date palm cultivars are partitioned into three gatherings, in particular delicate, semi-dry and dry. The fruit of any specific crop when left on the palm or presented to unreasonable curing conditions will lose dampness and build up a hard surface.

Dates with a hard surface texture are classified as second-grade dates. These dry dates are filled with nutrients with more benefits (Besbes et al. 2009). Different classifications can be found inside a similar gathering depending on natural product attributes, size and sugar content. Dates are devoured new, dried, or in different handled structures (Al-Abid et al. 2007). They are regularly devoured crisp in the wake of picking particularly at the fresh ripped stage. In a few cultivars, fruits are expended at the physiological development stage itself. Most dates, in any case, are devoured at the completely ready stage. The fruits at this stage are portrayed by low dampness content and hence are perfect for long period storage to be expended out of season. Any losses while collecting and handling in postharvest and advertising are high in most creating nations because of the frequency of physical, physiological and obsessive issue and to bug infection. Free radicals are involved in incessant incendiary ailments including rheumatoid joint inflammation. Free radicals assume an imperative part in the seriousness of rheumatoid joint inflammation and patients normally endure high oxidative pressure (Chaira et al. 2007). Antioxidants either engineered or normal are scavengers of free radicals and effectively affect human wellbeing and infection counteractive action. They may have a conceivable part in enhancing the incendiary condition in rheumatoid joint inflammation patients (Rahmani et al. 2014). The fluid concentrate of date organic product had in vitro

cell reinforcement movement because of the nearness of mixes with powerful free-
radical-scavenging action. So it was of significance to think about the antioxidant
action of a consumable part of date natural products separates in vivo, in order to
affirm their action in an organic framework. Since the palatable part of natural
products has been demonstrated to contain phenolic mixes, the methanolic and
water concentrates may indicate mitigating action (Mohamed and Al-Okabi 2004;
Biglari et al. 2008). In addition to its antioxidant activity, date palm fruits also
terminate allergic responses and the fruit extracts acts as an anti-allergic agent
(Karasawa and Otani 2012). The geographic origin of the date palms can be explored
by determining the phenolic content (Mansouri et al. 2005; Saleh 2011).

Date palm is socio-financially and customarily critical for populaces where the
way of life flourishes. Foundation of date palm forests made difference migrant
populaces in the past to settle and sort out groups and start cultivating. These
populaces turned into a centre point for advertising or exchanging items, a creature,
and different items. A totally new industry has additionally been produced in late
years around the date palm and dates (El Hadrami and Al-Khayri 2012). The dates
have a high substance of sugars, which can possibly build serum glucose and
triacylglycerol levels, and also serum oxidative pressure and weight file. No infor-
mation is directly accessible on the impacts of information utilization by solid
subjects on their serum glucose, lipids, and oxidative status (Rock et al. 2009).

1.2 Date Palm – Growth and Development

Date palm is a dioecious plant with singular male and female trees. The tree takes
5–7 years to blossom, and henceforth drawn out stretches of time are required before
the sex of the plant is identified. It is quiet east to proliferate the female trees by
branches or by utilizing tissue culture methods. In date palm, formative capture of
sterile sex organs happens before the finish of cell division. It is trailed by the gifted
cell separation and advancement of unisexual blossoms. Direct root meristem
recoloring with chromomycin is adequate to distinguish the sex of the date palm
plant. Blooms have three carpels yet on fertilization just a single creates and two
prematurely end. The state of the fruit is generally pretty much elongated or
ellipsoidal (Hammadi et al. 2009). Figure 1.1 represents unripe and riped date
palm in unripe and dried date palm seed. The seed, or pit, is hard and stogie formed,
somewhat pointed at the finishes, from grey to darker in shading, and with a little
developing life. The seed of the date palm fruit is bizarre where it stores the
nourishment materials for the developing embryo not as starch, but rather as hemicelluloses (Ashraf and Hamidi-Esfahani 2010).

Fertilization is a standout amongst the most vital pre-collect factors influencing
fruit quality in the date palm. In commercial estate, artificial pollination either using
hand or mechanical means is used in case of female trees using pollens from male
trees. Choice of a decent pollinizer is of primary significance in the date palm, as the
sort of the pollen parent influences fruit size and time taken for fruit aging, and

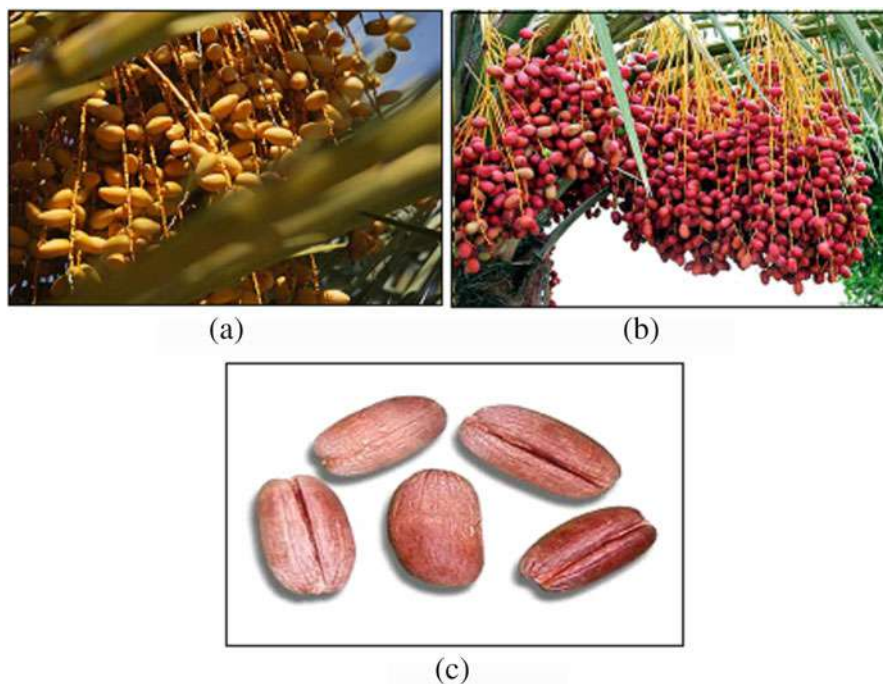


Fig. 1.1 Date palm – (a) Unripe date palm. (Reproduced from [http://www.junglemusic.net/New%20Plant%20Arrivals/Images3/Phoenix%20dactylifera%20fruit%20closeup%20\(Large\)%20\(Small\).JPG](http://www.junglemusic.net/New%20Plant%20Arrivals/Images3/Phoenix%20dactylifera%20fruit%20closeup%20(Large)%20(Small).JPG)) (b) Ripped date palm. (Reproduced from <http://realpalmtrees.com/palm-tree-store/canary-island-date-palm-seeds-pkg.html>) (c) Date palm seed

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115 additionally the chemical constituent of the organic product. Such impacts of the
 116 pollen male parent on different parts of date fruit improvement are alluded to as
 117 mataxenia (Bazza 2008). Because of its nutritional properties, date fruit as such can
 118 have an extensive range of applications, but at present the processing applications
 119 are very limited (Kamal-Eldin et al. 2012).

120 Fermentation is one of the most seasoned advancements ever utilized for the
 121 protection of sustenance and determining esteem included nourishment items from
 122 sustenance materials over the globe. Fermentation using microbes yield a few esteem
 123 included items for fluctuated applications other than the expansion of nourishment
 124 such as yogurt, vinegar, mixed drinks and so forth that are specifically consumed
 125 (Cagno et al. 2017). All natural products, plant and animal items that fit to be utilized
 126 as nourishment have been subjected to microbial fermentation with a specific end
 127 goal to infer advance results and items, for example, natural acids, amino acids,
 128 vitamins, and so forth (Chandrasekaran and Bahkali 2013). In spite of the fact that
 129 date palm sap is the rich wellspring of microbes, it could likewise fill in as a substrate
 130 during fermentation. As of late lignocellulosic biomass speaks to the most imminent
 131 feedstock for ethanol generation. Fermentative microflora from date palm could be
 132 used for fermentation using ethanol fermenting significant feedstocks. These

microbes could be altered using hereditary and metabolic building strategies for
higher production of ethanol (Gupta and Kushwaha 2011).

1.3 Variables Influencing Date Palm Development and Improvement

• Precipitation and Humidity

High precipitation and dampness at the time of blooming or later phases of fruit improvement may restrain the creation of date palms to an indistinguishable degree from deficient warmth unit. High stickiness and precipitation amid later phases of fruit advancement may cause certain physiological issue. Moreover, low relative moistness amid the fruit aging time frame may cause some physiological issue. High stickiness and precipitation pronouncedly affect the procedure of fertilization. Early precipitation amid flowering in the spring may cause the disease of the shut spathes with inflorescence spoil.

• Temperature

For appropriate date fruit maturing on the date palm, it is basic that the developing season is hot and free of precipitation amid the aging time frame. The normal ideal every day temperature from blooming until the point when the fruit aging is around 21 °C for early aging cultivars, 24 °C for mid season cultivars, and 27 °C for late maturing cultivars.

• Mineral nourishment

The presence of nitrogen is essential for effective growth and efficiency of date palm tree, and it is less delicate to other mineral supplements, for example, iron and boron, as contrasted to other fruit trees, for example, citrus.

• Growth regulators

The real increment in size of fruit is accomplished by the enlargement or vacuolation of the cells framed amid the early period of mitotic action. Auxins and gibberellins, splashed onto fruit groups, have been found to build fruit size and defer fruit maturing, with conflicting consequences for fruit compound structure. The inclination of the date palm flower to set parthenocarpic fruit if not pollinated might be identified with levels of endogenous hormones in the ovary of unpollinated flowers. Parthenocarpic date palm organic products may likewise be acquired by treating unpollinated flowers with hormones such as auxins, cytokinins or gibberellins. Such fruit are of low quality when contrasted with fruits delivered by hand fertilization and they won't age completely. Fruit aging is typically postponed in trees conveying a substantial harvest, which can be helped by fruit or bundle diminishing at a beginning period of development, with the goals of adjusting the quantity of green leaves and the quantity of fruiting packs (Yahia and Kader 2011).

170 1.4 Nourishing Constituents of Date Palm

171 Date palm fruits were found to contain the accompanying supplement creation:

- 172 • Carbohydrates – 44–88%
- 173 • Sugars – 60–80%
- 174 • Fats – 0.2–0.4%
- 175 • Proteins – 2.3–5.6%
- 176 • Fibres – 6.4–11.5%

177 The natural fruit are additionally rich in potassium, calcium and iron with little
 178 measures of protein (2%), lipids (under 2%), copper, chloride, zinc, sulphur and
 179 vitamins A, B1, B2 (Hasnaoui et al. 2010; Nehdi et al. 2010). Dates are rich
 180 wellsprings of copper, potassium, magnesium, selenium, and direct of calcium,
 181 iron, manganese, and phosphorus; and their normal utilization is accounted for to
 182 give the expected supplements to the human body. The high potassium and low
 183 sodium substance in dates are attractive for individuals experiencing hypertension.
 184 The presence of mixes, for example, phenolics with a possibility to scavenge free
 185 radicals, high antimutagenic impacts and to fortify the insusceptible framework may
 186 contribute towards the different pharmacological impacts (Baliga et al. 2011; Abdul
 187 and Allaith 2008). The unrefined fibre, which contains gelatin, lignin, hemicelluloses
 188 and cellulose, speaks to around 2–4% of fruit dry weight. Gelatin assumes an
 189 essential part in date surface. The protein substance of dates, which is accounted
 190 for to be of high nutritive esteem, goes in the vicinity of 1.5 and 2.0%, and the rough
 191 fat substance runs in the vicinity of 2.5 and 7.4%. The seed oil is made out of 45%
 192 oleic, 25% palmitic, 10% stearic and 10% linoleic corrosive, with some capric and
 193 caprylic corrosive substance. The relish and nature of dates are influenced by their
 194 natural acidic substance. The date palm kernel weighs about 12–15% of date palm
 195 fruit. It is filled with 5–6% of proteins, 10–13% of fat, 46–51% of fibre, 1–2% of ash
 196 and nearly 10% of moisture content in it (Mariod et al. 2017). The causticity of the
 197 fruit tends to increment with fruit development and afterward diminishes toward the
 198 start of the aging stage, while pH increments at development. High pH esteem means
 199 that dates is of high quality. Date corrosiveness achieves the largest amount amid the
 200 time of most quick development and reductions amid development and maturing.
 201 Palmitic corrosive is the most prevailing corrosive took after by capric and caprylic
 202 acids. Date fruits at the completely develop organize are rich in useful parts,
 203 including phenolic mixes. Tannins are the most prevailing phenolic mixes in date
 204 leafy foods intently connected with the fruit maturing process (Al-Farsi and Lee
 205 2008; Sahari et al. 2007). Dates comprise 70% starches, the vast majority of which is
 206 as sugars. In many assortments, the sugar content is totally modified sugar, which is
 207 quickly consumed by the human body. There is a specific absence of data on
 208 utilitarian constituents of dates and their potential incentive as useful nourishments.
 209 Useful sustenance is defined as those nourishments that give health benefits beyond
 210 fundamental nutrition (Assirey 2015; Sirisena et al. 2015).

1.5 Physiological Clutters

211

A few physiological issues can influence dates, consequently influencing their quality in the market. 212 213

• Obscuring 214

Both enzymatic and non-enzymatic browning happens in dates and increments with higher dampness content and higher temperatures. Enzymatic browning can be restrained at low oxygen focuses and low temperatures. 215 216 217

• Skin division (puffiness) 218

Skin division happens when the skin winds up dry, hard and fragile, and isolates from the flesh. It is said to be serious when the skin isolates from the flesh in an inflatable like manner. This issue creates amid aging of delicate date cultivars, which change in vulnerability. High temperature and high stickiness at a phase before the start of aging may incline the dates to skin division. Puffiness or indented partition, caused by high temperature as well as high dampness before the start of aging, may increment amid curing and influences just delicate cultivars. 219 220 221 222 223 224 225

• Sugaring 226

Sugar spotting is described by the presence of light-shaded spots under the skin and in the flesh and happens primarily in delicate date cultivars otherwise called rearrange sugar dates in which glucose and fructose are the principle sugars. Rate and importance of sugar spotting increases with increase in capacity temperature and time. Sugar spotting diminishes as the temperature diminishes and when the dampness content falls beneath 22%. So stockpiling at suggested temperatures limits this issue. Sugaring might be diminished by delicate warming of the influenced dates, however returned if adverse conditions conquer. 227 228 229 230 231 232 233 234

• Discolouration 235

Because of their high dampness content, delicate date cultivars are defenceless to a physiological issue known as inner breakdown which causes dark discolouration of fruits, on the off chance that they are not put away at the right temperature. 236 237 238

• White and Black Nose 239

White nose is portrayed by the nearness of a stained ring close to the calyx territory, which at times covers half of the fruit. It has been recommended that dry breezes for a long time amid the rutab phase of maturing can make the basal locale of the fruit age more than the rest, causing the ring appearance. This physiological issue might be because of calcium inside the fruit with the basal end containing less calcium than the apical end. Dark nose is fruit checking at the tip area of the fruit that turns dull shading. It is caused by high moistness. 240 241 242 243 244 245 246

247 • **Splitting**

248 It can be caused by various climatic conditions. Over-hydration, caused by a
249 sudden increment in stickiness, for example, unseasonal rain, can offer ascent to an
250 adjustment in turgor weight inside the fruit, bringing about splitting.

251 **1.6 Market Preparation Before Commercialization**

252 There are few preparatory stages for date palm fruit before it is provided in the
253 market for commercialization (Mahmoudi et al. 2008). Figure 1.2 demonstrates the
254 steps engaged with advertising readiness.

255 **1.7 Applications of Date Palm**

256 Date palm owing to its vast nutrient and mineral content is widely used for various
257 purposes. Figure 1.3 represents the benefits of date palm in various sectors.

258 **1.7.1 Medical Advantages**

259 Medicinal and health nourishments have as of late gotten tremendous enthusiasm
260 among the wellbeing experts and the general population. Subsequently, the

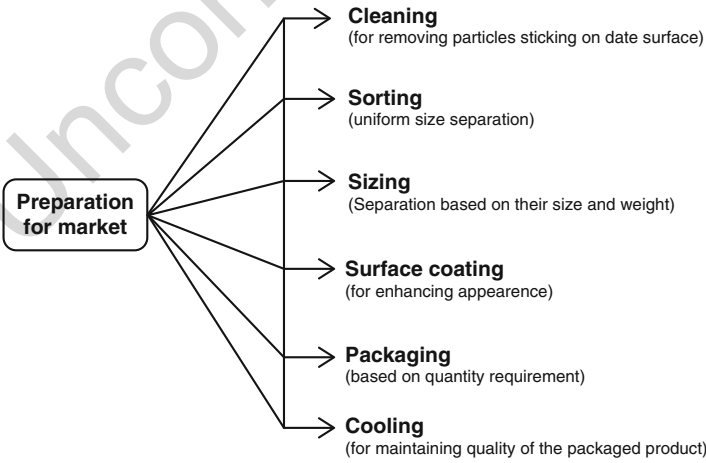
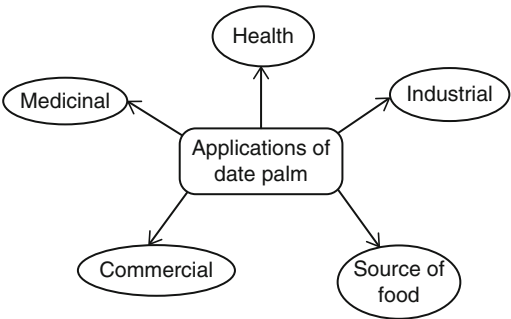


Fig. 1.2 Preparatory steps before commercialising

Fig. 1.3 Applications of date palm



worldwide wellbeing market has been overwhelmed with such items guaranteeing to 261
enhance wellbeing and also avoid ceaseless ailments. Due to expanded business 262
misuse of therapeutic sustenance, all assortments of products of the soil were 263
re-assessed for their phytochemical piece and medical advantages under both 264
research facility conditions and clinical settings (Vayalil 2012). 265

• **Gut Regularity** 266

Consuming dates can help counteract clogging. They’re a phenomenal wellspring 267
of dietary fiber. A lot of the fruit’s fiber is insoluble, the kind that advances ordinary 268
absorption. Concentrates of dates mash and palm sap have stimulatingly affect GIT 269
movement. All the more imperatively, the outcomes contribute toward the approval 270
of the conventional utilization of dates mash and palm sap for the treatment of 271
stomach related issue such as constipation (Souli et al. 2014). 272

• **Cardiovascular Benefits** 273

Dates are a decent wellspring of a few cardio-defensive supplements, including 274
potassium, copper and magnesium. Having ample potassium in one’s eating regimen 275
can help diminish hypertension, which may thusly bring down the danger of 276
showing stroke or heart attack. Copper and magnesium are imperative for blood 277
veins. Copper likewise keeps up the connective tissues in the heart and veins, while 278
magnesium maintains typical heart rhythms. Moreover, dates are a decent wellspring 279
of beta-D-glucan, a solvent fibre that can be especially compelling at decreasing 280
elevated cholesterol levels (Ishurd et al. 2002). 281

• **Absence of additional sugars** 282

Dates can be consumed to fulfil one’s sweet tooth while entirely constraining or 283
previous the additional sugars found in numerous refined nourishments - likewise 284
ensures cardiovascular wellbeing. Added sugars, or with any sort of sugar used to 285
sweeten a supper or sustenance item, have been connected to stoutness, hypertension 286
and undesirable cholesterol levels. Expending excessively numerous additional 287
sugars is related with a significantly more serious danger of dying from coronary 288
illness. 289

290 **1.7.2 Potential Benefits**

291 Vitamin C is absent in dates which is an important antioxidant commonly found in
 292 most of the fruits. They are as yet a decent wellspring of phytochemicals, in any case,
 293 which are generally present as phenols and carotenoids. A portion of these mixes
 294 display huge cancer prevention agent movement; they adequately protect cells from
 295 free-radical harm (Hamada et al. 2002). An eating routine rich in cell reinforcements
 296 or one focused on fruits, vegetables and other entire nourishments is generally
 297 thought to help ensure against growth, coronary illness and other perpetual condi-
 298 tions (Al-Humaid et al. 2010). Additionally presence of chemical constituents
 299 enhances the benefits of dates (Alshowiman 1990).

300 **1.7.3 Minerals from Date Palm**

301 • **Potassium**

302 Important electrolyte potassium is rich in dates. Potassium helps to control liquid
 303 levels and helps bring down the circulatory strain. It additionally makes the body less
 304 delicate to sodium, so people are more averse to endure a substantial spike in
 305 circulatory strain after a sodium-rich dinner. Expending potassium likewise benefits
 306 the nervous system, as the nerves depend on potassium communicates with each
 307 other.

308 • **Polyphenols**

309 Dates likewise contain polyphenols, a kind of gainful substance found in some
 310 plant-based nourishments. Polyphenols work as cancer prevention agents, shielding
 311 the cells from oxidative harm to the DNA, cell lipids and proteins that generally
 312 would cause ailment. While the impacts of date polyphenols on people requires
 313 assist examination, they demonstrate potential for ensuring one's wellbeing.

314 • **Dietary Fibre**

315 Dates fill in as a rich wellspring of starches, including dietary fibre. Fibre goes
 316 through the stomach related framework unaltered. Devouring fruits that contain fibre
 317 secures against coronary illness, and dietary fibre likewise benefits people with type
 318 1 and sort 2 diabetes. Fibres are the strong insoluble piece of date substance,
 319 basically made out of cellulose, hemicellulose, insoluble proteins and lignin. The
 320 measure of these filaments is higher in beginning periods of fruit life. In any case,
 321 amid the aging procedure, cellulase and pectinase chemicals show in the natural
 322 product separate insoluble polymers into littler dissolvable atoms. These filaments
 323 can be utilized as dietary strands because of oil and water take-up, and swelling limit
 324 (Shafiei et al. 2010).

Other advantages	325
• Date palm fruits help in expanding platelet count in patients experiencing dengue fever.	326 327
• Immune framework gets fortified and bone loss is prevented.	328
• Whole framework picks up vitality with expanded platelet count.	329
• It gives different minerals (potassium, fibre, and so on.) and vitamins required for development of human body.	330 331
• Night visual impairment (blindness) and paleness (anaemia) can be avoided.	332 333

1.7.4 Industrial and Commercial Applications 334

Date palm tree is fundamentally planted for its fruits. It has different uses too in the commercial and modern aspects. Besides, a portion of these results equalled or are more imperative than the date fruit itself (Weber 2010). Date palm tree requires heaps of daylight. The normal and most direct business utilization of date palm tree is in arranging. Seeing avenues fixed with date palm trees will bring out an extraordinary and tasteful atmosphere to the region. It can withstand high and low temperature yet should not dip under 20 °F. Dates seed oils, which are rich in a few unsaturated fats are utilized as a part of cleansers and beauty care products. High tocol content is present in date palm than other oils such as olive, etc. This indicates better oxidative stability of date palm (Nehdi et al. 2018). The chemical nature of date seed oil makes it reasonable as an element for oxalic acid. Date seed medical advantages incorporate defensive impacts against early diabetic complexities, counteract DNA harm, and secure liver and kidney. Regardless of its little size, date seed can be subjected to burning and utilized as a viable charcoal. The date leaves stalk or spine is long and thin yet is solid and can stand the heaviness of a few men. They are utilized as rooftop rafters, networks, wall, flooring for little cabins, basic furniture, and so on (Khan and Khan 2016). Date palm fruits are broadly delivered and speak to rich wellsprings of sugar, fibre, and phenolic cancer prevention agents. Date fruits give high sustenance crude materials because of its conceivable utilization at three advancement stages from an extensive variety of assortments. In spite of the high generation, date fruits are underutilized and more engaged research is expected to increase the value of this yield. Date fruits have a tremendous degree and potential for use as nourishment due to their wholesome and financial esteem. There is a vast potential to particularly create healthy products using the high-esteem fibre and phenolic cancer prevention agents found in the fruits and seeds (Ghnimi et al. 2017).

t1.1 **Table 1.1** Medical applications of different parts of date palm

t1.2	S. No	Parts of date palm	Uses
t1.3	1.	Leaf	Aphrodisiac and liver treatment
t1.4	2.	Flower	Fever, purgative and blood complaints
t1.5	3.	Fruit	Leprosy, bronchitis, asthma, fever, vomiting and tuberculosis
t1.6	4.	Seed	Inflammation, laxative, lesions and wounds
t1.7	5.	Gum	Genitor-urinary system diseases and diarrhea

360 1.7.5 Therapeutic Uses

361 Taking date fruits once a day amid pregnancy will help reinforce the uterine muscles.
 362 It will aid the conveyance and deflect the post-conveyance dying. Dates are rich in
 363 potassium, glycine, and threonine that will enact prolactin which is the milk hor-
 364 mone. It will advance the stream of milk, which is useful for a breastfeeding lady.
 365 Along these lines, it regards keep eating dates even after pregnancy. Dates are rich in
 366 Vitamins A, B1, B2, B3, B5 and C, fiber, calcium, phosphorus, sulfur, potassium,
 367 copper, magnesium, and manganese. In spite of its sugar content, it is utilized to
 368 re-establish wellbeing to the iron deficient and delicate because of its extraordinary
 369 wellspring of supplement content. The most ideal route is to eat them crisp and not in
 370 cooking or squeezing. The date is a low-glycemic record sustenance and its high
 371 characteristic sugar substance won't essentially raise your glucose levels. Date fruits
 372 to give alleviation from fever, astringent, bronchial asthma, chest and throat con-
 373 taminations. Table shows remedial utilizations of various parts of date palm (Kwaasi
 374 2003) (Table 1.1).

[AU2]

375 1.7.6 Source of Food

376 The date is the staple sustenance. Dates are additionally prepared into glue, syrup,
 377 stick, jam, date solid shapes, date sugar powder, date vinegar and even date liquor.
 378 Dates are presently promoted as chocolate secured dates and sprinkled with slashed
 379 walnuts and raisins. Most agriculturists will do specific separating while date fruits
 380 are creating for more profitable collect. These winnowed date fruits will be dried out,
 381 grounded and blended with different grains and utilized as feedstock (Ibrahim 2004).
 382 Overload dried dates are given as sustenance to animals such as horse and camels.
 383 The terminal bud and youthful date leaves, which are rich in phosphorus, potassium,
 384 nitrogen, and fiery debris, can be transformed into a serving of mixed greens or
 385 cooked as a vegetable dish (Al-Farsi and Lee 2011; Al-Shahib and Marshall 2003).

1.8 Destruction of Date Palm

386

In the same way as other different plants, a few palms are in risk of ceasing to exist in view of human action. In spite of the fact that date palm development in the date developing districts of the world has a long history, yet the endeavours consumed for the advancement of this imperative yield, though important, yet still deficient and fall beneath desires. The item quality is still low, the field and post-harvest misfortunes are very high and the date items and side-effects can no uncertainty be enhanced and the product blend more differentiated (Sawaya 2000; Jaradat and Zaid 2004). Production of Date palm is confronting significant issues, for example, low yields because of the absence of research, the spread of bugs, and additionally promoting imperatives. In the course of the most recent decade, profitability has declined in the customary developing zones. Pests and diseases caused by them have caused huge impacts upon date generation. Bayoud sickness which is caused by parasite undermines the date palms (Gassouma 2004). Therefore, the expenses of date production have outperforms incomes. In the meantime, the transportation of dates has declined to a base. Lessening in the profitable limit of date palms and the corruption of the nature of generation itself are the fundamental markers of debasement. Thus, the likelihood to gain a salary outside the desert garden, have incited mass movement. The maintaining date palms for the most part are limited. The outcome of this disregard is the running wild of the palm-forests, thickly developed with date palms, diminishing harvests and, subsequently. Regardless of the significance and expansive culture territories of ordinary date palm development, field and postharvest depletion are high, and techniques for estimating item quality and the utilization of date items and side-effects require change (Awad 2007). Amid the most recent 50 years, date palm forests have been subjected to corruption because of broad misuse coming about and because of the expansion in both the human populace and the quantity of residential animals. Likewise, the expanded capacity of most of the populace to profit by circumstances displayed by present day innovation has driven them to desert their date palms. Common variables have additionally added to the debasement of date palms, for example, dry spell, soil saltiness, bugs, natural change, and a decrease in the nature of ground water. Intense lack of trained and experienced workers with expanded wage requests, bringing about the disregard of numerous rural procedures required for appropriate date palm production. There is a recognizable shortcoming of government organizations for the augmentation and security of horticultural movement. Expanded pervasion of bugs and sicknesses bringing about a critical decrease in the efficiency of trees and have contributed altogether in destruction of date palm. The change of the present status of date palm development in the date producing nations and the upgrade of the nature of date items have turned out to be basic need that can't be overplayed (El-Juhany 2010).

426 Date palms must be comprehended to exist inside complex biological, social and
 427 economic organizations. Commercial products incorporate an expansive number of
 428 adjusted ecotypes. This perpetual dioecious plant is of extraordinary financial
 429 intrigue. To create natural dates, agriculturists must guarantee that natural organic
 430 composts are utilized to improve the sandy soil, and the dated must be permitted to
 431 age completely on the trees. The makers ought to consider, when fitting, the
 432 conceivable outcomes offered by naturally developed dates, as the natural market
 433 is developing quickly in numerous created nations. Thusly, as an ever-increasing
 434 number of buyers swing to natural sustenance, retailers will search for an entire
 435 scope of producing natural organic dates (Williams 2008).

436 1.9 Conclusion

437 Date palm is a customary product in the Arab world which has the ability to
 438 withstand unfavourable climatic conditions. The circulation of date palm is excep-
 439 tionally impossible to miss due to the inalienable prerequisite for hot atmosphere
 440 which is important for effective fertilization and fruit setting. Lately, in light of
 441 overexploitation, the decent variety of the date palm forests has declined. The
 442 generation and use of the date fruits likewise differs from nation to nation because
 443 of the impact of current ecological conditions. There are various components which
 444 impede the generation of date palm, for example, significant nuisances and sick-
 445 nesses, saltiness and dry spell, poor gather and postharvest hones. For a great many
 446 years date palm was engendered through ordinary reproducing which is a tedious
 447 and repetitive process. The utilization of the tissue culture systems gave date palm
 448 an enhanced productivity contrasted with different yields. The required data when
 449 accessible will upgrade our insight and thankfulness for the utilization of dates in
 450 our every day count calories. Because of its wealth and ease, dates remain a species
 451 with enormous potential and incalculable conceivable outcomes for future exami-
 452 nation. Considering the way that dates are generally modest, nutritious and are
 453 without dangerous impacts it is protected to propose that their utilization ought to be
 454 prescribed on a day by day the reason for better wellbeing, essentialness, and force.

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Abstract	In order to explore the renewable energy resources like biogas, there is a need to find the appropriate feedstock to avoid the depletion of fossil fuels and environmental deterioration. Date palm fruit is a suitable raw material with health promising features. Palm fruits also have the capability to produce biogas at a high quantity. Anaerobic digestion of palm fruit is a most valuable technique that has been evaluated as a promising feedstock to generate biogas like methane. In the event of biogas production, the anaerobic procedure assumes an essential part which gives higher help to the high amount of biogas generation. It is generally connected for the treatment of organic waste like palm natural products because of its high natural substance which helps in the generation of biogas. This chapter features the elements which impacting or influencing the anaerobic procedure and different kind of anaerobic reactors, for example, continuous stirred tank reactors, anaerobic filtration, anaerobic fluidized bed reactors, anaerobic contact process, upflow anaerobic sludge blanket reactors and so forth used for the methane gas generation. These reactors are organic procedures that have been disclosed to upgrade the biogas generation. This chapter also depicts the potential for biogas production from date palm fruit and additionally it reveals the upsides and obstacles for anaerobic digestion technology. Procedures to additionally enhance these methodologies alongside future research are outlined in this chapter.
Keywords (separated by ‘-’)	Renewable energy - Biogas - Palm fruits - Anaerobic digestion - Continuous stirred tank reactors - Anaerobic filtration - Anaerobic contact process

Chapter 5

Biogas Production from Date Palm Fruits

P. Senthil Kumar and C. Femina Carolin

Abstract In order to explore the renewable energy resources like biogas, there is a need to find the appropriate feedstock to avoid the depletion of fossil fuels and environmental deterioration. Date palm fruit is a suitable raw material with health promising features. Palm fruits also have the capability to produce biogas at a high quantity. Anaerobic digestion of palm fruit is a most valuable technique that has been evaluated as a promising feedstock to generate biogas like methane. In the event of biogas production, the anaerobic procedure assumes an essential part which gives higher help to the high amount of biogas generation. It is generally connected for the treatment of organic waste like palm natural products because of its high natural substance which helps in the generation of biogas.

This chapter features the elements which impacting or influencing the anaerobic procedure and different kind of anaerobic reactors, for example, continuous stirred tank reactors, anaerobic filtration, anaerobic fluidized bed reactors, anaerobic contact process, upflow anaerobic sludge blanket reactors and so forth used for the methane gas generation. These reactors are organic procedures that have been disclosed to upgrade the biogas generation. This chapter also depicts the potential for biogas production from date palm fruit and additionally it reveals the upsides and obstacles for anaerobic digestion technology. Procedures to additionally enhance these methodologies alongside future research are outlined in this chapter.

Keywords Renewable energy · Biogas · Palm fruits · Anaerobic digestion · Continuous stirred tank reactors · Anaerobic filtration · Anaerobic contact process

5.1 Introduction

Date palm (*Phoenix dactylifera*) is an essential antiquated monocots plant in the Saudi Arabia. It is made up of various natural products including leaves and seeds. Date palm parts are highly utilized in date creation and their primary utilization are to

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enhance organic matter of soil (Alananbeh et al. 2014). Date palm tree is an imperative tree for dry areas of the world, and it has constantly assumed an essential part in the social existences of the general population (Elluech et al. 2008). World date fruit generation achieved in excess of 7.7 million tons in 2014. An expected 12 million tons of date palm waste comprising of date palm trunk, fronds (stems and leaves), date flesh, and seeds are created on the planet consistently. The product of the date palm is one of the wealthiest natural product based wellsprings of protein. Date palm is one of the major natural products delivered in moisture free districts. It is a critical business edit in various districts of the world and is viewed as the third generally essential palm species in the worldwide farming industry, after coconut. The seeds of the date organic product, which are discarded after the date preparing, additionally contain 5–7% protein by weight. Various attempts were tried to utilize the date waste in a useful way. It produces a fruit date that is appreciated in all parts of the world. Because of this reasons the worldwide interest for dates and in addition its generation keeps on increasing. The present chapter is based on the efforts to extract energy from date palm fruit as methane-rich biogas.

5.1.1 Properties and Characteristics of Date Palm Fruit

Date palm fruit has an important part due to the upsides like agricultural, food providing, therapeutic, profitable, architectural, environmental characteristics and their various applications. As of late, this organic product has picked up noteworthy significance in worldwide business also. Amid the most recent two centuries, the world generation of dates has dramatically increased. Date organic products (*Phoenix dactylifera*) are of extraordinary significance in human sustenance attributable to their high substance of fundamental supplements, which incorporate various biomolecules (Lattieff 2016). Dates are rich in specific supplements and give a well-spring of quick vitality because of their high sugar content (70–80%). The vast majority of the sugars in dates are as fructose and glucose, which are effectively consumed by the human body. It has been built up that the date palm fruit product has different therapeutic properties like cancer prevention agent, antimutagenic, antioxidant, antimicrobial. The date organic product is recorded in society solutions for the treatment of different irresistible illnesses and cancer. Customarily they are utilized for sustenance, or to deliver desserts, sweet syrup (Dibs in Arabic), vinegar and alcoholic items. Sugars are the real substance components of the date, for the most part including glucose, fructose and little measures of cellulose and starch. The high health giving sugars of date palm squanders are great hotspots for organism maturation potential toward bio-energy creation (Gupta and Kushwaha 2011). The real parts of date palm biomass are cellulose, hemicelluloses and lignin. Additionally, date palm has high unstable solids substance and low humidity.

5.1.2 Global Production

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Date palm is one of the primary rural items in the Middle East also. The date palm *Phoenix dactylifera*, a tropical and subtropical tree, having a place with the family Palmae (Arecaceae) is one of humankind's most established developed plants. It has assumed an essential part in the everyday existence of the general population throughout the previous 7000 years. Tons of dates are generating from million date palm trees per year excluding secondary products like palm midribs, leaves, stems, fronds and coir. The generation of date palm fruits has been raised from 2.3 million tons in 1974 to 7.6 million tons in 2010. The heft of this yield comes, in a specific order, from Iraq, Egypt, Saudi Arabia, Iran, United Arab Emirates, Pakistan, Algeria, Sudan, Libya, and Tunisia (Bhansali 2010). The Arab world has in excess of 84 million date palm trees with the greater part in Egypt, Iraq, Saudi Arabia, Iran, Algeria, Morocco, Tunisia and the United Arab Emirates. In Iraq, nine million trees cover the center and southern parts of the nation, bringing about a surplus generation of dates also, other optional biomass. It is created to a great extent in the hot dry locales of the world especially in Gulf Cooperation Council (GCC) nations, and Saudi Arabia is one of the world's significant maker of dates. The availability of date palm trees in Saudi Arabia is about 23 million trees, which deliver about 780,000 tons of dates for every year (Al-Abdoulhadi et al. 2011). Dates creation in Saudi Arabia incredibly expanded for the previous two centuries and is likewise paralleled by high utilization. *P. dactylifera* is the essential yield in Oman, which transfers 82% of all organic product crops creation in the nation. Algeria produces in excess of 400 distinct assortments of dates with a yearly creation of more than 400,000 tons (Chandrasekaran and Bahkali 2013).

AU2

5.1.3 Feedstocks of Biogas Production

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The target on biogas production through better feedstock is increasing. The things like difficulties of inefficient biogas yield, high maintenance time, and high operating cost obstruct the most extreme execution of biogas creation in the anaerobic digestion process. These restrictions are profoundly reliant upon the accessibility, synthesis, and degradability of the feedstock utilized for biogas generation. The extraordinary potential lies in biogas generation from different feedstocks, for example, crop residues, livestock residues, municipal waste, landfill waste, food waste, and lignocellulosic feedstocks in light of their accessibility and plenitude. Nonetheless, the greater part of these feedstocks has moderate corruption rates and in that capacity requires longer maintenance times. Moreover, a portion of these feedstocks contains harmful intermediates or contain harmful mixes, which repress the biogas generation process. Biogas can be delivered from locally accessible

104 natural source by anaerobic processing. Locally accessible waste items for biogas
 105 generation include solid waste; sludge; and date palm wastes. Biogas is commonly
 106 created just from source that are effortlessly used by the microbial group in charge of
 107 changing these feedstocks into biogas. The improvement of imaginative innovations
 108 going for the usage of feedstocks that are promptly accessible however not effec-
 109 tively degradable would bring about an expansion in biogas creation. The real
 110 reasons why a few feedstocks are not perfect for biogas creation are: (a) they can't
 111 be processed by microbes, (b) assimilation by microbes is extremely troublesome to
 112 accomplish, (c) assimilation could be accomplished however in a moderate manner,
 113 and (d) the availability of inhibitors in the feedstock or the creation of inhibitory
 114 mixes amid microbial debasement.

115 **5.1.4 Date Palm Fruit as a Main Source**

116 Among the extraordinary types of inexhaustible feedstocks, biomass is without a
 117 doubt a standout amongst the most encouraging (Messineo et al. 2012). Around 16%
 118 of worldwide last vitality utilization originates from inexhaustible assets, with 10%
 119 of all vitality from customary biomass, essentially utilized for warming, and 3.4%
 120 from hydroelectricity. The biomass can be used for improving the quality of soil after
 121 proper treatment (Converti et al. 1999). The biogas quality depends on the type of
 122 waste material, characteristics of the material and also the fermenting conditions.
 123 The nature of biogas created by natural waste materials does not stay steady but
 124 rather shifts with the time of assimilation. An extensive variety of warm and
 125 biochemical innovations are available to change over the energy put away in date
 126 palm biomass to helpful types of energy. Due to the availability of moisture free in
 127 the date palm fruits, it is well appropriate for the thermal treatment like combustion,
 128 gasification and pyrolysis. Then again, the huge unpredictable solids in date palm
 129 biomass demonstrates its probability towards biogas creation in anaerobic absorp-
 130 tion plants, conceivably by co-digestion with sludge, animal wastes and food wastes.
 131 By the fermentation process, the carbohydrate content of date palm fruits can be
 132 converted into a biofuel. Various researches have been carried out the co-digestion
 133 process of agro waste for biogas production. *Phoenix dactylifera* has assumed a
 134 critical part of the everyday existence of the general population for the last
 135 7000 years. Today overall generation, use and industrialization of dates are consis-
 136 tently expanding because date natural products have acquired incredible significance
 137 in human nourishment attributable to their rich substance of fundamental supple-
 138 ments. The current investigation, intended to evaluate out of the biogas generation
 139 from date palm source.

5.2 Biogas Generation

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In the current decades, creation and utilization of biogas have pulled in particular consideration in view of vitality deficiency and rising costs of fuel in bringing in nations. In later a long time, administrations of India and China have started far-reaching endeavors to create biogas to manage the quick increment of the imported oil value. Biogas creation from natural waste items is a good choice since it joins both energy recovery and waste administration (Radeef et al. 2016). Biogas can be used for on-location warm vitality and power. Biogas speaks to a standout amongst the most very refreshing openings to use certain classifications of biomass to satisfy in part the earth vitality needs. Biogas normally alludes to a blend of gases delivered through the natural disruption of natural matter in the nonappearance of oxygen. The resultant vitality discharge permits biogas to be utilized as a biofuel to replace ordinary fossil vitality sources (coal, oil, flammable gas) in power and warmth generation, and furthermore as an adaptable sustainable power source to fuel vehicle. It also used to replace the diesel generated and local grid power. The generated biogas can be utilized for warm age, and after that sold to the next adjacent industrial facility. The part of biogas generation and catching innovation should be considered also. The establishment and working of biogas creation frameworks can give numerous advantages to clients and the more extensive group. Focal points incorporate vitality manageability, asset protection and natural preservation. The high use of reducing petroleum derivatives is considered unsustainable in view of their fewer source and nonrenewable nature. Biogas got from different natural sources can decrease the overwhelming reliance on these draining common assets and address the vitality weakness worries because of its inexhaustible (He et al. 2012). A few reports show that anaerobic process of the natural division of strong waste gives hopeful measures of biogas. Biogas is for the most part made out of 48–65% methane, 36–41% carbon dioxide, up to 17% nitrogen, <1% oxygen, 32–169 ppm hydrogen sulfide and hints of different gases (Ward et al. 2008). Not at all like a petroleum product, does biogas not contribute much to the environmental impact, ozone consumption or corrosive rain (Nath and Das 2004). This is one of the fundamental causes that anaerobic processing is an extremely vital part in addressing vitality difficulties of the future generations. The valorization of the created biogas is that it is vitality effective because of the low outflow of risky contaminations, for instance, volatile organic compounds (VOC) (Appels et al. 2011).

5.3 Anaerobic Digestion Process

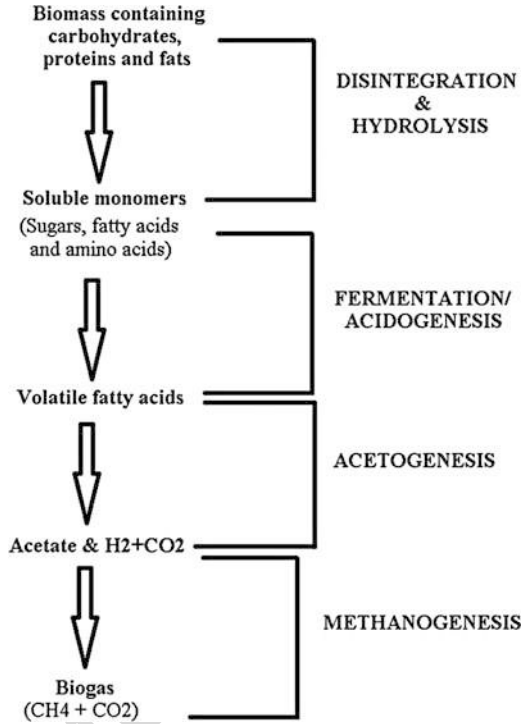
175

Enthusiasm for anaerobic digestion (AD) has been consistently developing in the course of the most recent decades, being increasingly as often as possible advanced by national projects for vitality generation from inexhaustible assets. Anaerobic

assimilation is an innovation confronting developing regards and expansive uses (Clarke and Alibardi 2010; Levis et al. 2010). Anaerobic assimilation is thought to be an eco-compelling innovation since it produces sustainable power source as methane, and furthermore decreases the discharge of ozone-harming substances by means of the biogas recovery (Kaewmai et al. 2013). Anaerobic Digestion (AD) is a natural procedure, which diminishes natural contamination and produces sustainable power source (biogas). This sort of bioprocess is viewed as an elective vitality source to non-renewable energy source. The capacity of anaerobic digestion process has identified newly which has the potential to convert biologically the hydrogen and carbon-di-oxide of sources into methane storage uses (Burkhardt et al. 2015). The high biodegradability and dampness substance of food waste are perfect attributes for biogas generation and digestate are utilized for conditioning the soil or as supplement feedstock. Biogas creation through anaerobic absorption innovation has progressed massively throughout the years. Because of high energy request and ecological worries as the total population expands, the drive for anaerobic digestion is inside research and the business for manageable energy. Anaerobic assimilation has been a standout amongst the most generally utilized handled for the adjustment of biosolid waste, for example, from the agro and civil waste to modern waste. In order to boost its effectiveness, anaerobic assimilation is currently generally utilized at fullscale to debase different natural feedstocks.

Anaerobic digestion is exceptionally ideal because of its ability of vitality recuperation by transformation of solids into biogas, odor decrease, and disposal of pathogens and mass decrease of solids. In anaerobic digestion, the organic biodegradable material is corrupted by microbes under conditions without oxygen, where biogas is delivered normally. Biogas is included for the most part 60–70% CH₄, 30–40% CO₂ and low measures of other trace gases. It incorporates assorted types of anaerobic microbes, which are in charge of the corruption of organic compounds and need time to adjust to the new condition before they begin to devour on organic matter to develop. To create biogas from absorbable materials by anaerobic absorption, the decay of natural squanders happens in four procedures at the same time: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Yang et al. 2015a, b). Steps associated with the anaerobic digestion process are indicated in the Fig. 5.1. Controlling these phases in an appropriate way of balance between their rates prompts the gas production to higher. Hydrolysis is a basic rate constraining procedure which corrupts insoluble natural materials, for example, lipids, polysaccharides, proteins and cellulose into its spine constituents (e.g. fatty acids furthermore, amino acids). The products from hydrolysis process are additionally separated into hydrogen (H₂, CO₂, acetic acid derivatives and volatile fatty acid (VFA) by acidogenesis process and further these products get converted in another product which is utilized for methanogenesis. In the next step, VFAs are processed to create acetic acid derivatives and H₂ by H₂ creating microbes/acetogens. In the last process where CH₄ is produced by an assortment of methanogenic microscopic organisms. The proficiency of this framework primarily relies upon the structure of the microbial group and natural variables, for instance, pH and temperature (Weiland 2010). The different gatherings of microscopic organisms taking part in the anaerobic

Fig. 5.1 Steps involved in the anaerobic digestion process



digestion have diverse ideal pH extents and large guarantee of effective assimilation 224
and gas generation. The procedure of biogas age from strong natural waste is 225
frequently completed by a few distinctive anaerobic microorganisms. 226

The procedure of acidogenesis also, methanogenesis need diverse pH for ideal 227
process control. Acidogenic microbes are less delicate and just require pH over 228
5, while methanogenic microbes are more suitable at pH range of 6.5–7.2 229
(Kathirvale et al. 2004; Appels et al. 2008). Hence, the ideal pH extend is 6.8–7.4 230
where both the microbes gathering can coincide. The VFAs produced amid the 231
anaerobic processing prompts the decrement in the pH. However, it can be countered 232
by the creation of alkalinity as carbon dioxide, ammonia furthermore, bicarbonate by 233
the methanogenesis microbes. The methane-producing process needs separate deg- 234
radation phases to be executed by the bacteria fermentative bacteria, syntrophic 235
acetogens, homoacetogens, hydrogenotrophic methanogens and aceticlastic 236
methanogens. The relationship among the above mentioned microbes adds to pro- 237
ficient anaerobic digestion and biogas creation (Weiland 2010). The last stage, 238
directed by methane forming microorganisms, is the most essential phase in biogas 239
creation where the methanogens change over their essential substrates including 240
acetic acid derivation, hydrogen and carbon dioxide into methane. In methane 241
development pathway, 75% of methane generation gets from decarboxylation of 242
acetic acid derivation and 25% begins from CO₂ and H₂. 243

244 The board utilization of this innovation originates from its potential preferences
 245 methanogenic procedure of anaerobic processing, and additionally on biodegrad-
 246 ability. To detoxify the phenolic compounds, pretreatment was found to be neces-
 247 sary. A wide assortment of anaerobic frameworks has been created to particularly
 248 treat squander anaerobically. Anaerobic assimilation in this way speaks to an
 249 adaptable procedure that can be utilized as conclusive change process in a
 250 biorefinery chain for every one of those substrates furthermore, remaining streams
 251 not further convertible to high esteem items. Including, the generation of methane, a AU3
 252 decrease of 30– half of the waste volume requiring extreme transfer, and a rate of
 253 pathogen obliteration, especially in the thermophilic procedure. The execution of the
 254 anaerobic procedures can be restricted by the inhibitory impacts of the phenolic
 255 mixes exhibit in palm effluent. Some straightforward phenolic mixes and poly-
 256 phenols inhibitory affect both general anaerobic assimilation and on the AU4

257 **5.3.1 Factors Affecting Anaerobic Digestion Process**

258 Anaerobic digestion, a microbial-subordinate organic process, is exceedingly subject
 259 to the presence of great environment to survive and process. Accordingly, the
 260 microbial groups will be straightforwardly influenced by the feedstock properties.
 261 This is on account of the feedstock, which assumes a part as the nourishment to be
 262 processed by the microorganisms, includes the significant living conditions inside
 263 the anaerobic assimilation framework. The microorganisms that take an interest in
 264 the process might be particular for each debasement step and in this manner could
 265 have distinctive ecological necessities. The anaerobic assimilation of natural mater-
 266 ial is a difficult process, including various diverse debasement steps. For the most
 267 part, the natural factors have a range, ideal esteem or pattern to take after for having a
 268 fruitful anaerobic assimilation process. Subsequently, the exploration techniques
 269 which had been and to be done for enhancing the biogas generation in view of the
 270 ecological variables will have a correct pathway to approach. Other than the natural
 271 factors, the cautious operational ability will be required with a specific end goal to
 272 guarantee a steady and fruitful anaerobic processing framework to work successfully
 273 and consistently. The biogas yield is influenced by numerous elements includes type
 274 and creation of substrate, microbial arrangement, temperature, pH, biodegradability
 275 and nutrient content. The factors influencing and affecting the anaerobic digestion
 276 are well explained in this chapter. Diminish in biogas generation was seen on
 277 account of fruit also, vegetable waste because of fast fermentation of these squan-
 278 ders, bringing about a bringing down of the pH in the bioreactor. Besides, the
 279 creation of bigger unstable unsaturated fats from such waste under anaerobic con-
 280 ditions restrains the action of methanogenic microbes. The expansion of
 281 co-substrates, for example, abattoir waste and sludge of fruit and vegetable waste
 282 stimulate the biogas generation under anaerobic conditions. In the meantime, these
 283 central understandings supported different of biogas generation upgrade techniques.

5.3.1.1 Temperature

284

Numerous analysts have announced noteworthy impacts of temperature on the microbial group, process energy and dependability also, methane yield. Temperature is an imperative parameter that significantly impacts anaerobic procedures. The working temperature is the main factor of the population of microbes' presence, particularly the assorted variety of the methanogen group in the anaerobic reactor (Leven et al. 2007). Underneath temperatures amid the procedure are known to diminish microbe development, substrate use, rates, and biogas generation (Trzcinski and Stuckey 2010). In addition, low temperatures may likewise bring about a release of cell vitality, a spillage of intracellular substances or on the other hand entire lysis. Conversely, high temperatures bring down biogas yield because of the creation of unstable gases, for example, ammonia which stifles methanogenic exercises (Fezzani and Cheikh 2010). Based on the three diverse temperature ranges namely psychrophilic (0–20 °C), mesophilic (20–42 °C) and thermophilic (42–75 °C), the anaerobic digestion process delivers the biogas. There are two regular temperature levels connected in the traditional anaerobic assimilation, which are mesophilic and thermophilic temperatures. Both temperature ranges have upsides and downsides from various viewpoints. Mesophilic anaerobic digestion has higher stability than the thermophilic. This can be clarified there is more differing microbial group can be found in mesophilic (37 °C) bioreactor. It moderately lower volume of biogas and will bring down volume loading compared with thermophilic anaerobic assimilation. The task in the mesophilic extend is more steady and requires a little vitality cost (Fernandez et al. 2008). Despite the fact that thermophilic anaerobic assimilation can accomplish higher natural substance corruption, it is constantly identified with the issue of the delicate process with inclined unstable unsaturated fat gathering. Other than that, there was a contention as far as vitality discussion because of the lower methane content had been created by a thermophilic reactor. Generally speaking, a temperature extends between 35–37 °C is viewed as reasonable for the creation of methane and a change from mesophilic to thermophilic temperatures can cause a sharp reduction in biogas creation until the fundamental population has expanded in number. Thermophilic are known to have a rate-advantage over the others because of a quicker response time and higher volumetric stacking rate, and accordingly exhibiting higher biogas efficiency. Psychrophilic are in huge consideration especially as far as creating biogas from low-quality wastewaters.

5.3.1.2 The pH

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A basic parameter which impacts the methanogens and which directly affects the biogas and methane generation. Most anaerobic frameworks work at close unbiased pH since methane aging happens inside the pH 6.5–8.5 territories with the ideal range from 7.0 to 8.0. Through neutralization process, the pH range was maintained

that need excessive utilization of chemicals, for example, sodium carbonate/bicarbonate or calcium carbonate since a few streams have outrageous pH esteems, and hydrolysis also, acidogenesis stages will diminish pH esteems. Extraordinary pH conditions amid anaerobic activity can't just furious natural execution and methane yield yet additionally influence film porousness and life expectancy. The methanogens are powerless to the encompassing pH esteem, which just can survive only under pH scope of 6.5–7.8. A scope of pH esteems appropriate for anaerobic assimilation has been revealed by different specialists, however, the ideal pH for methanogenesis has been observed to be around 7.0.

5.3.1.3 Nutrient Content

The most essential wholesome substance, for example, carbon and nitrogen are basic to help the anaerobic organic process. Nitrogen is fundamental for protein union and basically needed as a supplement by the microbes in the anaerobic reactors. Nitrogenous mixes in the natural squander are normally proteins which are changed over to ammonium by anaerobic processing (Sawayama et al. 2004). As ammonium, nitrogen adds to the adjustment of the pH esteem in the bioreactor where the procedure is occurring. The stability between carbon and nitrogen substance will be needed for a natural assimilation framework, which is usually depicted as carbon to nitrogen (C/N) proportion. The C/N proportion in the natural material assumes a vital part in anaerobic processing. The unequal supplements are viewed as a critical factor constraining anaerobic processing of natural squanders. Moderate debasement will be experienced when C/N proportion is too high, while the other way around will cause the gathering of the inhibitors, for example, alkali. For the generation of new cell mass microorganisms acclimatize ammonium. Smelling salts in high focus may prompt the hindrance of the natural procedure also, it restrains methanogenesis. For the change of nourishment and C/N proportions, co-absorption of natural blends are utilized (Cuetos et al. 2008).

5.3.1.4 Substrate Characteristics

Not a wide range of substrate is appropriate for experiencing the anaerobic assimilation, particularly when the biogas generation is the objective. For case, the poor mass exchange because of the lower water content, imbalance of nutrients and lower biodegradability. The rate of anaerobic processing is emphatically influenced by the sort, accessibility and nature of the substrate (Zhao et al. 2010). Distinctive sorts of carbon source support diverse gatherings of organisms. Before beginning an anaerobic procedure, the substrate must be portrayed for starch, lipid, protein also, fiber substance. The substrate ought to likewise be portrayed for the amount of methane that can conceivably be delivered under anaerobic conditions. Contrasted with lignocellulosic biomass, date palm fruit is substantially more desirable to be processed anaerobically due to its good characteristics. Other than of C/N

proportion, COD: N: Phosphorus (P) proportion had additionally been expected to keep up the digester activity (Annachhatre 1996). The prerequisites of different components as large-scale and micronutrient must be considered too. Sugars are viewed as the most imperative natural segment of municipal waste for biogas creation. Starch could go about as a compelling minimal effort substrate for biogas generation contrasted with sucrose and glucose (Su et al. 2009). The strong substance of the substrate in the bioreactor can essentially influence the execution of the procedure and the measure of methane delivered during the process.

5.3.1.5 Biodegradability

The biodegradability of the organic matter by the microbes is one of the major variables for a successful anaerobic assimilation process. It will specifically impact the rate of substrate use by primarily restricting the procedure of hydrolysis. This is generally portrayed as the biodegradability, which is significantly reliant on the constituents of the substrate. The water content basically restricts the mass exchange and organic matter solubilization inside the digester framework. In this way, the anaerobic assimilation of the high strong substrate will experience more difficulties and issues. Next, the unpredictability of substrate constituents, for example, the sugars, proteins, and lipids, will decide the biodegradability essentially. Moreover, the degradation of non-structural carbohydrates, lipids, proteins are more difficult to degrade due to its strong chemical bonding. Henceforth, the carbohydrate pretreatment or anaerobic digestion for a superior biogas generation. Other than that, the substrate with huge content of lipids (fat) was observed to be corrupted slower due to the availability of long-chain unsaturated fats (LCFAs).

5.3.1.6 Biomass Retention

Biomass maintenance is one of the basic observing factors for anaerobic assimilation. For this, the most widely recognized method is to decide the population of microbes in an anaerobic reactor by which it is particularly depicted as mixed liquor volatile suspended solids (MLVSS).

5.4 Anaerobic Reactors

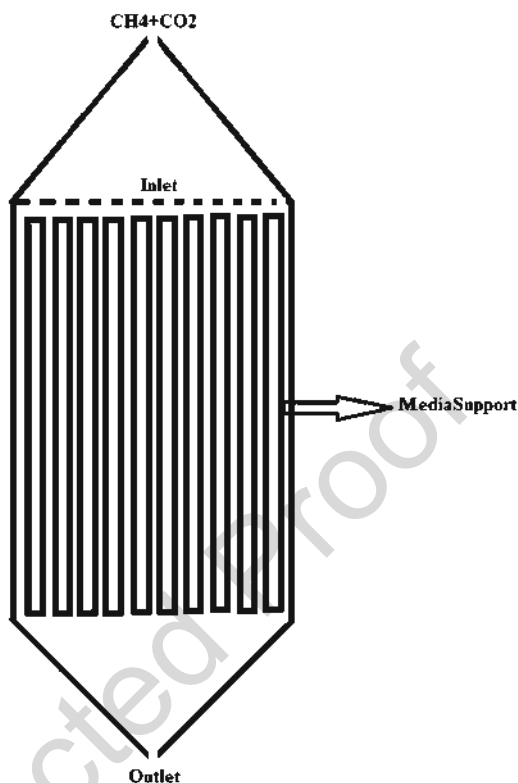
Anaerobic bioreactors have significant use for quick processing of strong natural waste constituents to decrease the ecological stack (Agdag and Sponza 2007). Bioreactor configuration has been found to apply a strong effect on the execution of a digester. an assortment of new bioreactor plans has been produced lately, which encourage a fundamentally higher rate of response for the treatment of food waste. Favorable position of anaerobic waste treatment frameworks as means for the

recuperation of non-regular vitality is progressively being perceived around the world. Anaerobic deterioration is an organically intervened process, indigenous to nature, and fit for treating squanders radiating from civil, agriculture, and modern exercises. These prompted improvement of different reactors, which are equipped for holding a considerably higher biomass focus than customary digesters. It is hard to assess the focal points and weaknesses of every framework in connection with other ideas. The most well-known anaerobic reactors are Anaerobic sequencing batch bioreactor, Anaerobic filtration, Plug flow reactor, Continuous stirred tank reactors, Lagoon system, Anaerobic fluidized bed reactor, up-flow anaerobic sludge blanket reactor, Anaerobic contact digester. This chapter discuss the anaerobic digestion strategy for the improvement of production biogas through date palm fruit waste. The methodology must be applicable and possible, and this will require a solid comprehension of the compelling elements of biogas generation by anaerobic digestion.

5.4.1 *Anaerobic Filtration*

The primary showing of this treatment framework originated from Young and McCarty, who productively worked an up-flow anaerobic channel to treat the rum refinery wastewater. It is widely in scale studies for the treatment of palm waste materials. Channel clogging is a noteworthy issue in the activity of anaerobic channels. Anaerobic filtration contains a channel medium where anaerobic microbial population—life forms that live without oxygen—can build up themselves. Such channels are generally used in the wastewater treatment. Such channels are generally utilized in the treatment of wastewater. An anaerobic channel is an anaerobic reactor with at least one filtration chambers in the arrangement. The principal anaerobic channels outlined utilized characteristic materials as help media, for example, stone and rock. These had a low voidage and obstructed with biomass and solids quickly. Plastic raschig rings were used in which the increase the time interval between blockages yet did not defeat the issue completely. As wastewater courses through the channel, particles are caught and the natural issue is corrupted by the dynamic biomass that is connected to the surface of the channel material. The channels can be worked under either an up-stream or on the other hand down-stream condition. The up-stream condition contains a high convergence of suspended biomass shaping a biofilm in the structure of the settled bed. The downstream bed contains a huge concentration of inorganic sulfur between the BOD and inorganic compounds. Upflow anaerobic channels (UAF) can be worked at either mesophilic or thermophilic temperature ranges. Thermophilic anaerobic filters are highly suitable for the treatment for high concentrated wastewaters particularly for the palm oil effluent (Mustapha et al. 2003). The anaerobic filtration has been effectively utilized in the treatment of date palm effluent on account of the advantages credited to it, which incorporates little reactor volume with low water powered maintenance time, capacity to withstand stun loadings, no strong partition/reusing and reasonableness of the

Fig. 5.2 Anaerobic filtration



reactor (Poh and Chong 2009). Anaerobic channels are utilized as an auxiliary 439
treatment in family level or decentralized wastewater treatment frameworks. With 440
respect to any anaerobic assimilation process, biogas can be recouped and changed 441
to vitality or light. It is highly utilized for the personal contact between the inflow 442
and microbial biomass, in this way taking into account a biomass maintenance time 443
longer than the HRT. Reusing can be connected for high-quality wastewaters. In this 444
manner, the AF shows incredible versatility for biomass to another carbon source 445
and to natural load vacillations. Contrasted with an anaerobic contact process, the 446
AF shown better sludge settlement. Accordingly, the AF could be more reasonable 447
to treat wastewaters with bringing down suspended solids. The higher speculation 448
cost ought to likewise be considered in applications. Figure 5.2 represents the 449
diagram of anaerobic filtration. 450

5.4.2 Plug Flow Reactor

451

Anaerobic plug flow reactors have been accounted for to be proficient for dry 452
anaerobic assimilation forms. This reactor is economical what's more, simple to 453

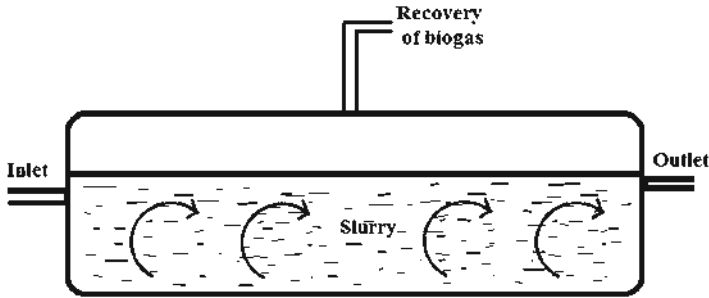


Fig. 5.3 Plug flow reactor

assemble which make them an appropriate innovation to enhance the occupations of the farmers (Lansing et al. 2010). The schematic representation of plug flow reactor is depicted in Fig. 5.3. The execution of biogas generation relies upon biomass substance creation and also process factors, for example, sustain focus, water driven maintenance time, pH, and temperature. The anaerobic plug flow reactor (APFR) is another customary process giving low groupings of VFA in the effluent, a high level of sludge maintenance and stable reactor execution. Plug flow reactors are long, direct troughs normally arranged over the ground. This kind of reactor is effective regarding productivity and conversion when compared with the ordinary single-phase CSTR. The APFR includes no inside disturbance and is stacked with the thick fertilizer of 11–14% aggregate solids and functions admirably at mesophilic or thermophilic temperature. The maintenance time is generally 15–20 days (Rajeshwari et al. 2000). This type of reactor has been accounted for to have the most noteworthy achievement rate in the United States, where 42% out of the 242 anaerobic digesters working at domesticated animals cultivates in 2015. This sort of reactor was used to give low beginning venture cost, high productivity and moderately simple activity and support in case of semi-solid waste (Sharma et al. 2000). Subsequently, in both industrialized and creating nations, the reactor has huge tendency to deliver biogas. Additionally, the reactor has been tried tentatively utilizing substrates, for example, pig manure, cattle deposits and urban natural squander, and so forth.

A plug flow reactor, a sort of reactor which is isolated into acidogenic and methanogenic stages along the stream way of the reactor, could enhance the reactor stability and treatment proficiency. By and by, a few deficiencies, for example, bring down mass exchange because of the absence of blending, warm stratification and strong sedimentation issues have been accounted in certain studies (Lansing et al. 2010). These issues can be controlled by the usage of compressors in plug stream reactors. The impellers permit insignificant blending for higher execution in the reactors. Plug flow reactor is constrained to cases in which the substrate contains low measures of sand, soil, coarseness that these polluting influences settle at the base of the reactor and prompt stratification of the reactor substance, requiring unavoidable release and cleaning of the digester. In addition, light coasting particles amass at the

highest point of the reactor and cause crusting issues. Nowadays, a mixed plug flow reactor was utilized to maintain a strategic distance from the settlement of particles at the base and to make an inflexible layer on the reactor substance.

5.4.3 Continuous Stirred Tank Reactors

The traditional continuous stirred tank reactor (CSTR) is the most regular suspended microbial development framework and has been generally used to create hydrogen (Fang and Liu 2002). CSTRs (Continuous Stirred Tank Reactors) are in round and hollow or rectangular shapes and utilize mechanical turbines for blending. Continuous stirred tank reactors are also known as closed tank digesters. The potential for natural transformation from the substrate to methane can be incredibly expanded because of the overall high shear pressure and serious blending (Ozgun et al. 2013). CSTR works at a persistent stream of reactants and items with a steady makeup in the reactor including exit stream having an indistinguishable synthesis from the tank. The mechanical instigator of the CSTR gives more zone of contact with the biomass in this way upgrading gas generation. CSTR utilizes microorganisms to process the natural substances in the wastewater under anaerobic condition. Amid this procedure, the BOD of the profluent is diminished in the meantime delivering biogas. To heighten this innovation and keep up a reasonable populace of the moderate developing methanogens, the CSTRs are generally joined with an inside or then again outer biomass division and reusing framework (Reungsang et al. 2013). A CSTR coupled film framework can accomplish a promising methane yield up to hypothetical esteem. Also, CSTR, for the most part, works at a lower biomass fixation (e.g. 5 g/L MLSS) contrasted with other high rate anaerobic reactors because of deposition of waste control issues, which comes about in a lower OLR (Organic Loading Rate) connected to the framework, constraining the biomethane potential from high stacking wastewater. Various digesters are being connected for AD process in both laboratory usage and in industrial use, continuous stirred tank reactor (CSTR) is one of most generally utilized for the anaerobic processing of high-strong food waste like date palm waste. A solitary CSTR is easy to work yet less effective in feedstock processing and biogas generation due to the “short circuit”. The short circuit in CSTR is found to be a major downside in the generation of biogas. Associating two reactors in arrangement (serial assimilation) is a suitable method to defeat the issues from single CSTR to build the biodegradation rate and also acquire more biogas generation. A few investigations have stressed the attainability of serial arrangement of CSTR. Blending yields better collaboration amongst microorganisms and substrates diminishes impediment to mass transmission and reduces the gathering of safe intermediates (Chong et al. 2013). Due to continuous blending in the reactor, the microorganisms get suspended. Application of biogas distribution expanded the COD evacuation proficiency, bio-methane age effectiveness, biomass maintenance capacity and the solids retention time (SRT) of CSTR. CSTR is simple to work and minimal effort without immobilization transporter. Besides, it normally

527 takes shorter start-up time compared with the anaerobic sludge blanket reactor and
 528 biofilm frameworks. Good mixing stimulates the contact between the organisms and
 529 food waste by consuming more energy. The activity of a traditional single CSTR is
 530 straightforward yet less proficient in based on the effluent quality. Therefore, a
 531 two-stage framework was found to have the more typical sort of framework. The
 532 two-stage CSTR framework is well known because of the effortlessness of the
 533 framework inactivity and its low capital when compared with the one stage CSTR.
 534 Also, the downsides related to the framework's structure and activity mode make it
 535 difficult to hold a high microbial population in the reactor. Because of blending and
 536 ceaseless blending, fast fermentation occurs, resulting in substantial VFA creation,
 537 which could prompt AD process. Recently, advances have concentrated on CSTR
 538 variations to make reactor execution through reactor volume enhancement.

539 **5.4.4 Lagoon System**

540 Anaerobic ponds or lagoons is most useable palm fruit anaerobic treatment around
 541 85% of the plant implemented this technique inferable from just its low capital and
 542 operational cost This approach viably empowers about 100% catch of the biogas
 543 created in all the lagoon ponds to decrease smell and GHGs (Green House Gas)
 544 outflows to the environment. Lake framework is one of the commonest treatment
 545 innovation because of its cost adequacy. An alternative to lessen digester cost is
 546 utilizing more affordable digester plans and lower cost development materials. This
 547 line of thinking can prompt be considering a persistent stream 'earthen digester',
 548 worked at encompassing temperatures, which is like present anaerobic ponds. This
 549 framework depends principally on microbial action to decrease natural material and
 550 supplements. Anaerobic lagoons are working as digesters where microbes break
 551 down the natural issue. Anaerobic tidal ponds are regularly used to treat modern
 552 wastewater or creature squanders from dairy or then again swine cultivates, or to fill
 553 in as the primary treatment advance in frameworks utilizing at least two lagoons in
 554 an arrangement. The anaerobic ponds digesters are intended for a generally low
 555 stacking rate worked with a long maintenance time and work well under warm
 556 climatic conditions and intensely subject to the surrounding temperature.

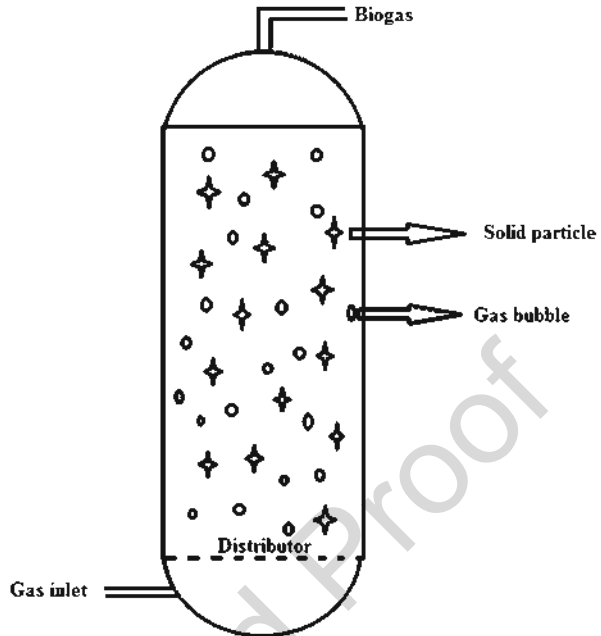
557 **5.4.5 Anaerobic Fluidized Bed Reactor**

558 Over the most recent two decades, anaerobic fluidized-bed reactors (AFBRs) started
 559 to be utilized as a part of food waste because of their ability for keeping high biomass
 560 fixations furthermore, thin biofilm thickness. In anaerobic fluidized bed reactor, the

barrier for bacterial connection and development is little dormant particles, for example, fine sand or alumina, kept in suspension by a quick upward stream of approaching wastewater. The design considerations provide more prominent protection from inhibitors and higher OLR. Moreover, execution of a thin biofilm on these medium particles and a great connection to biomass take into consideration great mass move effectiveness in the AFBR. AFBR depends on worthy fluidization attributes, for example, bed-extension tallness also, gas, fluid, and strong hold-ups. In any case, gas generation in AFBRs may acquire a bed-compression impact, bringing about the decrease of contact time between mass fluid and bioparticles, particularly for a huge scale AFBR. Anaerobic fluidized bed reactor (AFBR) is the treatment techniques for low-quality wastewater and it provides the excellent mass conversion between the substrate and the medium like a solid particle. FBR is a progressed stuffed bed framework, which allows the development of the bed amid activity (Alade et al. 2011). AFBR setup has pulled in an expanding consideration due to the maintenance of biomass onto a strong inactive biofilm bearer material with a huge particular surface region (Karadag et al. 2015). The reactors have been broadly utilized for the treatment of numerous food waste since the most recent two decades. The bearer materials are fluidized by the influent stream as well as through distribution of the supernatant fluid (Barca et al. 2015). FBR is a sort of anaerobic reactor gadget that has the limit of doing a few multiphase synthetic responses. The high up-flow fluid speeds give a bed development of just about 100%. The effectiveness of the fluidized bed reactor relies upon the idea of help material (Sowmeyan and Swaminathan 2008). The opposite stream fluidized reactor indicated high stability when over-burden is connected (Alvarado-Lassman et al. 2008). Little permeable fluidized media hold high biomass focuses in the reactor and in this way diminished HRT. Lower HRT (High Retention Time) and more prominent CH_4 generation demonstrated an advantage of fluidized bed over an anaerobic process.

Figure 5.4 shows the pictorial diagram of anaerobic fluidized bed reactor. In any case, gas generation in AFBRs may bring about a bed-compression impact, bringing about the diminishment of contact time between mass fluid and bioparticles, particularly for a substantial scale AFBR. The FBR can withstand high OLRs and a superior methane gas creation. Moreover, the capacity to evacuate surface strong particles of local wastewater utilizing the AFBR is superior to that of the UASB. This kind of reactor is more compelling for the treatment of soluble, or surface material nourish that is effectively biodegradable, for example, whey, whey permeates, black liquor condensate, etc. However, membrane fouling is a limitation for anaerobic fluidized bed reactors. It has been accounted for that proteins are the prevailing supporters of layer fouling at low temperature (Gao et al. 2014). To wipe out or diminish layer fouling, analysts have exhibited that a small amount of strong media such as granular activated carbon (GAC) or powder activated carbon (PAC) can be included, in light of the fact that they can successfully adsorb microbial metabolic items (Akram and Stuckey 2008).

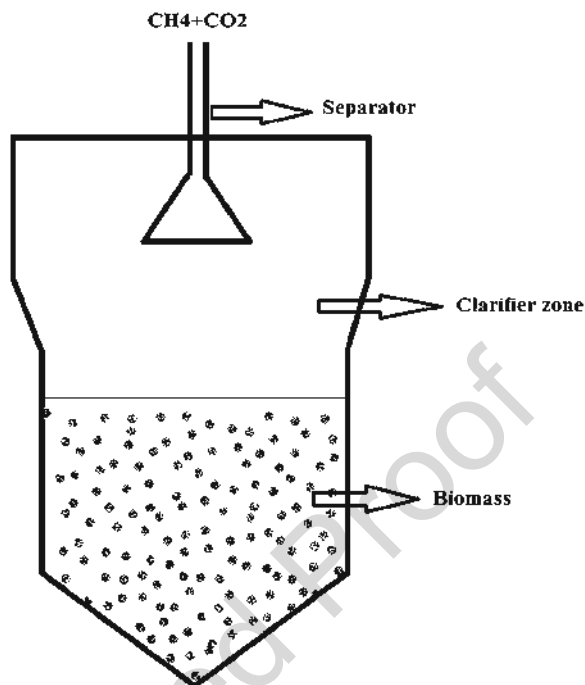
Fig. 5.4 Anaerobic fluidized bed reactor



5.4.6 Upflow Anaerobic Sludge Blanket Reactor

The UASB idea was produced by Lettinga et al. in the 1970s for methane creation. The up-flow anaerobic sludge blanket (UASB) reactor is the noticeable extensions in anaerobic processing framework for wastewater treatment and in excess of 1000 such sort of reactors is utilized as a part of worldwide (Tiwari et al. 2006; Chong et al. 2012). UASB reactor (Fig. 5.5) is very simple, compact and widely applied for the treatment of waste for the production of gas. The principle structure of the reactor is a thick slime bed situated in the base, which ensures great wastewater and biomass contact. This procedure has been successfully used to treat the extensive variety of modern affluent. The mystery of such a novel reactor configuration lies in its capacity to hold a high centralization of biomass as well settleable methanogenic slop granules in a thick slop bed at the base of the reactor; furthermore, besides, catch the created biogas through a gas-liquid separator (GLS) at the top. This reactor demonstrates a great execution for high-suspended strong wastewater and produces a huge volume of methane. The creation of fermentative hydrogen relies upon the impacts of HRT (High Retention Time) and OLR (Organic Loading Rate). The biomass and sludge from the organic waste settle in UASB reactor and the sludge gets digested by this reactor when the organic waste be in contact with the sludge. UASB reactor has been effectively been utilized for the treatment of various modern effluents incorporating those with high natural substance fit for restraining assimilation (Demirel and Scherer 2008). The suspended natural solids of date palm effluent have a high biogas potential which makes the transformation innovation

Fig. 5.5 Up flow anaerobic
sludge blanket reactor

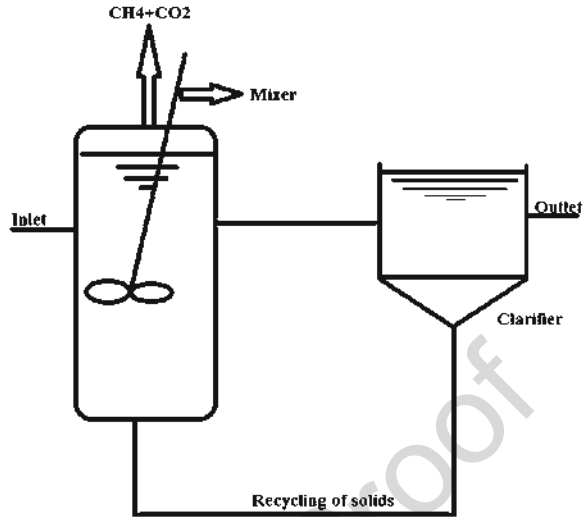


practical, which are the main thrust of UASB. Among the remarkable preferences, UASB requires low volume and space, highlights higher stream speed and biogas generation and fundamentally higher natural load rates. Moreover, the accessibility of granular permits treatment of higher COD stacking rates and providing satisfactory treatment at bringing down HRTs than is conceivable with the anaerobic filters (AF). UASB reactors can utilize thick bacterial granules, which fill in as a channel to counteract bacterial washout and which additionally give a bigger surface territory for speedier biofilm advancement and enhanced methanogenesis.

5.4.7 Anaerobic Contact Reactor

The anaerobic contact reactor is comprised of digester and sedimentation tank. The anaerobic contact reactor (ACR) is widely utilized for wastewater with high quantity of surface solids. In a few cases, high-rate mesophilic ACRs have been shown to be a manageable innovation for an extensive variety of modern wastewater, for example, food industry wastewater (Senturk et al. 2012) and pulp and paper mills (Capela et al. 2009). These reactors introduce comparative highlights to their oxygen-consuming partners like activated sludge reactors. Anaerobic contact assimilation includes the utilization of digester and sedimentation tank whereby the processed wastewater is left to coagulate and the wastewater is reused once more into the

Fig. 5.6 Anaerobic contact reactor



644 digester. ACR is more invaluable than regular anaerobic reactors, for example,
 645 up-flow anaerobic sludge blanket reactors (UASB). Figure 5.6 Schematic representation of anaerobic contact reactor.

647 Revealed focal points incorporate the contact procedure, quickly accomplished
 648 consistent state times because of blending, adequately short water powered maintenance times and moderately high gushing quality, less affected by stun stacking,
 649 ideal pH and constrained biomass washout. In order to maintain the organisms' quantity, the settled solids are move towards the reactor. The clarifier or pilgrim may
 650 have gravity settling or vacuum buoyancy. Settlement must be helped by degassing, cooling, filtration, or slanted plates. This approach was fruitful for the treatment of
 651 processed solids and enabled one to acquire fantastic effluents. Gas-lift blending is well known in these sorts of digesters. Great blending is likewise fundamental in this
 652 sort of reactor to guarantee uniform substrate and biomass concentration. Traditionally blending has been by paddles in a draft tube. Much of the system of the paddle
 653 type is submerged in the digester and maintenance is exceptionally troublesome. Another strategy for mixing is directed distribution of the digesters contents. Present
 654 day digesters are a large portion of the size and blending is significantly simpler.

661 5.5 Conclusions and Recommendations

662 Date palm natural product, a standout amongst the most nutritive and complete
 663 organic products regarding medical advantages is a perfect substrate for inferring a
 664 scope of significant worth included items in sustenance and nutraceutical businesses
 665 in the upcoming future utilizing bioprocessing innovations which will have a
 666 massive extension for the biogas production. For supporting the future manageable

palm fruit advancement, more exhaustive research on improving the biogas creation from date palm by anaerobic assimilation is basically required. Keeping in mind the end goal to guarantee the execution of anaerobic assimilation, RSM improvement of the manipulable elements (temperature, pH) by utilizing the specific bioreactor is very encouraged. The present chapter plainly shows that anaerobic assimilation is a standout amongst the best organic procedures to treat a wide assortment of date palm fruit. Additionally, this chapter demonstrates that anaerobic digestion is a standout amongst the best natural procedures to treat a date palm fruit for biogas generation. In any case, unique variables for example, substrate and co-substrate structure and quality, natural components (temperature, pH), microbial elements add to the proficiency of the anaerobic assimilation process and should be improved to accomplish the greatest advantage from this innovation as far as both vitality creation furthermore, natural waste administration. The examined reactors can be further investigated by taking into consideration of different measures, for example, extraordinary co-substrates, pre-treatment advances, added substances etc. the major elements of anaerobic assimilation and cost adequacy must be considered for the future activities. By working the anaerobic digester effectively, the used techniques had a positive reaction to the biogas creation. The prime preferences of this innovation incorporate that the procedure at the same time prompts minimal effort generation of biogas, which could be indispensable for meeting future vitality needs. In any case, unique components, for example, substrate and co-substrate structure and quality, ecological components (temperature, pH), furthermore, microbial flow add to the productivity of the anaerobic assimilation process and should be enhanced to accomplish most extreme advantage from this innovation. This innovation has enormous application later on for maintainability of both condition and horticulture, with the generation of energy as an additional advantage.

This chapter focuses the way that there is an extraordinary research movement around the globe, both in nations that deliver date palm and those in nations where the production is low yet the consumption is high. The anaerobic assimilation is a perplexing procedure, which the execution came about will be effectively affected by alternate variables, for example, organic loaded, start-up effectiveness, operation conditions, bioreactor design etc. The cooperation impacts of these diverse components might be amplified and turned out to be more imperative than its individual impact. The efforts were made to basically upgrade the biogas volumetric creation, yet not underlined to enhance the biogas quality. The basic examination of newer literature shows that much advance has been made in the innovative work of anaerobic systems for biogas creation. The green points of view of anaerobic reactors are biogas creation, high affluent quality, squander minimization, high limit, and impression proficiency (diminishing capital expenses) and bring down vitality prerequisites. Most research on reactors has concentrated on researching customary setups, for example, up-flow anaerobic sludge blanket reactor anaerobic fluidized bed reactor, continuous stirred tank reactors and so forth. The anaerobic pond is the basic strategy to produce biogas because of its minimal effort. The most suitable reactor for the generation of biogas from the date palm fruit is Upflow anaerobic sludge blanket reactor (UASB) as it produces higher measures of biogas,

for example, biomethane and biohydrogen. Be that as it may, it can't release completely clear profluent. For the further improvement of biogas AD that consideration be given to the blend of at least two of the previously mentioned factors influencing proficiency and to advance anaerobic digestion efficiency.

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CHAPTER 4

Characterization techniques for nanomaterials

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4.1 Introduction

Nanotechnology is used in sectors of science and technology such as energy, medicine and drugs, nanobiotechnology, nanodevices, optical engineering, cosmetics, bioengineering, nanofabrics, and also in the defense sector because of its large surface-area-to-volume ratio. Nanomaterials draw attention due to their unique physical, chemical, and mechanical properties from bulk solids and molecules. Nanomaterials are classified based upon their origin and structure. The classifications which depend upon the origin are: natural nanomaterials, artificial nanomaterials, zero-dimensional, one-dimensional, two-dimensional, and three-dimensional. Structural classification nanomaterials are classified into four types: carbon-based, metal-based, dendrimers, and composites. Size distribution is the most important information in dealing with nanomaterials. With decrease in size there is increase in portion of surface atoms. Nanoparticles make a connection between bulk materials and atomic structures [1,2]. When comparing to bulk materials, nanomaterials which are considered as low-dimensional material have unique thermophysical

properties and thermophysical characterization, which was found to be important in the field of nanoscience and nanotechnology. Small size, high surface area, easy blend with liquids, deep access to cells, strength, and ductility are some of the advantages found in nanomaterials. Some challenges, such as safety-related issues in exposure to engineered nanomaterials mainly in air and in water, loss of jobs in manufacturing and farming and easy availability of automated weapons are current concerns in the field of nanomaterials. The usage of nanomaterials has increased in various fields such as carbon nanotubes, medicine, information technology, nanorobots, nanocomputers, solar cells, and paper batteries, before labeling a nanomaterial, characterization of the material is needed. This chapter deals with the characterization techniques which are currently in practice within the field of nanomaterials [3,4].

4.2 Characterization techniques for nanomaterials

Nanomaterials have large surface-area-to-volume ratio that differs in orders of magnitude greater from the macroscopic materials. The size and structure of the nanomaterials depend upon factors such as surfactant additives, reactant concentrations, temperature, solvent conditions on the time of synthesis, and salt. In order to develop reproducible synthesis of nanomaterials, characterization of nanomaterials is found to be important. Characterization refers to the study of composition, structure, and other properties such as physical, chemical, electrical, and magnetic. Many techniques are available for the characterization of nanomaterials, but a degree of uncertainty is seen in each technique [5,6].

4.2.1 Characterization based upon nanomaterial properties

4.2.1.1 *Optical characterization techniques*

4.2.1.1.1 Confocal laser scanning microscopy

The main feature of confocal microscopy is its ability to produce images which are blur-free from thick specimens in different depths. Point to point information about images is gathered and reconstructed with a computer instead of projecting into an eyepiece. Depth of field, elimination of image degradation when images are out-of-focus and collection of images from thick specimens are some of the advantages of laser scanning confocal microscopy as compared to optical microscopy. Fig. 4.1 shows schematic representation of confocal laser scanning microscopy. The advantage is elimination of out-of-focus light by using spatial filtering

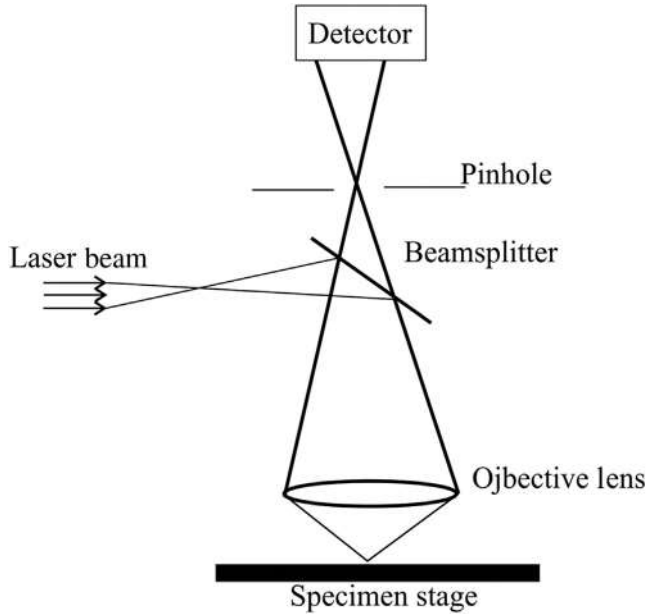


Figure 4.1 Schematic representation of confocal laser scanning microscopy.

when the specimen is thicker than the plane of focus. Different imaging modes such as single, double, triple, or multiple illumination modes are seen. Confocal microscopy uses raster scanning and scans the specimen point by point. The detection process was found to be slow and the axial resolution was found to be slow as compared to lateral resolution. Instead of illuminating the optical section, confocal microscopy illuminates the entire column and it causes photodamage [7].

4.2.1.1.2 Scanning near-field optical microscopy

The topography and the optical properties of nanomaterials can be measured using near-field optical microscopy. This method also provides details about the surface of the nanofeatures and their optical, as well as electronic, properties. The near-field scanner has an arbitrarily small aperture and it is illuminated at the back side with constant distance. The samples are scanned at a small distance below the aperture, and optical resolution of transmitted or reflected light is limited by the diameter of the aperture. 60–100 nm of optical resolution is normally attained, and the optical images are obtained by scanning the sample surface point by point and line by line. Some of the advantages of scanning near-field

optical microscopy (SNOM) include: high resolution of images up to 25 nm, analyzing of multiple properties and usage for different kinds of samples. Some of the disadvantages include: this type of scanning is limited to very low working distance and at extremely shallow depth of field, does not provide details of nonconductive soft materials and takes long scan times for large sample areas. This type of microscopy is generally seen in the field of nanotechnology, nanophotonics, nanooptics, life sciences, and in material research. Single-molecule detection is possible and dynamic properties at subwavelength scale are done using SNOM [8].

4.2.1.1.3 Two-photon fluorescence microscopy

Two-photon fluorescence Microscopy is used for studying biological systems. It is a nonlinear process which involves absorption of two photons whose combined energy is greater than the energy gap between the excited states and the molecule's ground. This energy gap is sufficient to make an excited electronic state in molecular transition. Two-photon absorptions by a fluorescent molecule is an excitation radiance's quadratic function. Deeper tissue penetration and less photodamage are some of advantages of two-photon fluorescence microscopy and lower resolution is the main drawback. This type of scanning is mainly seen in the fields of physiology, neurobiology, embryology, and tissue engineering. Two-photon fluorescence microscopy finds its special application in noninvasive optical biopsy [9,10].

4.2.1.1.4 Dynamic light scattering

Dynamic light scattering (DLS) is used for measuring the size of the particle and the measurement of molecules in suspension. Alternative names for DLS are photon correlation spectroscopy or quasielastic light scattering. Hydrodynamic size, shape, structure, aggregation state, and biomolecular confirmation can be obtained using scattering techniques. From submicron to nanometers of polymers scattering modalities, size distribution is obtained using a monochromatic light source. The temporal fluctuations are monitored using DLS. The particles which follow Brownian movement are measured by this technique, and the particle size, sample viscosity, and temperature influences the speed. Brownian motion causes the particle to diffuse through the medium. This instrument measures the scattered intensity at a fixed scattering angle with time. The static light scattering measures the scattered intensity as a function of angle. The

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Preface

Wastewater contains various types of pollutants that have to be removed before the water is directed to surface water or groundwater. This book focuses on wastewater treatment using green and eco-friendly materials. Sustainable solutions for wastewater treatment are addressed. This book presents an overview on environmental issues associated with direct and indirect wastewater uses and various types of pollutants present in water and their health effects. The applications of various types of green materials from agricultural waste and activated carbon, and magnetic materials for wastewater treatment are discussed. This book also includes detailed reviews on the removal of phenols and pesticides; and on the use of ionic liquid modified activated carbon for the treatment of textile wastewater. Since the book presents the fundamental techniques for wastewater treatment, it will bring great benefits to readers as they would gain better understanding about the green materials and their applications for wastewater treatment. We believe this book will be useful for environmental scientists, analytical chemist, chemical engineers, materials scientists, and all researchers who are working in the field of wastewater treatment.

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Coming together is a beginning; Keeping together is progress; Working together is success.
(By Henry Ford)

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Mu. Naushad
Eric Lichtfouse

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Ionic Polymer Metal Composites

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Keywords: IPMCs, Importance, Properties, IPMC Synthesis, IPMC Membrane and Electrodes, Principle, Applications.

Abstract. Electroactive polymers, or EAPs, are polymers that show an adjustment fit as a fiddle when invigorated by an electric field. Ionic polymer metal composites (IPMCs) are electro-dynamic polymers with great electromechanical coupling properties. They are proficient applicants in many progressed innovative applications, for example, actuators, artificial muscles, biomimetic sensors, and so forth. Type of membrane and electrodes determines the morphology and structure of IPMCs. IPMCs can be prepared using physical loading, chemical deposition and electroplating methods. The assembling of anodes for IPMCs is exceptionally basic in their electromechanical coupling. Optimization of force, determination of cations and molecule size dispersal inside the IPMC structure, and so on are the different components, which decides their proficiency. An ionic polymer-metal composite (IPMC) comprising of a thin Nafion sheet, platinum plated on the two side faces, experiences extensive twisting movement when an electric field is connected over its thickness. Then again, a voltage is created over its appearances when it is all of a sudden bends. IPMCs are best known for their proving advantages such as biocompatible, low activating voltage and more power efficiency.

Introduction

Ionic polymer-metal composites (IPMCs) refer to synthetic manufacturing of composite nanomaterials for artificial conduction of muscles with the help of applied voltage or electric field. IPMCs are made out of an ionic polymer composed of ionic macromolecules like Nafion, Acipex or Flemion with synthetically plated surfaces or physically covered conductors, for example, gold, platinum, etc. Under a connected applied voltage (1–5 V for common 10mmx40mmx0.2mm specimens), particle movement and redistribution because of the forced voltage over a piece of IPMCs result in a twisting deformation. If the plated terminals are organized in a non-symmetric design, the forced voltage can prompt a wide range of disfigurements, for example, winding, rolling, torsioning, turning, twirling, spinning and non-symmetric twisting deformation. Again if such deformations are physically connected to an IPMC strips they produce a yield voltage flag (couple of millivolts for regular little specimens) as sensors. IPMCs are a sort of electro active polymer. They work exceptionally well in a fluid domain and also in air. They have a drive thickness of around 40 of every a cantilever setup, implying that they can produce a tip compel of just about 40 times their own weight in a cantilever mode. Ionic polymer metal composites (IPMCs) are 'mechanically developed' electro active polymers (EAPs) [1]. IPMCs are much of the time known as 'delicate actuators-sensors' or 'manufactured muscles' a result of their electromechanical coupling conduct. The improvements on the polymer/metal composites in the mid 1930s have flagged the ascent of IPMCs effectively in inquire about. Regularly, an IPMC comprises of a thin film of an ionic polymer organized between two metal terminals on both the countenances. They are skilled in transducing the strain vitality into electrical vitality and the other way around. Their blend and planning assume a basic part in the proficiency of IPMCs based gadgets. They are discovered applications in an extensive variety of regions, for example, actuators, bio-mimetic sensors, counterfeit muscles, and some more. The light weight and adaptability are their additional points of interest, yet at the same time the tremendous cost is making far from commercializing such advances [2].

Structure of IPMCs

IPMC is composed of membranes made of polymeric ionic macro materials like usually of 200 μm thickness. The both sides of the composites are coated with electroless deposited metal electrodes of thickness 10 μm . A class of polymers like ionomeric molecules constitute these membranes with ionic groups at their side chains. The anionic counter ions are fixed in the polymer membranes neutralizing the charge in the polyelectrolyte matrix [3].

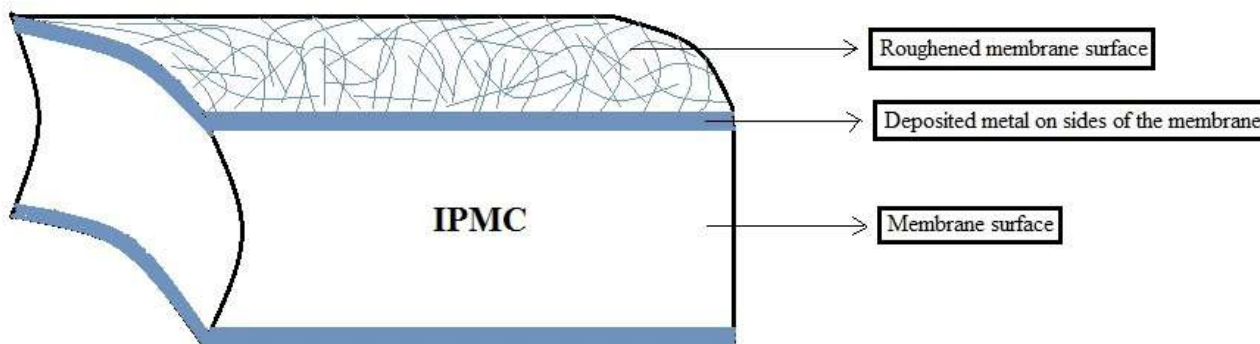


Figure 1: Structure of IPMC

IPMC is composed of the following components:

➤ Electrodes

The polymeric ionic membranes are usually coated with noble metals due to their benefits such as non-oxidising nature since IPMC mostly operates under liquid domain. Noble metals commonly employed in IPMC are gold (Au), silver (Ag), platinum (Pt), etc. Electroless plating or electroless deposition of metal technique is applicable for coating metals onto the surface and sides of IPMC. The plated metals are mainly used for conductivity with thickness of about 10 μm . Conductivity and thickness is directly proportional to each other. Increase in thickness increases conductivity of the plated noble metals. This stimulates the charges in the membrane surface and results in bending of the electrode due to activation. At the same time, stiffness of IPMC increases which also helps in deforming [4].

➤ Polymeric Membrane

Membranes made up of perfluorinated compounds are used for IPMCs. The three commonly used polymeric membranes are Flemion, Nafion and Acipex. Carboxylic acid groups are present at the ionic end groups of Flemion whereas Sulfonic groups are present in Acidex and Nafion. Owing to its advantages such as high mechanical strength, high thermal property, permeability and chemical stability, Nafion finds more commercial applications than Acipex and Flemion. Nafion is a class of synthetic polymers with ionic properties termed ionomers. It is mostly insoluble and derived by the reaction of sulfonated tetrafluoroethylene and sulfonyl fluoride vinyl ether. It can exist both as powder resin and copolymer. The molecular weight of Nafion ranges between 10^5 – 10^6 Da. Walther Grot was the first to discover Nafion membrane during 1960. Initially nafion was used as an ion-permeable membrane for fuel cells. Nafion is composed of a perfluorinated carbon as backbone, mobile cations, sulfonated side chain and water. The three dimensional structure is obtained due to polytetrafluoroethylene. The mobile cations are used to neutralize the acidic groups present in the structure. The alignment of polymeric chains depends on the water content and morphology because the membrane contains both hydrophilic and hydrophobic groups. The ionic class, being hydrophilic, are collected in firmly packed interconnected groups that are promptly soaked by water. The layer does not permit dispersal of anions through it while it is porous to water and cations. The morphology of nafion can be studied using various models as follows:

Table 1: Models used for defining the structure and morphology of Nafion membrane

S.No	Model Name	Working
1.	Cluster-Network	First found model through equal distribution of sulfonate ions.
2.	Rod	Sulfonic acids are arranged in crystal shaped rods
3.	Sandwich	Sulfonic acid attracts and transports through the two polymer layers
4.	Core shell	Poor ion core surrounds the rich ionic cores
5.	Water Channel	Self-arrangement of sulfonic acid groups into hydrophilic water channels

Synthesis of IPMC

IPMC are polymeric membrane with metal electrodes plated on their surface and side faces either chemically or electroplated. The metal particles are penetrated partially which increases the conductivity of cations. Bending occurs when electric field is applied between the metal electrodes. The noble metals are plated on the membrane by immersing the membrane inside the solution containing metal salt for certain period of time. Reduction of metal salt into metal particles occurs and a thick layer of metal particles gets deposited on the surface of the membrane thereby increasing the conductivity [5].

Chemical Deposition Method

The efficiency of nafion based IPMC can be increased by optimizing the manufacturing parameters like thickness, electrode, dimensions and sample size. IPMC can be prepared using chemical structured ethylene vinyl alcohol copolymers (EVOH) containing both hydrophobic and hydrophilic groups. The ionic hydrophilic groups enhance the uptake of water hence initiating the reaction. Ethylene vinyl alcohol copolymer first reacts with 1, 3 – propane sultone to form a complex which is modified using diisocyanate to form cross-linked polymer. The formation of complex structure was identified using Fourier Transform Infrared Spectroscopy (FTIR). The complex was immersed in prepared metal solution at 60°C for 1 hr. Finally IPMC was synthesised by chemical deposition of metal onto surface of EVOH complex formed. The metal gets deposited on the membrane. Platinum is the most commonly used metal because of its electrochemical properties and resistant to corrosion. On further cleaning and washing with deionised water, the metal deposited electrode can be obtained. When temperature is maintained, the membrane becomes white in colour. The reduction process was performed for three cycles to synthesise new IPMC [6]. The morphology characterization of produced IPMC was done using scanning electron microscopy (SEM).

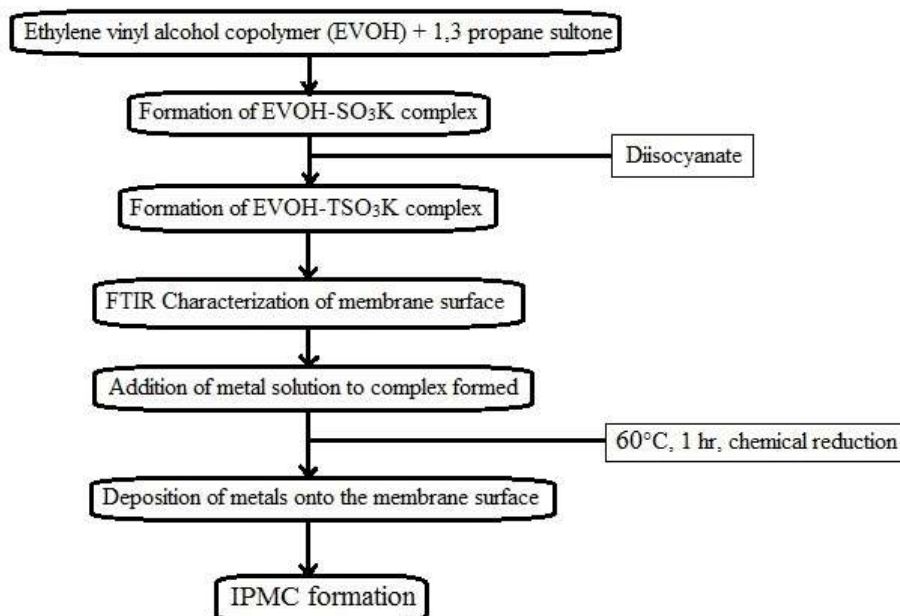


Figure 2: Chemical Deposition of IPMC formation

Electroplating Method

This method involves the application of electric field across the membrane for efficient deposition of metal on the surface of the membrane [7]. Electroplating process occurs in four steps as follows:

- **Roughening of membrane surface**

The initial step in electroplating method is to roughen the surface of the membrane so that adsorption of metal ions onto the membrane surface takes place efficiently. Sandblasting and sandpapering methods are used for this process. Sandblasting refers to the process of coating the surface using blasting machine. It consists of a nozzle, compressor and blasting pot while sandpapering is the act of grinding the surface with sandpaper. After roughening the surface through these techniques, cleaning is done to remove the impurities present either ultrasonically or chemically by heating with dilute acids.

- **Ion exchange**

This process involves the immersion of roughened membrane surface into metal solution for enhancement of ion adsorption. Metals like Platinum or silver can be used depending on their efficiency. The membrane strip is immersed into the metal solution for few hours for reduction of metal and binding on the surface.

- **Initial compositing**

In this step, the reducing agent is added to the solution containing membrane and metal. Sodium or lithium borohydride solution is used as reducing agent. Reduction is initiated by the reducing agents and the metals get reduced from their state. After metal reduction, it gets deposited as layers on the surface and at the sides of the membrane. A shiny black thick layer is formed in the membrane.

- **Surface electroding**

This process is mainly done for reduction of resistivity at the surface of the membrane. Another layer of noble metals are deposited over the first layer of metals plated. This is done to decrease the resistivity of the membrane and to increase the penetrating ability of first layer metal deposited.

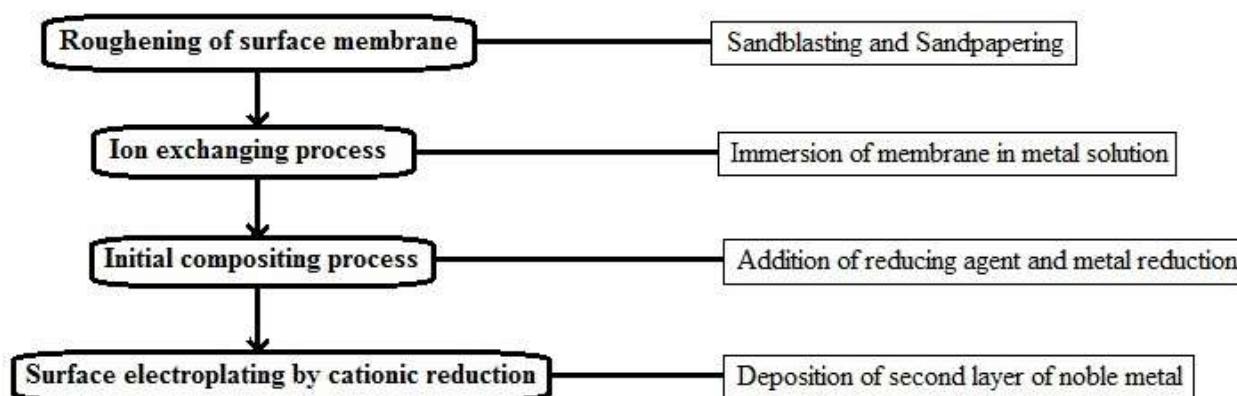


Figure 3: Steps involved in Electroplating process

Working of IPMC

The hydrophilic region is composed of ionic groups and cations while the hydrophobic region made up of polytetrafluoroethylene. Cations are mobile within the water groups and the anionic groups are immobile and are covalently attached to the hydrophobic fluorocarbon backbone. The movement of cations is responsible for activation of IPMC due to electrical induction. Therefore the mechanically movement of cations produces electrical signal and hence it functions both as activators, sensors and transducers. The increase in capacitance of transducer directly increases the activation since the expansion of transduction is directly proportional to the capacitance of the transduction. This process can be enhanced through deposition of metals on both the sides by

plating. Voltage is applied in the hydrated water region and electrostatic force exerts between mobile cations and immobile anions. Due to this effect, cations diffuse towards cathode and redistribute itself creating electron imbalances across the membrane. Anode region remain in ground state while cathode region starts stretching causing bend near the anode region. The cations dissolve and redistributes along with the water molecules producing differential swelling. Bending towards the anode and anode relaxation occurs in opposite direction. The parameters like speed, magnitude and direction depend on polymer composition, cationic type and electrodes. Voltage applied across the opposite sides of membrane causes initial bending of IPMC. While sudden bending of IPMC produces voltage, IPMC can act both as activators and sensors [8].

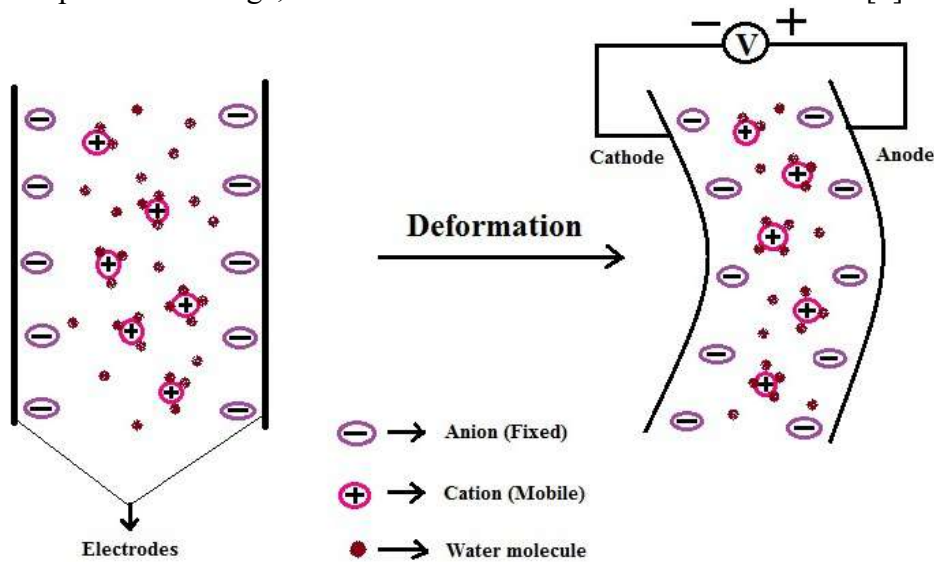


Figure 4: Working of IPMC before and after deformation

Characterization Parameters of IPMC

The bending of IPMC is influenced by various parameters such as stress, power, efficiency, strain, etc. The extent of bending directly depends on these factors which have to be monitored and controlled accordingly [9, 10].

- **Stress**

It refers to response of a material under applied pressure or force. The activators are being tested against this parameter to determine the withstanding ability of the material. Maximum stress applied to which the material can tolerate is defined as peak stress.

- **Power and efficiency**

It refers to the ratio of output to energy input. The rate of work output must be equal or greater than the input energy for the material to be efficient and for obtaining maximum result.

- **Actuation**

It is also termed as electromechanical coupling defined as amount of energy input that has been converted to output work. This includes the all the work done by the external actuator and also internal mechanical work done by the actuator itself.

- **Work hardness**

It is the measure of work produced in one actuator cycle standardized by actuator volume, barring electrolytes, anodes, control supplies or bundling. Particular power or energy to-mass proportion is the power yield per unit mass of actuator material.

- **Total cycle life**

It refers to the total number of work cycles the material undergoes. This factor depends on stress and also strain.

- **Strain measure**

It is the removal toward management per unit length of the material. It is the normal change in strain per unit time amid an actuator stroke. This occurs at low strains and high frequencies conditions only.

Properties of IPMC

IPMC finds various commercial applications owing to their unique properties only. Their potential to withstand factors like stress, strain, elastic modulus, bandwidth, etc has paved for its wide application in industrial and medicinal field.

- **Mechanical Properties**

Presently, after first detailing as dynamic polymeric material, IPMCs have been adjusted into imaginative materials for use in delicate activator/bio-mechanical applications on account of their huge twisting ability, simple handling, low driving voltage and simple scaling down. With a specific end goal to abuse the twisting movement from the IPMCs, numerous specialists endeavoured to utilize different stored metals from valuable metals (Au, Pt, Pd, Ag, and so forth) to change metals (Ni, Fe, etc) on Nafion membrane. Valuable metals, particularly Pt and Au, are the most surely understood for electroding metals [11]. Different endeavours to augment the IPMCs effectiveness, propelled materials, and handling techniques, used the composite terminals framework as well as the high usefulness ionic polymer. Pt/Ag composite cathode was saved utilizing an electrochemical technique to expand the electrical property-low resistance. The Pt/Au composite anode was tried to get high stable IPMCs. For the high mechanical properties of IPMCs, the carbon nanotube/Nafion nanocomposite was received utilizing a casting technique. Ionic fluid (IL) IPMC, a powerful approach to maintain a strategic distance from the restricted activation condition in water for customary IPMCs was proposed. Mechanical property can be identified by comparing between normal stress and normal strain using Nafion membrane. The stiffness and elastic modulus increased with nafion membrane nature itself. This indicates that the strain/stress depends on the polymer type and not on the electrodes. In spite of the fact that the manageable testing comes about demonstrate the inherent idea of the IPMC, an issue emerges when the IPMC works in a twisting method. Divergent mechanical properties of the metal particles (the terminal) and polymer organize appear to influence each other [12].

- **Electrical Property**

The electrical property of IPMCs can be evaluated using standard AC impedance method. It is studied that IPMC shows resistance nearly at high frequency and moderate capacitance at low frequency. For enhancement of surface conductivity, a thin layer of a profoundly conductive metal, (for example, gold) is sedimented over the platinum surface cathode. Understanding that water contained in the perfluorinated IPMC arrange is the dissolvable substance that can make valuable strains in the activation mode, another issue to manage is the 'deterioration voltage' [13]. As indicated by Faraday's law, increase in voltage alters the current in the system. In any case, a small increment in dc current is seen with a little change of voltage. It ought to be noticed that such water electrolysis prompts bring down thermodynamic effectiveness of the IPMC. The general conduct of the IPMC demonstrates a basic pattern of ionic movements caused under a forced electric field. In any case, it must be understood that, at low frequencies, the successful versatile modulus of the IPMC cantilever strip under a forced voltage is little. Then again, at high frequencies such moduli are bigger and movements are littler [14]. This is because at low frequencies water and hydrated particles have sufficient energy to spout out of the surface anodes while at high frequencies they are

present within the polymer. The idea of water and hydrated particle transport inside the IPMC can influence the moduli at various frequencies. This is of enthusiasm for a comparative similarity to ionic water driven activators. Clearly, water spillage is a specific drawback in accomplishing high effectiveness for the IPMC. This issue ought to be made plans to get considerably higher efficiencies and particular power for the IPMCs as activators and sensors [15].

- **Thermal Property**

With the persistent reduction in the extent of electronic and micromechanical gadgets, there is an expanding enthusiasm for high thermal conductivity materials for thermal scattering to maintain a strategic distance from basic harm to the gadgets [16]. Amid the previous two decades, thermal conductive polymeric materials have been given careful consideration. Boron (BN) and aluminum nitride (AlN) were acquainted with increment the thermal conductivity of polypropylene material. The thermal properties of two polypropylene composites filled individually with aluminum (Al) and copper (Cu) powders. Today plainly viable thermal conductivity is an imperative portrayal of thermal conductive properties of materials. The speculation of this examination found that with the proper filler content, the particles are found sufficiently close to each other to shape a persistent conductive way. At that point the thermal diffusivity of the composite should rise fundamentally [17].

Importance of IPMC

The IPMCs constitutes to a unique gathering of electro active polymers with changed properties. They are engineered composite materials for controlling for different applications. Their shocking properties, for example, activation, detecting, and so on has moved toward becoming exceptionally helpful in incorporating with other propelled advances for different applications. They are utilized as a part of actuators for changing over the electrical signs to mechanical twisting of the material. Reversibly, as a brilliant material, they can deliver voltage when a mechanical drive is connected on their surface. The ability in working even in the liquid situations without yielding the particular properties has expanded their significance. They turn into the practical parts of MEMS because of their similarity with such smaller scale mechanical frameworks. The application of IPMCs is begun from the essential application as actuators and has achieved propelled applications as a laparoscopic surgical device in the medicine. The creative ability of their potential fields of usage is past the farthest point of their present applications, and is anticipated that would perform later on look into future research [18, 19].

Applications

IPMC finds vast application in industrial and medicinal sector including functioning as activators, transducers and artificial muscles.

- **Industries**

Mechanical holder

IPMCs can be designed to function as micro and macro holders in gripping two membranes resulting in bending in opposite directions. The two IPMC actuators are set parallel to each other with top surfaces confronting each other. The terminals are connected to the best surface and the base surface of every actuator. Terminals are associated with each other and to one post of the power supply by electrical wire. The length of wire relies upon the required space between the two IPMC activators, based on requirement of application. The most significant benefit of such IPMC holders begins from their characteristic material delicateness in respect to ordinary activators. At present, multi-finger grippers that comprise of two, four, and eight fingers have been delivered [20]. Three-dimensional and linear actuators

IPMC activators are set in three dimensional networks and used along with three-phase generator box. IPMC activators consist of three membrane activators connected with each other and insulated

electrically with three sides facing externally. The tube is attached to the generator box and the terminals are located on sides of the actuators. The terminals are connected to the electrodes in the generator box. The major application of these types of activators is power mixing, production line feeding, etc. Linear activators are designed for producing manipulative robotics [21].

Meter measuring devices

Metering valves can be fabricated from IPMC. By applying an aligned measure of direct voltage/current to the IPMC metering valve connected to any tubes and, thus, shifting the level of twisting rearrangements of the IPMC, the control of watery liquid stream can be achieved. However alignment of such devices requires more effort and strain.

Musical Instruments

Due to mechanical flexing nature of IPMC materials, it creates a voltage and the way that if these materials are officially extended and twisted they make diverse recurrence yield signal, one can utilize them as a melodic instrument.

Microelectromechanical systems (MEMS)

Microelectromechanical system (MEMS) and microrobots designed with electroactive polymers and specifically IPMCs speak to an empowering innovation for assembling sensor furthermore, actuator microarrays, expendable microbiosensors for real time medicinal applications, and an assortment of microfabrication forms requiring the control of little materials. The IPMC actuator microarrays will have prompt applications in micromirror-based photonic optical fiber switches. Too, the IPMC microgrippers are incited with low voltages, are quick and can be cut discretionarily little from sheets of the IPMC material [22]. A wide assortment of electroactive clay materials are fused into engines, interpreters and controllers, in such gadgets as ultrasonic engines and inchworms. As opposed to electroceramics, IPMCs are rising as new incitation materials with uprooting abilities that can't be coordinated by the striction-constrained and inflexible ceramics. IPMC materials can be effortlessly framed in any coveted shape and can be utilized to assemble MEMS-sort components (actuators and sensors). They can be intended to copy the operation of organic muscles and they have exceptional attributes of low thickness and additionally high strength, extensive incitation strain consistent and intrinsic vibration damping. The IPMC sensors and actuators can be normally coordinated with the current MEMS innovation since they are effortlessly group processable and manufacturable and they can be made as little as craved and in any geometry that is sought, as we have demonstrated. IPMC-MEMS innovation will turn into an empowering new innovation to help in biotechnology too. Advancements, for example, the polymerase chain response (PCR), microsystems for DNA intensification and recognizable proof, the micromachined examining burrowing magnifying lens (STMs), biochips for discovery of unsafe compound and organic operators, and microsystems for high-throughput tranquilize screening furthermore, choice will especially profit by IPMC-MEMS reconciliation. IPMC-MEMS can likewise effortlessly incorporate into high yield dynamic detecting frameworks, for example, accelerometers and dynamic movement and constrain sensors too [23].

- **Medicine**

The nature of flexibility, stability and softness makes IPMC to be used in biomedical applications.

Artificial Cardiac muscles

Artificial ventricular help sort muscles can be made for heart patients with heart deformities related with cardiovascular muscle capacities. The potential IPMC gadget subsequently can keep away from thrombosis and comparable complexities, which are normal to current counterfeit heart, or heart-help gadgets, which may emerge when the blood stream makes rehashed contacts with non-natural or non-self surfaces. In pressuring a heart ventricle, the gadget must be delicate and electronically strong all together not to harm the ventricle. This resembles that the gadget ought to contain control means, for example, bradycardic (pacing) and tachyarrhythmic

(cardioverting/defibrillating) to encourage gadget operation in synchronism with the left ventricular withdrawal, and ought to be fit for transcutaneous energizing of the embedded batteries. the instrument is embedded basically in the ribcage of the patient yet is upheld on a slim adaptable stalk that stretches out to the mid-region. The stalk permits the systolic and diastolic cycles of the heart to proceed but then enables the body of the heart to make oscillations to the other side or the other without pointless confinement. It is likewise conceivable to put the supporting structure of the heart pressure device on the stomach muscle. These points of interest can be worked out at the time of clinical testing and operation of such devices. As modelled, this instrument produces helping or delicate pressure of the left ventricle of a poor functioning heart to create more interior weight and to direct more blood from at least one sides in simultaneous with the common systolic constriction of the ventricle. Furthermore, the framework can likewise give arrhythmia control of the pulsating heart. The delicate fingers designed join reasonably found cathodes for observing the ventricular stroke, volume and weight [24].

Medicinal tools and pumps

The IPMC activators can be received for use as a guide wire or a smaller scale catheter in biomedical applications for intra-hole endoscopic surgery and diagnostics. Little inward pits in the body can be explored by utilizing little strip or fiber-like IPMC activators. Peristaltic pumps can be produced using tubular segments of the layer of IPMC and arrangement of the anodes in suitable areas. Balancing the volume filled in the tube is manageable by applying suitable information voltage at the possible recurrence.

Energy Reapers

The use of IPMCs as energy saving system has accomplished much prominence in the current years. This is a quickly developing field in which the energy can be reaped from the liquid state with the assistance of IPMCs. The vitality gathering procedure can be from different sorts of streams including mobile immobile, and oscillatory streams. The capacity of IPMCs to change over the pressure energy to electrical energy is used in the stream situations. Various types of IPMC structures are utilized overwhelming fluttering banner facilitating IPMCs, IPMC cantilevers, etc. The energy reaping utilization of an IPMC strip cantilever is submerged in a liquid situation. The base excitation is considered for the displaying of IPMC strip submerged in a liquid state [25]. Trial work additionally been finished by checking the submerged vibration of the IPMC submerged and the relating electric reactions are noted for different resistors. It is required to be utilized expansive IPMC tests for accomplishing a couple of microwatts. The improvements in the outlining procedure of huge examples will absolutely help the energy saving instruments. The IPMCs are possess biocompatibility properties; henceforth they can be utilized even in the sticky moisture conditions. It has been suggested that the potential utilization of IPMCs for energy healing from smaller scale seismic or sea waves. Programming displaying is obligatory for the successful assessment of the IPMCs based frameworks for energy gathering applications.

Conclusion

The advancements in IPMCs based instruments and structures are extremely encouraging developments for future era coordinated innovations, which can bestow a larger number of yields as opposed to the current ones. The different elements decide the proficiency of an IPMC includes drive streamlining, reliance on cations for the electrochemical execution, preparation of cathode and the molecule estimate dispersion, and so forth. The electromechanical coupling of IPMCs is upgraded by expanding the charge thickness, which is gotten by plating noble metals like Pt on either side of the polymer layers. A few strategies have been settled on the synthesis of IPMCs, such as freestyle creation by discharging, casting solution and so on. The electroding procedure through the synthesis of IPMCs helps in minimizing their surface resistivity. The different execution parameters of IPMCs are data transmission, work thickness, effectiveness, elasticity modulus, and so forth. Demonstrating in IPMCs finds better understanding in their functions and

furthermore can distinguish the different factors that associate with the testing ones. The execution of IPMCs have made them imperative possibility for different applications, for example, coupled activator/sensor instrument, artificial cardiac assist muscles, energy gatherers, and so on. The high assembling expense and high reliance on IPMC's constrain thickness production ability decide their extent of commercialization. Facilitate advancements are to be sure keeping in mind the end goal to decrease the cost and thus acknowledgment of IPMC based devices. As the interest for energy develops, the requirement for more productive and helpful energy change instrument increases. One region of change is the utilization of direct energy transformation procedures and instruments. Smart materials are the establishment of current cutting edge instruments to change over energy from substance or electrical into mechanical energy to perform valuable work. In the field of detecting, these devices changes over mechanical energy into electrical or synthetic structures. The utilization of these materials appears extraordinary guarantee as choices for use in mechanical technology, biotechnology, sensors and other modern applications most importantly in medicinal field.

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Carbon Nanotube Composites

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Keywords: Carbon nanotube, high tensile strength, durable, young's modulus, size-dependent

Abstract. The discovery of carbon nanotubes is one of the remarkable achievement in the field of material science and it is a great advancement of Nanotechnology. A carbon nanotube is an expedient material used in several domains and paves way for the welfare of humans in many ways. Carbon nanotubes are Nano sized tubes made from graphitic carbons and it is well known for its exclusive physical and chemical properties. The market demand for the nanotubes has increased progressively due to its size dependent, structure and mechanical properties. The carbon nanotubes possess high tensile strength and it is also found to be the durable fibre ever known. It is also found to possess exceptional electrical properties. The carbon nanotube composites have an excellent young's modulus and higher tensile strength same as graphite carbon. This review plots the properties of carbon nanotubes and portrays the planning and properties of carbon nanotube composites. The wide application of carbon nanotube composites is also explained.

Introduction

Nanotechnology is a key solution that can be bridled to address a portion of the world's most basic advancement issues. Nanotechnology is one of the greatest empowering innovation which helps in solving many environmental issues with Nano sized objects. Nanotechnology is given immense attention in medical and other commercial applications due to its unique size. It is commercially manufactured in various categories such as fibres, materials, gadgets and frameworks. These materials possess specific physical and chemical characteristics with a unique size which lead to the advancement of nanotechnology in various domains. When this technology is prioritized and utilized properly it can rectify many basic environmental issues which prevails as a great hindrance in the livelihood of nearly 5 billion people living in the developing countries [1-2]. Carbon nanotubes are the advancements of Nanotechnology. In the previous thirty years, Carbon nanotubes are seemed to be one of the greatest breakthrough in the material science because of their wonderful properties they have pulled in exceptional intrigue from established researchers [3].

Many developed countries prioritize nanotechnology and they invest a huge amount in the nanotechnology research. The People's republic of China is one of the leading country investing a tremendous amount in Nano research and they have a certified nanotechnology textile industry. Israel is admirably leading the world in nanotechnology and they carry out many advanced types of research in this field. The United States of America which is one of the most capable nation globally has invested huge billions of dollars in this field and they have officially enunciated a national wide nanotechnology research center called Clinton nanotechnology in 2000. Europe has enunciated an enormously large nanotechnology program which are billions of Euros worth and they have formed many nanotechnology centers everywhere. Not only that, India which is one of the developing countries spend a large amount especially in this nanotechnology research. Many developed and developing countries believe that Nanotechnology is an excellent solution for many environmental problems remaining in the current scenario. The entire logically mindful and mechanically propelled world consider that nanotechnology is going to be the prodigious forthcoming technology which is highly capable of developing the standard of living and our reality with in a span of next 100 years [4].

The exceptional properties of carbon nanotubes produced tremendous movement in many regions of science and designing. The carbon nanotubes are exemplary because of its unique features and they possess an excellent thermal and mechanical properties when compared with other materials [5].

Nanotechnology is very much beneficial and shows numerous applications such as the production of field electron emitter, Nanoprobes, Nanotweezers and Nanobearings. The discovery of carbon nanotube composites remains as a propitious initiative in nanotechnology which is predominantly used for its unique physical properties [6]. This review article is intended to explain about the preparation and properties of carbon nanotube composites. It also gives a clear view on the different carbon nanotube composites

Carbon Nanotubes

A carbon nanotube is one of the identical discovery in the field of nanotechnology. It provides numerous applications to mankind and it is a remarkable achievement of our science community. The carbon nanotube was discovered by Sumio Iijima at 1990. The carbon nanotube is initially visualized using a High-Resolution Transmission Electron Microscope by subjecting the graphite molecule in Arc evaporation process in the presence of Helium gas. Iijima observed minute tube like structured carbon compounds accumulated in the core of the graphene cathode and these tubes comprise of concentric graphene barrels, commonly around 10 nm in diameter and are similar as fullerene [3]. The carbon element during sp^2 hybridization gives rise to various structural modifications. Kroto et al discovered the C_{60} structure of the carbon element in which the atoms are arranged in a honey comb like structure with open and closed edges. Correspondingly, at 1991 Iijima observed the tubular structure of the carbon which is called as a carbon nanotube. The two principle sorts of carbon nanotubes are single walled nanotubes and double walled nanotubes. Single-walled nanotubes (SWNT) is comprised of a solitary graphite sheet which is rolled into a hollow tube whereas the Multiwalled nanotubes (MWNT) comprises of a variety of nanotubes arranged like rings in the trunk of the trees [7].

Structure of Carbon Nanotubes

The structure of carbon nanotubes resembles the structure of fullerenes which is also known as bucky balls. The bucky ball structure consists of 60 carbon atoms organized as 20 hexagonal and 12 pentagonal faces clubbed to form a spherical sphere and when this sphere is elongated into a cylinder it forms the basic shape of the carbon nanotubes [8]. The three main classes of the carbon nanotube structure are arm chair, zig zag and chiral. In the arm chair and zig zag structure the hexagons are packed around the boundary whereas in the chiral structured carbon nanotube the hexagons are masterminded helically around the tube. The carbon nanotubes are usually distinguished into Single walled nanotube (SWNT) and Multi walled nanotube (MWNT). SWNTs are more adaptable than the multiwalled nanotubes because of their small diameter. Due to their increased flexibility, they curl around each other and don't stand straight. The multiwalled vary in their length from nanometers to a few micrometer and it is made up of an external diameter of 2.5 to 30 nm [3].

Synthesis of Carbon Nanotubes

The preparation of carbon nanotubes is limited by certain limitations such as the extent of purity and conformity. The carbon nanotubes are synthesized by various methods such as arc discharge method, laser ablation and chemical vapor deposition. Primatively the carbon nanotubes were produced by arc discharge method and this method is further used for the production of fullerenes and carbon fiber. As the technology gets advanced many innovative techniques have been followed in the production of carbon nanotubes. The carbon nanotubes are initially synthesized by arc discharge method and it is also used in the production of fullerenes. The arc discharge compartment is filled with a gas mixture of 10 Torr Methane and 40 Torr Argon. The negative side of the carbon electrode gives rise to carbon needles of 4 to 30 nm in breadth and 1 mm long. The two electrodes are placed in the centre of the arc discharge chamber and a DC Current of about 20 A to 20V is passed between the two electrodes. The combination of Argon, Iron and Methane is used in the production of the single walled nanotube. The arc discharge method and laser ablation method use the support of catalyst for the formation of

nanotubes. Chemical vapor deposition method (CVD) is used as an important method for the production of carbon nanotubes on a large scale. A mixture of acetylene, ethylene, methane, nitrogen and hydrocarbon gas is used in the vapor deposition chamber for processing of a substrate in the production of nanotubes at an optimal atmospheric pressure and temperature of about 700-900°C. CVD method is used to produce nanotube of lower cost and lower temperature. The silicon, alumina and glass are the preferred substrate for the production of nanotubes. The metallic catalyst such as Fe, Ni and Co are used for the deposition of the nanotubes in the substrate. The VanderWaals forces present in between the nanotubes help in the ordered growth of the nanotube in a parallel direction. The laser ablation is another method used in the production of single walled nanotubes by vaporizing the graphite rods using the laser in the presence of Co and Ni at 1200°C. With the reaction of the laser beam the nanotubes get settled at the end of the tube and the fully-grown nanotubes get segregated. Laser ablation is used for the mass production of the single walled nanotube and it uses cobalt coated silica for the organization of nanotubes [7-8].

Carbon nanotubes Composites

Carbon nanotubes cannot be used without adding a supporting medium to it so the nanotubes are reinforced with some supporting medium [8]. Carbon nanotube composites are filled with a combination of unique physical features which makes it preferable in many fields. The incomparable properties of the carbon nanotubes are the reason for using the carbon nanotubes as filler materials in composites. In ancient times the glass, silicon carbide, boron, alumina, glass and carbon are used as the reinforcements in the composites. The diameter of the nanotube generally varies from 1 to 100 nm of several millimeterlength. Due to the outstanding mechanical and thermal properties of carbon it is blended with composites and used. The carbon materials show a splendid mechanical property exhibiting tensile strength in the range of about 2.5 -3.5 Gpa. They possess Young's modulus in the range of 100–1000 GPa and strengths between 2.5 and 3.5 GPa [5]. Generally, the carbon nanotubes are reinforced in the polymer materials and in some cases, the ceramic and metal are used for producing carbon nanotube composites. The carbon nanotube composites are the emerging technology which eases the complicated process in the environment and used in many human activities [3].

Preparation of Carbon Nanotube Composites

Traditionally nanotube composites are prepared by simply mixing the Nano tubes with polymer solutions at an optimized condition and subjected to evaporation for removing the solvents and other solutions for the composites. This method has been used to prepare the polymer nanotube composites. Ultrasonic probes were used to blend the nanotube dispersions with the polymer solutions and the agitation created by the ultrasonic waves helps the polymer to get coated on the nanotubes. This method involving the blending of nanotubes with the solution is applicable only for few polymers because of restriction of some polymers towards solutions. Thermoplastic polymers are also used in the preparation of polymers. These thermoplastic polymers have the tendency to melt when heated and this melted polymer are coated on the surface of nanotube composites and this method is called as melt mixing method. Using the shear mixing the nanotubes are arranged and coated with the thermos polymers. Insitu polymerization method is also used to produce the carbon nanotube composites and here sonication is the key process used to blend both the polymer and nanotube. In this method after the preparation of nanotube, it is subjected to sonication process with HCl to obtain a fine distribution of polymers with nanotubes. The nanotubes are hybridized with a monomer such as aniline and subjected sonication and cooling in a cyclic manner. The single walled carbon nanotube composites and double walled carbon nanotube composites are prepared by various methods and immense care is taken to produce the composites without altering the thermal and mechanical properties of the composites. The perfect coating of polymer on the nanotubes provides highly efficient carbon nanotube composites [3].

Polymer Matrix Composites

The carbon nanotubes are often mixed with the polymer matrix for using it in various applications. In the preparation of polymer nanotube composites, the interfacial bonding between the nanotube and polymer matrix should be stronger. The understanding about the various features of the polymer and type of binding between the nanotube and the polymer matrix is significant in the production of polymer composites [5]. The incorporation of nanotubes with polymer helps in upgrading the abrasion resistance. However, it also increases the antiwear limit of the composite and tensile strength of nanotubes. The polymers such as polyaniline, polyimide, polyacrylamide and polypropylene are some of the widely used polymers that are usually reinforced with carbon nanotubes [7]. The polymer composites are formed with various sorts of polymers such as thermoplastics, thermosets and elastomers. The important parameter to be considered while producing polymer nanocomposites is the ratio of surface area of reinforcement to the volume of reinforcement. For better reinforcement of polymer with carbon nanotubes, it is pretreated with chemicals such as amines, silanes and some dispersants [9].

Ceramic Composites

Ceramic composites are another major class of carbon nanotube composites with high stability, conductance and nominal tensile strength. The ceramic composites have high stiffness and thermal conductivity, however, it is not easy to blend the carbon nanotubes with ceramic material like other polymers. Attaining a uniform blending and a very strong binding of carbon nanotubes and the ceramic material is quite difficult so various innovative techniques have been followed to produce ceramic composites. The arrangement of carbon nanotubes in the ceramic is quite difficult than in the polymer because of its rigidity. With the help of some thermal mechanical processing the polycrystalline ceramics which is used as a super plastic in many areas [3]. The combination of ceramic and carbon nanotubes are one of the unique types of CNT composites due to their enhanced electrical conductivity and thermal conductivity. This type of composites also acts as super plastics and they help as a lubricant in the process. The nanotubes blended with Fe-Al₂O₃ ceramic composites is generally prepared by hot pressing method [7].

Metal Composites

Carbon nanotubes reinforced in a matrix consisting of metals such as magnesium or aluminium is known as metal composites. The demand for the metal composites in the market is growing progressively and it is used widely in various applications. Metal nanocomposites are a low dense material possessing high Young's modulus and tensile strength. The metal composites are generally prepared by blending the nanotube with the metal matrix mixture and heated to high temperature. The tensile strength of the metal composites increases double the time than the pure metal from which it is prepared due to the incorporation of nanotube into the metal mixture. The prepared metal nanocomposites are coated using nickel, phosphorus and silica which is very helpful in lowering the abrasion and increasing the wear resistance [3].

Properties of Carbon Nanotubes

Physical properties

Carbon nanotubes are innovative strong composite materials. It resembles the structure of fullerenes and is comprised of hexagonal networks of graphitic carbon coiled into an excavated cylinder. The ends of the carbon nanotubes are capped with fullerene molecules. The nanotubes possess exceptional high Young's modulus, solidness, adaptability and high strength to weight ratio. The single walled carbon nanotube comprises a single sheet of graphene carbon and it is a distinct cylinder structure of 1-2 nm in diameter whereas the multiwalled carbon nanotubes comprise of a finely aligned graphene cylinders and the graphene cylinders are bound by weak van der Waals forces [10]. The single walled

carbon nanotubes are of 1 nm in diameter and their length is of some centimeter whereas the multiwalled carbon nanotubes are of 2-100 nm in diameter and the length extends up to several microns. The proficiency of the carbon nanotubes is based on the chirality, diameter and the type of the nanotube [5]. This nanotube can be used to construct largest Nano cable in the world of about 23,000 miles from outer space to earth in a without any barriers under the influence of high gravitational force [8].

Mechanical properties

Due to its superior mechanical property, the carbon nanotube composites are used in sensors and innuclear transportations. Basically, the carbon nanotubes possess a higher Young's modulus of about 1TPa and a satisfying tensile strength of about 11-63 GPa which enhances the mechanical property of the carbon nanotubes [11]. The carbon nanotubes reinforced with the polymer composites are best suitable material for many electronic applications and the blending of this carbon nanotubes with polymer solutions enhances the mechanical properties of the CNT's [12]. As the carbon nanotube and the graphite are moreover similar in their features the expectation for a material with high quality and solidness was increased. Graphite is wellknown for its amazing stiffness and tensile strength so it created a huge prospect on carbon nanotube after their discovery. The substantial measurement of the tensile strength at first is conducted with a transmission electron microscope and after that Atomic force microscope has been used to determine the stiffness constant of the multiwalled carbon nanotube [5]. Initially, Shaffer and windel are the two researchers who are very much interested in studying the mechanical properties of the carbon nanotube composites. According to their observations, the firmness of the composites very seemed to be low at room temperature [3]. Both the single walled nanotubes and the double walled nanotubes possess high bending constant due to its high tensile strength [13]. The carbon nanotube is highly vulnerable to stress and strain above its optimal limit of elasticity and they have the tendency of regaining its original structure even after subjecting it to a heavy stress whereas the other fibers don't possess this much amount of tolerance to stress and strain. Salvetat et al tried to measure Young's modulus of the catalytically produced MWNT using atomic force microscopy and he observed that Young's modulus was found to be at 27 GPa. The measurement of SWNT is little complicated however it is measured using the nanostressing stage and Young's modulus for SWNT was found to be 320–1470 GPa and a tensile strength of 30 GPa [3].

Electrical properties

The carbon nanotubes are very well known for its peculiar electrical properties which distinguish it from other materials. The outstanding electrical property of nanotube composites is mainly dependent on two factors such as diameter and geometrical property of the nanotube which are the major factors responsible for the fluctuation of the conducting and semi conducting behavior of the nanotubes [8]. The electrical behavior of carbon nanotubes will be fluctuating based on the type of the tube and it keeps on wavering tube to tube. The carbon nanotubes possess amazing electrical properties and sometimes it is incorporated into the non-conducting polymers to increase the conductivity of the polymer. The polypropylene combined carbon fibers showed an electrical conductance of 9–18 wt-%. Polyaniline is one of the promising polymer composites which exhibits an exceptional conductance with higher efficiency. The polyaniline incorporated with carbon nanotubes showed an increased conductance when compared to other materials because of the barrier less charge transfer between the polymer and the nanotube [3]. The atomic structure of the nanotube also plays a major role in the electrical behavior of the nanotube because of the varying geometry the geometry of the tube in different contact location. Moreover, the resistance also gets varied in the different point of contact locations on the nanotube [8].

Thermal properties

In 1996, Treachy et al performed various laboratory studies to determine the thermal properties of the Multi walled carbon nanotubes using TEM [3]. The single walled nanotube composites and the double walled nanotube composites exhibit high thermal conductivity even at room temperature and they

possess exceptional thermal properties [14]. The blending of the carbon nanotube to the polymer brings a change in the thermal conductivity of the polymer. The thermal conductivity of a flawless polymer generally varies from 0.1 to 1 W/Mk. The thermal conductivity of the single walled carbon nanotube composites is found to be at around 1750 to 5800 W/Mk whereas for the multi walled carbon nanotube composites it is in the range of 3000 W/Mk [15]. Addition of even a small concentration of carbon nanotube into the polymers gradually increases the thermal conductivity [16]. The carbon nanotube composites are preferred because of their thermal management. The nanotube composites are usually used to control the liberation of heat from the electronic devices and other sources. The CNT can easily control the build up of heat inside the devices and other electronic instruments [17]. The parameters influencing the thermal properties of composites are the angle proportion, volume portion, arrangement of the strands, and the bond between the polymer and nanotube in the nanotube composites [18]. The thermal conductivity of the carbon nanotubes is greater than that of the diamond. The thermal conductivity of the carbon nano tubes is measured using the phonons [7].

Application of carbon nanotubes composites

Carbon nanotube composites are one of the emerging latest technology which has become an essential part of the livelihood of the public and it is known for its unique properties which makes it more versatile in the market. These nanotubes can be used as electrodes in the various chemical process. Due to the weak van der Waals force prevailing between the individual nanotubes that can be used in the various nanoelectromechanical process. It can be also used in the extraction of silicon from the silicon surface without applying a voltage with the help of nanoindenter [8]. The carbon nanotubes reinforced with the polymer composites are used in a wide range of applications such as transportation, electronic gadgets and fuel cells [11]. Polymer composites are very much helpful in packaging materials and they are used in the production of sports goods. Most of the electronic devices and sensors used nowadays are made up of nanocomposites [9].

Future Studies

The carbon nanotube composites have been an emerging technology in various industrial sectors. Much advance has been made over the most recent couple of years in composite fortification utilizing carbon nanotubes. Furthermore, numerous analysts are spreading out with the creation of novel structures by inventive preparing strategies. The unique properties of the carbon nanotube composites had increased the research option in this field. New innovative techniques for manufacturing the CNT composites should be discovered. Many new strategies to enhance the reinforcement of the nanotube into the polymer should be determined. Methods for controlling the debonding of the nanotube from the polymer / ceramic matrix should be enunciated. Other problems regarding the stress transfer and improper blending should be enhanced using chemical process. In the event that this advance proceeds apace, we can expect a proceeding with brilliant future in this interesting what's more, possibly extremely valuable zone.

Conclusion

Carbon nanotubes are one of the greatest inventions of this century and it created a great revolution in the field of material science. It has become an important material in many industrial and domestic appliances. The carbon nanotubes possess unique mechanical and thermal properties with higher stiffness and strength. It possesses a versatile modulus higher than 1 TPa and a tensile strength close to 200 GPa which makes it a strongest material when compared to other fibers. To increase the and enhance the features of the carbon nanotubes it is reinforced with a polymer or ceramic matrix. This review clearly explains the different unique properties of the carbon nanotube composites. In any case, the genuine estimation of CNTs lies in their range and expansiveness of properties, in particular, their electrical, warm, attractive and optical properties. The debondment and the strength of the reinforcement of the polymer with the carbon nanotubes are the important parameters which affects

the quality of the CNT. The details mentioned in the chapter gives an elaboration of the carbon nanotube composites.

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Polymer Electrolyte Membranes

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Abstract. Polymer electrolyte membranes (PEM) with good properties are essential for the improvement of electrochemical operations. The increase in properties of polymer electrolyte membranes will develop the performance of polymer electrolyte membranes in the fuel cells. The importance of polymer electrolyte membranes is increasing recently due to its activity and simplicity in energy associated applications like automobiles and various portable applications. PEM has various properties like proton conductivity, chemical stability, mechanical properties, thermal stability and so on. These properties are enhanced and influenced by various factors like morphology, the molecular weight of the membranes, chemical structures, cross linkages etc. The present chapter attempts to summarize about the properties of polymer electrolyte membrane involved in the different types of electrochemical utilizations.

Introduction

Due to the increasing concern in the world related to the lack of fossil fuels researchers have been focussed on the search of new power generators and energy storage arrangement. Continuous usage of fossil fuels leads to serious problems like ozone layer depletion, acid rain, global warming, pollution, climate change and so on [1]. Hence, we need alternative renewable energy like fuel cell for the generation of power. Over the three decades, numerous scientists have found the usage of polymer electrolyte membranes in different applications like electrochemical devices which incorporated with super capacities [2]. The membrane selection for this application depends on the factors like cost effectiveness, chemical stability, mechanical strength, permeability and so on [3]. Polymer electrolyte membrane is most important solid electrolyte used for the conduction of protons, the partition of gases and insulation of electrodes [4]. They are naturally more secure than those established salt-fluid dissolvable electrolytes in lithium batteries as there will be no issue of interior shorting or electrolyte spillage utilizing the polymer electrolytes. Mostly the polymer electrolyte membranes are non-flammable. The application of solid polymer electrolytes could beat the spillage issue related with fluid electrolytes. The polymer electrolyte membranes have several advantages like less leakage of toxic gases and liquids, easy manufacture of polymer electrolyte membranes for fuel cells and high energy batteries and simple fabrication than the other electrolytes. Recently, several advancements have been made in the development of polymer electrolyte membranes together with other related innovation progressions. They are commonly applied in fuel cells in which the polymer membrane act as a polymer membrane. Polymer electrolyte membrane fuel cells contain admirable properties like low working temperature, high productivity, low discharges, high life span, no spillage of electrolytes etc [2,5].

Polymer electrolyte membrane fuel cells are alternative to the various electrochemical applications. Recently, the application of polymer electrolyte membranes in the fuel cells is increasing because the fuel cells are steadily based on the conductance of electrolytes. In fuel cells, they act as a separator to avoid the blending of reactants and carries the electrons by the outer way to the cathode in the fuel cell. polyperfluorosulfonic acid (poly-PFSA) such as Nafion and perfluorinated ionomer (PFI) membranes and dow membranes are widely used polymer electrolyte membrane due to it's on account of its incredible chemical and thermal stability [6] and also found useful in various fuel cells. The membrane can be developed through the inclusion of inorganic fillers (e.g. SiO₂, ZrO₂, and TiO₂), acidic additives (e.g. heteropolyacids), polymer blends, or

organic–inorganic hybrid polymers. The regulation of properties of polymer electrolyte membrane is done by the chemical structure of the polymer, polymer molecular weight and molecular weight dissemination, morphology of the polymers, the cross-linked structure of polymers and bonding forces between polymeric chains and so on. Generally, the polymer electrolytes have developmental phases like dry polymer electrolytes, gel polymer electrolytes, and composite polymer electrolytes. Dry solid composites do not have organic liquids and polymer host plays a major role as a solid solvent. The ionic conductivity in the dry solid composites is very low. The gel polymer electrolytes comprised of plasticizers with high ionic conductivity. In the composite polymer electrolytes, ionic conductivity is increased due to the availability of appropriate fillers in it [2]. Polymer electrolyte membranes have specific properties like chemical and electrochemical stability, sufficient mechanical strength, low penetrability to reactant fluids/gases, and furthermore high proton conductivity [7]. With a specific end goal to understand the capability of fuel cells there is a requirement for novel electrolyte membrane materials based on membrane morphology, proton and mass transfer, and chemical and mechanical properties. The purpose of this review is to discuss the various properties of polymer electrolyte membranes and their importance in research and development have been explained.

Properties of Polymer Electrolyte Membranes

Proton conductivity

Proton conductivity is a deciding property of PEM for identifying the performance of PEM in fuel cell utilization. The materials which are used in fuel cells should have high proton conduction in order to get high voltage. Hence more researchers are focussed on developing proton conducting materials. It guarantees high power density output and low internal resistance of fuel cells. Proton conductivity is influenced by several factors, for example, relative humidity, ion exchange capacity, temperature, and polymer morphology. Since number of protons are accessible for transport, higher ion exchange capacity (IEC) gives higher proton conductivity. In any case, too high ion exchange capacity regularly causes overabundance swelling of membranes. Therefore, it is fundamental to control IEC at a sensible level. Likewise, water is assumed as an essential part in proton conduction. In proton conductivity, water is an important aspect because it creates an impact on the formation, dimensions and ionic pathways in polymer electrolyte membranes (PEM). The increase in water content leads to the segregation of PEM components into hydrophobic regions and hydrophilic cluster aspects. Using nanochannels, the cluster domains are joined together to form cluster network installed in a fluorocarbon phases. Water also acts as a barrier for proton transport. Without the guide of water atoms, protons and sulfonate anions are firmly fortified together prompting to a great degree of low proton conductivity. Because of this, proton conductivity is highly dependent on the relative humidity. In any case, it ought to be noticed that at the temperatures over the breaking point of water (100°C), relative humidity diminishes with expanding temperature, and thusly pressurization of the system is regularly expected to guarantee high relative humidity. Proton conductivity also gets affected by polymer morphology. The proton conductivity depends on the factor like proton mobility during the transport mechanism [8].

Moreover, the existence of water and proton conduction increases rapidly in PEM. At lower temperature 0°C and higher temperature 100°C, the PEM electrolyte membrane like Nafion becomes improper because of dependence of conductivity on water which reduces the conductivity due to the properties of water [9]. The introduction of inert hygroscopic fillers like SiO₂, TiO₂, reduces the proton conductivity of PEM. Integrating inorganic binary component into the PEM like Nafion increases proton conductivity. In order to operate the PEM at high temperature, these inorganic components are applied as additives to hold the water in the membrane which leads to raising of proton conductivity. In Nafion membrane, the proton conductors like heterocycle compounds [10] including triazole [11] and polyfunctional phosphonic acid [12] were added. Formation of bifunctional fillers like zeolite and silicon in the polymer electrolyte membrane reduces the property loss like proton conductivity in the PEM. The changes in the structure of the

polymers also bring out the changes in the proton conductance. The fall of proton carrier in the PEM, decreases the proton conduction and damages the membrane. Expanding the sulfonic acid functional group content and the hydrophilic aggregate domain size brings about increment in the proton conductivity. Accordingly, streamlining of the level of sulfonation and hydrophilic area morphology is important to outline a PEM having high proton conductivity with reasonable mechanical properties. The table 1 displays types of polymer electrolyte membranes used in fuel cell applications and its proton conductivity. The variations in the experimental conditions like moisture content, temperature, data analysis bring out the changes in the proton conductivity of PEM.

Table 1 Selected polymer electrolyte membranes and its proton conductivity [13]

S.NO	Types of polymer electrolyte membrane	Proton conductivity (S/cm)
1.	Sulfonated poly (ether ether ketone ketone)	0.040
2.	Poly vinyl alcohol blend	0.004
3.	Crosslinked poly (vinyl alcohol) using sulfosuccinic acid	0.015
4.	Sulfonated polyimide	0.120
5.	Sulfonated copolyimide	0.082

There are two sorts of proton conductivity directions they are tangential/in-plane conductivity and normal/through-plane conductivity. Generally, proton conductivity is deliberated along the plane of the film, since the estimation of the conductivity in the in-plane direction is significantly simpler to do with higher security, reproducibility, and exactness. Yet, in practice, the membrane need proton conduction opposite to the film. In this way, the through-plane conductivity of the film may have a noteworthy impact on the execution of power generation. The estimation of proton conductivity is typically executed by a four-test or two-test AC impedance strategy. Since the estimation of in-plane conductivity is considerably less demanding to work than the estimation of through-plane conductivity particularly at low relative humidity and the in-plane conductivity has been broadly used to describe the proton conductivity of a PEM. it is essential to building up an easy and successful strategy for estimation of through-plane proton conductivity since through-plane conductivity can be added to the fuel cell. The proton conductivity (σ) is determined by the following Eq.1. [14]

$$\sigma = \frac{L}{RA} \quad (1)$$

Where L is the thickness of the membrane, R is the impedance of the membrane and A is the area of the two electrodes.

Thermal stability

It is notable that fuel cells are especially worked at elevated temperature due to the benefits of high CO resistance, easy water management, and quick electrochemical energy and hence thermal stability is considered as a significant property of PEM which is normally assessed by thermogravimetric analysis (TGA). The polymer electrolyte membranes operating at a high-temperature range (100-200°C) displays high proton transport in the fuel cell applications. Utilization of thermally stable polymer electrolyte polymers has several benefits like rise of reaction kinetic rates, decreases catalyst poisoning and electrode flooding. So, it is treated as an important property of the polymer electrolyte membrane. Consolidating hygroscopic fillers into the PEM raises the thermal stability and it is also influenced by concentration and stability of cross links between sulfonic groups of Nafion membranes. alkyl sulfonated aromatic polymer electrolyte membranes have high thermal stability when compared with other materials. The water absorption capacity in the aromatic polymers can be induced through the inclusion of aryl sulfonate and alkyl sulfonate groups. Membrane morphology and its structure result in valuable properties of Nafion

PEMs, for example, thermal stability and ionic conductivity. Perfluoropolymers show high warm steadiness than the other polymer membranes. In aliphatic PEM addition of cross-linking structure and inorganic materials would rise the thermal stability [15,16]. The consolidation of particles into their structure reduces the thermal stability. The thermal disintegration is continued in three phases like loss of water; loss of sulfonic gatherings, signifying a breaking of the C–S bonds; and the decimation of the membrane network. The strong reliance of the Nafion thermal stability is based on the nature of the counterion. Nafion films demonstrate enhanced warm steadiness as the extent of the counter cation diminishes. The thermal of different alkali metal exchanged Nafion films will appear in the form like



Some of the studies showed that the Na^+ Nafion film has high thermal stability than the other alkali metal exchanged Nafion films like K^+ and Li^+ film [17].

Mechanical properties

The mechanical properties of the PEM are considered as most important because of its practical applications and lifetime. Additionally, it also influences fuel cell durability. PEM having reasonable mechanical properties, that is, elasticity, tensile strain, and strength has a higher resistance to the effect compel from the high-stream rate fuel gas, and accordingly its thickness can be diminished. The improvement of a PEM with high mechanical quality, high ionic conductivity, and lower thickness is a critical issue for a superior PEM. The assessment of membrane mechanical properties is normally performed by a tensile test. High elastic anxiety and substantial lengthening at break recommend great mechanical properties of the membranes. More than 20MPa of tensile stress and elongation along 20% is required for the good PEM. The mechanical stability is high in random copolymers because of the existence of aromatic backbones. The characterization of mechanical properties of PEM is carried out using dynamic mechanical analysis (DMA). Sometimes there is a presence of optimum proton carrier in the polymer electrolyte membrane. Rise of proton carrier in the PEM leads to the decrease of mechanical stability. Hydrophobic domains are in charge of giving appropriate mechanical properties to the PEMs which keep from dissolving in proton transporter (i.e., water) or different solvents, for example, methanol and from H_2 and O_2 (or air) gasses when connected in power module operations. The major factors like the molecular weight of the polymers, molecular weight distribution of the polymer, structure plays a major role in controlling the mechanical properties namely tensile strength, flexibility, and toughness of the polymer electrolyte membranes [18]. Among them, polymer molecular weight is an essential factor influencing membrane mechanical properties, and the higher the molecular weight, the higher the mechanical quality. In order to increase the mechanical strength of the membrane, membranes are reinforced with the fibers which play a vital role in enhancing the mechanical stability. This is due to the existence of porous films on the surface of the film. The legitimate cross linking of PEM enhances the mechanical strength and reduces the solubility of polymers in water when it is applied in fuel cell applications. The factors which affect the mechanical properties of the membranes are moisture content and temperature. These factors show effects on mechanical properties lower break stress and higher break strain. Several types of research showed that inclusion of an inorganic filler, crosslinking, and annealing treatment would stimulate the mechanical properties of the polymer electrolyte membrane.

Ionic conductivity

PEMs are basically utilized as a part of electrochemical applications; ionic conductivity is important amongst the most critical properties. In other words, a great PEM ought to have proper ionic conductivity. Accordingly, the PEM with positive and negatively charged groups are carried by the inorganic materials. For a PEM, ionic conductivity is a basic portrayal that should be considered. The ionic conductivity depends on the availability of the water content. The increase in water content, the ionic conductivity of the membrane increases. Based on the water content, the

ionic conductivity measurements are calculated. There are two types of ionic conductivity are utilized in the fuel cell applications. They are in-plane and through-plane conductivities. The conductivity occurs along the surface of the membrane direction are called in-plane conductivity and the conductivity takes place across the thickness of the membrane direction are called through-plane conductivity.

Chemical stability

Sustaining chemical and mechanical integrity of the membrane over the expected lifetime is a major necessity, and it merits consideration as of now in the beginning time of membrane improvement. Due to the loss of functional groups or constituents, PEM meet with chemical degradation caused by HO and HOO radicals which are shaped in situ through association of H₂ and O₂. Several types of research have been carried out in the chemical degradation of PEM (19,20). It is clearly known that chemical degradation of PEM occurs from chemical attack by hydrogen peroxide radicals, bringing about breakage of the membrane and consequent loss of mechanical quality and proton conductivity, hence prompting an expansion in resistance and declining cell performance. It is conceivable to recreate the corruption of PEMs utilizing a quickened test medium, for example, Fenton's reagent. Worse oxidative stability of the membranes leads to failure during the fuel cell operation. The evaluation of oxidative stability is done by immersing them into the Fenton's reagent. Their dissolving capacity determines the oxidative stability. Fenton's reagent is a strong oxidizing capacity which consists of hydrogen peroxide and Fe²⁺. Generally, low amount of Fe²⁺ is utilized along with the combination of large amounts of hydrogen peroxide are applied in which Fe²⁺ is oxidized into Fe³⁺ and form hydroxyl radical and a hydroxide ion in the process then it is further reduced to Fe²⁺ and form hydroperoxy radical and a proton. This strategy is viewed as one of the standard tests to gauge the relative oxidative stability and to enhance the accelerated fuel cell operating conditions. But there is no connection between oxidative stability and durability of the membranes. The radical oxidation develops the degradation of polymer electrolyte membranes. The evolution of radicals is created from the cathode side due to the permeation of oxygen. Hence it is most significant to produce the polymer electrolyte membrane (PEM) with high oxidative stability.

Permeability

The basic material property of polymer electrolyte membrane is permeability of PEM towards fuels. Fuel cell efficiency and the lifetime of the fuel cells is based on the membrane permeability. By decreasing the thickness of the polymer electrolyte membrane, the permeability of the membrane gets raised. At the time of fuel cell operation, the fuels like hydrogen or methanol get penetrated inside the cell and simultaneously ion conduction occurs. Due to the fuel permeation, the voltage gets decrease and efficiency of fuel cell also affected. Additionally, radical generation also takes place which makes the membrane to undergo chemical degradation due to the penetration of hydrogen into the fuel cells [21]. Hence, the fuel permeability should be low in polymer electrolyte membranes. There are two methods are available for the evaluation of fuel permeability in the fuel cell. They are ex-situ and in situ methods. Ex-situ method is widely applied for the determination of methanol diffusion. In this method, two types of reservoirs are used and these are separated by sample membrane. The passage of liquid is prevented by the membrane and allows only permeate molecules to pass through. The injection solution consists of methanol and pure distilled water. The diffusion process starts after the injection of solution and measured by gas chromatography. In the in-situ method analyze the fuel concentration in the fuel cell operation. This method measures the permeation of hydrogen and oxygen by using chronoamperometry [22]. Though the evaluation is more difficult than the ex-situ, this method gives the appropriate result of fuel cell operation.

Water uptake capacity

Water uptake should be given important consideration in electrochemical applications because it gets immersed into the water. The water uptake capacity is measured using mass

contrasts between the wet and dry membrane. The weight percentage take-up was dictated by the accompanying condition which was mentioned in Eq. 2

$$WU(\%) = \frac{W_w - W_d}{W_d} \quad (2)$$

Where W_d is the mass of the dry membrane, W_w is the weight of the wet membrane, respectively.

Through the humidified H_2/O_2 gas streams water is carried into the fuel cell. Availability of water in the membrane is transferred by two ways namely osmotic drag of water from the anode to cathode and diffusion. The dry membranes in the fuel cell lead to less performance of electrolyte. Water uptake capacity is a major property required in polymer electrolyte membranes. This property can be enhanced by the introduction of the inorganic binary component to PEM. In order to retain proton conductivity of the polymer, water uptake capacity is highly needed because the water molecules play a vital role in proton transport mechanisms. High water uptake capacity increases proton conductivity and simultaneously raises the mechanical properties of polymer electrolyte membranes [23]. In ion conducting process, water molecules are more responsible for the transport of proton and hydroxyl ions across the Hydrophilic domains are helpful in holding the water that makes the PEM in proton transport [24]. The water gets retained in the membrane due to the lower toughness and lower free volume that occurs in the existence of a high degree of PEM cross link density. Thus, optimization of cross like density is needed for PEM properties. The hydrolytic stability is normally assessed by measuring the progressions in mechanical properties, weight reduction, IEC, and proton conductivity. Various studies showed the water uptake capacity of polymer electrolyte membranes and their characterization of physical structures using a technique like IR spectroscopy are discussed.

Most of the researchers are focussed on the water uptake capacity of the polymer electrolyte membrane because it is connected with the property like ionic conductivity. The morphological changes in the ionic cluster and crystallinity occur by pretreatment of the membrane which leads to the creation of impact on water uptake capacity of PEM. This property is based on drying method employed and membrane drying at room temperature has higher water uptake capacity than the membrane drying at elevated temperature. Most of the investigations noted that water uptake capacity is low at a higher temperature. With the addition of inorganic filler into the hybrid membranes, the water uptake capacity gets increased. The water uptake capacity is connected with the hygroscopic interior for the inorganic filler, plasticization effect of the nanoparticles. It is realized that other than the sulfonic acid groups in membrane hygroscopic Si-OH gatherings could likewise assimilate and hold water atoms, which expanded the substance of bound water. Moreover, the Nano sized particles had huge particular surface areas, which influenced the hybrid membrane to uptake high water content. In any case, there are additional studies asserting the presence of an optimized substance of inorganic fillers in the hybrid membranes enhances the water uptake capacity.

Future outlook

The broad research endeavors around the world, the need still exists for new polymer films that could have good properties. Hence, several studies need to be carried out to identify the new polymer electrolyte membrane (PEM) with better properties and to be used in various applications. Researchers should focus on the evolution on the methanol stable membranes in order to decrease the methanol crossover. Usage of future PEM in the research and development require high durability thus it should be enhanced through reinforcement. Further studies should describe in measuring the properties of PEM through different techniques.

Conclusion

Several research and development strategies are available for several electrochemical usages. But these applications will require the membrane material with stringent properties that is suitable for large scale production. This review paper presents new ideas and summarizes the details regarding polymer electrolyte membrane properties based on recent literature. Currently, the well-developed fuel cell technology is based on polymer electrolyte membranes. This review article develops to understand the properties of the membrane and the more extensive utilization of the membrane. On the basis of above investigations, it is clearly mentioned that the based on the properties of polymer electrolyte membranes, their applications in the fuel cells are increasing. Though there are poor properties for some of the PEM, the usage of polymer electrolyte membrane is raising. The information contained in this chapter will give valuable information in the future.

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Diffusion of Multiwall Carbon Nanotubes into Industrial Polymers

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Abstract. Carbon nanotubes (CNTs) are made out of carbon atoms connected in hexagonal shapes, with every carbon molecule covalently attached to three other carbon particles. The properties of nanotubes have made scientists and organizations think about utilizing them in many fields. For instance, since carbon nanotubes have the most noteworthy quality to-weight proportion of any known material. Nanocomposites of adjusted multi walled carbon nanotubes (MWCNTs) installed in a polymer matrix yield a one of a kind mix of warm and electrical properties and mechanical quality. The composites combine the vast pseudo capacitance of the directing polymers with the quick charging/releasing two-fold film impedance and incredible machine-driven possessions of the carbon nanotubes. The electrochemically co-stored composites are the most homogeneous and demonstrate an unordinary communication between the polymer and nanotubes, offering ascend to a reinforced electron delocalisation and conjugation along the polymer chains.

Introduction

The assets and utilizations of CNTs and associated constituents have been extremely dynamic investigation. CNTs have high adaptability, low mass thickness, and extensive viewpoint proportion (ordinarily >1000), while anticipated and some trial information show to a great degree high pliable segment and qualities for these constituents. Singular single-walled carbon nanotubes (SWCNTs) can be metallic or semiconducting. SWCNTs and MWCNTs touched off a firestorm of enthusiasm for these exceptional particles in view of their remarkable properties furthermore, potential applications. CNTs fortified cover composites are in effect progressively utilized as a part of automobile, marine and aviation applications in light of their fantastic power-driven properties. Without a doubt, this blend of machine-driven and power-driven properties of individual nanotubes makes them the perfect fortifying specialists in various applications of CNTs. The carbon nanostructures, for example, fullerenes furthermore; CNT nanofibers are increasing wide acknowledgment as the innovative materials because of their magnificent physical goods, slim erection and simple accessibility. The utilizations of CNT-polymer system composites (CNPCs) have been foreseen to have immense impact on gathering and development based endeavors due to their lightweight and assistant/non-fundamental multi-functionalities [1].

CNTs are regularly blends of different chiralities, distances across, and lengths the nearness of contaminations furthermore, different imperfections. Additionally, CNT combination has been found to altogether hamper the machine-driven properties of made nanocomposites. Finally, because of their little size, CNTs are ordinarily twisted and wound, and along these lines, discrete CNTs implanted in a polymer just show a division of their potential. In this manner, the sublime assets of CNTs cannot so far be completely converted into high quality and solidness completed items.

In perspective of the first, there has been a huge push to build up the furthestmost appropriate environments for the exchange of powered load to singular nanotubes in a polymer complex. An essential attempt is the productive scattering of discrete nanotubes and the foundation of a solid concoction proclivity with the encompassing polymer network. Distinctive systems for CNT manufactured change have been shown exceptionally productive in familiarizing utilitarian moieties that subsidize with superior nanotube dispersing. Aside from enhancing the substance proclivity of

CNTs to polymer networks, the different change techniques moreover aid compelling handling to shape CNT/polymer parts with improved machine-driven and power-driven properties [2].

The comparison statement of outcomes got from an awesome quantity of non-strengthened and CNT fortified polymers. The outcomes are for sure very uncovering; much of the time, an upgrade of the electrical conductivity by a few requests of size is gotten by the expansion of CNTs. In spite of the fact that an extremely expansive scope of both thermosetting and thermoplastic lattices have been utilized and orderly patterns are hard to perceive, clearly in a manner of speaking little measures of CNTs are prerequisite to achieve for the most part high estimations of electrical conductivity. Clearly, result unaided can guarantee the imminent business common sense of CNT constituents, given clearly that down to earth dispersing methodologies are used. Finally, the substitution of carbon dim, the most routinely mechanically used CNTs for the course of action of power driving polymer composites is depended upon to significantly influence an extensive variety of mechanical applications.

Properties of MWNTs

MWNTs have fantastic properties and are being utilized in a substantial number of business applications [3]. The properties of MWNTs are:

- (i) Electrical: MWNTs are extremely conductive when properly joined into a composite structure.
- (ii) Morphology: MWNTs have a great viewpoint extent with extents regularly in excess of 100 times the estimation, and in particular, cases essentially developed. Their completing and solicitation is develop regarding perspective extent, and additionally on the level of ensnarement and the straightness of the tubes, which in this manner is a component of the equally the grade and estimation of defects in the conduits.
- (iii) Physical: Defect-free, individual, MWNTs have a splendid flexibility and when consolidated into a composite, for instance, a thermoplastic or thermoset blends, can on a very basic level grow its quality.
- (iv) Thermal: MWNTs have a warm steadfastness in excess of 600 °C, in perspective of the level of deformations and to certain degree on the perfection as extra impulse in the thing can in like manner catalyze crumbling.
- (v) Chemical: MWNTs are an allotrope of sp² hybridized carbon and as needs be consume great creation steadfastness. Regardless, one can functionalize the nanotubes to overhaul equally the eminence and dispersibility of complexes.

Difficulties in Commercialization of MWNTs

The difficulties in commercialization of MWNTs include the following:

- (i) Purity: Many MWNTs forms cause extensive remaining metallic impetus which can be inconvenient to execution.
- (ii) Scattering: These have better dispersability into arrangements or polymers than SWNTs, however the nature of the scattering got is a basic factor in the execution of the last item.
- (iii) Defects: The quantity of deformities is subject to the quantity of layers inside MWNTs. The high perspective proportion of MWNTs contributes a great part of the estimation of their utilization.

Quality Assurance Parameters

Observational systems, for example, SEM, TEM and AFM are utilized for portraying MWNTs and can be utilized to get information, for example, length, distance across and number of dividers. Moreover, thermo gravimetric analysis (TGA) is utilized to gauge the remaining mass, the temperature at the onset of oxidation and the temperature of the greatest oxidation rate. The state of the subsidiary bend gives subjective data regard to the consistency of the example with reference to polydispersity of the material. A high, limit top demonstrates a restricted circulation of measurements and insignificant tube absconds [4].

Synthesis of Carbon Nanotubes

Conversely, with polymers, which are commonly incorporated in the fluid stage, carbon nanotubes are created through an assortment of amalgamation strategies that ordinarily include the response of a vaporous carbon feedstock to frame the nanotubes on impetus particles. Different synthetic vapour admission frames have been made to create SWNTs and MWNTs, all including the reaction of a vaporous carbon composite as feedstuff. A champion among the best, pitiful, and adaptable CVD methodology is the considerable weight CO handle, cannot use pre-formed stimulus particles not in the least like most other CVD frameworks. Substrate development and synergist gas stream CVD containers have demonstrated the capacity to create amazingly long CNTs from various carbon gas sources; notwithstanding, a significant number of these methods create MWNTs with changing grades of controller concluded the quantity of dividers or the imperfection thickness. Reactant gas stream methods indicate additional guarantee for modern versatility than substrate development techniques because of the higher CNT yield [5].

The diverse SWNT association procedures regularly produce masses of SWNTs with polydisperse estimation, extent, chirality, and flaw thickness, considerable approximating the polydisperse sub-nuclear loads and extended erections conveyed in conventional polymer association. The primary difficulties in SWNT blend is the capacity to regulate the circulation of polydisperse SWNT properties. The supervisor changes in such way are found in the CoMoCat strategy, which devours nearly command over SWNT separate over, and substrate CVD-advancement techniques, which make nanotube assortments of largely constant extent.

SWNTs and Sub-Atomic Composites

The inescapable use of buildings is because of the gained ground mechanical properties that come to fruition in view of filling a host material with some reinforcing particle or fibre. These elements or strands are visible glass strands, carbon filaments, or even carbon dark. Also, if the fortifying part is electrical conductive and outlines a saturating framework inside the matrix, the conductivity of the compound especially increases. Molecular composites will be composites where singular particles, for example, polymer chains are utilized as fortification as opposed to plainly visible filaments. Regularly, the filler particle is an inflexible pole polymer [6].

Sub-atomic scale fillers of great perspective proportion have a considerably developed amount thickness and superficial region thickness than customary grouts at a similar volume part. In addition, with sub-atomic scale fillers of high viewpoint proportion, a greater amount of the polymer grid is related with the filler and fewer load is related with the non-strengthened polymer network. Fundamental models for the scrambling of compound modulus with filler point of view extent, bulk segment, and course of action consolidate the administer of mixes.

i) SWNT Scattering in Polymer Lattices

The central strategies for creating SWNT/polymer compounds is arrangement mixing, where the SWNTs are scattered in a dissolvable and blended through the polymer complete fiery tumult; the complex is then shaped through hastening or throwing a flick and dissipating the dissolvable. This strategy experiences the greater part of the issues related with SWNT scattering talked about beforehand; the SWNTs must be isolated from each other, consistently scattered (commonly using ultra sonication, and balanced out inside the dissolvable to anticipate re-conglomeration.

Various solvents comprising toluene and chloroform have been utilized for nanotubes, with restricted scattering prompted by ultra-sonication. The utilization of surfactants in watery arrangements portrayed above is the most widely recognized method used to scatter SWNTs as people and little packages. Nevertheless, the utilization of surfactant SWNT scatterings in complexes is dangerous in light of the fact that the surfactant will then stay in the compound and influence the transportation possessions [7].

SWNTs enables that scattered in solvents that are extra traditional and might enhance convergence goods in the polymer network; in any case, this system may trade off the predominant electric stuffs of SWNTs. Functionalization methods may cut SWNTs as well as present imperfections while upsetting π conjugation and diminishing electric stuffs. SWNTs functionalized by means of natural diazonium science could permeate at considerable inferior stacking standards in polystyrene compounds than immaculate SWNTs.

Various mechanical systems ordinarily used to deliver regular composites have additionally been utilized to commandingly blend nanotubes into a polymer dissolve. Dissolve mixing uses extraordinary heats and solid trim strengths to blend SWNTs into a polymer framework. This strategy is a great part of the time used as a piece of present day circumstances for the plan of near buildings when the congregation polymer is indecipherable [8].

Nevertheless, this strategy is restricted to low centralizations of SWNTs because of preparing troubles because of consistency increments and conceivable polymer corruption; these thickness increments are considerably advanced than those watched for customary complexes or carbon dark based composites. A great part of the exploration on these points is constrained to a straightforward approach of: (1) Use a trial technique, and (2) evaluate the method by essentially measuring last item properties (i.e., consistency, conductivity). This approach needs any displaying or representation of sub-atomic stage conduct, energy, accumulation, or system arrangement.

ii) SWNT–polymer framework interfaces

The major trouble is the utilization of nanotubes is that they devour great angle proportion sub-atomic measurements and a vast particular surface region, with the end goal that it is hard to set up great interaction with powerful freight exchange among the polymeric grid and this exterior region.

The objective is to limit the measure of unconfirmed network; a superior parameter is "filler surface zone each component volume of composite". This objective is better achieved by a great filler amount thickness with extraordinary viewpoint proportion and surface zone (as because of SWNTs). This preferred standpoint of SWNTs over MWNTs identifies with the root inspiration for nanocomposites: break even with property upgrade at bring down volume division because of increments in filler surface region per volume. SWNT packages or totals cannot manage stack the way that people do.

Different systems have existed concentrated to beat these issues. Covalent functionalization of SWNTs with the system can be utilized to accomplish convincing weight trade; this method has even been utilized to functionalize the outside surface of carbon fibres (called "assessing" the fiber) in polymeric composites for a comparable reason. SWNT sidewall functionalization can proceed in two different ways.

- (i) Straightforward functionalization intended to build disband in useful diluents by adding useful gatherings to the SWNT side divider (as portrayed previously).
- (ii) System of really making covalent bonds among the polymer grid and the nanotube sidewalls.

Covalent functionalization of nanotubes with polymers as "joining from" SWNTs, i.e., functionalizing originators as an afterthought divider took after by polymerization of monomers to shape polymers covalently bound to the SWNT. i.e., pre-shaped polymer atoms responding through useful end gatherings to associate with SWNTs. The main trouble with the "uniting to" method is polymer versatility while the boss trouble with the "uniting from" approach includes response control. All things being equal, these systems have ended up being very compelling in enhancing scattering and interfacial anxiety exchange amongst nanotubes and the polymer framework [9].

A comparable strategy for enhancing scattering and convergence quality is the development of piece co polymers with nanotubes, as appeared by PBO–SWNT co polymers what's more, UV-started polyacrylamide-nanotube (PAM–CNT) co-polymer thin films. The possessions of these flicks demonstrate that the nanotubes extraordinarily enhance stack bearing.

The quality of the gore can be measured by the gore trim quality, which is the amount of the basic gore shear worry at which matrix nanotube association comes up short. In non-covalently fortified convergences, the attachment among the SWNT furthermore, lattice predominantly originates from electrostatic associations, van der Waals collaborations, and distortion because of contrasts in coefficient of warm extension. The belongings of the polymer close to the convergence vary from the mass, especially in demonstrating a high shear quality.

Gore contact amongst filler and network is risky for unbending bar polymer too since they are regularly immiscible in different polymers and tend to stage distinct as portrayed previously; the convergence among the filler and network is regularly set apart by a frail biphasic locale. In any case, the nearness of alluring hydrogen field between the filler spine and the network changes the free vitality of blending and prompts phenomenal scattering and interfacial contact. Various components affect the level of hydrogen holding, counting steric availability, dispersing of hydrogen holding functional gatherings and the capacity of the inflexible bar polymer to hydrogen bond with its neighbours. [10].

7. MWNTs and Composite Materials

The advancement of strategies for the standard amalgamation of carbon nanotubes has created extraordinary enthusiasm for misusing their astounding physical properties. The conductivity, quality, flexibility, strength, and sturdiness of shaped compounds may all be considerably enhanced by the expansion of nanotubes. Moreover, great interfacial holding is required to accomplish stack exchange over the CNT-grid interface, an essential condition for enhancing the power-driven possessions of the compound. The high perspective proportion of some carbon nanotubes may likewise empower them to be lined up with one hub of the composite. In different applications, their high centre electrical conductivity offers the potential for making coordinating polymers. To be financially perceptive in such mass applications, their anticipated execution must be acknowledged at low focuses [11].

i) Polymer/MWNTS Composite fibres

The tractable properties of strands created from the polymer/ MWNTS composites take after comparative patterns. For instance, polypropylene/MWNTS composite strands show a critical increment in versatile modulus with expanding MWNTS focus, however no change in elasticity. At low MWNTS focuses, the elasticity, largely controlled by the diffusion of imperfections, decreases, due to an expansion in the recurrence conveyance of deformities related with the nanotubes closes. In spite of the fact that the nanotubes have a high viewpoint proportion of ~1000, they are moderately short, ~20 μm , and henceforth on a full scale do not go about as persistent fortifying stages run of the mill in great enactment fibre-fortified composites. In addition, if the interfacial grip is poor, it brings about untimely composite disappointment since the fortifying nanotubes just haul out of the lattice without adding to the quality or, then again firmness of the material.

At advanced focuses, there are additional communications amongst the MWNTs, and break spread is hindered, bringing about expanded elastic quality watched for the compound flicks. This is further enhanced when surrenders in the nanotubes erection are evacuated by strengthening at high temperatures. Nevertheless, there are some huge contrasts in the physical properties of the strands in contrast with the composite films. The technique for creation of the flicks does not advance huge introduction of the MWNTs in a favoured course, the conveyance being irregular. Significant picks up in the mechanical properties of the two films and filaments might be normal after making upgrades to the interfacial holding between the MWNTs and the polymer framework [12].

The exterior conductivity of the compound flicks happens at low MWNTS fixations, while the filaments hold their protecting properties up to moderately high MWNTS fixations (~10 vol %). The MWNTs inside the strands are all around scattered and lined up with the fibre pivot. Henceforth, at low focuses there is less likelihood of the MWNTs framing a nonstop leading way along the span of the complex fibre.

ii) Alteration of MWNTs with polymers

The modification of CNTs by polymers may be segregated into two classes, including either non-covalent or covalent holding amongst CNT and polymer. Non-covalent CNT change concerns the physical adsorption and furthermore wrapping of polymers to the surface of the CNTs. There are two fundamental systems for the covalent chemical bonding (grafting) of CNTs relying upon working of polymer chains. The "uniting to" approach includes a blend of a polymer with a particular sub-atomic weightiness ended with responsive gatherings or fundamental antecedent. In a resulting response, the polymer bind is appended to the surface of nanotubes by expansion responses. A detriment of this strategy is that the united polymer gratified is restricted because of the moderately stumpy reactivity and great steric prevention of macromolecules [13].

iii) Application of MWNTs

There are a substantial number of present and developing applications for MWNTs. These include:

- (i) Enhanced Structural Composites: MWNTs as non-woven or woven textures or tar mixed buckypaper when immersed with thermoset tars have demonstrated significant increment in firmness and quality of composite structures, for example, auxiliary covers and golf club shafts for aviation application.
- (ii) Water filtration layers: High viewpoint proportion, high mechanical quality and vast particular surface empower extremely productive filtration media.
- (iii) Electrically Conductive Polymers: MWNTs are reasonable for these applications particularly because of its high conductivity and high perspective proportion. The required conductivity level can be accomplished with significantly lesser loadings than for regular arrangements, for example, metal particulates or carbon dark. Applications incorporate electrostatic release security in wafer preparing manufacture, antistatic elastomeric and plastic segments for vehicle fuel line segments, plastics rendered conductive to empower electrostatic splash painting of car body parts, RFI protecting materials, and the sky is the limit from there [14].

Diffusion of CNTs

MWNTs have been scattered into arrangements of chose lattices utilizing a great vitality ultrasonic test. The low consistency of the arrangement permits the CNTs to move uninhibitedly through the framework. This was done in two phases, at first utilizing a high-control ultrasonic test to scatter the MWNTs in toluene. Therefore, the diffused suspension was blended with a weaken arrangement of polystyrene (PS) in toluene utilizing an ultrasonic shower. This two-stage approach was utilized to limit the danger of tube burst amid handling and maintain a strategic distance from disturbance of the polymer structure by the intense ultrasonic test. The blend was thrown on glass and the dissolvable evacuated to yield MWNTS-doped film. The sonication approach is constrained to grids that unreservedly break up in like manner solvents. It is in this way not especially alluring for mechanical scale forms. A more reasonable strategy for creating MWNTS/polymer composites includes shear blending taken after by expulsion or, then again infusion trim to create antiques in the required shape.

At any given temperature, diffusion proficiency is identified with mechanical vitality contribution to the blend. Expanding the living arrangement time and additionally the rotor speed can increment the vitality input and thus enhance the scattering. Comparative bends are created when the temperature of the soften is transformed or when a polymer with various liquefying qualities is utilized. Advanced vitality effort was essential with expanding MWNTS fixation because of an expansion in liquefy consistency.

- (i) Surface Resistivity. The minimal effort polymers utilized as a part of the large-scale manufacturing of electronic parts and gadgets are covers, on which charge can collect with conceivable harm because of electrostatic release. Conductive grout expansion is normally used to incite conductivity for electrostatic control. When blended into liquid polymer, filler particles frame

into chains or systems, giving directing pathways. Carbon dark is the most generally utilized filler material, in spite of the fact that carbon filaments, metallic powders, and glass strands covered with metals have likewise been used. These fillers likewise diminish from the capacity to reuse scrap materials, expanding squander transfer costs. Therefore, the carbon dark substance must be limited (to the permeation edge) to hold these alluring properties and decrease costs.

The expansion of a little convergence of MWNTs to a polymer framework can have a noteworthy effect upon its electrical possessions. At focuses as low as 0.05 vol %, the exterior resistivity of flicks created utilizing PP as the lattice tumbled from its virgin polymer estimation of $>10^{12} \Omega/\text{square}$ to an estimation of $\sim 10^5 \Omega/\text{square}$, which demonstrates that the MWNT-PP film has a permeation limit as low as 0.05 vol %. With polystyrene or its high-affect variation (HIPS) as the framework, comparative outcomes were discovered when low fixations of MWNTs were presented. Be that as it may, for the ABS network, the expansion of up to 0.5 vol % MWNTS had little impact upon surface resistivity, maybe a sign of isolation of the MWNTs into a specific stage yet lacking congruity through the network. At higher MWNTS focuses, the exterior resistive of the MWNTS-PS what's more, MWNTS-PP films tumbles to $<100 \Omega/\text{square}$, moving toward the incentive for unadulterated carbon dark or metals.

(ii) Great shear blending to scatter MWNTs may bring about tube cracking. For polystyrene with 0.5 vol % MWNTs, nanotube distance diffusions at general interims amid blending have been measured.

(iii) Ductile Assets: The diffusion of low fixations of MWNTs into the chose polymers delivered a momentous decrease in superficial electrical resistivity, their impact on the malleable possessions was moderately little. Around, for the most part a little increment in flexible modulus and an abatement in rigidity. This diminishment in elasticity can be credited to an increment in the recurrence conveyance of deformities related with the nanotubes that start disappointment. Deprived convergence holding among the nanotubes and the network will likewise affect the power-driven possessions of the flicks. This permits fibre haul out and subsequent disappointment of the film. A conceivable cure is to change the superficial attractiveness of the carbon nanotubes. Various exterior handling strategies, including functionalization methods, are measured for this reason. At higher MWNTS fixations, the adjustments in the power-driven possessions of the flicks are more articulated. For polystyrene/MWNTs composites comprising from 2.5 to 25 vol % MWNTs, At the bring down fixations, the elasticity diminishes from the flawless polymer estimation of 40 MPa, as it were surpassing it when the MWNTS content is over 15 vol %. At the point when the basic flaws and polluting influences show in the as-arranged MWNTs are evacuated by warming to graphitization temperatures, the polystyrene/ MWNTS composites produced using them demonstrate moved forward execution. Atomic system estimation demonstrates that the descending contacts among nanotube polymer boundaries are considerably higher than that among neighbour films of a MWNTS, and these abrasion strengths assume just a trivial part in deciding the boundary quality. The van der Waals strengths, emerging mostly from the hydrogen union associations among the π -obligations of MWNTS exterior and the hydroxyl adjacent gatherings of the polymer lattice, are controlled by the polymer atomic erection, particularly its capacity to shape requested spirals nearby singular nanotubes [15].

i) Polymer composite handling

To expand the upside of CNTs as successful fortification for great quality polymer composites, the CNTs ought not to frame totals, and should be very much scattered to improve the interfacial cooperation with the lattice. A few handling techniques accessible for manufacturing CNT/polymer composites in light of either thermoplastic or thermosetting frameworks. An advanced convergence cooperation between the CNT side-dividers and the network bring about a proficient load exchange to the "hard" segment of the composite.

ii) CNT-based films and strands

For some applications, stringy materials are more appropriate than mass materials. Likewise, fibre generation strategies have a tendency to be well matched for the arrangement of nanotubes

inside the polymer lattice. In an option approach, CNT arrangements have turned into filaments utilizing a dry-stream wet turning system. Another strategy utilized as of late to frame composite-based strands from arrangement is electro spinning. This strategy includes electrostatically lashing a fly of polymer arrangement out of a spout onto a metal counter-terminal.

iii) Power-driven possessions of CNT complexes

The one-dimensional erection of CNTs, their stumpy thickness, their high viewpoint proportion, and exceptional power-driven possessions make them especially alluring as fortifications in composite materials. The variety of numerous parameters, for example, CNT sort, development strategy, concoction pre-treatment and also polymer sort and handling technique has given some reassuring outcomes in creating moderately solid CNT–polymer composites.

iv) Electrical properties of carbon nanotube/polymer composites

Nanotube compounds display permeation conduct, in which the nearness of consistent nanotube organize grades to an emotional increment of their electrical conductivity. Physical constraints of compound ingredients, for example, the electrical conductivity, the permeation limit (t) and the basic type have been seriously concentrated to accomplish CNT conductive complexes at stumpy grout focuses.

Doping CNT Composites Through the Polymer Part

CNTs in composites might be charge-exchange doped specifically by the encompassing polymer material, which brings about a change in electrical conductivity and a move of the Fermi level and a relating change of the coefficient. The doping is emphatically reliant on the cooperation amongst polymer and CNTs and in that; capacity is affected by their relative focus, and by the handling conditions.

Future Research Needs

Innumerable other functionalization procedures have been endeavoured for inflexible pole polymers in sub-atomic complexes, which have not yet been connected to CNTs; such procedures may turn out to be helpful in forthcoming investigation endeavours. The distinguishing proof of MWNTs as polymers is precise, useful, also, essential for explore advance for MWNT applications, especially those that exploit MWNTs' unbending nature and great mechanical properties. Various trial ponders have been distributed as of late where nanotubes are essentially thought to be an obscure, one of a kind, innovative factual. In a number of these investigations, nanotubes are essentially blended or scattered utilizing a few set up polymer handling system with no investigation, hypothesis, model, or portrayal of the significant collaborations of singular nanotubes, predominantly because these examinations do not have the applied structure for asking such questions. Considering nanotubes as polymers opens the request up to a broad assortment of prior examination and models that location these issues.

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Edited by
K.R.V. Subramanian, Tubati Nageswara Rao and
Avinash Balakrishnan



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Preface

Nanofluids are dilute liquid suspensions of nanoparticles with at least one of their principal dimensions smaller than 100 nm. Nanofluids are a new class of nanomaterials that offer significant advantages of superior thermophysical properties such as thermal conductivity, viscosity, stability, and specific heat with higher values of base numbers (Nusselt, Prandtl, Darcy, etc.) when compared to base fluids. Owing to their enhanced properties as thermal transfer fluids for instance, nanofluids can be used in a plethora of engineering applications ranging from use in the automotive industry to the medical arena to use in power plant cooling systems as well as computers.

Phase change materials as nanoparticles have been used in nanofluids to simultaneously enhance the effective thermal conductivity and specific heat of the fluids. Nanofluids have been demonstrated to be able to handle their role in some instances as a smart fluid. In the sub-area of power conversion technology, improving heat-transfer performance for lower-temperature nanofluids, and developing plant designs for higher resource temperatures to the supercritical water region would lead to an order of magnitude (or more) gain in both reservoir performance and heat-to power conversion efficiency. Engine oils, automatic transmission fluids, coolants, lubricants, and other synthetic high-temperature heat transfer fluids found in conventional truck thermal systems—radiators, engines, heating, ventilation, and air-conditioning (HVAC)—have inherently poor heat transfer properties. These could benefit from the high thermal conductivity offered by nanofluids. A principal limitation on developing smaller microchips is the rapid heat dissipation. However, nanofluids can be used for liquid cooling of computer processors due to their high thermal conductivity. There is a new initiative which takes advantage of several properties of certain nanofluids to use in cancer imaging and drug delivery. This initiative involves the use of iron-based nanoparticles as delivery vehicles for drugs or radiation in cancer patients. Magnetic nanofluids are to be used to guide the particles up the bloodstream to a tumor with magnets.

Looking at the possible uses of nanofluids, a variety of different possibilities open: transportation (engine cooling/vehicle thermal management), electronics cooling, defense and space, nuclear systems cooling, heat exchangers, biomedicine and other biomedical applications, heat pipes, oil recovery, fuel cell, concentrated solar technology, solar water heating, chillers, domestic refrigerator, diesel combustion, drilling, lubrications, thermal storage, and many others.

This book deals with some of the technologically most important engineering applications of nanofluids as well as cutting edge research areas. It also attempts to deal with some practical engineering challenges facing nanofluids. One of the most crucial issues related to nanofluids is the stability of the nanoparticles suspension. The agglomeration of nanoparticles results in the settlement and clogging of microchannels and also the decreasing of thermal conductivity of nanofluids. The nanofluids research has seen a large amount of experimental works, it is still in initial phase and there are several open issues, like the lack of agreement regarding the results obtained by different researchers, and the lack of theoretical understanding of the mechanisms responsible for changes in the properties. In fact, there are many important variables and issues related to the production and the usage of nanofluids, which may cause significant discrepancy in the acquired experimental data. The type of nanoparticle, its size, its shape, and distribution are important properties that cannot be easily measured nor well-defined or properly reported in the publications. The type of base fluids used, the method for the nanofluid production, use of surfactants and stabilization additives, including pH adjusters, etc. are other important factors.

We, the editors, Subramanian, Rao, and Avinash have drawn upon our own research thrusts, work, and proposals in nanofluid technology and strived to bring the application areas to the forefront with the challenges. We would like to express our sincere thanks to our management, viz.,

Gandhi Institute of Technology and Management (GITAM) School of Technology, Bangalore, India (Prof. P.V. Sivapullaiah, Pro Vice Chancellor, Prof. Vijaya Bhaskar Raju, Director) as well as Suzlon Energy Ltd., Gujarat, India, for supporting this endeavor. Our thanks are also due to the distinguished authors who have contributed their might. We finally thank our family members for their support.

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DFT Study on Interaction of Estrone and Imidazolium-Based Hydrophobic Ionic Liquids

*Sai Saravanan Ambi Venkataramanan and
Ramalingam Anantharaj*

Abstract

Affinity of estrone on imidazolium-based hydrophobic ionic liquids was computed at the B3LYP/6-31G(d) level. Columbian interactions and other closed-shell interactions, in general, were observed to be pivotal to the binding of the EDC species on visualizing the optimized structures as well as probing the proximity of electronegative and electropositive groups between estrone and ionic liquids. The interaction strength was also studied using calculation of binding energy values of each system. [BMIM]⁺[PF6][−] was found to be the most binding ionic liquid. Estrone was found to be highly bonded in the vicinity of [PF6][−] species with a binding energy of −9.57 kcal/mol. The Ionic Liquids under study, [BMIM]⁺[NTF2][−] and [BMIM]⁺[BF4][−], also illustrated promising binding nature with binding energies of −7.63 and −8.61 kcal/mol. AIM analysis was carried out to validate the nature of intermolecular interactions by calculating the topological properties at (3,−1) bond critical points.

Keywords: DFT, endocrine disrupting compounds, computational quantum chemistry, molecular interaction

1. Introduction

Chemical substances that inhibit the reception sites in endocrine systems in our body are collectively termed as endocrine-disrupting compounds (EDCs). These carcinogens are proliferating in large quantities in all forms of water media, ranging from domestic water to ocean streams [1]. Although these contaminations are extremely minimal in quantity, such as in the order of ppm, these prove to be a significant competitive inhibitor and obstruct the transmission of endocrine hormones to certain parts of our bodies leading to a diverse array of problems, including development of cancerous tissues and abnormal change in sexual orientation of a person altogether. Recent research works in the domain of wastewater treatment have shed some light on this issue stating that most wastewater discharge plants and sewage treatment plants currently being operated in the industry are also affected by exposure to EDCs [2].

Ionic liquids have been reported as novel green solvents in various domains ranging from catalysis [3] to extraction [4], owing to its ease in screening of these solvents by subtle manipulation of thermodynamic variables. A review publication by Tomasi



International Conference on Intelligent Systems Design and Applications

ISDA 2018 2018: **Intelligent Systems Design and Applications** pp 627–639

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Part of the [Advances in Intelligent Systems and Computing](#) book series (AISC,volume 941)

Abstract

Narrowing of blood vessel due to plaque deposition is known as stenosis that acts as prime indicator of the coronary artery diseases (CAD). Coronary cine angiography (CCA) is a digital imaging modality used for the assessment of severity of coronary bifurcation lesions in the coronary arteries. Angiography based stenosis diagnosis is done as subjective analysis by the clinicians that results in overestimations or underestimations of detected stenosis. In stenosis, mostly the plaque deposition occurs at the left main coronary artery (LMCA) branch. Bifurcation angle at site of LMCA act as significant indicators of presences of stenosis. The proposed work involves segmentation of LMCA using various segmentation techniques such as Morphological based segmentation, Hessian detection and Active contour segmentation. Active contour segmentation provides clear visualization of LMCA structure when compare to all other segmentation methods. Then, computation of automatic bifurcation angle measurement at bifurcating regions of LMCA such as left anterior descending (LAD) and left circumflex (LCx) in both normal and stenotic images of CCA is performed. The diagnostic performance of stenosis yields a detection accuracy of 92%. The outcome of proposed work is found to be quantitative tool for the clinicians in accurate analysis of prediction of stenosis and also helpful during stent replacement surgical procedure in percutaneous coronary interventions.

Keywords

[Left main coronary artery](#) [Coronary Cine Angiogram](#)



International Conference on Intelligent Data Communication Technologies and Internet of Things

ICICI 2018: **International Conference on Intelligent Data Communication Technologies and Internet of Things (ICICI) 2018** pp 741–750

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Abstract

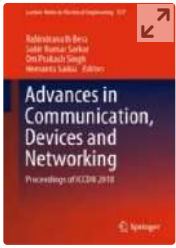
Cell image segmentation becomes important and yet difficult task in quantitative cytopathology. The main objective is to develop an algorithm to segment and calculate the amount of neutrophils using morphological operators. The current work focuses on extraction of neutrophils from the peripheral blood smear was taken and it’s stained using Leishman stain to obtain differential leukocyte count. The particle analysis is done by extorting the edges to isolate the appropriate elements from the surrounding image after suitable thresholding technique. The preliminary results in this study reveals the potentials of using particle analysis method in cell image segmentation for automation and further used for classifying.

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Part of the [Lecture Notes in Electrical Engineering](#) book series (LNEE,volume 537)

Abstract

Autonomous navigation is of utmost importance for people suffering from visual impairment problems in their daily life. At present, a device known as Electronic Travelling Aids (ETA) is used by the visually impaired to detect static objects. As it is to be held by hand, it limits them from performing some of their activities. The objective of this project is to provide a hands-free module which focusses on dynamic objects (car) in an outdoor environment. This is achieved by using Raspberry Pi module, camera and ultrasonic sensor. The vehicle is captured by the camera in real time and detected using image processing techniques and Haar Cascade classifier. The ultrasonic module scans for the obstacle in three different directions, and then intimates the user to move away from the obstacle using an audio output, which is provided through headphones. The above-mentioned modules are incorporated into a waist belt. This prototype would be a better choice than the existing modules as it is long-lasting, hands-free, detects dynamic objects and helps the user in dauntless navigation in the outdoor environment.

Keywords

[Visual impairment](#)

[Raspberry pi](#)

[Haar cascade classifier](#)

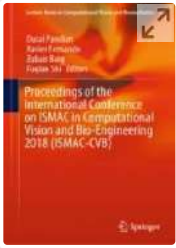
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ISMAC 2018: **Proceedings of the International Conference on ISMAC in Computational Vision and Bio-Engineering 2018 (ISMAC-CVB)** pp 1825–1834

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Conference paper | [First Online: 02 January 2019](#)

1702 Accesses | **1** Citations

Part of the [Lecture Notes in Computational Vision and Biomechanics](#) book series (LNCVB,volume 30)

Abstract

Sleep apnea is a breathing disorder which occurs during sleep. Sleep apnea causes more health-threatening problems such as daytime sleepiness, fatigue and cognitive problems, coronary arterial disease, arrhythmias, and stroke. However, there is an extremely low public consciousness about this disease. The most common type of sleep apnea is *obstructive sleep apnea* (OSA). Polysomnography (PSG) is the widely used technique to detect OSA. *Obstructive sleep apnea* is extremely undiagnosed due to the inconvenient and costly polysomnography (PSG) testing procedure at hospitals. Moreover, a human expert has to monitor the patient overnight. Hence, there is a requirement of new method to diagnose sleep apnea with efficient algorithms using noninvasive peripheral signal. This work is basically aimed at detection of sleep apnea using a physiological signal electrocardiogram (ECG) alone which is taken from free online apnea ECG database provided by PhysioNet/PhysioBank. This database consists of 70 ECG recordings. A detailed time- and frequency-domain features and nonlinear features extracted from the RR interval of the ECG signals for observing minutes of sleep apnea are occurred in this work. Time-domain features mean HR ($P = 0.0093$, $r = 0.3593$) and RR interval mean (ms) ($p = 0.0003$, $r = 0.376$), frequency-domain features VLF power (%) ($P = 0.00659$, $r = 0.1081$) and HF power (%) ($P = 0.00135$, $r = 0.41138$), and nonlinear analysis feature SD1 ($P =$



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Chapter 6 - A Medical Image Retrieval System in PACS Environment for Clinical Decision Making

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Vijay Jeyakumar¹, Bommannaraja Kanagaraj²

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Abstract

Image retrieval plays a major role in an integrated healthcare environment for various purposes, such as computer-aided diagnosis, medical education, Tele-surgeries, evidence-based medicine, and many more. In the retrieval system, two kinds of approaches are mainly followed: Text-Based Image Retrieval (TBIR) and Content-Based Image Retrieval (CBIR). The former approach requires lot of human effort and time, also subject to human perception. The latter approach pays greater attention to global and local information, such as the color, shape, region, and texture of an image. The major drawback of CBIR is its inability to distinguish the characteristics of heterogeneous medical images. Considering the limitations of both approaches, an integrated framework is proposed, based on the distinct characteristics of TBIR and CBIR. In both approaches, the related feature descriptors of images and terms of documents are extracted. In order to reduce the irrelevant features in CBIR, a modified ant colony optimization with a relevance feedback mechanism is incorporated. In this proposed framework, the performance of CBIR, TBIR, and their fusion (combination of TBIR and CBIR) is analyzed and the precision of each approach is 78.8%, 85.9%, and 94.8%, respectively.

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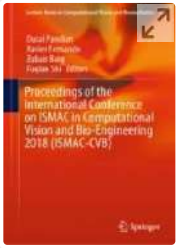
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A Study on Comparative Analysis of Automated and Semiautomated Segmentation Techniques on Knee Osteoarthritis X-Ray Radiographs

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Part of the [Lecture Notes in Computational Vision and Biomechanics](#) book series (LNCVB,volume 30)

Abstract

Arthritis is a most common disease in the worldwide population targeting knee, neck, hand, hip, and almost all the joints of the human body. It is a frequently noticed problem in elder people, especially women. The severity of the disease is analyzed using the older KL grading system. Traditionally, the detection of various grades of OA (osteoarthritis) is interpreted by just a visual examination. A traditional modality, X-ray images are considered as the data for the project. The images are segmented using different segmentation techniques to extract the articular cartilage as region of interest. From the literature, eight different segmentation techniques were identified out of which seven are automated and one is semiautomated. By implementing those techniques and evaluating their performance, it is inferred that block-based segmentation, center rectangle segmentation, and the semiautomated seed point selection segmentation performs well and provides sensitivity, positive prediction value and dice Sorenson’s coefficient of 100%, respectively, and specificity of 0%.

Keywords

[Arthritis](#)

[X-ray](#)

[Osteoarthritis](#)

[Tibio-femoral disk](#)

[Automated segmentation](#)

[Semiautomated segmentation](#)

Influence of Design Parameters on Composite and Noncomposite Space Truss Structure Analysed Using ANSYS



P. Sangeetha, R. Senthil and P. Naveen Kumar

Abstract A space frame is a skeleton structural system assembled using linear elements so arranged that forces are transferred in a three-dimensional manner. Architects and engineers aim for new structural forms to accommodate large unobstructed areas. Space frames satisfy the objectives, and it provides lightness, economy, and speedy construction. Previous research investigation in the composite space truss, proved that using concrete slab acting compositely with the top chord member is to reduce the buckling of the compression chord members and also improve the overall behaviour of the space truss structures. The advantages of the composite space truss, gives confidence to use as floor system in the multistorey buildings. The composite space truss is influenced by various design parameters like cross-sectional area of the tubular member, support condition, module size and their depth, concrete strength and concrete slab thickness. The analysis of composite and noncomposite space truss as roof as well as floor for the building of size $30\text{ m} \times 30\text{ m}$ was carried out using ANSYS software for varying design parameters. The overall maximum central deflection for the models was observed and compared with the codal provision. The load–deflection behaviour of the models was plotted, and the optimal solution for the noncomposite and composite space truss was arrived.

Keywords Composite space truss · Finite element analysis · Support condition Optimization

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K. S. Vijay Sekar et al. (eds.), *Advances in Manufacturing Processes*, Lecture Notes in Mechanical Engineering, https://doi.org/10.1007/978-981-13-1724-8_11

111

On Mechanical and Thermal Properties of Concretes with Rubber as Partial Replacement to Well-Graded Conventional Aggregates



Srinath Rajagopalan, P. Sreehari, B. Mahalingam
and K. Mohammed Haneefa

Abstract The disposal of used automobiles tyres is a major environmental concern of the day. Annually, there are 1.2 billion tyres seeking disposal issues globally. Concrete as a major construction material can potentially adopt processed rubber waste—derived from tyres as a partial replacement for aggregates. The present study is focused on mechanical and thermal properties of concretes with rubber as partial replacement to well-graded conventional aggregates. The study includes replacement of 10, 20, 30 and 100% of coarse aggregate with waste tyre aggregates and was compared with conventional M30 grade concrete. Concretes were subjected a thermal cyclic heating of 50 °C for a period of 7 days. The results showed that the weight of the rubber concrete is reduced by 12% compared to the conventional concrete and the strength of the concrete reduces with the increase in rubber content. At ambient temperatures, the rubber concrete was found thermally stable. The compressive strengths were found increasing after cyclic heating of 50 °C for a period of 7 days. This effect may be due the effect of Portland pozzolana cement which has 30% of fly ash in it. From this study, it can be concluded that rubber waste concretes can be a potential candidate for structural and non-load bearing structures at ambient temperatures.

Keywords Compressive strength · Concrete · Rubber tyre waste
Cyclic heating · Fly ash

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Advances in Materials and Metallurgy pp 365–373

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Mechanical Characterization and Robustness of Self-compacting Concrete with Quarry Dust Waste and Class-F Fly Ash as Fillers

[B. Mahalingam](#) , [P. Sreehari](#), [Srinath Rajagopalan](#), [S. Ramana Gopal](#) & [K. Mohammed Haneefa](#)

Conference paper | [First Online: 02 September 2018](#)

941 Accesses | **2** Citations

Part of the [Lecture Notes in Mechanical Engineering](#) book series (LNME)

Abstract

Self-Compacting Concrete (SCC) is a special type of concrete which does not require any form of external forces to get compacted. However, it behaves similar or better to conventionally vibrated concrete when it gets hardened. The present study focuses on developing SCC with a constant powder content of 600 kg/m³ with 450 kg/m³ of cement.

Design of Piles for a Berthing Structure on Artificial Slope



S. V. Sivapriya, R. Sundaravadivelu and S. R. Gandhi

Abstract In present study, a new berthing structure is proposed for slope stable dredging activity. A slope with a weak soil structure comprising gravel, sand–silt clay, stiff silty clay, and terra firma at various depths is stabilized with ground improvement techniques. The pile makes dredging difficult for a single-slope angle. To overcome this difficulty, different slopes are recommended for different depths. This study analyses the slope stability for such a design by finite element modeling. Modeling shows that the factor of safety is > 1.5 for the varied slope structure, thus proving that the design is effective in preserving the slope stable.

Keywords Slope stability · Static · Dredging

1 Introduction

Dredging activities may result in slope instability caused by factors such as saturation, swell, coupled with seepage, and pore pressure. For example, dredging of slopes comprising cohesive soil leads to negative pore pressure, which increases the short-term safety of the slope. The most important factor that influences slope stability is the slope angle; it is particularly sensitive when the slope angle is 15° . Soil type and vegetation are other factors that affect slope stability [1], and it is important to understand the stability of slopes during dredging activities and erection of piles.

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Cozero Divisor Graph of a Commutative Rough Semiring

[B. Praba](#), [A. Manimaran](#) , [V. M. Chandrasekaran](#) & [B. Davvaz](#)

Conference paper | [First Online: 24 January 2019](#)

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Abstract

In this paper, we define the ideal generated by an element in the commutative rough semiring (T, Δ, ∇) . The characterization of this ideal along with its properties are also studied. The cozero divisor graph of a commutative rough semiring is defined using

Bounds of Spreading Rate of Virus for a Network Through an Intuitionistic Fuzzy Graph

Ganesan Deepa, Bashyam Praba, Vellankoil Marappan Chandrasekaran, Krishnan Rajakumar, Krishnamoorthy Venkatesan

Book Editor(s): Arun Kumar Sangaiah, S Shantharajah, Padma Theagarajan

First published: 05 July 2019

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Citations: 1

Summary

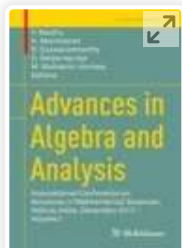
We consider an intuitionistic fuzzy graph. The energy of such an intuitionistic fuzzy graph is determined and the lower and the upper bounds with real and complex roots of the energy of an intuitionistic fuzzy graph are derived. There are no exact methods to analyze the virus spread in the user flow of the website. Hence we made an attempt to find the virus spread in a network in terms of the energy of an intuitionistic fuzzy graph. These concepts are explained and illustrated by taking the website network of the web navigation of <http://www.pantechsolutions.net/>.

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Bounds of Extreme Energy of an Intuitionistic Fuzzy Directed Graph

[B. Praba](#), [G. Deepa](#) , [V. M. Chandrasekaran](#),
[Krishnamoorthy Venkatesan](#) & [K. Rajakumar](#)

Conference paper | [First Online: 24 January 2019](#)

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Abstract

We are considering the website network <http://www.pantechsolutions.net/> of the web navigation of the customers. This website network can be representing as an intuitionistic fuzzy directed graph by means of considering the navigation of the customers. In this intuitionistic fuzzy directed graph,

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Optimization of Electric Field Distribution Along a 400-kV Composite Insulator

[C. Archana](#)  & [K. Usha](#)Conference paper | [First Online: 19 September 2020](#)

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Abstract

Polymeric insulators are being widely used over ceramic insulators due to their tremendous merits. However, due to absence of the intermediate metal part, electric field and potential distribution along these insulators are non-uniform, which can be minimized by using suitable corona ring and grading ring. The aim of this work is to provide an optimum design of corona ring and grading ring for a 400-kV suspension-type polymeric insulator. Finite element method-based software is used for simulation purposes. This paper presents the results of 3D

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Mathematical Modelling of Embedded Switched-Inductor Z-Source Inverter for Photovoltaic Energy Conversion



T. Divya and R. Ramaprabha

Abstract Z-source inverters provide single-stage power conversion for photovoltaic (PV) interface as it does the job of boosting and DC-AC conversion. The topology presented here is derived by fusing the switched-inductor cell (SL) in an embedded switched Z-source inverter which eliminates the problem of inverter leg short circuit (SC). Its output voltage varies over a wide range without any requirement of a time delay in turning on the power switches. This inverter generates high gain factor for the same structural elements in comparison with other topologies and is expected to give continuous input current, and hence, it is more suitable for PV and fuel cell interface. The mathematical model of ESI-ZSI along with PV array is presented in this chapter. The advantageousness of the ESI-ZSI inverter over few basic inverters will be presented by comparing the parameters of the similar existing topologies reported in the literature.

Keywords Z-source inverter · Modelling · PV module · Incremental conductance

1 Introduction

Energy conservation has been a central topic for many government schemes owing to the decrease in conventional energy resources with the rapid increase in energy demand. First preference is given to solar energy or in other words, photovoltaic (PV) energy, because of its abundance in nature, green, and inexhaustible [1, 2]. Existing PV panels have a lower and varying range of input voltage, and thus, the energy converted by photovoltaic panels, intended for any specific application, should be conditioned by a suitable inverter for further use. Also in many applications, the single-stage architecture is often preferred to realize PV interfaced applications due to its considerable reduction in power loss. Such conditions demand for a buck-boost type inverters, and one such inverter to convert and boost the PV voltage for required applications is presented in this paper with PV interfacing.

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Design and Implementation of Secured Cloud-Based Remote Home Access Through an Application for Smart Infrastructure



Annadanam Subbarathinam Shashank Karrthikeyaa,
Ramakrishnan Priyadarshini, Gunasekaran Revathi,
and Santhanam Sakthivel Murugan

Abstract Internet of things (IoT) is one of the most swiftly growing technologies predominantly and prevalently existing, creating a profound impact on the quality of living with each passing day. It encircles newer and better technologies such as smart cities, smart electric grids, remote smart homes. These technologies are emanating from the integration of the existing systems with the physical world that creates much better ones. Remote home access (RHA) is one of the emerging concepts of IoT enabled smart homes. Remote home access service is a system by means of which a user can remotely monitor the status of his devices and control them as well even from outside his/her home. This paper deals with the design and implementation of a system in which the requests of the users generated within the home or outside can intelligently be managed and controlled by cloud-based services. The functionalities of the system that is proposed here are classified into various service groups such as monitoring, controlling, security, authenticating, authorizing, managing, logging, and user groups. As a part of the RHA architecture, the connectivity between the cloud and the user application is encrypted using Secure Sockets Layer (SSL) certificates to prevent the infringement of user's privacy and the authentication is afforded based on Open Authorization 2.0 (OAuth 2.0) framework for better security.

Keywords Internet of things · Remote home access · Secure sockets layer · Open authorization 2.0

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Advances in Smart System Technologies pp 639–654

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A Survey on Crack Detection Algorithms for Concrete Structures

[M. J. Anitha](#) , [R. Hemalatha](#) & [S. Radha](#)

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Abstract

Crack detection is gaining much attention nowadays due to localization and identification of cracks in the civil structures accurately. The aim of crack detection on images is to automatically detect the cracks or defects considering the properties of civil structures. Among various civil structures, concrete structures are the most important one which is having both domestic and industrial applications. Detection of cracks in

concrete structures will be very important in present scenario. Some of the prevailing crack detection methods are manual inspection method, acoustic and vibration-based method, electrical and magnetic methods, visual and optical methods. This survey paper jointly summarizes the various methodologies and issues of automatic crack detection. Performance metrics like accuracy, sensitivity, and specificity are used to analyze the experimental evaluation of different papers effectively. Finally, various challenges and the future research directions of the crack detection techniques are discussed.

Keywords

Concrete surface inspection

Defect detection

Crack detection

Artificial neural network

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Image processing

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Study of Statistical Distribution and Morphology of Particles in a Polymer Matrix by Foldscope Imaging Technique

[P. Kaythry](#) , [A. Madhan](#) & [K. Rajkumar](#)

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Abstract

Design and material engineers are focusing on strengthening and toughening of the polymer matrix by introducing secondary particles. However, particle distribution is a control parameter to ensure the properties of polymer materials. Further, the agglomeration of the fine particle affects polymer composite performance.

The chosen process may affect the statistical distribution and aggregation of secondary particles in the polymer composite. There is a lack of simple and affordable technique to evaluate the particle distribution, morphology and degree of agglomeration of particles in the polymer matrix. In this paper, the origami crafted microscope called foldscope is used to find out the particle distribution in the polymer matrix. Initially, the fillers/particles are mixed in the epoxy matrix through an ultra-sonication technique. The experiments are conducted by varying the size of filler (30, 80 and 120 grit) with sonication parameters such as power rate (70, 80 and 100%) and processing time T_{on} (45, 90 and 135 s) with constant 3% filler in weight. With the above parameters, Taguchi L17 array was constructed, and the process parameters were optimized to the high degree of uniform distribution. From the particulate polymer composite, the images captured by foldscope were further analyzed by ImageJ technique for determination of the statistical distribution of particles. The processing parameters of 80% power, T_{on} 135 s for 120 grit size exhibited excellent particle distribution and higher tensile strength.

Keywords

[Polymer matrix](#)

[Foldscope](#)

[Ultra-sonication](#)

[Particle distribution](#)

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Exploring the possibilities of security and privacy issues in health-care IoT

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1. Introduction

Internet of Things (IoT) is a network of smart, self-configuring devices embedded with sensors and actuators that use diverse networking technologies to connect objects in the physical world to the web. IoT-enabled devices are designed and developed for a wide range of applications such as building and home automation, smart city, smart grid, smart agriculture, transportation, military, and health care, etc. Health-care industry particularly is expected to reach greater heights due to increasing health awareness among the people and increased access to insurance facilities. On the other hand, health-care services are becoming costlier and out of reach to a section of the population thereby a large section of the society will be at high risk as the number of chronic diseases is increasing with simultaneous aging of major population. Development of IoT-enabled devices, systems, and applications made health-care pocket friendly and easily accessible. Currently, the entire world is experiencing a pandemic situation due to coronavirus disease, COVID 19 outbreaks [1], wherein nearly 2.5 million positive cases were identified as on date [2] and 0.18 million deaths. In such pandemic situations, to avoid community spread, doctors nowadays are available for video consultation in most parts of the globe with the help of applications developed for such purpose. In the near future, it is expected that such growing technology would move the medical checks from hospital to patient's residence, so-called remote patient monitoring systems that would avoid unnecessary hospitalization if correctly diagnosed and will help a large section of society who cannot afford for such facilities. With such developments in IoT-based health-care systems and services, it is expected

that the quality of treatment will be improved thereby improving the health of patients.

In spite of the massive potentiality of IoT in health care, the complete communication infrastructure is weak from the security point of view and may result in loss of privacy for the patients. Security and privacy with respect to health-care data are the most important requirements that would bring remarkable challenges and openings to manufacturers, developers, service providers, and consumers. The most important security issues influencing the developing health-care IoT systems arise out of the security flaws present in the technologies used in building health-care IoT for relaying health-care data. Most of the IoT devices are constrained devices. A constrained device possesses limited power, limited memory, limited computation and communication capability, and is low cost. The communication in health-care IoT is wireless and hence vulnerable to various attacks. Typically in health-care IoTs, the patient's physiological parameters are sensed by the devices called body sensors. Body sensors relay the measured physiological parameters and the related events to the cloud that carries data analyses. Privacy in health-care IoT systems should be protected at every stage starting from the device till data analyses at the cloud which helps to disclose patient's health-related sensitive information. The privacy of users and security of patient's health-related information poses new challenges that need to be addressed in the health-care IoTs. The objective would be to identify the security and privacy challenges in health-care IoT and discuss possible solutions for constrained environments. In such environments there is a possibility of an attack in two different ways:

1. Attack in the network between the gateway and the devices or between the gateway and the cloud server
2. Attack between the cloud server and the end user (uses smartphone or any other external consoles)

Some of the attacks which are likely to occur in health-care IoT environment are spoofing attack, eavesdropping attack, data manipulation, malware Infection, and power analysis attack. To address the abovementioned attacks, the types of required security services such as confidentiality, data integrity, authentication, and secured firmware updates are to be defined properly. The most important aspect is to protect the cryptographic keys. The objective of the chapter is to explore the possibilities of various security and privacy issues possible in such scenarios. The security challenges in IoT health-care systems will be discussed in details. As the attacks occurring in

IoT devices are very difficult for the end users to detect, prevent, and apply corrective measures, appropriate security mechanisms to address the security challenges will be explained in detail.

On the other hand, various wireless communication protocols such as Bluetooth, Zigbee, LoRaWAN, etc. are emerging in IoT devices apart from WiFi. As the IoT devices are connected via such protocols and due to increase in the usage of such devices in a variety of applications, security breaches are found to be critical and the number of attacks is also increasing. Hence the type of attacks related to protocol usage in health-care scenarios will be discussed. Finally, as IoT devices run on various microcontrollers with proprietary real-time operating system (RTOS), field firmware upgradation of these devices is very essential by the manufacturers to understand the threats. Since the threats related to microcontrollers vary with the different types of controllers used in various devices, the different types of threats related to different controllers will be addressed. Over and above, in this proposed chapter, we would like to discuss the existing cryptographic algorithms or mechanisms available to address the security issues in IoT health-care devices and discuss the possible solutions. The challenge is to identify the limitations and explore the possibilities for further progress in IoT enabled health-care systems.

The rest of the chapter is organized as follows. In [Section 2](#), a conceptual framework of IoT-based health-care system, communication, and protocol architectures are presented. [Section 3](#) gives an introduction to applications of IoT in health-care. [Section 4](#) elaborates upon the challenges involved in IoT health-care. [Section 5](#) gives an insight into security and privacy issues in IoT health-care and proposes a possible solution in terms of a security model. [Section 6](#) summarizes the discussions and possibilities for further developments.



2. IoT health-care framework

IoT-based health-care system enables real-time monitoring of patients with expected medical emergencies like heart attack, hypotension, hypertension, respiratory disorder, etc., via connected smart devices. The IoT devices capture the required physiological parameters of the patient under monitoring and forward the collected health data to the cloud via the Smartphone application to which the IoT devices are connected. The

physiological parameters such as heart rate, blood pressure level, oxygen level, etc. stored in the cloud are shared with the concerned physician for remote monitoring. Center of Connected Health Policy (CCHP), a nonprofit organization, in its case study found that there was nearly 50% reduction in 30-day readmission rate because of such remote monitoring on patients with heart failure severity [3].

Fig. 1 depicts the conceptual framework for effective remote patient monitoring with heart disease. The IoT device shown in Fig. 1 uses noninvasive technique to capture heart rate measurements exactly at the ulnar side of the forearm in the wrist. The sensor will be embedded within the strap of a watch and will be strapped in the wrist. The IoT device is connected to the smartphone application. The device can capture the heart rate and use the data connection of the smartphone to transfer the heart rate data to the cloud. The data stored in the cloud can be shared with the concerned doctor or even to the insurance company. At the cloud server, machine learning and training can be used to look for patterns in the data that is collected from an individual and make better decisions in the future and alert the individual or the concerned physician regarding the possible medical emergency. This allows the device to learn automatically without human

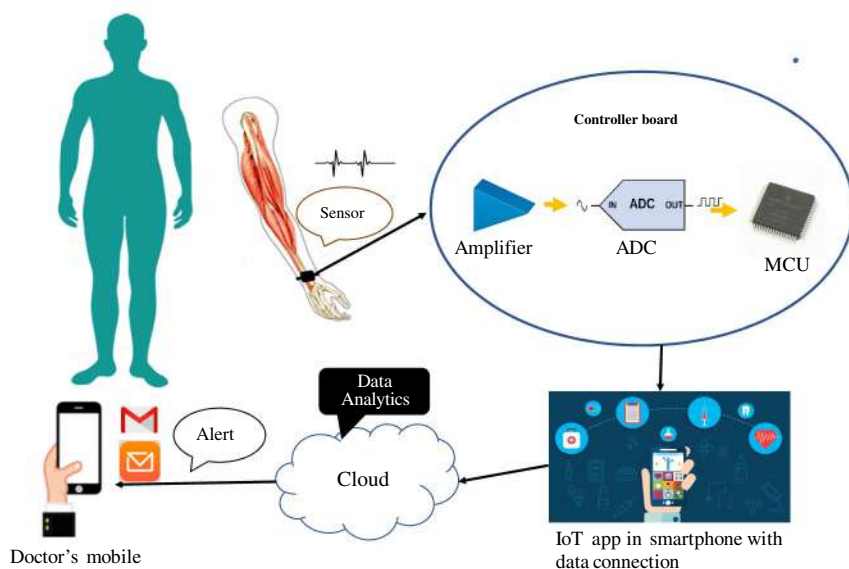


Fig. 1 Conceptual framework for remote patient monitoring and health care via wearable.

intervention or assistance and adjust actions accordingly. Whenever the individual is stressed, it gets reflected on the data that is stored in the cloud and the same thing can be intimated to the individual or the physician by generating a chart of the heart rate data over a period.

Fig. 2 depicts the communication architecture framework for IoT health-care system. IoT-based health-care system can completely automate patient care with developing new technologies and health-care facilities. Protocols such as Bluetooth, 802.11, 802.16, 802.15.4, Zigbee, etc., can be used to transfer the physiological parameters captured by the IoT device to the cloud as depicted in Fig. 2. The health data stored in the cloud can be shared with the concerned physician thereby reducing unnecessary visits and improving resource management efficiently. Such IoT-enabled systems are capable of performing data analyses over the cloud and thereby storing only the final reports in the form of graphs or bar charts instead of raw data. Machine learning, deep learning, and Artificial Intelligence can be used to look for patterns in the data that is collected from an individual and make better predictions and alert the concerned physician regarding the possible medical emergency. Hence IoT-based health-care systems provide time alerts with better accuracy thereby improving the efficiency of remote patient monitoring. On the other hand, IoT-based health-care systems

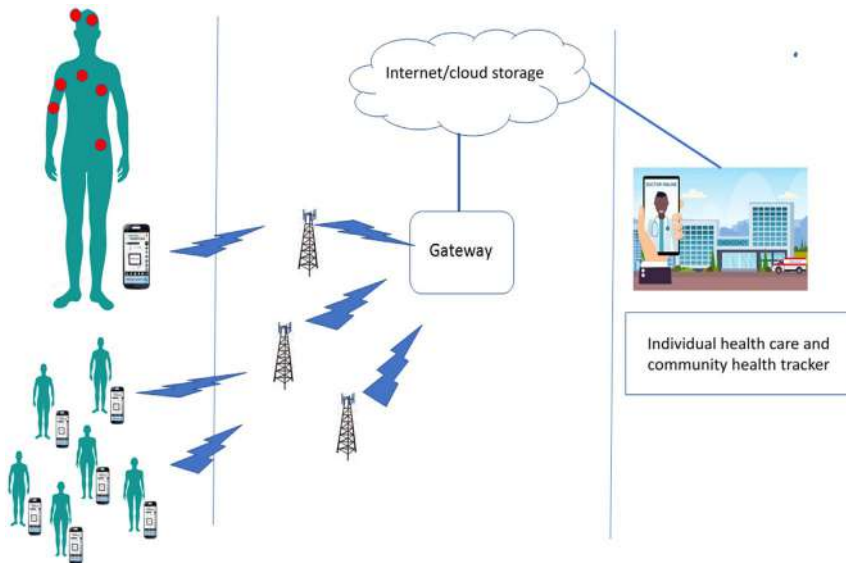


Fig. 2 Communication architecture framework for IoT health-care system.

collect a huge amount of data about the patient's health history that can be used to support medical research in terms of statistical study. Most of the IoT-based application follows five-layer protocol architecture model, in which Link and PHY layer supports 802.11/802.15.1/802.15.4/802.16/, Network layer supports IPv4/IPv6/6LoWPAN, transport layer supports TCP/UDP, and application layer supports http/COAP/MQTT/WebSockets [4]. As discussed in Ref. [5] IoT health-care system devices use IPv6 and 6LoWPAN systems for data transmission over 802.15.4 protocol. Data are replied back by the 802.15.4 enabled devices with user datagram protocol (UDP) at the transport layer.



3. IoT health-care applications

The innovation in the field of IoT is expected to enable a wide variety of applications across the globe. The various IoT health-care applications currently used by the doctors, patients, insurance companies, medical research institutes, and various other organizations that are directly or indirectly participating in patient's health care are real-time body temperature measurements, heart rate measurements, noninvasive glucose level measurements, blood pressure monitoring, continuous monitoring of blood oxygen levels, IoT-enabled fully automated systems for physically challenged people etc. [5]. Nowadays health-care industries talk about ingestible sensors that can monitor the medication level in the body round the clock, thereby send an alert in case of any irregularities and hearing aids that are connected to a smartphone with Bluetooth technology. Halo Neuroscience, a Silicon Valley firm and Thync, a venture-backed start-up had come up with gadgets in the form of headsets that send low-level electric current to the targeted region of the brain thereby improving the mood [6, 7]. The rise in IoT has come up with devices with computer vision and artificial intelligence (AI) technology that reads the environment and helps the visually impaired patient to detect obstacles and navigate accordingly [3]. The most important facility that should be noted in all the applications introduced so far is the availability of health-care data. The health-care data collected from the patients are stored in the cloud and analyzed, thereby complete statistical details about the patients in the form of charts or bar graphs can be made available for the physicians irrespective of the date, time and venue, that avoid manual maintenance and makes doctor's work easier than before.



4. Challenges

4.1 Security and privacy

As the collected health-care data is stored in the cloud for further processing and sharing, the most important challenge faced by IoT health-care system is security and privacy issues. There is a possibility that the hackers steal the personal information of patients and as well as the information pertaining to top physicians with which they can create fake identities to buy certain important drugs and even medical emergency equipment. Another possible cyberattack is that the hackers can steal the patient's personal data and can initiate a fraudulent claim with the concerned insurance company. Data protection becomes an important challenge with respect to IoT health-care systems as the amount of data involved is huge and sensitive too.

4.2 Lack of standardization

As per the current practical scenario, no unified standard exists; solutions that are available are basically domain specific for particular application vertical. The different types of devices introduced into the market by different manufacturers, when interconnected, pose real challenges as different devices follow different protocols and standards which in turn complicate the process of data collection, processing, and aggregation. The lack of nonuniform standards and data formats may adversely affect the scalability of IoT health-care systems to a greater extent. Developing unified standards may seem impossible due to domain knowledge differences, but an effort to develop interoperability is a challenging task [8].

4.3 Accuracy in decision-making

Most of the IoT health-care applications require continuous monitoring of patients round the clock. Apart from that the number of devices involved in measuring the health-care data is several numbers based on the requirement and hence the amount of data involved is huge. As the devices follow different communication protocols, data processing and data aggregation are becoming difficult. This, in turn, affects the accuracy in decision-making by doctors [3]. The issue aggravates with the number of devices.

4.4 Device type

Another challenging task is to decide the technology to develop miniaturized IoT devices that need to be embedded in some form with the patients to collect the physiological parameters. Most such devices are constrained in terms of power, memory, computation, and communication capabilities. Deciding appropriate embedded parts and integrating them into the required IoT device is a challenging task. The choice should be such that it should not harm the patients under observation.

4.5 Software development and maintenance

Software application development involves four stages namely: setup, development, debugging and testing, and publishing. In the development of IoT health-care applications, the participation of concerned medical experts in terms of sharing their experience and suggestions will ensure better quality. At the same time, for the application to be sustainable, there should be frequent updates based on the current advances in the medical science, new types of diseases and disorders, methods of early detection of such diseases, and posing new diagnostic challenges. Additionally, there is a requirement of customized computing platforms for IoT health care with suitable application program interfaces (APIs), disease-oriented libraries and appropriate frameworks as the requirements are highly demanding and sophisticated [5].

4.6 Cost-effective

Actual requirement is, the IoT-based health care must be low-cost facilitating affordability by a common man. Achieving low-cost IoT health-care technologies pose a new challenge to most of the developed countries.



5. Security and privacy issues in IoT health-care

Smart IoT devices in health-care systems provide many advantages but they pose a lot of challenges with respect to security and privacy issues related to health-related data of the patients.

5.1 Privacy issues

In health-care systems, the complete details of the patients under observation are maintained in the form of health records. The most important

requirement in such scenarios is, all these health records must be kept highly confidential, and otherwise, this can become a target for cyberattacks leading to the disclosure of private data resulting in privacy issues. Since the communication of such patient's personal data in IoT health-care systems is done wirelessly, the attackers can inject eavesdropping attack by stealing information that the smart IoT devices, mobile phones, and computers exchange over the network. Therefore protecting the data exchanged over the network becomes an important requirement. Different countries have different laws to protect patient's health data. But the users of such systems are not very much aware of what is happening to the health data collected from them. For example, people from different age group and different work culture, use fitness wearable devices and think that the physiological parameters collected are protected under certain rules and regulations, but the reality is quite different [9]. In addition to all these privacy issues, there is a possibility that the attackers may steal location details of such patients as all these devices are connected to the smartphone application via the data connection.

5.2 Security requirements and challenges

Following are the general security requirements with respect to the IoT health-care systems:

- **Confidentiality:** Providing privacy and secrecy of health-care information to prevent unauthorized access.
- **Integrity:** Ensuring that message is not altered during the transition.
- **Authentication:** Authenticating the participating connected devices before granting a limited resource, or revealing information.
- **Flexibility:** Security technique chosen must work in any kind of environment and it must support the addition of devices, in general, it must be flexible.
- **Scalability:** Techniques chosen must support scalability, which forms an important issue in IoT-enabled systems, i.e., the technique must be applicable for both smaller networks and larger ones.

One of the important challenges in IoT-based systems is to provide very good security with limited resources. The challenges in providing security for IoT health-care systems are [10]:

- First challenge is that there must be a good compromise between minimization of resource consumption and maximization of security level. At the same time, resource constraints should be taken care.

- Security mechanism hosted on a device is dependent on the capabilities and constraints of sensor node hardware.
- Third challenge is that the lack of predefined topology facilitates attackers for passive eavesdropping, active interfering, leaking of secret information, interfering message, impersonating nodes, etc.
- Fourth challenge is that communication is through radio, Wire-based security scheme impractical for such applications [11].
- Fifth challenge is that the topology is not fixed. Variations in the number of connected devices are expected to be arbitrary fashion. Failures may be permanent or intermittent.
- Sixth challenge is that the overall cost should be as low as possible.

Constraints in IoT health-care systems can be defined in three different ways as node constraints, network constraints, and physical limitations. The constraints and the corresponding challenges are:

- **Limited energy:** IoT devices have limited battery life and hence a simple key establishment technique consuming less computation power must be used.
- **Limited communication bandwidth:** Due to bandwidth constraints the key establishment techniques must allow only small-sized data to be transferred at a time.
- **Limited memory:** The selected security technique must use less memory at the same time it should provide a higher level of security.
- **Limited communication range:** Limited energy supply also limits the communication range. To overcome this, a sort of network processing should be performed where a selected set of nodes takes care of aggregating and forwarding the data to cloud.

5.3 Security threats in IoT health-care systems

Considering the sensitivity of the health data exchanged among the connected devices in IoT health-care systems, attacks are possible on different levels from devices, to applications and cloud. Interoperability of IoT devices leads to vulnerabilities and the related challenges [9]. The following are the important security threats possible in the case of IoT health-care systems:

(i) Denial of Service (DoS) attacks

DoS attacks cause communications links to be lost or unavailable. Such attacks threaten health-care service availability, network functionality, and device responsibility. The system loses its basic functionality to implement

the requirements. It may happen in different forms from devices to protocols and storage.

Jamming is a popular Denial of Service attack where the adversaries interfere with the communication frequencies of the sensor nodes. Here the adversaries select few jamming nodes from the entire networks. The possible solution, in this case, is the proper choice of spread spectrum technique. But the complexity involved with respect to computation and the cost involved will be huge [10]. To be more specific, the adversary targets a single system with several compromised devices and crashes the entire framework making data unavailable, successfully injecting distributed denial of service (DDoS) attacks [9].

(ii) Tampering

In this case, the adversaries can get access, and become successful in compromising some IoT devices that can be used as a portal to steal patient's sensitive health data that is termed "Medjacking" by TrapX, a solution provider for security issues during June 2015. Additionally, the adversary can get access to the security credentials of the users. One of the best defense mechanism for such an attack is manufacturing devices with self-destruction capability whereby devices vaporize memory contents in case of intrusion and this may prevent leakage of information. Another solution is proposing an efficient fault-tolerant protocol that maintains proper functioning of the network even if some nodes are compromised. But exploring the possibilities of implementing such mechanisms in IoT-based systems pose a new challenge.

(iii) Modification and fabrication

As mentioned in the previous attack, once the adversary succeeds in compromising few IoT devices, he/she can access the sensitive health data and modify them misleading the other entities involved in the IoT network. On the other hand, the hacker can inject false messages into the network and confuse the other connected entities, introducing fabrication attack. The best defenses against this type of attacks are making use of proper encryption and authentication techniques.

(iv) Replay attack

The adversary after successfully compromising the IoT device can replay the existing messages at some later point of time thereby threatening data freshness. The best defenses against this type of attacks are making use of proper time stamps and cryptographic nonce.

(v) Unauthorized data access

Each IoT-based health-care system application will have a huge number of users and the data involved in such a scenario is huge. In such scenarios

preventing unauthorized access to the health data and related resources becomes an important issue. The best defenses against this type of attacks are making use of appropriate access control and authentication mechanisms.

(vi) Hardware and Software Compromise

In such cases, the attackers succeed in tampering IoT devices and configure the compromised devices with malicious codes. In addition to that an attacker explores the software vulnerabilities and malfunction IoT devices [5]. As discussed earlier, one of the best defense mechanisms for such an attack is manufacturing devices with self-destruction capability whereby devices vaporize memory contents in case of intrusion and this may prevent leakage of information.

(vii) Exploiting the vulnerabilities of protocol standards

The attackers may exploit the possible vulnerabilities with the defined protocol standards for injecting malicious activities into the networks. For example, If MAC sublayer of IEEE 802.15.4 standard use CSMA/CA with RTS/CTS, in which RTS/CTS packets are used to reserve channel access to transmit data. There is a possibility that an adversary intentionally injects RTS packets continuously to a targeted node by ignoring CTS reply packets thereby flooding the link of the targeted node [10]. Such nodes are often termed as malicious nodes or self-sacrificing nodes. The best solution is that a node can limit itself in accepting connections from the same identity. A particular node will not accept more than fixed number connections from the same identity and there should be a proper selection of this threshold.

(viii) Cyber Security Attacks

As the IoT-based health-care systems rely on the cloud for storage and analyses, the cybercriminals can inject attacks such as hidden https tunnels, hidden DNS tunnels, and ransomware and botnet attacks. In hidden https tunnels, the attackers use the https tunnels meant for actual data communication for its own command and control that looks like normal traffic over long periods of time [12]. On the other hand, the cybercriminals can insert malicious software or stole health-care information into DNS queries and responses that can even bypass the firewalls. Ransomware is a form of malware that encrypts the victim's information and demands a ransom to restore access to data, whereas botnets are created by infecting systems with malicious software and make those systems slave to the botnet creator. Currently, it is found that the rate of occurrence of both ransomware and botnets in IoT health-care systems is less when compared to other applications [12].

5.4 Possible solutions

Following security mechanisms can be considered at the stage of design, development, production, and deployment of IoT health-care devices:

(i) Encryption

Encryption ensures confidentiality. The sensitive data can be protected by creating secure links. Appropriate encryption algorithms can be used to create required certificates that can be used to exchange health-care data securely.

(ii) Authentication

Manufacturers need to issue certificates for IoT devices for verifying the identity of the authorized users in the network.

(iii) Integrity

IoT health-care data exchanged wirelessly must be signed with the created certificates so that data is not altered during the transition that ensures data integrity.

Suppose the IoT health-care framework uses the devices Xbee module mounted on an appropriate microcontroller, the security features in Xbee include 128-bit AES encryption, two security keys namely network key and link key that can be preconfigured or obtained during joining, and support for a trust center. The security features available with Xbee satisfies the security requirements such as message integrity, confidentiality, and authentication. In such scenarios, all the participating devices can be predistributed with the link key and the coordinator node can be made responsible for selecting a network key for encryption and distributing the network key encrypted by the link key to the joining devices. Data transmissions are always encrypted with the network key that is hop to hop, and can optionally be end-to-end encrypted with the Application Support Sublayer (APS) link key [13]. On the other hand, three cryptographic layers are defined in Wasmote encryption libraries namely link layer, application layer, and secure web server connection, if Wasmote is chosen as the microcontroller. As per the link layer, all the participating nodes in the network share a common predistributed key that can be used to encrypt the data using AES 128. This process can be carried out using specific hardware integrated in the same Zigbee radio, thereby the efficiency of energy consumption of devices can be taken care. In this kind of setup, if a malicious node sends a message, the message will be discarded in the first hop itself and hence link layer itself will be able to ensure that no third party devices can get connected to the network thus providing efficient access control. Apart from access control, Wasmote encryption libraries can also provide solutions to common

security issues such as authentication, confidentiality, integrity, and repudiation with Waspnote hash files, Waspnote AES files, and Waspnote RSA files, respectively. Hence acceptable security level can be achieved with the device used in the IoT health-care framework, which is in turn dependent on the secured storage of keys.

Suppose, if a device without predistributed keys wishes to join the network, at least a single unprotected key must be sent to enable encrypted communication. This one-time exchange of unprotected key may end up with sniffing attack [14] that would lead to compromise security of the whole network. On the other hand, most of the device type mentioned in such application scenarios is not tamper-resistant and hence there is a possibility that an attacker succeeds in accessing the secret keys and other privileged information. The solution for the first case is to use only preconfigured keys as discussed earlier and in the second case, logic needs to be developed to erase the security credentials if tampering is detected. The resilience of the framework can be further increased by proposing logic to periodically change the network key in regular intervals of time so that known plaintext attack can be avoided.

Exploring the possibility of the second level of security by developing lightweight digital signature algorithm using Waspnote hash files, Waspnote AES files, and Waspnote RSA files available with Waspnote encryption libraries will be a great challenge [15]. Here the signature can be generated using the private key of the signer and the signature is attached along with the hash code of the message before transmission. The receiver has to verify the signature using the public key of the signer. Once the signature is verified, the link will be established between the two devices and the message will be transmitted. The challenge here will be making the entire process lightweight suitable for constrained environments by choosing a complex number computed from a small prime number within a specific range for computing signature parameters instead of large prime numbers to avoid computational overhead.



6. Summary

In this chapter, we have discussed the possible communication and protocol architecture of IoT health-care systems. Overview of various applications of IoT in health care is discussed along with the challenges involved. It is understood that due to sensitive data handling, security and privacy become an important challenge in the design, development, and

deployment of IoT health-care systems. The chapter also explored the privacy issues, security requirements and challenges, security attacks, and a short discussion about the possible solutions. It is understood that security factor must be taken care at various levels starting from devices to networks and finally cloud. Confidentiality, integrity, and authentication are the required services for maintaining security in IoT devices. Extensive care should be taken to design a proper security technique that suits IoT systems. A trade-off between the requirements and resources of IoT determines which security mechanism should be employed for a particular application.

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3. Assessment and intelligibility modification for dysarthric speech

From the book [BAND Voice Technologies for Speech Reconstruction and Enhancement](#)

P. Vijayalakshmi, M. Dhanalakshmi and T. Nagarajan

<https://doi.org/10.1515/9781501501265-004>

Abstract

Dysarthria is a motor speech disorder that is often associated with irregular phonation and amplitude, incoordination and restricted movement of articulators. This condition is caused by cerebral palsy, degenerative neurological disease and so on. The pattern of speech impairment can be determined by the amount of compromise detected in the muscle groups. That is, the dysarthrias have global effect rather than focal effects on speech production systems of phonation, articulation and resonance. Clinically, assessment of dysarthria is carried out using perceptual judgment by experienced listeners. One of the limitations of perceptual assessment is that it can be difficult even for highly trained listeners to differentiate the multiple dimensions of dysarthric speech, as dysarthria has multisystem dysregulation. Although many researchers are involved in developing assistive devices, acoustic analyses are carried out on each of the subsystems independent of each other. As dysarthria affects the speech system globally, a multidimensional approach is required for the assessment and an associated intelligibility improvement system to develop an assistive device. This chapter will describe the significance and methods to develop a detection and assessment system by analyzing the problems related to laryngeal, velopharyngeal and articulatory subsystems for dysarthric speakers, using a speech recognition system and relevant signal-processing-based techniques. The observations from the assessment system are used to correct and resynthesize the dysarthric speech, conserving the speaker's identity, thereby improving the intelligibility. The complete system can detect the multisystem dysregulation in dysarthria, correct the text and resynthesize the speech, thus improving the lifestyle of the dysarthric speaker by giving them the freedom to communicate easily with the society without any human assistance.

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BAND Voice Technologies for Speech Reconstruction and Enhancement

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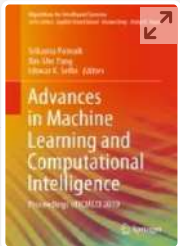
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Kinect-Based Outdoor Navigation for the Visually Challenged Using Deep Learning

[Anand Subramanian](#) , [N. Venkateswaran](#) & [W. Jino Hans](#)

Conference paper | [First Online: 26 July 2020](#)

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Abstract

In this paper, we propose an outdoor navigation system, intended for people with visual impairments. Our system makes use of a Microsoft Kinect which is reconfigured for mobile use with a portable power supply. An object detection model was trained to detect commonly found obstacles on roads, namely cars, pedestrians, bicycles and

motorcycles, based on the inputs from the Kinect. In the process, we select an optimal object detection model for an embedded environment by carrying out extensive training, benchmarking and experimentation on three single shot detection models (SSD) with different feature extractors and a RetinaNet model, while also applying quantization techniques to obtain real-time performance with relatively minor losses in performance. The detections from the network are leveraged to calculate the distance between the person and the object detected, using the depth map from the Kinect, and the information is relayed to the user using a text-to-speech system, through Bluetooth earphones paired to the system. The entire setup is constructed on a white cane, where a Raspberry Pi 3B is connected to the Kinect for reading the input frames and performing onboard processing. The results of testing the model in outdoor footage indicate its viability as a tool for outdoor navigation.

Keywords

[Kinect](#) [Object detection](#) [Deep learning](#)

[SSD](#) [Smart cane](#)

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Chapter 8 - Cyber physical systems for healthcare applications using compressive sensing

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Abstract

Lately, healthcare devices have gone through a very expeditious development. The conventional systems have been contingent upon providing the patients with vast advantages and the relationship that prevails between the patients and the medical [cyber physical systems](#) are becoming healthier and powerful. A very tremendous development has been started for human welfare by medical [cyber physical systems](#) and this has keyed up a great improvement to the human community. The main objective of the proposed system is to support and monitor the patients using real time data that is obtained from the patients on consulting and evaluating the various parts of their body. Real time images are captured from the patients and these images are stored in the cloud for clinical examination and for a patient database. For efficient storage of the data in the cloud, the compressive-sensing algorithm has been applied. Further, the images in the cloud database can be retrieved and reconstructed using appropriate recovery algorithms. Doctors analyze the data that is saved in the cloud, diagnose the disease and provide necessary medication to the patients. Parameters such as percentage of reduction in the total amount of samples and the PSNR value were studied. And 53% of reduction in the samples was obtained throughout the proposed system. Thus, an ensuring on-cloud healthcare clinic has been developed for healthcare industry.

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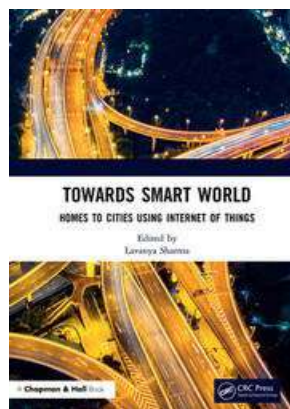


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Chapter



Importance of Augmented Reality and Virtual Reality in Our Daily Life

By Vallidevi Krishnamurthy (</search?contributorName=Vallidevi Krishnamurthy&contributorRole=author&redirectFromPDP=true&context=ubx>), D. Venkata Vara Prasad (</search?contributorName=D. Venkata Vara Prasad&contributorRole=author&redirectFromPDP=true&context=ubx>), Ganesh Kumar (</search?contributorName=Ganesh Kumar&contributorRole=author&redirectFromPDP=true&context=ubx>), B. Surendiran (</search?contributorName=B. Surendiran&contributorRole=author&redirectFromPDP=true&context=ubx>), Arjith Natarajan (</search?contributorName=Arjith Natarajan&contributorRole=author&redirectFromPDP=true&context=ubx>), Akshaya Natarajan (</search?contributorName=Akshaya Natarajan&contributorRole=author&redirectFromPDP=true&context=ubx>), Dattuluri Rushitaa (</search?contributorName=Dattuluri Rushitaa&contributorRole=author&redirectFromPDP=true&context=ubx>)

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ABSTRACT

Augmented reality (AR) has widespread applications in every field imaginable. This technology has proven to be an inflection point in numerous verticals, improving lives and improving performance. In this chapter, the various possible applications of AR in the medical field is explored. The objective of using AR in medicine or generally in any field is the fact that AR helps in motivating the user, making sessions interactive and assists in faster learning. This chapter discusses the applicability of AR in the field of medical diagnosis. AR technology reinforces remote collaboration, allowing doctors to diagnose patients from a different locality. Additionally, it is believed that a much more pronounced effect can be achieved by bringing together the cutting-edge technology of AR and the lifesaving field of medical sciences. AR is a mechanism that could also be applied in the learning process. Similarly, virtual reality (VR) could be used in the field where more practical experience is needed such as driving, sports, and neonatal care training. Experiments were conducted on the newly developed VIRECAR system, which is based on the virtual environment, for learning the vehicle driving process.

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Chapter 4

Crucial Role of Data Analytics in the Prevention and Detection of Cyber Security Attacks

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ABSTRACT

Data analytics plays a major role in retrieving relevant information in addition to avoiding unwanted data, missed values, good visualization and interpretation, decision making in any business, or social needs. Many organizations are affected by cyber-attacks in their business at a greater frequency when they get exposure to the internet. Cyber-attacks are plenty, and tracking them is really difficult work. The entry of cyber-attack may be through different events in the business process. Detecting the attack is laborious and collecting the data is still a hard task. The detection of the source of attack for the various events in the business process as well as the tracking the corresponding data needs an investigation procedure. This chapter concentrates on applying machine learning algorithms to study the user behavior in the process to detect network anomalies. The data from KDD'99 data set is collected and analyzed using decision tree, isolation forest, bagging classifier, and Adaboost classifier algorithms.

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INTRODUCTION

Data Analysis can be applied in many disciplines of data mining, cyber security to study the behavior of data for anomaly detection. In anomaly detection a profile of the normal data is developed and then data that does not agree with it as an anomaly (Dimitar et al., 2017). Broadly speaking, dataset used in various analyses can be split into two subdomains, inliers and outliers, in which the outlier's data behaves abnormally (Fabrizio et al., 2016). Using the outlier's data, it is possible to detect the anomalous behavior at a certain point of time in an application. Outlier detection can belong to three families, namely supervised, semi-supervised, and unsupervised. Mostly the outlier dataset is analyzed using the unsupervised methods based on statistical, deviation, distance based, density based, angle based, isolation based, concept based, cluster size/density based, etc.

The application where the data behave anomalously can be fields of Data mining (Zhangyu Cheng, 2019), sensor technology (Yu HsuanKuo et al., 2018), Cyber-attack (Simon D.Duque Anton et al., 2019) (Filipe Falcão et al., 2019), HTTP/HTTPS protocol (Hieu Mac et al., 2018) (Ya-Lin Zhang et al., 2018), weather data (Tadesse Zemichael et al., 2019) Network Intrusion Detection System (Zouhair Chiba et al., 2019) etc. Normally, outlier detection methods can detect the outliers accurately. In many cases, they end up with non-outliers as outliers and outliers as non-outliers. So a biased method will do this task well efficiently to detect the anomalous behavior of the data.

The main idea behind the work is to do the network traffic analysis. Using this analysis, the network administrator can have a watch on the traffic pattern to identify anomalous traffic. In order to have familiarity with the analysis, historical data is used to develop mathematical model. For the development of the model the data set available from Kaggle is used which is freely available to the public.

The objective of this paper is to detect network based anomalies using the publicly available dataset. All the parameters are cautiously considered and class required for this analysis is tracked. The training and testing data splitting was conveniently decided in applying the decision tree, random forest and bagging classifier algorithms. Python is used in this research work to detect the network anomalies and accuracy was also evaluated. The contribution that was emphasized in this chapter is as follows:

- To detect network-based anomaly detection systems
- Apply the decision tree, isolation forest, random forest, Ada Boost and bagging classifier on data set
- Study the performance accuracy of these methods in detecting the anomalies

The organization of the paper is as follows. Background Section details the literature survey and the Intrusion Detection Section discusses the anomaly detection used in this paper. The methods used for analysis are decision trees, random forest, isolation forest, bagging classifier, and Ada Boost classifier are discussed. The Methodology section details the applicability of the unsupervised anomaly detection algorithm used in this work, and the results obtained by applying these methods using the dataset KDD'99. Conclusion section provides the summary of the work done and future work of this proposed chapter.

BACKGROUND

(Zhangyu Cheng et al, 2019) applied anomaly detection methods to detect the local and global outliers using Isolation forest and local outlier factor with low complexity to prune the data set. Also applied ensemble method to improve pruning accuracy and improve the outlier detection rate. (Yu-HsuanKuo et al, 2018) proposed a regression model to fit the sensor data to detect the outliers using contextual outlier detection methods. (Filipe Falcão et al, 2019) used 12 types of detection methods that belong to a family of algorithms for the dataset that is prone to system and network intrusion detection. (Hieu et al, 2018) targeting the web attack of SQL Injection, Cross-site Scripting(XSS), XPath Injection, Local File Inclusion(LFI), Server-side Template Injection, Code Injection, OS command Injection, Server side Request Forgery, and Others. They analyzed and detected malicious patterns in the HTTP/HTTPS requests using regularized deep autoencoders. (Ya-Lin et al, 2018) proposed the Anomaly Detection with partial Observed Anomalies using the three methods, isolation forest unsupervised method, support vector machine supervised method, and the cost sensitive strategy PU learning based method on the different datasets. Also the problem of malicious URL detection was also demonstrated.

(Tadesse et al, 2019) used benchmark weather data sets to handle the missing values by applying the five strategies of mean imputation, MAP imputation, reduction, marginalization, and proportional distribution with IF, LODA and EGMM unsupervised anomaly detection algorithms. (Simon et al, 2019) adapted the three algorithms, one class support vector machines, Isolation Forests and time series Matrix Profiles algorithms to detect the process behavior in industrial enterprise dataset. Out of which Matrix profile was able to detect the attack that occurs multiple times. (Dimitar NikolaevKarev et al, 2017) used unsupervised machine learning algorithm Isolation Forests to identify intrusion models using HTTP log data. (Qing et al, 2018) applied anomaly detection in spatio-temporal data to investigate multiple types of traffic data. (Xing Yang et al, 2019) applied a density-based local outlier

factory detection algorithm to determine the outlier in network flow data streams, and also used the LSTM model for prediction.

(Timofey et al, 2018) used code vector representation to detect the kotlin code fragments in the programming language community that is available in the GitHub repository. In this analysis, Local Outlier Factor, Isolation Forest, and Autoencoder neural network methods were used to detect the code anomalies. (Zouhair Chiba et al, 2019) combined the suricata signature based detection and anomaly detection isolation forest methods in Network Intrusion Detection System to detect and protect from intruder's network attacks in the network environment by monitoring network traffic. (Degang et al, 2019) studied the anomaly detection of abnormal signals in wireless devices based on four dataset using isolation forest algorithm.

OUTLIER ALGORITHMS USED FOR ANOMALY DETECTION

This section provides the significance of outlier methods in cyber security related applications, intrusion detection systems. As per Hawkins, Outlier is an observation which deviates so much from the other observations as to arouse suspicions that it was generated by a different mechanism (Hawkins, 1980). There are a lot of areas in which these kinds of outliers exist or are created and the need of study arises. For example, The birth of a child to Mrs.Hadlum happened 349 days after Mr.Hadlum left for military service. Average human gestation period is only 280 days. Here 349 days is observed which is an outlier (Barnett, 1978). Some of the sample applications of outlier detection are in Health Care, Finance Domain, Sports arena etc.

Outlier detection distinguishes outlier data from normal data using either: abnormality detection which compares new data to a model of normality or outlier classification which classifies new data as either normal or abnormal. Outlier detection can also use time-series or sequence analysis to detect changes in temporal patterns (John Wang, 2014).

INTRUSION DETECTION

An intrusion is a series of activities in computer network systems that compromise security of the system. An intrusion can be an external attack or internal misuse of the system. An intrusion can compromise confidentiality, integrity, availability and also other security aspects in various ways (Xiangyang, 2003).

The classifier will consume time to detect intrusion and this in turn will have impact on the accuracy. (Kajal Rai et al, 2016). Accuracy and time estimate are considered as a major factor to evaluate the intrusion detection algorithms. Accuracy

can be defined as the number of correct predictions. It can be computed as shown in Equation(1)

$$\frac{(TP + TN)}{(TP + TN + FP + FN)} \quad (1)$$

Where TP is True Positive, TN is True Negative, FP is False Positive and FN is False Negative

METHODOLOGY

Decision trees can detect the malicious activities for a large set of data as they provide rules that can be understood easily. (Kajal Rai et al, 2016). Random forest classifier is very effective in classifying the attack since it is an ensemble algorithm. (Nabila Farnaaz and M A Jabbar, 2016).

Few data points will be identified as anomalies which is susceptible to a process called isolation. Isolation forest detects anomalies by following the process of isolation differs basically from other methods of anomaly or intrusion detection (Fei, T. L, 2008).

Neural network, rule learning, statistical models and ensemble methods are some machine learning algorithms to detect intrusion. Ensemble methods performs well during training process. One advantage of bagging classifier is that it takes less time to build the model and provides low false positives when compared with algorithms of similar kind. (Gaikwad, et al, 2015). Detections of false positives and the minimization of the false negatives can be achieved using AdaBoost (ArifYulianto, et al, 2019). Due to these various advantages of machine learning algorithms, the following is applied in this proposed work: i) Decision tree, ii) Random forest, iii) Isolation forest, iv) Bagging classifier, and v) Adaboost classifier.

Data Set

For the study the data set is taken from Kaggle repository. The URL of the data source is present in the reference. The data has 42 columns and 125974 rows. 100,780 records are used to train the model and the remaining 25194 used for testing the models. The 41 fields are attributes and the 42nd field is the class label normal, dos, probe etc. The preprocessing is a pre requisite for the machine learning algorithms. The machine learning data set should be tuned to suit our needs. This is done by preprocessing.

Preprocessing

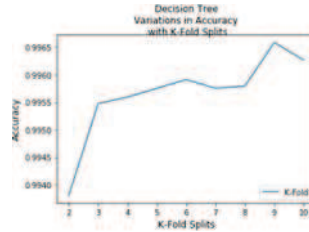
The categorical data are converted to discrete values. The data is normalized using min max normalization. The attributes of the data set are like that of Duration, Protocol, Type of service, Source Bytes, Destination Bytes, Type of the message, Login details, Login type owner or guest, Error rates, Type of attack. Using the above data set the algorithms are analyzed.

- i) **Decision tree:** A decision tree is represented by a tree like graph having nodes and edges. The root and the intermittent nodes represent the test attribute and the leaf represents the class label. (Kajal Rai et al, 2016). Decision tree is the well-known classification method for data mining. The reasons for it are: i) Decision tree is very fast to train and test the data, ii) Its results are very easy to understand for human operators and visualize, iii) Its results are used to mine rules (Atilla Ozgur et al., 2012).

In proposed decision tree the target variable is the class label which indicates the type of attack. The predictor variables used in the study to name a few are protocol, type of service, length of the data etc. During training, the decision tree technique partitions examples of data records in the training data recursively until a stopping criterion is met. After each partition, the set of training examples falling in a branch of the decision tree has less loss inconsistency with respect to the target class. A typical stopping criterion for not further partitioning a branch is that all the examples are of the same target class, and the branch becomes a leaf in the decision tree.

The structure of a decision tree shows the correspondence between the predictor variables and the target variable for the proposed problem. The decision tree divides the problem space into a number of sub-regions with all the training examples in one sub-region having the same target value. The sub-regions can then be used to classify the target value of real test data. Each path from the root node of a decision tree to a leaf node of the decision tree represents a pattern of the predictor variables or a sub-region that is useful in predicting the value of the target variable (Xiangyang, 2001). The accuracy is estimated and is given in Figure 1. The average accuracy score is calculated as 0.9956.

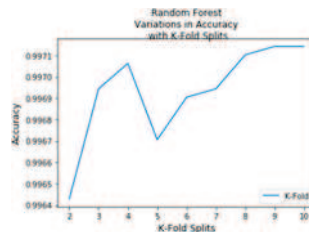
Figure 1. Accuracy using Decision Tree K-fold splits whereas $K=10$



- ii) **Random Forest:** Random forest method is used for prediction type of problems. The performance in Random forests is high due to ensemble. The ensemble is achieved with a set of decision trees that are generated using subspaces of data selected randomly. Let D be a training dataset in an M -dimensional space X , and Y be the class feature with a total number of c distinct classes. The method for building a random forest follows the steps as taken from (Bharathidason, 2014)

The accuracy is estimated and is given in Figure 2.

Figure 2. Accuracy using Random Forest with K-fold splits where as $K=10$



- iii) **Isolation forest:** The Isolation forest also belongs to the family of ensemble learning algorithm. The algorithm builds a group of isolation trees using a recursive and randomized tree partitioning procedure. An isolation tree belongs to a family of binary tree. The trees represent a nested collection of partitions of the finite dimensional feature space, grown iteratively in a top-down fashion, where the cuts are axis perpendicular and random (Guillaume Staerman, 2019). Isolation forest has high degree of adaptability and highly efficient. Due to these merits it can be used in parallel computing algorithms. Due to these merits it is very helpful in detecting the anomalies. (Sahand Hariri

et al, 2019). In Isolation forest the observations are selected by the random selection of features. The algorithm uses the split value used to split the tree. The split value is selected between the two extremes of the selected feature. The number of splits depends upon the path length from the root to the leaf (Fei, T. L, 2008), (Fei, T.L, 2012). The maximum depth for the tree is varied and for each varied value, accuracy is calculated and is given in Figure 3. Also by varying the number of trees, accuracy is calculated and is given in Figure 4.

Figure 3. Accuracy in Isolation Forest by varying Number of Trees

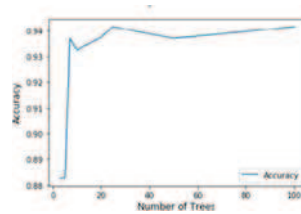
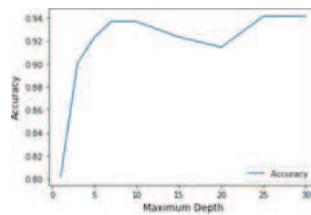
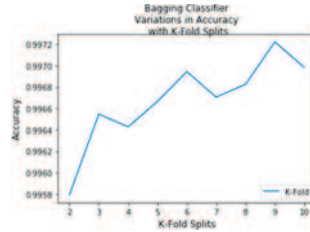


Figure 4. Accuracy in Isolation Forest by varying Maximum Depth



- iv) **Bagging classifier:** Bagging gets its name from Bootstrap Aggregating. This method follows ensemble learning. The underlying principle of bagging is to create different classifier and to ensemble them parallel. This method also distributes the training data randomly among the classifiers (Xiao-Dong et al, 2010). The accuracy is estimated and is given in Figure 5.

Figure 5. Accuracy using Bagging classifier with K-fold splits where as K=10



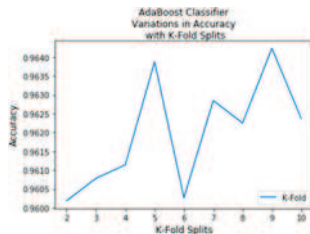
- v) **Ada Boost Classifier:** The aim of Ada Boost is to improve the accuracy of the classification by combining several weak learning algorithms. The training is done to each weak learning algorithm using a set of training data. The training is done by adjusting the weights of all the samples iteratively. Let us consider N training samples $X = \{(X_1, Y_1), (X_2, Y_2), \dots, (X_N, Y_N)\}$ where X_i denote the i^{th} sample and Y_i the class label for the sample can be -1 or +1. Initializations are done to the parameters, the number of iterations, the weak classifier count, weights of the data instance (Freund et al, 1999).

The Ada Boost algorithm has the following main steps:

- Step 1: Sampling step:** In this step, some samples (D_t) are selected from the training set, where D_t is the set of samples in the iteration t.
- Step 2: Training step:** In this step, different classifiers are trained using D_t , and the error rates (ϵ_t) for each classifier are calculated.
- Step 3: Combination step:** Here all trained models are combined.

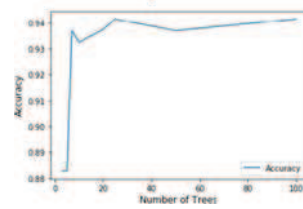
The accuracy is estimated and is given in Figure 6. The average accuracy score is 0.9619.

Figure 6. Accuracy using Ada Boost Classifier with K-fold splits whereas K=10



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Figure 7. Accuracy using Ada Boost Classifier when the trees are varied



The execution time for finding accuracy is given in Figure 8 for various algorithms.

Figure 8 Execution time of the various algorithms in millisecond



Accuracy for each of the algorithms as per above analysis are summarized and presented in Table 1.

Table 1. Accuracy values by applying confusion Matrix

Algorithm	Accuracy in %
Decision tree	33
Random forest	100
Bagging classifier	100
Adaboost classifier	67
Isolation Forest	100

As per figure 8, execution time for each of the algorithms in seconds are presented in Table 2.

Table 2. Execution time estimates

Algorithm	Execution time in seconds
Decision tree	0.00806
Random forest	0.00088
Isolation forest	0.00073
Bagging classifier	0.00188
Adaboost classifier	0.00063

The contribution of this work is as follows.

- Decision tree, random forest, isolation forest, bagging classifier, Ada Boost was applied to detect the network based anomalies.
- Applied decision tree, the split of training and testing aided to know that the class distribution was true. Since it is large set of data, 10-fold cross validation was used to reduce the overfitting. Prediction accuracy obtained is 33%.
- Isolation forest was applied to identify the anomalies by locating the split point in the data distribution. Prediction accuracy calculated by varying number of Trees and maximum depth is 94%.
- Bagging classifier with 10 fold splits was used to reduce the overfitting and error. Prediction accuracy obtained with 10-fold split is 99.72%
- Ada Boost classifier was used to tally the prediction made from decision tree to decide on the final classification. Prediction accuracy computed with 10-fold split and varied trees is 99%
- Detection was effective to identify the anomalies in the data set.
- 7.Mitigation in detecting network based anomalies

Using the mathematical equation of the models derived, one can do proactive analysis. One can apply the real time traffic data to the model classify whether this data will be classified as attack or not. If the data traffic details end up in classifying as attack then the network administrator can block the traffic from the IP address or the protocol used, setup a firewall to avoid attack. Hence such analysis will help to analyze the traffic and derive a conclusion based upon the outcome of the models

CONCLUSION

Three records are taken as a sample for testing the model generated using the various classifiers. The same three records are subjected to each of the models. When comparing the accuracy value of each algorithm, it was observed that decision tree needs more training to increase the accuracy level. Ensemble methods of learning give better performance. In the case of the decision tree the result indicates that the training is to be increased to improve the performance. In this data set Ada Boost classifier is performing to a lesser extent. When comparing the execution time for different algorithms, it is clearly seen that Ada Boost classifier performs better than other algorithms.

FUTURE RESEARCH DIRECTIONS

To evaluate the performance of intrusion detection, some of the metrics like F1 score, precision, recall can also be studied further. Various other machine learning algorithms can also be implemented and be studied for intrusion detection. The results discussed made use of the open data set available but to check with realistic data from a live website will be still interesting.

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Chapter 9

Use–Case of Blockchain in Cybercrime and Cyberattack

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ABSTRACT

Cybercrime involves unlawful activities done by the individual in cyberspace using the internet. It is cyberbullying, financial theft, code-hack, cryptojacking, hacking, etc. The main difference between cybercrime and cyberattack is that cybercrime victims are humans. The crime associated with the latter is that of a computer network, hardware or software. Cyberattack activities include ransomware, viruses, worms, SQL injection, DDoS attacks, and government and corporate are potential targets. Cyber security provides a specialised approach to the protection of computer systems from cybercrimes and cyberattacks. As of now, no cyber defence is 100% safe. What is considered safe today may not be secure tomorrow. Blockchain enables a new way of recording transactions or any other digital interaction within the network with security, transparency, integrity, confidentiality, availability, and traceability. This chapter explains in detail about cyber risks and how blockchain can be used to avoid risks in financial and insurance frauds.

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INTRODUCTION

Cyber Crime (Broadhurst & Chang, 2012) makes use of digital technologies in committing a crime. In other words, the latest techniques with the application of internet access private data through unlawful activity and thereby doing a crime. It includes attacks on data center, child pornography, financial and e-Commerce data. Cybersecurity (Ahmad, 2019) prevents cybercrime with cryptographic techniques, virtual private networks(VPN) and firewall. VPN provides a means to access personal information over public network internet. Cybercrime broadly classified into three groups.

1. Crime against individuals, such as Computer Vandalism, transmitting a virus, unauthorised access/control over a computer system (Chattopadhyay & Mitra, 2018, 2020), intellectual property thefts.
2. Crime against an organisation, such as unauthorised access to its computer, cyber terrorism on the government, spreading illegal information (Chelliah et al., 2019) and usage of pirated software.
3. Crime against society, such as uploading child pornography, indecent activities in the public places, sale of banned articles and gambling online.

Common Types of Cyberattacks

1. Denial of service (DoS) and distributed denial of service (DDoS) attacks: These attacks overwhelm the system resources, thereby prevents it from servicing the request. It dramatically reduces the system ability to respond to the service request. Some of Dos and DDoS includes Transmission Control Protocol (TCP), synchronous (SYN) flooding or SYN attack, Ping-of-death attack (PoD) or long ICMP attack, Smurf attack, Botnets or bots and Teardrop attack.
2. Man-in-the-middle attack: A malicious actor eavesdrops the conversation between sender and receiver and then access information that they are trying to send one another. The attacker sends and receives data meant for someone else without the sender and receiver knowing until it is too late. He works to fork the TCP connection into two connections, one is between the sender and attacker, and the other is between attacker and receiver.
 - a. IP spoofing attack: The attacker modifies the IP address field on a packet with a fake address instead of the sender's correct IP address.
 - b. Replay attack or playback attack: The attacker catches and preserves past communications, and then he attempts to repeat or delay it.

Use-Case of Blockchain in Cybercrime and Cyberattack

3. Phishing attack: The attacker sends malicious emails pretending that it comes from the trusted source.
 - a. Spear phishing attack: It is similar to a phishing attack where an attacker uses email spoofing or cloned websites.
4. Drive-by download attack: This attack installs spyware, adware, malware and even an unwanted program that are not of interest to the end-user.
5. Password attack or password cracking: This attack aims to steal the user's password and relevant login credentials and also called a brute force attack or cracking.
6. Structured Query Language (SQL) injection attack: Attacks on database-driven sites.
7. Cross-site scripting (XSS) attack: This attack embeds malicious code into the script of a genuine website to get information of users in that site.
8. Eavesdropping attack: Listens to others conversation by intercepting the communication link between them without being identified. There are two types of eavesdropping attack, namely passive and active.
9. Birthday attacks: Cryptographic cyber-attacks that are done against hash algorithms used for verifying the integrity of a message.
10. Malware attack: An unwanted software is being installed on the victim's computer without his/her consent. Though the effects of the malware may not be immediate, it ends in bringing harm to the victim's computer. Some malware includes macro virus, file injector virus, system infectors, stealth virus, polymorphic virus, trojan horse, ransomware, spyware and worm.

Blockchain

A blockchain is a distributed decentralized ledger (Karthika & Jaganathan, 2019) that records all the transactions that take place on the peer to peer network. It provides an immutable source of truth that can be accessed by users in the network. In simple words, it is a one way linked list of groups of transactions. It offers greater transparency by making the ledger available to anyone in the network. The users are identified with their public key, and hence they stay anonymous in the blockchain network. The transactions within the Blockchain cannot tamper as it links with the hash value of the forthcoming blocks. For example, if a hacker wants to tamper a transaction in the n^{th} block, he has to persuade all the successive blocks in Blockchain to change the hash value. Hence, immutability is one such major security feature of blockchain technology. There are two types of Blockchain, such as public Blockchain and private Blockchain.

- **Public Blockchain:** Anyone can connect to the public Blockchain with no access restrictions. It offers incentives for those who secure the Blockchain by correctly adding the blocks to it. Bitcoin and Ethereum are the most known public blockchains.
- **Private Blockchain:** Only the administrator has the right to add the user to the private Blockchain with access restrictions. Both the participant and validator access are restricted. Hyperledger fabric is the most known private Blockchain.

BACKGROUND: CYBERSECURITY TECHNOLOGIES

Cyber Security technologies deal with protecting computer systems and preventing illegal access to data. It protects hardware, software, networks and its data. It is mandatory for any computer system or network to have cybersecurity technology where sensitive information is being stored and transferred. As no cybersecurity technology is foolproof, there is a need to identify and adopt new technologies to strengthen cybersecurity steadily. Some of the existing cybersecurity technologies include Machine Learning and Deep Learning, Behavioral Analytics, Embedded Hardware Authentication and Zero-Trust Model.

Machine Learning and Deep Learning

Machine learning plays a vital part to provide cybersecurity. It pre-emptively detects cyber threats and strengthens security infrastructure through penetration testing, real-time cybercrime mapping and pattern detection. Moreover, Deep learning helps in analysing data such as transaction, real-time communications and logs to identify threats or unwarranted activities.

Cyber-attack named “WannaCry” attacked nearly 2 lakh computers over 150 countries in May 2017. It encrypts the files on the computer and makes them unreadable. The target of the attack was to acquire special decryption software. Another attack called “ransomware” targets individuals and large organisations, including the U.K.’s National Health Service, Spanish telecom giant Telefonica, Chinese schools, U.S.-based delivery service FedEx, and Russian banks. The total losses of this attack estimate to approximately \$4 billion. There were about 10.5 billion malware attacks in 2018 alone. Humans cannot handle these large volumes of attacks. Machine learning helps in identifying attacks. It applies algorithms on previous datasets and makes a statistical analysis to get assumptions about a computer’s behaviour.

Use-Case of Blockchain in Cybercrime and Cyberattack

Machine Learning can uncover threats and automatically suppress them before they cause severe damage to the system. Microsoft in early 2018 has identified a Trojan malware with its window defender anti-virus software that employs various layers of machine learning to detect recognised threats. Here are some lists of companies that use machine learning to reinforce cybersecurity. These include Microsoft, Chronicle, Splunk, Sqrrl, Blackberry and Demisto. Machine learning in cybersecurity provides solutions for threat detection and response, data protection and application security. The following examples show how machine learning helps in cybersecurity.

- Phishing and spam filtering: ML helps in filtering phishing and spam using classification algorithms, thereby detecting malicious activity with predefined parameters.
- Forensic analysis: Clustering benefits forensic analysis (Karie et al., 2019) where it throws some light on the type of attacks and how data are compromised.
- Incident response and risk management: Association rule learning presents recommendations to mitigate risks and how to respond to incidents.
- Prevention and threat modelling: ML algorithms support to predict fraudulent activity before it evolves into a costly data theft or breach.

Though ML contributes to cybersecurity with its classification and clustering models, it's likely to act maliciously pretending the threat as a normal.

Behavioural Analytics

Behaviour Analysis considers improving advanced cybersecurity technologies. It helps in determining patterns on network activities to identify real-time cyber threats. For example, an unusual rise in data transmission pattern from a specified user could probably indicate a cyber-attack. One of the benefits of using Behaviour Analysis is to detect insider threats. The behavioural analysis finds out the following types of anomalies within an organisation:

- Schedules: A potential threat exists if an employee logs into the network outside his regular working hours. It may trigger further inquiry or needs an extra layer of security.
- Applications: The risks associated with using unauthorised or different application than using a typical application, especially browser may indicate a threat in accessing the network.

- Geography: When an employee logs onto the network from different geological location, it could indicate some risks to cybersecurity.
- Devices: Employee accessing the network from a computer with different machine ID rather than his regular machine ID can be a reason for the alert.

Even though each of the above methods can give details about cyber risks, behaviour analysis becomes more effective when an organisation considers all of these factors concurrently.

Embedded Hardware Authentication

A password/PIN is no longer sufficient to offer foolproof identity verification. It can be stolen by anyone to have illegal access to the system. One of the emerging technologies for confirming a user's identity is embedded hardware authentication. It relies on a dedicated physical device held by an authorised user, offers a way to gain access to the computer system in addition to the password. The device generates a unique key that must be used with the password for user authentication. Intel has launched the Sixth generation vPro Chips, and hardware enabled multifactor authentication solution, designed to establish identity protection. Intel Authenticate tries to address the issue of data breaches originating from stolen user credentials with the help of new security technology. It checks identity by combining three factors such as personal identification number, mobile phone and fingerprint. One issue with hardware-based authentication is that legitimate users cannot log in to the system if the hardware device is stolen or lost.

Zero-Trust Model

Zero Trust cybersecurity model does not automatically trust anything inside or outside the network. It must verify everything trying to connect onto the network before granting any access. It allows only authenticated users and devices can access applications and data and also protects it from advanced threats on the internet. Some of the issues when using a zero-trust model for cybersecurity are

- Reduced data compromise and malware propagation
- Lateral movement restriction and hiding in unmanaged network communication pathways.
- Software vulnerability exploits have less impact
- Phished credentials lose value
- Declining deployment of shadow IT

Blockchain Cybersecurity

Blockchain cybersecurity (Piscini et al., 2019; Mathew, 2019) is one of the latest cybersecurity technologies that's gaining attention nowadays. It works based on blockchain technology's decentralized peer-to-peer network concepts (Sowmiya & Poovammal, 2019). Every user in the network holds the responsibility to ensure the authenticity of newly added data. The blockchain technology safeguards the data from attackers with their impenetrable network. Moreover, the application of blockchain with Artificial Intelligence can bring a better system for cyber threat detection.

Blockchain in Cybercrime

The new battle by the companies is cybercrime. Cybercrimes can slither in any business, medical care, university, government, or military system to gather information and record data. Prevention of cyber-crime will be an important priority for financial firms, notably as the volume of data is growing enormously and would be increasingly high in the near future. Distributed ledger technology and artificial intelligence have a great potential to revolutionise the storage and exchange of financial data, and this could be the solution to overcome the risk of cyber-criminality in financial organisations. This technology may not have been fully developed yet, and financial firms will have to snap it up prior to diverse implementation.

Technology alone would never be a remedy for the effective fight against cybercrime; the observation of systems and suspicious activity requires human experience and expertise. But it is critical to overcome cybercrime (Taylor et al., 2019) that the right systems be implemented to manage data most securely and to provide experts with the most effective tools to operate, which is a pending issue for Blockchain.

According to Lone (2019), Digital evidence (Graham & Smith, 2020) plays a vital role in investigating digital crimes due to criminal activities done by the persons. While investigating cybercrimes, extreme care should take for these parameters, i) guarantee integrity, ii) authenticity and iii) auditability of digital evidence (Tian et al., 2019). Blockchain technology assures capability for enabling a secured and transparency of transactions (events/actions). According to Lone (2019), cyber forensics should implement this technology for these reasons, i) improved transactional efficiency, ii) the reduction of fraud, and iii) reduced costs of transactions due to increased transparency and absence of third-party validation. Below are some of the promising use cases of Blockchain Technology in Cyber Forensic (Gopalan et al., 2019) and how the department of cybercrime wing collaborates for betterment in tracking, monitoring and capturing the cybercriminals.

1. Digital Forensics Chain

Forensic Chain (Lone & Mir, 2019) is a blockchain-based solution to keep and trace digital crimes. Blockchain is a type of data structure that facilitates the creation and storage of transactions done and shares it across all participating peers in a distributed computer network. Blockchain uses cryptography to secure and build an indispensable audit trail to record and store transactions occurring within the network. Forensic-Chain consists of blocks made up of details like location, time-stamp with date, and these details are hashed and recorded in the chain by a smart contract.

2. Hotel Chain

A new product named as HotelChain using Blockchain Technology is developed by a start-up company Zebi for the Department of Law Enforcement, Andhra Pradesh to track criminals and missing persons in that state. It combines Blockchain and AI to store information about hotel guests. HotelChain stores the daily transactions that happened in the hotel and is shared with the local police station. Both the parties (Hotel authorities and Police) get benefited due to reduced paper documents, online data, and less difficult process for legal obligation. Data available in HotelChain can be compared with the police database for finding criminals and any missing persons. Currently, it is implemented in Vishakhapatnam city and is encouraged in other countries, like Japan and Singapore.

CASE STUDY 1: FINANCIAL FRAUDS

Financial fraud (Hyvärinen et al., 2017) occurs when someone denies cash or capital and damages the pre-planned budget employing tricky plans. Individual persons can be misdirected, or other unlawful practices that lead to wholesale fraud or extortion of speculation is also termed as financial fraud. Forthcoming sections give a significant clarification of Financial Frauds and examine how Blockchain Technology helps in forestalling this sort of tricks.

Tax evasion and money related cheats have become the most recent subject of conversation as this has influenced the monetary divisions a ton. Somebody could utilise your data and access your records and complete exchanges. The end client needs to store his insight with the goal that he/she can't be an injured individual for such sort of digital assaults. In the present market, blockchain is an enthusiastically prescribed procedure that assists with checking these defects in the framework and secure the electronic instalments in monetary associations.

Frauds impact association of assorted types and sizes over a broad scope of enterprises and geologies. Results can be immediate, through money related misfortunes, or aberrant, through fines and reputational aftermath. In 2018, firms overall lost more than \$7 billion to inward misrepresentation plans, as per a 2018 Report to Nations by the Association of Certified Fraud Examiners (ACFE) - which broke down 2,600 genuine instances of word related extortion from organisations across 125 regions and 23 ventures. Tending to the danger of misrepresentation is a critical test for all associations.

Types of Financial Fraud in Businesses

Too often, an entrepreneur discovers the point of no return that even the most faithful worker may commit money related frauds. The worker may steal organisation information when circumstances arise or if the worker is in severe monetary problem and needs quick money. The four basic types of financial fraud are:

1. *Misappropriation*, also called robbery, which is the illicit utilisation of assets by an individual who controls those assets. For instance, an accountant may utilise organisation cash for his own needs. Commonly, misappropriation stories don't make it into the paper since specialists are humiliated to such an extent that they decide to keep the undertaking calm. They usually settle secretly with the thief as opposed to confronting open investigation.
2. *Inner robbery*, which is the taking of organisation resources by workers, for example, taking office supplies or items the organisation sells without paying for them. Interior burglary is regularly the guilty party behind stock shrinkage.
3. *Adjustments and payoffs*, which are circumstances in which representatives acknowledge money or different advantages in return for access to the organisation's the same old thing. The employee makes a situation to pay more for the merchandise or items than would generally be appropriate. That additional cash discovers its way into the employee's pocket who encouraged the entrance. As a general rule, settlements and payoffs are a type of pay off, yet not many organisations report or dispute this issue and take severe actions against the committers.
4. *Skimming* is a process performed by the workers by making deceitful receipts and takes cash without making any passage in income book.

Why Fraud Takes Place and How Is It Tackled

An absence of interior oversight joined with a high-pressure workplace gives the perfect conditions to hierarchical extortion to happen. A review by PwC, a worldwide

evaluator, presents that 52% of internal on-screen characters include in such tricks, 24% are from top-level on-screen characters. As indicated by PwC's "Worldwide Economic Crime and Fraud Survey 2018" - which assembled information from 7,200 respondents across 123 unique regions - utilisation of a blockchain-improved framework for data trade may assist with diminishing the dangers and expenses to the notoriety of ranking directors perpetrating misrepresentation. Right now, associations address extortion by building up an implicit rule, drawing in with outer evaluators and giving the position to interior review groups. The utilisation of information observing instruments and examination additionally adds to bring down misfortunes and quicker recognition of misrepresentation cases, as announced by the ACFE. The ACFE report additionally referred to the most well-known technique for starting extortion discovery. It didn't depend on innovation by any stretch of the imagination, however, through worker tips and whistleblowing, speaking to 40% of cases.

If Blockchain technology screens the exchanges and records of the bank, cheats could have been forestalled or identified at the beginning period. Lately, numerous exponential budgetary tricks surfaced out in the open and private banks. As revealed by the Reserve Bank of India, noting an RTI, state-run banks have said upwards of 8,670 "credit extortion" cases totalling nearly thousands of crores throughout the last five monetary years.

Digital tackles and information altering issues have presented extreme dangers. Blockchain is an energetically prescribed procedure to check these ailments. Indeed, according to Juniper Research, \$290 million was put into the improvement of the worldwide blockchain industry in the central portion of 2016. Money related associations were the first to ensure their electronic instalments utilising Blockchain.

Blockchain as a Solution

Blockchain stores the record of transactions that are time-stamped and each block is linked with its previous block by hash pointer. Blockchain innovation gives a close to continuous review trail of data. Along these lines, regardless of whether deceitful action occurs, there is a primary method to distinguish and label the related exchanges. With regards to advanced digital wallets, it is practically challenging to find a fake transaction. The money sent starting with one digital wallet then onto the next can't surpass the sum recorded in the sender's wallet. It is extremely hard for employees in the organization to alter digital records.

For organisations that don't yet deal with direct instalments in digital monetary forms, they can, in any case, influence the advantages of blockchain innovation to disincentivise extortion. For instance, when archiving budget reports, expectations sheets or some other computerised record inclined to alter, put away, traded or crushed, such exercises can be naturally "logged" on a blockchain.

The way toward logging these exchanges to open blockchains is known as tying down, where just the hash of that movement is recorded as exchange and kept in a chain. These blockchain exchanges would then be able to be perceptible to anybody, for full open responsibility, or just to those conceded consents to view or access the first documents for assessment, for example, outer evaluators or controllers. At present, it could help to manage fiscal report misrepresentation plans, which include exaggerating resources, incomes and benefits, and downplaying liabilities, costs and misfortunes. Potential fraudsters who know about this discernibility and the lastingness of these records are thus improbable to complete their ideal plans.

Blockchain doesn't comprehend a wide range of extortion, particularly when the exchanges occurring is disconnected. The innovation's primary role is to serve a critical misrepresentation investigator and uprightness implementation to handle genuine issues like degenerate work and altering land records.

How does the Blockchain Technique Help to Fight Fraud?

In Blockchain, the computerised records consolidate into blocks, and such blocks make a chain cryptographically and sequentially interfacing system with one another through cutting edge numerical calculations. Each block has an unusual arrangement of records with an association with the past one. The hashing is performed by 'n' quantities of PCs over the system. Each block registers the equivalent computerised count and has its one of a kind advanced mark. When another block is enrolled, the member gets notice of the equivalent. The data on this block can't be changed or adjusted. The members can just enhance the current old data.

Blockchain For Avoiding Identity Fraud

Character extortion makes a potential hazard to Mastercard organisations and money related establishments. Such organisations become caution and send alarms to their clients if a character misrepresentation happens. Despite strict principles and different consents laid, crooks gain admittance to classified information. Such criminals take essential data and use it without due endorsements. Blockchain has made it conceivable to make a sealed computerised character of people. If all the personality data are placed in a blockchain with consents, just allowed gatherings would have the option to confirm exchanges while approved groups appreciate restricted access.

CASE STUDY 2: INSURANCE FRAUDS

The banking and insurance industries have open arms Blockchain. The insurance industry understands that it needs to remain competitive, thus simplifying processes and meeting the demands of digitally knowledgeable clients. Blockchain technology can help insurance firms overcome the challenges of today and create transparent and credible operations (Raikwar et al., 2018). The authors will outline several of the challenges facing organisations and how Blockchain can mitigate these problems in future, to understand the current insurance industry landscape fully.

Challenges Within the Insurance Industry

Insurance companies face several challenges in the context of complex compliance issues, limited mature market growth, fraudulent claim activity, payment transactions for external parties and the handling of vast quantities of data. Insurers should also develop from the emphasis on compensating for financial losses to physical risk prevention to compete effectively with disruptors by increasing their data visibility. Furthermore, many insurers have asked how to streamline processes and secure sensitive information due to their move to digital transactions. There are growing concerns about the high costs and safety of using digital valets.

Blockchain to the Rescue

Although Blockchain may not be at the end of the day with the insurer's problems, it provides underlying technology which encourages confidence, transparency and stability. However, insurers have already employed a few ways to mitigate the above challenges by using the technology: i) security; (ii) big data; (iii) third-party transactions; (iv) intelligent contracting and (v) reinsurance. But, there are never-ending opportunities and insurance companies and start-ups are exploring fully-fledged technology insurance applications, which includes (i) detection and prevention of fraud, (ii) insurance for property and casualties, (iii) Health and (iv) Reinsurance.

I) Fraud Detection and Risk Prevention

Blockchain technology stores insurance claims in immutable ledger that helps to eliminate common insurance frauds.

Key points

Use-Case of Blockchain in Cybercrime and Cyberattack

- a. The cost of insurance fraud goes over \$40B per year, and standard methods are hard to detect.
- b. By fusing claims data between insurers, Blockchain's distributed ledger technology can move forward fraud detection.
- c. Blockchain technology can save insurers the cost of paying for governmental and subscription data to avoid fraud by facilitating better data sharing.

Fraud Detection Using Blockchain Technology

Insurers could record permanent transactions on a distributed directory, with granular access controls for data security protection. Storing claims information on a shared list would help insurers work together and find suspicious behaviour. Blockchain technology would take a considerable amount of coordination between insurers to stop fraud, but in the long term, it would prove extremely beneficial. An effort to counter fraud based on a blockchain could begin with fraudulent claims being shared to help us find bad behaviour patterns. Applying this technology, insurers can reap the following three benefits: (i) removing or dealing with multiple accident complaints; (ii) owning and reducing counterfeiting through digital certificates; and (iii) reducing premium diversions, e.g. for unlicensed brokers selling insurance and pocketing premiums.

ii). Property and Casualty (P&C) insurance

A joint lead and insurance contracts can improve the efficiency of property and casualty insurance to achieve smart contracts.

Key points

- a. P&C reports that data has been dispersed through several places controlled by various parties, making it a challenge to resolve claims.
- b. Blockchain technology allows automated data collection, analysis and possibly up to 3x quicker and 5x cheaper than currently, some types of P&C claims.
- c. Applications processing and payments are accelerated by automated "smart contracts," which spares insurers more than € 200b per year.

P&C Insurance on a Blockchain

Blockchain technology can codify business rules and automate claims management using intelligent contracts while offering a permanent trail of audit, allowing

policyholders and insurers to scan and manage physical assets digitally. Intelligent agreements using blockchain technology can transform paper contracts into programmable code that automates the processing of claims and calculates insurance liabilities for all concerned.

For example, when the accident occurs, the insurer informs immediately by linking the intelligent contract with the sensors in a vehicle. The smart contract can inform medical teams and towing services, start the process of insurance claims and inform the insured person that the assistance is being provided. New information such as police reports and crash photos can be added to the claim by the Smart Contract, thus simplifying the payout process by minimising human intervention.

iii) Health Insurance

It improves interoperability and keeps the medical records secure by adopting blockchain technology into the ecosystem of health insurance industry.

Key points

- a. The demand for patient confidentiality results in insurers often not having full access to the medical history of their patients.
- b. The lack of information may lead to denials of insurance claims.
- c. Patient information can be encoded with Blockchain technology, facilitating information transmission while maintaining patient privacy.

Healthcare Using Blockchain Technology

An industry-wide, synchronised repository of health care data can maintain patient privacy while saving billions each year from the industry. Checking the medical data of patients can be returned and shared case-by-case by Blockchain Technology. The blockchain system maintains the distributed ledger with a cryptographic signature for every record rather than forcing insurance providers to accumulate data from different databases. The signature cryptographically indexes the contents of each document and sets the time signature without saving sensitive blockchain information. Due to the shared ledger, medical data can be checked by insurers and suppliers whenever the document is modified. In the meantime, the Blockchain could provide permissions to comply with regulations, while anonymising and sharing data for research.

iv). Reinsurance

Blockchain technology facilitates the flow of information and payments between insurers and reinsurers by ensuring reinsurance contracts through smart contracts.

Key points

- a. Reinsurance protects insurers, for example, during a natural disaster, when a large number of claims occur at once.
- b. Blockchain technology can reduce risk in information sharing with smart contract's automation process.
- c. Insurance helps people dissipate the risk of natural disasters and alleviates unforeseen events.

Reinsurance Using Blockchain Technology

Blockchain technology has the potential to improve current reinsurance processes. With the use of blockchain techniques, complete premium transactions can occur on the computer systems of insurers and reinsurers, ending the need for book reconciliations for every claim between institutions. Reinsurers can be better able to assign capital for claims almost in real-time with data shared in an immutable directory and enable them to both processes and settle claims more instantly without relying on primary insurers for the data surrounding each claim.

Use-Cases (Insurance)

I. Blockchain Use Case: Etherisc (Fraud Detection – Insurance)

Blockchain start-up technology Etherisc has built up an insurance product with a blockchain capacity, which was openly tested in October 2017. The flight delay program based on crypto-currency permitted passengers to buy flight insure using either cryptocurrency or fiat money like USD and Euro. Other development products include insurance for hurricanes, and crop insurance.

Smart contracts power Etherisc's products. A contract is a paper agreement that can be enforced by law between two or more parties, but an intelligent contract is an agreement between two or more parties which can be enforced by code. With multiple 'oracles' or data sources, the Etherisc smart contract can independently verify claims. Etherisc may, for example, drone videos, compare satellite images, and weather station to the pictures provided by the insured when processing a crop insurance claim. This automatic examination can detect fraudulent claims before the

human review. Blockchain should be more commonly used as a tool for preventing fraud.

II. Blockchain Use Case: Insurwave (P&C Insurance)

The blockchain-powered marine hull insurance platform Insurwave was launched by a collaboration of organisations— including EY, ACORD, Guardtime, Microsoft, and A.P. Møller-Maersk. The platform is now commercial and is planned to deal in its first 12 months of operation with the risks of over 1,000 commercial ships and 500,000 automated transactions. In the future, the group plans to implement its platform in other types of business insurance such as freight, aviation and logistics.

The Insurwave platform provides ship location and safety conditions information in real-time to both insurers and insureds. The establishment of marine insurance premiums is, as the blockchain company R3 puts it, “notoriously complex.” Products such as Insurwave are designed to make the audit trail impossible to change more accessible to this complexity.

The process of making claims can be speeded up with reliable information stored on a vessel. It can also contribute to increasing access to data for shipowners and insurance agents. Information such as shipping, geographic location can help insurers analyses the risk they take and help ship owners to assess better the type of insurance they require.

III. Blockchain Use Case: MedRec (Health Insurance)

MedRec is a collaborative MIT Health Content Management Program. It indexes medical documents on the Blockchain instead of stored medical data directly in the chain, enabling providers with permission to access reports. This helps ensure patient confidentiality while creating a trail that facilitates patient information finding and verification in the Blockchain. While MedRec is still a proof of concept academic project, it provides a model to understand the secureness of medical data using blockchain technology. Today, Blockchain companies have essential regulatory and compliance obstacles to deal with the insurance industry to be successful.

IV. Blockchain Use Case: B3i (Reinsurance)

In October 2016, B3i is a consortium formed to explore blockchain technology by some of the most notable names in the insurance and reinsurance industries. AIG, Allianz, Aegon and Swiss Re are among the members. In 2017, B3i launched the Smart Contract Management System, a type of disaster reinsurance system for Property Cat XOL contracts. Each platform reinsurance contract is written as smart

contracts on the same shared infrastructure with executable code. If an event such as an earthquake or a hurricane occurs, the smart contract evaluates participants' data and automatically calculates their payments. After testing and reception of feedback by 40 companies, the B3i pilot program concluded in September 2018 and is scheduled to launch live at the start of 2019.

Running blockchain technology-based reinsurance policies helps in allocating capital and undertaking insurance policies to bring the insurance industry greater stability. Instead of relying on primary insurers for data loss, reinsurers can directly request coverage from the Blockchain.

Moving Towards a Blockchain-Powered Insurance Industry

Although blockchain technology is still in its early stages, it is already in the insurance industry with various promising use cases and applications. Both giant insurance carriers such as Allianz and Swiss Re and small blockchain technology start-ups are alike leveraging solutions. However, despite this overwhelming interest in blockchain technology, there is a large amount of room to cover before the insurance industry can make a significant impact.

Insurance companies must align themselves from an industry viewpoint to blockchain technology standards and processes. Although blockchain technology can help insurers collaborate and share information more efficiently, the insurers themselves have to be ready to work with each other. It is also necessary to further develop the technology itself. Public blockchains where anyone gains access to the ledger, because of privacy and security concerns, are not feasible for the insurance industry. Blockchains still under active development is private, permissible.

Finally, it is highly regulated in the insurance sector to protect consumers against abuse and insurance companies against excessive risk and bankruptcy. Legal and regulatory insurance frameworks must evolve and provide clear guidance for the success of blockchain technology.

CONCLUSION

Ginni Rometty, Chairman, President and CEO of IBM, said, "Cybercrime, is the greatest threat to every profession, every industry, every company in the world". Blockchain Technology, a shared distributed ledger, is a better answer for encountering cybersecurity threats. In this chapter, the authors discussed various cybersecurity threats and detailed two such scenarios, financial and insurance. Blockchain Technology can lend a helping hand for preventing, finding, and eradicating cyber threats. Due to the properties like immutability, transparency and security, the above

said technology would play a vital role in building effective solutions for handling cybercrimes. At this stage, Blockchain Technology is in its infancy stage, and the authors have to consider the parameters such as scalability, time taken for completing a transaction (writing a block in chain), and domain where the chain is implemented.

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Chapter 6

Deep Learning–Based Malware Detection and Classification

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ABSTRACT

Malware analysis is an important aspect of cyber security and is a key component in securing systems from attackers. New malware signatures are being created continuously and detection techniques need to keep pace with them. The primary objective is to propose a solution which detects malicious files in real time by evaluating each file. Other objectives are to assess the threat level of the malware and recognize the family of malicious file. Hence, to cover all the needs and to fulfill the motivation, a deep neural network is more suitable to detect and classify the malware. Convolutional neural network-based system MalNet-D is designed to detect the presence of malware, and subsequently, to classify the detected malware into the family in which it belongs, a variation of MalNet-D termed as MalNet-C is proposed. Images of the executable files, both malignant and benign, are used as input data, which is trained by the respective MalNet. This is used to detect and classify malware into families. The system achieved 93% accuracy in malware detection and 96% accuracy in malware classification.

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Eye Blink Detection Using Back Ground Subtraction and Gradient-Based Corner Detection for Preventing CVS

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Abstract

Many individuals experience eye discomfort and vision problems when viewing digital screens for extended periods leading to Computer Vision Syndrome (CVS). The solutions to digital screen- related vision problems are by insisting suitable preventive actions by obtaining regular eye care. The proposed work uses Viola Jones algorithm for detecting the eyes, eye blink using background subtraction, gradient based corner detection and it is capable of detecting common cases of fatigued behaviour linked with prolonged computer use by tracking the eye blink rate. Hence, this proposed system could significantly reduce the symptoms among regular computer users leading to improved health habits.



Previous

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Keywords

Backgroud Subraction; Blink Rate; Corner Detection; CVS; Eye Blink; Viola Jones Algorithm



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Eye Blink Detection Using Back Ground Subtraction and Gradient-Based Corner Detection for Preventing CVS

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Abstract

Many individuals experience eye discomfort and vision problems when viewing digital screens for extended periods leading to Computer Vision Syndrome (CVS). The solutions to digital screen-related vision problems are by insisting suitable preventive actions by obtaining regular eye care. The proposed work uses Viola Jones algorithm for detecting the eyes, eye blink using background subtraction, gradient based corner detection and it is capable of detecting common cases of fatigued behaviour linked with prolonged computer use by tracking the eye blink rate. Hence, this proposed system could significantly reduce the symptoms among regular computer users leading to improved health habits.

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Keywords: Backgroud Subraction, Blink Rate, Corner Detection, CVS, Eye Blink, Viola Jones Algorithm

1. Introduction

Computers have become an integral part of our daily life. Spending time hours together in front of visual gadgets like personal digital assistant, computer monitor and television have increased rapidly among the current generation [1]. One of the by-products of this attitude computer vision syndrome (CVS), also referred as digital eye strain,

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Entropy Analysis on Planar Anamorphic Images

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Abstract

Anamorphosis is an art of drawing, which creates illusion effect over the drawn image plane, and the impact of the illusion is nullified when the specific viewing position is used to view the drawn image. In digital imaging domain, the effect of anamorphosis is analyzed quantitatively by the amount of distortion present in the anamorphized image. This study on the anamorphized image suggested that the optimal combination of parameters can create the better-anamorphized image.

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Keywords: Anamorphosis, Projection, Renyi Entropy Shannon's Entropy.

1. Introduction

Anamorphic images are unique images which, when seen from the correct perspective reveals the intended image. Viewing from the other angles shows a distorted version. Some anamorphic images need the right attitude as well as some individual devices to view the image [1-4]. The former images are a planar anamorphic image, and the latter is known as mirror anamorphic images. Figure.1 shows the different types of anamorphic images. Mirrors could be conical, cylindrical, or pyramid. Traditionally, anamorphic images are part of the arts. European art and architecture introduced an advanced linear perspective projection in the form of anamorphosis [5]. Moreover, the anamorphized images are used to hide the secret details into it. "The Ambassador" image of the Hans Holbein the Younger, National Gallery, London, 1533 is the best example for anamorphic image with secret detail, which hides the skull image into it. The skull image is visible only when "The Ambassador" image is viewed from the particular direction

[6]. Jean Francois Nicéron [7] created the anamorphic image with the help of grid construction. Hunt et al. [8-9] derived the equation to generate planar and mirror anamorphic images and analyzed the generated images with the conventional methods of anamorphosis in the digital era. Anamorphic image generation over the complex surface is a complicated process. Paola et al. [10] suggested the simplest way of creating the anamorphic projection over the complex surface to overcome the problems associated along with the anamorphic image generation. Above studies of anamorphic image generation highly depends on the anamorphic drawing in the real-world environment. There is a limited amount of work related to digital anamorphic image generation and analysis.

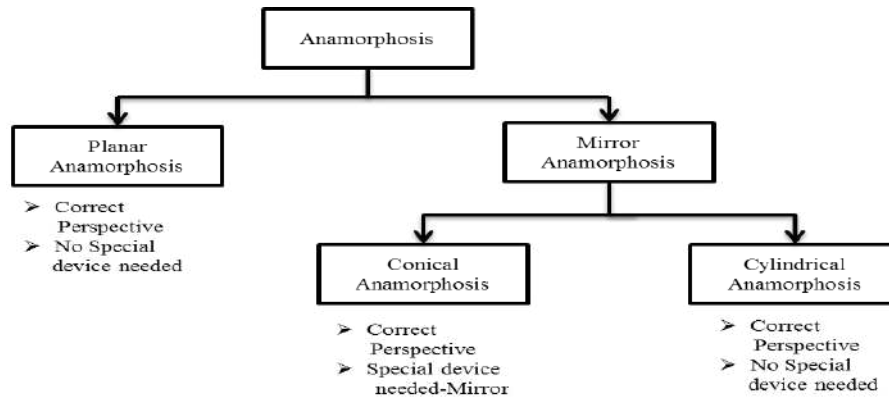


Fig. 1. Type of Anamorphosis

In this work, we have automated the process of planar anamorphization using the computers, i.e., given an ordinary image, and a user-specified the perspective, the algorithm generates an anamorphic image automatically. Here, the light rays equations are used to generate the anamorphic images. A given image can be anamorphized in various ways depending upon the perspectives. A perspective is characterized by three parameters, (i) viewing angle, (ii) viewing distance and, (iii) viewing height.

Since the anamorphized image tools distorted from the incorrect perspectives, we would like to maximize the distortion. We have addressed "What is the best way to anamorphize the given image?" or in other words, "How to maximize the distortion?". This depends on the above stated three parameters and can be called as optimum anamorphic parameters. In this work, the set of parameters maximize the anamorphic distortion that is sought by comparing the entropies and relative entropies of the given and anamorphized images.

The organization of this paper is given as follows: Section 2 explains the anamorphic image generation process. The entropy of the anamorphic images is analyzed in Section 3, and Section 4 gives the conclusion of this work.

2. Anamorphic Image Generation

The anamorphic image generation process in the digital imaging field transforms the pixel of the two dimensional image matrix into another image matrix using the Eq(1-2) [6].

$$y' = \frac{y}{\sin(\alpha)} \cdot \frac{1}{\left[1 - \left(\frac{y}{h}\right) \cos(\alpha)\right]} \quad (1)$$

$$x' = \frac{x}{\sqrt{[h^2 + d^2 + y^2]}} \cdot \sqrt{[h^2 + (d + y)^2]} \quad (2)$$

The relation between the observer height (h), distance (d) from the image and viewing angle (α) is expressed in Eq. (3).

$$\tan(\alpha) = \frac{h}{d} \quad (3)$$

While transforming the pixel from the original image matrix to anamorphic image matrix, it creates gaps in anamorphic images. These gaps are filled using the three different interpolation methods named as sample and hold, nearest neighbor, and linear interpolation methods [11-12]. The flow diagram of anamorphic image generation process is given in Fig.2.

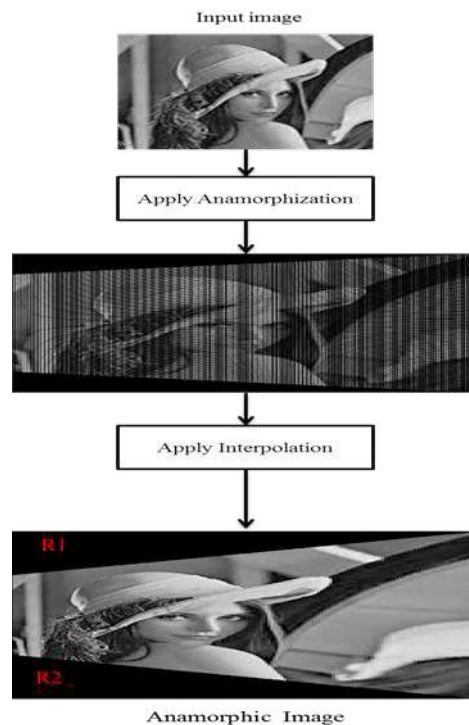


Fig. 2. Anamorphic image generation

3. Entropy Analysis

In this section, the anamorphic images are analyzed using their entropies. Scaling up/super-resolution of the images does not change the entropy value, i.e., both the original and the scaled-up images have the same entropy values. However, this is not true for the anamorphic images, i.e., the original image and the anamorphized image can have different entropies. In other words, the information contained in the scaled-up images does not change, whereas the anamorphic transformation tries to reduce the information content. The entropy reflects the amount of information present in an image. We have used Shannon and Renyi entropies [13-15] to analyze the anamorphic images generated from section 2. Eqs. (4) and (5) give the Shannon and Renyi entropy formulae.

$$\text{Shannon's Entropy} = - \sum_k p_k \times \log_2(p_k) \quad (4)$$

The Renyi entropy is the extended form of Shannon's entropy which is given below,

$$\text{Renyi Entropy} = \frac{1}{1-q} \log_2 \sum_k p_k^q \quad (5)$$

where, the index k runs from 0 to 255, and p_k is the probability associated with a particular gray level which can be computed from the image histogram. In Renyi entropy, the value of q is defined as greater than 1 and when the value of q is equal to 1, Renyi entropy turns into Shannon entropy.

The anamorphic transform changes the rectangular/square matrix into a trapezoidal shape. The pixels in regions 1 (R1) and 2 (R2) in Fig. 2 are not considered for entropy calculations. Entropy analysis takes anamorphic images from different combinations of d , h , and α . Figure. 3 depict the anamorphic image generation process for the different values of d , h , and α .

3.1. Impact of different interpolation schemes on the entropy of the anamorphic images

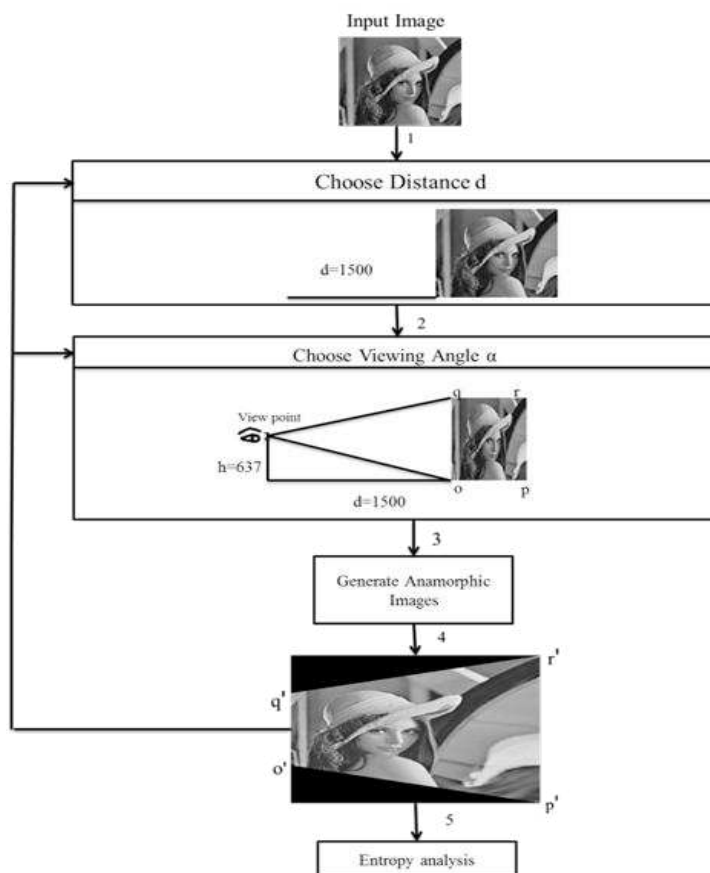


Fig. 3. Entropy analysis on anamorphic images

First, the effect of different interpolation schemes on the entropy of the anamorphic images is studied. Figure. 4 shows the Shannon and Renyi entropy of the anamorphic image (512 x 512-Lena image) as a function of α , for three different interpolation schemes. In Fig. 4, d is fixed, and the corresponding h is computed through Eq. (3), for various α . Fixing d at 1500, for $\alpha = \{20^\circ, 30^\circ, 40^\circ, 50^\circ, 60^\circ, 70^\circ, 80^\circ\}$, the corresponding heights are, $h = \{546, 693, 755, 953, 1212, 1785, 3402\}$. The Fig.4 tells us that as α decreases the entropy decreases, for all the three interpolation schemes. We have already discussed that it is more difficult to recognize the original image in the anamorphic image generated with lower α . This means that entropy decreases at α values (since the entropy measures the information content of the image). Fig 4 depict both Shannon and Renyi ($q=5$) entropy, and the trends are the same in both cases. It can also be observed from Fig. 4 that the plots show the same behavior for all interpolations. Further, results in the paper have used linear interpolation.

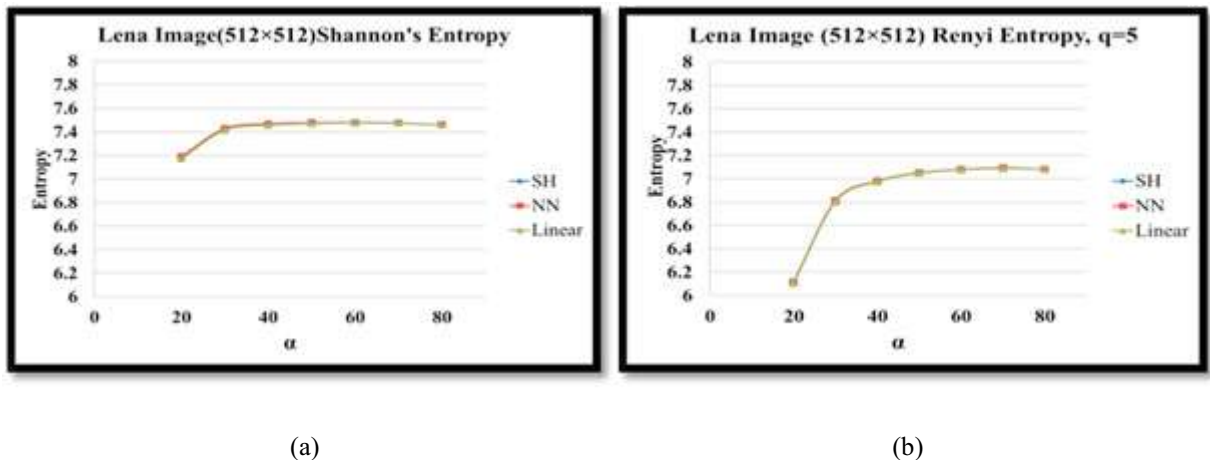


Fig. 4. Shannon and Renyi ($q=5$), entropy of Sample and Hold (SH), Nearest Neighbor (NN), Linear interpolation techniques used in Lena anamorphic image generation (a-b).

3.2. Effect of α , d and h on the entropy of the anamorphic images

The effect of α , d , and h on entropy is explored. Eq. (3) tells us that the same α can be obtained for various combinations of d and h . Different combinations of d and h can produce the same α , which is clearly shown in Fig. 5 (i.e., 3D plot of Eq. (3)). For an example, $\alpha = 20^\circ$ is obtained for four different combinations of $(d, h) = (1500, 546)$; $(1750, 637)$; $(2000, 728)$; $(2500, 909)$.

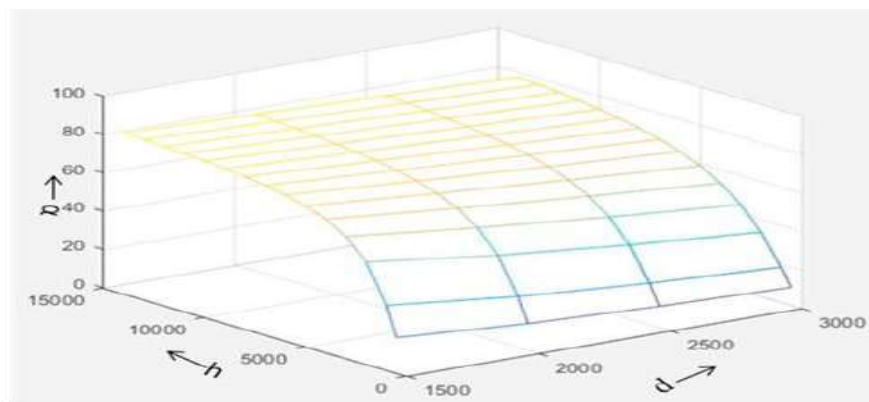


Fig. 5. 3D plot of Eq. (3) for various α , d and h

Figure 6 shows the Shannon and Renyi entropy of the anamorphic image (512 x 512-Lena image) as a function of α , with the corresponding d and h values. We can see that at lower α values entropy decreases, and we can also note that the lower d and h values for the given α , decrease the entropy, for both Shannon and Renyi entropies. The variation is more clear in Renyi entropy with $q=5$. Since we desire lower entropy to get the better anamorphic effect, the image rotations/orientations result in lower entropy is of our interest. To conclude, lower α , lower d , and lower h decrease the entropy, i.e., the information content is difficult to recognize the anamorphic images generated with lower α , lower d , and lower h which is depicted in Fig.7.

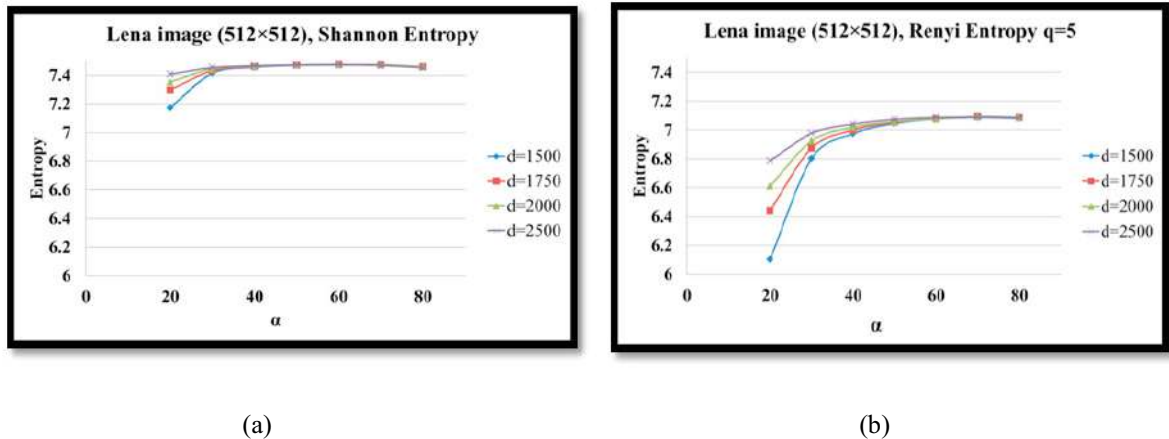


Fig. 6. Anamorphic images entropy (Shannon, Renyi Entropy $q=5$) analyses based on distance 1500, 1750, 2000, 2500 over target Lena image.

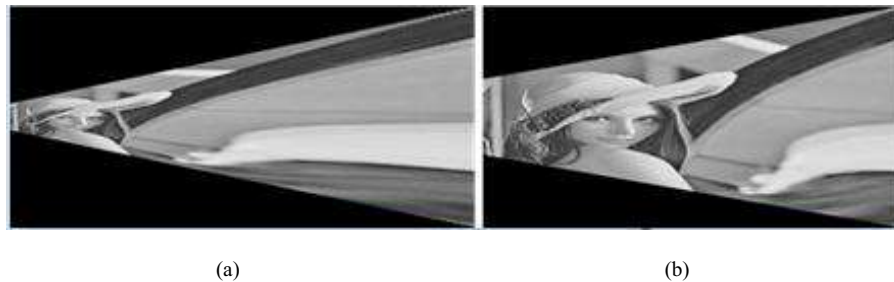


Fig. 7. Different combination of α , d and h (a) $\alpha=20$, $h=546$ and $d=1500$ (b) $\alpha=20$, $h=728$ and $d=2000$ involved in anamorphic image generation.

The same analysis is taken place on the other two images, which also results in the same. Figure 8 depicts the Renyi entropy values as a function of α and d in a 3D plot. Even though the h is not shown in Fig. 8, it should be kept in mind that h changes along with α and d .

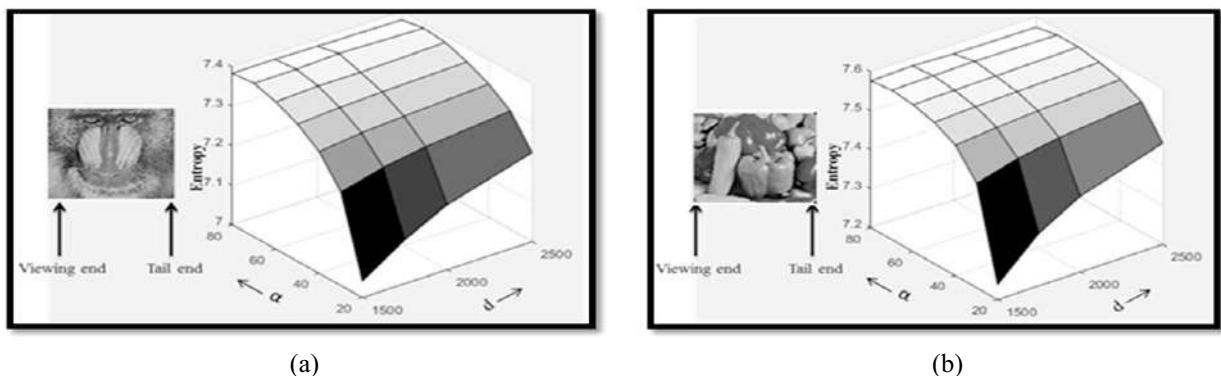


Fig. 8. Entropy analysis of the anamorphic images

4. Conclusion

This work has analyzed the anamorphic images using Shannon and Renyi entropies, for various viewing angle, distance, and height. It was hypothesized that the application of anamorphic transformation reduces the entropy, at appropriate rotations of the image on which the transform is being applied. The hypothesis was checked through systematic simulations, and the results have exposed that the entropy reduces at lower viewing angle, distance, and height. We have also found that Renyi entropy is more suitable for analyzing the anamorphic images.

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Optimized Feature Integration and Minimized Search Space in Content Based Image Retrieval

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Abstract

The semantic gap between the user request and retrieval result is an important but unsolved problem in the content-based image retrieval (CBIR) systems. This paper introduces a new multi-level structure in a CBIR system to bridge the semantic gap using the combination of low-level visual contents of an image. The initial stage of the proposed system depends on the statistical information of the color images which gives the most prominent images for the further level of the process. In the next step, low-level features such as color and texture details are extracted using dominant color descriptor (DCD) and radial mean local binary pattern over the query and selected images. Subsequently, Particle Swarm Optimization (PSO) is applied over both the color and texture similarity measure between the query and selected images. Finally, this multi-level system is experimented on OT-scene and Corel-10k databases to assess the performance and it gives 78.43% and 52.34% average precision rate.

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Keywords: Content-based image retrieval; Mean, Particle Swarm Optimization (PSO); Standard deviation.

1. Introduction

In recent years, digital image growth is tremendously increasing in different domains like web, medical, education, and remote sensing, etc. While searching for images in the huge image archive, content-based image retrieval (CBIR) system gives relevant images without the help of keywords generated by human experts [1]. The content based image retrieval system automatically extracts the details about the image and searches for similar details

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around the whole image database. Once it finds the similar details, the image corresponding to those details is retrieved as the closely matched image which is placed at the top of the retrieval results. The image details are in the form of color, texture, shape and interest points, etc. [1]. Color is the significant low-level descriptor of an image because of its powerful differentiating behavior expressively used in the object identification task. Moreover, color is invariant to image size and orientation [2]. Color features can be expressed in the way of global and local using the following techniques such as color histogram [3], color moments [4,5], joint histogram [6], dominant color descriptors (DCD) [7], color correlograms [8], color coherence vector (CCV) [9] and the color layout descriptors [10], etc. The texture is also an influential descriptor for providing relevant results in CBIR systems with the help of structural arrangement and orientation details of pixels available in the object of an image. Most commonly used texture descriptors are gray level co-occurrence matrix (GLCM) [11], edge histogram descriptors (EHD) [12], local binary pattern (LBP) [13] and Gabor wavelet transform [14], etc. The CBIR system based on any one of the features among the three low-level features has less number of adequate results. Hence, the integration of more than one feature based CBIR system is introduced to improve the relevant retrieval [15-23]. However, the semantic gap still remains high, whereas the retrieval accuracy depends on the features and how much each feature contributes to similar image retrieval. The above-mentioned feature integrated CBIR systems assign an equal weight for each feature of the image. This reduces the retrieval accuracy of the CBIR system since every feature does not equally contribute to the image to give the discriminant feature representation. Moreover, the retrieval time of the CBIR system is proportional to the number of images present in the image database and the feature vector count of the extracted features. Thus, there is a need for an optimized weight assignment for each feature used to describe the image and relevant image selection method to reduce the search space of the retrieval system.

The proposed framework design supports the CBIR system in the form of integrating color, and texture features by giving optimized weight for each extracted features which improve the retrieval accuracy and uses the statistical measure of the image to reduce the search space of the retrieval system. This approach considerably reduces the size of the database used in the retrieval task which is directly proportional to the comparison space of the similar image retrieval system. Thus, the retrieval time of the proposed system is considerably less. Moreover, this framework is explored over two databases (Corel-10k and OT-scene) and the performance of this framework is compared with various existing multi-feature combined CBIR systems.

The structure of this paper is framed as follows: Related works are described in section 2, the proposed features of the integration technique are explained in section 3; Section 4 shows the experimental results and discussion. Section 5 gives the conclusion of this work.

2. Related work

The image retrieval system based on the traditional color and texture feature extraction methods gives equal weightage for fusing the extracted features, which limits the retrieval accuracy of the CBIR system within a certain range [27]. On the other hand, the significant color and texture features of the image are extracted from Zernike chromaticity distribution moments and the Contourlet domain respectively. However, these features also share the same weight to give retrieval accuracy of the CBIR system around 70% over the Wang's databases [28]. The extracted feature of the images does not always have an equal probability of information about the image. Thus, feature selection approaches were introduced in the field of image retrieval. These feature selection methods give high weightage to the most prominent feature vectors among the other set of features extracted from the same image. Younus et.al [25] extracted four different features details (i.e.: color histogram, color moments, color co-occurrence matrix and wavelet energy) of the database images and performed clustering using the PSO based K-means clustering algorithm.

Then, the distance measure calculated between the query features and database image features cluster centers. This reduces the search space of the image retrieval system however the feature clustering the high dimensional feature vector takes more time for convergence. The color, texture and shape features of the database images are integrated using the PSO method which has high retrieval precision compared to the retrieval accuracy of each

feature individually involved in the image retrieval process. However, image retrieval time based on this method is directly proportional to the number of images involved in the image retrieval process [26]. The image selection rule based on color mean and its standard deviation reduces the search space of the image retrieval system [28]. Even though it uses the image selection rule for reducing the search space, the integration of different kinds of features shares the same weight which is the drawback of this system. Like optimal weight assignment for the different kinds of feature, the feature extraction algorithm also plays an important role in CBIR since feature representation only holds discriminant details of the image. The popular color feature extraction method takes the dominant color information available in the image by quantizing the pixel intensities. There are two different kinds of image quantization techniques (i.e. (i) predefined range based image quantization (ii) clustering based image quantization) are available in color feature extraction. The clustering based image quantization represents the color details more approximately than the certain ranges involved in quantized color feature extraction. In texture feature extraction, the local structural arrangement of the image is extracted using the binary pattern available in the local region [13, 26]. Here, every raw pixel acts as a threshold for binary pattern creation. This representation is highly sensitive to a small amount of noise. To overcome this drawback, radial mean and angular mean local binary patterns are introduced [29]. These studies reveal that the optimized combination of image representation in the reduced subspace is still an active research area of CBIR.

This work concentrates to reduce the retrieval time of the CBIR system by selecting the set of prominent image's corresponding features for similarity measure calculation. Moreover, this work uses the discriminant details of the image in the compact representation and integrates them by assigning the optimal weight for them.

3. Proposed work

The standardized process of the optimized features integration based CBIR framework is depicted in Fig.1. The proposed CBIR framework is comprised of two-level of the process in a similar image retrieval task. Here, the first level fully depends on the statistical information of the images. Second level deals with the color and the texture information of the selected images.

The initial step of the proposed technique is to extract the statistical, color and texture feature of the database images. The following section gives details about the feature extraction techniques involved in this work.

3.1. Statistical information

The statistical information [28] such as mean and standard deviation are assessed separately from R, G, and B color channels of the RGB color space query image using Eqs. (1) and (2). Subsequently, image selection rule is formed by the combination of these two statistical measures.

$$Mean(I_c) = \frac{1}{M \times N} \sum_{i=1}^M \sum_{j=1}^N I_c(P_{ij}), c = \{R, G, B\} \quad (1)$$

$$Std(I_c) = \left(\frac{1}{M \times N} \sum_{i=1}^M \sum_{j=1}^N (I_c(P_{ij}) - Mean(I_c))^2 \right)^{\frac{1}{2}}, c = \{R, G, B\} \quad (2)$$

where c is the color channel information of an image. M and N are the row and column size of a specific color channel of the image I_c . $I_c(P_{ij})$ indicates the value of the pixel in the i^{th} row and j^{th} column of the particular color channel image.

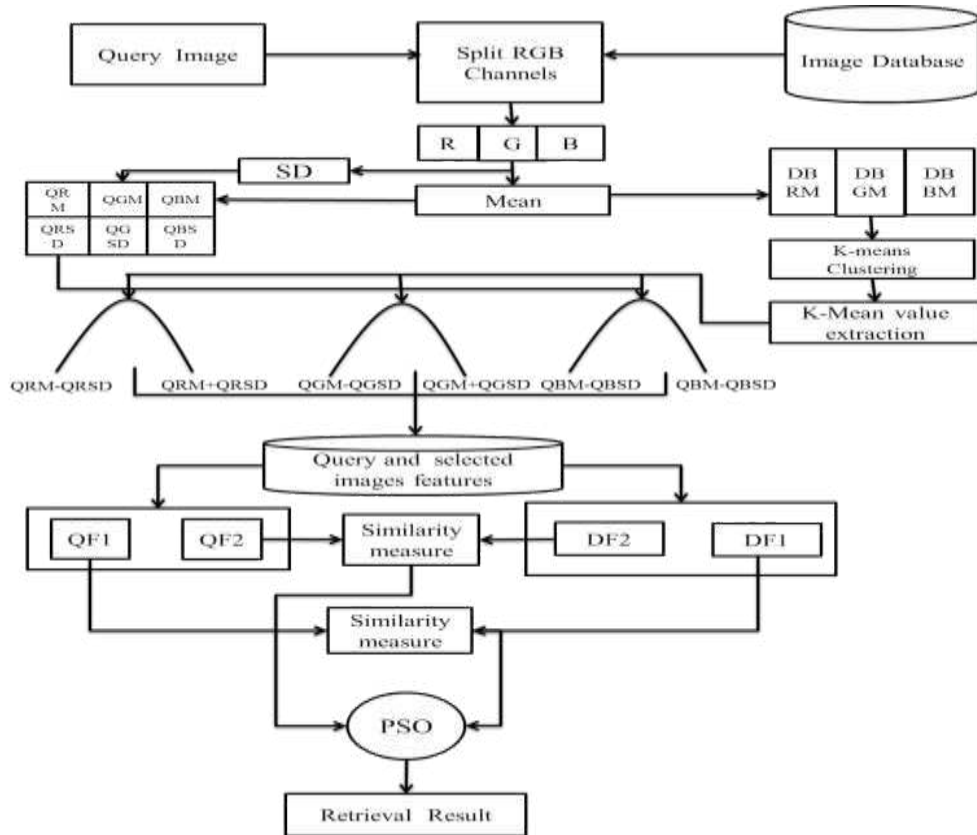


Fig. 1. Optimized feature integration based image retrieval.

3.2. Image selection

After the evaluation of the statistical information of the query image, low-threshold (LT) and high-threshold (HT) values are estimated through Eqs. (3) and (4) [34].

$$LT(I_c) = Mean(I_c) - Std(I_c), c = \{R, G, B\} \quad (3)$$

$$HT(I_c) = Mean(I_c) + Std(I_c), c = \{R, G, B\} \quad (4)$$

3.3. K-Means Clustering

First order color moment (Mean) of each image in the database is evaluated by Eq. (1). Then, the K-means clustering algorithm is applied over the first order (mean) statistical measure of the R, G, and B color channels of the database images.

If the calculated cluster mean information lies between the low-threshold and high-threshold from Eqs. (3) and (4). Then, the particular class images are selected for the next level of the process. This framework takes the features

of these images for the retrieval process. This work forms 50 cluster means on the database images.

3.4. Color feature

The dominant color information of the image is extracted by applying K-means clustering over the HSV color channel of the image [30]. Here, the initial seed points of the K-means clustering algorithm is derived from the mean and maximum value of each channel. The dominant color information of the image is extracted by applying K-means clustering over the HSV color channel of the image [30]. Here, the initial seed points of the K-means clustering algorithm is derived from the mean and maximum value of each channel.

$$\text{Initial seed points}(c) = \frac{Ic_{mean}}{k} + (c-1) * \frac{Ic_{max}}{k} \quad (5)$$

where, Ic_{mean} - Image channel mean. Ic_{max} - Image channel maximum. k - total number of cluster. c - indicates the cluster and it takes values from 1 to k . Based on the initial seed points the dominant color information of the image is extracted from the query and database images.

3.5. Texture feature

The structural arrangement information of the image is extracted from the radial mean value of the local region involved in texture feature extraction [29].

$$BP(I_c)_{p,r} = \sum_{l=0}^{p-1} s\left(\overline{I_{l,r_{1,...,n}}} - I_c\right)^2, s(d) = \begin{cases} 1, d \geq 0 \\ 0, d < 0 \end{cases} \quad (6)$$

where p indicates the number of equal distanced pixels considered in the circular neighbourhood in different radii ($r=1,...,n$). r holds the different radius values, I_c is the centre pixel value of the sub image and $\overline{I_{l,r_{1,...,n}}}$ gives mean value of the intensities I in the l^{th} pixel direction at different radii (i.e:1,...,n).

3.6. Distance measure

The color feature distance [30] is calculated using the Eqs (7-9),

$$D(Q, DB) = \sum_{i=1}^K \min \left(\sum_{j=1}^M D(C_i, C_j) + D(H_i, H_j) \right) \quad (7)$$

Where, i and j takes the values from 1 to K and M respectively. C_i and C_j indicate dominant color of the query image and database images. H_i and H_j hold the query and the database images dominant color occurrence information.

$$D(C_i, C_j) = \sqrt{(CH_i - CH_j)^2 + (CS_i - CS_j)^2 + (CV_i - CV_j)^2} \quad (8)$$

$$D(H_i, H_j) = \sqrt{(H_i - H_j)^2} \quad (9)$$

where, CH_i , CS_i , CV_i , CH_j , CS_j and CV_j indicates the query and database images H, S and V channels dominant color information

The texture feature distance is calculated using the D1 distance measure given in Eq (10),

$$D1(qif, sif) = \sum_{s=1}^m \left| \frac{qif_s - sif_s}{1 + qif_s + sif_s} \right| \quad (10)$$

where, qif - query image feature, sif - selected image feature. s takes the value from 1 to length of the feature vector.

3.7. Normalization

Normalization limits the similarity measure of the selected images color and texture features to [0, 1]. The proposed framework implements the Min-Max normalization [32] to the color and texture similarity measure separately through the Eqs. (11).

$$ND(i) = \frac{D1_f(i) - \min(D1_f)}{\max(D1_f) - \min(D1_f)}, \quad i = 1, 2, \dots, L \quad (11)$$

where L is the total number of selected images. $D1_f(i)$ denotes the feature distance information of the i^{th} image in the selected images.

3.8. Optimal weight based feature integration

The Particle Swarm Optimization (PSO) algorithm emulates the mutual experience sharing the behaviour of the birds in the flock [24, 25, 31]. The PSO algorithm is applied over the similarity measure of the two different feature datasets (i.e., color and texture) of the selected images, this improves the CBIR system performance in terms of retrieval precision. Here, PSO takes average precision as a fitness function and converge to achieve high precision rate. Before applying the PSO algorithm on the similarity measure of the selected image features, parameters involved in PSO needs to be initialized. The parameters of the PSO algorithms are the number of iteration (30), number of particles (20), dimensional of each particle (2), velocity, weight and acceleration coefficients. After each iteration, the local and global best position of the particle is stored in $pbest$, and $gbest$ variable respectively and the velocity of each particle is obtained from Eq.(12) and the position of the particle is updated using the Eq.(13).

$$vl_i^{(t+1)} = w * vl_i^{(t)} + a1 * r1 * (pbest - p_i^{(t)}) + a2 * r2 * (gbest - p_i^{(t)}) \quad (12)$$

$$p_i^{(t+1)} = p_i^{(t)} + vl_i^{(t+1)} \quad (13)$$

where, $a1$ and $a2$ are the acceleration coefficients. Here, $a1$ and $a2$ are set to 2 which maintains the balance between particle's individual and social behavior. $r1$ and $r2$ are random variables which takes the value between 0 to 1. w - inertia weight which is fixed as 1.

The $gbest$ value at the end of 30th iteration is taken as the optimal precision rate and its corresponding two dimensional particle position information acts as a weight for the color and texture feature respectively.

3.9. Performance measure

The average precision measure [28] on the retrieved results is evaluated using the Eqs (14-15).

$$\text{Precision} = \frac{\text{Number of relevant images retrieved}}{\text{Total number of images retrieved}} \quad (14)$$

$$\text{Average Precision} = \frac{\sum_{i=1}^{TDB} P(i)}{TDB} \quad (15)$$

where, $p(i)$ and TDB represents the precision and total number of images in the database.

4. Experimental results

The proposed multiple features integrated CBIR framework is implemented in the MATLAB R2013a environment with the dual-core processor, 2 GB memory and 64 bit windows operating system and its performance is investigated over the Corel-10k¹ and OT_scene² databases. Figure. 2(a) shows sample images from the Corel database. Corel-10k contains 10000 images of resolution either 126×187 or 187×126 which are equally grouped into 100 classes. Therefore, each class has 100 images. OT-scene database has totally 2,688 images of 8 distinct groups such as coast, forest, intercity, highway, mountain, open country, tall buildings and street. In this database, all the images are in the resolution of 256×256, each group contain different number of images in to it and some of the images from this database is shown in Fig. 2(b).



Fig.2. Sample images from the (a) Corel (b) OT scene database

In order to estimate the retrieval accuracy, each image of the database acts as a query to perform the similar image search. The retrieval precision of the color and texture feature involved in this proposed work is depicted in Fig.3.

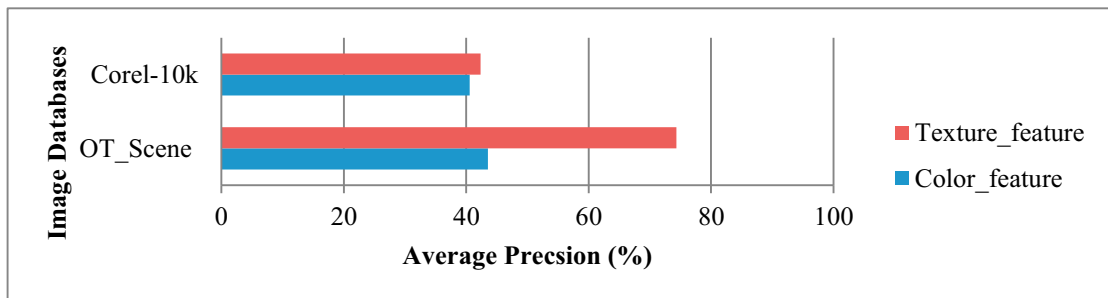


Fig.3. Average precision rate of the color [30] and texture feature [29] of the proposed work.

¹Corel-10k Database: <http://www.ci.gxnu.edu.cn/cbir/Dataset.aspx>

²OTScene Database: <http://cvcl.mit.edu/database.htm>

The retrieval accuracy of the color feature extraction method used in Corel-10k and OT_scence database is low compared to the retrieval accuracy of the texture feature extraction method involved in this work. However, retrieval results obtained from color and texture feature extraction methods are not always the same. Thus, integration is needed between them. Figure 4 gives the results of assigning the same weight for each feature involved in feature integration and PSO based feature integration method.

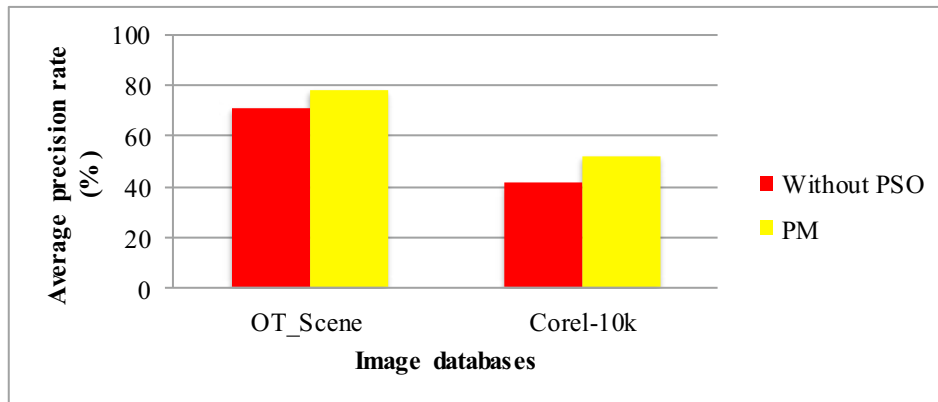


Fig. 4. Average precision rate of color [30] and texture feature [29] integration with equal weight (without_PSO) and with PSO (PM)

The retrieval precision of the feature integration method using the PSO gives more relevant result than the feature integration based on equal weight assignment. Moreover, Fig.4 reveals that the feature integration without the optimization techniques, results is improved compared to the retrieval result of the individual feature based CBIR system. It shows that the feature integration approach has a high impact on the individual feature based CBIR system. Moreover, the image does not have an equal probability of feature into it (i.e.: not all the features equally contribute in representing the image). Thus, PSO based feature integration system has achieved a high retrieval rate of 78.43% and 52.34% over OT_scence and Corel-10k database respectively in CBIR system. Figure 5 shows the retrieval results of the state-of-the-art CBIR techniques based on the combination of multiple features. The feature integration method suggested by Fadaei et.al [32] achieved 55.74% and 43.62% precision over the OT-Scene and Corel-10k. Even though PSO based integration is preferred in [32] this work, the choice of feature extraction methods is responsible for the result. Likewise, the color and texture features based on the PSO based clustering method limits the average precision of the OTscence and Corel-10k databases as 57.98% and 42.11% respectively. Moreover, Fig. 5 illustrates that the feature integration method [26] by sharing equal weight has low performance in CBIR system.

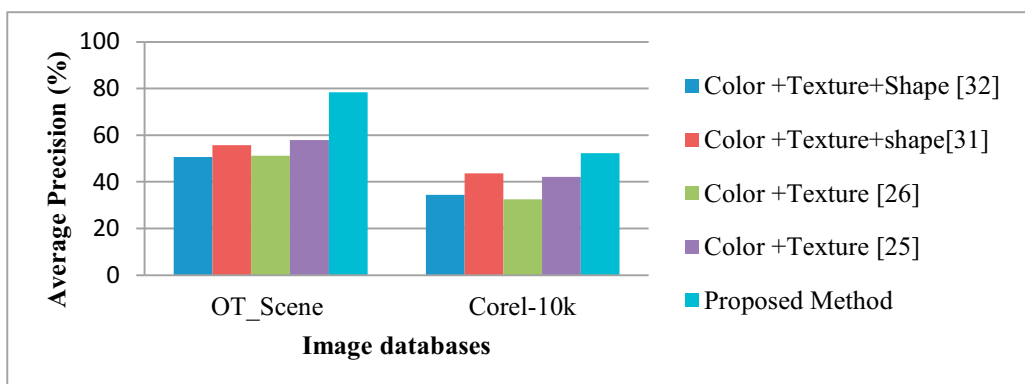


Fig. 5. Average precision rate of feature integrated methods [32],[31],[26],[25], and proposed method.

The effect of the image selection rule is studied and the corresponding results are given in Fig. 6. The number of images involved in the optimized CBIR is minimized by the mean and standard deviation based image selection rule used in the initial level of this work. Thus, the search space of a similar image search is narrow down which increase the retrieval speed of the proposed CBIR system.

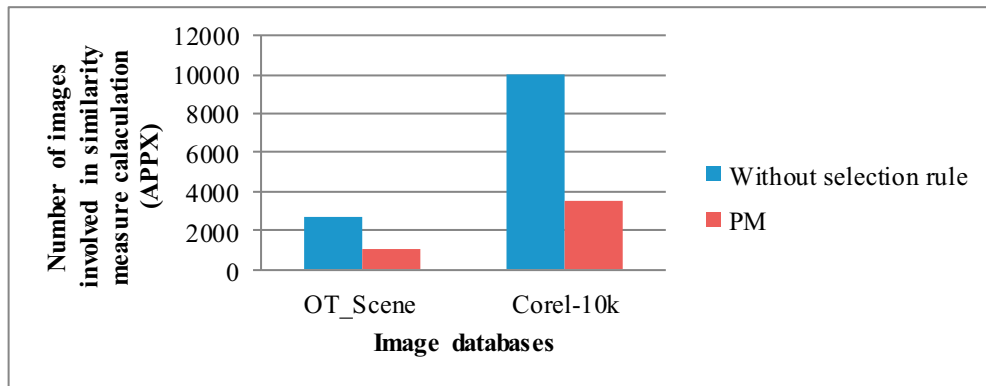


Fig. 6. Number of images involved in proposed and other CBIR system

5. Conclusion

The proposed work reduces the search space of the retrieval system based on the mean and standard deviation of the images involved in the retrieval task and clustered mean of the database images. Moreover, the proposed work achieved high retrieval accuracy over the OT-Scene and Corel-10k databases by integrating the prominent color and texture features of the image with the help of the PSO technique. The performance in the proposed work is high compared to the other state-of-the-art techniques of the CBIR systems.

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Object Detection In Underwater Acoustic Images Using Edge Based Segmentation Method

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Abstract

Image segmentation techniques play a vital role in partitioning the image into segments. These techniques are used for detecting the objects in the images. The real challenge in the acoustic image segmentation lies in differentiating the sea floor, sediments and the objects. Due to the typical characteristics and low resolution of the acoustic images, segmentation techniques such as region based, morphological based and edge based methods are not suitable. The sediments will also be traced along with the objects that makes the detection process a very difficult one. In this research paper, edge based segmentation method that uses the morphological operations for identifying the edges followed by a object tracing algorithm is proposed. The images used in this work are captured in real time using Edgetech 4125 Side scan sonar device. The acoustic images are first pre-processed using Wiener and Median filters and a morphological gradient is obtained by subtracting the morphologically dilated and eroded image. Next the edge map of the acoustic images are obtained using binarization method by which the object's boundary is made visible. Finally a Moore's object tracing algorithm is used for detecting the objects in the images.

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Keywords: Acoustic; Edges; Object; Morphological; Segmentation; Sonar;

1. Introduction

Underwater exploration is a challenging task as it involves searching for things that are unusual and unexpected. It helps in managing the ocean resources. Image processing plays a major role in revealing the mystery and the wealth of deep sea. The acoustic imaging system helps to capture the images that are present under water such that it is useful for any further investigation and exploration.

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Acoustic instruments are used for searching the surface of the ocean. Today, Sonar systems become a common acoustic-based technology for underwater exploration. SONAR (Sound Navigation And Ranging) is a technology used to detect and locate objects under the water. Side scan sonar [26] is one of such instruments used for detecting the objects in seafloor. The side scan sonar helps in accurate mapping of large sections of the seabed, locate pipeline or cable routes, obstructions and other features. Specifically, shipwreck location, mine hunting, downed aircraft search and lost cargo operations all require the use of side scan sonar.

The images of the seafloor are taken using sound as the source. This is due to the degradation in the optical visibility range in sea water which is caused by the presence of suspension, turbidity of water, unavailability of light source in deep sea. The sound waves are used to capture images in spite of turbid water and low visibility. The acoustic energy penetrates the mud and silt that causes turbidity and has the capability of capturing images in deep sea where human's presence is impossible. Hence the range of acoustic systems is greater than the optical systems. But the resolution capacity of acoustic imaging systems is lower than the optical image system.

Edge detection is a preprocessing technique that aims at identifying the boundary of the objects. There are many image processing techniques using various filters that detect the edges. The edges in the images are obtained by calculating the first and second order derivative [2][3]. These techniques may detect true edges if the foreground object is distinguishable from the background in an image. In case of texture images where the boundary is very different to differentiate, these filtering techniques may lead to false edges. The images used in this work are acoustic images obtained by side scan sonar. The acoustic images contain speckle noise caused by the instrument [9]. So there is a need for new edge detection technique that differentiates the object in the sea floor from the sediments and surface. This work aims at finding the true edges that are real objects using morphological techniques and then a boundary tracing algorithm is used for object detection.

2. Related Work

The acoustic images obtained from side scan sonar are texture images that contain seafloor, sediments and objects (both living and non living). Many researchers focus on detection and classification of the object lying under the sea bed. Many different works have been carried out for segmenting the acoustic images and to detect the objects. Some of the works similar to our proposed research work have been reviewed. In order to perform image segmentation, a combination of texture and spectral analysis [1] was proposed. For analysing the spectral features, Directional Filter Bank (DFB) was used and for deriving the texture features, Grey Level Co-occurrences Matrices (GLCM) was used. The acoustic images contains the texture features containing different regions. An active contour model is then applied to the original image. The segmentation method proposed by [4] readjusts the weights attached to each feature by modifying the feature selection step. The drawback of the method is the sensitivity to initialization.

A novel method was proposed by [6] for segmenting the side scan sonar images. This uses K-means clustering algorithm which is an unsupervised learning algorithm used to segment the image into various regions. The region based segmentation methods are well accepted ones for object detection. The authors [7] have done object detection in three steps. An object detection model is first used for positioning the objects and in next step, background location is determined using background prior. These steps are followed by region merging segmentation method. This method seems to be an automatic method for object detection in underwater images. Medical images are considered to be similar to underwater acoustic images as both are texture and gray scale images. Based on Tsallis and Shannon entropy a new edge detection algorithm was proposed for recognizing the human organs in the medical images. Due to the noise and geometric features [8] of the images, the edge detection techniques cannot be used for identifying the true edges.

Some methods perform image enhancement before detecting the objects from the images. As a preprocessing step in object detection dynamic brightness assignment is done [9]. The author [10] has done a comparative study on edge detection algorithms which were applied on noisy image using morphological filter. A work has been carried out by [11] for detecting the edges using the combination of mathematical morphological operators such as erosion, dilation, opening and closing.

Other than the texture images morphological operators have been generalized and used on complex signals [12]. Edge detection becomes more challenging when the objects remain in the dark regions. The traditional operators perform edge detection by first applying the gradient operators and then performing threshold. The method which uses pseudo top-hat transformation of the mathematical morphological edge detection algorithm [13] proves

to detect the edges in the dark regions and also preserves distinguished features. In this method, thresholding is done using recursive quad tree decomposition scheme. Hidden Markov Chain (HMC) model along with non decimated wavelet have been used by [14] for detecting the edges in the images. EM (Expectation Maximization) algorithm has been used for training the model and Viterbi algorithm has been used for revealing the hidden state of each coefficient.

Many research works have been carried out for side scan sonar images including correction of brightness variation and patching gaps [15]. Due to the constantly changing attitude of the towfish the images are difficult to read. A voting based approach [16] applied directly to the edges recognizes the objects using priori known models. The drawback of this method is recognizing a single segment in the image. Detection, classification and identification of objects in side scan sonar [18][22] was done using six different screening algorithms. A marker based watershed transform [19] was used for detection of objects in salient regions and their cast shadows. Acoustic shadows provide useful information about the object's shape and are considered as salient regions. The work proposed by [20] has used mean shift clustering based segmentation technique for isolating the regions in an image. The reliability aware fusion of features were computed and used for different data set. For automatic detection of objects in underwater acoustic images obtained by forward looking sonar, the object's echo shape is segmented by removing the ground echo shape. This separated shape is compared to the simulated reference shape to know its orientation or to identify the shape using shape matching method.

A symmetric bank of Gabor filters are used for filtering the images and then a morphological closing operator [23] was applied on the filtered image. Then active contour model are used for segmenting areas with different textures. The advantage of this method is multiple texture regions are identified easily. This method doesn't use edge features for segmenting the regions. In order, to reduce the high computational effort and time, programmable logic technology was used by [24]. In this work, they have divided the image into three regions such as acoustic highlight, seafloor reverberation and acoustic shadow areas. They have applied adaptive methods for different regions. A 3D segmentation method [25] for underwater acoustic images has been done. They have used RANSAC (RANDOM Sample And Consensus) algorithm through which a super quadric primitives are directly recovered from raw data without any pre-segmentation processing. Using evolutionary algorithms [29] have done 3D reconstruction of underwater scenes using DIDSON acoustic sonar image sequences.

In the literature, many researchers have used various segmentation algorithms for object detection. In the generic images, the objects were separated into background and foreground objects and were easily differentiated using region based and morphological based segmentation algorithms. But the object detection in the acoustic images are really challenging as they are texture images. It is very difficult to differentiate the objects from sea floor and sediments. In our research, we have used edge based segmentation method and object tracing methods for object detection.

3. Segmentation Techniques

The edges in the images can be detected using segmentation techniques. The segmentation techniques can be classified as region based and edge based segmentation.

3.1 Region based segmentation techniques

There are methods such as thresholding, region growing, region splitting and region merging that determines the edges in the objects. As the edges are the changes in the intensity of the pixels, the neighboring pixels are examined to determine the connected components. The region based methods considers the image as a whole and starts to evaluate all the pixels in the images.

3.2 Edge based segmentation techniques

The change in the intensity can be identified by differencing adjacent pixels. The process of finding the first order derivative can be done by convolving the filter to the image. Based on the values in the filters, the edge detectors are classified into Robert, Prewitt, Sobel and Canny. These edge detectors identify the edges in both horizontal and

vertical directions. They use two different templates for determining the horizontal and vertical edges. The complete edge map is obtained by adding the horizontal and vertical edges.

Some of the edge detection operators such as Robert and Sobel don't perform edge linking. So the object boundary may not be visible. But the Canny edge detector identifies the edges and also performs the edge linking by smoothing the image, localizing the edges and thresholding for finding the true edges. The acoustic images that are texture images containing only seafloor and sediments. These are considered to be the connected components and it leads to clumsy edges.

4 Proposed Method for Edge Detection in Acoustic Images

The edge map is generally used for tracing the objects in an image. Identifying the true edges is the challenging task in detection. In acoustic images, this process is even more crucial since the sediments and the sea floor cannot be differentiated from the object in the obtained edges. The proposed method for edge detection first uses the Wiener filtering to remove the speckle noise. The speckle noise is the granular noise caused by the sonar which is used for acoustic image acquisition. The filtering process smooths the image and preserves the high frequency components. Next step is smoothing the image using median filter which removes the small objects which is the sediments in our acoustic image.

Morphological processing is generally used for finding the shape of the objects by obtaining the local minimum and local maximum. This process includes erosion and dilation. The morphological gradient is used to obtain the edges in the images by using the difference of the dilated image and the eroded image. The resultant edge map is compared with the state of art edge detection techniques such as Canny and Sobel and used for tracing the objects in the images. The Figure 1 shows the block diagram for edge detection process.

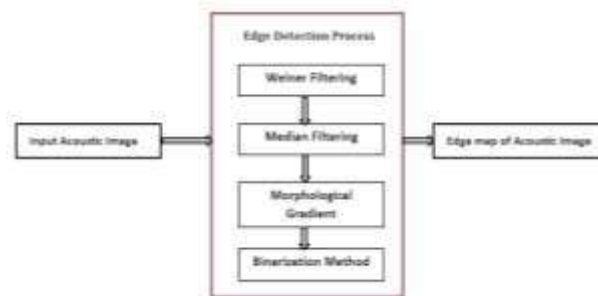


Figure 1: Block Diagram for Edge Detection Process

5. Results and Discussion

5.1 Experimental Results

The figures 2 shows the experimental results of the edge detection process for the input acoustic images 1 and 2. Figures 2.b) and c) represents the output of the preprocessing stage after applying wiener and median filters respectively. Figures 2.d) and e) indicates the output of Canny and Sobel edge detectors. The Figure 2.f) denotes the output of the proposed system. The output of both the Canny and Sobel operators reveals that they have detected false edges and ignored true edges. One of the characteristics of Canny edge detector is the edge linking property. It is obvious from the figure that the sediments and the sea floor also gets linked to create false edges. In Sobel, output true edges have been ignored. But the output of our proposed morphological based edge segmentation have detected only the true edges that is boundaries of the true objects and have avoided the edge linking.

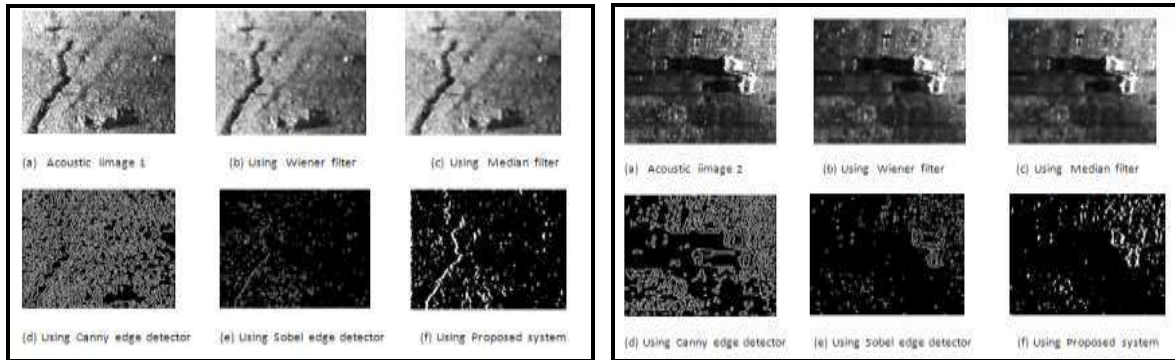


Figure 2: a) Acoustic Image1 b) Output of Wiener filter c) Output of Median Filter d) Output of Canny edge detector e) Output of Sobel edge operator f) Output of Proposed system

6 Boundary Tracing

Boundaries are the set of pixels in which the elements are edges in the binary image. The objects in the acoustic images are detected using the Moore's neighbor algorithm. Using this procedure, the boundary of the objects in the acoustic images are traced.

Procedure: Moore's neighbor algorithm

Input: Binary image with detected edges as white pixels

Output: Pixels forming the boundary of an object

- 1: Scan the pixels from leftmost corner of the image till a edge pixel is found
- 2: An edge pixel is considered as the starting point for tracing
- 3: Using eight neighborhood, the connected components for the starting pixel is determined.
- 4: A boundary is drawn over the connected pixels
- 5: The process is repeated till all the pixels are scanned

6.1 Experimental Results

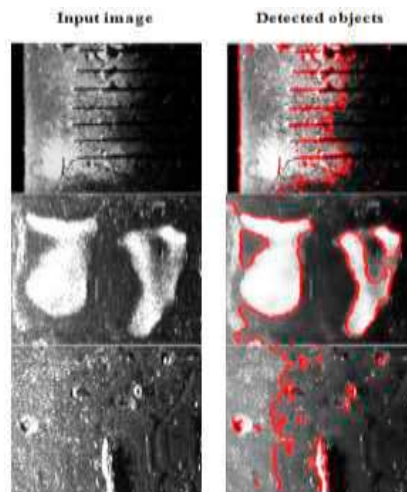


Figure 3: Objects Detected in Acoustic images using edge based segmentation and boundary tracing method

7. Conclusion

This work aims at detecting the objects in the acoustic images. Before detecting the objects, the edges available in the images are identified. The speckle noise in the images is removed using Wiener filter and to still smooth the image, median filter was used. After preprocessing the image, edges are obtained by finding the morphological gradient. The morphological gradient is obtained by differencing the dilated image and the eroded image. The dilation process thickens the edges in the image whereas the erosion process shrinks the boundaries. When gradient is calculated only the true edges are retained and the false edges are ignored. The output of these steps leads to a binary image with edges. The objects in the acoustic images are detected using Moore's object tracing algorithm which uses the neighborhood operations to find the connected components. In visual perception the results show that the objects in the acoustic images are traced in a better way.

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Resource Scheduling Algorithms for Cloud Computing Environment: A Literature Survey

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Abstract

Nowadays, resource scheduling in cloud environment is a challenging task as the number of customers increases for utilizing the cloud services. In this cloud environment, allocation of suitable resources to the corresponding VM depends on the QoS requirement of the specified applications. Researchers have developed so many resource scheduling

algorithms. However, the service providers in cloud environment still find it difficult to choose the appropriate algorithm for their applications. This is due to the heterogeneity of resource types, interdependencies, uncertainty and dispersion of assets in the cloud environment. This paper reviews all the available load balancing algorithms in a nutshell.

Keywords

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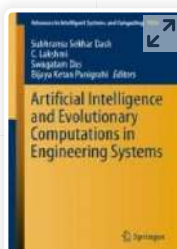
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Modern Parking Business Using Blockchain and Internet of Things (IoT)

[Varun V. Narayanan](#), [M. V. Ranjith Kumar](#) , [Kartik Saxena](#), [P. Madhavan](#) & [N. Bhalaji](#)

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Abstract

This paper aims to deliver a sustaining business model by analyzing the market-trends of the bitcoin, develop a blockchain-based transaction system to run the errand and deploy an IoT-based, low-investment platform for ensuring profits in the long run. The existing monetary systems and investment platforms are discussed

in detail and various inferences have been drawn from the trend of cryptocurrencies and world economy. An example of running a fully-automated, modern parking facility is used to demonstrate how this business would continue to grow as the demand-supply chain can be partially controlled. To the best of our knowledge from extensive literature survey, it can be a very promising investment for corporates and governments.

Keywords

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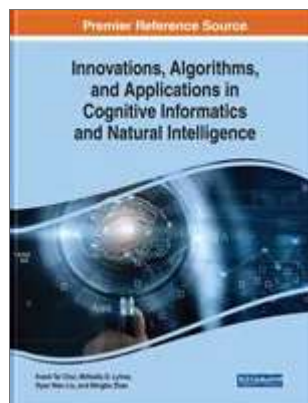
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Inter-Hemispherical Investigations on the Functional Connectivity in Controls and Autism Spectrum Using Resting State fMRI ☒

S. Vidhusha, A. Kavitha

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Abstract

Autism spectrum disorders are connected with disturbances of neural connectivity. Functional connectivity is typically examined during a cognitive task, but also exists in the absence of a task. While a number of studies have performed functional connectivity analysis to differentiate controls and autism individuals, this work focuses on analyzing the brain activation patterns not only between controls and autistic subjects, but also analyses the brain behaviour present within autism spectrum. This can bring out more intuitive ways to understand that autism individuals differ individually. This has been performed between autism group relative to the control group using inter-hemispherical analysis. Indications of under connectivity were exhibited by the Granger Causality (GC) and Conditional Granger Causality (CGC) in autistic group. Results show that as connectivity decreases, the GC and CGC values also get decreased. Further, to demark the differences present within the spectrum of autistic individuals, GC and CGC values have been calculated.

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Introduction

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Autism is a brain disorder that involves multiple functional networks. Many researchers have indicated the variations present in the autistic individuals (Aghdam et al. 2018). While a growing number of studies indicate that functional connectivity analysis between selective brain regions can highlight pivotal differences in typical controls and autism patients, multiple studies and reports differences within the spectrum of autism (Aseña, 2016). The autism spectrum is mainly categorized into low functioning and high functioning autism (DSM-V, 2013). A few studies suggest strong connections in sub regions of the high functioning autistic brain with a deficiency in long range connectivity (Chei et al. 2015). According to Derdikman et al. (2013) persistent atypical fMRI records (Aghdam et al. 2018) indicate that the brain functions differently in autism. Such differences might be explained by a combination of factors such as task regression field of view and low pass filtering.

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Task based studies dominated functional neuroimaging till functional scans of resting subjects were acquired and the correlation of a seed (Wang, Y., 2014) defined in the frontal-parietal cortex with respect to the rest of the brain was computed. This revealed that even in the absence of a task, regions performing similar functions or regions that would be modulated by a task exhibit functional connectivity (Ding et al. 2006). Numerous studies have been experimented with EEG and MEG analysis that highlight variations between controls and autism subjects using brain signals (Blinowska, 2011). But, to intuitively signify the relative differences in the brain regions for low functioning and high functioning autistic individuals, has sparked an interest in analyzing the functional connectivity using resting state fMRI (rs-fMRI).

rs-fMRI studies have also confirmed the existence of a default mode network, that is particularly active during resting periods and whose activity diminishes while performing a task. This network has been found to include the posterior cingulate cortex (PCC), ventral medial prefrontal cortex (vmPFC), inferior parietal lobule (IPL), lateral temporal cortex (LTC), dorsal medial prefrontal cortex (dMPFC), and parahippocampal gyrus (PHC) (Dodel et al, 2005). Of these, posterior cingulate cortex, medial and lateral parietal cortex and medial prefrontal cortex were chosen (Torres, G., 2013) as the task negative regions (i.e. regions whose activity decreased during the performance of an attention-demanding task) while from other fMRI studies (Goswami et al, 2006) task positive regions- intra parietal sulcus (IPS), frontal eye field (FEF) and middle temporal region (MT) were identified (Subbaraj, P. K et al, 2014) and from the connectivity based correlation and conjunction analyses (Goswami et al, 2006) these task positive and negative regions were found to be anti-correlated. The study focused on control subjects while also a comparison on the task positive and negative regions in autism subjects with those in the control has also been performed.

Functional connectivity provides a measure of temporal correlations between secluded physiological events (Kana et al, 2006). It is different from effective connectivity which depends on an apriori model for the cases of causal mode of relationship. Functional connectivity using fMRI (Chengaiyan, S., & Anandhan, K., 2015) was studied on the regions of motor cortex of resting state human brain using the relevance of product moment correlation of BOLD time courses. Functional connectivity measures can be tested for its implication and the reliability of functional connectivity among the nodes infers the strength of the integration of nodes (Van Den Heuvel et al, 2010) is allied in the functional network.

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Start to Finish Automation Achieve on Cloud with Build Channel: By DevOps Method

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Abstract

Innovations through IoTs urge software developing industry need to come up with new life cycle model instead than usual. Process of software developments should be go along with advancements life cycle. This brings the attention for native and adoptable software life cycle process that is required for current industry standards. Manufactures are integrating the methodologies of software development process in a single bundle as automation with support of cloud with DevOps. The operation engineers, development engineers and QAs participate together for building the software applications will spin into minutes instead of days. Automation is the ultimate demand for DevOps approach. This approach advents continual automation to the software life cycle is known as delivery. This continually performs the tests and analysis of code. The developers provision and build the software into their cloud environment. Every step in the continuous delivery can be repeated in a several time a day depending on how much new applications need to release. Automation in DevOps improving speed of development, precision, consistency and increases the number of delivery.

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Keywords: Cloud; DevOps; Automation;

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Visual Speech Recognition using Fusion of Motion and Geometric Features

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Abstract

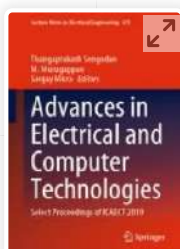
The Visual Speech Recognition (VSR) system performance is highly influenced by the selection of visual features. These features are categorized into static and dynamic features. This work proposes to exploit both lip shape (static-geometric features) as well as the temporal sequence of lip movements (dynamic-motion features) to build a combined VSR system with fusion both at feature level and model level. The digit dataset for VSR system is evaluated on the benchmark (using Discrete Wavelet Transform (DWT), Discrete Cosine Transform (DCT), and Zernike Moments (ZM)) systems. First, the Motion History Image (MHI) is calculated from all visemes from which wavelet and Zernike coefficients are extracted and modeled using a simple GMM L-R HMM. This proposed method shows a significant improvement in performance of 85% for MHI-DWT based features, 74% for MHI-DCT and 80% for MHI-ZM features. Geometric features are extracted using an Active Shape Model (ASM). Two types of fusion, namely feature fusion and model fusion are used. In feature level fusion, the motion features (MHI-DWT, MHI-DCT, and MHI-ZM) with geometric features (ASM) and modeled using GMM L-R HMM. The performance improves for combined features with an accuracy of 96.5% for DWT-ASM, 84% for DCT-ASM, and 93% for ZM-ASM. Model level fusion is performed using a two stream HMM model with stream weight of DWT-ASM, DCT-ASM, and ZM-ASM features. A weighted model level fusion results in further improvement, with an accuracy of 98.2% for DWT-ASM, 85% for DCT-ASM and 94.5% for ZM-ASM. The proposed work result achieves high recognition for VSR systems compared to the benchmark systems (DWT, DCT, and ZM).

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Keywords: Motion History Image, Zernike Moments, Active Shape Model, Hidden Markov Model, Discrete Wavelet Transform, Discrete Cosine Transform, Gaussian Mixture Model

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Tweet Classification Using Deep Learning Approach to Predict Sensitive Personal Data

[R. Geetha](#) , [S. Karthika](#) & [S. Mohanavalli](#)

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Abstract

Twitter is one of the most successful online social networks that present user's opinions, personal experience, daily activities and ideas to the world. The analysis of user tweets gives various interesting perspectives of vulnerable cyber-crimes and information losses in the microblogging platforms. This research work analyzes 280 k tweets that were queried using 23

personal cyber-keywords to predict personally sensitive tweets. The personal tweets were annotated based on the proposed rules developed from the privacy standards defined by well-established organizations like NIST. The most influential textual features are extracted using auto-encoders optimized with word embedding techniques. The manually annotated tweets were trained and modeled using recurrent neural network to classify tweets as sensitive and insensitive personal tweets. The sensitivity model was evaluated with activation functions like ReLU, sigmoid, and softmax under varied hyper-parametric conditions. The model with three hidden layers with ReLU and softmax resulted in the accuracy of 75% in identifying personally sensitive tweets.

Keywords

[Twitter](#) [Personal information](#)

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Sensitive Keyword Extraction Based on Cyber Keywords and LDA in Twitter to Avoid Regrets

[R. Geetha](#)  & [S. Karthika](#)

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Abstract

Twitter is the most popular social platform where common people reflect their personal, political and business views that obliquely build an active online repository. The data presented by users on social networking sites are usually composed of sensitive or private data that is highly potential for cyber threats. The most frequently presented sensitive private data is

analyzed by collecting real-time tweets based on benchmarked cyber-keywords under personal, professional and health categories. This research work aims to generate a Topic Keyword Extractor by adapting the Automatic Acronym - Abbreviation Replacer which is specially developed for social media short texts. The feature space is modeled using the Latent Dirichlet Allocation technique to discover topics for each cyber-keyword. The user's context and intentions are preserved by replacing the internet jargon and abbreviations. The originality of this research work lies in identifying sensitive keywords that reveal Tweeter's Personally Identifiable Information through the novel Topic Keyword Extractor. The potential sensitive topics in which the social media users frequently exhibit personal information and unintended information disclosures are discovered for the benchmarked cyber-keywords by adapting the proposed qualitative topic-wise keyword distribution approach. This experiment analyzed cyber-keywords and the identified sensitive topic keywords as bi-grams to predict the most common sensitive information leaks happening in Twitter. The results showed that the most frequently discussed sensitive topic was 'weight loss' with the cyber-keyword 'weight' of the health tweet category.

Keywords

[Twitter](#)[Cyber-keywords](#)[Privacy leaks](#)[Regrets](#)[Social media](#)

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Social Media Veracity Detection System Using Calibrate Classifier

[P. SuthanthiraDevi](#)  & [S. Karthika](#)

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Abstract

In the last decade, social media has grown extremely fast and captured tens of millions of users are online at any time. Social media is a powerful tool to share information in the form of articles, images, URLs and, videos online. Concurrently it also spreads the rumors. To fight against the rumors, media users need a verification tool to verify the fake post on

Twitter. The main motivation of this research work is to find out which classification model helps to detecting the rumor messages. The proposed system adopts three feature extraction techniques namely Term Frequency-Inverse Document Frequency, Count-Vectorizer and Hashing-Vectorizer. The authors proposed a Calibrate Classifier model to detect the rumor messages in twitter and this model has been tested on real-time event#gaja tweets. The proposed calibrate model shows better results for rumor detection than the other ensemble models.

Keywords

[Rumor](#)

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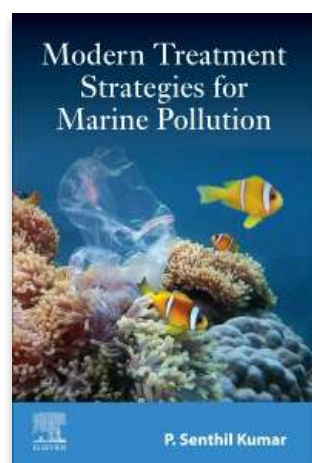


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Modern Treatment Strategies for Marine Pollution provides an overview of assessment tools that identify contaminants in marine water, also discussing the latest technologies for removing these contaminants. Through templated and consistently structured chapters, the author explores the importance of seawater to our marine ecosystems and the devastating effects pollutants are causing. Sections cover the emission of toxic pollutants from industries, wastewater discharge, oil spills from boarding ships, ballast water emission, abnormal growth of algal blooms, and more. Techniques explored include huge diameter pipelines erected for removing floating debris from seawater, which is denoted as a primary idea for cleaning contaminants.

The book includes numerous case studies that demonstrate how these tools can be successfully used. It is an essential read for marine ecologists and oceanographers at the graduate level and above, but is also ideal for those looking to incorporate these techniques into their own work.

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Enzyme inhibitors play a pivotal role in pharmaceutical and nutraceutical industries. The primary understanding of the action of inhibitors helps pharmacologists during the design process for developing new therapeutic drugs. Most drugs treat various chronic and life threatening diseases owing to their specificity and the potency of enzymes which they can inhibit. Enzyme inhibitors are used to screen various levels of diseases which propel the growth of inhibitors. The potential for enzyme inhibitors in the therapeutics market is very high as the biochemical properties and classes of enzyme inhibiting products are readily available.

The other broad aspect of enzyme inhibition is their application in analytical sensors. These sensors assist in monitoring various environmental factors. Understanding the mechanism of inhibition and regeneration of enzymes is a general problem of great importance for many biochemists and biotechnologists especially when using immobilized enzymes.

This reference compiles applied information about enzyme inhibitors used in medicine and environmental monitoring applications. Chapters presented in this volume cover special topics including biosensors, crop improvements in agriculture, biofuel production, pesticide and heavy metal detection, and drug therapy for human diseases such as breast cancer, neurological diseases and viral infections.

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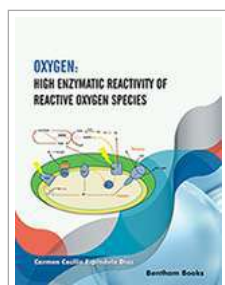
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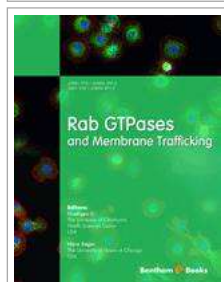
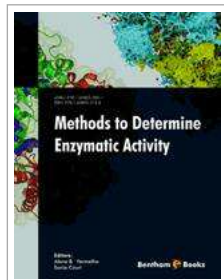
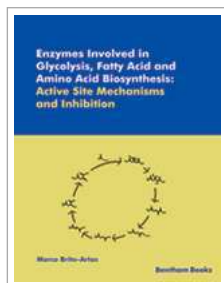
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Subramanian Senthilkannan Muthu
Editor

Environmental Footprints of Recycled Polyester

 Springer

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Series Editor

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This series aims to broadly cover all the aspects related to textiles science and technology and clothing science and technology. Below are the areas fall under the aims and scope of this series, but not limited to: Production and properties of various natural and synthetic fibres; Production and properties of different yarns, fabrics and apparels; Manufacturing aspects of textiles and clothing; Modelling and Simulation aspects related to textiles and clothing; Production and properties of Nonwovens; Evaluation/testing of various properties of textiles and clothing products; Supply chain management of textiles and clothing; Aspects related to Clothing Science such as comfort; Functional aspects and evaluation of textiles; Textile biomaterials and bioengineering; Nano, micro, smart, sport and intelligent textiles; Various aspects of industrial and technical applications of textiles and clothing; Apparel manufacturing and engineering; New developments and applications pertaining to textiles and clothing materials and their manufacturing methods; Textile design aspects; Sustainable fashion and textiles; Green Textiles and Eco-Fashion; Sustainability aspects of textiles and clothing; Environmental assessments of textiles and clothing supply chain; Green Composites; Sustainable Luxury and Sustainable Consumption; Waste Management in Textiles; Sustainability Standards and Green labels; Social and Economic Sustainability of Textiles and Clothing.

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Editor

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LCA (Life Cycle Assessment) on Recycled Polyester



Aravin Prince Periyasamy and Jiri Militky

Abstract Polyester is a synthetic material which is produced from the petroleum products. The various environmental impacts are associated with polyester from manufacturing to end of life. Therefore, the manufacturing of recycled polyester (rPET) is an important process as concerned with environmental impact and also inevitable. The rPET has a wide scope of their potential applications similar to virgin polyester. Generally, life cycle assessment (LCA) technique investigates the environmental impacts of the particular products from its cradle to grave. Therefore, it helps to identify the critical phase which creates the maximum impact on the entire product life cycle. So, it is significant to understand the environmental impact of rPET, nevertheless, LCA on rPET is foreseeable. The data from the LCA can initiate preliminary steps to reduce the environmental burdens from the products, also it provides the detailed information on how it affects the ecosystem. In this chapter we discussed about the LCA on rPET, initially, the brief introduction will be provided about the present manufacturing techniques of rPET. Various issues associated with sustainability of rPET manufacturing, importance and methodology of LCA on rPET were explained in detail. Based on the LCA results, the important parameters with respect to the sustainability of rPET would be present in this chapter.

Keywords Cradle to grave · Polyester · Recycling · LCA · GWP

1 Introduction

The several natural fibers were chiefly used for the production of textiles and garments until the seventeenth century [1, 2]. Either way today's situation differs, according to the development of synthetic fibers in the late 1930s, these fibers are now largely used for textiles [3]. Polyester fibers are the examples of synthetic fibers containing ester groups in their main polymeric chain [4]. Polyethylene terephthalate (PET) having the ester group and generally known as polyester. In 2018, 106 million tons of global

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production compared to 25% cotton fibers, however, polyethylene terephthalate produced and consumes higher than any other textile fibers [5]. Eco-friendly industries and eco-friendly industrial practice has been promoted by the awareness created on environmental concerns. In the case of environmental benefits, the classical 3R can be implemented in the rPET industry, also it must be promoted to make awareness to the consumers [6, 7]. As it is known recycling is not new with vast history [8]. Last two decades, the awareness of sustainability and waste management results protection towards to the environment by practicing the more and more recycling process. Humanity poses large problems mainly due to plastic and polymeric waste in which crude oil is the first non-renewable materials which is the raw materials to produce various thermoplastic materials including the textile fibers. Majority of the synthetic materials consists of larger molecular size and rigid structure resulting non-biodegradable and non-decomposable. Accounting into the problems above it is advisory to recycle plastics and polymers and recycling motivates to decrease or lower landfill expenses, compared to virgin plastics recycled polymers are cheaper and further energy can be recovered from the plastic through various process [9]. 60% of the global PET produced with high-molecular weight further utilized to produce the textile fibers and 30% of PET is utilized to produce the bottles and other articles [10]. According to the reference [11], 70–80% of crude oil is used to produce virgin polyester, among them only 30–40% were recycled. Therefore, it is necessary to take attention which increase the recycling percentage, resulting the reduction of the environmental burdens by landfilling as well as carbon emission. In order to reduce our carbon footprint, larger companies receive tons and tons of paper and plastic which is recyclable. However, some of the statistics says 91% of plastics are not recycled, apart from that people buy millions of plastic bottles (food, beverages, water etc.) per minute [12]. In 2015, approximately 20% of textiles were reused in Sweden [13], in 2018 it can be increased to 40% as per the Swedish Environmental Protection Agency (SEPA) [14] and is predicted to increase further 20% in 2020. Figure 1 shown the recycled PET bottles% in various forms in the USA. Public imagination has been gathered by the idea of using recycled PET materials including bottles, molded articles, textile fibers, buttons etc. The concept of recycling has become green option, since it reduces the energy requirement for the production of virgin PET also reduce the consumption of non-renewable resources.

Generally, the textile wastes can be classified into three types, which are [15]:

- Wastes from pre-consumer stage
- Wastes from post manufacturing
- Wastes from post-consumer stage

Pre-consumer stage waste is defined as waste generated during the production, for example in textile productions, short fibers in the spinning, yarns in both weaving and knitting and fabrics from garment cutting and many. Generally, these wastes can be reused and produce different products, for example the short fibers were used to produce the coarser (i.e. thicker) fabric. After manufacturing, products having the defects are classified into the wastes from post manufacturing stage, perhaps it can

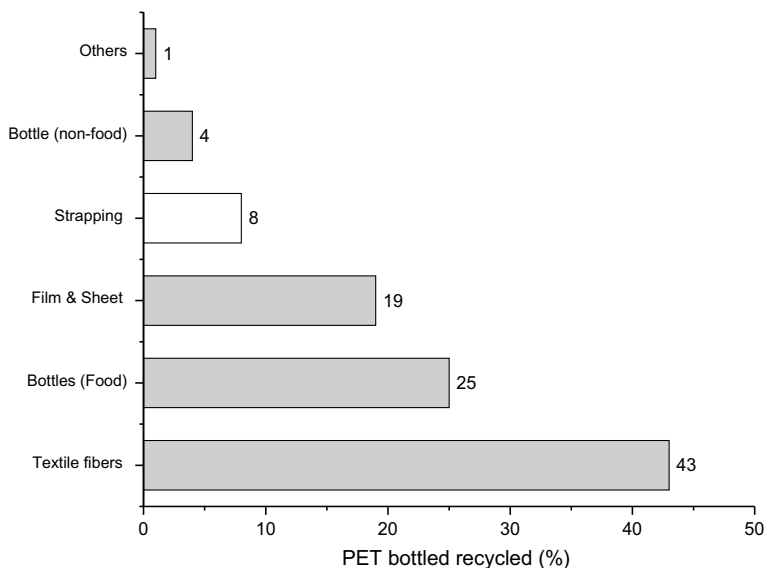


Fig. 1 Percentage of PET bottles recycled in various forms in the USA (2017)

be sold to very less price to the consumers or it will be reused and produced as same or different products.

To make rPET it includes the recycling of the accessories and beverage bottles as an example. Figure 2 summarizes the various routes of recycling and reuse of textiles. In any process waste is inadvertent and it has to be reused for the improvement of the environment. Recycling is the best solution for the polyester textile which drastically reduced the carbon emission and saves the energy as compared to virgin PET manufacturing.

If the materials were recovered from the waste use it again is called as reuse, whereas, after recovering, modify into the product is called recycling, meanwhile the recycled product is higher values than the original product is called as upcycling and lower values is called downcycling. There are four approaches for the recycling which is well explained in Fig. 3. Primary recycling defines the recycle of waste into original products. Recycling the post-consumer plastic waste into new products with reduced properties may classified into secondary recycling. Production of fuel or monomer from the PET waste are classified into tertiary recycling approach [17].

2 The Life Cycle Assessment Methodology

LCA is the method to evaluate the environmental performance of the products throughout the cycle, starting from raw material to its last stage of cycle. In accordance

to the ISO standard, life cycle assessment can be conducted with four phases namely (Fig. 4) [18–20]. First stage comprises of aim of study and describe all the products that are assessed. In the second stage of inventory the raw material is acquired to the process of development to its final information of the product are collected [21]. In order to develop, calculate the data of discharge from the process of the life cycle of the product in this stage energy consumption, raw material requirement, environmental emission and discharged are figured and calculated. The third stage is impact assessment stage the data of inventory are translated into the effect of human health, ecological health and resource depletion. The last stage of the life cycle assessment is the interpretation where the results are interpreted and discussed. The four stages of LCA has been described graphically in Fig. 4.

- Goal and scope,
- Inventory analysis,
- Impact assessment and
- Interpretation.

The first phase is “goal and scope” where the purpose of LCA study can be well explained. It is clearly discussed in ISO 14040 and 14044 standards. Inventory analysis deals with the energy and material requirement to produce the products

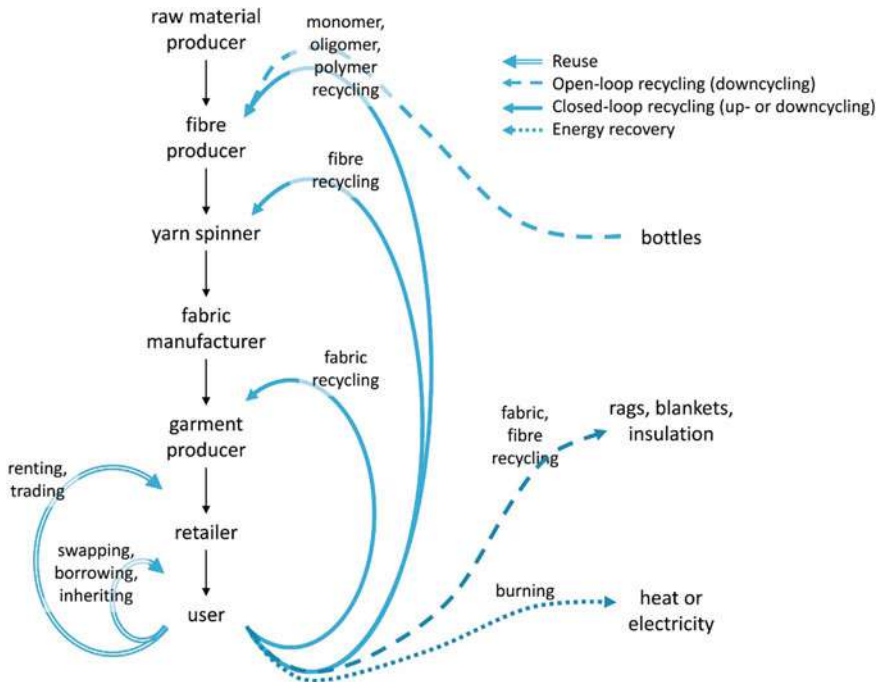


Fig. 2 Recycling and reuse routes for textile wastes, (reused under the terms of the Creative Commons Attribution license from Journal of Cleaner Productions, Elsevier Publications [16])

Refining Biomass Residues for Sustainable Energy and Bioproducts

Technology, Advances, Life Cycle Assessment, and Economics



Edited by
R. Praveen Kumar
Edgard Gnansounou
Jegannathan Kenthorai Raman
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Technology, Advances, Life Cycle
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Preface

The advent of biochemical engineering leads to the way for invention of enormous amount of bioproducts which ranges from food to fuel. Increase in demand and environmental concerns leads to the search for new and renewable technologies for the production of various value-added bioproducts. On the other hand, waste management is a prime concern nowadays as their generation was increasing due to the increasing population and improvement of people's lifestyle. Proper disposal of these wastes is examined through various technologies and reported by researchers around the world. Biorefinery technology may be a one-stop solution for management of residual biomass thereby reducing the amount of waste and producing value-added products. The concept of biorefinery is expanding, and a huge number of ideas are blooming out these days in this area. Those ideas should be properly disseminated to the community to make aware of technologies. This book entitled "Refining Biomass Residues for Sustainable Energy and Bioproducts" may be a platform for knowledge dissemination. This book consists of more recent data pertaining to the research report, which is divided into eight parts covering the major areas of biorefineries.

The first part is about the concept of integrated biorefinery systems for waste management; in this part, solid waste biorefineries and its potential applications were discussed in detailed by the authors. The second part is about the sources and operation of waste biorefineries. This part discusses about the different feedstocks and their modes of conversion.

The third part is about the industrial waste biorefineries. Microbial fuel cell using industrial waste and utilization crude glycerol that is obtained as a byproduct from biodiesel industries were investigated. In the fourth part the agroindustry waste biorefineries are studied. This part covers the production of various bioproducts using agroindustry wastes. The fifth part is about the food industry waste biorefineries. This part covers recovery and treatment of food waste for the production of platform chemicals. In the sixth part the potential advantage of marine source based biorefineries has been elaborately discussed.

The seventh part is about the life cycle assessment of waste biorefinery models. The life cycle assessment plays a vital role in the application of biorefinery concept in industrial scale. This part discusses about *Jatropha*-based biorefinery and comparative life cycle analysis of synthetic detergents and biosurfactants. The concluding part is about the economics and cost analysis of waste biorefineries. This part extensively discusses about the economics and cost analysis. Also the process design, techno-economic, and life-cycle assessments of selected sugarcane-based biorefineries in the South African context were also discussed.