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RECENT TRENDS IN CHEMICAL SCIENCES AND ENVIRONMENTAL SCIENCE

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First Edition

Editors

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Dr. Rajesh Kumar Singh,

Dr. Yashvant Rao

Thanuj International Publishers

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About the Editors

Dr. Azad Kumar currently serves as an assistant professor in the Department of Chemistry, M.L.K (P.G.) College, Balrampur. Dr. Kumar received the B.Sc. Hons Degree (2007), M.Sc. degree (2009), M.Phil. degree (2010) in Chemistry from Dayalbagh Educational Institute, Dayalbagh Agra, and the Ph.D. Degree (2018) in Chemistry from Babasaheb Bhimrao Ambedkar University (A Central University), Lucknow. Dr. Kumar is also a member of several scientific societies. His research and teaching interests include theory and application of nanomaterial synthesis and their applications, hybrid composite, photocatalysts and polymer. Dr. Kumar has published 20 research papers in peer-reviewed journals and international and national journals. Dr. Kumar is the editorial member of some international journals. Dr. Kumar is also the reviewer of some international journals. Dr. Kumar is teaching for the last 10 years in various institutes.

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Dr. Yashvant Rao presently obliges as a Nodal Officer cum Lab Manager at District Virology Laboratory, New Sadar Hospital Sahibganj-816107 Jharkhand. The District Virology Lab is installed and standardize for Global Pandemic COVID-19 (RT-PCR test) and till now 115k test completed within 6 months. Dr Rao received the B.Sc. Hons Degree (2007) at KSSPG College Faizabad Affiliated from Dr RML Awadh University Faizabad, M.Sc. (2010) from Babasaheb Bhimrao Ambedkar University (A Central University), Lucknow, M.Phil, And Ph.D. degree (2014 and 2018) in Nanoscience and Nanomedicine respectably. Dr Rao is also a member of several national and international scientific societies. Dr Rao has awarded Distinguished Scientist Award (2021) (Elsevier), Young Scientist Award (2019) National Research Association. Research and teaching based interests include theory, synthesis (green, chemical and physical), characterization (molecular and structural) of nanodevices for biomedical with application for polymer and protein based nanodevices. Dr Rao has published 14 research papers in peer-reviewed journals of springer, ACS, RSC, Nature, Future Sciences. Dr Rao has served as an editorial member of many international journals. Dr Rao completed research and teaching for more than 8 years in various institutes.

Preface of book

Our intention in publishing this book was to discuss and interpret all of the major issues in the chemical and environmental science disciplines, because this book covers such a broad range of chemical and environmental science research area. Rather, we have selected the themes and challenges, briefly defined them and demonstrated how they connect, clarified the terminology, and indicated where further research may be accessed. We hope that the result is an excellent introduction to 'chemical and environmental science. It is primarily aimed towards researchers in chemical science and related fields, but it should be accessible to new researchers as well. We have explored into more depth on issues that have received little attention elsewhere. There are several useful sources for topics such as chemical science, environmental science, nanotechnology, ionic liquids, solid waste management, photodegradation, Nanomaterial, adsorption of hazardous metals, and conducting polymers.

However we attempted to provide up-to-current knowledge, we are well aware that books may soon go out of date if they seek to provide too much detail, so we concentrated on basic concepts that should not go out of fashion too quickly. Our book differs somewhat from other texts in the chemical and environmental sciences in its concentration. We have focused on ideas and theories because we feel that a solid grasp of them will be more useful in the long run than specifics of present systems, services, and approaches. We've also highlighted the dimension since we feel it's critical to understand where the discipline and its components originated from and why some things are the way they are.

This approach is based on the research, with several references provided at the end of each chapter for convenience. Our intention is that the content of this book will be sufficient to provide a fundamental knowledge of the entire field, and that readers will refer to the references for more information and examples of the parts of which they are most interested. The conclusion words and captions, as well as the important references, at the conclusion of each chapter are intended to present the main points in a factual way.

ABOUT THE BOOK

In this book, we have selected the 19 research and review articles for publication. The chapters in this book reflect a wide range of fundamental and applied research in the chemical sciences, environmental science and interdisciplinary subjects. This book is a unique collection of full research papers as well as reviews. **In the 1st chapter**, describes advances of aviation fuel derived from renewable sources is a "DROP-IN" alternative for air transport as it has a similar high energy density and meets all the required fuel specifications. Major challenges faced by the industry with respect to the development of alternative aviation fuel are - high quality standards requirements, safety issues, wide range of operational conditions and drop-in kind with traditional aviation jet fuel. **In the 2nd chapter**, To describes significant optical features of luminescent materials have drawn immense appreciation in all walks of life including organic dyes, metal-organic frameworks, lanthanide compounds, semiconductor-based quantum dots, and carbon-based nanodots, which attribute numerous applications to these Luminescent materials. Moreover, they have been proven important in various applications, including gas storage and separation, heterogeneous catalysis, light-harvesting, chemical sensing, bio-imaging, and drug delivery. **In the 3rd chapter,** describes introduction of mixed ligand dithiolate complexes of cobalt, synthesis of mixed ligand complexes of cobalt (II) with dithiolate (1-methoxy carbonyl –1- cyano ethylene -2,2- dithiolate) and nitrogen donors. **In the 4th chapter,** Mixed ligand complexes of the type $[Ni(L)_n(dithio)]$ n=1 or 2 L= OPD, and various substituted pyridines, dithio=$(NaS)_2C=C(CN)$ COOMe.H_2O have been synthesized and characterized. **In the 5th chapter,** discussed about conducting polymers (CPs) are chemical compounds or mixtures of compounds composed of structural units formed during the polymerization process. The prospective uses of CPs, particularly in the realm of electronic manufacturing, have piqued the curiosity of researchers. I**n the 6th chapter,** BiOCl nanomaterial have been acknowledged as potential and promising environmental remediation material because of their low costs, low toxicities, and enormous stabilities as well as resourceful photocatalytic activities of various hazardous environmental pollutants including dyes, pesticides and several other organic pollutants etc.**In the 7th chapter**, discuss about polyaniline (PANI) which is reviewed as environmental remediation. **In the 8th chapter**, describe a the low cost activated carbon based adsorbent derived from the fruit of *Kigelia Africana* (KA), was characterized for effective removal of Pb (II) from its aqueous solution and determine the rate of adsorption. **In the 9th chapter**, discuss about Ionic liquid which has emerged as intriguing modern material in science and technology. To better comprehend and investigate the unusual and fascinating characteristics of ionic liquids. **In the 10th chapter**, to prepare the nanocomposites of Titania by solution impregnation method and used as photocatalyst for the degradation of acetic acid at various factors. **In the 11th chapter**, discuss about health and socioeconomic conditions which are inextricably linked. A substantial beneficial influence on economic success is ensured by the general population's well health. Cardiovascular complexity is the single most serious health problem in India. Hypertension is a key risk factor for cardiovascular disease. **In the 12th chapter**, discuss about waste management. There is need for framing policies for effective management of waste and above all implementation of them by the authority and adherence to them by the general public. **In the 13th chapter** highlights the potential of Hierarchical Nanostructured 3D Flowerlike BiOX (X=Cl, Br, I) microsphere as a remarkable technology towards the environmental remediation processes of various hazardous and persistent environmental pollutants. **In the 14th chapter,** to prepared the nanoparticles of zirconium oxide and characterized them by the some characterization techniques. **In the 15th chapter,** discuss about waste management which involves the procedures and actions necessary to manage waste from generation to disposal. This covers waste collection, transportation, treatment, and disposal, as well as waste management process monitoring and control, as well as waste-related legislation, technology, and economic processes. **In the 16th chapter,** discuss about the role of probiotic milk in human health. The numerous perceived health benefits and the growing awareness about probiotics have caught the attention of the food industry. Food companies are increasingly manufacturing foods with incorporated probiotic bacteria, which fall under the new category of foods called Functional Foods. **In the 17th chapter,** discuss the recenttrend and modification in TiO2 nanostructured based super hydrophobic surfaces ofdifferenttypeofmaterials.Furthertheapplicationpotentialoftheartificialsuper hydrophobic surfaces such as self-cleaning; water/oil separation and anti-fogging etc.**In the 18th chapter,** reviews the iron polyphenols interaction which cause to the colour formation during the sugar processing. The chemical structure of various phenolic acid which presents in sugar cane juice are interact with the Fe(III) through chemical reaction or by changing conditions which results in the various colourant formation during sugar formation are described. **In the 19th chapter,** discuss about carbon footprint which is used to calculate the individual carbon emission which includes to the atmosphere every day. in the recent years causes lots of carbon emission and in turn increase the global warming, which is harmful to the present, and future of the earth and its living beings.

Contents

CHAPTER: 1

PROGRESS AND TRENDS OF PRODUCTION OF RENEWABLE FUELS VIA CATALYTIC MODE

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Abstract

Air transport is completely dependent upon liquid hydrocarbon fuels because of their requirement of high energy density. Aviation fuel from renewable sources is a “DROP-IN” alternative for air transport as it has a similar high energy density and meets all the required fuel specifications. This chapter describes advances in this area and future challenges. Major challenges faced by the industry with respect to the development of alternative aviation fuel are - high quality standards requirements, safety issues, wide range of operational conditions and drop-in kind with traditional aviation jet fuel. Liquid biofuels are the only low-CO_2 emission option for substituting traditional aviation turbine fuel (ATF), as they have high specific energy content and can be blended with commercial ATF. Hydrogenated vegetable and animal fats and oils, Fischer-Tropsch (FT) based on biomass, Renewable Synthesized Iso-Paraffinic (SIP) fuel to jet fuel are some of the option available to produce aviation fuel and are included in approved ASTM standard. The feedstock can be classified into three categories based on the downstream process:

1. Oil containing biomass
2. Lignocellulose biomass
3. Sugars and Starch biomass.

The first two categories is processed via thermal or catalytic or combination of these two routes to produce fuel, while the third category of feedstock is converted via enzymatic or catalytic or combination of these two routes.

Keywords –Renewable Jet, Hydroprocessing, Biotechnology, FT synthesis and Pyrolysis.

1. INTRODUCTION

Depleting fossil fuel reserves, increasing energy needs due to industrialization and modernization, along with growing awareness of global warming, a constant thrust is provided towards significance of securing alternatives to petroleum based fuels. [1] The aviation industry consumes approximately 10.8 exajoules (EJ)/year of fossil fuel energy. Also around 12% of the global transport sector CO_2 emissions are from aviation sector, out of which 80 % emissions are from long distance flights (>1500km), due to ever increasing aviation load [2] and no practical alternative [2,3,4]. Aviation Turbine Fuel (ATF) is required to meet stricter specifications (ASTM D 1655) than any other transportation fuel making it all the more difficult to find appropriate alternatives [5]. The fossil derived jet fuel is expensive and is subjected to market volatility. Massive change in the current aviation engine design along with complex lengthy management approvals would be needed if one has to move away from this type of fuel. Air transport is completely dependent upon high energy density liquid hydrocarbon fuels and an alternative; cheaper, renewable fuel with similar properties to liquid hydrocarbon fuels is needed. [6]

The development of alternative aviation carbon neutral fuel started way back in 2005. Hydrogen-powered airplanes need a larger tank for fuel storage, would be extremely capital intensive and would also reduce efficiency (increased storage space) [6]. Photovoltaics require further developments and are presently not commercially viable. Hence for a transition from fossil based fuels to a more sustainable carbon neutral growth for aviation sector, a mid-term solution in terms of second and third generation bio-fuels would help bridge this gap and enable a smoother transition along with reduced CO_2 emissions over the longer term [6]. Liquid bio-fuels can be produced through different routes such as by processing lipids (used/unused) or by processing bio-oils (pyrolysis oils) or by processing syn-gas via hydroprocessing,[1, 2, 7-10] hydrothermal, [10,11] transesterification [7-10] or by Fisher Tropsch synthesis (FTS for gas to liquids) [1, 7-10]. All processes have their advantages and disadvantages and the most sustainable and economical route to produce sustainable aviation bio-fuels would prevail [4-8, 11-16].The research and developments carried out by various organizations working around the world lead to successful synthesis of renewable bio-aviation fuel having specifications similar to that for fossil based jet fuels [16]. The Bio-fuels was categorized based on the process of development and detailed specifications along with test methods for these specifications were listed as a new ASTM standard, ASTM D 7566 for aviation turbine fuel containing synthesized hydrocarbons [5]. The different specifications are listed in table 1.

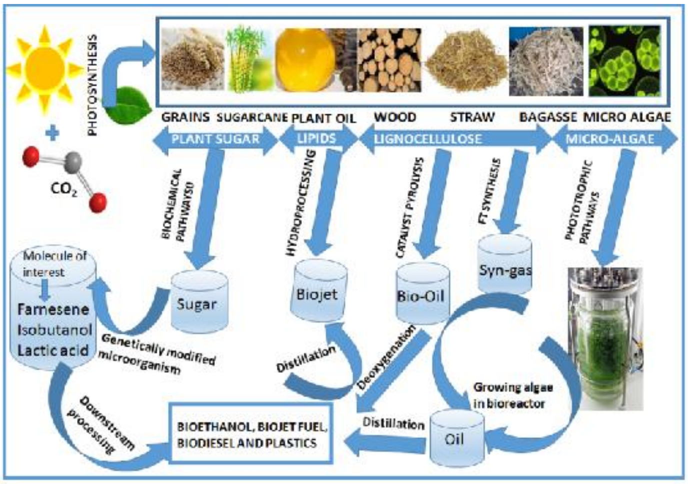

Fig.1: Schematic representation of screening and engineering for the progress and trends of renewable jet fuel

This chapter presents the progress and trends in renewable jet fuels, the technological advances in different routes being researched upon for production of bio-aviation fuels and their ASTM specifications. The chapter focuses on hydroprocessing of lipids, the effect of different catalysts, operating conditions, kinetics, energetic, reactions mechanisms involved and major reasons for catalyst deactivation are discussed. The chapter also provides details about development of Fischer Tropsch synthesis, chemical, biotechnological (including fermentation), and thermochemical routes (Fig. 1) for production of bio-aviation turbine fuels. Fig1 shows the various conversion pathways for the production of renewable jet fuel based on the availability of biomass. In biochemical route, using plant sugar as feed stock, genetic engineering is a hot and challenging area of research to produce molecules (shown in Fig.1), that can be convert to aviation fuel. Phototrophic pathways also involve the selection and genetic modification using algae as feedstocks to produce molecule of interest. Hydroprocessing, FT synthesis and pyrolysis routes require the use of new catalysts and novel processes for upgradation to produce fuel commercially.

2. AVIATION TURBINE FUEL CONTAINING SYNTHESIZED HYDROCARBONS (ASTM D 7566)

The conventional fossil based aviation turbine fuel was classified based on ASTM D 1655 specifications. The ASTM D 7566 covers specifications for manufacturing of aviation turbine fuel that consists of conventional fossil based fuels and synthetic blending components. There have been no changes in original specifications for aviation fuel and the fuel manufactured, certified and released to all the requirements of ASTM D 7566 specifications, meets the requirements for ASTM D 1655 turbine fuel [5]. Explicit specifications for batches originating from Fischer Tropsch Synthesis (FTS) and for batches originating from Hydroprocessing of Esters and Fatty Acids (HEFA) for the production of Synthetic Paraffinic Kerosene (SPK) are provided [5]. The test properties for characterization of FT and HEFA based SPK are broadly classified into 9 classifications, namely composition, volatility, fluidity, combustion, corrosion, thermal stability, hydrocarbon composition, non-hydrocarbon composition and additives. Among these hydrocarbon composition, non-hydrocarbon composition and additives were specifically added for synthesized hydrocarbons and were previously not included in ASTM D 1655 turbine fuel classification. The hydrocarbon composition class details specifically the amounts of cyclo-paraffins, aromatics, parraffins and combined carbon and hydrogen mass percentages (table 1). The non-hydrocarbon composition class details the specific amounts of heterogeneous atoms such as nitrogen, oxygen, sulfur, metals and halogens present in these synthesized hydrocarbons (table 1). As the origin of these hydrocarbons is from oxygen containing renewable compounds and presence of slightest amounts of oxygen in the final processed products may lead to oxidation reactions and gumming, hence anti-oxidants are a must in these synthesized hydrocarbons. Additives in another class included specifically for limiting the amount of anti-oxidants present in these synthesized hydrocarbons (table 1). Apart from these additions there is a relaxation in terms of fluidity for batches of both FT-SPK and HEFA-SPK with freezing point specifications of -40 ^oC as compared to -47 ^oC in case of Jet A1. The temperature for thermal stability evaluation has also been increased to 325 ^oC (FT-SPK and HEFA-SPK) from 260 ^oC (Jet A1) so as to provide a recurring, batch-by-batch verification of process stability and compositional consistency for these synthesized paraffinic kerosene (table 1). Also in addition a limit to fatty acid methyl esters (FAME) content in the HEFA-SPK has been set to <5 ppm (table 1). In totality the final blended turbine fuel needs to meet the specifications of Jet A1 (table 1) as mentioned in ASTM D 7566 and ASTM D 1655.

3. HYDROPROCESSING OF LIPIDS

Hydroprocessing of lipids, classified mainly as glycerides (triglycerides, diglycerides, monoglycerides), free fatty acids and their derivatives including phospholipids, produces liquid bio-fuels with properties similar to hydrocarbon based fuels. Researchers have used different sources of lipids for hydroprocessing reactions such as jatropha,[7-17] soyabean oil,[18-20] sunflower oil,[21-24]palm oil,[25, 26] rapseed oil,[27-29] pomance oil, [30,31] tall oil,castor oil, [33,34] and many more. They have hydroprocessed these sources of lipids either directly or co-processed these oils with crude based gas oils [7, 11, 13, 18, 19, 22-25, 49]. Model compounds such as tristerian, triolean, tricaprylin, caprylic acid, stearic acid, oleic acid, etc have also been hydroprocessed over different catalysts in presence of hydrogen and inert atmospheres to understand the reaction mechanisms and intermediate compounds formed [48, 49, 33-36].

Lipids contain generally oxygen and nitrogen as impurities and these need to be removed by hydrotreatment over non-acidic supports such as γ-Al2O3 or activated carbon [50, 17, 24, 32] with strong hydrogenation functionality provided by mono-metallic Pd, Pt, Ni etc or bi-metallic catalysts such as Pt-Re, NiW, NiMo, CoMo. Acidic supports such as zeolites, silica-alumina, silico-aluminophosphates, titanosilicates etc, [51-53] along with hydrogenation functionality are used as bi-functional catalyst to perform hydrocracking, hydrogenation, hydroisomerization reactions [51]. The properties of the catalyst materials such as hydrogenation functionality, acidity, porosity, surface area, hydrothermal stability etc can be tuned and surface morphology controlled to favor a particular set of reactions and increased catalyst life and performance. These hydroprocessing reactions require hydrogen as an input along with lipid source, in fact nearly 300-420 m3 of H2/m3 of vegetable oil is required to obtain desirable hydrocarbons [56].

High hydrogen consumption is one of the factors delaying the commercial success for lipids hydorprocessing into bio-aviation fuels. Researchers have also investigated single-step processes for production of bio-fuels with reduced hydrogen consumption [61-63]. The primary reactions involved during the hydroconversion of lipids is depproponation (-C_3H_8) (table 2a) where the glycerol linkage of the lipid molecule is hydrogenated and a propane and corresponding acid/aldehyde molecule is formed [63]. Deoxygenating of the corresponding intermediate acid/aldehyde (table 2a) occurs via three oxygen removal pathways mainly

1. Decarboxylation (-CO_2),
2. Decarbonylation (-CO),
3. Hydrodeoxygenation (-H_2O)

After removal of oxygen molecule the corresponding hydrocarbon is further cracked and isomerized into aviation range hydrocarbons (table 2a). To minimize the hydrogen consumption and reduce the loss of hydrogen as a water molecule during deoxygenation reactions, researchers are focusing on maximizing decarboxylation as compared to hydrodeoxygenation [61].

FT-SPK – Fischer-Tropsch Hydro processed Synthesized Paraffinic Kerosene

HEFA-SPK – Hydroprocessed Esters and Fatty Acids Synthesized Paraffinic Kerosene

Table 1 Detailed specification as per ASTM D 7566 for batches of FT and HEFA – SPK[47]

Test Properties	**Method**	**Jet A1**	**FT-SPK**	**HEFA-SPK**
COMPOSITION				
Acidity, total mg KOH/g (max)	D 3242	0.1	0.015	0.015
Aromatics, vol % (max)	D 1319	25	-	-
Sulfur, mercaptan, C mass % (max)	D 3227	0.003	-	-
Sulfur, total mass % (max)	D 4294	0.03	-	-
VOLATILITY				
Distillation temperature, °C:	D 86			
10 % recovered, °C (max)		205	205	205
50 % recovered, °C		Report	Report	Report
90 % recovered, °C		Report	Report	Report
Final boiling point, °C (max)		300	300	300
T90-T10, °C (min)		40	22	22
Flash point, °C (min)	D 3828	38	38	38
Density at 15°C, kg/m^3	D 4052	775-840	730-770	730-770
FLUIDITY				
Freezing point, °C (max)	D 5972	-47	-40	-40
Viscosity −20°C, mm^2/s (max)	D 445	8		
HYDROCARBON COMPOSITION				
Cycloparaffins, mass % (max)	D2425	-	15	15
Aromatics, mass % (max)	D2425	-	0.5	0.5
Paraffins, mass %	D2425	-	report	report
Carbon and Hydrogen, mass% (min)	D5291	-	99.5	99.5

On processing lipids directly over a hydrocracking catalyst (bi-functional catalyst with strong hydrogenation functionality and acidity), resulted in increased formation of cracked kerosene range hydrocarbons with increased isomerisation activity. A maximum yield of 78% bio-jet fuel yield was obtained using algal oil as the lipid source over a ZSM-5 based catalyst. The yield of renewable aviation range hydrocarbons also increased on increasing the temperatures form 360 to 450 ^{o}C, due to increased reaction severity. Hydrocracking of lipids at lower temperatures (<300 C) has also been investigated using Platinium and Nickel based catalysts [61, 36, 39] over jatropha [65, 43] and castor oil lipids. Increased bio-aviation kerosene yields have been reported, but longer catalytic evaluations for catalyst stability, life and activity are yet to be performed over these catalysts. Pilot scale evaluations with stable catalyst performance over Ni-W/Silica-Alumina catalyst system have been reported for the production of bio-aviation fuel in literature [65].The renewable aviation fuel obtained has also been evaluated as per ASTM D 7566 standards and it meets all the specifications for aviation turbine fuel [55].

Catalyst deactivation

Stable catalyst performance with increased catalytic activity is very much necessary for commercial success of hydroprocessing of lipids and investigation on the catalyst deactivation behaviour for improving catalyst life as well as activity have also been carried out [46, 55]. Researchers have studied the impact of products originating from hydrotreating of hetroatoms, such as H_2S, NH_3 and H_2O on catalyst activity and selectivity [46, 56, 61]. Laurent and Delmon [58], showed that ammonia strongly inhibits both hydrodeoxygenation reactions and decarboxylation reactions whereas inhibition effect of water was less as compared to that of ammonia. The catalyst should have high hydrothermal stability due to presence of water in the reaction media. The presence of water increases the hydrolysis of carboxylic esters intermediates formed but has very slight week inhibiting effect on various reactions. [46] It inhibits slightly the hydrogenation activity of the catalyst and leads to increase in oxygen containing compounds [46, 59]. It although favours water gas shift reactions leading increased catalyst bed temperatures [60] and promotes slightly isomerisation reactions due to increase of Brønsted acidity [55-56]and helps in reducing char [60].The sulphur from the catalyst active sites (edges) is exchanged with oxygen due to presence of water which reduces catalyst activity. This exchange of sulphur from edge sites is reduced by using by-metallic (CoMo, NiMo) catalyst [61]. The inhibition effects of high concentrations of water may also be prevented by addition of H_2S generating agents in the bio-feeds. The presence of H_2S led to competing reactions and lowered considerably the hydrodeoxygenation /decarboxylation ratios [56]. The activity of the sulfided catalyst, during the hydroprocessing of vegetable oils, decreases primarily due to gradual sulphur removal from the active sites. In case of petroleum derived sources, the sulphur present in the feed replenishes the sulphur lost from the catalyst surface, where as in case of oxygenated feeds like vegetable oils, there is constant depletion of the active sites due to loss of sulphur from the catalyst surface [50].

Another reason for loss of catalytic activity would be due to inaccessibility of the bulky reactant molecules to the active sites due to coke deposition on the catalyst surface. Kubička and Horáček, [45, 56] studied the deactivation during deoxygenation of vegetable oils and indicated that the degradation of active sited by loss of sulfur was not fully reversible. Kubička and Horáček,[50] used pulses of DMDS and a constant feeding of DMDS to resulfide the catalyst active sites and observed the changes in selectivity of products. In absence of DMDS, hydrodeoxygenation (HDO) reaction was 3-4 times faster than decarboxylation (HDC) reaction, where as in presence of sulfur containing species, the extent of hydro-deoxygenation reactions were reduced and decarboxylation reactions were favored. They observed that a constant feeding of di-methyl-disulfide (DMDS) doped vegetable oil reduced the catalyst deactivation, occurring due to insufficient sulfur [60]. It also improved the catalyst stability towards deoxygenation reactions. Continuous catalyst reactivation with sulfur-containing feed was more effective as compared to reactivation using pulses, which leads to stable catalytic performance [55, 61].

4. Fischer–Tropsch (FT) synthesis to renewable jet fuel

Fischer–Tropsch (FT) synthesis is effective technology in the production of clean hydrocarbon fuels from syngas.In order to make use of biomass as feed stock and produce aviation fuels as products, there are three pathways (Fig. 1): conversion of biomass to synthesis gas, conversion of synthesis gas to oil, and oil refining to aviation fuels. Iron and cobalt-based catalysts are commonly in FT synthesis [74, 75]. Cobalt FT synthesis catalysts are considered by many to have advantages over iron based catalysts such as high conversion per pass, long lifetime, and selectivity toward higher hydrocarbons. Despite the diversity of technologies, when FT synthesis is viewed from a product perspective, there are only two basic types of products that are industrially produced by FT synthesis. The first one is the product fromhigh-temperature Fischer Tropsch (HTFT) synthesis using Fe-based catalysts operated at 300-320 °C and higher temperature. The second is the product from low-temperature Fischer Tropsch (LTFT) synthesis employing mainly Fe- and Co-based catalysts at temperature from 170 °C to 270 °C. It is necessary to find out that F-T synthesis can be manipulated to make the refining production of aviation turbine fuel easier.

5. Biomass conversion pathway to renewable jet through biotechnology platform

Biomass contributes around 10% of the world energy consumption and is currently used mostly for heating and cooking. Resourcing feedstock is a major challenge for biomass conversion processes. The use of lignocellulose, non-edible part of plant and also non edible plant such as Jatropha would create pathways in the direction of sustainability. Charcoal, ethanol derived from corn (maize), methane-rich biogas, non-edible plants like Jatropha, wood and straw comprise biofuels. The major part goes towards heat, with the rest used for electricity and transportation. But biofuels have the potential to deliver 25% of the world's projected energy needs of 623 exajoules by 2035 [51]. In addition to controlling global warming, this would augment jobs, especially in the rural areas while ensuring energy security.

Biomass conversion through biochemical route induces use of micro-organisms (yeast and bacteria) and converts it to fuel and chemicals. Genetically modification in the microorganism is the goal of research along with technological aspects to produce molecule of interest. To achieve it, countries will try to make an effort in the development of biofuel technologies [60]. Countries notably like Sweden, Austria, Brazil and China, endeavored huge strides in this respect. Even though many other countries have huge amount of biomass resources but they are not making the most of their resources: in Australia and India, for example, millions tones of straw are still burned in fields after the harvest each year; this 'waste' could be used to generate energy. We believe that biomass conversion pathways have an industrial and technological challenge that must reconcile the technical performance, environmental performance, social acceptability and economic viability [60].

Table 2.Different reactions occurring during hydroprocessing of lipids with heat of reactions (a) and kinetic parameters (b) for conversion into bio-aviation fuel.

Reaction $\Delta H_r^o = \sum \Delta H_{f\,Products}^o - \sum \Delta H_{f\,Reactants}^o$	ΔH_r^o **, MJ/mole**
Depropanation $C_{57}H_{116}O_6(v) + 3H_2(g) \xrightarrow{\Delta\ Catalyst} C_3H_8(g) + 3C_{18}H_{36}O_2(v)$	-1.02
Decarboxylation $C_{18}H_{36}O_2(v) \xrightarrow{\Delta\ Catalyst} CO_2(g) + C_{17}H_{36}(v)$	+0.03
Decarbonylation $C_{18}H_{36}O_2(v) + H_2(g) \xrightarrow{\Delta\ Catalyst} CO(g) + H_2O(v) + C_{17}H_{36}(v)$	+0.07
Hydrodeoxygenation $C_{18}H_{36}O_2(v) + 3H_2(g) \xrightarrow{\Delta\ Catalyst} C_{18}H_{38}(v) + 2H_2O(v)$	-0.079
Hydrocracking $C_{18}H_{38} + H_2 \xrightarrow{\Delta} C_{12}H_{26} + C_6H_{14}$	-0.04
Hydrocracking $C_{17}H_{36} + H_2 \xrightarrow{\Delta} C_8H_{18} + C_9H_{20}$	-0.04

Table 3 shows the production yields from various pathways with specifications in terms of hydrocarbon type. Through biochemical pathways using algal biomass as feed stock, depending on the processing conditions, the yield of jet fuel is 3 times more than that from sugar fermentation, approximate 1.5 times more than FT synthesis and alcohol to jet route. Thus biochemical pathway though still in infancy but is most promising future route to produce aviation biofuel. Pyrolysis route provides least amount of jet yield among the different discussed routes in Table 3.

But based on the availability of feed FT synthesis are most promising pathways for the production of aviation jet fuel. The production yield of jet fuel via FT synthesis is approximate 2 times more than that of sugar fermentation pathway and almost same as alcohol-to-jet route. But paraffinic composition is less through FT route (<70%) compared to alcohol-to-jet route (97%). So based on biomass, technology, food security and production yield, FT Synthesis and hydroprocessing routes are found to be attractive route in the production of renewable Jet fuel.

Table 3 Production yields from various pathways with specification discussed in this chapter.

S.No	Pathways	Biomass	Jet fuel yield gal/BDT	Hydrocarbon type analysis	
				Aromatics vol% paraffins mass%	
1	Biochemical	Microalgae biomass	8-122	report	report
2	Alcohol-to-jet [6,86]	Corn, wood straw	11-79	0.01	97.45
3	Sugar fermentation	Sugarcane, wood, straw	24-43	2.6	40
4	FT	Biomass coal and wood	9-88	<1	<70
5	Pyrolysis	Corn strover, wood, biomass	19	report	report
6	Hydroprocessing	Animal and plant lipids	30-50	<8	92

6. CONCLUSIONS

This chapter shows the progress and trends in renewable jet fuels via different pathways, which has been summarized in Fig.1. Feedstock availability is a major challenge for biomass conversion processes. The use of lignocellulose, non-edible part of plant and also non-edible plant oils such as jatropha, would create pathways in the direction of sustainability. The oil containing biomass and lignocellulose biomass is processed via thermal or catalytic or combination of these two routes to produce fuel, while the sugars and starch biomass is converted via enzymatic or catalytic or combination of these two routes. Hydroprocessing route to producing alternative biofuels has become a well-established technology, though economically not yet cost-competitive due to the higher cost of animal and plant derived triglycerides/lipids. Inherently, hydroprocessing of lipids requires hydrogen. Moreover, despite various developments in catalysis and process, specifically for conversion of lipids into fuels, there are few reports available on reaction pathways, kinetic, diffusion and thermodynamic properties of these lipids and the specific bio-based products thus obtained. Nature of different intermediates produced over different catalytic systems during lipid processing and their effects on the entire process and on the catalyst has also not been studied in detail. In this chapter, we have described different possible commercial routes for the production of renewable jet fuel, challenges related to catalytic requirements and technology implementation concerns from environmental point of view.

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CHAPTER: 2

THE MEDICINAL IMPORTANCE OF LUMINESCENT AND FLUORESCENT ANALOGUES

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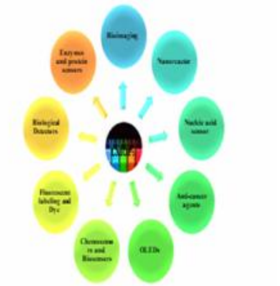
Abstract

The significant optical features of luminescent materials have drawn immense appreciation in all walks of life including organic dyes, metal-organic frameworks, lanthanide compounds, semiconductor-based quantum dots, and carbon-based nanodots, which attribute numerous applications to these Luminescent materials. Moreover, they have been proven important in various applications, including gas storage and separation, heterogeneous catalysis, light-harvesting, chemical sensing, bio-imaging, and drug delivery. In recent times, biologically important luminescent metal contain drugs have attracted great interest in bioinorganic chemistry.There is great potential in the application of these materials to cell bio-imaging. The most effective and useful tool for tracking the bio-distribution of luminescent compounds into the cell and cellular uptake of the species is cell bioimaging. A researcher has recently studied the cellular uptake which is monitored by CFM (Confocal Fluorescence Spectroscopy) of bioactive luminescent silver(I) diethylbarbiturate complexes, and these studies have demonstrated that this luminescent compound may develop potent anticancer agents in the future by suggesting that mitochondria and DNA are the potent biological targets for new drug discovery. This review will focus on a brief discussion on the various biological applications of luminescent and fluorescent metal-organic complexes, fluorescent heterocyclic compounds, nanomaterials, and luminescent inorganic molecules. This effort will help new researchers working in the field of luminescent and fluorescent-based medicinal chemistry development.



Graphical Abstract

Keywords: Metal-organic frameworks; Luminescence; Biosensors; Fluorescence; Biological activity.

1.0 INTRODUCTION

Bioactive luminescent metallodrugs have attracted great interest in bioinorganic chemistry in the last few years, owing to the potential application of the luminescent compounds to cell bio-imaging, which is a useful tool for tracking the biodistribution of luminescent species into the cell, as well as the cellular uptake of these species. The cellular uptake studies monitored by confocal fluorescence spectroscopy (CFM) of bioactive luminescent silver(I) diethylbarbiturate complexes, recently tested as anticancer agents, have demonstrated that these complexes can access the cytosol and nucleus of A549 and MCF-7 tumor cells. These findings are suggesting that mitochondria and DNA are potent biological targets [1]. Moreover, LMOFs (Luminescent metal-organic frameworks) key structural and chemical features make them appealing candidates for measuring levels of biochemical compounds or for imaging contrast agents. Numerous different LMOFs display low cytotoxicity, which is important for eventual *in vivo* screening[2]. Furthermore, to design specific affinity, the wide range of metal and organic building blocks that can be incorporated into their structures allows for judicious tuning of the material's light absorption and emission properties to avoid interference with those of the desired analyte. LMOFs can also be modified post-synthesis, enabling specific molecular recognition [3]. Additionally, this versatility of LMOFs opens up possibilities for cell or tissue-specific targeting in bio-sensing applications [4]. The LMOF can be re-used multiple times, as the binding and fluorescence events are typically reversible.

Furthermore, the incorporation of targeting groups through simple post-surface modification allows for greater binding to and uptake of the LMOF particle by the intended cell target. Enlightenment solely of the region of interest, by using an LMOF's essential fluorescence, can achieve a better diagnosis. Hence, by creating a multimodal imaging system this diagnosis can then be coupled to therapeutic delivery. However, the lack of literature on MRI with non-toxic metal cluster LMOFs reveals the need for development in the field and attention for key biological properties, such as cytotoxicity and clearance times. In addition, the lack of variation of LMOFs being used shows that there need to develop novel LMOFs as highly efficient bio-sensing platforms. On the other hand, the biological applications have been very limited due to the challenging issues; however, the chemo sensing applications of LMOFs have been abundantly reported in the literature. Due to the highly tunable characteristics, LMOFs are attractive candidates as biosensors and contrast agents for certain analyses and as Nano reactors for biochemical reactions through rapid and efficient catalysis [5]. Hence, to expand the biological efficiency of LMOFs, the most important issues to address include the necessity for high affinity, increased biocompatibility, recyclability, and low cytotoxicity, particularly for *in vivo* study [6]. The vast diversity of metal and organic linker building blocks available in combination with prudent PSM approaches. This may enable the successful synthesis of LMOFs that are highly sensitive and selective for molecular recognition with as little interference as possible in the PL spectra of the target analyses in the complex biological environment [7]. Therefore, such high-affinity LMOFs have been adopted for favorable interactions with targeted cells and tissues. Additionally, in the literature, many studies describe LMOFs as highly selective probes for the evaluation of biological macromolecules like proteins [8], nucleic acids [9], and smaller biomolecules like glucose [10], amino acids [11], and many others [12]. They can also function analogously to synthetic enzymes like peroxidases or catalases [13]. Revolutionary work on bio-molecular recognition includes the detection of dipicolinic acid (DPA) molecules, a structural constituent of *Bacillus anthrax* spores, and various other virulent bacteria [14]. The researcher utilized luminescent Eu-doped $Gd(BDC)_{1.5}(H_2O)_2$ MOF NPs complexes with Si-coated Tb monoamide derivatives to form a highly sensitive probe for the detection of DPA [14]. In the last few years, many other groups have developed sensing platforms for DPA molecules, including bimetallic (Eu^{3+}/Tb^{3+}) MOFs [15] and Tb-MOFs [16]. In light of the numerous advantages of LMOFs, in this review, we have discussed the biological application, bio-sensing, and bio-imaging applications of luminescent MOFs which will encourage new researchers to develop new medicinally important luminescence compounds in the future.

2.0 Various biological applications of luminescent and fluorescent compounds

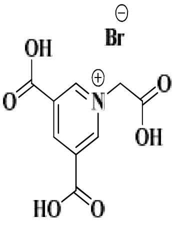
2.1 LMOFs as a nucleic acids sensor

Sensors produce detectable signals due to the response of physical or chemical properties and they are a critical extension of human insight in the modern era in many aspects worldwide. This is largely because we are more sensitive to the physical environment such as light, temperature, pressure, or humidity than to the chemical or biological environment. Still, suitable chemical or biological compositions are strongly connected to the quality of life. In addition, chemicals in the environment such as heavy metals, explosives, and toxins can affect human health whereas molecule and ion concentrations inside a human body such as metabolites, metal ions, hormones, and proteins reflect the human’s health. Consequently, the development of selective and highly sensitive sensors to identify important analytes has long been a main focus of research for many areas including medical diagnostics, environmental monitoring, and industrial quality control.

Moreover, target recognition and signal transduction are two components of the sensor. The target recognition element can be any biological or chemical entity such as small organic molecules, nucleic acids, peptides, carbohydrates, proteins, or even whole cells. Ideally, this element should have a low detection limit (high affinity), low interference (high specificity), long shelf life, wide dynamic range, fast response time for detecting a wide range of analytes with the same class of recognition element. However, nucleic acid detection also presents a risk for self-recognition, and self-activation in response to host nucleic acids is associated with many autoimmune diseases. Improper detection of self-molecules is prevented through the subcellular separation of receptors, degradation of self-nucleic acids by endogenous nucleases, and specialization of innate receptors that detect conserved microbial features absent from the host. Here, we discussed the new luminescent organometallic compounds as a sensor for the detection of nucleic acid.

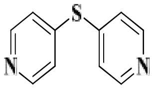
N,N-bis(2-hydroxyethyl)dithiooxamidatocopper(II) [$Cu(H_2dtoa)$] (1)

Zhu et al. have reported the detection of HIV DNA and thrombin using the MOF, N, N-bis(2-hydroxyethyl)dithiooxamidatocopper(II) [$Cu(H_2dtoa)$] **(1)** with high sensitivity and selectivity in 2012. Firstly, they compare the fluorescence intensities between free probe DNA and the complex probe of DNA-$Cu(H_2dtoa)$. Fluorescence intensities recover 156% and 502% in the presence of target DNA (50 nM) and thrombin (100 nM), respectively. A novel strategy of a MOF, $Cu(H_2dtoa)$, as a sensing platform for assaying biomolecules was presented by the researcher which will open the door of the applications of MOF in the sensing[17].



$H_3CmdcpBr$

(2)



dps

(3)

$[Cu_3(Cmdcp)_2(dps)_4(H_2O)_4(SO_4)]n$

(4)

Furthermore, Yang et al. have synthesized a water-stable three-dimensional Cu-based metal-organic framework (MOF) $[Cu_3(Cmdcp)_2(dps)_4(H_2O)_4(SO_4)]n$**(4)** supported by a tritopic quaternized carboxylate and 4,4′-dipyridyl sulfide as an ancillary ligand. The synthesized ligand was further subjected for the sensing of human immunodeficiency virus 1 double-stranded DNA and Sudan virus RNA sequences, respectively, with detection limits of 196 and 73 pM, respectively. Their results convincingly suggest that P-DNA1@1 and P-DNA-2@1 systems function as highly selective sensing platforms for the detection of HIV ds-DNA and SUDV RNA sequences in vitro, respectively.Furthermore, the introduction of T0' to 80' to the P-DNA-2@1 system results in significant fluorescence enhancement, whereas no obvious fluorescence enhancement was observed in the case of T100'. In addition, they further designed one base mutated target RNAs T50A' and T80A' as interfered RNA sequences for T50' and T80', respectively. This finding may guide the synthesis of more 3D MOFs with bigger pores from flexible zwitterionic carboxylates of low symmetry to detect longer HIV ds-DNA or SUDV RNA sequences. This type of MOFs may also find potential application in the early diagnosis of HIV and ebolavirus disease as well as other virus-associated infectious diseases having no effective vaccines and treatments [18].

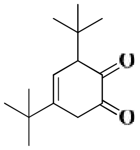
$Cd(L).(HDMA)_2(DMF)(H_2O)_3$ (5)

$Zn(L).(HDMA)_2(DMF)(H_2O)_6$ (6)

Additionally, In 2014, aromatic ligand, bis-(3,5-dicarboxy-phenyl)terephthalamide (H4L), two metal-organic frameworks, $Cd(L).(HDMA)_2(DMF)(H_2O)_3$**(5)** and $Zn(L).(HDMA)_2(DMF)(H_2O)_6$**(6)**, were synthesized using a solvothermal method by wang et al. The synthesized compounds were further utilized for the sensing of DNA strands, which is attributed to their different affinities for single and double-stranded DNAs. This biological screening of compounds 1 and 2A was performed by a fluorophore (fluorescein, FAM) labeled ssDNA probe (P). In order to assess the sensitivity of these sensing platforms, the fluorescence spectra of the suspensions containing 2 ($0.5\ \mu g\ \mu L^{-1}$) and P (100 nM) with various concentrations of T (0-200 nM) were measured. Researchers have also tested the effect of the amount of MOFs on their sensing efficiency. It was found that an increase in the MOF amount led to an increased quenching efficiency but a decreased recovery efficiency. However, at the same time, the probability of direct absorption of the target on the vacant surface of the excess compounds increased during the hybridization process, which suppresses the hybridization of the target with the fluorophore-labeled ssDNA probe and leading to the decreased fluorescence recovery efficiency. Another advantage of their MOF-based DNA sensing platforms is their ability to distinguish between complementary and incompatible sequences. It was observed that the fluorescence enhancement (FP+MOF+Tx_FP+MOF, FP+MOF, and FP+MOF+Tx are the fluorescence intensities of the suspension containing P and MOF before and after the addition of target DNA, measured at 522 nm) upon the addition of T1, T2, and T3 is 81.6%, 49.8%, and 9.0%, respectively, of the value of T. Due to their high sensitivity and selectivity, the MOF-based sensing platforms described by the researcher are applicable for the practical qualitative and quantitative detection of DNA sequences [19].

2.2 LMOFs as a Nanoreactor

Luminescent Metal-organic frameworks nanoparticles have been attracting materials for a researcher from both scientific and application perceptions, bearing a nano-sized cavity space compressed in a permeable inorganic nanoshell. Over the last decade, developments in this field have demonstrated their different properties, which derived from the presence of interior void space, are useful for wide applications such as nanoreactors [20-21], drug-delivery vehicles [22-23], and contrast agents for molecular imaging [24-25]. Specifically, the nanoparticles are considered as potent candidates for nanoreactor systems when the catalytic species such as noble metal nanocrystals are incorporated in the interior cavity of the porous shell; this is the reason for a weak point in conventional nanoparticle-based catalysts. Additionally, the selectively functionalized internal cavity is the most dynamic component, which allows chemical reactions to occur confined within the protective space in the performance of this type of nanoreactor. There is imitated research available in the literature for this particular field, hence, this significant and challenging area must be addressed for full exploitation of the potential of LMOFs nanoparticles in nanoreactor applications. Herein, we have discussed some research that described the efficiency of LMOFs nanoreactor.



3,5-di-*tert*-butylcyclohex-4-ene-1,2-dione

(7)

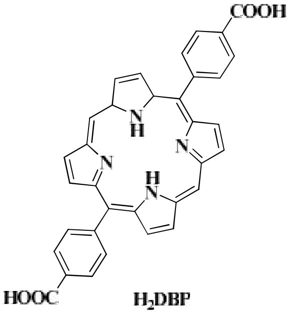
In 2011, Lykourinou and co-workers have reported the corresponding o-quinone product 3-5, di-tert-butylocyclohex-4-ene-1,2 dione **(7)** synthesis by the oxidation of the chromogenic substrate 3,5-dit-butyl-catechol (DTBC) at 420 nm and subjected for enzymatic catalytic activity. This group demonstrated the successful immobilization of microperoxidase-11 into a mesoporous MOF consisting of nanoscopic cages, which exhibited superior enzymatic catalysis performances compared to mesoporous silica material MCM-41. Considering the richness of mesoporous MOF structures, the present studies also open a new avenue for enzyme immobilization as heterogeneous biocatalysts. This group exploring and designing new mesoporous MOFs to immobilize different kinds of enzymes for catalysis applications under various conditions [26].

Here, in 2014, Lyu et al. have proposed a new strategy that directly synthesizes protein-embedded MOFs. In their study cytochrome c (Cyt c), which has important applications in bioanalytical field, was chosen as a model protein, which we attach to zeolitic imidazolate framework (ZIF-8) **(8)**. In their findings, to explore the mechanism behind the 10-fold increase in the apparent activity of the Cyt c in ZIF-8, they determined the enzymatic Michaelis-Menten kinetics of Cyt c in ZIF-8 concerning H_2O_2 concentration. They found that the embedded Cyt c shows a K_m value of 2 mM and a V_{max} value of 200 μM/min, while the K_m and V_{max} of free Cyt c is 15 mM and 80 μM/min, respectively. The researcher achieved rapid, sensitive, visible detection of highly explosive organic peroxides using the Cyt c-MOF complex. Given the variety of proteins and the ever-expanding pool of MOFs, this new method for the preparation of protein-MOF composites opens opportunities for combining their properties and functionalities, thus displaying novel key features enabling new applications in biosensors, biofuel cells, analytical devices, and industrial biocatalysis [27].

2.3 LMOFs Bioimaging Applications

The first X-ray image was captured by Wilhelm Roentgen of his wife's hand in 1896 and a new era dawned in the history of medical diagnosis. Many non-invasive methodologies have been invented after the inception of X-ray technology for medical imaging and successfully applied to fields ranging from clinical diagnosis to research in cellular biology and drug discovery. Biomedical imaging research has leveraged the benefits of significant advances in electronics, information technology, and, more recently, nanotechnology. Imaging of biological specimens both in vitro and in vivo has long relied on light microscopy (fluorescence and luminescence imaging) and is currently attracting increasing attention as technological advances provide enhanced capabilities. Another technology that has grown remarkably as a tool in medical diagnostics, especially for soft tissues, is MRI. The development of multifunctional nanoparticles is a step further in the same direction. Luminescence bioimaging offers a unique approach for visualizing morphological details of tissues with subcellular resolution and has become a powerful tool for the manipulation and investigation of microspecies from living cells and animals [28-29]. In this review, we focus on the recent progress in luminescent chemodosimeters for photoluminescent bioimaging of various metal cations, anions, amino acids, and neutral molecules in living biological samples. This chapter will briefly review the recent methods in imaging with a particular focus on optical imaging using luminescent nanoprobes, their design and applications in bioimaging.

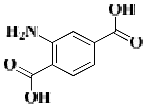
Lu et al. have reported the rational design of a Hf-porphyrin nanoscale metal-organic framework in 2014. The new porphyrin derivative, 5,15-di(p-benzoato)porphyrin (H_2DBP) **(9)**, was synthesized by a condensation reaction between 4-(methoxycarbonyl)benzaldehyde and dipyrrylmethane, DBP-UiO ($Hf_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(DBP)_6$) **(10)** was synthesized by a solvothermal reaction between $HfCl_4$ and H_2DBP in N,N-dimethylformamide (DMF).



H_2DBP

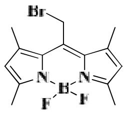
(9)

Furthermore, in vitro PDT of the synthesized compounds was performed on human head and neck cancer cells SQ20B, which are resistant to cisplatin and radiation therapy. Histologies of tumor slices exhibited macrophage infiltration in tumors of the DBP-UiO treated group and indicated that significant fractions of tumor cells were undergoing apoptosis/necrosis [30].



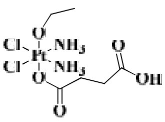
Amino-BDS

(11)



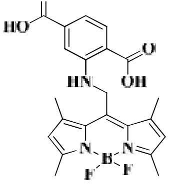
Br-BODIPY

(12)



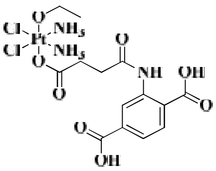
ESCP

(13)



BDC-NH-BODIPY

(14)



BDC-NH-ESCP

(15)

Likewise, In 2009, Taylor-Pashow et al. have reported the Fe(III) NMOF particles with the framework formula of $Fe_3(\mu_3\text{-}O)Cl(H_2O)_2(BDC)_3$**(16)** were synthesized in modest yields (typically∼ 20%) by heating a solution of equimolar $FeCl_3$ and terephthalic acid (BDC) in DMF at 150 °C with microwave heating.

Furthermore, the synthesized MOFs were subjected to in vitro optical imaging and anticancer therapy. Additionally, Cytotoxicity tests of RGD-targeted 1c@silica gave cytotoxicity (IC_{50}) 21 µM) similar to that of cisplatin (IC_{50}) 20 µM). The generality of this approach should allow the design of a wide range of nanomaterials for imaging and therapeutic applications [31].

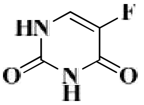
$Gd(BDC)_{1.5}(H_2O)_2$ (16)
$[Gd(1,2,4\text{-}BTC)(H_2O)_3].H_2O$ (17)
Gd0.95(BDC)1.5(H2O)2:Eu0.05 (18)
Gd0.95(BDC)1.5(H2O)2:Tb0.05 (19)

In 2006, Rieter and co-worker have reported the synthesis of $Gd(BDC)_{1.5}(H_2O)_2$**(16)** and $[Gd(1,2,4\text{-}BTC)(H_2O)_3].H_2O$ **(27)** nanorods (where BDC is 1,4-benzenedicarboxylate) by stirring an optically transparent microemulsion of $GdCl_3$ and bis(methylammonium)benzene-1,4-dicarboxylate in the cationic cetyltrimethylammonium bromide (CTAB)/isooctane/1-hexanol/water system. They rationalize that NMOFs **16** and **17** contain a large number of Gd^{3+} centers and would therefore give very large relaxivities on a per-particle basis.

As per the observed result, nanorods of **16** are much more efficient in enhancing the water signals in *T*1-weighted images than clinically used OmniScan. Ethanol dispersions of these doped nanorods are highly luminescentupon UV excitation with characteristic red and green luminescencefrom $Eu^{3+}$and Tb^{3+}, respectively. These results suggestthat NMOFs **16**, their findings can be used as potential target-specific multimodal imaging contrast agents [32].

nano-Yb-phenylenevinylenedicarboxylate-3 (nano-Yb-PVDC-3) (20)

Moreover, Collet et al. have reported nano-Yb-phenylenevinylenedicarboxylate-3 (nano-Yb-PVDC-3) **(20)**, a unique MOF based on a PVDC sensitizer-ligand and Yb^{3+} NIR emitting lanthanide cations in 2013. The principal aim of this study was to test nano-Yb-PVDC-3 in cells as NIR imaging agents for a biological system. They choose human cancer (HeLa) and mouse (NIH 3T3) cells as representative cell lines. The researcher further evaluated the Cellular Uptake of these compounds and the internalization of nano-Yb-PVDC-3 **(20)** by the cells was confirmed with confocal microscopy and inductively coupled plasma (ICP) spectrometry experiments. It can be started from their findings that the stability, combined with cytotoxicity results, is favorable for using nano-Yb-PVDC-3 **(20)** as a biological probe for in vivo applications [33].



5-fluorouracil

(21)

In addition, Lucena et al. reported the preparation of the drug 5-fluorouracil **(21)** incorporated in Cu-BTC MOF and evaluated for their cytotoxic activity. The experiment was demonstrated during the prolonged drug release 48 hours. Firstly, 39.4% of the drug was released from the MOF in the first 30 minutes; this can be attributed to the drug in its free form as showed in the DSC curve. These results are according to the peritonitis test that showed a decrease in levels of TNF-α and NO in the tumor site, which may have contributed to the maintenance of the required levels of these substances in the activation of caspase that activate apoptosis. Their MOFs showed the controlled release properties, low toxicity to normal cells, and also an indication of anti-inflammatory activity which could act as an adjuvant treatment [34].

2.4 LFMOs as a sensor for enzymes and proteins

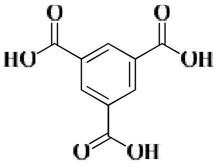
Biosensors for highly sensitive, selective, and rapid quantification of specific biomolecules make great contributions to biomedical research, especially molecular diagnostics. In the past few years, biosensing has proven to be an innovative and effective technique in several fields including the environment and biomedical applications. Modern biosensors can be miniaturized, mass-produced, and easily transported. Real-time analysis can be measured by Biosensors, which is tremendously useful for monitoring rapid changes in biological fluids. Further, Chemical biosensors are based on the presence of a biological element, which is specific for the analyte, and stable under normal conditions of use and storage [35]. The first glucose oxidase biosensor was developed in the early

1960s after that the electrochemical biosensors have studied [36]. Electrochemical biosensors can be potentiometric, amperometric, or impedimetric biosensors, where the biochemical signal is transduced into a quantifiable amperometric signal [37]. Several recognition elements have been used in biosensors, such as nucleic acids, receptors, antibodies, whole cells, and different classes of enzymes. Biosensors can be developed and characterized on this basis, optical, calorimetric, or acoustic, but the most widely used biosensors depend on the electrochemical proprieties of transducers and analytes. However, Enzyme-based amperometric biosensors have been widely studied over the last few decades as they are easy to miniaturize, robust, and can operate with small sample volumes of rather complex matrices. The production of a current is monitored when a fixed potential is applied between two electrodes in this type of biosensors [38-39]. Hence, here below we have discussed the current research on sensing of enzymes and proteins which is based on luminescent organometallic frameworks.

PtNPs/Ru-PEI@ZIF-8/CS (22)

In this direction, Xiong et al. have reported an ultrasensitive “off-on” electrochemiluminescence biosensor for the determination of telomerase activity by using self-enhanced Ruthenium-polyethylenimine (Ru-PEI) complex doped zeolitic imidazolate framework-8 (Ru-PEI@ZIF-8) with high electrochemiluminescence efficiency as electrochemiluminescence indicators and an enzyme-assisted DNA cycle amplification strategy. They have first characterized the construction of the proposed electrochemiluminescence biosensor by ECL measurements after every step. The results from the study indicated that the PtNPs/Ru-PEI@ZIF-8/CS **(22)** film displayed a strong electrochemiluminescence signal, which revealed that the proposed Ru-PEI@ZIF-8 had superior electrochemiluminescence property. All these results observed by researchers indicated that the proposed electrochemiluminescence biosensor was successfully fabricated [40]. Furthermore, the detection performance and stability of the proposed biosensor were checked by the researcher. The observed results indicated that the proposed biosensor presented good performance in the detection of telomerase activity and could act as an effective assay for telomerase activity measuring. It was observed that the electrochemiluminescence response increased with the increase of Hela cell numbers. A relatively stable electrochemiluminescence response was observed at each cell number. These proofs proved that the proposed electrochemiluminescence biosensor had proper stability for telomerase activity measuring [40].

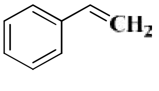
On the other hand, the proposed electrochemiluminescence biosensor was further evaluated for their Anticancer Drug proficiency. Hence, for introducing the proposed biosensor to clinical cancer research, the proposed electrochemiluminescence biosensor was applied in the anticancer drug screening. These results indicated that the proposed electrochemiluminescence biosensor by researchers could become a powerful tool for cell apoptosis monitoring based on anticancer drug screening [40].



1,3,5-benzene tricarboxylate

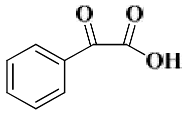
(23)

Furthermore, in the year 2014, Tan and co-workers have attempted to explore the intrinsic peroxidase-like activity of Cu^{2+} based MOFs by employing $Cu_3(BTC)_2$ (BTC=1,3,5-benzene tricarboxylate) **(23)**, also known as HKUST-1 **(23)**, as a model MOF and thiamine (TH) (Vitamin B1) as a peroxidase substrate, respectively. Furthermore, the changes of TH absorption spectra in the presence of HKUST-1 **(23)** and H_2O_2 suggest the formation of TC with a more stable rigid structure [41]. In addition to their work, the MOFs were further subjected to the determination of vitamin B1 in tablets and urine samples. As seen from observed results, the recoveries of vitamin B1 in tablet samples were between 99.56 % and 116.35 %, while the recoveries between 99.35 % and 102.33 % were obtained for urine samples. The results indicate that the proposed fluorescent method can be used to detect vitamin B1 in tablets and urine samples and this method has no obvious system error of detection [41].



Styrene

(24)



PGA

(25)

Furthermore, Lian et al. have reported the synthesis of an Sc-based metal-organic framework with MIL-53 type configuration was synthesized (Sc-MOFs), and the luminescent Eu-doped MOF is developed in 2017. These MOFs were further evaluated for the sensing efficiency of PGA **(25)**. Their result indicates that the enhanced effect of Eu@MOFs caused by PGA **(25)** is not influenced by the simultaneous components, and this shows that it can further use the sensor for the detection of PGA **(25)** in serum and urine [42]. On the other hand, to explore the detecting potential of Eu@MOFs for further application, the detection limit tests in serum and urine were conducted. This can satisfy the daily needs for the monitoring of urinary PGA **(25)** and also suggests the extreme sensitivity of Eu@MOFs as a probe for detecting PGA **(25)** [42].

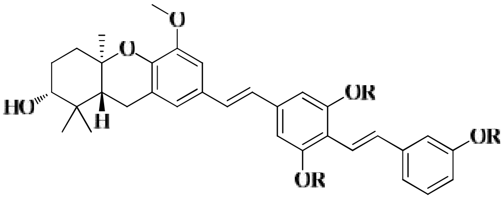
$Ce(NO_3)_3\cdot 6H_2O$ (26)

Additionally, In the year 2016, Zeng and co-worker reported the preparation of a kind of cerium(III) coordination polymer nanoparticles employing ATP molecule as bridging ligand by simply mixing the precursors (ATP and $Ce(NO_3)_3\cdot 6H_2O$) **(26)** in Tris-HCl buffer and further evaluated for detection of sensing of glucose and H_2O_2. It was observed from the result that the concentration of glucose in human serum, measured by the proposed method in their work, was close to the reference value provided by the hospital with the GOD-PAP method. The good accuracy (the recovery was in the range of 98.5% to 106 %) and the high precision (RSD) demonstrated the applicability of ATP-Ce-Tris CPNs as an effective sensor for glucose detection in human serum [43].

Further, in the year 2016, Yin et al. have developed a facile approach for the preparation of protein-embedded MOFs by using bovine hemoglobin (BHb) as the organic component and zeolitic imidazolate framework-8 (ZIF-8) as the inorganic component, respectively. This hybrid composite was further applied for visual detection of hydrogen peroxide (H2O2) and phenol. The developed method revealed a high selectivity, good sensitivity, and rapid response time towards the target compounds. The successful real-sample applications demonstrate the great potential of the ZIF-8@BHb hybrid composites in biological and environmental analysis [44]. Due to their high sensitivity, good selectivity, rapidity, and simplicity, we believe that the luminescent-based biosensors will indubitably find wide applications in biological research, clinical diagnostics, and drug discovery.

2.5 LFMOs as Anti-cancer agents

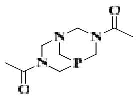
Cancer is one of the leading health hazards and the prominent cause of death for decades and chemotherapy is considered a significant option for the cure of cancer. Among applied approaches for the treatment against cancer the major objective of many marketed chemotherapeutic medications [45], is the introduction of apoptosis of cancer cells. Currently, medicinal chemists have focused on various heterocyclic derivatives in the efforts to develop appropriate anticancer drugs. However, in recent times, researchers have focused on luminescent-based nano compounds and organometallic compounds for the imaging of cancer cells in the human body. There is an urgent need for novel selective anticancer analogues with negligible side effects due to toxicity to normal cells, decreased drug activity, and development of drug resistance, which are responsible for deficiency in cancer treatment [46]. Numerous anticancer agents are currently in clinical trials and used for the treatment of different kinds of cancers. Here, we have attempted to discuss some research on luminescent-based organometallics compounds which are evaluated for anti-cancer activity.



(27), R=MOM
(28), R=H

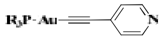
In the year 2009, Kuder and co-workers have reported the preparation of three natural schweinfurthins and more than 40 analogues, and assays on these compounds have afforded some understanding of structure-activity relationships in this family. Further schweinfurthins were evaluated as chemotherapeutic agents and would be benefit from the characterization of their mechanisms of action. As observed in the result, the schweinfurthins display potent growth inhibition and differential activity in the NCI’s 60-cell screen.

In this screening, the SF-295 cell line is among the most sensitive to schweinfurthin-induced growth inhibition, while the human-derived lung adenocarcinoma A549 cells display only moderate growth inhibition upon comparable treatment. These findings further suggest that the structural changes introduced in compound **28** do not alter the differential activity observed with the schweinfurthins [47].



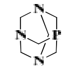
3,7-diacetyl-1,3,7triaza-5-phosphabicyclo[3.3.1]nonane

DAPTA (29)



PR3= PTA(I); DAPTA (II)

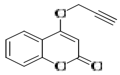
(30)



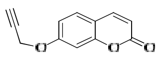
1,3,5triaza-7-phosphaadamantane

PTA

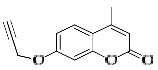
(31)



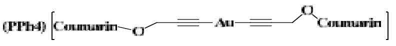
32



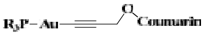
33



34

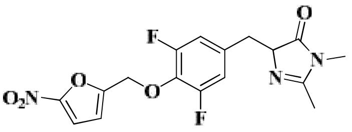


32-34a



PR3 = PTA (32-34b); DAPTA (32-34c)

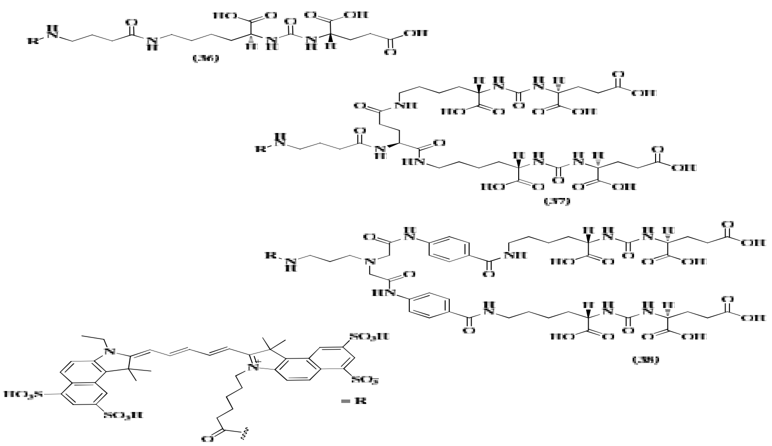
Furthermore, Arcau and co-workers have reported the synthesis and characterization of three propynyloxycoumarins together with the formation of three different series of gold(I) organometallic complexes in 2013. Additionally, the biological evaluation focused on determining the effects against tumor cell growth in HT-29 colon carcinoma and MDA-MB-231 breast cancer cells as well as inhibition of the activity of the enzyme TrxR, which represents a well-established molecular target of gold species. The activities of **32-34b/c**, I, and II were similar to that of $PPh_4[AuCl_2]$, in which gold(I) was unstable coordinated and readily presented to interact with thiols/selenols as present in TrxR. Moreover, their activity was also similar to that of some other recently studied complexes of the alkynyl gold(I) triphenylphosphane type [48].



DFHBI-NF

(35)

In addition, Xu et al. and co-workers have reported the dual activated fluorescent probe based on RNA mimics of GFP for the detection of NTR. They have used DFHBI and 2-bromomethyl-5-nitro-furan to synthesize 5[3,5-difluoro-4-(5-nitrofuran-2-ylmethoxy)-benzylidene]-2,3dimethyl-3,5-dihydro-imidazol-4-one (DFHBI-NF) **(35)**, which blocks phenolate formation using a protecting group. Further, they used flow cytometry to confirm the above results. They observed that fluorescence was improved significantly when both Broccoli and NTR were present. According to their observed results, DFHBI-NF **(35)** could image NTR in living cancer cells. Their findings open new possibilities for developing various genetically encoded fluorescent biosensors based on RNA/DFHBI complexes [49].



(36)

(37)

(38)

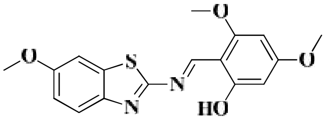
= R

In the year 2018, Kwon et al. have reported novel multivalent PSMA inhibitors with glutamate-urea-lysine structures to improve inhibition characteristics. Precursors of the novel inhibitors were prepared from glutamic acid with di-tert-butyl ester. In vitro PSMA inhibition studies were carried out by a fluorescence-based NAALADase assay method. Their observation might be clarified by the chemical structures of the compounds. Whereas compound **(36)** had three carboxylic acids, compounds **(37)** and **(38)** had six. Furthermore, unlike compound **(38)**, the linker of compound **(37)** consisted of glutamine amino acid. Consequently, the researcher considered that the amino acid structure of compound **(37)** contributed to quick clearance, which could be a reason for the deficiency of intensity in the liver. The observed results suggest that the developed inhibitor could be a favorable imaging probe for prostate cancer and that the dimeric system by a glutamine linker could show positive effects on the diagnosis of cancer [50].

2.6 LFMOs as an Antibacterial and Antifungal Agents

Many diseases lead to human death and the reason behind this morphology is the different bacterial infections to mankind. Among them, mycobacterial infectious disease is a serious threat globally. Due to lengthy treatment periods, some microbes have become resistant to prophylaxis. Mycobacteria are generally responsible for tuberculosis disease which is the primeval enemy of the human. It is a vital cause of morbidity and mortality in poor low-income countries as well as in developing countries due to of non-availability of reliable laboratory facilities. Furthermore, in the past few years, the problems of multidrug resistance (MDR-TB) microorganisms have reached an alarming level in many countries around the globe. Infections caused by various bacteria pose a serious challenge to the medicinal community hence there is an urgent need to develop novel anti-microbial drug candidates. Despite this knowledge, various researchers have reported biologically active heterocyclic derivatives and their complexes which are effective against bacteria, fungi and tumors, as well as biochemical and pharmacological properties [51-53].

Furthermore,the fungal pathogens *Candida albicans*, Aspergillus, and *Cryptococcus neoformans* are transitioned from a rare curiosity to a leading cause of human death. The administration of infections caused by this microorganism is intimately dependent on the efficiency of antifungal drug candidates. The increasing populations of individuals with decreased immune function increase the risk of fungal infections that are most susceptible to opportunistic pathogens. For that reason, there is serious attention has been focused on the development of novel antifungal analogues [53-54]. Among antifungal agents, fluorescent organic derivatives having excellent photophysical properties ease of production, availability, in terms of fluorescence intensity and quantum yields led to much more attention in the field of chemosensors, biological studies such as cell imaging and antimicrobial activities. Hence, the utilization of nano-scale fluorescent or luminescent materials in the treatment and detection of metal ions and drug-resistant bacteria is of prime importance. Here, we have discussed a few research that shows the antibacterial and anti-fungal importance of luminescent and fluorescent-based organometallic analogues.

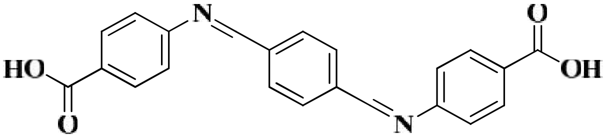


(E)-3,5-dimethoxy-2-((6-methoxybenzo[d]thiazol2-ylimino)methyl)phenol

(39)

Alpaslan et al. have reported a new Schiff base, (E)-3,5-dimethoxy-2-((6-methoxybenzo[d]thiazol-2-ylimino)methyl)- phenol **(39)**, was prepared from the reaction of 2-amino-6-methoxybenzothiazole and 2-hydroxy-4,6-dimethoxybenzaldehyde. The synthesized compounds were further evaluated for their antibacterial and antifungal activities for their minimum inhibitory concentration. It was observed from the results that the compound has a higher antifungal effect on C. Albicans ATCC 60193 and C. tropicalis ATCC 13803 compared to the antibacterial effect. Similarly, the Schiff base has a stronger antibacterial effect against E. faecalis ATCC 29212, B. subtilis ATCC 6633, E. coli ATCC 25922, E. coli ATCC 35218, P. aeruginosa ATCC 27853, and P. Vulgaris ATCC 13315 compared to S. aureus ATCC 25923. The Schiff base showed better antifungal activity than antibacterial activity. Antifungal activity of Schiff base was found to be dose susceptible depending on the concentration of 32 mg/mL [55].

Further, Calangian et al. have reported the synthesis of carbon nanoparticles (FCNPs) using hydrothermal carbonization and Cladophora vagabunda as a raw material. The antibacterial assay against *S. aureus*, *E. coli*, and cytotoxic activity using brine shrimp lethality test was performed to determine the biological activity of synthesized FCNPs from C. vagabunda. These findings suggest that the as-prepared FCNPs from C. vagabunda exhibit inactive cytotoxicity and can be potentially used for bio-imaging and drug delivery [56].

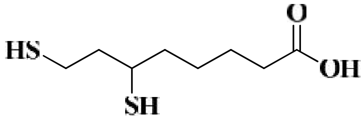


4,4'-{benzene-1,4-diylbis[(Z)methylylidenenitrilo]}dibenzoic acid

(40)

Furthermore, in the year 2018, Mahajan and co-workers have reported a simple, selective, and sensitive method for the detection of Co^{2+} ions using fluorescent organic nanoparticles. The fluorescent small compounds were synthesized (4,4'-{benzene-1,4-diylbis-[(Z)methylylidenenitrilo]}dibenzoic acid) (BMBA) **(40)** to explore its suitability as a sensor for Co2+ ion and biocompatibility in form of nanoparticles. The antibacterial activity retained by BMBA **(40)** for *E. coli and Bacillus sps* bacterial culture was with MIC of 6.25 - 100 µg/mL and 3.12 to 100 µg/mL, respectively. The antibacterial activity obtained for BMBANPs and BMBA **(40)** exhibits better performance compared with the reported organic compounds [57].

On the other hand anti-TB, the biological evaluation was also carried out the check the potency of the synthesized fluorescent nano moleculesFrom the result, it is noteworthy that BMBANPs depicted outstanding anti-tubercular activity as compared to the standard drug streptomycin against *M. tuberculosis* at 6.25 µg/mL. Whereas the parent compound, BMBA **(40)** revealed rational activity with the MIC of 50 µg/mL. Here, bioactive properties of BMBANPs and BMBA **(40)** show effective anti-TB activity against *M. tuberculosis* $H_{37}RV$ strain as compared to the reported compounds [57].



Dihydrolipoic Acid (DHLA)

(41)

Moreover, Liu et al. have proposed a new strong UV photochemical reduction synthesis of water-soluble luminescent Ag NCs using DHLA **(41)** as the capping reagents to stabilize the Ag NCs in the solution in 2014. Further, the antibacterial ability of the Ag NCs was tested on the *M. tuberculosis* $H_{37}Rv$ strain. Ag NCs inhibit respiration and growth of the cell, break permeability of the outer membrane and destroy the structure of the membrane, resulting in cell decomposition and death eventually [58].

Additionally, In the year 2011, Mutalik and co-worker have reported the synthesis of a series of La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III) and Yb(III) complexes with the Schiff base (PHC) **(42)** derived from the condensation of 8-formyl-7-hydroxy-4-methyl-coumarin with 3-amino pyridine. Furthermore, antibacterial and antifungal activities of ligand and its complexes are tested against two bacteria such as *S.Aurease*, *E.Coli,* and two fungi *A.Niger*, *C.Albicans*. Norfloxacin for bacteria and Grisiofulvin for fungi were used as standard drugs. From the observed results, it is clear that the metal chelates display significant antimicrobial activity than that of the free ligand molecule. The complexes **(43), (46),** and (**50)** were most active among the other complexes. From the above biological results, it was concluded that these compounds serve as good fungicides and better bactericides [59].

PHC = $C_{16}H_{12}O_3N_2$ (42)

(43) L1 = $[La(PHC)_2(NO_3)(H_2O)_2].2H_2O$.

(44) L2 = [Pr (PHC)2(NO3)(H2O)2].2H2O.

(45) L3 = $[Nd(PHC)_2(NO_3)(H_2O)_2].2H_2O$.

(46) L4 = $[Sm(PHC)_2(NO_3)(H_2O)_2].2H_2O$.

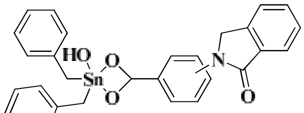
(47) L5 = $[Eu(PHC)_2(NO_3)(H_2O)_2].2H_2O$.

(48) L6 = $[Gd(PHC)_2(NO_3)(H_2O)_2].2H_2O$.

(49) L7 = $[Tb(PHC)_2(NO_3)(H_2O)_2].2H_2O$.

(50) L8 = $[Dy(PHC)_2(NO_3)(H_2O)_2].2H_2O$.

(51) L9 = $[Yb(PHC)_2(NO_3)(H_2O)_2].2H_2O$.



4-6
(52-54)

In 2010, Cai et al. have reported the synthesis of 3-(1-oxo-1H-2,3-dihydroisoindol-2-yl)benzoic acid (1, mHpba, positional isomer of our previously reported 2- and 4-(1-oxo-1H-2,3-dihydroisoindol-2yl)benzoic acid (oHpba 2 and pHbpa 3, respectively)) and three correlated organotin carboxylates with general formula Sn(OH)(bz)2L (**52, 53, 54** bz = benzyl, HL = mHpba, oHpba, and pHpba, respectively). It can be proposed that this remarkable and unique fluorescent property of phthalimidine derivatives might be useful in exploiting some sensory and diagnostic applications [60].

3.0 Conclusion

Since the discovery of LMOFs in 1995, their potential has been recognized for a wide variety of applications. Their luminescent properties, in combination with their unique structural conditions, make LMOFs exciting candidates for sensing, catalysis, adsorption, therapeutics, and imaging. Throughout this review, we have comprehensively discussed the fundamental properties of LMOFs, types of LMOFs, well-established synthesis approaches, and various PSM strategies for enhancing their functional capabilities and expanding their potential chemo- and biosensing applications. Despite advancements in sophisticated instrumentation in analytical fields, the demand for a novel and alternative approaches for rapid screening and therapeutic applications has grown tremendously over the past decades. In line with such development, the great potential of LMOFs in sensing applications has also been recognized due to their superior properties (e.g., high sensitivity, selectivity, and molecular payload), meritful structural characteristics (e.g., thermally and chemically stable crystal structure, tunable porosity, multiplexed luminescent attributes), and feasibility of scaled-up synthesis.

Accordingly, various biological and chemical sensing applications of the LMOFs have been extensively investigated. The use of LMOFs for such applications has been validated in the body of publications covering the target subjects. It is anticipated that future attempts to explore the new and novel combinations of metal ions and organic linkers will yield advanced LMOF platforms with enhanced sensing capabilities in various fields including molecular sensing and bioimaging. A thorough literature survey on the sensing potential of LMOFs has revealed a paradigm shift towards the use of methodical approaches to enhance the sensitivity and selectivity of LMOFs with a specific focus on reversibility. A major aim of LMOF-based sensor research in the future will be to develop nanoscale LMOFs with enhanced sensing capacities and reversibility under controlled environmental conditions. Another important factor driving the research on these coordination compounds will be transforming these exciting potential applications into actual products that meet daily needs. The active participation of material scientists, chemists, and biologists on a single platform can enable the successful transformation of LMOF science to product-based technology in the future.

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CHAPTER:3

SYNTHESIS, CHARACTERIZATION OF SOME MIXED LIGAND COMPLEXES OF COBALT FORMED WITH 1 METHOXY CARBONYL-1-CYANOETHYLENE-2, 2- DITHIOLATE AND VARIOUS NITROGEN DONOR

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Abstract: This paper describes introduction of mixed ligand dithiolate complexes of cobalt, synthesis of mixed ligand complexes of cobalt(II) with dithiolate (1-methoxy carbonyl –1- cyano ethylene -2,2-dithiolate) and nitrogen donors like pyridine, β–picoline, γ-picoline, orthophenylenediammine and characterization by elemental analysis, molar conductance, IR., UV-vis., ESR spectroscopy and thermo gravimetric analysis (TGA).

Keywords: Co(II),Dithiolate and Nitrogen donor.

INTRODUCTION

Dithiolate complexes involving cobalt and various 1,1 and 1,2-dithiolate ligands have been of interest because of various interesting features and applications associated with them. Cobalt (II) complexes have diverse structural, electronic and magnetic features. Their electrochemical behavior is also of considerable interest. Oxidation of cobalt (II) to cobalt(III) is facile process. In dithiolate complexes, cobalt (II) is generally oxidized to cobalt (III) state. Structural feature of square plannar cobalt (II) complexes are worthy of mention. In some of these complexes symmetry has been found lower than D_{4h}. Cobalt forms variety of complexes, clusters with dithiolate ligands. Dithiolate complexes have application, such as: photoluminescent[1], semiconductor[2], nonlinear optical material[3], molecular conductor[4], catalyst[5-6], magnetic properties[7], and antimicrobial activity[8].

Molecular structure, two and three legged piano stool geometry of the cobalt dithiolate complexes have been reported by many workers.[9,10]Synthesis and D_{2h} symmetry of cobalt(II) complex of the dianion of cyclopentadienedithiocarboxylic acid has been reported by Kalbacher *et al.*[11].

The electrochemical behavior of the cobalt dithiolate complexes have been studied by many workers[12-16]. Synthesis and planar structure of cobalt dithiolate complex, [Co(η^5-C_5R_5){SNC(Ph)S}](R=H or R=CH_3, η^5-C_5R_5 = η^5-cyclopentadienyl, SNC(Ph)S= 1-phenylmethanimine-N,1-dithiolato) have been reported by Kato *et al.*[17]. This complex [Co(η^5-C_5R_5){SNC(Ph)S}] undergoes reversible one electron reduction which was ascribed to process from Co^{III} to Co^{II}. Recently Cerdeira *et al.*[18] derived a new series of $[M(cbdt)_2]^{-2}$ (cbdt= 4-cyanobenzene -1,2-dithiolate, M= Zn, Co, Cu, Ni, Au, Pd) complexes. These complexes show square planar coordination geometry and redox properties.

Mixed ligand complexes of CpCo(Dithiolene) with pyridinium-dicyanomethylide group have been reported by Nomura *et al.*[19]. These complexes show metal centered and ligand centered reduction wave.

Synthesis, square-pyramidal structure and magnetic property of cobalt dithiolate complex $[Hpy]_2[\{M(mnt)_2\}_2]$(M=Fe or Co, Hpy= pyridinium, mnt= maleonitrile dithiolate(2,3-disulfanyl maleonitrile)] have been reported by Rodriques *et al.*[20]. Mori *et al.*[21] have studied oxidation properties of cobalt dithiolate complexes, Co(η^5-[C_5H_5)($C_8H_4S_8$)] ($C_8H_4S_8^{2-}$= 2-{(4,5-ethylenedithio)-1,3-dithiole-2-ylidine} -1,3-dithiole-4,5-dithiolate(2-)) and [Co(L)(C_3S_5)](L= η^5-C_5H_5, η^5-C_5Me_5, $C_3S_5^{2-}$=4,5-disulfanyl-1,3-dithiole-2thionate) and crystal structure of Co(η^5-C_5Me_5)(C_3S_5)Br. The complex [Co(η^5-C_5Me_5)(C_3S_5)Br] behaves as an insulator. Nomura *et al.*[22] have reported paramagnetic and diamagnetic complexes [CpNi(bdtodt)] and [CpCo(bdtodt)](Cp = η^5-cyclopentadienyl,bdtodt:benzo[1,3]dithiol-2-one-5,6-dithiolato) and electrochemical behavior.

Gurashi[23] have studied synthesis and effect of substitution on symmetry of mixed ligand complexes of dithiolate, [M(dha)(Htddt)(tddt)] (M = Co, Ni), (Hdha = 3-acetyl – 4-hydroxy – 6-methyl – 2-pyrrone, Htddt = 1,3,4 – thiadiazole – 2,5 – dithiol).In mixed ligand dithiolate complex of cobalt(II), octahedral symmetry of Co(II) is reduced by the substitution of an Hdha ligand by Htddt ligand. Mixed ligand complexes of cobalt and other transition metal have appeared in literature[24-35].

Singh*et al.*[36] have synthesized mixed ligand complexes of Co(II) with nitrogen donor (pyridine, α-picoline, β-picoline, γ-picoline, orthophenylenediammine) and sulfur donor(1,1-dicyanoethylene-2,2-dithiolate(i-MNT^{2-}) or 1-cyano-1-carboethoxyethylene-2,2-dithiolate (CED^{2-}). They revealed distorted octahedral stereochemistry around Co(II) in these complexes.Bajia *et al.*[37] have reported synthesis of mixed ligand complexes of Co(II),$[Co\{S_2P(OR)_2\}_2(C_5H_5N)_2]$(R= o-, m-, p-$C_6H_4Me$, CH_2Ph, ($S_2P(OR)_2$) = Bis(O,O'-ditolyl/dibenzyl dithiophosphato), C_5H_5N= pyridine), $[Co\{S_2P(OR)_2\}_2(NH_3)]$($NH_3$= amine).They have reported distorted octahedral geometry of pyridine complex and distorted trigonal bipyramidal of amine complex.

In this chapter we describe mixed ligand complexes of cobalt (II) formed with dithiolate (1-methoxycarbonyl-1-cyanoethylene-2, 2- dithiolate) and nitrogen donor ligands like pyridine, β-picoline, γ-picoline, orthophenylenediamine

EXPERIMENTAL

Materials and method

All the chemicals were of laboratory reagents grade.Cobalt was determined gravimetrically after decomposing organic part of the ligands by aquaregia. Sulfur was estimated as $BaSO_4$. Melting points were taken in an open capillary and are uncorrected.The molar conductance of the millimolar solutions of the complexes in DMSO was measured using systronics conductivity meter 304 with dip type cell. UV-vis. spectra was recorded on AnSI/IEE / Shimadzu quartz cells in (200-1000nm)/ (400-1100nm) region. IR spectra were recorded 500-4000cm^{-1} as KBr pellets on Perkin Elmer. ESR spectra were recorded on varian E-112 spectrometer at liquid nitrogen temperature (LNT) in DMSO. Thermogram was recorded on Perkin Elmer thermal analysis instrument.

Synthesis of the ligand

The ligand (1-methoxycarbonyl-1-cyanoethylene-2, 2- dithiolate) was prepared by reported method[38].Finely crushed NaOH (4g,0.2mol) was poured in 12ml methanol and solution of methylcyanoacetate

(5.5ml, 0.1mol) and CS_2 (5ml, 0.1mol) in 10ml methanol was added with constant stirring and cooling by maintaining the temperature in range of 15-20^oC. The yellow product obtained was filtered off.

Synthesis of Complexes [Co ($CS_2C=C(CN)COOMe$)L] L= Py, β -pic, γ-pic and OPD (o-phenylenediamine).

(1) [Co($CS_2C=C(CN)COOMe$)(OPD)]. $5H_2O$

To 20 ml of an aqueous solution of cobalt acetate (1.09g, 5mM), 20ml of methanol solution of OPD (0.54g, 5mM) was added. The solution was thoroughly mixed and an aqueous solution of the ligand ($(NaS)_2C=C(CN)COOMe.5H_2O$) (1.5gm, 5mM) was added dropwise followed by addition of 20 ml distilled water. Deep green colored product was washed with water alcohol and ether, dried over $CaCl_2$.

(2) [Co ($CS_2C=C(CN)COOMe$)$(py)_2$]

To 25 ml of an aqueous solution of cobalt acetate (1.24g, 5mM), 2.5 ml of pyridine in ethanol was added. The solution was thoroughly mixed and an aqueous solution of the ligand ($(NaS)_2C=C(CN)COOMe .5H_2O$)(1.5gm, 5mM) was added dropwise followed by addition of 20 ml distilled water. Green colored product was washed with water, alcohol and ether, dried over $CaCl_2$.

(3) [Co ($CS_2C=C(CN)COOMe$)(β-pic)$_2$]

To 25 ml of an aqueous solution of cobalt acetate (1.24g, 5mM), 3ml of β-picoline in ethanol was added. The solution was thoroughly mixed and an aqueous solution of the ligand ($(NaS)_2C=C(CN)COOMe .5H_2O$)(1.5gm, 5mM) was added dropwise followed by addition of 20 ml distilled water. Green colored product was washed with water, alcohol and ether, dried over $CaCl_2$.

(4) [Co (CS_2C=C(CN)COOMe)(γ-pic)$_2$]-

To 25 ml of an aqueous solution of cobalt acetate (1.24g, 5mM),3 ml of γ- picoline in ethanol was added. The solution was thoroughly mixed and an aqueous solution of the ligand ($(NaS)_2C$=C(CN)COOMe .5H_2O) (1.5gm, 5mM) was added dropwise followed by addition of 20 ml distilled water. Green colored product was washed with water, alcohol and ether, dried over $CaCl_2$.

RESULTS AND DISCUSSION

Molar conductance

Molar conductance of the complexes, [Co(py)$_2$(CS_2C=C(CN)COOMe)], [Co(β-pic)$_2$(CS_2C=C(CN)COOMe)], [Co(γ-pic)$_2$(CS_2C=C(CN)COOMe)] and [Co(OPD)(CS_2C=C(CN)COOMe)].5H_2O in 10^{-3}M solution in dimethylsulfoxide have been observed at 30µ Scm^{-1}. These values suggest non electrolytic nature of these complexes.

Table.1 : Colour, molar conductance, analytical data of the complexes.

S.N.	Complex	Colour	Mol. Wt.	M.P./ (dec.°C)	Found (Cal.) (%)		Molar Conductance in 10^{-3} M DMSO (µS cm^{-1})
					M	S	
1	[Co(OPD)(S_2C=C(CN)COOMe)].5H_2O ($C_{11}H_{21}N_3O_7S_2Co$)	Dark Green	429.9	165 – 170	12.5 (13.7)	13.5 (14.8)	30
2	[Co(py)$_2$(S_2C=C(CN)COOMe)] ($C_{15}H_{13}N_3O_2S_2Co$)	Green	389.9	110	14.5 (15.1)	15.1 (16.4)	30
3	[Co(β-pic)$_2$(S_2C=C(CN)COOMe)] ($C_{17}H_{17}N_3O_2S_2Co$)	Green	417.9	130 – 135	12.9 (14.09)	14.1 (15.3)	30
4	[Co(γ-pic)$_2$ (S_2C=C(CN)COOMe)] ($C_{17}H_{17}N_3O_2S_2Co$)	Green	417.9	160 – 165	13.2 (14.09)	14.5 (15.3)	30

IR Spectra

IR spectral data have been presented in table 2. Strong bands of ν(C-S) vibration have appeared at 1007-1036 cm^{-1} in all complexes. The characteristic frequency ν(C=$CS_{2)}$ have been observed in the region (1383-1443 cm^{-1}).[43] Bands at 2183-2196 cm^{-1} in all complexes are attributed to the ν(C≡N)vibrations[41,43]. The compounds having ester functions are expected to show ν(C=O) band in the region (1600-1700 cm^{-1}) and ν(C-O) band in the region (1100-1200 cm^{-1})[43]. In these complexes, these bands have been found in the region 1612-1662 cm^{-1} and 1133-1171 cm^{-1}.The band of pyridine ring for the presence and coordination has been found at (625-635cm^{-1})[39,41]. The band for monosubstituted rings has been observed at 690 - 780 cm^{-1}. ν(=C-H) (aromatic ring) bending mode for orthophenylene diammine[40] has been found at 759 cm^{-1}. Aliphatic ν(C-H) vibration and aromatic ν(C-H) vibration of the complexes have been observed in the region 2924-2987 cm^{-1} and 3000 cm^{-1} respectively. A broad band in all complexes has been found at 3383-3415 cm^{-1} due to presence of water.

Table.2. Important IR bands (cm^{-1}) of the complexes.

S.N.	Complexes	¬(C≡N)	¬(C=O)	¬(C-O)	¬(C=CS$_2$)	¬(C-S)	Coordination of nitrogen donor ring	Substituted ring(o,m,p)
1	[Co(OPD)(S_2C=C(CN)COOMe)].5 H_2O ($C_{11}H_{21}N_3O_7S_2Co$)	2196	1619	1171	1443	1036	625	759
2	[Co(py)$_2$(S_2C=C(CN)COOMe)] ($C_{15}H_{13}N_3O_2S_2Co$)	2184	1632	1142	1429	1009	625	–
3	[Co(β-pic)$_2$(S_2C=C(CN)COOMe)] ($C_{17}H_{17}N_3O_2S_2Co$)	2183	1662	1133	1383	1007	635	750
4	[Co(γ-pic)$_2$ (S_2C=C(CN)COOMe)] ($C_{17}H_{17}N_3O_2S_2Co$)	2183	1612	1133	1383	1009	627	807

UV-vis. Spectra

Electronic spectral data of the complexes have been presented in table (3). In the visible region all of these complexes show absorption band at around 600 nm. The complex having OPD ligand shows additional band at 720 nm. Electronic absorption spectra are supportive of square planar type of geometry in these complexes[42].

Table.3- UV-Visible data for the complexes.

S.N.	Complexes	Solvent	λ_{max}(nm)
1	[Co(OPD)(S_2C=C(CN)COOMe)].5H_2O ($C_{11}H_{21}N_3O_7S_2Co$)	DMF DMSO	270,330, 372 450, 620, 720
2	[Co(py)$_2$(S_2C=C(CN)COOMe)] ($C_{15}H_{13}N_3O_2S_2Co$)	DMSO	260, 287, 340, 380,600
3	[Co(β-pic)$_2$(S_2C=C(CN)COOMe)] ($C_{17}H_{17}N_3O_2S_2Co$)	DMSO	267, 337, 376, 607
4	[Co(γ-pic)$_2$ (S_2C=C(CN)COOMe)] ($C_{17}H_{17}N_3O_2S_2Co$)	DMSO	260, 336, 375, 596

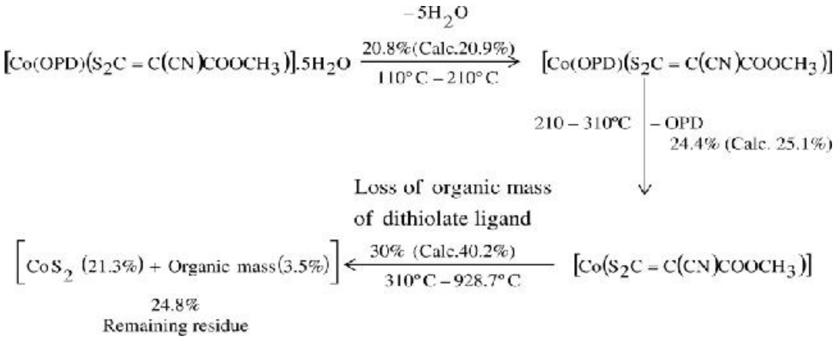
In UV region, [Co(py)$_2$(CS_2C=C(CN)COOMe)], [Co(β-pic)$_2$ (CS_2C=C(CN)COOMe)], [Co(γ-pic)$_2$(CS_2C=C(CN)COOMe)] and [Co(OPD)(CS_2C=C(CN)COOMe)].5H_2O show bands at 260 nm, 287 nm, 340 nm, 380 nm; 267 nm, 337 nm, 376 nm; 260 nm, 336 nm, 375 nm and 270 nm, 330 nm, 372 nm. Presence of similar bands in UV region supports presence of similar moiety (pyridines) in these complexes.

ESR

ESR spectra of the complexes [Co(py)$_2$(CS_2C=C(CN)COOMe)],[Co(β-pic)$_2$(CS_2C=C(CN)COOMe)], [Co(γ-pic)$_2$(CS_2C=C(CN)COOMe)] and [Co(OPD)(CS_2C=C(CN)COOMe)].5H_2O recorded at room temperature in Dimethyl-sulfoxide solution does not give signals and hence are not informative. ESR spectrumof the mixed ligand complex [Co(OPD)(S_2C=C(CN)$COOCH_3$].5H_2O recorded at L.N.T. in Dimethyl sulfoxide solution shows presence of eight lines . In cobalt(II) systems, eight lines are expected in view of I = 7/2 for this nucleus. ESR indicates that cobalt is present as divalent ion in this complex. $g_{av}$and A_{av} calculated from the spectrum found as 2.02 and 42. Value of g_{av} is similar to those reported for metal dithiolate complex. The value of A_{av} show considerable delocalization of electrons. g_{av} also suggest covalent nature of bonding.

Thermogravimetric analysis

Thermal behavior of the complexes, [Co(OPD)(S_2C=C(CN)$COOCH_3$)] .5H_2O was recorded in the temperature range 37.94°C to 928.7°C. Thermogram of complex indicated the total weight loss of 75.2% in above mentioned temperature range, which occurred in three steps. Decomposition of complex starts from temperature 110°C leading to loss of five water molecule (20.8%) upto temperature 210°C. In the second step decomposition, orthophenyl enediammine molecule (24.4%) is lost in temperature range 210°C to 310°C.



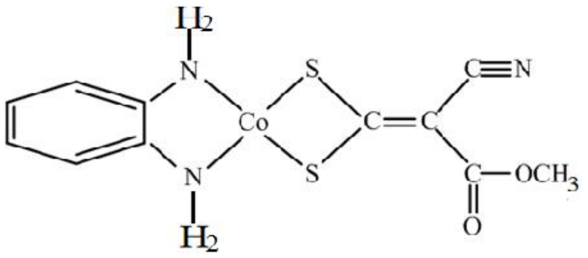
In third step decomposition, weight loss (30%) in the temperature range 310°C to 928.7°C corresponds to decomposition of organic part of dithiolate ligand. The decomposition of organic part of dithiolate ligand is not completed upto temperature 928.7°C. End product is expected to be metal sulfide (CoS) and remaining organic part of dithiolate ligand.

Table 4 : Temperature and Weight loss data for complex [Co(OPD)(S_2C=C(CN)$COOCH_3$).$5H_2O$]

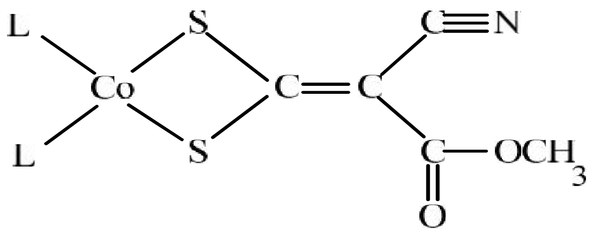
Steps	Temp. Range °C	Wight loss%		Lost fragments	Remaining residue
		Found	Calculated		
I	110 – 210	20.8	20.9	$5H_2O$	CoS(21.3%)+ organic mass(3.5%) (Total mass – 24.8%)
II	210 – 310	24.4	25.1	OPD	
III	310 – 928.7	30	40.2	Organic Part of dithiolate ligand	
		75.2	86.2		

CONCLUSION

On the basis of foregoing discussions and literature, the structure of the mixed ligand complexes of dithiolate of cobalt have been proposed tentatively.



and



$C_6H_8N^{-}_{2}$ = O-Phenylene diammine, L= Pyridine, α-Picoline, β-Picoline, γ-Picoline

Fig 1: Proposed structure of mixed ligand complexes of dithiolate of cobalt(II).

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CHAPTER:4

SYNTHESIS AND CHARACTERIZATION OF SOME MIXED LIGAND COMPLEXES OF NICKEL (II) FORMED WITH 1-METHOXY CARBONYL –1- CYANO ETHYLENE-2,2- DITHIOLATE LIGAND AND NITROGEN DONORS

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Abstract: Mixed ligand complexes of the type [Ni(L)$_n$(dithio)] n=1 or 2 L= OPD, and various substituted pyridines, dithio=$(NaS)_2C=C(CN)$ COOMe.H_2O have been synthesized and characterized by elemental analysis, molar conductance measurements, IR, electronic and ^{1}HNMR,spectral studies, thermal gravimetric analysis. These complexes are of non-electrolytic nature as expected. Geometry around metal ion is either square planar or octahedral. Dithiolate ligand coordinates in bidentate chelating manner through its two sulphur atoms and nitrogen donors are monodentate except for which acts in bidentate chelating manner OPD For which acts in bidentate chelating manner. Thermogram of $Ni(OPD)_2(S_2C=C(CN)COOMe)]$.$2H_2O$ reveal that water present in the complex is not coordinated to metal.

Keywords: mixed ligand, dithiolate, nitrogen donor.

INTRODUCTION

Synthesis, characterization of complexes of nickel with 1,1- and 1,2- dithiolates have been focus of active research.[1-4] Nickel generally forms square planar complexes with bulkier sulfur donors. The planar complexes of nickel were of considerable importance from the view point of electrical conductance studies.[5] Simple complexes, salts, heterobimetallic complexes, clusters formed with nickel and dithiolate ligands have been reported.[6-9] The dithiolate complexes of nickel have been investigated for their number of applications, such as: molecular conductor[10], catalyst[11], antibacterial and antifungal activity[12], antioxidants[13], thin films material[14], nonlinear optical materials[15] and near IR dyes[16].

Mixed ligand complexes of nickel formed with sulfur and nitrogen donors have also been reported.[17-24] These complexes have similarity with those of nickel dithiolates. However their electronic and structural properties may be tuned by choice of nitrogen and sulfur donors. Mixed ligand complexes of nickel have also been investigated for their various applications, like: molecular conductors[25], nonlinear optical materials[26-27], semiconductor[28], transmetalating agent[29], vulcanization accelerators and anticholinesterase activity[30], sensitizer[31], light energy conversion materials and biological agent.[32]Nickel(diimine)(dithiolate) complexes have been reported by Alkam *et al.*[33] and Benedix *et al.*[34]. Recently Singh *et al.*[35], have reported synthesis, characterization, luminescent properties and biological activity of mixed ligand complexes of dithiolate with nitrogen donor ligands like pyridine and picolines.In this communication we report synthesis, characterization of some mixed ligand complexes of nickel formed with 1-methoxy carbonyl –1- cyano ethylene -2,2- dithiolate and various nitrogen donors, like orthophenylene diamine, pyridine, β-picoline, γ- picoline.

EXPERIMENTAL

Materials and method

All the chemicals used in this study, were of laboratory reagents grade.Nickel was determined gravimetrically after decomposing organic part of the ligands by aquaregia. Sulfur was estimated as $BaSO_4$. Melting points were taken in an open capillary and are uncorrected.The molar conductance of the millimolar solutions of the complexes in DMSO was measured using systronics conductivity meter 304 with dip type cell. UV-vis. spectra were recorded on AnSI/IEE using quartz cells in 200-1000nm region. IR spectra were recorded 500-4000cm^{-1} in KBr pellets on Perkin Elmer.^{1}H NMR spectra were recorded on av 300 spectrometer in DMSO solution. Thermogram recorded on Perkin Elmer thermal analysis instrument.

Synthesis of the ligand

Ligand was synthesized as reported in literature[36].Finely crushed NaOH (4g, 0.2mol) was poured in 12ml methanol and solution of methylcyanoacetate (5.5ml,0.1mol) and CS_2 (5ml,0.1mol) in 10 ml methanol was added with constant stirring and cooling by maintaining the temperature in range of 15-20°C. The yellow product obtained was filtered and dried over $CaCl_2$.

Synthesis of Complexes $[Ni(S_2C=C(CN)COOMe)L]$ L= Py, α–picoline(pic), β-picoline, γ-picoline and OPD(o-phenylenediamine).

(1) $[Ni(OPD)_2(S_2C=C(CN)COOMe)]\ .2H_2O$

O-phenylenediammine (1.08gm, 10mM) in methanol (30ml) solution was added with stirring to a 30 ml aqueous solution of nickel acetate (2.5gm, 10mM). Deep green coloured solution was obtained. To this solution, 30 ml of ligand $((NaS)_2C=C(CN)COOMe.5H_2O)$ solution (3.09gm, 10mM) was added with stirring, which yielded a green product. The product separated out by filtration and washed with water, alcohol, ether and dried over $CaCl_2$.

(2) $[Ni(py)_2(S_2C=C(CN)COOMe)]$

2.5 ml pyridine (30mM) was added with stirring to a 25 ml aqueous solution of nickel acetate (1.25gm, 5mM). Blue coloured solution was obtained. To this solution, 25 ml of ligand $((NaS)_2C=C(CN)COOMe.5H_2O)$ solution (1.545gm, 5mM) was added with stirring which yielded a greenish brown coloured product . The product separated out by filtration, washed with water, alcohol, ether and dried over $CaCl_2$.

(3) $[Ni(\ \text{-pic})_2(S_2C=C(CN)COOMe)]$

3 ml β-picoline (30mM) was added with stirring to a 25 ml aqueous solution of nickel acetate (1.25gm, 5mM). Blue coloured solution was obtained. To this solution, 25 ml of ligand $((NaS)_2C=C(CN)COOMe.5H_2O)$ solution (1.545gm, 5mM) was added with stirring which yielded a brown coloured product. The product separated out by filtration and washed with water, alcohol, ether and dried over $CaCl_2$.

(4) $[Ni(\gamma\text{-pic})_2(S_2C=C(CN)COOMe)]$

3 ml γ-picoline (30mM) was added with stirring to a 25 ml aqueous solution of nickel acetate (1.25gm, 5mM). Blue coloured solution was obtained. To this solution, 25 ml of ligand $((NaS)_2C=C(CN)COOMe.5H_2O)$ solution (1.545gm, 5mM) was added with stirring, which yielded a orange coloured product. The product separated out by filtration and washed with water, alcohol, ether and dried over $CaCl_2$.

RESULTS AND DISCUSSION

Molar Conductance

Molar conductance of the complexes, $[Ni(OPD)_2(S_2C=C(CN)COOMe)]\ .2H_2O$, $[Ni(py)_2(S_2C=C(CN)COOMe)]$, $[Ni(\beta\text{-pic})_2(S_2C=C(CN)COOMe)]$ and $[Ni(\gamma\text{-pic})_2(S_2C=C(CN)COOMe)]$, in 10^{-3}M solution in dimethylsulfoxide have been found in range 10-40µS cm^{-1}. The conductance value of all complexes indicates nonelectrolyte behavior.

Table 1 : Colour, molar conductance, analytical data of the complexes.

S.N.	Complex	Colour	Mol. Wt.	M.P./ (dec.°C)	Found (Cal.) (%)		Molar Conductance in 10^{-3} M DMSO (µS cm^{-1})
					M	S	
1	$[Ni(OPD)_2(S_2C=C(CN)COOMe)].2H_2O$ $(C_{17}H_{23}N_5O_4S_2Ni)$	Green	483.7	110	11.5 (12.1)	12.2 (13.2)	20
2	$[Ni(py)_2(S_2C=C(CN)COOMe)]$ $(C_{15}H_{13}N_3O_2S_2Ni)$	Greenish brown	389.7	84	13.5 (15.0)	14.5 (16.4)	30
3	$[Ni(\beta\text{-pic})_2(S_2C=C(CN)COOMe)]$ $(C_{17}H_{17}N_3O_2S_2Ni)$	Brown	417.7	80 – 85	13.1 (14.0)	14.2 (15.3)	10
4	$[Ni(\gamma\text{-pic})_2(S_2C=C(CN)COOMe)]$ $(C_{17}H_{17}N_3O_2S_2Ni)$	Orange	417.7	90 – 95	12.8 (14.0)	13.9 (15.3)	20

Infrared Spectra

IR spectral bands of the complexes have been shown in Table 2. ν(C=C), ν(C-S), ν(C≡N) in the complexes have been found at 1410-1450 cm^{-1}, 1030-1050 cm^{-1}, 2210-2250 cm^{-1} respectively[38]. ν(C≡N) has been observed at very high frequency. The C≡N band has been found split in all the complexes that suggest lower symmetry of these complexes as expected. ν(C=C) frequency in dithiolate kind of compound is often quite different than that of ethylene bond. In highly conjugated dithiolates, ν(C=C) is observed in low region (1320-1530cm^{-1}). νC=O frequency usually observed at 1710 cm^{-1} is also lowered because of excessive conjugation. In compounds containing $=CS_2$ groups, three important frequencies at ~940 cm^{-1}, 1100 cm^{-1}, 1300-1500 cm^{-1} are observed. Also many low intensity bands may be observed in lower frequency region. A vibration of pyridine ring[35,37]which is sensitive to coordination has been observed at 620-660 cm^{-1} in complexes. C-H deformation of aromatic ring in o, p and m-substituted aromatic ring has been found at 690-780cm^{-1}.[37] Aliphatic ν(C-H) vibration has been found at 2910 cm^{-1} and aromatic ν(C-H) vibration ~3000 cm^{-1} for aromatic ring. A broad band at ~3450 cm^{-1} is indicative of presence of lattice water because lower energy vibration for coordinated water has not been found in complexes. Thermogram of $Ni(OPD)_2(S_2C=C(CN)COOMe)]\ .2H_2O$ suggest that water present in the complex is not coordinated to metal.

Table.2. Important IR bands (cm^{-1}) of the complexes.

S.N.	Complexes	¬(C≡N)	¬(C=O)	¬(C-O)	¬(C=C)	¬(C-S)	Coordination of nitrogen donor ring	Substituted ring(o,m,p)
1	$[Ni(OPD)_2(S_2C=C(CN)COOMe)].2H_2O$ $(C_{17}H_{23}N_5O_4S_2Ni)$	2220	1560	1120	1450	1030	640	740
2	$[Ni(py)_2(S_2C=C(CN)COOMe)]$ $(C_{15}H_{13}N_3O_2S_2Ni)$	2210	1540	1120	1410	1030	650	–
3	$[Ni(\beta\text{-}pic)_2(S_2C=C(CN)COOMe)]$ $(C_{17}H_{17}N_3O_2S_2Ni)$	2250	1680	1110	1420	1040	620	790
4	$[Ni(\gamma\text{-}pic)_2(S_2C=C(CN)COOMe)]$ $(C_{17}H_{17}N_3O_2S_2Ni)$	2220	1640	1110	1420	1050	660	810

UV-visible spectrum

UV-visible spectrums of these complexes have been recorded in DMSO solvent. From observed peak at 441, 600 and 800 nm for the complex $[(OPD)_2Ni(S_2C=C(CN)COOMe)]\ .2H_2O$ octahedral geometry around nickel ion is indicated[49]. These may be attributed to $3A_{2g}\rightarrow 3T_{1g}$ (P), $3A_{2g}\rightarrow 3T_{1g}$(F) and $3A_{2g}\rightarrow 3T_{1g}$(P) transitions respectively. Two higher energy bands at around 450 and 475 nm have been found in all the complexes and first is split suggesting lower symmetry of these complexes. In $[(\gamma\text{-}Pic)_2Ni(S_2C=C(CN)COOMe)]$ this band is unsplit but a shoulder has been found 455nm with it. However in $[(OPD)_2Ni(S_2C=C(CN)COOMe)].2H_2O$ band at ~441 does not show splitting. Electronic absorption spectrum of $[(py)_2Ni(S_2C=C(CN)COOMe)]$ in DMSO displays absorption bands at around 450-475(split) and very weak one at 600nm that supports square planar geometry around Ni (II) ion in this complex.[39] For the complex $[(\beta\text{-}pic)_2Ni(S_2C=C(CN)COOMe\ )]$ band at ~450-475(split) and very weak one at 600nm shows square planar environment in this complex. Band at 460 nm with shoulder at 475 and very weak absorption at ~600nm found in $[(\gamma\text{-}pic)_2Ni(S_2C=C(CN)COOMe)]$ is also indicative of square planar geometry around Ni(II) ion in this complex.

Table3. - UV-Visible data for the complexes.

S.N.	Complexes	Solvent	λ_{max}(nm)
1	$[Ni(OPD)_2(\ S_2C=C(CN)COOMe)].2H_2O$ $(C_{17}H_{23}N_5O_4S_2Ni)$	DMSO	265, 310, 345, 441, 605, 805
2	$[Ni(py)_2(S_2C=C(CN)COOMe)]$ $(C_{15}H_{13}N_3O_2S_2Ni)$	DMSO	260, 295,342, 450, 495, 600
3	$[Ni(\beta\text{-}pic)_2(S_2C=C(CN)COOMe)]$ $(C_{17}H_{17}N_3O_2S_2Ni)$	DMSO	260, 297, 345, 447, 476, 605
4	$[Ni(\gamma\text{-}pic)_2(S_2C=C(CN)COOMe)]$ $(C_{17}H_{17}N_3O_2S_2Ni)$	DMSO	264, 295, 342, 447, 485, 560, 610

In the UV region CT bands at around 265 nm have been found in all the complexes. Bands found in UV region of electronic spectra of these complexes are comparable by and large. UV spectra of these complexes show presence of similar moieties.

^{1}H NMR spectrum

^{1}H NMR spectra of these complexes [(OPD)$_2$Ni(S$_2$C=C(CN)COOMe)] .2H$_2$O, [(β pic)$_2$Ni(S$_2$C=C(CN)COOMe)] and [(py)$_2$Ni(S$_2$C=C(CN)COOMe)] have been recorded in DMSO. In ^{1}H NMR spectrum of the complex [(OPD)$_2$Ni(S$_2$C=C(CN)COOMe)] .2H$_2$O, three signals have been observed. Multiplets at δ-6.37– 7.48 were attributed to aromatic protons of OPD. A broad signal observed at δ-4.22 attributed to N-H protons of the amine. Signal observed at δ- 3.47ppm is attributed to OCH$_3$ proton. In ^{1}H NMR spectrum of [(β-pic)$_2$Ni(S$_2$C=C(CN)COOMe)], signal δ- 2.31 is attributable to methyl proton linked with pyridine ring, multiplet for protons of pyridine ring has been observed at δ-7.30 – 8.39 position. In this complex, OCH$_3$ signal is not found well resolved at ~4 ppm. In ^{1}H NMR of the complex [(py)$_2$Ni(S$_2$C=C(CN)COOMe)], broad singlet observed at δ~ 8.08 is attributable to pyridine ring. In this complex, OCH$_3$ signal seems to have merged with signal of H$_2$O protons as evident from the broadness and shape of the peak.

Table.4- ^{1}H NMR spectral data of complexes.

S.No.	Complex	Aliphatic(ppm)	Aromatic(ppm)		
		OCH$_3$	Aromatic Proton (ppm)	CH$_3$	NH$_2$
1.	[Ni(OPD)$_2$(S$_2$C=C(CN)COOMe)].2H$_2$O (C$_{17}$H$_{23}$N$_5$O$_4$S$_2$Ni)	3.47	6.37 – 7.48	–	4.22
2.	[Ni(py)$_2$(S$_2$C=C(CN)COOMe)] (C$_{15}$H$_{13}$N$_3$O$_2$S$_2$Ni)	–	8.08	–	–
3.	[Ni(β-pic)$_2$(S$_2$C=C(CN)COOMe)] (C$_{17}$H$_{17}$N$_3$O$_2$S$_2$Ni)	–	7.30 – 8.39	2.31	–

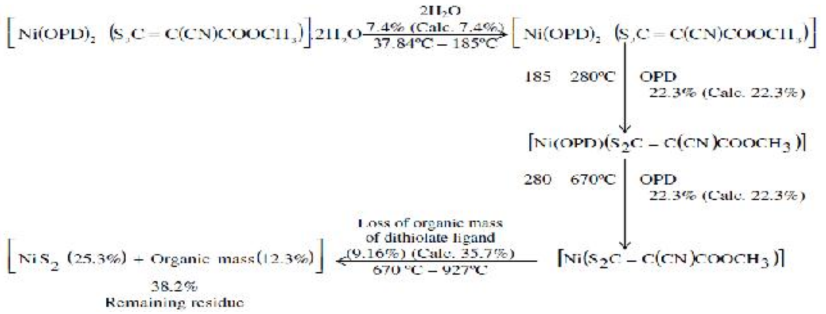
Thermogravimetric analysis

Thermal behavior of complex [Ni(OPD)$_2$(S$_2$C=C(CN)COOMe)] .2H$_2$O has been observed in the temperature range of 37.8-927.5°C. Thermogram of complex indicated the total weight loss of 61.1% upto temperature 927.5°C which occurred in four step. In the first step decomposition, two water molecule are eliminated with weight loss (7.4%) in the temperature range 37.84-185°C. In the second step decomposition, weight loss (22.3%) show decomposition of orthophenylenediamine molecule in the temperature range 185- 280°C. In third step, weight loss (22.3%) show decomposition of other orthophenylenediamine molecule in the temperature range 280- 670°C. In fourth step, the decomposition of organic part of dithiolate ligand undergoes continuously in temperature range 670–927.5°C.

Table.5 : Temperature and Weight loss data for complex [Ni(OPD)$_2$(S$_2$C=C(CN)COOCH$_3$).2H$_2$O]

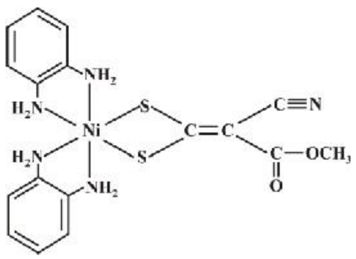
Steps	Temp. Range °C	Wight loss%		Lost fragments	Remaining residue
		Found	Calculated		
I	37.8 – 185	7.4	7.4	2H$_2$O	NiS$_2$ (25.3%)+ organic mass (12.3%) (Total mass -38.2%)
II	185 – 280	22.3	22.3	OPD	
III	280 – 670	22.3	22.3	OPD	
IV	670 – 927.5	9.1	35.7	Organic part of dithiolate ligand	
		61.1	87.7		

The decomposition of organic part of dithiolate ligand in the complex is not complete upto temperature 927.5°C. Remaining residue (38.2%) should contain metal disulfide NiS$_2$ and some organic part of the dithiolate ligand.

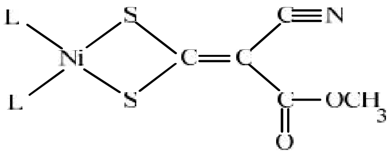


CONCLUSION

On the basis of foregoing discussions and earlier literature, following structure of the mixed ligand complexes of nickel have been proposed tentatively.



and



$C_6H_8N_2^-$ = O-Phenylene diammine, L= Pyridine, α-Picoline, β-Picoline, γ-Picoline

Fig.1 : Proposed structure of mixed ligand complexes of dithiolate of nickel(II).

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CHAPTER:5

CONDUCTING POLYMERS: A REVOLUTIONARY MATERIAL

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Abstract: Conducting polymers (CPs) are chemical compounds or mixtures of compounds composed of structural units formed during the polymerization process. The prospective uses of CPs, particularly in the realm of electronic manufacturing, have piqued the curiosity of researchers. The relative simplicity of processing, cost effectiveness through mass manufacturing, and manufacture of portable electronic devices are the benefits of CP over traditional materials. The Nobel Prize in Chemistry was awarded to MacDiarmid, Heeger, and Shirakawa in 2000 for the creation and development of CPs.A variety of CPs derivatives, for example, have drawn special interest in the field of nanoscience and nanotechnology due to their extraordinary properties such as electrical characteristics, reversible doping-dedoping procedure, controllable chemical and electrochemical properties, and simple processibility.

Keywords: Polymer, Conducting Polymer, Polyaniline, Polypyrrole

Introduction

Polymers have long been used as insulating materials. For example, metal cables are coated in plastic to insulate them. However, there are at least four major classes of semiconducting polymers that have been developed so far. They include conjugated conducting polymers, charge transfer polymers; ionically conducting polymers and conductively filled polymers. The conductively filled conducting polymers were first made in 1930 for the prevention of corona discharge. The potential uses for conductively filled polymers have since been multiplied due to their ease of processing, good environmental stability and wide range of electrical properties. Being a multi-phase system in nature, however, their lack of homogeneity and reproducibility has been an inherent weakness for conductively filled polymers. Therefore, controlling the quality of dispersion to obtain homogeneous conducting polymer composites is critically important. The report of electrical conductivity in ionic polymers in 1975 attracted considerable interest. Since then, various ionically conducting polymers or polymer electrolytes have been prepared for a wide range of applications ranging from rechargeable batteries to smart windows. Polymer electrolytes are also highly process able. The ionic conduction mechanism requires the dissociation of opposite ionic charges and the subsequent ion migration between coordination sites, which are generated by the slow motion of polymer chain segments. Consequently, polymer electrolytes normally show a low conductivity and high sensitivity to humidity. They often become electrically non-conducting upon drying [2]. The properties of polymers such as strength, elasticity, plasticity and toughness often compare with those of metals and offer a lot of very important advantages over the latter, normally light weight, greater workability and economy. The important fundamental property which distinguishes metals from polymers is their very high electrical conductivity of the order of - 10^{4}-10^{6} Ω^{-1} cm^{-1}[3]. Polymers have generally very high resistivity with conductivity around 10^{-14} Ω^{-1} cm^{-1} and this low electrical conductivity has led to widespread use of polymers as electrical insulators [4]. In spite of the low inherent conductivity of polymers, several attempts were made by researches to make them electrically conducting. Conducting polymers so far developed fall into two distinct groups. The first generation conducting polymers were made by incorporating conductive filler or additives into the normally insulating polymer [5]. Examples are

Rubber + Graphite powder → Conductive rubber.
PVC powder + Nickel powder → Conductive PVC.
Polyester film + Al powder → Metalized polyester film

Polymer: A polymer or a macromolecule is a material composed of long molecular chains that is composed of well-accepted multiple repeating units like beads on a string, originates a characteristic of highrelative molecular massand attendant properties [1]. These play a significant role in human life as our body is made of a lot of polymers. The humans are using polymer from ancient time in the form of wood, skin and fibers. The polymers are light weight, easy to fabricate, poor conductor of electricity as well as poor thermal conductor and unaffected by chemical attack and decay.

Conducting Polymers: Conducting polymers (CPs) are the chemical compound or mixture of compounds consisting of structural units created through a process of polymerization.The interests among the researchers on CPs are due to the potential applications of it particularly in the field of electronic industry. The advantages of CP over conventional materials are the relative ease of processing, cost effectiveness by mass production and fabrication of portable electronic devices. The importance of CPs is exemplified by the Nobel Prize award in Chemistry in 2000 to MacDiarmid, Heeger and Shirakawa for the invention and development of CPs [2,3,10]. Because of their extraordinary properties such as electrical characteristics, reversible doping-dedoping procedure, controllable chemical and electrochemical properties and simple processibility, a variety of CPs derivatives, etc, have drawn special interest in the field of nanoscience and nanotechnology.

Polyacetylene (PA): Polyacetylene (PA) usually refers to an organic polymer with the repeating unit $(C_2H_2)_n$. The name refers to its conceptual construction from the polymerization of acetylene to give a chain with repeating olefin groups. In the mid 1970s, PA was accidentally fabricated by accident by Shirakawa, the first polymer capable of conducting electricity [10]. Hatano et. al are the first to state the electrical conductivity of the order of 10^5 S/cm for trans PA sample [2]. Little had suggested that accurately substituted PA molecule would show superconductivity at ambient temperature [3].

Polythiophene) (PTh): Polythiophene **(**PTh) are polymerized thiophenes having a sulfur heterocycle. They can become conducting when electrons are added or removed from the conjugated π-orbitals via doping. It is an important CP that manufacture the environmentally and thermally stable materials and useful as an electrical supercapacitor, non-linear optics, polymeric light emitting diodes (PLEDs), eletrochromic, photoresists, antistatic coatings, sensors, batteries, electromagnet shielding materials, solar cells, memory devices, transistors and imaging materials[4].

Polyaniline (PANI): Polyaniline (PANI) is a CP of the semi-flexible rod polymer family. It can also be defined as a simple 1,4-coupling product of the monomeric aniline molecule. Among all the above classes PANI is of much importance worldwide because of its unique properties. PANI was first explained in the mid-19th century by Henry Lethe by who studied the electrochemical and chemical oxidation products of aniline in acidic media [5].

Polypyrrole (PPY): Polypyrrole (PPY) is a type of organic polymer formed by polymerization of pyrrole. PPY was shown to be a CP in 1968. Among the numerous CPs, PPY has been widely studied [6], which is due to its ease of preparation, superior redox properties, stabilized oxidized form, capacity to give towering conductivity, water soluble, commercially accessible and valuable electrical and optical properties. Pyrrole blacks have been known for a century initially obtained as powders by chemical polymerization of pyrrole.

Poly (3,4-ethylenedioxythiophene) (PEDOT): Poly (3,4-ethylenedioxythiophene) **(**PEDOT) is a CP based on3,4-ethylene dioxyl thiophene monomer. Advantages of PEDOT are optical transparency in thin, oxidized films, very high stability and reasonable band gap and low redox potential [7]. It can be used in lots of different applications such as antistatic coating of polymers and glass, high conductive shell, organic light emitting diode displays, nano-fiber electrodes for unit stimulation, solar cells, cathode material in electrolytic capacitors, printing wiring panels, textile fibres with colour varying properties, transparent electrodes for thick-film electroluminescence, source gate and drain in the quickly developing organic semi-conductors field [8].

Poly(phenylenevinylene) (PPV): Poly(phenylenevinylene)(PPV) is a diamagnetic substance, capable ofelectroluminescence and has an extremely low electrical conductivity of the order of 10^{-13} S/cm having a structure which is intermediate between that of PA and PP. Oriented PPV is highly crystalline, mechanically strong and environmental stable. The electrical conductivity enhances upon doping with iodine, ferric chloride, alkali metals or acids but with less stability. Generally, unsubstituted unaligned PPV shows reasonable conductivity with doping ranging from 10^{-3}-100 S/cm synthesized via the popular Gilch route [9].

Poly(p-phenylene)sand Poly(phenylene)s: Poly(p-phenylene) (PPP) is the precursor to a CP of the rigid-rod polymer hostfamily made of repeating p-phenylene units and converted to its conducting form using an oxidant or a dopant. PPP is the first example of the non-acetylenic hydrocarbon CP that can be doped to attain the conductivity comparable to PA [10].This is the first case of the non-acetylenic hydrocarbon polymer that can be doped with electron acceptor or an electron donor to offer conducting properties. Ballard et. al synthesized PPP via derivations of cis-dihydrocatechol achieved from bacterial fermentation using benzene as a transformation substrate in a homo-polymerization way [11].

Synthesizing Methods of Conducting Polymers

CPs can be synthesized by any one of the following methods:

Chemical Method: CPs have been chemically synthesized through the oxidation or reduction of monomers and polymerization of corresponding monomers. One of its advantages is the chance of mass production at a reasonable price. Numeral studies have been applied to increase the yield and quality of the manufactured product attained via oxidative polymerization method. The principles of chemical route do not order the use of electrochemical methods [12]. For example, poly (3-hexylthiophene) is renowned and frequently studied CP that is almost generally produced chemically.

Electrochemical Method: Electrochemical synthesis of CPs is very important among the different reported methods of synthesis, since it is simple, cost-effective, can be performed in a single section glass cell, reproducible and the fabricated films have required thickness and uniformity. The most widespread electrochemical technique for preparation of electrochemical polymerization is anodic oxidation of appropriate electroactive functional monomers; cathodic reduction is used much less often. In the previous, synthesis of a polymer film and doping of counter ions as a consequence of oxidation happen simultaneously [13].

Photochemical Method: Chemical and ECP methods have been the main procedures of finding polymers in the industry and scientific research laboratories [14]. However, during the previous two decapods, photochemical preparation, though awfully studied, has been reported to present few advantages in that it is a quick and inexpensive method and it is not destructive to the surroundings. The method is useful for the fabrication of some CPs.

Metathesis Route: Metathesis is defined as the chemical reaction between two compounds that results in the interchange of one part of each to form two different compounds. Metathesis polymerization is divided into three categories: ring-opening metathesis of cyclo-olefins; metathesis of alkynes, acyclic or cyclic; and metathesis of diolefins. Evans et. al studied the metathesis of aniline and 1,2-Dihydroquinoline derivatives [15]. Synthesis of acetylene-based typically conjugated polymers by metathesis polymerization and polymer properties are studied by Masuda [16].

Concentrated Emulsion Method: The emulsion polymerization method is a heterophase polymerization procedure where three segments can be classified: the water segment, the latex particle segment and the monomer droplet segment. The main mechanism in it is a radical polymerization. Methods with one segment present in the arrangement are bulk and solution polymerization, where the monomer as a solvent and the initiator are in the identical segment [17]. The synthesized polymer remains soluble either in the monomer or in the solvent until high modification.

Inclusion Method: Inclusion polymerization is a unique one-dimensional polymerization which proceeds in a canal (channel) of inclusion compounds. It generally manufactures composite materials at the atomic or molecular level. So, this kind of polymerization can unlock the path to unique low-dimensionality composite materials with enormous potential [18]. These materials have a potential possibility to show some characteristic properties in the inclusion state due to their one-dimensional structure. For instance, the inclusion of an electro-conductive polymer might fabricate a molecular wire.

Solid State Method: Solid State polymerization is a procedure in which the polymer chain lengths are enlarged by heat in the lack of oxygen and water, either by vacuum or removal with an inert gas to push away the by-products of reactions. The reaction is controlled by temperature, pressure and the diffusion of by-products from the core of the pellet to the shell. It is a key move often used after melt-polymerization for the intention of enhancing the mechanical and rheological properties of polymers prior to injection blow molding [19]. This method is extensively useful in the industrial production of bottle-grade PET, films and advanced industrial fibers.

Plasma Polymerization: Plasma polymerization is a novel process to manufacture thin films from a group of organic and organometallic preliminary materials. Plasma polymerized films are pinhole-free and highly cross-linked and thus are insoluble, thermally stable, chemically inert and mechanically strong. Additionally, such films are extremely coherent and adherent to a range of substrates comprising a conventional polymer, glass and metal surfaces [20].

Pyrolysis Method: Pyrolysis is described as the chemical decay of organic materials by heating to elevated temperatures. It has established as a precious process for the investigation and detection of organic polymeric substances in the plastic and rubber production, dentistry, ecological shelter and in the failure testing. This method permits the direct study of very small sample quantity without the necessity of time consuming sample preparation. Spectroscopic methods can give a detection of the monomeric species present; though, pyrolytic degradation plays a significant function in the concluding assignment of the structure. Synthetic and natural polymer analysis is extensively done by pyrolysis gas chromatography [21].

Applications

Supercapacitor (SC): Supercapacitor (SC) is the common term for a family of electrochemical capacitors.CPs are a subject of interest for many researchers due to their multiple applications. SCs have been emphasized on the growth of new customized electrode materials with superior performance [22].The substances for the electrode of SCs are generally transition metal oxides, high surface carbons and CPs. SCs based on CPs have benefits such as superior capacitive energy density and low material cost. Superior electrical conductivity, better pseudo-capacitance and rapid doping/dedoping rate throughout the charge/discharge procedure are their key benefits. CPs have some disadvantages also such as small life cycle and slow ion transport.

Polymeric Light Emitting Diode (PLED): During last two decades, polymeric light emitting diodes (PLEDs) synthesized from CP have drawn international attention as contestants for the next generation of emissive flat panel displays and the same organic structures have been utilized as light detector appliances similar to photodiodes or solar cells. CP ultrathin film employed as a hole injection layer for organic optoelectronic equipment such as organic light emitting diode also has been an issue of importance in current time. In the hole injection layer, CPs plays a crucial role to effectively insert holes from the anode into the device [23].

Sensors: A sensor is a device that receives a signal or stimulus and responds with an electrical signal. The reason for the output of a sensor to be limited to electrical signals is related to the present development of signal processing, that is almost exclusively performed using electronic devices. The application of CPs in sensor technologies includes the CPs as an electrode modification in order to enhance sensitivity, to impart selectivity, to suppress interference and to give a support matrix for sensing materials [24].

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CHAPTER:6

BiOCl NANOMATERIAL: SYNTHESIS, CHARACTERIZATION AND ENVIRONMENTAL APPLICATIONS

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Abstract: BiOCl nanomaterial have been acknowledged as potential and promising environmental remediation material because of their low costs, low toxicities, and enormous stabilities as well as resourceful photocatalytic activities of various hazardous environmental pollutants including dyes, pesticides and several other organic pollutants etc. Several synthesis methods of BiOCl nano-micro structures including physical, chemical and biological methods were highlighted. The various characterization methods for these assemblies including nanowires, nanosheets, nanoflakes and flower-like structures were reviewed. The review emphasized the various environmental pollutants remediation and degradation abilities of these BiOCl nano-micro structures. BiOCl found to be remarkable nanomaterial with extraordinary potential in the field of environmental clean-up and remediation technology.

Keywords: BiOCl, Synthesis, Characterization and Environmental applications.

1. Introduction:

As the world's population has been increasing exponentially day by day, the level of pollution will surely make its way accordingly on this planet which will lead critical situation of environmental remediation. As far as the traditional methods for environmental remediation have been concern to [1], they are not well enough to fulfil the necessity of environmental clean-up in a broad way and can generate secondary pollutants so there is a strong need to develop better and advanced technologies to address and solve these issues [2,3]. Advanced oxidation processes have been considered as the latest methods for environmental remediation [4,5]. Various types of advanced oxidation processes have been available today and among these photocatalysis found to be an ideal and important method for environmental remediation [5,6]. For these reason, not just the process of advanced oxidation [7] but the materials involved in it such as nano-macro micro or bulk materials, have also been getting promising attentions [8,9]. Among them, photocatalytic degradation using semiconductor material and light source has been the most applicable method in this century because of low cost, simplicity, easy and complete mineralization of organic pollutants and to achieve the pollution removal in this sustainable world view [10]. Now a day various types of semiconductor materials with special nano/microstructures found to be available for photocatalysis. Among these, Bi based nano/microstructures for photocatalysis have been attracted attention. Various types of Bi based nano/microstructures have been synthesized till the date and oxyhalides have been found to be the most applicable photocatalyst among them [11]. A tremendous scientific literature and published work already present in the scientific domain using Bi based oxyhalides to degrade various types of hazardous as well as environmentally persistent pollutants and BiOCl already gained a significant popularity among other bismuth based oxyhalides in this regard [12-15].

Various hierarchical structures of BiOCl like nanowires [16,17] nanoflakes [18], nanoflowers [19], nanofibers [20], nanobelts [21], nanosheets [22] as well as several other assemblies [23,24] have been synthesized using various physical, chemical and biological methods [25]. BiOCl also exhibited photocatalytic activity in different light sources such as ultraviolet, visible and solar light. Due to simple synthesis, low cost, low toxicity, stability and ability to absorb UV, visible as well as sunlight made BiOCl nanomaterials a privileged choice over other oxide based semiconductor resources [12-15].

Thus the present study was an attempt to understand the synthesis, characterization and photocatalytic activity of BiOCl nanomaterial. In this review, various synthesis methods, characterization techniques and applications of BiOCl nano/microstructures have been discussed in details.

2. Synthesis of BiOCl nano/microstructures :

During past few decades a lot of work have been done in the field of the synthesis of BiOCl nano/microstructures have been done using various physical, chemical and biological methods. This section mainly describe several common methods used for the synthesis of BiOCl nano/microstructures, mainly including hydrolysis, hydrothermal, solvothermal, template method and biological methods.

2.1 Hydrolysis methods:

Hydrolysis method found to be the simplest method used for the synthesis of BiOCl nano/microstructures. Various precursors such as $BiCl_3$, $Bi(NO_3)_5$. $5H_2O$ or Bi_2O_3 have been extensively used for synthesis of BiOCl nano/microstucture. Ye et al. synthesized flowerlike BiOCl by using $Bi(NO_3)_5$. $5H_2O$ as source of Bi at room temperature and prepared 4-5 micrometer in sized material [26]. Wang et al. synthesized micro-nano particles with a fine ferrite plate structure of BiOCl. These particles have been synthesized using SDBD and HCl [27]. Armelao et al synthesized BiOCl using $BiCl_3$ at 65 ^{0}C for 6 h in the Acetyl acetone as well as HCl as solvents [28]. Song et al. synthesized irregular BiOCl nanosheets by using $Bi(NO_3)_5.5H_2O$ as source of Bi at room temperature [29]. Seddiqi et al. used sodium bismuthate and hydroxylammonium chloride for synthesis of BiOCl nanoshpere. In this method best results obtained when 24 gm of hydroxylammonium chloride was used [30].

2.2 Hydrothermal Methods:

In hydrothermal synthesis temperature and reaction time found to be the critical, limiting and most influential factor to decide the shape and size of the nanoparticles. Hu et al. synthesized square like BiOCl in the presence of sodium citrate and argued with the important role sodium citrate in the shape/size dependencies [31]. Xiong et al. also synthesized square like BiOCl using Mannitol and provided the evidence of the important role of Mannitol in the synthesis [32]. Xie et al. used one pot synthesis of flower like BiOCl and provided the influence of time in the formation of hierarchical flower like BiOCl nanostructure [33]. Liu et al. used PEG assisted synthesis for BiOCl naono/microstructure and further elucidated the influential role of PEG in the size and shape of the BiOCl [34]. Biswas et al. used one-step synthesis of BiOCl microstructure and in this process structural chlorine has been obtained by generation of chloride ions in the system [35].

2.3 Solvothermal Process:

Solvothermal Processes have also been found to be similar with hydrothermal process. In this process solvent, temperature and reaction time have been the most significant factors to decide the size and morphology of the nanoparticles. Song et al. synthesized BiOCl nanoflower using pyridine as solvent in solvothermal process. In this process volume ratio of water to pyridine played an important role [36]. Effect of temperature and reaction time in the synthesis of BiOCl microsphere was investigated by Mera et al. and highest photocatalytic activity of BiOCl has been obtained at 155 ^{0}C in 18 h [13]. Tian et al used DEG solvent for synthesis of BiOCl nanosheets with tunable thickness. $FeCl_3$, $CoCl_2$ and NaCl were used as Chlorine source. It was found that these metal ions played an important role in modulating the thickness of 2D BiOCl nanostructure [37]. Gao et al. used ethylene glycol as solvent at 160 ^{0}C for 12 h for the synthesis of BiOCl microsphere. They reported that adjusting the concentration of $Bi(NO_3)_5$ $.5H_2O$ controlled the different size of BiOCl [38]. Senasu et al. used green solvethermal process for the synthesis of BiOCl microsphere without any surfactant or capping agent or any other structure directing agent. They reported uniform micro-sphere of 50-60 nm [14].

2.4 Template method:

In this method substance was used as a template or stabilizing agent or structure directing agent for the nanoparticles. Ascencio-Aguirre et al. used tannic acid as stabilizing agent. Acidic medium was used for the synthesis [39]. CTAC was used as capping agent by Li et al. for synthesis of square like ultrathin BiOCl nanosheets [18]. L-lysine was used as capping agent by Chen et al. for the synthesis of BiOCl nanoflower. They reported two methods for synthesis of BiOCl using L-lysine. $BiCl_3$ and $Bi(NO_3)_5$ $.5H_2O$ were used as precursor [19,40]. Soft capping agent namely PVP/ehtylenediamine/dextrose were used by Ramirez-Meneses et al. Among these ehtylenediamine promote a defined rectangular plate-like morphology of BiOCl [41].

2.5Biological method:

To reduce the consumption of toxic chemical and make methods more environmental friendly or green oriented, the recent scientific works shifted toward the green synthesis of these photocatalyst. Now a day's nanoparticle was also synthesized by using bio-mediums such as plant extract or microbial or any other biological mediums. These biological mediums found to be able to work as stabilizing agent in the synthesis process. Garg et al. firstly reported synthesis of BiOCl using plant extract of *Azadirachta indica, Ocimum santum* and *Saraca indica* [42]. Yan et al. used butterfly wings for synthesis of 3D hierarchical BiOCl [43]. Recently, we have also synthesized BiOCl nano material using costal plants recently can got tremendous success. To the best of our knowledge BiOCl has never been synthesized using any costal plant extracts till date [44].

3. Characterization of BiOCl nano/microstructures:

Knowing the synthesized material or catalyst is also very important task to understand the nature and structure, shape as well as the size of the generated material/product or catalyst. Various sophisticated analytical methods and based instrumentations are available today to understand it at very tiny level. To determine the various properties of nano/microstructures various characterization methods are available whose can sensitive enough to give reliable, reproducible, stable, and precise as well as authenticate results at very tiny levels.

Table 1 summary of the experimental technique used in the characterization of nano/microstructures

Techniques	Main information derived
XRD	Crystal structure, composition, crystalline grain size
SEM-HRSEM, T-SEM-	Morphology, dispersion of NPs.
EDX	elemental composition
HRTEM	NP size, size monodispersity, shape, aggregation state, Study defects.
FTIR	Surface composition, ligand binding
UV-Vis	Optical properties
BET	Surface area
DLS/PSA	Hydrodynamic size, detection of agglomerates
PL	Optical properties – relation to structure features such as defects, size, composition
TGA	Mass and composition of stabilizers
AFM	NP size and shape in 3D mode.
XPS	Electronic structure, elemental composition, oxidation states, ligand binding.

These include various spectroscopic and microscopic analytical techniques. Some methods related to their structure like XRD (X-Ray Diffraction), IR (Infra-Red spectroscopy), RAMAN, XPS, EDX/EDS etc., some methods related to their morphology like SEM (Scanning Electron Microscopy), TEM (Transmission Electron Microscopy), AFM (Atomic Force Microscopy) etc., some methods related to their particle size like PSA, DLS, BET etc., some methods related to their photocatalytic activity like PL, TGA, DTA, DSC, UV-VIS DRS, etc. are applicable with the requirement. Size and shape are most important parameters studied in the characterization of nano/microstructures. Table 1 is showing the summary of the experimental technique used in the characterization of nano/microstructures [45] and their specific applications to understand the specific characteristics of nano-micro materials at very tiny levels.

4Application of BiOCl nano/microstructures for environmental remediation:

BiOCl nano/microstructures exhibit versatile photocatalytic activity among a very broad class and category of pollutants such as dyes, pesticide, pharmaceuticals, organic solvents etc. Most of the research article published used dye molecules as targeted pollutant. We also used carbamate pesticides in degradation study using flower like BiOCl which was first of its kind report.

Methomyl and Oxamyl highly water soluble pesticide easily degraded in solar light under experimental conditions. Very few research studies have been done on pharmaceuticals and organic solvents as pollutants. Table 2 shows the short comparison of photocatalytic degradation of various pollutants using BiOCl nano/microstructures.

Table 2 Environmental remediation using BiOCl nanomaterial

Material	Pollutant	Light source	Outcomes	Reference
Flowerlike BiOCl	Rhodamine B (RhB) dye	visible light	BiOCl exhibited much higher photocatalytic activity than commercial TiO_2 (P25).	[26]
BiOCl having ferrite plate structure	methylene orange	500 W xenon lamp	Better photocatalytic activity than P25 photocatalyst.	[27]
BiOCl nanosheets	Perfluorooctanoic acid (PFOA)	UV irradiation	BiOCl exhibited 1.7 and 14.6 times higher photocatalytic activity than commercial In_2O_3 and TiO_2 (P25)	[29]
flake-like BiOCl	methylene blue and methyl orange dyes	UV-Vis irradiation	100% degradation in approximately 30 min.	[30]
Square-like BiOCl	methyl orange	Simulated sunlight irradiation.	Higher photocatalytic activity than that prepared without sodium citrate.	[31]
square-like 2D BiOCl	Rhodamine B	visible light	Higher photocatalytic activity than commercial BiOCl and TiO_2 (anatase)	[32]
Flowerlike BiOCl	Rhodamine B	visible light	Higher photocatalytic activity than that of other BiOCl and TiO_2	[33]
Sheet-shaped BiOCl	methyl orange	ultraviolet light and simulated solar light	Fast degradation has been observed compared to reference BiOCl	[34]
flake-like BiOCl	Methyl Orange	modeling sunlight	higher photocatalytic activity than TiO_2	[36]
BiOCl nanosheets	Rhodamine B	visible light	higher photocatalytic activity than TiO_2	[37]
BiOCl microstructure	Rhodamine B, ofloxacin, norfloxacin and ciprofloxacin	UV irradiation	99% toward degradation of all pollutants.	[14]
square-like BiOCl	Rhodamine B	visible light	97% of RhB degraded within 20 min.	[18]
BiOCl nanoflower	Rhodamine B	visible light	Represented higher photocatlytic activity than other catalyst repoted in literature.	[19]
Flowerlike BiOCl	Rhodamine B	visible light	Higher photocatalytic activity than their sheet-like counterparts.	[40]
plate-like BiOCl	methylene blue	UV-Vis irradiation	Higher photocatalytic activity than TiO_2: BiOCl composites and equal to commercial TiO_2.	[41]
BiOCl nanoflower	Methyl Orange and Bisphenol A	visible light	Higher photocatalytic activity of *Azadirachta indica* extract mediated synthesis of BiOCl	[42]
3D hierarchical BiOCl/Au	Rhodamine B	visible light	93.8 % degradation efiiciency in 20 min.	[43]
BiOCl	Oxamyl	Solar light	95% degradation in 180 min.	[44]
BiOCl pallete	Azure B and Oxamyl	Solar light	95 % degradation in 60 min (Azure B) and 150 min (Oxamyl)	[46]
Flowerlike BiOCl	Methomyl	Solar light	100 % degradation in 150 min.	[6]
Flowerlike BiOCl	Oxamyl	Solar light	100 % degradation in 150 min.	[47]
BiOCl microsphere	Carbamazepine	simulated sunlight irradiation	Best performance achieved at pH 4.	[48]
BiOCl microsphere	Carbamazepine	simulated sunlight irradiation	9.48 times higher than TiO_2 (P25)	[49]
BiOCl microsphere	Carbamazepine	visible light	CBZ degrades 70% after 180 min.	[38]
BiOCl microsphere	Carbamazepine	Solar light	Ethylene glycol mediated BiOCl exhibit highest photocatalytic activity.	[50]

BiOCl nanosheets	Carbamazepine	simulated sunlight irradiation	91.9 % degrades in 30 min.	[12]
BiOCl microspheres	Carbamazepine and sulfamethoxazole	UV light irradiation	exhibited superior photocatalytic activity to TiO_2 (P25)	[51]
BiOCl nanosheets	Ibuprophen	UV light irradiation	Detailed study about degradation pathway	[52]
BiOCl nanosheets	Atenolol	simulated sunlight irradiation	100 % degrades in 60 min.	[53]
Fe-dopdes BiOCl nanosheet	Levofloxacin	Visible LED light	95 % degrades in 60 min.	[15]
Grey BiOCl nanocrystals	Methylene blue	Visible light irradiation	Higher than that of white BiOCl.	[54]

5 Conclusion:

BiOCl is a very promising photocatalyst. Various researches have been done on the synthesis, characterizations and environmental applications of BiOCl nano/microstructures. Very simple, easy, environmental friendly, cost effective methods have been developed by the scientists. Very detailed literatures have been available for the characterization methods of BiOCl nano/microstructures. Also versatile applicability in photocatalytic degradation of various pollutants including dye, pesticide, pharmaceuticals etc. has been reported by environmental scientist. The present review supports the all the characteristics described above. Thus we conclude that BiOCl is the twentieth century photocatalyst for environmental remediation.

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CHAPTER: 7

POLYANILINE (PANI) NANOMATERIAL FOR ENVIRONMENTAL REMEDIATION

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Abstract:

The intense growth in civilization and industrialization leads to release of hazardous, toxic compounds, heavy metals into environment causing adverse effects on living beings. Therefore, to minimize and control the ill effects, appropriate methods have to be implemented. In this chapter polyaniline (PANI) have been reviewed as environmental remediation.

Keywords: Nanomaterial, Polyaniline, Pollution, Hazardous Compounds.

Introduction

With growth in civilizations and industrialization, there is an increase in the release of hazardous compounds, toxic heavy metal ions and dyes into water bodies, which is of public concern. As a result, appropriate treatment methods have to be implemented in order to minimize and prevent water pollution. The discovery of nanotechnology has opened the door for the development and use of various Nano adsorbent for the removal of pollutants from water. Polyaniline (PANI) nanocomposites are noble adsorbents that have gained popularity in identifying water pollution issues and have also been reported in various literatures. In this chapter, focus mainly has been given on the synthesis of PANI nanocomposites in brief and their application as efficient adsorbents for water treatment in the form of environmental remediation. Detailed discussions on applications of these materials are compared for the adsorptive removal of heavy metal ions and dyes from waste water.

Literature of Research:

The existence of various toxic pollutants in natural water bodies originating from different activities such as textile industry, mining operation and steel manufacturing is still a global challenge. Hence; it is almost important to develop efficient technologies and remedial methods to remove such pollutants from waste water before its release into the environment. Among several water treatment processes (coagulation, membrane filtration, chemical reduction and precipitation, reverse osmosis), adsorption technology is an efficient technology to treat waste water due to exceptional advantages such as its low cost, high efficiency and regeneration . For many years, there has been an ongoing research on the development of high efficiency materials for water pollutants, which can effectively adsorb and remove them from industrial waste water. Conducting polymers (CPs) including polypyrrole (PPy), polyacetylene (PA) and polyaniline (PANI) have attained great attention for water treatment, due to their unique properties such as easy synthesis, tunable structure and the presence of ideal functional groups. Hence, CPs has been widely used in materials such as chemical sensors, electrochromic devices, surface coating for corrosion protection and water treatment. Among these conducting polymers, PANI has been extensively studied due to its low cost, ease of synthesis, good environmental stability, unique doping/de-doping property and relatively high surface volume ratio. Environmental Remediation Owing to the rapid economic and industrial development including metal plating facilities, tanneries, mining operations, batteries, paper 25 industries, fertilizer industries, and pesticides, etc., heavy metal pollution is being a serious environmental problem.

Methodology:

Synthesis of polyanilines

Polyaniline have different chemical structures which depend upon the oxidation number of the polymer backbone, and exists in several states. The overall representation of the polyaniline structure are often described by the subsequent molecular formula (Figure 1) Where y = 1, 0.5 and 0 correspond to completely reduced polyaniline (leucoemeraldine), the half oxidised polyaniline (emeraldine) and fully oxidised polyaniline (pernigraniline), respectively. (Figure 1):

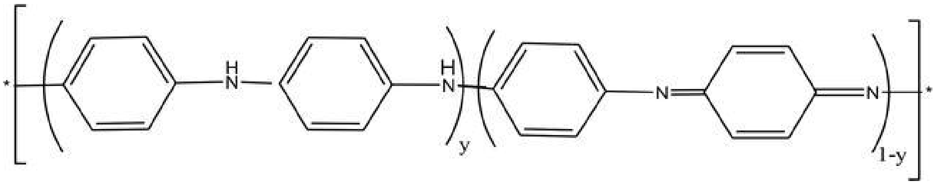

Figure 1 The general structure of polyaniline.

Where y = 1, 0.5 and 0 correspond to completely reduced polyaniline (leucoemeraldine), the half oxidised polyaniline (emeraldine) and fully oxidised polyaniline (pernigraniline), respectively.Upon doping, PANI is often interconverted from one oxidation number to a different the interconversions are often clearly seen as presented in Figure 2.

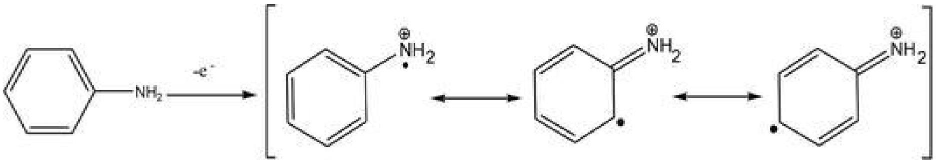

Figure 2. Oxidation of aniline monomer during polymerisation of aniline.

There are two general methods for synthesis of conducting polymers through electrochemical oxidation of the monomers or chemical oxidation of the monomers, viz. electrochemical polymerisation and chemical polymerisation.

Electrochemical polymerisation

Electrochemical polymerisations are often administered by employing one among the three techniques: (i) applying a continuing current (galvanostatic), or (ii) applying a continuing potential (potentiostatic), and (iii) by applying a possible scanning/cycling to the solution of aniline. Polymerisation process is performed in strongly acidic aqueous electrolyte employing a radical polymerisation mechanism which allows a formation of anilinium radical cation by aniline oxidation on the electrode. Electrochemical polymerisation strongly depends on the subsequent factors: 1. low pH which is required for preparation of conductive polymeric materials, 2. the dopant anion incorporated into polymer to work out the morphology, conductivity, rate of polymerisation growth and influences degradation process and 3 Inert electrode like Pt, Au and graphite 4. The electrochemical process is more advantageous since film properties like thickness and conductivity are often controlled by the synthesis parameters, including the present density, substrate, pH, nature and concentration of electrolyte. a) Chemical polymerisation like electrochemical polymerisation, chemical polymerisation is additionally administered in an acidic medium like acid (HCl) and formic acid (HCOOH) which helps in yielding primary polymer. For this process to occur, a dopant or oxidant is required. The dopant reagents used for this doping process are the oxidising agents like ammonium persulfate (APS), ferric chloride ($FeCl_3$), peroxide (H2O2) and ceric nitrate (Ce(NO3)3). The p vital role of the oxidant is to withdraw a proton from an aniline molecule, without forming a robust coordination bond either with the substrate intermediate or with the ultimate product. The general mechanism involved during polymerisation of aniline proceeds dominantly through radical mechanisms. Radical mechanisms are often further subdivided into initiation, chain propagation and termination steps, these results into stable intermediate resonance structures. The three different stages of polymerisation are illustrated in Figures 2–4. Step 1: initiation step (oxidation of aniline monomer) The initial step of aniline oxidative polymerisation is that the generation of the aniline cation radical within the oxidation of aniline with an oxidant as shown in Figure 2 .The aniline cation radical undergoes resonance to achieve the foremost stable and reactive radical cation which is free from steric hindrances. This step is that the slowest step within the reaction, hence it's deemed because the rate determining step (RDS) in aniline polymerisation. Step 2: radical coupling and rearomatisation Head to tail coupling of the N¬ and para¬ radical cations takes place (Figure 3), yielding a dicationic dimer species. This dimer further undergoes the method of rearomatisation which causes it to return to its neutral state, yielding an intermediate referred as p-aminodiphenylamine .These processes also are amid the elimination of two protons.

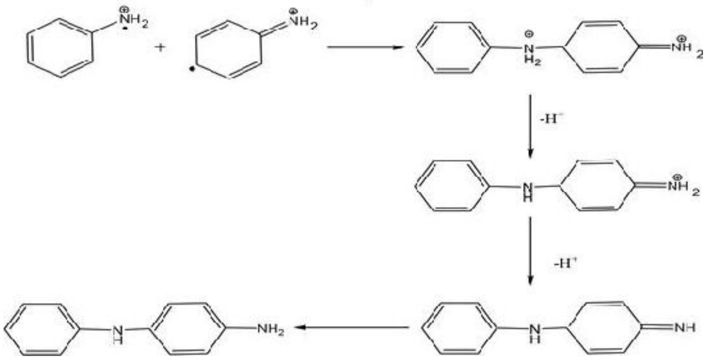

Figure 3.Mechanism of Formation of dimer.

Step 3: chain propagation

The dimers are immediately oxidised and then react with a stable aniline cation radical via an electrophilic aromatic substitution, followed by deprotonation and rearrangements to give the trimer as seen in Figure 4 .The trimer further undergoes oxidation and reacts with aniline cation radical to form a tetramer and so on.

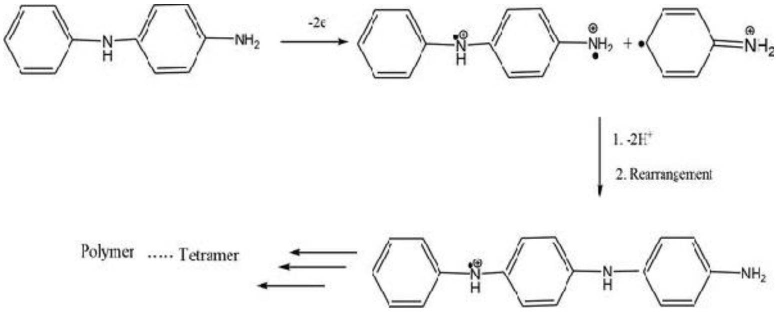

Figure 4.Formation of a trimer and polymer formation

Synthesis and characterisation of polyaniline nanocomposites

Different nanocomposites supported polyaniline are reported for wastewater remediation so as to reinforce the removal efficiency of polyaniline. Counting on the tactic of synthesis, a spread of PANI based nanostructures and nanocomposites are often developed for instance, Ren et al. reported PANI/PAN (polyacrylonitrile) nanocomposite synthesized via in–situ polymerization of ANI monomer using DBSA and APS to get a Nano fibrous structures. Rachna and associates reported zinc ferritePANI nanocomposite prepared following similar preparation method and monomer using toluene as a solvent and CuSO4. The SEM image showed that the nanocomposite had a smooth surface. Tanzifi et al prepared PANI/carboxymethyl cellulose/titanium dioxide PANI/CMC/TiO2 nanocomposite in acidic medium using an equivalent polymerization route and APS as an oxidizing agent. The nanocomposite structure formed uniform spherical particles. PANI@Ni(OH)2 nanocomposite was prepared by Bhaumik et al. via in–situ polymerization using APS and hydrazine hydrate. Hallajiqomi et al. synthesized PANI/PVP nanocomposite via in–situ polymerization using KIO3 and PVP as oxidizing agent and surfactant, respectively. The nanocomposite showed irregular structural morphology. PANI/reduced graphene oxide (RGO) nanocomposite was synthesized by Li et al. following an equivalent polymerization route using APS as an oxidizing agent. The nanocomposite exhibited a lamellar structure. In another study, Harijan and Chandra reported a PANIGO nanocomposite synthesized by similar preparation method and therefore the nanocomposite was composed of sheetlike morphology. Wang et al. synthesized PANI/αZrP with plate–like structures via in–situ polymerization using an equivalent oxidizing agent. In another study, Abdolahi et al. synthesized uniform PANI nanofibers through interfacial polymerization with different sizes starting from micro to nanometers. Goldpolyaniline (AuPANI) nanocomposite was prepared by simple interfacial polymerization, performed in an immiscible water/toluene biphasic system using tetrachloroaurate, as an oxidant. The TEM images of AuPANI Nanocomposite showed rodlike Au nanoparticles embedded during a PANI matrix. Dhachanamoorthi et alprepared PANIiron oxide (Fe3O4) ternary nanocomposites with improved crystallinity upon addition of Fe3O4 by mechanical mixing approach. Similar method was used for the synthesis of PANIzinc oxide (ZnO)

This knowledge will further broaden the appliance scope of PANI and supply the idea for the researchers to hunt the new application of PANI within the future. This current research focuses on the thermally conductive polymeric composites, fibres/polymeric matrix wavetransparent composite materials, electromagnetic shielding polymeric composites, ablationresistance polymeric composites, surface/interface modification, mechanisms. In the last decade, the heavy metal removal through PANI systems has attracted far more interests due to their reversibility and high heavy metal removal efficiency. PANI with different morphologies and PANI nanocomposites are synthesized to be used for the heavy metal removal from the waste water system. Wang et al. used PANI to get rid of Hg(II) from water solution and proposed that the Hg(II) adsorption on PANI was thanks to the complexation between Hg(II) and nitrogen binding sites on the polymer backbone of PANI. However, this proposed mechanism wasn’t been verified during this work. Kumar et al. prepared the PANI on the surface of jute fiber with 1, 4phenylenediamine as chain terminating reagent, which could effectively remove Cr(VI) from wastewater. Zhang et al. synthesized PANI nanofibers doped with vitriol without adding of seed fibers, oligomers, and other templates, which showed an honest Cr(VI) removal performance with a maximum uptake around 95.79 mg g . Olad et al. studied the Cr(VI) removal efficiency and kinetics on the PANI film and powder at different oxidation states., The PANI film was relatively difficult to organize during a great deal during a short time compared with powder form. Additionally, PANI film with a smaller specific area might restrict the penetration of Cr(VI) into the inside of PANI film, resulting in a comparatively lower ability for Cr(VI). Against this, PANI powders with a rough surface were an honest candidate for highly efficient Cr(VI) removal due to their large specific area , and simple bulk production. Guo et al. fabricated the bulk quantity 1D PANI nanowire/tubes with the rough surface by an easy chemical oxidation method, which couldn't only rapidly and effectively remove Cr(VI) from solution in one step through reducing Cr(VI) to Cr(III) also as simultaneously adsorbing the . Reduced Cr(III), but even be easily regenerated for reuse. Normally, the ES sort of PANI might be oxidized to the PB form after treated with Cr(VI) and therefore the PB form might be reduced by directly treated with acidic solution as proved by MacDiarmid et al.This could help PANI be regenerated after treated with Cr(VI) and reused. However, it's still a challenge to sustainably recycle the PANI powders after Cr(VI) treatment and therefore the interactions between PANI and Cr(VI) are still unknown. More recently, a replacement method to recycle the PANI adsorbents by introduction of the magnetic nanoparticles is developed. Gu et al. have fabricated the Fe O /PANI nanocomposites by surface initiated polymerization (SIP) method, during which the ES form PANI served because the coating layer to guard the Fe O nanoparticles from the acid dissolution. The prepared Fe O /PANI nanocomposites showed an honest Cr (VI) removal performance within the entire pH range and therefore the presence of Fe O core favored the recycle of Fe O /PANI nanocomposites. After recycling, the Fe O /PANI nanocomposites might be easily regenerated by the 1 mol L toluene sulphonic acid (PTSA) solution and reused for Cr (VI) removal.

Polyaniline and its composites for wastewater treatment:

The application of PANI for wastewater treatment has been widely studied thanks to its exceptional structure that consist abundant amine and imine functional groups .The nitrogen atoms on these functional groups possesses lone pairs of electrons to facilitate chelation and adsorption of pollutants .However, PANI has disadvantages like poor mechanical properties and process ability also as low solubility. These limitations contributed to its high conjugation and powerful electrostatic interaction between chains, which decreases its performance and limit its commercial application. Composites formation overcomes the above drabacks. Polyaniline composites are often considered a cloth consisting of PANI matrix and one or more components like semiconductors, metal nanoparticles, and organic compounds, inorganic compounds also as biological and natural products so as to enhance polymer backbone properties or extend its functionalities. For the preparation of composite materials successfully, several methods like physical mixing, sol–gel technique, in–situ chemical polymerisation, and emulsion technology and irradiation technique are employed. Since then, various PANI composites are reported for the removal of pollutants from waste water using, chemical reduction, photocatalytic degradation and adsorption technology. From these methods, adsorption has been identified as a important technology, thanks to its flexibility and ease of design, minimum cost, easy operation. Different polyaniline based composites for adsorption of pollutants is widely studied. Samani et al. reported PANI/PEG (polyethylene glycol) composite for the removal of hexavalent chromium ions (Cr (VI)), which had the utmost adsorption capacity (qmax) of 68.97 mg/g. Debnath et al Reported a PANI/lignocellulose composite with qmax of 1672.5 mg/g for azo dye (CR) removal. PANI/chitosan was studied by Janaki et al. for the removal of dyes (CR, Coomassie Brilliant Blue (CBB), and Remazol Brilliant Blue R (RBBR)). They obtained the utmost capacities to be 322.58, 357.14 and 303.03 for CR, CBB and RBBR, respectively. PANI/silica ($SiO2$) gel was reported by Karthik et al with qmax = 63.41 mg/g for the removal of Cr (VI). However, most of those PANI composites have lower removal efficiency and adsorption capacity, due to their irregular structure resulting from agglomeration, poor water dispersion and reduced area .Numerous researches are aimed toward the event of nanostructured PANI composites with improved area and maximum adsorption capacity.

Application of polyaniline nanocomposites as adsorbents for water treatment

Recently, polyaniline nanocomposites are used as adsorbents for the removal of varied pollutants from waste water .More studies are aimed on the adsorption of organic dyes and heavy metals ions thanks to their good interaction with PANI nanocomposites functional groups. Within the study of interaction between PANI nanocomposites and pollutants, various adsorption parameters like pH, contact time, adsorbent dose, and temperature, nature of the adsorbent and concentration of the pollutants are investigated. From these parameters, the adsorption capacity of nanocomposites is often determined to verify the potential of the PANI nanocomposites as adsorbents for water purification as remedial tool.

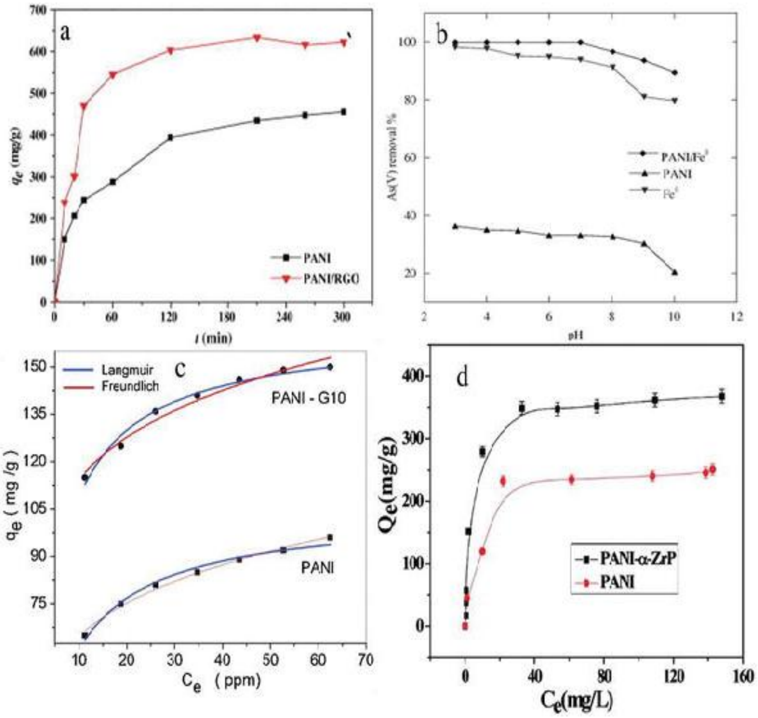

Figure 5 Comparison of PANI and PANI nanocomposites for the removal of various pollutants (a) kinetics [32], (b) pH effect [43], (c) isotherms [33] and (d) equilibrium adsorption capacity

i) Adsorption of heavy metals

The general sources of heavy metals are weathering of rocks thanks to their abundance in nature and mining industries as a results of mineral process of metal ores .Various heavy metals known to pollute water include nickel, cadmium, lead, mercury, chromium, arsenic and copper. The pollution by these toxic metals may be a global concern due to their acute toxicity and enduring accumulation .Heavy metals are problematic since they're mutagenic, carcinogenic, aren't biodegradable and may formvarious species.

Table 1. Some of PANI nanocomposite for heavy metal adsorption

Adsorbent	Pollutant	q_{max} (mg/g)	pH	Conc. (mg/L)	Adsorbent dose (mg)	Pollutant	q_{max} (mg/g)	pH	Conc. (mg/L)	Adsorbent dose (mg)
PANI/PAN	Cr(VI)	67.03	2	5	10	CR	147	2	50	7
PAMpDA@Fe_3O_4	Co(II)	116.3	6	50	50	MO	48.8	—	10	30
PPy-PANI/Fe_3O_4	Cr(VI)	303.0	2	100	50	Rhodamine B RHB	1000	2	10	500
Fe_3O_4/GO/PANI	Cr(VI)	153.4	6.5	100	50	CR	94.28	2.6	82	140
PANI@Ni$(OH)_2$	Cr(VI)	625.0	4	100	10	CR	99.6	7	100	1000
PANI/zeolite	Cr(VI)	—	2	50	200	CR	222.22	4	200	1000
PANI/PVP	Mn(II)	50.30	7	100	250	Reactive Black 5	811.30	5	10	6

PANI nanocomposites for adsorption of heavy metals ions A PANI/RGO nanocomposite was reported by Li et alfor the removal of Hg(II) ions from solution . It had been shown that the PANI/RGO had high equilibrium adsorption capacity as compared to PANI (Figure 5a). The obtained monolayer maximum adsorption capacity was 1000 mg/g at pH 4, 33°C and 400 mg/L for 200 mg adsorbent dose. Bhaumik et al. reported a PANI/Fe0 nanocomposite for the removal of arsenic (As), which had Langmuir maximum adsorption capacity of 232.5 and 227.7 mg/g for both As(III) and As(V) at pH 7, 25°C and 1 mg/L for 10 mg of PANI/Fe0 nanocomposite. The obtained pH effects results (Figure 5b) showed higher removal efficiency by the nanocomposite as compared to the neat PANI. Harijan and Chandra reported a PANI/GO for the removal Cr(VI) from solution . It had been demonstrated that the nanocomposite had high Langmuir maximum capacity of 192 mg/g at pH 6.5, 30°C and 100 mg/L for 25 mg of PANI/GO as compared to the neat PANI (Figure 5c). Table 1 shows a number of the

PANI nanocomposites reported for removal of varied heavy metal ions under different experimental conditions

ii)Adsorption of organic dyes

Organic pollutants are generally materials that comprise of aromatic rings in their structure. Numerous organic pollutants including dyes, chlorinated, aliphatic and phenolic compounds are carcinogenic and mutagenic. Dyes are of major concern thanks to their wide application in textile, paper, pigment and plastic industries. Their presence in water systems leads to water decolouration, which may negatively affect aquatic life by influencing the photosynthetic process. A number of PANI based nanocomposites for dye removal are given in Table 2.

Adsorbent	Pollutant	q_{max} (mg/g)	pH	Conc. (mg/L)	Adsorbent dose (mg)
PANI/MWCNTs	CR	147	2	50	7
PANI/PA 6	MO	48.8	—	10	30
$ZnFe_2O_4$-PANI	Rhodamine B RHB	1000	2	10	500
PANI/CMC/TiO_2	CR	94.28	2.6	82	140
PANI/Fe^0	CR	99.6	7	100	1000
PPy–PANI NFs	CR	222.22	4	200	1000
Starch/PANI	Reactive Black 5	811.30	5	10	60

Table 2.Some of the PANI based nanocomposites for dye adsorption.

Conclusion:

This chapter encompasses the work done on PANI nanocomposites/nanostructures for the removal of heavy metal ions and dyes from solution. Adsorption technology was studied thanks to its flexibility in design and operational simplicity. The utilization of PANI nanocomposites as adsorbents has been investigated for adsorption of pollutants due to their inherent properties like high area, environmental stability, and easy preparation. The literature showed that a various morphological structures are often obtained, which depend strongly on the tactic of synthesis, and thus have various effects on the adsorption of the pollutant. For instance, PANI based nanocomposites and nanostructures are preferable prepared via insitu polymerization. It had been demonstrated that the pH, contact time, temperature, adsorbent dosage, concentration, nature of adsorbent and therefore the presence of competing ions have an influence on the removal efficiency of nanocomposites. Hence, optimization of adsorption parameters has been studied for the removal of heavy metals such Cr(VI), Hg(II), As(V), Co(II) and dyes like CR, MB, MO, MG and RB5 from wastewater using various PANI nanocomposites and nanostructures. Overall, these nanocomposites display improved removal efficiency towards heavy metals and dyes adsorption. Hence, data during this chapter provides insight into PANI based materials for effective use as economically valuable and convenient adsorbents for the removal of dyes hazardous compounds and heavy metals ions from wastewater.

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CHAPTER:8

ACTIVATED CARBON DERIVED FROM BALAM KHIRA (*KIGELIA AFRICANA*) USED FOR REMOVAL OF Pb (II) ION FROM ITS AQUEOUS SOLUTION

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ABSTRACT

A low cost activated carbon derived from the fruit of *Kigelia Africana* (KA), was characterized for effective removal of Pb (II) from its aqueous solution. The derived carbon from *Kigelia Africana* (CKA) had micro porous and meso porous pore size distribution with high surface area (799 $m^2\ g^{-1}$) and high carbon content (79.42 %).The batch experiments are carried out to investigate the effect of process parameters such as solution concentration, pH, temperature, contact time, CKA amount on adsorption. The maximum adsorption was found at pH 5.0 (on 97 % for 2.5 g/l CKA in 50 mg/l Pb (II) initial concentration). The Langmuir, Freundlich and Temkin models were modeled to evaluate the equilibrium adsorption data. The adsorption isotherm data was best fitted by Langmuir model with adsorption capacity 79.87 mg/g (R^2 =0.99) at 30^0 C. Thermodynamic study demonstrates spontaneous and endothermic nature of the adsorption. Kinetic studies were examined using different kinetic models (Lagergren first order and pseudo second order) and found pseudo second order kinetic data are well fitted for adsorption process.

Keyword: Low cost activated carbon (CKA), Pb (II), isotherm models,Lagergren first order, Pseudo second order

1. Introduction

Lead is the one of such highly toxic element that is found both naturally and as introduced contaminant in the environment. In recent time, Pb has been introduced into natural water from a variety of sources such as acid battery manufacturing, metal plating and finishing, ammunition manufacturing, tetraethyl lead (TEL) manufacturing and ceramic and glass industries are the major sources of lead pollution [1]. Lead poisoning in humans causes severe damage to the kidney, nervous system, reproductive system, liver, and brain and causes sickness or death. Severe exposure to lead has been associated with sterility, abortion, stillbirths, and neonatal deaths. The permissible limit for Pb (II) in wastewater given by the Environmental Protection Agency (EPA) is 0.05mg/ dm^3 [2]. The presence of excess lead in drinking water causes diseases such as anemia, encephalopathy, and hepatitis. Lead ions have an affinity for ligands containing thiol and phosphatic groups and they inhibit the biosynthesis of heme, causing damage both to the kidney and liver; this behavior of lead is similar to that of calcium. However, Pb can remain immobilized for years, and hence it is difficult to detect the metabolic disorders it causes [3].

There are various methods developed to remove the heavy metals from the aqueous solutions and wastewater. Traditionally, the most widely applied methods for heavy metal removal from waste water are chemical and electrochemical precipitation, cationic and anionic ion-exchange resins, ion-flotation, evaporation, membrane filtration, reverse osmosis, adsorption, etc. However, adsorption systems have been widely employed in the purification of wastewater. Adsorption is surface phenomenon in which collection or accumulation of substance on the surface of the solid or liquid takes place. It is a physicochemical process in which dissolved molecules are attached to the surface of an adsorbent by physical or chemical forces. Adsorption technology is currently used extensively for the removal of organic and inorganic micro pollutants from aqueous solutions [4]. However, its application for the treatment of wastewaters is not economical. Taking these criteria into consideration, the search for low cost and easily available adsorbents has led many investigators to seek more economic and efficient techniques using natural and vegetal adsorbents [5-10].

The objective of the present work was to evaluate the analytical potential of CKA for an effective removal of Pb (II) from its aqueous solutions. The physical and chemical properties of the CKA were evaluated and the effect of process parameters such as solution concentration, pH, temperature, contact time, CKA amount on adsorption was studied. Adsorption equilibrium and kinetic have been studied under the optimum adsorption conditions. The Langmuir, Freundlich and Temkin isotherms were applied to evaluate the adsorption properties in the batch experiments. In addition, the pseudo first order and pseudo second order kinetic models were also applied to examine the uptake kinetics of Pb (II) in the adsorption process.

2. Materials and methods

2.1 Biosorbent characterization

2.1.1. SEM analysis

Theparticle morphologies of the CKA were studied using scanning electron microscope of JEOL (JSM 6490 LV). Samples were mounted on aluminum stab with the help of double-sided tape. Mounted stabs were coated with gold palladium prior to analysis using a Polaron sputter coater.

2.1.2. Infrared spectroscopy (FTIR)

The CKA (2 mg) was mixed with 200 mg of KBr and then pelleted. The FT-IR spectra of the pellets were recorded using a Fourier Transform Infra-Red Spectrometer (FTIR) Thermo Scientific (Nicole 6700).

2.1.3. X-ray diffraction (XRD)

Crystallographic parameters of the activated carbon produced by optimum preparation condition were obtained from X-ray diffraction studies. Powder X-ray diffraction patterns were recorded on a Rigaku Miniflex II desk top X-ray diffractometer at 30 kV and 15 mA using CuK radiation.

2.1.3. BET surface area

The surface area and pore characteristics of the derived adsorbent CKA was determined from nitrogen adsorption/desorption isotherms at 77 K (boiling point of nitrogen gas at 1atm pressure) using a surface area analyzer (BELSORP-max, Japan).

2.1.4. Point of Zero Charge (PZC) for adsorbent

The PZC characteristic of CKA was determined by solid addition method using 0.1M KCl and 0.002M citrimide solutions. KCl and citrimide solution (40 ml) was taken in 100 ml stopped conical flask. The initial pH values of the solutions were adjusted between 2 and 12 by adding either 0.1N HCl or 0.1N NaOH. The total volume of the solution in each flask was adjusted exactly to 50 ml by adding the KCl and citrimide solution. The initial pH of the solution was then accurately noted. The CKA (0.5 gm) was added to each flask. The suspensions were shaken and allowed to equilibrate for two days with intermittent shaking. The final pH values of the supernatant liquid were noted. The difference between the initial and final pH values ($\Delta pH = pH_i - pH_f$) were plotted against the initial pH value. The point of intersection of the resulting curve at which change in pH is zero gives the PZC.

2.1.5 Reagent and solutions

All reagents used were AR-grade chemicals. Stock solutions (1000 mg/l) of the test solution were made by dissolving required amount of $Pb(NO_3)_2$ in double distilled water. The pH of the test solutions was adjusted using dilute HCl (0.1 N) and NaOH (0.1 N). The CKA was derived from an inexpensive, abundantly available and eco-friendly vegetal source of Balam Khira (*Kigelia Africana*).

2.1.6. Preparation of the activated carbon from *Kigelia Africana*

The fruit of*Kigelia Africana*(Hindi name Balam Khira) obtained from the local area of Lucknow, Uttar Pradesh (India) was used as a precursor for activated carbon employing $ZnCl_2$ activation method. The raw material was first washed with distilled water to remove any water soluble impurities and ashes on the surface then dried at 65^0 C to remove the moisture and other volatile impurities. The precursor was then crushed in a pestle and motors and sieved it to desired particle size. The chemical activation of the powdered precursor was done with $ZnCl_2$ at a ratio of 2:1 (activating agent/ precursor) over 24 hours at 60^0C for activation, followed by carbonization at 550 °C in a muffle furnace for 1h in presence of nitrogen (flow rate of 150 ml/min STP). After cooling, the produced material was washed with 0.5N HCl, hot water and finally cold distilled water to remove residual organic and mineral matters;it was then dried at 110°C for 12 h and sieved to the desired particle size by standard sieves. The product derived so was referred to as CKA.

3.1. Experimental adsorption

3.1.1. Batch studies

The adsorption equilibrium was probed by batch technique in 250 ml conical flasks contacting the CKA (1.0 g/L) with 100 ml of lead solutions of known concentrations (25–1000 mg/L), shaking at 120 rpm for 2h at room temperature (30 ^{0}C), followed by filtration (0.45 µm) and subsequent analysis of residual Pb (II) concentration in the filtrate (AAS on flame mode by lead-hollow cathode lamp and wavelength 283.0 nm). The effect of adsorbent dose, adsorbate concentration, temperature, pH and contact time was investigated. For determining the effect of pH on Pb (II) adsorption, initial pH of solutions were adjusted to the desired value (2–7) using 0.1 N HCl or 0.1 N NaOH. The amount of Pb (II) adsorbed by the adsorbent at equilibrium was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

Where C_0 and C_e are initial and equilibrium concentrations (mg l^{-1}) Pb (II) in the solution, V the volume (l), m the weight (g) of the adsorbent and q_e is the amount Pb (II) adsorbed by the adsorbent at equilibrium (mg g^{-1}).

Results and discussions

Biosorbent characterization

The SEM images shown in Fig.1 clearly demonstrate the porosity and surface texture of new adsorbent material.

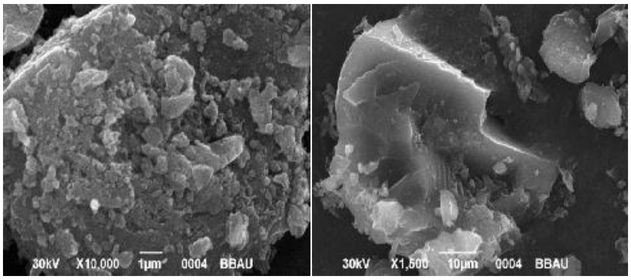

Fig. 1. SEM images of CKA at different magnifications

The CKA was found to contain following elemental compositions-

Table 1: Elemental composition of CKA

Elements	Percentage (%)
C	79.42
O	18.57
K	0.01
Na	0.02
Mg	0.91
Ca	1.07

Fourier transform infrared (FT-IR) spectroscopy provides evidence for the presence of specific functional groups on the surface of carbon material. Several characteristics bands were observed in the FT-IR spectrum shown in Fig. 2each of the bands has been assigned to specific functional group reported in literature. The details of band assignments to functional groups are shown in Table 2.

Table 2: List of specific functional group present in FT-IR spectrum of CKA

Frequency (cm^{-1})	Bond	Functional group	References
3035.5	=C—H stretching,	Alkenes	[11]
2879.2	-C—H stretching,	Alkane	[12, 13, 14]
2774.1	H-C=O, C—H stretch,	Aldehyde	[14]
1607.6	-C=C stretching,	Olfinics	[13]
1500.1	-C=C stretching,	Aromatic compound	[15, 16]
1053.6	-C—O stretching ,	Acids, Alcohols, Phenols,	[17]
680.5	-C=C—C, C-H,	Alkene	[18]

In IR spectra of activated carbon after deposition of Pb(II) some new peaks are also observed due to increased sharpness of surface of activated carbon. The surface of carbon becomes smooth and sharp that some broad peak converted in to multiples and also arises new peaks at 1214.9 cm^{-1}, 1004.9 cm^{-1} and 795.5 cm^{-1}.

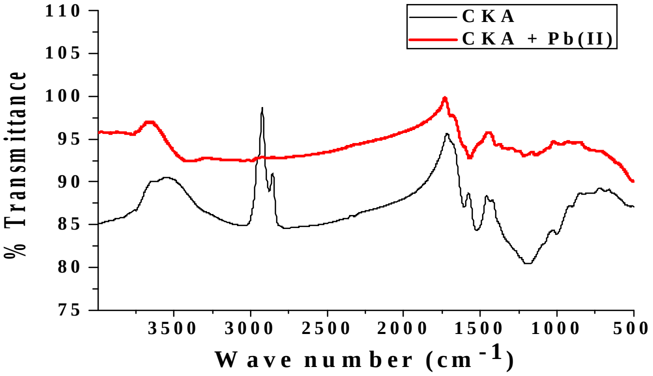

Fig. 2. FT-IR spectrum of activated carbon derived from CKA

The BET (Brunauer-Emmett-Teller) surface area (S_{BET}) was measured by means of standard BET equation applied in the relative pressure range of 0.05–0.10. The BET analysis reveals that the CKA had a surface area 799.91 m^2g^{-1}, which was primarily contributed by micropores. The average pore diameter of CKA was found to be 4.72 nm, which is an indicative of its micropores character as defined by IUPAC (International Union of Pure & Applied Chemistry).

Table 3: Surface parameters of activated carbon derived from CKA

(V_m) (cm^3 g^1)	(S_{BET}) (m^2g^{-1})	(V_T) (cm^3g^{-1})	d_{avg} (nm)	R_p (nm)
83.78	799.91	0.9443	4.72	1.21

X-ray diffraction spectrum shown in Fig.3 illustrates that the treated carbon derived from KA fruit under optimum preparation condition is crystalline in structure. There are three broad peaks centered on 2Θ value of 24^0, 42^0 and 83^0 are visible in the XRD spectrum. Two broad diffraction peaks centered around 2Θ values of 24° and 42° are attributed to the reflections from the (002) and (10) diffraction peaks of carbon material. These reflections are compulsory for activated carbon and indicate better layer alignment with an increased regularity in crystal structures. The presence of broad peak around $2\Theta = 83^0$ is not clearly described. These results and description are also explained by Devarly et al [19] and Ting Yang et al [20].

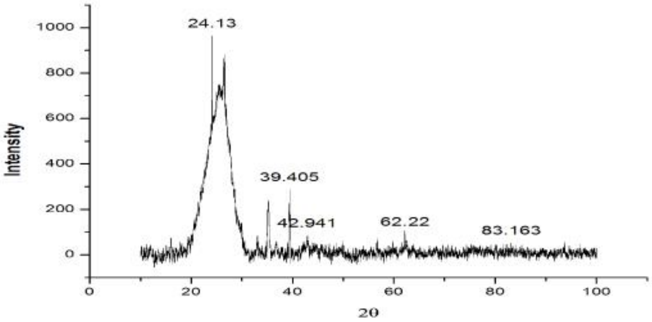

Fig. 3. XRD spectra of activated carbon derived from (Balam Khira)*Kigelia Africana*

The surface potential of the adsorbent may be influenced by the pH value [21] of the coexisting liquid bulk phase. The pH value, at which the surface charge is zero, is called the point of zero charge (PZC). The surface will be positively charged at $pH < pH_{PZC}$ and negatively charged at $pH > pH_{PZC}$. Since, pH_{PZC} of the CKA was found to be about 6.6, at any $pH < pH_{ZPC}$, the surface of TBH will be positively charged and at $pH > pH_{ZPC}$, the surface will be negative.

Effect of process parameters on Pb (II) adsorption

Effect of pH

The effect of pH on adsorption of Pb (II) on to CKA is shown in Fig. 4. The pH of the solution has a significant role on the removal of heavy metals, since it determines the surface charge of the adsorbent, the degree of ionization and speciation of the adsorbate. In order to establish the effect of pH on adsorption of Pb (II) on to the CKA, equilibrium studies at different pH values were carried out in the range of 1–7 at 50 mg/l and 100 mg/l, respectively. The maximum percent removal of Pb (II) ions on to CKA was observed at pH 4.5 – 5.0. Above and below this pH, extent of adsorption of Pb (II) onto CKA was found to be quite low. Above pH 7.0, Pb (II) starts precipitating as $Pb(OH)_2$ and hence studies in this range are not conducted. The ion exchange mechanism between H^+ions at the CKA surface and metal ions may follow two reactions [22]

$$2(\text{S-COH}) + M^{2+} \rightarrow (\text{S-CO})\,2M + 2H^+,$$

$$\text{S-COH} + MOH^+ \rightarrow \text{S-COMOH} + H^+,$$

where S is the adsorbent surface. The Pb (II) speciation diagram indicates that in the highest sorption range, the dominant species of adsorption are $Pb^{2+}$and $PbOH^+$[23].

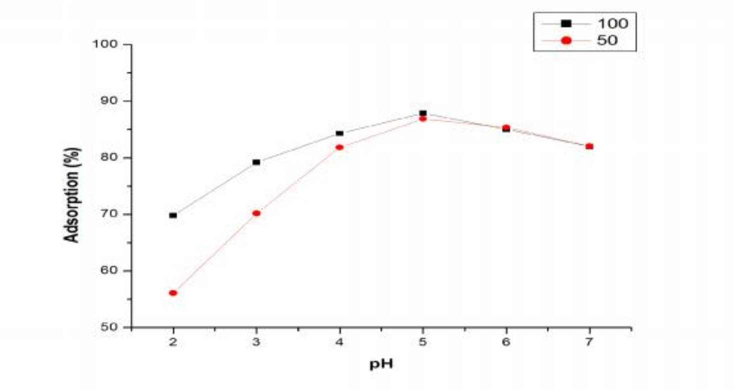

Fig. 4.Plots illustrating the effect of pH on adsorption (%) of Pb (II) onto CKA (1 g/l, 30^0 C)

In acidic solution, the surface being positively charged, the adsorption of $Pb^{2+}$and $Pb(OH)^+$ species are not favored. Because electrostatic attraction between positively charged adsorbent surfaces and positively charged metal ion surfaces is not possible, it seems that some non electrostatic forces are also involved in adsorption process.

Effect of initial Pb (II) concentration

The adsorption capacity of the CKA obtained from experimental data at different initial concentration of Pb (II) are shown in Fig.5 As observed from result, the adsorption percentage of the adsorbent decreased with increasing adsorbate concentration . The CKA amount was fixed 1.0g and equilibrated for 2 h, 30^0 C (120 rpm) at the initial Pb (II) concentration was increase from 25 mg/l to 150 mg/l.

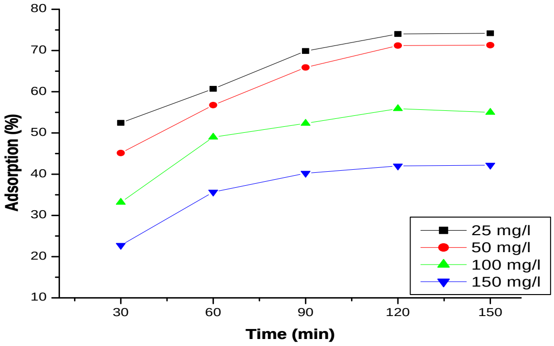

Fig. 5. Plots illustrating the effect of initial Pb (II) concentration on adsorption (%)(CKA 1g/l, 30^0,pH 5)

Effect of adsorbent dose

The effect of adsorbent dosage on the percentage removal of Pb (II) at pH 5 has been shown in Fig.6. The CKA amount was varied from 0.5 g to 3 g and equilibrated for 2 h , 30^0 C (120 rpm) at 50 mg/l and 100 mg/l Pb(II) initial concentration, respectively. It can be seen from the figure that initially the percentage removal increases very sharply with the increase in adsorbent dosage but beyond a certain value (2.5–3 g/l) the percentage removal reaches almost a constant value. This trend is expected because as the adsorbent dose increases the number adsorbent particles increases and thus more Pb (II) is attached to its surface.

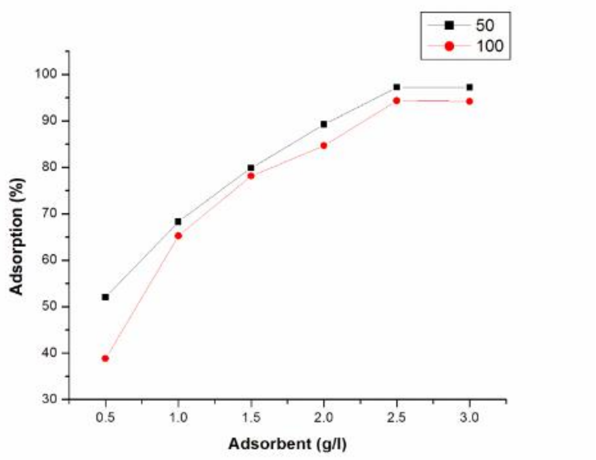

Fig. 6. Plots illustrating the effect of adsorbent dose on adsorption(%) of Pb (II) (Conc.50,100 mg/l, 30^0C, pH 5)

Adsorption equilibrium

Several equilibrium isotherm equations were applied to optimize of an adsorption system for the adsorption of Pb (II) onto the CKA. The Freundlich isotherm[24] is employed by assuming a heterogeneous surface with a non uniform distribution of heat of adsorption over the surface which may be written as:-

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (2a)$$

The above equation can be linearized as

$$lnq_e = lnK_F + \frac{1}{n} lnC_e \qquad (2b)$$

Where q_e (mg/g) is the amount of solute adsorbed per unit weight of adsorbent, C_e (mg/l) is the equilibrium concentration of solute, K_F (mg/g) is the Freundlich constant which indicate the relative adsorption capacity of the adsorbent and 1/n is the constant indicate the intensity of adsorption.

The Langmuir equilibrium isotherm[25] is based on the fact that the adsorption occurs at specific homogenous site within the surface of adsorbent and monolayer sorption onto a surface with a finite number of identical sites assuming that there are no interaction between adsorbed molecules on the surface, may be written as:-

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \qquad (3a)$$

Which can be linearlized as

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (3b)$$

Where q_e (mg/g) is the amount of solute adsorbed per unit weight of adsorbent, C_e (mg/l) is the equilibrium concentration of solute, q_m is the monolayer adsorption capacity (mg/g) and is a constant, and K_L is a constant related to the free energy of sorption (K_L α $e^{-\Delta G/RT}$). It is the reciprocal of the concentration at which the adsorbent is half-saturated. Using plot of experimental data as $C_e/q_e Vs1/q_m$, values of the constants were evaluated.

The Temkin isotherm[26] is given as:-

$$q_e = \frac{RT}{b} ln(K_T C_e) \qquad (4a)$$

Which can be linearized as:-

$$q_e = B_1 lnK_T + B_1 lnC_e \qquad (4b)$$

Where $B_1 = RT/b$, b is the Temkin energy constant (J mol^{-1}). The factor K_T in this isotherm explicitly takes into account the interactions between adsorbing species and the adsorbent. A plot of q_e *vs* lnC_e enables the determination of the isotherm constants b, B_1 and K_T from the slope and intercept, respectively.

Table 4: Adsorption characteristics' of Pb (II) on to CKA

S.No.	Adsorption isotherm	Isotherm parameters	R^2
1	Freundlich	K_F 8.82 n 2.11	0 .96
2	Langmuir	K_L 0.051 qm 79.87	0 .99
3	Temkin	B_1 41.64 K_T 2.13	0 .98

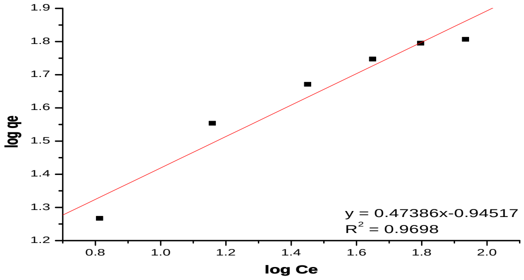

Fig. 7. Freundlich adsorption isotherm of Pb (II) on to CKA at 30^0 C

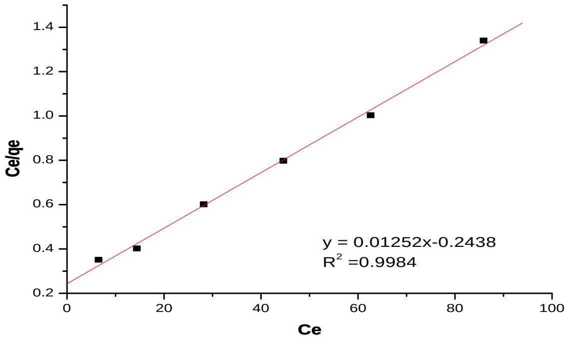

Fig. 8. Langmuir adsorption isotherm of Pb (II) onto CKA at 30^0 C

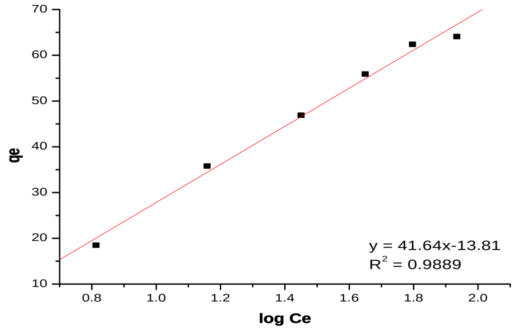

Fig. 9. Temkin adsorption isotherm of Pb (II) on to CKA at 30^0 C

Kinetics of adsorption

Adsorption kinetics was studied by monitoring the progress of the adsorption process at different time intervals. Fig.5 clearly demonstrates that the amount of adsorption was found to increase up to 90 min. and finally attained a constant value up to 150 min. for 25, 50,100 and150 mg/l initial Pb (II) concentration, respectively. Several kinetic models were tested with observed experimental results in order to describe the mechanism of adsorption process. The results of the two models are represented in Fig.10 and 11. The kinetic parameters of each model are tabulated in Table 5.

Lagergren first order Kinetics

The Lagergeren first order rate expression [27] is written as:-

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303}t \qquad (5)$$

Where q_t and q_{eq} are the amount adsorbed at time t and at equilibrium, t is time K_{ad} is rate constant for adsorption. A log (q_e - q_t) *vs*. time plots give a straight line, (Fig.10.) K_1 was calculated from the slope at temperature 30^0 C and data are presented in Table 5.

Pseudo second order kinetic

The pseudo second order kinetic equation [27] is given as:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \qquad (6a)$$

The integration of the equation leads to:

$$\frac{t}{q_t} = \frac{1}{K_2 q_{e2}^2} + \frac{1}{q_{e2}}t \qquad (6b)$$

Where K_2 is the rate constant (g mg^{-1} min^{-1})

The slope and intercept of the plot between t/q_t*vs*. time gives the value of q_e and $K_{2,}$ respectively (Fig.11) and data are shown in Table 5.

The data shown in Table 5 illustrates that the pseudo second order kinetic equation represent the adsorption data well satisfactorily with R^2 = 0.99 that are obtained from linear regression methods. Such representative plots are shown in Fig. 10 and 11, respectively.

Table 5 :Kinetics parameters for adsorption of Pb (II) at different initial concentration on to CKA

Lagergren first order kinetics

Pb (II) conc. (mg/g)	K_1 (min^{-1})	q_e (mg/g)	R^2
25	0.050	177.82	0.93
50	0.059	309.02	0.91
100	0.056	119.11	0.93
150	0.049	111.13	0.98

Pseudo second order Kinetic

Pb (II) conc.(mg /g)	K_2 (gm min^{-1})	q_e (mg/g)	R^2
25	5.1×10^{-4}	90.68	0.99
50	4.2×10^{-4}	85.54	0.99

100	5.6×10^{-4}	67.11	0.99
150	5.5×10^{-4}	53.13	0.99

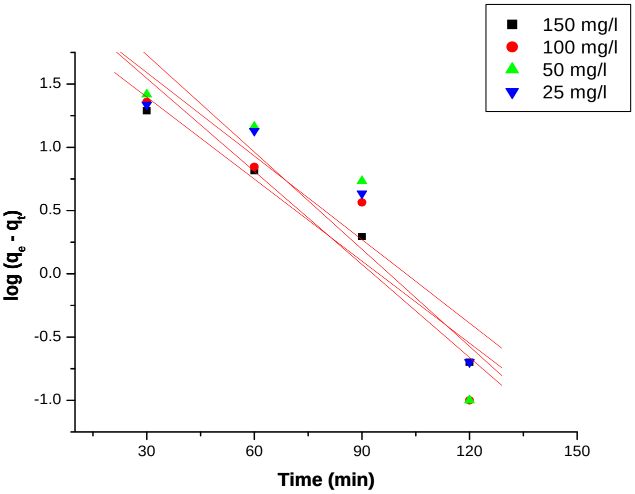

Fig. 10. Lagergren first order plots for the adsorption of Pb (II) on to CKA (pH 5.0, CKA 1 g/l and 30^0 C)

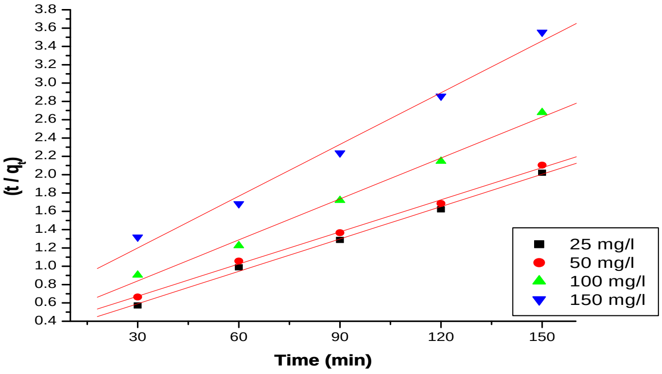

Fig. 11. Pseudo second order plots for the adsorption of Pb (II) on to CKA (pH 5.0, CKA 1 g/l and 30^0 C)

Thermodynamics of adsorption

The temperature range used in this study was 20 – 60^0C. The values of equilibrium constants (K_c) at 20, 30, 40, 50, and 60 ˚C, Pb (II) initial concentration 50 mg/l and CKA amount 1g/l at pH 5 were calculated using the following relation [28].

$$Kc = \frac{C_{Ac}}{C_e} \qquad (7)$$

Where C_{Ac} and C_e are the equilibrium concentrations (mg/ l) of Pb (II) on the adsorbent and in solution, respectively

$$\Delta G^0 = -RT \log K_c \quad (8)$$

Where T is the absolute temperature, R gas constant and ΔG^0 is the standard free energy change. The values of enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated using the following relation:

$$\log Kc = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \qquad (9)$$

ΔS^0 and ΔH^0 were calculated from the slope and intercept of linear plot of log K_c *vs* 1/T. The vant's Hoff plot for Pb (II) on CKA is shown in Fig.12. The thermodynamic data are given in Table 6.

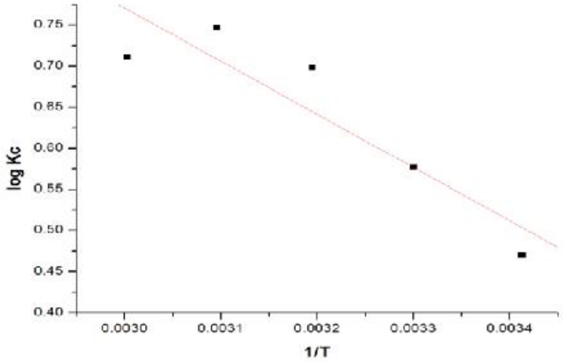

Fig.12. Vant's Hoff plot for Pb (II) on to CKA

Table 6 :Thermodynamics parameters at different temperature for the adsorption of Pb (II) on to CKA

Temperature (◦C)	K_c	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (kJ mol^{-1})
20	2.95	- 2.63		
30	3.78	- 3.32		
40	4.99	- 4.16	12.36	0.0518
50	5.58	- 4.59		
60	5.14	-4.53		

The endothermic nature of the adsorption was confirmed by the thermodynamic parameters as shown in Table 6. The negative value of ΔG^0 is an indication of the spontaneous nature of the process.

Apparent enthalpy of adsorption ΔH^0 also confirms the endothermic nature of the adsorption process.

Conclusions

The synthesized CKA produced from Kigellia Africana fruit seems to have great potential to remove Pb (II) from waste water. The various equilibrium models such as Freundlich, Langmuir and Temkin were tested to describe the equilibrium adsorption. However, Langmuir isotherm was found most suitable as representative of the equilibrium adsorption data. The kinetic modeling of the Pb (II) adsorption onto CKA indicates that adsorption process is pseudo-second order with the R^2-0.99. Different thermodynamic calculations indicate that the sorption process is feasible, spontaneous, endothermic and positive value of ΔSsuggests the increased randomness. The adsorption properties of studied system depend on several factors such as surface area of adsorbent and solution condition such as pH and adsorbate concentration. The waste material used for the preparation of CKA is widely available and inexpensive hence it is expandable for industrial purpose.

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CHAPTER:9

STUDY AND INVESTIGATE THE INTERESTING AND FASCINATING CHARACTERISTICS OF IONIC LIQUIDS: A REVIEW

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Abstract

A salt in liquid form is known as an ionic liquid (IL). In certain cases, the term has been confined to salts with a melting point below a specified temperature, such as 100 degrees Celsius (212 degrees Fahrenheit). Ordinary liquids like water and gasoline are mostly made up of electrically neutral molecules, whereas ionic liquids are mostly made up of ions. Liquid electrolytes, ionic melts, ionic fluids, fused salts, liquid salts, and ionic glasses are all terms that describe these compounds.There are several applications for ionic liquids. They're strong solvents that can also be employed as electrolytes. Because of their low vapour pressure, salts that are liquid at near-ambient temperatures are useful in electric battery applications.An ionic liquid is formed when a salt melts without disintegrating or vaporising. At 801 °C (1,474 °F), sodium chloride (NaCl) melts into a liquid mostly composed of sodium cations (Na+) and chloride anions (Cl). When an ionic liquid cools, it frequently transforms into an ionic solid, which can be crystalline or glassy.

Keywords: Ionic liquid, green chemistry, ionic bond, salts,

1. Introduction

Chemistry has significant impact on our daily lives, as the organic compounds are widely distributed and for survival of life on earth sustainable development should be our first priority. Human has inclined the ingenious balance of our ecosystem towards the instability. In the mid- 1990s, a new concept of “benign by design” or green chemistry was developed by Anastas and coworkers (Anastas & Farris, 1994). Green chemistry principles have attracted the researcher aiming towards, minimum waste and cost effectiveness research. Recently, there has been an improvement in extensive interest for improving health and aesthetics values of every individual (Meyers, 1999). This can be accomplished in chemical industry, via designing new chemical reaction or modifying the current chemical processes. A range of conventional organic solvents are used in chemical industry, which often have negative impact on climate change, depletion of ozone layer and formation of smog etc. (Lide, 1995; Wypych, 2000). The prevention of pollution and waste minimization are significant challenges, which will require some alternative processes.

Ionic liquids (ILs) are generic terms for a class of materials, consisting utterly of ions & being liquid below 100^0C. ILs is ionic compounds usually liquid at room temperature. ILs can be stable over a wide range of temperature (300-400°C), so they are thermally stable. ILs won’t change their chemical state and physical state, so electrically stable.

2. History of Ionic liquids

Initially, S. Gabriel and J. Weiner (Gabriel & Weiner, 1888) synthesized the first room temperature ionic liquid ‘ethanol ammonium nitrate’ (T_{melt} =52-55 ^{0}C). After this, Paul Walden, (*Walden,* 1914) reported the synthesis of ionic liquid “ethyl ammonium nitrate” (T_{melt} =12^0 C). In 1970s & 1980s halogen anions with pyridinium cations are used as electrolytes in batteries. The various reported methods are exhibits for synthesis of neutral ionic liquids mostly in 1990s, commonly phosphorus hexafluoride anion and boron tetrafluoride anions are used. The stability of these anions is the major factor still they are toxic in nature. In recent years, magnetic ionic liquids are synthesized using tetrachloroferrate as an anion with 1-butyl-3-methyl imidazolium as a cation (Hayashi & Hamaguch, 2004). These ILs are less toxic, highly stable and more environmentally benign in nature then earlier ILs.

3. Properties and Characteristics of Ionic liquids

Ionic liquids exhibit special features like thermal stability, nonvolatility, high polarity, temperature-dependent miscibility with water, wide temperature range, variety of structural availability and nonexplosion (Table 1) (Zhang *et al.,* 2006; Deetlefs *et al.,* 2006; Rooney *et al.,* 2009). ILs mostly do not have any smell and don't ignite. They are usually safe in nature. The dermal toxicity of all of ionic liquids is very low and safe to use in research fields. Ionic liquid catalysts provide the considerable attention on immobilized or biphasic catalyst, ILs containing metal or nonmetal supported on polymer or mineral, easy recyclable and separation (Lei *et al.,* 2017; Dai *et al.,* 2017; Welton, 2004; Kirchner, 2009; Sanjay, 2008; Wasserscheid & Welton, 2008). Interesting advantage of ionic liquids is their immobilization on the solid surfaces. ILs have few disadvantages over numerous uses such as most of the ionic liquids are not easily biodegradable, expensive and some the fluorinated anions are toxic in nature.

Table 1: The general physical properties of ionic liquids are given below.

1.	A salt	Cation and or anion slightly large
2.	Liquidous range	Often $>200^0$C
3.	Freezing point	Preferably below 100^0C
4.	Viscosity	Normally <100cP, workable
5.	Polarity	Moderate
6.	Thermal stability	Usually high
7.	Dielectric constant	Implied < 30
8.	Specific conductivity	Usually < 10 $mScm^{-}$
9.	Molar conductivity	< 10 Scm^2mol^{-1}
10.	Electrochemical window	>2 V, even 4.5 V
11.	Solvent or catalyst	Excellent for many organic reactions
12.	Vapour pressure	Usually negligible

4. Structures of Ionic liquids

ILs are found an irregular shape in nature that helps to prevent the packing of ions near together. They are non-symmetrical in nature and usually big in shape.

The nature of cations and anions affect the properties of ionic liquids. In ILs cations and anions control the electrical & thermal stability. The common cations and anions structures are shown in Figure 1.

- **Cations in ILs:** Cations are generally organic in nature

Examples: Ammonium based, Imidazolium based, Phosphonium based, sulphonium based etc.

- **Anions in ILs:** ILs may be inorganic or organic in nature.

Examples: Inorganic anions: Cl^-, F^-, Br^-, I^-, BF_4^-, PF_6^- etc.

Organic anions: alkyl sulphonates, tosylates etc.

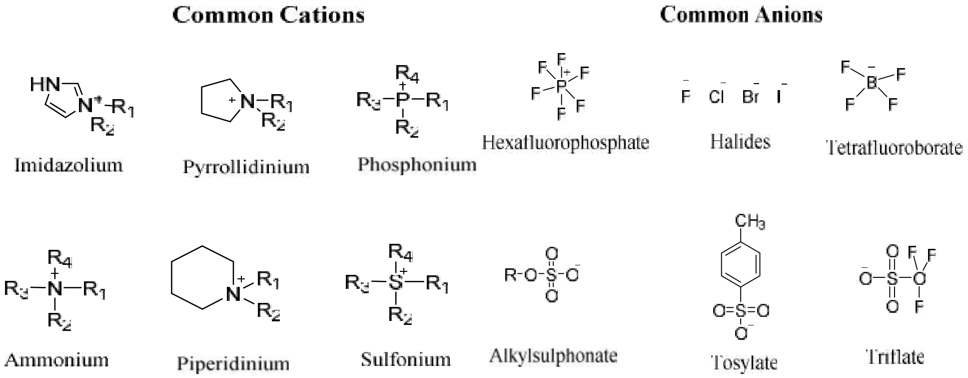


Figure.1. Thecommon examples of cations and anions for the formation of ionic liquids

5. Classification of Ionic liquids

As the ionic liquids are emerging, their chemical diversity has also grown. These ionic liquids have been further classified as below:

(i). Room-temperature ionic liquids (RTILs)

Room-temperature ionic liquids (RTILs) are ‘’molten salts” composed of ions with melting point below 100 °C. They generally composed of an organic anion and/ or cation with variety of tunable interaction, which remains them liquid below room temperature. Recently, a variety of RTILs can be synthesized via using different cations/anions combinations, and significantly different structures are possible depends on their components.

RTILs are works as green solvents as well as catalyst for various organic synthesis. These have direct application in energy storage, electrochemistry and to understand the molecular structure of RTIL-air interface in chemistry and physics. Some of the RTIL are shown in Figure.2. (Hallett & Welton, 2011; Bara *et al.*, 2009; Lei *et al.,* 2014; Lei *et al.,* 2014; Chatel & MacFarlane, 2014; Mai & Koo, 2016).

N-alkyl-N-methyl pyrrolidinium

N-alkyl pyridinium

1-alkyl-3-methyl imidazolium

acetate

Figure2. Some examples of the RTILs

(ii). Task- specific ionic liquids (TSILs)

Task -specific ionic liquids (TSILs) are the recent generation of ionic liquids, formed when a functional group is covalently attached to the anion or cation (or both) of ionic liquids. The TSILs having competency to acts not only as a reaction but as a regent or a catalyst in various chemical reactions (Wasserscheid &Welton, 2008) . The recent synthesis for most of TSILs is two-step method, there are different synthetic approaches used for the synthesis of different types of TSILs. In TSILs, the preference for supporter materials is very significant in case of supported ionic liquids.

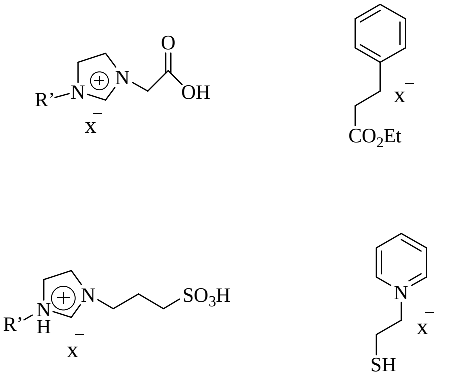
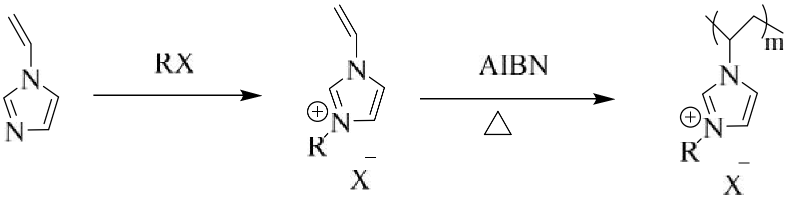


Figure3. Some examples of the TSILs

One of the economical TSILs is non-imidazolium-based ionic liquids, which includes the study of green solvents, catalyst, green synthesis and efficient recycling of catalysts (Yue *et al.,* 2011; Ruckart *et al.,* 2015). There few examples of TSILs are shown in Figure 3 (Neto *et al.,* 2019; Hallett & Welton, 2011; Welton, 1999).

(iii). Polyionic liquids (PILs)

Polyionic liquids (PILs), as an ingenious class of polyelectrolytes that are composed of repeating units of ionic liquids with polymeric backbones. The combination of ionic liquid and polymers keeps them highly effective material for composite in material science. The repeating unit of Ionic liquids in PILs illustrate their chemical and physical properties such as ion conductivity (up to 10^{-3} S cm^{-1}), thermal stability (300 °C or even higher), solubility, nonflammability and electrochemical stability (up to 5 V *vs.* Li^+/Li^0), determining on bases of cation-anion pair, shows to resemblance with ILs (Zhang *et al.,* 2020; Qian *et al.,* 2017; Rojas *et al.,* 2014). The common synthesis of PILs from N-vinyl imidazolium based IL monomer (Yuan&Antonietti, 2011) is shown in Scheme 1.



Scheme1. Synthesis of PILs from N-vinyl imidazolium-based IL monomer

The recent example of PIL, includes the incorporation of organic redox moieties such as nitroxide 2, 2, 6, 6-tetramethylpiperidine-1-oxyl (TEMPO) or anthraquinone (AQ) derivatives as counter anions into PDADMA-type PILs. This is used in electrochemical energy storage technologies such as as electrocatalysts in fuel cells, metal–air batteries, as lithium batteries or as electrolytes in redox flow batteries (Hernández *et al.,* 2017).

(iv). Supported ionic liquid membranes (SILMs)

Supported ionic liquid membranes (SILMs) made up of a thin microporous support belonging the pores which are filled by an ionic liquid. SILMs have been considerably used in selective separation and purification of mixed organic compounds. SILMs also having unique properties as similar to ILs such as greater viscosity, negligible vapour pressure and minimization of solubility which overcome the instability of supported liquid membranes (de los Ríos*et al.,* 2012; Wickramanayake *et al.,* 2014; Scovazzo *et al.,* 2009).

(v). Ionic liquid supported on Metal−Organic frameworks (MOFs)

Ionic liquid supported on Metal−Organic frameworks (MOFs) are consist of huge set of ionic liquid which are impregnated metal-organic framework composites. MOFs are generated by direct contact method to provide the performance for separation of gas as sorbent (Ferreira*et al.,* 2019).

IL acts as a medium for MOF synthesis consisting various properties such as the proficiency to simultaneous dissolving ability of both inorganic and organic precursors, chemical stability, high thermal stability, and extremely low volatility (Khan*et al.,* 2013; Parnham & Morris, 2007; Liu *et al.,* 2013; Liu *et al.,* 2016; Zhang *et al*., 2016).

6. Methods for the Preparation of Ionic liquids

1. Alkylation: Imidazolium, ammonium, phosphonium based and pyridinium based ionic liquids are formed by providing a suitable nucleophile (a precursor) with an alkylating agent like haloalkane (Kianfar & Mafi, 2021; Amarasekara, 2016; Earle *et al.,* 2006; Dupont *et al.,* 2000; Mutelet *et al.,* 2005; Kolle & Dronskowski, 2004).

2. Anion Exchange: This is two-step method for synthesis of ionic liquid for example hexafluorophosphate is obtained by using two-step process of imidazole diacetyl cation (Kianfar & Mafi, 2021; Amarasekara, 2016; Donata *et al.,* 2006; Earle *et al.,* 2006). In this method, a mineral anion replaced an elemental salt.

3. Solvent-free synthesis: This method also involves two steps process, for the formation of non-alcoholic ionic liquid. In first step of alkylation, haloalkanes are used as an alkylating agent and in second step replacement of undesirable halide salts using double anion exchange (Kianfar & Mafi, 2021; Amarasekara, 2016; Mutelet *et al.,* 2005). The unwanted halide salts can affect the catalytic activity of ionic liquids.

4. Synthesis of Chiral: The asymmetric synthesis of crystal ionic liquid had significant role as a solvent and catalyst. The crystal ionic liquid are generally prepared by using alkylation of pre-crystal precursor such as amino acids, terpenes, sugars and other chiral compounds and then anion exchange process (Kianfar & Mafi, 2021; Amarasekara, 2016; Mutelet *et al.,* 2005).

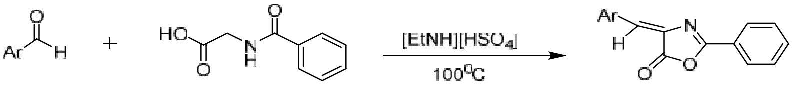
5. Special performance processes for synthesis of ILs: In recent years, the scope of utilization of ionic liquids needs high scale production of functional ionic liquids (Amarasekara, 2016; Mutelet *et al.,* 2005).

7. Applications of Ionic liquids

Ionic liquids have been regarded to be suitable environmentally friendly, as a recyclable catalyst for synthesis of various organic compounds, fuel-cell application, conversion of biomass to renewable feed stock, extraction of metals and processing, Lithium batteries storage, other technology and chemical sciences.

1. Solvents applications: Ionic liquids have been used as solvents for extraction of metals (Chen *et al.,* 2015), solvents in many enzymatic reactions and organic synthesis (Scheme 2) (Parveen *et al.* 2015).

2. Catalysis applications: Ionic liquids have been used catalyst in various organic synthetic reactions (Chen *et al.,* 2015). For example, Parveen *et al.* (2015) reported the synthesis of 4- arylidene-2-phenyl-5 (4*H*)-oxazolones by the reaction of substituted heterocyclic/aromatic aldehydes and hippuric acid in presence of ionic liquid $[Et_3NH][HSO_4]$ at 100^0C. It was facile and stereoselective reaction affording high yield and took short time for completion. The advantage of this method is that replacement of acetic anhydride by using ionic liquid in reaction which acts as catalyst as well as solvent (Scheme 2).



Scheme 2.: Synthesis of 3,5-disubstituted oxazolone derivatives

3. Industrial applications: 'BASIL' (Biphasic acid scavenging utilizing ionic liquid) was developed by BASF's, which provides a tremendous breakthrough for chemical processes in industry. In past few years, the production of acids as by-products with many chemical processes commonly hydrochloric acid (HCl) was obtained, which decomposed the main chemical product or other side reactions. To protect the reaction products from decomposition, the acids required to be scavenged. Initially triethylamine used as a scavenger, after that 1-methylimidazole was applied as an acid scavenger and give rise to excellent results (Maase *et al.,* 2004).

4. As new functional materials applications: In recent years, ILs are used as lubricants, in preparation of polymers & gels, preparation of liquid crystals and epoxy ionic liquids resin (Yin*et al.,* 2020). For example, the polymerization of L-aspartic acid provides polyaspartic acid by using methylimidazolium hydrogen sulfate as a catalyst under microwave irradiation (Yang *et al.,* 2012).

5. Energy applications: Due to increasing requirement for sustainable energy, ILs applied as energy storage & conversion of material and devices (Díaz *et al.,* 2014; Yasuda & Watanabe, 2013; Lee *et al.,* 2009; Belieres & Angell, 2007).

6. As an Electrolytes application: ILs used as an electrolyte in fuel cell and Lithium ion batteries as an evolving field due to high electrochemical, conductivity, and thermal stability. In Lithium ion batteries, carbonate-based electrolytes are used since these having highest energy density and secondary batteries can even be developed (Díaz *et al.,* 2014; Yasuda & Watanabe, 2013; Lee *et al.,* 2009).

7. Pharmaceutical applications: When pharmaceutically active anion combined with pharmaceutically active cation, they formed a compound having medicinal properties. For example, the combination of an anionic antimicrobial with an antimicrobial active imidazolium cation leads to new microbiologically active ionic liquids or "Bionic liquids". The combined effectiveness of Bionic liquids is greater than the key elements (Postleb *et al.,* 2013; Amarasekara & Razzaq, 2014; Amarasekara, 2011).

8. Agricultural applications: The commercial herbicides caused the plants exhibits resistant towards herbicides; hence herbicide-resistant weeds species are increasing. To avoid the penetration of herbicides in plants tissues, other negative impact and to increase the efficiency of agrochemicals, the use of herbicidal ionic liquids maximizing in agricultures (Schütte *et al.,* 2017; Kaczmarek *et al.,* 2020; Łęgosz *et al.,* 2016).

9. Applications in technology: Ionic liquid epoxy worked as tough polymer matrix in cryo composite fuel tanks, is used by NASA as rocket propellent in recent years (Yin *et al.*, 2020; Jouyandeh *et al.*, 2021; Amarasekara, 2011). This IL epoxy used as corrosion prevention paint for ship.

10.ILs used in production of biofuel from algae (Zhou *et al.*, 2014), dissolving cellulose (Zhou *et al.*, 2014; 646], waste processing (Postleb *et al.*, 2013; Amarasekara & Razzaq, 2014; Amarasekara, 2011).

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CHAPTER: 10

FABRICATION OF Cu/TiO$_2$ NANOCOMPOSITES AND THEIR PHOTOCATALYTIC APPLICATION FOR THE DEGRADATION OF ACETIC ACID IN WASTE WATER

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Abstract

In the present study, prepared the nanocomposites of Titania by solution impregnation method and used as photocatalyst for the degradation of acetic acid in the presence of nanocomposites of Titania. The resulting powders were copper titanium dioxide. The alcohol route of synthesis, adopted here, yielded dark black homogeneous powder of copper titanium dioxide. The obtained yield of the product was more than 90% of the expected theoretical yield. In which the material has the nanodiamension. The prepared material was subjected to XRD analysis which gives the information about the presence of phase rutile and anatase both phases were present in the prepared sample. It is found that, in samples sintered at 400 ^{0}C both anatase and rutile phases were presented and rutile phase was more dominant, while in samples without sintered the exclusive formation of polycrystalline anatase and rutile phase separately was occurred. Applying the Scherrer's calculations through which particle size was found 16 and 72 nm in case of copper Titania and pure Titania respectively. The prepared sample of Titania and copper Titania were subjected to photocatalytic degradation of acetic acid were done. The degradation of acetic acid occurs efficiently. The prominent degradation was found in case of oxalic acid in the presence of nanocomposites Cu/TiO$_2$.

1. INTRODUCTION

Photocatalytic degradation is a rapidly expanding technology for the treatment of wastewater contaminated with organic pollutants such as acids, dyes, pesticides and non biodegradable materials. Photocatalytic degradation is the advanced oxidation process to degrade the water contaminants such as acids, dyes, pesticides and non biodegradable materials, which exhibit chemical stability and resistance to biodegradation. In recent years interest has been focused on the use of semiconductor materials as photocatalysts for the removal of organic and inorganic species from aqueous or gas phase. This method has been suggested in environmental protection due to its ability to oxidise the organic and inorganic substrates.

Several catalysts have been studied as photocatalysts for the degradation purpose. These include: TiO$_2$ [26–28], ZnO [22,25], ZrO$_2$, SnO$_2$ and WO$_3$ [29–32], ZnS [22], CdS [20,21], a-Fe2O$_3$, g-Fe$_2$O$_3$,[23,24], , Cr$_2$O$_7$ [34], AgCl/Al$_2$O$_3$ [35], niobium oxides [36], lanthanide tantallates (LnTaO4 where Ln can be La, Ce, Pr, Nd and/or Sm) [37], ZnO/TiO$_2$ [38], TiO$_2$/SiO$_2$ and TiO$_2$/Al2O$_3$ [39]. Titanium dioxide (TiO$_2$), commonly known as Titania, is one of the most commonly used photocatalysts. Because of its high oxidative power, stability, and non-toxicity, it promises a broad range of uses as a photocatalysts. Advantage of using TiO$_2$ as photo-catalyst are: (a) using TiO$_2$, the process occurs under ambient conditions.(b) using TiO$_2$, the oxidation of the substrate to CO$_2$ is complete in most cases and (c) it is comparatively inexpensive and remains quite stable in contact with different substrate. TiO$_2$ has also played a leading role in the active research for the utilization of solar energy. The TiO$_2$ based, dye sensitized, photo-electrochemical cells are receiving a great deal of attention as a possible candidate for converting solar energy into electricity on a large scale.

Extensive investigations have been reported on the photocatalytic degradation of organic compounds such as chlorinated compounds, chloro- and nitrophenols, dyes, pesticides and aromatic compounds. However, the possibility of using photocatalytic reactions for the degradation of trace acids dyes and pesticides in water have been receiving much attention in recent years. Semiconductor-mediated photocatalytic oxidation is becoming one of the possible environment-friendly techniques for the removal of trace organic pollutants, includingpesticides in water. Titanium dioxide is a well-known photocatalyst for water and air treatment as well as for catalytic production of gases. The general scheme for the photocatalytic destruction of organics begins with its excitation by supra band gap photons, and continues through redox reactions where OH radicals, formed on the photocatalyst surface, play a major role.

2. EXPERIMENTAL

2.1 Synthesis of TiO_2 nanocomposites

Titanium dioxide (TiO_2) nanoparticles were synthesized by the modified sol-gel method [30, 31]. Titanium tetraisopropoxide (Ti [OCH $(CH_3)_2]_4$ (TTIP), Aldrich, England), absolute ethanol (C_2H_5OH, Merck, Germany), and ammonia (NH_3, Merck, Germany) were used as the starting materials for synthesizing TiO_2nanoparticles. Titanium tetraisopropoxide (20 mL) was dissolved in 250 mL absolute ethanol and mixed until a homogeneous solution was obtained. The mixture of TTIP and absolute ethanol was loaded into a cellophane membrane and suspended for 1 h in a clear solution containing 1 : 1 ratio of ethanol (95%) and deionized water and 7 mL of ammonia solution (25%) as shown in Figure 1. After the completion of the dialysis process, the suspension was centrifuged at 7500 rpm for 10 min, washed with deionized water, and then dried in an oven at 60°C for 24 h. The white powders were then calcined in a furnace at a temperature of 400°C for 3 h.

2.2 Synthesis of Cu/TiO_2

In this study, Cu/TiO_2 nanocomposites were prepared by solution impregnation method. In this method suitable quantity of prepared TiO_2 was dispersed in alcoholic solution of copper acetate. The dispersion is agitated continuously for 4 hour at temperature which is just below of boiling point of alcohol. After the treatment the residue will removed through filtration and will sintered for 1 hour in presence of air at 400 ^oC by kipping it in a silica boat inside muffle furnace. After sintering and slow anilling to room temperature, The Content was taken out from furnace and was stored in closed and air tight bottles and was used as photocatalyst.

2.3: Photo-degradation studies

Photo-catalysed oxidative degradation reaction of organic substrates is holds lot of potential in pollution abatement as well as in synthetic Organic Chemistry. Although in literature several photocatalyst have been cited for this purpose many of then suffer from one or more disadvantage, particularly with regard to either then being highly expensive and chemically unstable. TiO_2 is well known semiconductor that has also been widely used as photocatalyst. In this study, to investigate the photo-degradation behavior of a prepared TiO_2 vis-à-vis synthesized Cu/TiO_2 nanocomposites towards photo-degradation of acetic acid

3. RESULT

3.1. X-ray diffraction analysis

Phase identification in the samples was attempted by analyzing them using X-Ray Diffractometer (Bruker AXS D8 Advance System, Germany). The obtained X-Ray diffraction patterns of few representative samples are shown in Figures 4.1 and 4.2. The observed pattern of peaks, when compared with the standard JCPDS database, suggested that, in commercially obtained TiO_2 samples, major peaks at 2θ angles 25.5, 37.2, 48.3 and 55.40 correspond to anatase phase, whereas major peaks at 2θ angles 26.9, 28.2, 42.6and 54.2^0 indicate the presence of rutile phase. In case of Cu-TiO_2 sample, the observed XRD pattern indicates not only a decrease in the peak intensity, compared to $TiO_{2,}$ but even the absence of some originally observed TiO_2 peaks. This is, probably, due to the decrease in the crystallinity, grain fragmentation and partial amorphization, when the samples were wet impregnated by copper acetate.

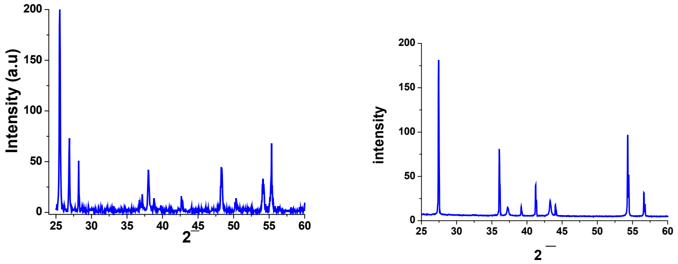

Fig-.2: Observed XRD pattern of TiO_2 andCu/TiO_2

3.2.2: Determination of Average size of Particles/ Grains in samples

Utilizing the observed X-ray diffraction data of samples, Scherrer's calculations were attempted to know the average size of particles/grains in the samples. Although, Scherrer's calculations are only approximate in nature, but definitely provide a first-hand idea of the average size of the particles/ grains in the samples, which may be quite accurate, provided the size of particles/ grains is below 100 nm. The results of Scherrer's calculations are presented in Table 1. The results suggest average size of the particles/ grains in the samples lying in nm range.

TABLE -1: Average size of particles/grains in the samples of TiO_2 and Cu/TiO_2

sample	Particle size from Scherrer's calculation *(nm)
Cu/TiO_2	80
TiO_2	35

3.2.3. SEM (SCANNING ELECTRON MICROSCOPY)

The morphology of the samples was investigated by scanning electron microscopy and it resumes the most interesting outcomes. Fig 3.3 A and 3.3 B clearly show that both the prepared samples are obtained agglomerate in nanometric dimension. The doping of copper is indicating that the particle size reduce due the penetration of copper in the lattice of titanium dioxide.

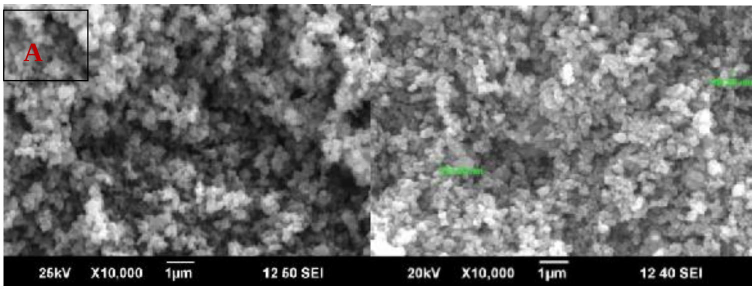

Fig. 3: Observed SEM image of (A) TiO_2 (B) $Cu\text{-}TiO_2$

3.2.4. Surface area analysis (B.E.T)

The specific surface area, pore volume and average pore size of the TiO_2 and Cu/TiO_2as-prepared photocatalyst were characterized by using the N_2 adsorption technique *BET*. Table -2 summarizes their physical properties. The TiO_2 modified by Copper are fragmentized to some extent during thermal treatment, leading to a marked increase of the *BET* surface areas and the average pore radius size and decreasing of the pore volume.

Table-2: Phase ssurface areas, pore volume, average particle sizes of TiO_2 and Cu/TiO_2

Sample	Phase	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore radius (nm)
TiO_2	R+A	6.4	0.018	11
Cu/TiO_2	R+A	13.2	0.031	6

3.3: Photo-degradation of acetic acid

The samples of TiO_2 and Cu/TiO_2 were used as photocatalyst in the photo-degradation of Acetic acid. A suitable quantity of the photo-catalyst was dispersed in the substrate solution and the reaction mixture was illuminated with UV – Visible light, while kept under agitation. The results presented in this Section comprise the residual concentrations of substrate in the reaction mixture, measured at different time intervals.In this study, photo-catalytic degradation of Acetic acid was investigated. The measured values of residual concentration of acid in the reaction mixture at different times of illumination (or reaction time) have been shown in Tables 3-5 and Figures 4.3 – 4.6. It is clear from the results shown that both TiO_2 and Cu/TiO_2 are proving as an effective photo-catalyst for the degradation of organic acid. However Cu/TiO_2seems to be more effective as photo-catalyst for the degradation of acetic acid.

TABLE -3: Observed variation in Acetic acid concentration with time in the reaction mixture

Reaction Time (min)	**Amount of Photocatalyst: 20 g/ L**					
	Reaction Temperature 30 °C					
	TiO_2			**Cu-TiO_2**		
	10.6ò10^{-3} M	**5.3ò10^{-3} M**	**2.65ò10^{-3} M**	**10.6ò10^{-3} M**	**5.3ò10^{-3} M**	**2.65ò10^{-3} M**
0	10.6	5.3	2.65	10.6	5.3	2.65
60	8.8	4.5	2.20	8.0	4.2	2.0
120	7.6	4.0	1.8	6.6	3.5	1.4
180	6.8	3.4	1.4	4.2	3.0	1.0
240	5.8	3.0	1.0	3.2	2.2	0.5

TABLE -4: Observed variation in Acetic acid concentration with time in the reaction mixture

Reaction Time (min)	**Initial concentration of Acetic acid: 10.6ò10^{-3} M**			
	Reaction Temperature 30 °C			
	TiO_2		**Cu-TiO_2**	
	Amount of TiO_2 20 g/ L	**Amount of $TiO_2$40 g/ L**	**Amount of Cu-TiO_2 20 g/ L**	**Amount of Cu-TiO_2, 40 g/ L**
0	10.6	10.6	10.6	10.6
60	8.8	8.4	8.0	6.4
120	7.6	7.2	6.6	6.2
180	6.8	6.2	4.2	4.0
240	5.8	5.4	3.2	3.0

TABLE -5: Observed variation in Acetic acid concentration with time in the reaction mixture

Reaction Time (min)	**Initial concentration of Acetic acid: 10.6ò10^{-3} M**					
	Amount of Photocatalyst: 20 g/ L					
	WPC		**TiO_2**		**Cu-TiO_2**	
	RT 30 °C	RT 40 °C	RT 30 °C	RT 40 °C	RT 30 °C	RT 40 °C
0	10.6	10.6	10.6	10.6	10.6	10.6
60	10.6	10.6	8.8	7.4	8.0	6.4
120	10.6	10.6	7.6	6.5	6.6	5.2
180	10.6	10.4	6.8	5.2	4.2	3.8
240	10.6	10.2	5.8	4.0	3.2	2.4

3.5. Effect of Temperature

The effect of system temperature on photocatalysis has not attracted enough attention. But In present research, it is found that the temperature has a great effect on the photodegradation of methyl Red. The photocatalytic efficiency can be increased about 2-3 times if the temperature increased from 30 to 40 Because the solar energy include UV light, which can be used to activate the photocatalytic course, which is increase the temperature of photocatalytic system. The experiments showed that Methyl Red cannot be photodegraded if TiO_2 or UV light was not used, indicating that Methyl Red cannot be pyrolyzed by heating with the heating temperature which was less than 40 °Cand self degraded by absorbing irradiation. Only when TiO_2 and UV light were both used, the Methyl Red was efficiently degraded shown in table 3.2-3.3 and fig 3.4-3.5 and 3.6. The obvious decrease of concentration of dye shows that the TiO_2 and Cu/TiO_2 can serve as an effective photocatalyst.

3.6 Effect of concentration

Effect of dye concentration Keeping the catalyst loading concentration constant at 25 g/liter of the dye solution, the effect of varying amounts of the acid was studied on its rate of its degradation (from 50 x 10^{-4} to 25 x 10^{-4} M) as given in Table 3.2 and 3.3. With increasing concentration of MB the rate of degradation was found to decrease. This is because as the number of dye molecules increase, the amount of light (quantum of photons) penetrating the dye solution to reach the catalyst surface is reduced owing to the hindrance in the path of light. Thereby the formation of the reactive hydroxyl and superoxide radicals is also simultaneously reduced. Thus there should be an optimum value maintained for the catalyst and the dye concentration, wherein maximum efficiency of degradation can be achieved.

3.7. Effect of pH

The photodegradation reaction was also carried out under varying pH conditions from (2 to 7), by adjusting with NaOH, with TiO_2 kept at constant amounts of 25 g/ L of citric acid solutions. The reaction was found to have low rates at neutral ranges of pH. While at lower cases it was found to increase at 2 to 3 pH. The photodegradation is maximum at 2-3 pH but at 4 pH the photodegradation is rapidly decrease and after increasing pH the photodegradtion slightly increase. This implies that acidic conditions are favourable towards the formation of the reactive intermediates that is hydroxyl radicals is significantly enhanced, which further help in enhancing the reaction rate. On the other hand in neutral medium conditions the formation of reactive intermediates is relatively less favourable and hence less spontaneous.

Table-12: Effect of pH on photodegradation of acids with temperature.

pH	Degradation % at 30 °C	Degradation % at 40 °C
2	46	54
3	38	42
4	24	34
5	30	35
7	23	28

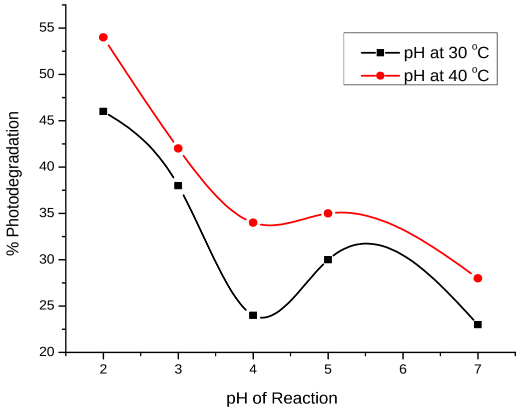

Fig.4. Showing the effect of pH on photodegradation at two defferent temperature

3.8. Effect of photocatalyst

It is clear from the results shown in table 3.2 - 3.23 and fig.3.4 - 3.5 that both TiO_2 and Cu/TiO_2 are proving as an effective photo-catalyst for the degradation of Acids. However Cu/TiO_2 seems to be more effective as photo-catalyst for the degradation of acids. The prominent degradation of acids was found in 3 hour study in the presence of Cu/TiO_2 in comparison to the prepaed TiO_2.

3.9. Effect of photocatalyst amount

It is clear from the results shown in table 3.2 that both TiO_2 and Cu/TiO2are proving as an effective photo-catalyst for the degradation of Acids. But when the amount of photocatalyst increases the photodegradation of acids also increase. It is observed that Cu-TiO_2 is the more effective photocatalyst than TiO_2

3.9. Kinetic study

The pseudo-first-order rate constant (*k*, min^{-1}) for the photodegradation reaction of Acids were determined through the following relation where, *k* can be calculated from the plot of ln(*Ct/Co*) against time (*t*), *C*0 and *C* denote the initial concentration and reaction concentration, respectively.

$$\ln C_o/C_t = k_1 t \text{ ……………………………………………………..…} (1)$$

In addition, the linear feature of plots of $\ln(C_o/C_t)$ versus time (Fig.3.7 and 3.8) indicates that this photocatalytic degradation reactions follow the pseudo-first-order rate law. The rate constant of the photocatalysis at 30 ^{o}Cis min^{-1}.

4. CONCLUSION AND DISSCUSION

Photocatalysis deals with reactions which are initiated by electronically excited molecules generated by absorption of suitable radiation in the visible or near ultraviolet region. Photocatalytic reactions are occurring in the presence of semiconductor and light. Researchers are using photocatalysts for oxidative degradation of various non-biodegradable wastes. In the present study, to prepare the nanocomposites of titania by solution impregnation method and photocatalytic degradation of some target materials such as acids in the presence of nanocomposites of titania which was prepared by the solution impregnation method, was done. The resulting powders were copper titanium dioxide. The alcohol route of synthesis, adopted here, yielded dark black homogeneous powder of copper titanium dioxide. The obtained yield of the product was more than 90% of the expected theoretical yield. In which the material has the nanodiamonsion.The prepared material was subjected to XRD analysis which gives the rutile and anatase both phases were present in the prepared sample. It is found that, in samples sintered at 400 ^{0}C both anatase and rutile phases were presented and rutile phase was more dominent, while in samples without sintered the exclusive formation of polycrystalline anatase and rutile phase separately was occurred.Applying the Scherrer's calculations through which particle size was found 16 and 72 nm in case of copper Titania and pure Titania respectively. The prepared sample of Titania and copper Titania were subjected to photocatalytic degradation of acids e.g. oxalic acid, tartaric acid, citric acid and acetic acid were done.The degradation of carboxylic acids such as acetic acid, oxalic acid, citric acid, and tartaric acid occur efficiently. The prominent degradation was found in case of oxalic acid in the presence of nanocomposites Cu/TiO_2.

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CHAPTER: 11

EFFECT OF PERIODONTITIS ON CARDIOVASCULAR DISEASES AND BLOODPRESSURE

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ABSTARCT

A country's health and socioeconomic condition are inextricably linked. A substantial beneficial influence on economic success is ensured by the general population's well health. Cardiovascular complexity is the single most serious health problem in India. Hypertension is a key risk factor for cardiovascular disease, and the present prevalence of hypertension among Indians is concerning. Periodontal health, which appears to be unrelated yet is highly essential, is connected to hypertension. Oral health, on the other hand, remains one of the most ignored health issues.There is practically no statistical data on oral health concerns in India at the moment, and as a result, periodontal disease has attained 'iceberg' status. A concerted national effort on periodontal status is critical in order to give better treatment in antihypertensive medication and other systemic illnesses related with periodontal disease. Political, social, organisational (both government and nonprofit), and professional commitment and support are urgently required to bring this country's oral health up to level with general health in order to achieve good overall health.

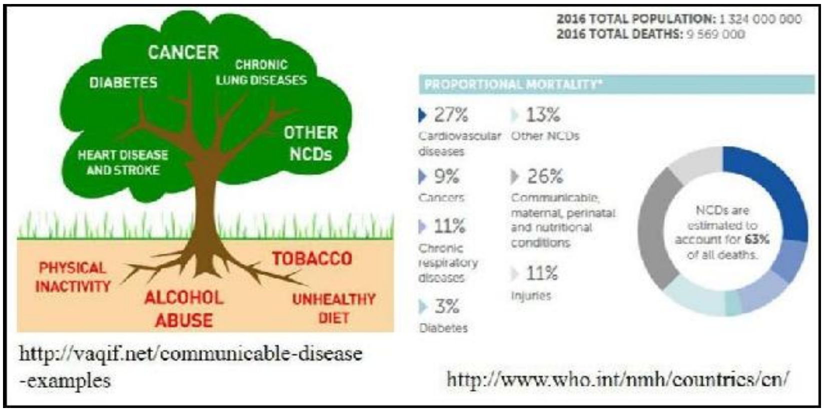
Keywords: cardiovascular, oral health, hypertension, blood pressure

Introduction

According to a recent survey report lead by world health organization (WHO) in 2018, non-communicable diseases (NDCs) pose a serious threat to the humanity in present time scenario and their prevalence is reaching almost epidemic portion indeveloped as well as developing country.[1] NDCs were the main responsible factor leading to 71% death (41 million out of 75 million) occurred globally in 2016. NDCs majorly manifest in the form of four diseases: Cardiovasculardisease, chronic respiratory disease, Cancers, and diabetes (written in descending order in terms of their effect on the global morbidity, **figure 1**). With the rapid increase of urbanization and changein lifestyle, NDCs are not only leading to cause of death but also undermining the work force productivity and thereby making a hard challenge to the economic prosperity. In almost every country, the poorestand the vulnerable populations are facing theworst situationof NDCsasthey have the least access to detect and treat the diseases. The most affective disease among NDCs is cardiovascular disease which has led to happen 27% death in India in 2016 (**Figure 1**). The major cardiovascular risk factoris high blood pressure which isoftentermedas hypertension. Hypertension is a chronic condition of concern to a population of a country like India which is under going through a socioeconomic evolution. There are several responsible factors which leadto hypertension. This report aims at spreading the awareness on periodontal health, a seemingly uncorrelated but extremely important factor, in controlling blood pressure and fetching betterefficacy during antihypertensive therapy based on a very recent medical survey report.[2] An overview of the cardiovascularsystem and blood pressure has been introduced first followed by a description of the risk factors of hypertension and its prevalence in India. Subsequent sections narrate what is periodontal disease all about and it’s correlation with the blood pressure followedbythenecessityoftheawareness.

Cardiovascular system and blood pressure

Cardiovascular system is the blood transport system of body.[3-6]there are three principle components of cardiovascular system: heart, blood and blood vessels. Blood vessels are categorized into three major parts:Arteries, veins and capillary. Arteries supply oxygen rich blood to the different organs of the body. In return body dumps carbon dioxide (CO_2) in veins whichdeliver the blood back to heart. Heart transfers the CO_2rich blood to lungs through pulmonaryartery and the purified oxygen rich blood comes back to heart through pulmonary vein. Thepurified blood again circulated to the body through arteries. Thus a cyclic process continues(**Figure 2**).

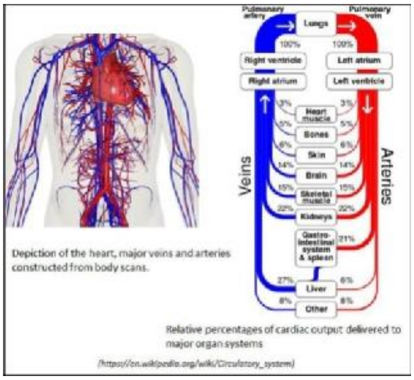


http://vaqif.net/communicable-disease-examples

http://www.who.int/nmh/countries/cn/

Figure1: Non-communicable disease**,** their root cause and their impactof morbidity in India.

Blood also transports nutrients (such as amino acids and electrolytes), oxygen, CO2, hormones, etc. to the cells and helps in fighting against diseases, stabilizing temperature and pH.Thus cardiovascular system plays crucial role in helping the body to survive. When blood passes through the blood vessels it produces apressure on the muscularwall of the vessels.This pressure is termed as blood pressure. Arteries receive the blood from heart. So blood pressure is more inarteries compare to veins. When the heart is full of blood, certain part of the heart contracts. Thisprocess is called systole. Immediately after the systole, pressure increases in arteries and thepressure is called systolic blood pressure, SBP (normally 120 mm of Hg). After systole, heart receives blood from the body and this time blood flows atnormal pressure.This is termedasdiastolic blood pressure (normally80mm ofHg). Blood pressure is generally categorized in threec lasses i) (120 &80) , ii)between (120&>80) and(140 &>90)and iii) (140&>90)orhigher.



Depiction of the heart, major veins and arteries constructed from body scans.

Relative percentages of cardiac output delivered to major organ systems

(https://en.wikipedia.org/wiki/Circulatory_system)

Figure2: Cardiovascularsystem

Hypertension

Hypertension is a medical condition wherein blood flows through the blood vessels at high pressure. Hyper tension is categorized in three classes viz.(i)above normal(>140/90mmofHg), (ii) moderately high (>160/100 mm of Hg) and (iii) very high (>180/110 mm of Hg). The primary riskfactors responsible for hypertension are: old age, obesity, high salt diet, stress, smoking and drinking and chronicin flammation. Prevalence of hypertension is one of the most killing factors intoday'sworld. It is the single bigge strisk factor forheart disease, stroke and other cardiovascular problems. If hypertension is not taken care at proper time, it could lead to heart attack, heart disease, congestive heart failure, atherosclerosis (fatty buildup in the arteries that causes them to harden), stroke, kidney damage,vision loss, erectile dysfunction, memory loss, fluid in the lungs, chest pain or discomfortand peripheralartery diseaseand many other life threatening complications.[7,8]

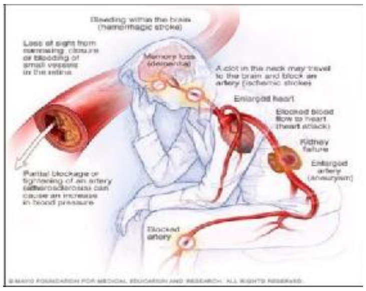
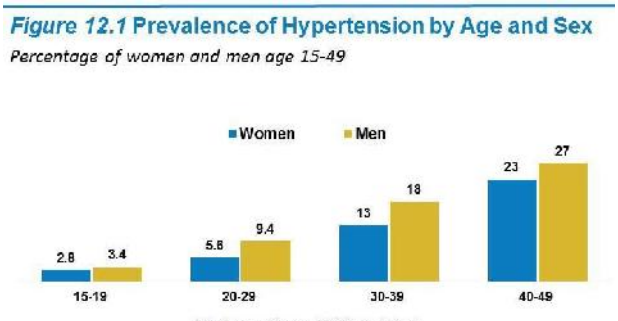


Figure 3: Complexities due to high blood pressure

Prevalence of hypertension in India

For the firs time during 2015-2016 the National Family Health Survey (NFHS), a large-scale and multi-round survey which is conducted in are presentative sample of households through out India,included the blood pressure measurement to accesses the existence of hypertensive patient among Indian population. Data were collected intwenty-ninestates and six unionterritories covering boththe rural and urban population. The survey revealed that 22.4% of total population suffers from hypertension.The study also represents that the hypertension increases sharply with increasing age for both the men and women.



http://www.rchiips.org/NFHS/about.shtml

Periodontal disease

Meaning of “Peri” is around and “odontal” relates to teeth. Periodontal diseases are infections ofthe structures around the teeth, which include the gums, periodontal ligament and alveolar bone.[9] After many years of research it has been identified that the bacteria in the dental plaque are the main villaincausing period ontal disease.There fore it is important to know what are dental plaques and how are they formed.Dental plaque (Figure5) is a structurally and functionally-organized soft sticky biofilm which builds up on our teeth [10-16]. Plaque is colorless but with passing time itbecomes yellowish. According to Dr. Susan Kinder Haake of UCLA's Periodontic InformationCenter, plaque can be classified in three ways: i) by its attachment to the gum line ii) by it sattachmentto the tooth surfaceiii) by association with its diseasestate.

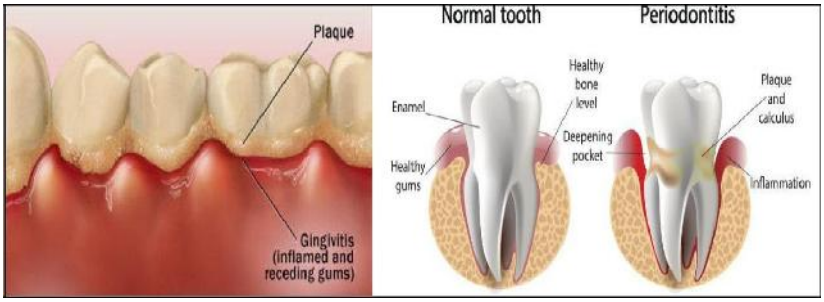


Figure5: Ignoranceondental plaque leadstogingivitis which end supcausing periodontitis.

More than700 different types of bacteria remain present in our mouth.[10]Dental plaque forms via an ordered sequence of events, resulting in a structurally- and functionally-organized community of such bacteria. Development of plaquegetsa boost when the food containing carbohydrates such as sugar, milk, soft drinks, cakes, raisins or candy are stuck to the surface of teeth.The oral bacteria grow vigorously on the surface of the sestuck foods.

The sebacteria metabolize dietary carbohydrates to acid. A low pH environment is generated which againac celebrate the competitive growth of the bacteria. The species responsible for healthy enamel are sensitive to the low pH environment. Absenceof suchs peciesasa consequence of externa lperturbation (sugar rich food) leads to formation of caries which paves the way of plaque mediated dental diseases. **Figure 6** shows aschematicre presentation about how diseasespreads in dental plaques.[17]

Soitis clear that removal of plaqueis extremely important.Plaquewhich are not removed by daily brushing lead to the formation tartar which are hardeninnature.Removal oftartaris more difficultas it accumulates at the gum line (Figure5). Overtime accumulation of plaque, bacteria, tartar increases on the gum leading to a reddish, swollen gum tissue and sometimes bleeding whilebrushing the teeth. This state is known as “gingivitis” (Figure 5) which is the early stage ofperiodontitis. In general, gingivitis is a mild form of the disorderedness of gum tissue. Natural health of gum tissue can be regained from gingivitis by regular brushing, flossing and scaling by a professional dentist.However if gingivitisisignoreditdirectsto“periodontitis”.Inperiodontitis,gums are pulled awayfrom theteethforming pockets(figure5). In this scenario,plaque continuesto increasing bellow the gum line. Body’s immune system tries to prevent the bacterial growth inthe plaque. The fight between immune system and bacterial toxin causes to break the teeth boneand destroys the holding tissue and eventually ends up in a situation where the teeth need to beremoved. Due to interaction between the immune system and bacterial toxin, periodontal disease is inflammatory in nature.This inflammatory nature has drawn the attention of scientists, researchers and medical practitioners to find the link between periodontal disease and its impacton blood pressure whose signature is closely associated with the cardio vascular disease, one oftheworst global burden on human health in this existingera

Present status of periodontal disease among Indians?

As per the report by National Oral Health Survey of India (2002-03) the % prevalence of periodontal disease was57.0,67.7,89.6and79.9intheagegroups12,15,35-44and65-74years, respectively.[18] After that there has not been any organized study regarding the status of theperiodontalhealth amongIndians up to now.

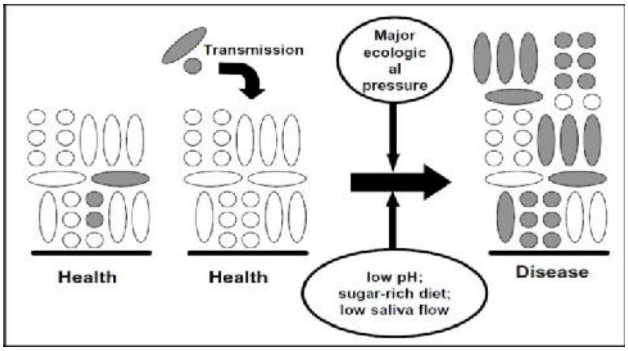


Figure 6: Potential pathogens (grey) may be present in low numbers in plaque, or transmitted in low numbers to plaque; both situations may be compatible with health.A major ecological pressure will be necessary for such pathogens to outcompete other members of the resident microflora (white) and achieve the levels (numerical dominance) needed for disease too ccur.

Howis periodontal disease connected with theCVD

Thepro-in flammatory cytokine shave been found to increase systemically with periodontal disease progression and diminish after therapy. The same cytokines rush was also observed in a theromatous lesions. Creatinine reponse protein (CRP), an inflammatory marker known to be associated with CVD is also found to consistently be elevated in people with periodontal disease. Several studies also found a direct association between the bacteria that cause periodontal disease and CVD. Pgingivalis, T. forsythia and A.actinomycetem comitans and Pr. Intermedia, the known period ontal pathogens have been found in atheromatous plaque. The Oral Infection and Vascular Disease Epidemiology Study (INVEST), a prospective cohort study data showed that there was a dose dependent relation between carotidplaquethickness and period on talbone loss.In summary,there are multiplestudies that strongly suggest a biologically plausible association between period on taldisease and CVD through various mechanisms.

How is periodontal disease connected with the blood pressure?

Periodontal disease is a chronic inflammatory disease. To understand the effect of periodontal disease on blood pressure it is necessary to understand the how inflammation arising due toimmune response leaves its impact on the blood pressure. Blood circulation throughout the entirebody happens through theblood vessels.Interior surface of the blood vessels is separated from the rest of the vessel wall by a surface,endothelium, which is constructed by a single layered cell called endothelial cells (Figure 7). During the pathogenesisofhy pretension it has been observed tha tseveral adhesive substances such as vascular cell adhesion molecule-1(VCAM-1) and intercellular adhesion molecule-1(ICAM-1)are expressed.[19]

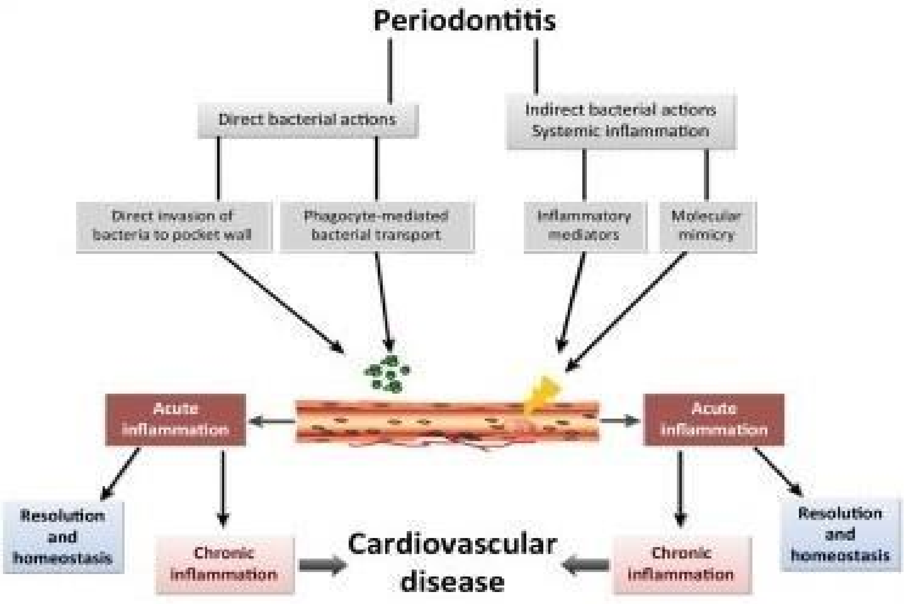


Figure7: Effectof periodontitis on CVD.

Any Inflammation in body increases the level of VCAM-1 and ICAM-1 which dictate leukocyte binding to the endothelial celllining.[20-24]Leukocyte binding increases over time and leads to functionalism balance of endothelial cells. Endothelial cells maintain the natural blood pressure profile by synthesizing vasodilators such as nitric oxide (NO), prostacyclin (PGI2) and endothelium derived hyperpolarising factor (EDHF) and vasoconstrictors such as endothelin-1, thromboxane(TXA2), and angiotensinII.[20] Vasodilation is a process when the blood vessels relax leading to low blood pressure whereas in vasoconstriction the blood vessels contracts leading tohigh blood pressure. A perfect balance between vasodilation and vasoconstriction is extremely important to maintain normal blood pressure. In case of hypertension a persisting imbalance has been seen between PGI 2and TXA2.[24] There fore it is obvioust hat the inflammation has significant role in the regulation of blood pressure.InFigure8,it is depicted how in flammationregulatesthe blood pressure.[20]

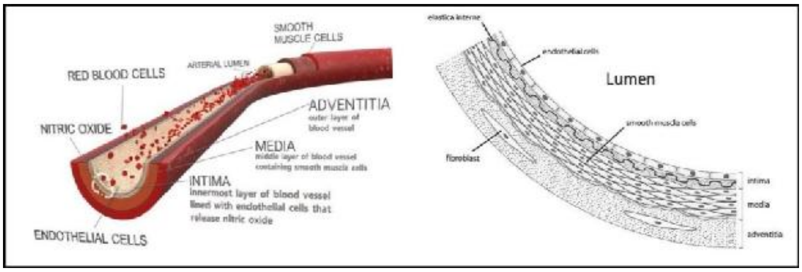


Figure 8: Endothelium and endothelial cells.

In periodontal patient, cerum high sensitivity CRP (hs-CRP), a cardio vascular risk factor, has been found at higher level and thehs-CRPlevel decreased significantly after period ontal treatment.[22,23] The hs-CRP has been assumed to be a sensitive indicator which link schronic inflammation and periodontal.Hs-CRP might be responsible factor causin gendothelialmal function.[24,25] In experimental rats it has been noticed that due to the period on taldiseasethe level of CRP inflammatory biomarkers increases.[24] Also, it has been illustrated in earlier reports that the total surface area of inflammation inpresence of period ontitisis similar to the size of a palm. All theseevidences strongly suggest that periodontal disease is intimatelyrelated to the blood pressure regulatory system. Howe vera dedicated study is necessary to find out the relation between periodontal health and the blood pressure profile of individuals.

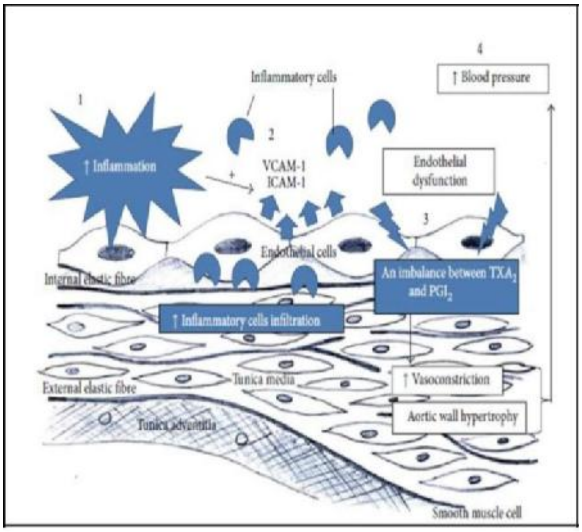


Figure 9: (1) Inflammatory stimuli induce the expression of cellular adhesion molecules such as vascularcelladhesion molecule-1(VCAM-1) and intracellularadhesion molecule-1(ICAM-1) on endothelial cells. (2) Increased VCAM-1 and ICAM-1 expressions recruit more leukocytes to thesite of inflammation. (3) Leukocytes infiltration and production of cytokines lead to oxidativestress and inflammation, which result inendothelial dys function, affecting the balance of synthesis between vasodilators and vasoconstrictors. The imbalance favors vasoconstriction and adverse vascularre modeling, (4) consequently leading to elevation ofblood pressure.

Significance of the awareness

Very recently Dr. Pietropaoli and histeam have published are trospective study inareputedpeer-reviewed journal, “Hypertension”, about the impact of periodontal disease on the blood pressure profile of hypertensive adults aged years with and without periodontal disorder. [2] They examined and statistically analyzed the data obtained by the National Health and Neutrition Examination Survey (NHANES) of United States of America (USA) in between 2009 and 2014on4095period ontalpatients out of which 3626 were under the treatment of hypertension and406were not. Based on dental examination 52 % of the hypertensive patients had periodontal disease with 37.8% moderate, 11.5% severe and 2.9 % mild disease severity. Among 460 untreated hypertensive patients, the mean systolic blood pressure (MSBP) was 2.8 to 7.6 mm Hg higher inpresence of periodontal disease as compare to the patients where periodontal disease was absent. On the other hand, the MSBP was 2.3 to 3 mm of Hg higher in treated hypertensive patients with period ontitisthan those without period ontitisir respective of sexandracial/ethnicsubgroups.This seemingly small bloodpressure changeis very similar to the lowering of blood pressure which canbe achieved by reducing daily salt intake by six grams, a tea spoon full of salt. Their studies also revealed that the hypertensive patients often need more than one drug to achieve adequate bloodpressure profile and it leads to several side effects of the medications along with the burden ofcosts. The presence of periodontal disease stimulates these side effects and people with gum disease were20percentless likelytoreach healthy blood pressure ranges, compared with patients in good periodontal health.

All their observations suggest that the presence of periodontal disease which is inflammatory innature can have detrimental effects on the efficacy of antihypertensive treatment and there by leading to a state of elevated cardiovascular complexities. In a recent interview Dr.Pietropaoli said "Physicians should pay close attention to patients' oral health, particularly those receiving treatment for hypertension, and urge those with signs of periodontal disease to seek dental care"and "Likewise, dental health professionals should be aware that oral health is indispensable to overall physiological health, including cardiovascular status"(22).From the health studies performed in India, it has been seen that hypertension is increasing at an alarming rate and the percentage prevalence of period ontaldisease is also very high asperthe oral health survey of India(2002-2003). So the awareness on periodontal disease and its impact on blood pressure among physicians, dentists and common people is one of the most needed health issuesof India at present time.Health and socioeconomic status of a country are closely associated with each other. A soundhealth of the overall population ensures a strong positive impact on the economic prosperity. InIndia, the single largest challenge to the health is cardiovascular complexity. Hypertension is oneof the major risk factors of the cardiovascular disease and the current prevalence of hypertensionamong the Indian population is alarming. Hypertension is interlinked with periodontal health, aseemingly irrelevant but extremely important factor. However, oral health is still one of the mostneglected health topics. There is even no statistical data on oral health issues at present times inIndia and because of this periodontal disease has achieved its ‘iceberg’ status. A dedicated effortat the national level is extremely important on periodontal status to provide better treatment in antihypertensive therapy and other systemic diseases associated withperiodontal disease.Political, social, organizational (both government and non governmental) and professional dedication and support are urgently needed to make oral health of this countrycomparable withgeneral healthforachieving good over all health.

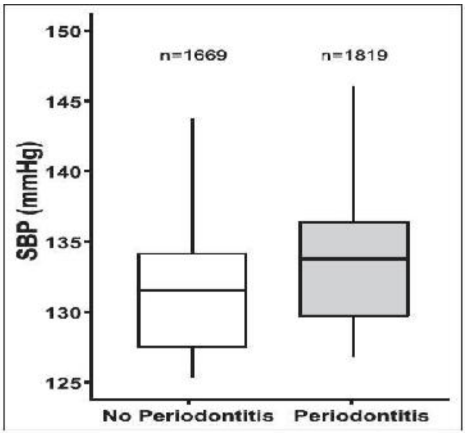


Figure 10: Box plots of systolic blood pressure (SBP) in treated hypertensive US adults aged ≥30year with and without periodontitis: National Health and Nutrition Examination Survey 2009 to2014.

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CHAPTER: 12

A REVIEW ON SOLID WASTE MANAGEMENT

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ABSTRACT

Pollution is increasing and most of our cities are becoming unhealthy, except some who are more efficient in managing waste. The highest amount of world's waste is generated in India as per the World Bank data. The municipal waste generated every year is around 2.01 billion tons, which is predicted to rise to 3.4 billion tons by 2050 due to rapid urbanization, population growth and economic development. The metro cities of India like Mumbai and Delhi are resting on the mounds of wastes, the condition of the civic bodies also gets reflected in the fact that the height of Ghazipur landfill site has reached 65m which is just 08m less than the height of Qutub Minar. Only about 75-80% of the municipal waste gets collected in India and in it merely 22-28% is processed and treated, while the rest is transported to the suburbs and disposed of randomly which causes imbalance in the ecosystem and causes health issues in the public. Therefore there is need for framing policies for effective management of waste and above all implementation of them by the authority and adherence to them by the general public. If this is not done properly, it will lead to nuisance to the general public as well as the sustainability of the ecosystem will be at risk.

Keywords: Waste Management,Municipal Solid Waste, Integrated Solid Waste Management, Composting

1.0INTRODUCTION

Heaps of garbage is a common sight everywhere today. The only omnipresent thing is waste in the form of rotting piles that speck our landscape, pollute our rivers, wells and lakes. Even the idea of a clean village is no longer true because waste has overcome the rural-urban divide very successfully.

The materials which are unwanted and disposed of by man are termed to be waste materials. Man has always created or generated waste materials which are either by-product of his activities, for which he could not find any further use, or products which have reached the end of useful life and cannot be used furthermore. In recent times waste has become a significant global issue with increasing volumes of waste being generated due to increase in the global population, rise in the living standards and poor management of waste.

Although the generation of waste is as old as human being is, its management was not a challenge because Mother Nature's waste management plans were sustainable and because of small population, vast area of land was available for disposal. Rapid urbanization and industrial diversification has led to migration of people from villages to cities which have resulted in the surge of population and generation of enormous quantities of municipal, plastic, hazardous and biomedical waste. The nature has been overburdened, the natural processes of treatment and disposal are not sufficient enough in the present time to solve the problem; hence there is need for framing policies for effective management of waste and above all implementation of them by the authority and adherence to them by the general public. If this is not done properly, it will lead to nuisance to the general public as well as the sustainability of the ecosystem will be at risk.

As there are challenges in the disposal of waste, its impacts on the environment and the general public are very high causing serious health issues. Improper disposal of waste has led to the formation of dumping yards which often results in spread of diseases and contamination of water bodies and soils. The impacts of this on the economy cannot be ignored and managing them poses a major problem. Small competitive and labour intensive industries which are not effectively regulated by administration are the source of hazardous solid waste which is recognized as major problem in developing countries. India produces 277.1 million tons of solid waste every year according to World Bank report of 2018 which is assumed to touch 387.8 million tons by 2030 and 543.3 million tons by 2050. As per the India Today Report of 2019, 1.5 lakh metric tons (MT) of solid waste is generated in India every day. Almost 15000 MT of garbage remains exposed in the environment, increasing the pollution levels. Out of all the total waste collected, only 20% waste is processed, while the remaining 80% is dumped in landfill sites. The major source of solid wastes in our country is industrial activities, agriculture and agro-industries, medical facilities, commercial centers and household sectors.

2.0 Solid Waste

The issue of dealing with the solid waste is one of the biggest challenges to the authorities of both small and large cities in developing countries. In India it is a different scenario, along with producing a lot of solid wastes in the country, we also import it from outside, for example Electronic gadgets i.e., mobiles and its accessories.

Classification of Solid Waste

Solid waste can be broadly classified as follows

1. Depending on the origin: Domestic, industrial, commercial, construction or institutional
2. Depending on the contents: organic material, glass, metal, plastic paper etc.,
3. Depending on the hazardous nature: toxic, non-toxin, flammable, radioactive, infectious etc.,

Based on the Source of Generation, it can be further classified as

a. Municipal Solid Waste (MSW)

It consists of household waste, construction and demolition debris, sanitation residue and waste from streets generated mainly from residential and commercial complexes. As per the Ministry of Environment, Forest and Climate Change; it includes commercial and residential waste generated in municipal or notified areas in either solid or semi-solid form excluding industrial hazardous wastes but including treated bio-medical wastes.

Municipal Solid Waste (MSW) normally includes 51% organic waste, 17% recyclables, 11% hazardous and 21% inert waste. However, about 40% of it is not collected at all and hence lies littered everywhere, ultimately finding its way to the nearby drains and water bodies, resulting in clogging as well as pollution of surface water. The unsystematic collection of waste and its transportation leads to the creation of dumping place in the open. This leads to generation of leachate which contaminates ground and surface water in the surroundings. The gaseous emissions from them also contribute to global warming.

b. Industrial Solid Waste (ISW)

In a majority of cases it is termed as hazardous waste as they may contain toxic substances are corrosive, highly inflammable, or react when exposed to certain things e.g. gases.

c. Biomedical waste or hospital waste

It is usually infectious waste that may include waste like sharps, soiled waste, disposables, anatomical waste, cultures, discarded medicines, chemical wastes, etc., usually in the form of disposable syringes, swabs, bandages, body fluids, human excreta etc. These can be a serious threat to human health if not managed in a scientific and discriminate manner.

3.0 Waste Management System in India

India faces a great waste management challenge. India generates 62 million tons of waste each year. About 43 million tons (70%) are collected of which about 12 million tons are treated and 31 million tons are dumped in landfill sites. Increase in the waste generation is the result of economic development, urbanization and industrialization. This increase has led to the formation of many legislations and regulations for treatment and disposal of waste. All these regulations come under the umbrella of Environment Protection Act, 1986. There are separate laws for each class of waste. In 2016, the ministry revised the Solid Wastage Management (SWM) Rules which had been in place for 16 years, This policy is important as it includes for the first time the informal sector i.e., the rag pickers in the waste management process Despite of all this, experts still believe that India’s waste management system is not flawless.

4.0 Need for Waste Management

Disposing of waste has huge environmental impacts and can cause problems. The majority of collected waste is usually buried in landfill sites, most of the times it is thrown away unsystematically. It may rot with bad odor, in the process methane gas is generated which contributes to the greenhouse effect and is also an explosive. Solid Waste Management reduces or eliminates the adverse impact on the environment & human health. The main aim of waste management is to lower the impact of environmental pollution and health issues on the general public**.** It is associated with the process of generation, storage, collection, transport or transfer, processing and disposal of solid waste materials in a way that best addresses the societal issues.

Mainly two types of waste management methods are in practice

a. Centralized method: It involves the collection of municipal waste from all over the local area and is dumped outside the city/nagar panchayat limits. The process involves door-to-door collection of solid waste by rag pickers, taken over by the collection team who later discard it in the landfill.

b. De-centralized method: This model is seen in a very few places like Suryapet in Andhra Pradesh and Bangalore in Karnataka. Here in the waste is collected ward-wise and segregated into bio-degradable and non-biodegradable. The biodegradable waste is whereas the non-biodegradable waste is categorized into paper, plastic, metal and other waste which can be recycled. This is passed on to the recyclers for upcycling or downcycling by the recyclers or treated using various methods.

5.0 Treatment methods for solid waste

a. Thermal treatment: This method also known as “incineration” is the combustion of waste in the presence of oxygen, converting the waste into carbon dioxide, water vapour and ash. This is termed as “Waste to Energy method”. The main advantage of this method includes waste volume reduction, curtailing the transportation costs and decreasing greenhouse gas emissions. On the other hand, pollutants of burning may be released into the atmosphere, and cause health issues.

b. Pyrolysis and gasification: This method involves thermal processing in the absence of oxygen or with less amount of air.

c. Biological treatment methods: The decomposition of biodegradable components of waste using micro-organisms generating organic compost used as healthy fertilizer.

d. Landfills and open dumping:

Sanitary landfills include the controlled disposal of waste in a well defined area with a minimal contact between waste and the environment. Dumps are the open areas where waste is throwed away allowing it to expose to natural elements, stray animals and birds. There is absence of monitoring and no leachate collection system, which leads to the pollution of both land and water resources.

6.0 Integrated Solid Waste Management (ISWM):

This method includes recycling of the waste collected before disposal into something useful. This reduces the amount of waste needing treatment, cost of its handling and disposal to landfills. Recycling also reduces the quantity of energy necessary to make new products, thus helping to conserve the natural resources.

“Kabadiwalahs”, local waste dealers are informal waste collectors in India who collect waste from the ragpickers or sometimes from the apartments and other households. They collect and sort out the dry waste into aluminium, plastic, paper, glass, etc., and handover to the recyclers.This large network of informal sector aids in effective management of waste at local levels. After the segregation of waste, the second step involves converting the biodegradable waste into compost and non biodegradable one is treated before the final disposal.This method is an efficient one in management of waste and needs to be practiced to overcome the issues of waste.

7.0 Municipal Solid Waste Management-Karnataka

In Karnataka, the largest amount generated is municipal solid waste (21,43,280 metric tons), followed by hazardous waste (86,137 metric tons) and biomedical waste (27,095 metric tons). The major cities like Bangalore, Belgaum, Gulbarga, Hubli-Dharwad, Mangalore, Mysore and other taluka places in the state, mostly dumped the solid waste in open sites outside the municipal limits. Ever since the implementation of MSW Rules, 2000, few of the Municipal Corporations and Urban Local Bodies (ULBs) are in the process of identifying landfill sites and also focusing on waste recycling system to dispose the non-recyclable wastes. Scientific waste disposal is a community activity, as the community is accountable for production of waste, the management of waste disposal should also start at the source itself i.e., by the citizens. In Karnataka, some of the ULBs have attempted in creating awareness among the general public to segregate waste before handing over to the collector. There are various residential welfare associations who are involved in the door to door collection of household waste. In the city municipal areas (i.e., ULBs), door-to-door waste collection is done by civic authorities successfully. Apart from these, the other stakeholders who have a crucial role in MSW management are rag pickers, NGOs and self-help groups who help in reusing or recycling the waste.

8.0 Rules and regulations associated with SWM

Under the 74th Constitutional Amendment, Disposal and management of Municipal Solid Waste is one of the 18 functional domains of the Municipal Corporations and Nagar Panchayats. The various rules and regulations for solid waste management are:

1. The Bio-Medical Waste (Management And Handling) Rules, 1998
2. Municipal Solid Waste (Management And Handling) Rules 2000
3. The Plastic Waste (Management And Handling) Rules, 2011
4. E-Waste (Management And Handling) Rules, 2011

There are other court cases that find their importance in terms of Solid Waste Management in India:

1. Almitra Patel vs. Union of India
2. B. L Wadhera vs. Union of India.
3. Judgement of Karnataka High Court towards Mandatory Segregation at Source

9.0 Responsibility of Individuals

Waste is the responsibility of every individual. Making use of a efficient waste reduction strategy either at home or at work by following the simple **4 R’s** principle will aid in effective waste management. This will not only reduce the quantity of solid waste been thrown into the landfills, but can turn the waste into a resource, thus saving our fast depleting natural resources.

The **4 R’s** are

Reduce:

1. Purchasing items by lesser packaging, refillable items and more durability.
2. Carrying personal cloth bags
3. Avoiding use of disposable items plastics.
4. Curtailing on the excessive use of paperwork

Reuse:

1. Donating old clothes, books, phones and lots more to the ones in need rather than disposing it.
2. Reusing of old bottles, jars as storage bins
3. Purchasing of rechargeable items rather than disposable ones.

Recycle:

1. Segregation of waste for better disposal
2. Purchasing of recycled/green products.
3. Composting organic waste directly at the source itself so that minimum amount reaches the landfill.

As per the report from IIT Kanpur there is potential of recovering at least 15 per cent or 15,000 MT of waste generated every day in the country. This can also provide employment opportunities to about 500,000 rag-pickers.

Recovery or reclaim - Waste to Energy

This process deals with turning waste into fuel for manufacturing processes or equipment designed to produce energy. In the conversion ofwaste to energy, the major hurdle is that almost 50% of treatment plants are non-functional because most of the wastes received by the treatment facilities are mixed wastes, which require additional manpower for segregation.

Recent researchers have given the idea of conversion of organic wastes into fuel pellets, which can be used as a substitute for coal as well as activated carbon Also, once the water is extracted from the food waste while its treatment it can be passed on to an anaerobic digester. The gas produced therein can also act as a fuel source.

10.0 Waste Management Initiatives in India

The government has advised all the stakeholders to stick on to the "golden rule" of the 4R's-Reduction, Reuse, Recycling and Reclaiming which will contribute significantly to effective waste management and sustainable development. Some of the major initiatives taken by the central government are as follows

Swachh Bharat Abhiyan (SBA) or Swachh Bharat Mission (SBM)

This mission was initiated on 2 October 2014 with the aim of making the country clean and free from defecation on 150th birth anniversary of Mahatma Gandhi. This mission also aims in promoting the maintenance of clean surroundings in the domestic as well as commercial places. Awareness programs on reducing waste and waste management are organized under this scheme by various stake holders in the country.

Swachh Survekshan

Ministry of Housing and Urban Affairs has introduced this scheme in 2016 to encourage large-scale citizen participation, in creating awareness among all segments of society, to work together to make their cities and towns a better place to live.

11.0 The way forward

Rules of waste management in India are based on the principles of "sustainable development", "precaution" and "polluter pays". The increase in waste generation as a consequence of economic development has resulted in the framing of subordinate legislations under the umbrella law of Environment Protection Act, 1986 (EPA for regulating the mode of disposal and treatment of generated waste. Solid Waste Management (SWM) is one among the fundamental services provided by municipal authorities to strive for the cleanliness of the cities. Conversely, almost all the municipal authorities dump their solid waste at a dump yard within or outside the city arbitrarily. There is need for changing the thinking of individuals as well as the stake holders and reinvent new methods for treating the waste.

Most of the cities are set to be developed as smart cities. This is an opportunity for the Civic bodies have to redraw long term vision in solid waste management and rework their strategies as per the changing lifestyles. The civic bodies should reinvent the garbage management in cities so that it can be processed and not land filled. To follow this, households and institutions must segregate their waste at source itself so that its management as a resource can be effective. The Centre is aiming to do away with landfill sites in 20 major cities. If this happens, there will be no spare land for dumping garbage; the ones which already exist are in a critical state. The authorities should think on the construction of Compost pits in every locality for the processing of organic waste. Community participation has a direct role on efficient waste management, hence more of awareness programs have to be organized and importance of solid waste management explained. These are some of things which need attention from the government which will help to aid in the existing problem of waste management.

Conclusion

The key to efficient waste management is to ensure proper segregation of waste at source and to ensure that the waste goes through different streams of recycling and resource recovery. The civic bodies allot more than three-fourth of solid waste management budget for collection and transport, very less remains for its processing. It should be strived to allocate more of the budget for the processing and treatment of the waste so that the burden of dealing with it is reduced. There is need for a comprehensive and sustainable waste reduction and recycling program as well as proper means of ensuring enforcement of the regulations waste management to bring about a positive change.

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CHAPTER:13

HIERARCHICAL NANOSTRUCT RED 3D FLOWERLIKE BiOX (X=Cl, Br, I) MICROSPHERE: A STATE OF ART TECHNOLOGY TOWARDS ENVIRONMENTAL APPLICATIONS

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Abstract: The present book chapter highlights the potential of Hierarchical Nanostructured 3D Flowerlike BiOX (X=Cl, Br, I) microsphere as a remarkable technology towards the environmental remediation processes of various hazardous and persistent environmental pollutants. The work has emphasized the selected case studies on three dimensional flowers like structures of Bismuth oxyhalides exclusively. The chapter also summarizes the selective synthesis and characterization domains of bismuth oxyhalides nanomaterials to better understand their assemblies and structures along with specific applications. A significant inside in the key challenges and future prospects associated with this technology has been also included with this chapter.

Key Words: Nanotechnology, Bismuth Oxyhalide, 3D- hierarchical structure, applications.

Introduction:

Nanoscience covers the study of nanoscale materials on the basis of various properties such as size, morphology and composition. Nanotechnology has captured exceptional diligence during last two decades, since 1991 with carbon nanotube discovery [1]. Since nanomaterials offer their imminence in resourcefully eradicating environmental contaminants present in various forms, they have a wide range of application in environment remediation and are being studied extensively [2,3]. Due to its large surface area, nanomaterials are good adsorbents as well and are used widely as photocatalysts for purification [4,5].

Initially nanomaterial size was taken into consideration due to their extraordinary properties as compared to their bulk counterparts, for an instance band gap of quantum dots can be tuned by simply size variation [6]. Offlet research communities are focused on varying composition and, morphologies of nanoparticles, there are many morphological structures of nanoparticles have been prepared so far, like rod shaped, plate shaped, needle shaped, flower shaped etc. [7]. At the beginning TiO_2 was studied exhaustively because of its excellent photocatalytic activity, but the major drawback associated with TiO_2 is it is incompetent in visible and solar light. As time goes by many more semiconductor photocatalysts have been synthesized among which, Bismuth Oxyhalides (BiOX) have gained phenomenal interest of scientists [8,9]. In past decade scientific studies have been devoted to hierarchical structures and synthesis of hierarchical bismuth compounds specially oxyhalides [10]. The hierarchical structures contribute to their outstanding ability to reflect light and utilize its maximum surface area, thus it is more active than bulk as well as conventional nanoparticles for environmental remediation [11,12].

Due to their substantive utility, synthesis of nanoparticles is of paramount interest and various methods of synthesis have been developed. Moreover, owing to their handiness and ease, solvothermal and hydrothermal methods of synthesis are most widely used for bismuth oxyhalides [8,9]. Apart from environmental remediation, like air and water treatment, hierarchical BiOX nanoparticles have extra ordinary applications in the fields like medicinal, cosmetics, energy and environment etc. [8-12]. This chapter is dedicated to the study of different methods of synthesis, characterization and environmental applications of BiOX nanoparticles.

Synthesis, characterization and environmental applications of hierarchical BiOX (X=Cl, Br,I):

Song et al. (2010) synthesized Hierarchical structured bismuth oxychlorides using solvothermal method. XRD, FE-SEM, TEM, HRTEM, FTIR, SAED, XPS, BET surface area and PL were the main characterization techniques used in present study. MO and simulated sunlight system was used for photocatalytic evaluation. BiOCl nanoflower could degrade 100% of MO in 8 min. under experimental conditions. BiOCl nanoflower exhibit higher photocatalytic activity than P25 [13].

Ren et al. (2012) synthesized hollow/flower-like BiOI microspheres using precipitation method. XRD, FESEM, BET surface area, UV-Vis-DRS and PL were the main characterization techniques used in present study. RhB and visible light system was used for photocatalytic evaluation. Results indicated that microsphere having 500-800 nm in size. Photocatalytic experiments results represented that BiOI completely degraded RhB in 180 min. under experimental conditions. They reported that BiOCl nanoflower exhibit higher photocatalytic activity than P25 [14].

Wei et al. (2013) synthesized Mn-doped BiOBr microspheres using hydrothermal method. XRD, FESEM, TEM and SAED were the main characterization techniques used in present study. RhB and simulated sunlight system was used for photocatalytic evaluation. Total 5 samples undoped BiOBr, 0.5% Mn doped BiOBr, 1% Mn doped BiOBr, 5% Mn doped BiOBr and 10% Mn doped BiOBr were synthesized in present study. Results indicated that microsphere having 2 µm in size. They reported that 1% Mn doped BiOBr exhibit higher photocatalytic activity. It degraded 1lmost 100% of RhB in 140 min. under experimental conditions [15].

Ye et al. (2013) synthesized flowerlike BiOCl using hydrolytic synthesis. XRD, FESEM and UV-Vis-DRS were the main characterization techniques used in present study. RhB and visible light system was used for photocatalytic evaluation. As prepared BiOCl having 4-5 µm in size. Flower-like BiOCl completely degraded RhB in 20 min under experimental conditions. They reported BiOCl nanoflower exhibit higher photocatalytic activity than P25 [16].

He et al. (2013) synthesized flower-like bismuth oxybromide microspheres using solvothermal synthesis. They used $Bi(NO_3)_3 \cdot 5H_2O$, polyethylene glycol 600 and IL [C16mim]Br as precursor in the synthesis process. (XRD, FESEM, ESD and UV-Vis-DRS were used for characterization. RhB using visible-light system was used for photocatalytic evaluation. They reported that BiOBr were having 1-2 µm in size and spherical in shape. In this study total 4 types of photocatalyst were used for comparative photocatalytic evaluation. They reported that flower-like BiOBr exhibit higher photocatalytic activity than other photocatalyst under investigation. In 60 min. BiOBr flower-like microspheres, BiOBr hollow microspheres, BiOBr nanoplates and P25 exhibit 99, 79, 32 and 7% efficiency, respectively [17].

Yu et al. (2013) synthesized Flowerlike C-doped BiOCl nanostructures using wet-chemical method. They used $Bi(NO_3)_3 \cdot 5H_2O$, polyacrylamide (PAM), KCl in the synthesis method. In this method polyacrylamide (PAM) was used as both chelating and doping agents. Total 5 samples undoped and C-doped with 0.2, 0.3, 0.4 and 0.5 g of PAM were synthesized in the present investigation. XRD, SEM, XPS and raman spectroscopy were the characterization methods used in present investigation. They used MO or phenol and UV light system for catalytic evaluation. They reported 46% and 98 % efficiency for undoped and C-doped with 0.4g PAM BiOCl, respectively for MO and UV system in 40 min. They also reported 25% and 65% efficiency for undoped and C-doped with 0.4g PAM BiOCl, respectively for phenol and UV system in 180 min. [18].

Zhang et al. (2013) synthesized 3D flower-like BiOClBr using solvothermal method. They used $Bi(NO_3)_3 \cdot 5H_2O$ and ethylene glycol as precursor in the synthesis method. XRD, FE-SEM, XPS, FT-IR, BET surface area, UV-Vis-DRS and XRF were the main characterization methods used in present investigation. RhB and visible light system were used for photocatalytic evaluation. They reported that undoped BiOClBr and I-doped BiOClBr having 2-3 and 1 µm respectively in size. Total 5 samples BiOCl, BiOClBr, BiOBr, I-doped BiOClBr and BiOI with wide range of band gap from 1.71 to 3.1 eV were used for phtocatlytic evaluation in present study. They reported that I-doped BiOClBr exhibit higher photoctalytic than other. It represented 100% efficiency for RhB in 60 min. [19].

Chen et al. (2013) synthesized Flower-Like BiOX (X=Cl, Br, I) using template method. XRD, FESEM, TEM, HRTEM, SAED, UV−vis DRS, and N_2 adsorption−desorption techniques were used for characterization purpose. . RhB and visible light system was used for photocatalytic evaluation. They reported that BiOBr exhibit higher photocatalytic activity among BiOX. BiOBr degraded 100% of RhB in 40 min under experimental conditions [20].

Gneyam et al. (2013) synthesized Hierarchical Nanostructured 3D Flowerlike BiOClxBr1−x using hydrolysis method. XRD, FE-SEM, particle size, zeta potential and BET surface area were the main characterization techniques used in present study. RhB and visible light system was used for photocatalytic evaluation. Total 6 types of samples with different molar ration of Cl &Br, BiOCl and BiOBr have been synthesized in the present study. They reported that $BiOCl_{0.875}Br_{0.125}$ exhibit 100% efficiency to degrade RhB in 120 sec. under experimental conditions. To know the versatility of as prepared photocatalyst Acetophenon (AP) and visible light system also used photocatalytic evaluation. $BiOCl_{0.875}Br_{0.125}$ also degraded 90% of AP in 180 min. [21].

Sun et al. (2014) synthesized 3D flowerlike BiOCl using solvothermal method. They used XRD, SEM, TEM, HRTEM and SAED analysis for characterization purpose. MO and UV light system was used for photocatalytic evaluation. BiOCl microflower having 1-2 µm in size. They reported that as prepared 3D flowerlike BiOCl easily degraded 100% of MO dye with few minutes [22].

Zhang et al. (2015) synthesized Flower-like $BiOCl_xI_y$ using solvothermal method. XRD, SEM, TEM, EDX and BET surface area were the main characterization techniques used in present study. Adsorption of MO dye was used for catalytic evaluation. Flower-like $BiOCl_xI_y$ having 1 µm in size. Flower-like $BiOCl_xI_y$ synthesized using 2:1 molar ration of Cl and I was exhibit highest photocatalytic activity. It adsorped 100% of MO dye in 10 min. under experimental conditions [23].

Gnayem et al. (2015) synthesized 3D Sunflower-Like Bismuth Doped $BiOCl_xBr_{1-x}$ nanomaterial using reduction method. XRD, HR-SEM, XPS, UV-Vis-DRS and BET surface area were the main characterization techniques used in present study. Chlorobenzene, Benzene, Toluene, Xylene and visible light system were for photocatalytic evaluation. Total 11 samples with different molar ratio have been synthesized in the present study. They reported that 3%Bi-doped $BiOCl_{0.80}Br_{0.20}$ and 2% Bi-doped $BiOCl_{0.125}Br_{0.875}$ catalyst were exhibit higher photocatalytic activity [24].

Wu et al. (2016) synthesized 3D flower-like $BiOCl_xBr_{1-x}$ using hyderothermal synthesis. XRD, FE-SEM, TEM, UV-Vis-DRS, XPS, raman spectra and PL were the main characterization techniques used in present study. Total 7 types of samples with different molar ration of Cl &Br, BiOCl and BiOBr have been synthesized in the present study. Photocatalytic air purification method has been used for the evaluation of activity. They reported that $BiOCl_{0.5}Br_{0.5}$ exhibit higher photocatalytic activity among all photocatalyst under investigation. This catalyst was represented 57.3 % efficiency for NO removal under experimental conditions. $BiOCl_{0.5}Br_{0.5}$ exhibit 3 and 19 times more photocatalytic activity than BiOBr and BiOCl [25].

Song et al. (2016) synthesized 3D flowerlike BiOX using solvothermal method. XRD, FESEM, BET, XPS, PL and UV-Vis-DRS were the main characterization techniques used in present study. RhB and visible light system was used for photocatalytic evaluation. As prepared BiOX having 2 µm in size. Among all three types of BiOX, BiOCl exhibit higher photocatalytic activity [26].

Gu et al. (2017) synthesized hierarchical BiOX (X=Cl, Br, I) microflowers using precipitation method. XRD, FESEM, TEM, HRTEM, UV-Vis DRS and N_2 adsorption-desorption techniques were used for characterization purpose. RhB and UV-Visible light system was used for photocatalytic evaluation. All BiOX microflowers having 1 µm in size. BiOCl microflower exhibit highger photocatalytic activity than BiOBr and BiOI. BiOCl degraded 99.4 % of RhB in 6 min. under experimental conditions [27].

Qi et al. (2018) synthesized Hierarchical flower-like BiOIxBr(1-x) nanomaterial using solvothermal synthesis. XRD, FE-SEM, XPS, PL and BET surface area were the main characterization techniques used in present study. They used MO or Bisphenol A (BA) and visible light system for photocatalytic evaluation. Total 5 types of samples have been synthesized using molar% of KI in the synthesized material. These samples were denoted as R0, R25, R50, R75, and R100 and represented the molar % of Iodide 0, 25, 50, 75 and 100 respectively. They reported that R75 ($BiOI_{75}Br_{25}$) exhibit higher photocatalytic activity among them for both MO and BA samples [28].

Key challenges and future prospects:

The important key challenges associated with BiOX technology have always been conjugated with the better synthesis methods and characterization techniques. As the various meso- micro structures of BiOX are having varied dynamic stabilities and fluctuations in their shape-sizes in the synthesis medium thus better stabilization agents are also a need of the hour to make this technology more sharp. Some of the safety issues have also been associated with their nanostructures thus better green technological domains or use of herbal mediums can give a significant gain in the future prospect sense.

Conclusion:

An inclusive outline of the expansion of nanotechnology has been discussed in the light of bismuth oxyhalide nanomaterilas for environmental remediation. In this chapter various properties such as size, shape, morphology and composition have been discussed, with a special focus on morphological development of nanomaterials and synthesis of hierarchical structures and their use in environmental remediation, Because of their worthwhile quality the hierarchical BiOX have extensive application range and are most widely studied semiconductor nanoparticles now a days. More significant studies related to the green technological domains are needed to make this state of art technology a better environmentally feasible platform.

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CHAPTER:14
FABRICATION, CHARACTERIZATION OF ZIRCONIUM OXIDE NANOPARTICLES

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Abstract

Zirconia has received much attention from the materials research community due to its attractive intrinsic properties such as hardness, shock wear, excellent acid and alkali resistance, low frictional resistance, and high melting temperature· It has been widely used in applications, such as gas sensors, solid oxide fuel cells (SOFCs), catalysis, catalysis carriers, and orthopaedic implants.However, bulk zirconia synthesized by the conventional methods usually have relatively low specific surface area (<100 m^2 g^{-1}) and microporosity, which limit some of its applications.In this study, to prepared the nanoparticles of zirconium oxide and characterized them by the some characterization techniques. *The* zirconia is nontoxic and less volatile, thus making it more environmentally friendly and easier to reuse.

Keywords: Zirconium oxide, nanoaprticles, inorganic, ceramic

INTRODUCTION

Over the years, Zirconium oxide (ZrO_2) which is also referred to as zirconium oxide or is an zirconia inorganic metal oxide that is mainly used in ceramic materials, zirconium oxide succeeds zirconium as the compound of the element zirconium that most frequently occurs in nature. [1] Ceramics have been largely used because of their chemical and physical properties, such as excellent chemical resistance, high refractoriness and ionic conductivity. To achieve such desirable properties, the synthesis condition must be well controlled to obtain fine powders with a narrow particle size distribution that enhance reactivity and densification**.**

In recent years, zirconia has received much attention from the materials research community due to its attractive intrinsic properties such as hardness, shock wear, excellent acid and alkali resistance, low frictional resistance, and high melting temperature·[2] It has been widely used in applications, such as gas sensors, solid oxide fuel cells (SOFCs), catalysis, catalysis carriers, and orthopaedic implants.[2-6] However, bulk zirconia synthesized by the conventional methods usually have relatively low specific surface area (<100 m^2 g^{-1}) and microporosity, which limit some of its applications. [6] Much research has been focused on increasing the specific surface area of zirconia. Synthesis of mesoporous zirconia has received significant attention, due to its high surface area, uniform pore size distribution, and large pore volume· [7]

1.1CRYSTAL STRUCTURE

Zirconium dioxide it has a tetragonal structure and is a white crystalline oxide of zirconium. [8] From normal temperature to elevated temperatures the pure zirconia structure transform from monoclinic structure. The pure zirconia is an instability material for temperature change. Therefore several oxides add to the zirconia to stabilize the material· [9]Pure zirconium dioxide exists at atmospheric pressure in three different polymorphs; monoclinic, tetragonal and cubic. Below 1170^{0}C, monoclinic phase is stable, between 1170^{0}C and 2370^{0}C, zirconia exists in tetragonal phase while above 2370^{0}C zirconia transforms to cubic phase [10].

1.2 PROPERTIES

These nanocystalline particle exhibit size dependent properties and novel optical, electronic, magnetic mechanical properties that cannot achieve using their bulk counterparts·[11-14]zirconium is a heavy metal of which 0.016% is found on the earth, thus it occurs more frequently than the elements chorine and copper. Its great hardness, low reactivity and high melting point have made it the oldest mineral that can found on the earth.[15]

Zirconium dioxide has a high thermal stability. It does not melt below 2680^0 C, which is why it is used in high temperature ceramics, such as crucible or furnaces. Since in addition it has a high mechanical stability and is very resistant to abrasion, it serves to e.g. improve the properties (especially the scratch resistance) of varnishes and coatings or as finishes to furniture [16]. Zirconium metal is also used for making zirconium inorganic and organic compound. Many example of the synthesis of zirconium complexes for catalytic applications are described in literature. [17-18]

Several interesting physical properties make zirconium dioxide a technologically important material for various purposes. The chemically stable, hard and high melting oxide can be further improved in its thermo mechanical properties by intentional addition of impurities, allowing the production of ceramic materials with high hardness, rigidity and thermal stability [19] The high oxygen ion conductivity over wide ranges of temperature and oxygen partial pressure makes yttrium-stabilized zirconium (YSZ).an important solid electrolyte for a number of electrochemical applications. Thus oxygen sensors based on zirconium dioxide are applied for the control of combustion processes in vehicle engines of furnaces or to monitor the oxygen concentration in metal melts recent publication deals with YSZ as a solid electrolyte well suited for fuel cells. [20]

Also in heterogeneous catalysis, ZrO2 is of increasing importance, both as supporting materials for metal catalysis and as a catalytically active metal oxide on its own. All these application require a detailed knowledge of the structure, phase transition and morphology of $ZrO_{2,}$ as well as appropriate method to influence them intentionally beside the addition of foeign cation, the choice of suitable precursors and the control of the preparative condition are factor determining the structural and morphological properties of the oxide phase [10].

Many different method of producing nanosize zirconium oxide powder where describe in the literature, such as sol-gel processing, hydrothermal processing, and precipitation method [21]. Among these methods listed above, hydrothermal synthesis meets the increasing demand for the direct preparation of crystalline ceramic powders and offers a low temperature alternative to conventional powder synthesis technique in the production of anhydrous oxide powders. This technique can produce fine, high purity and stoichiometric particles of single and multi component metal oxides.[22]

The best known process for the production of metallic zirconium is the Kroll process [23]. In this reaction zirconium is produced by the reduction of zirconium tetrachloride with an active metal such as magnesium at 800–900 °C. Elsewhere in the literature, the preparation of metallic Zr nanoparticles by ultrafast laser ablation of a zirconium rod in isopropyl alcohol has been described [24]. This process produces a colloidal solution of zirconium nanoparticles. the presence of the zirconium as a catalyst ensure an effective method for the synthesis of high purity and good quality CNTs (Carbon nanotubes).

In the recent years, there is a growing interest in the application of nanopartical as sorbents for pollutant removal [25-28]. Compared with traditional millimeter or micron-sized materials (mm to um) nanoscale particle have quite different physicochemical properties. The surface properties could be changed when the material becomes nano-scaled. Most of the atom on the surface of nanoparticles are unsaturated and can easily bind with other atoms. Due to the huge specific area and the absence of internal diffusion resistance, nanoscale sorbents may have superior performance for removing contaminants (e.g. high adsorption capacity and fast adsorption kinetics). [28-29, 25, 30]

When zirconium oxide mixed with other metal oxides they shows some other different properties which is also very useful just like The ceria-zirconia mixed oxide are likely to be attractive as three-way catalyst for vehicles[31-33] as materials for intermediate temperature solid oxide fuel cells[34,35] and as catalysts for wet air oxidation (CWAO) of organic pollutant[36-38] because of their unique redox properties and their high oxygen storage capacity[39].it was shows that the incorporation of Zr(IV), with a smaller ionic radius than that of Ce(IV) in the structure of CeO_2 increases its oxygen storage capacity[40-41] and thermal stability[31]. More ever, mixed oxide of cerium and zirconium are supports of interest for noble metals in the context of an application in catalysis and more specifically in CWAO.

The TiO_2-ZrO_2 mixed oxides are also extensively used as supports with metals, non-metals, and metal oxides for various catalytic applications. These supported catalysts have also been thoroughly investigated by different techniques. The influence of TiO_2-ZrO_2 on the dispersion and surface structure of the supported active components as examined by various techniques. A variety of reactions catalyzed by TiO_2-ZrO_2 and supported titania-zirconia mixed oxides, namely; dehydrogenation, decomposition of chlorofluoro carbons (CFCs), alcohols from epoxides, synthesis of 1-caprolactam. In addition to catalytic applications, these mixed oxides have also been employed for various other purposes such as photoconductive thin films, gas sensors, and in fuel cell and ceramic technologies. Interestingly, both titanium dioxide (TiO_2) and zirconium dioxide (ZrO_2) single oxides exhibit excellent catalytic properties for various reactions and both have been used as supports to disperse various noble and transition metals for distinct catalytic applications.**[42]**

In particular, mesoporous oxides of yttrium and zirconium have been synthesized using a variety of surfactant template molecules and transitionmetal precursors.**[43-45,46-48]** Only a few papers have appeared on the synthesis of mesoporous yttria-stabilized zirconia, although yttria-stabilized zirconia is the material of choice for use in solid oxide fuel cells (SOFC).**[49]** Ozin**[50]** used cetyl trimethyl ammonium bromide as a template to synthesize mesoporous yttria-zirconia with a high surface area (116 m^2/g) and a high thermal stability. However, the zirconia precursor must be modified with ethylene glycol for the synthesis of mesoporous yttria-zirconia.

Firstly, zirconia is nontoxic and less volatile, thus making it more environmentally friendly and easier to reuse. Secondly, zirconia is more stable at high temperature and reducing environment, which maintains its catalytic activity at high temperature.**[51]** These all contribute to a better performance for catalytic reaction at high temperature, and drawing much attention from the research community. However, in order to have a comprehensive understanding of the features and mechanisms of zirconia catalyst, we should know the structure and properties of zirconium dioxide. There are some physical and chemical properties of zirconium is given below.

1.3PHYSICAL PROPERTIES

Zirconia is an important ceramic material with attractive physical and mechanical properties. It has a melting point of 2680˚C, and a boiling point of 4300˚C. At room temperature, the density of zirconia is about 5.68 g/cm3, and Moh's hardness is about 7.

Beside the high temperature stability and hardness, zirconia also possesses relatively high toughness and strength. Another special property of zirconia is its low thermal conductivity, combined with the non-magnetic electrical insulator nature, making it a potential candidate for many thermal applications. **[53, 54]**

1.4 CHEMICAL PROPERTIES-

Zirconia is a chemically inert material; it has a good corrosion resistance in acids and alkalis. Zirconia is also an amphoteric material, which has both acidic and basic properties. Another outstanding property of zirconia is stability under reducing conditions, which makes it an important material in catalytic field. **[55]**

1.5 APPLICATIONS-

Zirconium dioxide has various properties and it is used in different field.

i. Stabilized zirconia is used in oxygen sensor and fuel cell membranes because it has the ability to allow oxygen ions to move freely through the crystal structure at high temperatures.**[56]**
ii. Single crystal of the cubic zirconia is commonly used as diamond stimulant in jewellery.
iii. It is also used in optical devices **[57]**. And ceramics biomaterial **[58]**.
iv. The very low thermal conductivity of cubic phase of zirconia also has led to its use as thermal barrier coating, or TBC in jet and diesel engines to allow operation at higher temperature.
v. This material is also used in dentistry in the manufacture of sub frame for the construction of dental restorations such as crowns and bridges.**[59]**

vi. It is used as an alloying agent in materials that are exposed to corrosive agents such as surgical appliances, explosive primers, vacuum tube and filaments.

vii. The powder of zirconium is highly flammable and consequently has military applications, such as in the production of explosive materials for munitions.[60]

viii. There have been lots of studies on depositing ZrO_2 onto one dimensional carbon nanotube (CNT) and applying ZrO_2-CNT nanocomposites for various applications, such as catalyst supports for fuel cells, biocompatible matrix for protein immobilization and transistors.

ix. Marine pumps seals and soft guides. Roller and guides for metal tube forming.

x. Zirconium dioxide is also found in varnishes for electric items, in nail polishes, in ink jet printer inks, and other products.

xi. It is also known as abrasive and is found (like titanium oxide) as a white pigment in porcelain.

xii. Moreover, hip joint endoprosthesus and other high performances medical ceramics benefit from the advantages of zirconium dioxide.

xiii. Zirconia is an insulator at ambient temperatures, but will turn into super ionic conductor at very high temperature. Because of its good biocompatibility, high hardness and strength.

xiv. Zirconia is chemically and thermally stable, combined with its unique amphoteric characteristic, makes it an ideal candidate for catalyst. For example, the hydrogenation of aromatic carboxylic acids, the decomposition of nitrous oxide, the isomerization of alkanes, and many other reactions.

xv. The ZrO_2 nanorods with different sizes were used to estimate their potential application in humidity sensor, which is important in many fields such as meteorology, industrial and agricultural process control, food production, and physicochemical processes in pharmaceuticals.[61]

xvi. The high melting point makes zirconia a good refractory material, and it finds important utilization in high temperature applications.

xvii. It can also be used as hot metal extrusion dies, due to its refractory nature as well as high hardness, high toughness and strength.

xviii. metal oxide-graphene nano composites have great potential for applications in fuel cells, lithium ion batteries, solar cells, super capacitors, etc.

1.6 ADVANTAGES OF ZIRCONIUM DIOXIDE-

Zirconia, as a well-known catalyst, possesses both the common advantages of transitionmetal compound catalysts and its own unique merits

1. Zirconia, as a well-known catalyst, possesses both the common advantages of transitionmetal compound catalysts and its own unique merits.
2. The high melting point and hardness is a big advantage for zirconia as a catalyst, which allows it to perform in extreme environments such as high temperature catalysis
3. The amphoteric property is considered to be another advantage, the relative acidic and basic sites present on the surface of metal oxides alter the catalytic properties.
4. Chemically inert, a significant requirement with respect of catalytic uses
5. Stable under reducing conditions, making it possible in catalytic reduction reactions.
6. Moreover, zirconia has many practical advantages such as nontoxic, easy to handle, able to reuse, and less expensive, thus making it an important acidic catalyst in chemical industry.

2.1 EXPERIMENTAL PROCEDURE

Starting with 0.423 gm bis cyclopentadienyl zirconium (IV) chloride dissolve in 20 ml ethanol in one neck flask under vigorous stirring, after few minutes 5ml PEG (polyethylene glycol) was added into the above solution when the complex completely dissolve in the solution 10ml dil nitric acid HNO_3 added in the solution, all the reaction was performed under argon gas atmosphere using condenser. Reaction is maintained at 115^0C for one and half an hours after completion of reaction, left the solution for whole night. And centrifuged the solution, obtained precipitates were washed properly with ethanol to remove the soluble impurities, to discard the remaining solvents and then dried in rota vapour. Finally, crystalline ZrO_2 were obtained after calcination at 500^0 C for 2 hours in muffle furnace.

2.2 CHARACTERIZATION TECHNIQUES-

Property characterization of nanomaterials is challenging because of the difficulties in manipulating structures of such small size. New tools and approaches must be developed to meet new challenges. Due to the high size and structure selectivity of nanomaterials, their physical properties could be quite diverse, depending on their atomic-scale structure, size and chemistry. A typical example is carbon nanotube, which is made of concentrically cylindrical graphite sheets with a diameter range from one to 400 nanometers and length of a few micrometers. Characterizing the mechanical properties of individual nanotube, for example, is a challenge to many testing and measuring technical properties because of the following constraints. First, the size (diameter and length) is rather small, prohibiting the application of well established testing techniques. Tensile and creep testing require that the size of the sample be sufficiently large to be clamped rigidly by the sample holder without sliding. This is impossible for one-dimensional nanomaterials using conventional means. Second, the small size of the nanostructure makes their manipulation rather difficult, and specialized techniques are needed for picking up and installing individual nanostructures. Therefore, new methods and methodologies must be developed to quantify the properties of individual nanostructures. The characterization of the as prepared nanostructures (nanoparticles, nanorods etc) will be performed using XRD, SEM with EDS characterization techniques.

RESULT AND DISCUSSION-

4.1 COMPOSITIONAL ANALYSIS

FTIR spectroscopy is a useful tool to understand the functional group of synthesized materials. figure1 show the FTIR spectra of the synthesized ZrO_2 particle respectively. The broad peak located at 3424.6 cm^{-1} are associated with the –OH stretching vibration of adsorbed water and the peak at 1734.6 cm^{-1} implies that the presence of ketone group. The band structure located at 1382.2, 2929.8, 1618.8, 2339.0 cm^{-1} corresponds to presence of alkane, alkene, alkyne group.a peak 1529.1, 1453.8 cm-1 shows the presence of strectch aromatic group. And the peak at 1027.2 cm-1 indicates that –CN in aliphatic amine group is also presence here.

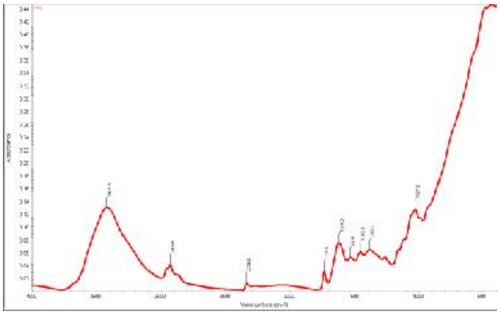

Figure 1-FTIR spectra of synthesized ZrO_2 nanoparticles

4.2 MORPHOLOGICAL ANALYSIS OF ZrO_2-

The morphology and size information of the zirconium oxide was investigated by SEM analysis. The sample exhibited spherical like morphologies. The average size of the zirconium oxide nanoparticle was found in fig.3 (A) 0.5 µm. The same process was repeated for the synthesis ZrO_2 nanoparticle and their size determined fig.3 (B) (C) (D) depicts the morphology of the product and the average size of ZrO_2 particle was found to be around 1µm.

The formation and composition of crystalline ZrO_2 nanoparticles are justified from EDX measurements. The measurement shows the presence of 39.15% Zr and 60.85% O (atomic percentage),which reveals that the Zr and O as the only elementary species in the sample indicate that, high purity and no any other impurity in the sample.

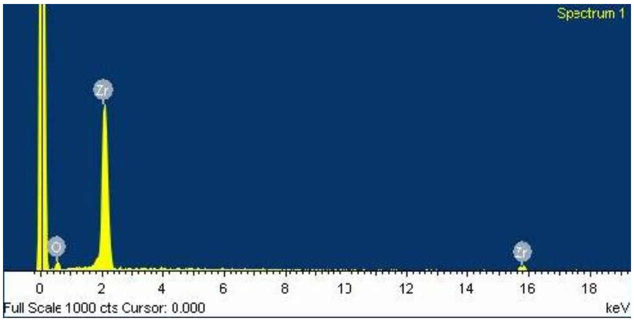

Figure 2- EDX imageof ZrO2nanoparticle

Element	Weight %	Atomic %
O K	21.42	60.85
Zr L	78.58	39.15
Total	100.0	100.0

Table 1- Total percentage of ZrO_2

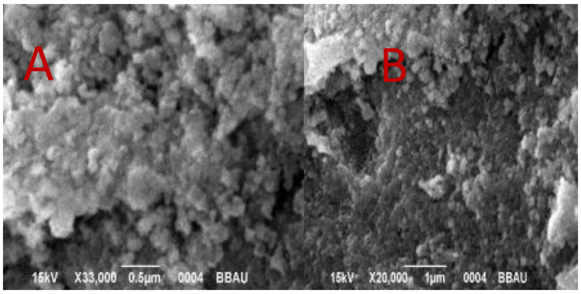

Figure 3 SEM images of ZrO_2 nanoparticles: (A),(B)

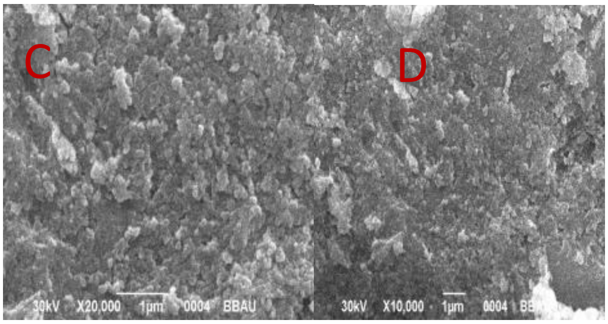

Fig 4.SEM image of Zirconium Oxide nanoparticles (C), (D)

CONCLUSION-

This paper reports a simple and rapid method for the synthesis of metallic zirconium nanoparticles. The spherical shaped particles with average size of 0.5 and 1 µm were obtained, which was confirmed by SEM, XRD,studies. This work would be meaningful to provide a methodology to synthesize ultrafine nanomaterials

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CHAPTER:15

SOLIDWASTEMANAGEMENT FOR THE SUSTAINABLE DEVELOPMENT OF ENVIRONMENT

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Abstract

Waste management involves the procedures and actions necessary to manage waste from generation to disposal. This covers waste collection, transportation, treatment, and disposal, as well as waste management process monitoring and control, as well as waste-related legislation, technology, and economic processes.Waste can be solid, liquid, or gaseous, and each has its own removal and management procedures. Waste management is concerned with all forms of waste, such as industrial, biological, domestic, municipal, organic, biomedical, and radioactive wastes. In some situations, trash can endanger human health.Throughout the waste management strategy, there are health concerns. Health problems can occur both indirectly and directly, directly, through solid waste disposal, and indirectly, through the consumption of water, soil, and food. Human activity, such as the mining and processing of basic resources, generates waste. Trash management is to decrease the negative impacts of waste on human health, the environment, global resources, and aesthetics.

INTRODUCTION

Waste is a left over a redundant product or material of no or marginal value for the owner andwhich the owner wants to discard. Characteristics of being a waste are not intrinsic property of an item but dependon the situation in which item appears as defined by the owner or in other word show the owner values the items. To become a waste is depending on factors such as time, location, state, income level and personal preferences.Ageneraldefinitionof wasteis given by UNEPas:“Wastes are substances or objects which are disposed of or are intended to be disposed of or required to be disposed of by the provisions on national Law”

SolidWaste:

Definition of solid waste is waste in solid state which may be solid or liquid as sludge or as freechemical phase. This originates from defining solid waste as waste that is not water or air borneand has no transporting media like water and air that must be cleaned. In other words, we can saywastes arising from human and animal activities that are normally solid that are discarded asuselessorunwanted.

Solidwaste materials on the basis of their origin andnature are broadly classified as-

1. Municipal Waste
2. Industrial waste
3. Hazardous waste
4. Inert waste
5. Household wastes
6. Clinicalor Healthcare waste
7. Commercial waste
8. Radioactive waste
9. Biodegradable waste
10. Non-Biodegradable Waste

Municipal Waste: It generally refers to solid waste from household, streets and public places, shops, offices and hospitals. It also includes the waste generated by commercial, government and educational sectors.

Industrial waste: wastes produced by the manufacturing industries activities such as rubbish, ashes, special wastes and hazardous waste. Industrial waste has greater potential for recycling due to their worse effect on environment and human beings.

Hazardous Waste: Hazardous waste poses substantial danger immediately or over of time to environment, plants, animal life and public health. Hazardous waste has the following characteristics-

(a) Ignitability
(b) Corrosively
(c) Reactivity
(d) Toxicity

Principal sources of hazardous waste are from chemical industries, hospitals and Biological Research institutes.

Inert Waste: Waste that has virtually no environmental or health threat on disposal. Clean waste ceramic material and uncontaminated soil comeunder this category.

Household Waste: Wastes produced in domestic household and gardens due to many residues arise from household domestic activity and gardening activity.

Clinical or Healthcare waste: Clinical or Healthcare waste is generated by healthcare activities. The main sources of this type of waste are Hospital wastes, Dentist, Biomedical research laboratories etc.

Commercial waste: Commercial waste is produced by the commercial business activities. This is like household waste but contains more paper products.

Radioactive waste: Radioactive waste produced by Nuclear Power projects, Military nuclear weapons production, hospitals and research laboratories.

Biodegradable waste: Biodegradable waste is produced by degradation of material by microbialaction.

Non-Biodegradable Waste: Waste which cannot be decomposed or degrade by the biological process is known as “Non-biodegradable wastes”. Most of them include inorganic waste is non-biodegradable.

They remain on earth for thousands of years without any degradation or decomposition. Therefore, the threat caused by the missal so more dangerous. An example is the plastic which is usually used in almost every area. Other cases are cans, metals, and chemicals for agricultural and industrial uses.They are the chief causes of air, water and soil pollution and diseases like cancer.

Issues with Solid Wastes:

If solid waste is properly managed may constitute serious problems in the surroundings as well a senvironments. The various issues arising of ill managements may raise the in numerable harmful effects as below: -

1. **Public Health Issue-**Accumulated solid waste easily accessible by insects, animals and human beings may cause a health issue over a period of time. The waste may spread the infected vectors such as rats, cockroaches, flies and seagulls etc. which may cause various diseases in domestic animals and human beings.
2. **Nuisance:** If Solid waste accumulates over a period of time due ineffective waste disposal cause a nuisance such as odors, flies etc. become a problem for neighbors and aesthetic problem forc ommunity.
3. **Environmental Issue:** Waste which is lying for long period may cause contamination ofenvironmentas water pollution, air pollution and soil pollution.
4. **Resource Issue:** Waste pertain resources that can be used to save the other resources i.e space used for waste collection for long period which in not managed /disposed of.
5. **Economy Damage and Loss:** In urban area where large amount of waste is collected per day and no easy way of disposal area vailable within short distance may cause high cost of disposal of waste.The disposal of waste may reduce the GDP ofcountry.

RemedialactionforSolidWaste:

Solid waste generated due to the above said factors must be removed for clean environment and better eco-system. Thesolid waste may beremoved by some effective manner as-

1. Land Fill
2. Incinerators
3. Compost
4. Recycling

LANDFILL

Land fill technique is often confused with "open dump". Open dumping of waste can cause irreparable damage to environment by polluting land, water and air adversely affecting human, animal and crops health and lowering poorquality of life. The 2000 Rules, therefore, prohibitopen dumping and requires municipals authority to safely dispose of solid wastes in engineered landfills. The rules further mandate treatment of the organic fraction of solid waste before final disposalin the land fill sites.There are five principles which should be strictly adhered to-

1. Solid waste must be collected, transported and deposited in controlled manner.
2. Solidwastesshould bespreadinthinlayers.
3. Dailygroundcover ofabout sixinchesshould beapplied onelayer.
4. No open dumping to avoid air pollution.
5. All the factors which are likely to allow deposited wastes to contribute to water pollution must be eliminated.

Schedule III of Rule 2000 provides guidelines for the basic landfill requirements for selection and design. Guidelines includethe following provisions regarding site selection-

1. In area falling under the jurisdiction of "Development Authority". It is the responsibility of those authorities to identify the land fill site and to hand over the site to the concerned municipal authority for development, operation and maintenance.

BasicrequirementsforsiteSelection:

Sl.No.	Place	Minimumsitedistance
1.	Habitation	500 metre
2.	Waterbodies (river, lakes)	200 metre
3.	Canals, Drainage systems	30 metre
4.	Highways, Railways	300 metrefrom centerline
5.	Coastal regulation zone	No Landfill permitted
6.	Flood prone area	No Landfill permitted
7.	Airports	20 kilometre
8.	Earthquake prone areas	500 metre from faultline fracture

2. Selection of landfill sites must be based on examination of environmental issues. The department of urban development of the state or the union territory must coordinate with the concerned organization to obtain the necessary approval and clearance.
3. Landfill sites must be planned and designed with proper documentation of a phased constructionas well asclosureplan.
4. Landfill sites must be selected to make use of nearby waste processing facilities. Otherwise, waste processing facility must be planned as anintegral part of the land fillsites.
5. Existing landfill sites that will continue to be used for more than five years must be improved in accordance with the specifications that aregiven in Schedule III of rule 2000.
6. Biomedical waste must be disposed off in accordance with the Biomedical waste"Management and handling "Rules 1998, and Hazardous waste must be managed in accordance with hazardous wastes "Management and handling "Rules 1989 as amended.

Incinerators:

Incineration of solid wastes serves the function of reducing the volume of these wastes from their raworcollected states to more manageable levels, thus obtaining lower transportation costs to the ultimate disposalsite.

The maindisadvantage of technique is that both capital and operating cost are high and equipment is expensive.

Two types of incinerators are generally used for unsorted wastes-

1. **Batchtype plant:** It is manually stoked and has relatively smallrated capacity.The operationis intermittents othere is a lack of uniform burning temperature.This promotes in adequate com bustion and thus an attendant heavy output of particulate matter, less than optimal volume reduction and unstableresidue.
2. **Continuous Feed Plants:** It has larger storagebins,automaticfeedhoppers and veritiesofty pemoving grates and ash removal systems. The unit maintains uniform combustion temperature range, can be fitted with pollution control devices yields a stable residue. The reason for rapid growth of incineration is the volume reduction and operated with controlled furnace temperature.

It is designed as turboelectric generator plant using solid wastes as fuel. Unsorted waste is passed through shredder, dried by the hot gases, discharged from combustor and injected intothe combustorat high pressure.Then waste is fluidized as they pass through the chamber. The plan is tha the hot gases produced will drive the gasturbine which will drive electrostatic precipitator and hot gasses will be expelled at atmospheric pressure.

The incinerators shall meet the following operating and emission standards,namely: -

A. Operating Standards

(1) The combustion efficiency (CE)shall be atleast 99.00%.

(2) The combustion efficiency is computed as follows:

$$C.E. = \frac{\%CO2}{\%CO2 + \%CO} \mathbf{x100}$$

Emission Standards Parameters Concentrationmg/Nm3at (12% CO2 correction Particulate matter: 150

(1)Nitrogen Oxides :450

(2)HCl :50

(3)Minimum stack height shall be 30 metres above ground

(4)Volatile organic compounds in ash shallnot be more than 0.01%.

Composting: Composting is indeed the biological way of transforming organic materials like garbage and discarded food into a useful fertiliser that may improve soil and plants. Composting merely accelerates the decomposition process by creating a perfect habitat for bacteria, fungus, and other decomposing organisms (such as worms, sowbugs, and nematodes) to perform their work. Compost is the decomposed stuff that results, which typically looks like fertile garden soil. Compost, sometimes known as "black gold" by farmers, is high in nutrients and may be utilised in gardening, horticulture, and agriculture.

Biodegradable waste is converted to a soil like substance (Compost) which isvaluable soil amendment and fertilizer. Farmers and gardeners throughout the world have beenpracticing composting by pacing vegetable manures and animal manures in piles or pits fordecompositionprior to use.Many composting initiatives are not formally linked to the official system and therefore strugglewithorganizational, financial and institutional problems.Composting schemes vary in terms of scope, technology and management. The most important schemes of India are:

Scope	**Technology**	**Management**
Backyardcomposting	Boxcomposting	Individualcomposting
Neighborhoodcomposting	Windowcomposting	Communitycomposting
Marketwastecomposting	Vermicomposting	Municipalcomposting
Centralizedcomposting	Pitscomposting	Privatecomposting
	Cocomposting	

StandardsforComposting

1. The waste processing or disposalfacilities shall include composting,in cineration, palletization, energy recovery or any other facility based on state of-the-art technology duly approved by the Central Pollution Control Board.
2. In case of engagement of private agency by the municipal authority, a specific agreement between the municipal authority and the private agency shall be made particularly, for supply of solidwaste and other relevant terms and conditions.
3. In order to prevent pollution problems from compost plant and other processing facilities, thefollowingshould becomplied: -

i. The incoming wastes at site shall be maintained prior to further processing. To the extentpossible, the waste storage area should becovered. If, such storage is done in anopenarea, I tshall be provided with impermeable basewith facility forcollection.

ii. Necessary precautions shall betakento minimize nuisance of odor, flies, rodents, bird menace and fire hazard.

iii. Incase of break down or maintenance of plant, waste intake shall be stopped and arrangements be worked out for diversion of wastes to the land fill site.

iv. Pre-process and post-process rejects shall be removed from the processing facility on regular basis and shall not be allowed to pile atthesite.

v. In case of compost plant, the windrow area shall be provided with impermeable base. Such abase shall be made of concrete or compacted clay, 50 cm thick, having permeability coefficient less than 10–7 cm/sec. The base shall be provided with 1 to 2 per cent slope and circled by lined drains for collection of leachate or surfacerun-off.

vi. Ambientair quality monitoring shall be regularly carried out particularly for checking odor nuisance at down-wind direction on the boundaryof processing plant.

vii. In order to ensure safe application of compost, the following specifications for compost quality shall bemet, namely

Parameters	Concentration not to exceed *(mg/kg dry basis , except pH value and C/N ratio)
Arsenic	10.00
Cadmium	5.00
Chromium	50.00
Copper	300.00
Lead	100.00
Mercury	0.15
Zinc	1000.00
C/Nratio	20-40
PH	5.5-8.5

Recycling: "recycling" means the process of transforming segregated solid wastes into raw materials for producing new products, which mayor may not besimilar to the original products.

Recycling involves recovering and re processing usable materials that otherwise might end up aswaste.There covered material can be transformed into useful products that can pre-empt consumption ofvirgin resources in manufacturing.Use ofrecycled material susually requires less energy needed to manufacture a product compared with manufacturing the same product with raw materials. It also helps save energy and associated green house gas emissions across the multiple phases of product lifecycle, e.g., during extraction and manufacturing, and from decomposition. Commonly recyclable materials includepaper, cardboard, glass, plastics, metals, etc. Recycling of inorganic materials of solidwasteis often well developed through the activities of in formal sectorsal though municipal authority seldom recognizes.

SolidwastemanagementinIndia

The primary responsibility and duty for solid waste management goes to Municipal authorities, State legislation and local acts including special provisions for Collection, Transportation and disposal of waste. The Supreme Courtof India directed against the PIL (Public interestlitigation Application no.888 of 1996) in March 1999 that Central Government, State government and Municipal authoritiestakea necessary action against the proper disposal of Solid wastes. Ministry of Environment and Forest issues Rules 2000 for solid waste management in September 2000 under Environment Protection act 1986.

Glimpsesof Schedule I of 2000Rule

S.No.	Steps	CompletionDate
1.	Setup waste processing and disposal facilities	December 200 3or Earlier
2.	Monitor the performance of processing and disposal facilities	Onceevery six months
3.	Improve existing landfill sites as per provisions of the rules	December 2002 or Earlier
4.	Identify Landfill sites for future use and make site sready for operation	December 2002 or Earlier

ScheduleIIof2000Rule

Under Schedule II of the Rules, municipal authorities have been further directed to set up and implement improved waste management practices and services for waste processing and disposal facilities.

Standard for waste processing and disposa lfacilities are defined in Rules and municipal authority are required tomeet the specifications and standards specified in Schedule III andIV.

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CHAPTER: 16

ROLE OF PROBIOTIC MILK IN HUMAN HEALTH

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ABSTRACT

The numerous perceived health benefits and the growing awareness about probiotics have caught the attention of the food industry. Food companies are increasingly manufacturing foods with incorporated probiotic bacteria, which fall under the new category of foods called Functional Foods. Probiotic dairy products such as yogurts containing *L. acidophilus* and *Bifidobacterium* spp. constitute a significant amount among the commercially available probiotic foods. Functional foods have been developed in most food categories and even by conservative estimates, the global market size alreadyexceeds that for organic foods. In addition to providing consumers options for improving their health and well-being, functional foods such as probiotics in dairy products are an attractive market sector, providing new economic opportunities.

Keywords: Probiotics, dairy products, *Bifidobacterium,* probiotic food.

INTRODUCTION

Probiotic food products have been consumed by human beings in the form of fermented foods, for many years [1, 2, and 3]. According to the report by FAO/WHO, probiotics are: "Live microorganisms which, when administered in adequate amounts, confer a health benefit to the host". The most common types of probiotics are Lactic acid bacteria and include specie fromthe Lactobacillus, Pediococcus *andBifidobacterium* genera. Various species including *Lactobacillus rhamnosus* and *Bifidobacterium* have mainly been used as probiotics over the years [4,5]. An important characteristic of probiotic bacteria is that they need to survive through the gastro intestinal track of the host. As *S. thermophilus* and *L. bulgaricus* are not expected to survive and grow in the host's intestinal tract, they are not categoried as probiotics by most scientists by the fermentation of milk with cultures of streptococcus thermophilus and lactobacillus delbrueckii ssp. bulgaricus, however, yogurt-like productsare Probiotic bacteria are grow in the host's intestinal tract, they are not categorized as probiotics by most scientists and are therefore considered as yogurt cultures [6]. Hence a probiotic yogurt will typically contain conventional yogurt starters and additional probiotic bacteria so as to provide health benefits in humans by creating an improved balance in the flora of the intestines [7]. Besides of these advantages of probiotics, and probiotic food there is very less information is available on the synergistic effects of prebiotics and hydrolyzed milk on the growth and survival of bifidobacteria spp., which could lead to new products for the dairymarket.

FERMENTED MILK AND PROBIOTIC BACTERIA

Fermented milk has been used throughout the history of mankind. Nearly every civilization have developed some type of fermented milk product such as buttermilk, labneh, acidophilus milk and yogurt, which were familiar to many people, although the fermentation process was not defined yet. Yogurt, which came from the Turkish term in the eighth century as- yoghurut [8] and the spelling, changed over time to the present spelling in the eleventhcentury.Yogurtisdefinedas-productobtained made by substituting L. Bulgaricusby other Lactobacillus species for the fermentation of milk or yogurt containing probiotic bacteria[9]. The fermentation process of dairy products and its bacteria have received great attention over the decades after discovering the importance of viable bacteria infood for health benefits. At the beginning of the last century first scientific work had been done by Metchnikoff to investigate the beneficial effects of fermented milk for human health. Numerous scientific studies have been published describing the health benefit associated with the consumption of fermented dairy products [10].The lactic acid bacteria (yogurt bacteria; Lactobacillus delbrueckii ssp. bulgaricus and Streptococcus thermophilus) do not inhabit the human and animal intestinal tract, nor do survive passing through the digestive system [11]. Therefore, to get the beneficial health effects associated in the fermented dairy products, there has been and increase interest in the incorporation of the intestinal species Lactobacillus acidophilus and Bifidobacterium species in the fermented milk products [12,13,14], these include fermented liquid milks, ice cream, yogurt, and cheese and in soya milk and soya yogurt [15,16,17]. A probiotic is defined classically as a viable microbial dietary supplement that beneficially affects the host through its effects in the intestinal tract. This definition, however, was initially intended for use with animal feed products. For human nutrition, the following definition has been proposed: Probiotics are viable microorganisms that are beneficial to the host when administered in appropriate quantities[18].

In the last decade, the use of probiotics in Fermented dairy product and feed product applications has a noticeable interest anddevelop. These organisms play significant role in lowering the pH of the large intestine through the release of lactic and acetic acid[19]. A large number of probiotic strains Isolates from food, especially dairy products, but also from many applications samples for human, and nutrients for animals. All commercially available isolates of the genera Lactobacillus and Bifidobacterium were identified and compared with reference strains from official culture collections (ATCC, DSMZ, LMG, CCUG, andothers). As bifidobacteria are used as probiotic cultures in commercial dairy products, the questions arose, which species are used? [20,21]. In general, there are 56 species of lactobacillus and 29 species of Bifidobacteria, which used worldwide in dairy products[14].

In consequences bifidobacteria have been used only to limited extent in commercial fermented milk [31, 1] in However, the main species of lactobacillus and Bifidobacteria had been reported in literature such as; L. lactis, L. casei, L. paracasei and more. B. longum, B. infantis, B. breve, B. lactis and B. bifidum [14]. Recent experience revealed that B. animalis had been applied frequently in fermented dairy products due to the fact that this species is somewhat less sensitive against acidification (pH below 4.2) and elevated oxygen tolerance, which is remarkable within the Bifidobacteria [22, 23]. Bifidobacteria are unique in many other respects.

Human related sequence of bifidobacteria differs from both homo and hetero-fermentative bacteria in that they metabolize carbohydrates by aspecial enzyme called Fructose-6-Phosphate Phosphoketolase (F6PPK), which also metabolize Fructooligosaccharides (FOS) which are polymers of fructose and cannot be metabolized by either human digestive enzymes or most undesirable gut microorganisms.

The use of Bifidobacteria in fermented milk shows that it has very slow properties and it requires specific growth factor, known as bifidogenic factors, these are carbohydrates such as N-acetyl-D-glucosamine and lactulose found in human milk [24] and processed milk products, respectively. — Unlike yogurt bacteria, probiotic bacteria grow very slow. Moreover, it has shown that breast-fed infants have higher numbers of Bifidobacterium than bottle-fed ones[25].

The use of bifidobacteria in fermented milk has many benefits to human and animals by several mechanisms [26, 25,27,28]. Therefore, it has been very important to determine the efficacy of the product containing probiotics, such as the acceptance of the product by the consumers and the survival of probiotic microorganisms during its production. In general, the food industry has applied the recommended level of 106 CFU/g at the time of consumption for Lactobacillus acidophilus, bifidobacteria and other probiotic bacteria [14,29]. Although milk contain the essential nutrients for the growth of bifidobacteria, but the level of amino acids and peptides insufficient to provide the ideal condition for rapid their growth and survival[30,31] spite that fermented milk is the preferred carrier for bifidobacteria.

The growing understanding of the relationship between diet and health increased the demand for food with specific benefit beyond their basic nutrition such as improving the health and well-being ofhuman.

This food is called functional food However; Functional food has defined as one, which provides a specific health benefit over and above its normal nutritional status [32]. Moreover, the functional foods must remain as foods (not capsules, etc.) and they must also reveal their effects in amount that can usually be expected to be consumed in thediet. It has been suggested that food will use as functional when it has shown beneficial effect on one or more target in the body and that beside their nutritional effectssuch as well-being and health of the host[33].

The old generation of functional foods indicates of using supplements to the food to increase their nutrition and health effects such as vitamins and micronutrient. However, in the new concept of functional foods there was more interest in the gastrointestinal interactions [34], that led for more interest in the dominated organisms in the gastrointestinal tract (indigenous microflora) which found to beneficially effect human health, which known as probiotic bacteria. Therefore, the use of probiotic micro-flora was one of the most promising areas for the developmentoffunctionalfoodsintherecentstudies [35] because of what probiotics has established a great benefit to human health.

Bifidobacteria were the most dominated organisms in the gastrointestinal tract and their viability and metabolic activity have shown very beneficial effects on the health of the gastrointestinal tract [36] and that always related to the presence of a suitable environment and nutrients, which are very important for the viabilityand activity, for bifidobacteria to use it in the bowel as carbon and energy source, these compound were referred toas bifidogenic factors [37].

At present, probiotics products and especially probiotics dairy foods are marketed successfully all over the world because of their acceptance of consumer and the awareness about their positive aspect for the health benefits.

Health benefits for human Health benefits

Bacteria have a reputation for causing disease, but a growing body of scientific evidence suggests that you can treat and even prevent some illnesses with foods and supplements containing certain kinds of live bacteria. For example, Metchnikoff related the longevity of Bulgarians to the present of Lactobacillus bulgaricus in the souring milk -yogurt. Moreover, in the Northern Europeans consume a lot of these beneficial microorganisms in the dairy products, because of their tradition of eating foods fermented with bacteria, such as yogurt and cheese, these beneficial bacteria have named later asprobiotics.

Probiotic microflora displays numerous health benefits beyond providing basic nutritional value. The health benefit reported of probiotics is the improvement in gut health and the prevention of intestinal infections and stimulating the immune system [38]. Infection prevention is increasingly preferred over using the traditional action by chemotherapy with antibiotics, that rise the concern over development of antibiotic resistance has placed probiotics at thefore.

The principal mechanism for this action is known as competitive colonization or competitive inhibition [39, 40, 41, 42]. This is described as the creation of probiotic bacteria in the human intestine, which acts as a vital barrier to invasion by pathogens in the gastrointestinal tract of the human host. Over 90% of the total cells in the body are present as bacteria in the colon, getting 1012 CFU (Colony Format Unite) for every gram of large intestinal contents [43, 44]. Under natural conditions, a protective gut microflora develops and there is no need for a bacterial supplement [45] but the changing food habits and lifestyle force us to take processed food, which affects our access to, and colonization, by probiotics. Moreover, we also consume antibacterial substances ranging from vinegar to antibiotics. To reside in the gut, when ingested, probiotic bacteria are resistant to gastric acidity and bile salts [46] and therefore pass through the upper gastrointestinal tract and have the ability to adhere to the intestinal mucosa. Further, the probiotics‘secretion of by products such as lactic acid and acetic acid lower the pH in the intestine and producing hydrogen peroxide inhibiting the growth of pathogens and helped to speed pathogens through the intestines [47,48].

The enhancement of the immune system is another reported health benefit of probiotics [49,50], as it appears that this effect by balancing control of pro-inflammatory and anti-inflammatory cytokines [51,14] and therefore probiotics are considered as immune-stimulatory agent and an important tools to prevent intestinal inflammation, stop gut mucosal dysfunction and decrease hypersensitivity[52].

Recently, there is a relatively large volume of scientific literature basis supporting the use of probiotics for diarrhoea has started to become established. Probiotics have been shown effectiveness in the prevention of several types of diarrhea, including antibiotic-associated diarrhea, bacterial and viral diarrhea (including travelers‘ diarrhea), as well as that caused by lactose intolerance [53]. It is thought that this action is due to the secretion of antimicrobial polypeptides known as bacteriocins and that by; reduction in gastrointestinal pH through stimulation of lactic acid-producing bacteria; a direct antagonistic action on gastrointestinal pathogens; competition with pathogens for binding and receptor sites; improved immune function; and competition for limited nutrients [54). It seems that the effect of probiotics on traveller's diarrhea depends on the bacterial strain used and the destination of the travelers[55]. Observational data suggest that consumption of fermented dairy products is associated with a lower prevalence of colon cancer, which is suggested that probiotics are capable of decreasing the risk of cancer [56].

The Mechanisms described by Inhibition of carcinogens and pro-carcinogens, Inhibition of bacteria capable of converting pro-carcinogens to carcinogens [57]. Moreover, probiotic and especially bifidobacteria has shown to increase the α- and β-galactosidase activities in the faecal samples after feeding with the fermented milk containing probiotics, which is considered to be an important probiotic quality, as it supports lactose digestion in the intestine and compensates for lactase-deficiency[14,58,59]. Playne [60] suggested that Health benefits imparted by probiotic bacteria are strain-specific and not species- or genus- specific. For example the strains *Lactobacillus rhamnosus* GG (Valio), *Lactobacillus paracasei* Shirota (Yakult), and *Bifidobacterium Lactis* Bb12 (Chr. Hansen), *L. acidophilus* La5 (Chr. Hansen) have the strongest human health efficacy data, against some or all of: lactose intolerance; rotaviral diarrhea; antibiotic- associated diarrhea and some other bacterial diarrheas and infections. *B. animalis* found to stimulate the immune response *in vivo* [61,62]. Moreover, it has improved in control study the useful of *Bifidobacterium lactis* strain Bb12 in prevention of acute diarrhea in infants [63,64,65] and same by *Lactobacillus* GG[66].

Bifidobacterium lactis Bb12 well known in their ability to improve the growth of children when supplement in their formula. Candida can also be suppressed or controlled by viable *L. acidophilus*. It is also thought thatnon-viable forms exert such control but to a lesser extent[67].

The only prebiotics for which sufficient data have been generated to allow an evaluation of their possible classification as functional food ingredients are the inulin-type fructans, which include native inulin, enzymatically hydrolyzed inulin or oligofructose, and synthetic fructooligosaccharides [68, 69,72].

INULIN

Inulin is natural food ingredient, which found in many vegetables and obtained industrially from chicory roots [70]. Usually GFn is the symbolized use for inulin as polysaccharides mixture, where G is the glucose moiety, F is the fructose moiety and (*n*) equals the number of fructose moieties linked by β (2→1) linkages (Figure 2.1). This bonding renders it resistant to hydrolysis, both in the stomach and the intestine [71]. The degree of polymerization (DP) of inulin typically ranges from 2to 60. Usually 10% of the inulin extracted from chicory roots is sucrose and fructose, and 30% is oligosaccharide (DP=10). The production process of inulin naturally from chicory roots is by diffusion in hot water, followed by refining and sprydrying.

The nutritional properties of inulin as a supplement to the healthy foods is obtained when inulin is not broken down in the upper digestive systems of human and should be given energy value of 6.28 kj/g [71], fermented by the intestinal flora causing increase in the biomass, producing of short chain fatty acids and decrease in the pH, and significant increase of bifidobacteria in the colon and inhibits the growth of less beneficial bacteria, [72]. So using these ingredients in food allows improving the nutrition value of the products, by reducing the calorie content and increasing the bifidus-promotingcapacities.

Inulin has natural taste, colourless and minimal influence on the natural characteristics of the products. Inulin is highly soluble fiber ingredient, which gives its more importance in the dairy industries such as milk drink, yogurt, and cheeses. Combining inulin with sweetness improves the taste of products giving more sugar-like sweetness. Atconcentration of 40-45% inulin form a fatty tasting solution, which make it highly used in the free-fat products to give the smooth creamy texture and taste; Inulin has successfully applied in fat-reduced table spread, cheese product, meat products, frozen desserts, fillings, sauces and meat replacers. [73,74].

Using the food as vehicles for inulin considering in its ability to keep the inulin save to the intestine where the bifidobacteria inhabit, but yogurt has shown to be the best choice for that purpose. However, bio-yogurt - with inulin showed problem in transferring the short chain length of the inulin because of the possibility to interfere too much with the inter-micellar bonding of the casein, that why it is important to watch the optimum level of casein to give maximum gel to natural yogurt with inulin. Moreover, the different effect of the yogurt culture or *Bifidobacterium spp.* on the different levels of oligosaccharides which generate undesirable acids when utilize some of the inulin and the effect of the inulin on the gel strength, viscosity and flavour of the natural yogurt.

OLIGOSACCHARIDES

Oligosaccharides of various types found in common foods such as fruit, vegetables, milk and honey [75]. Oligosaccharides often have between 2-10 polymers of sugar. It is often contain low levels of monosaccharide and di- or polysaccharides. They have various properties depended on their molecular- weight; low molecular- weight can used in food freezing temperature andthe high once use for thickness and increase body and mouth feel.

Grittenden and Playne [76] have selected food grade oligosaccharides and listed them: Fructo-oligosaccharides (FOS), Galacto-oligosaccharides (GOS), Lactulose, Lactosucrose, Malto-oligosaccharides, Isomalto-oligosaccharides, soybean- oligosaccharides and xylo-oligosaccharides in the commercial productions. Of these food grade oligosaccharides there are some of them, which have the bifidogenic effect and health promoting properties; such as Fructo- oligosaccharides andGalacto-oligosaccharides.

GALACTOOLIGOSACCHARIDES

Galacto-oligosaccharides (GOS) are found in the human milk and proved to have the bifidogenic promoting effect for the breast-fed infants [77,78,79]. GOS is primary production from Cow‘s Whey-derived lactose [80]. The lactose solution is converted to GOS by the action of β-galctosidase, which has transgalactosylation activity (Figure 1). GOS have a DP of 2 to 10 units, which are able to pass through the upper gut without hydrolysed by digestive enzymes, to reach the large intestine and beneficially affects the host by stimulating the growth and/or activity of target floraonly.

GOS found in the breast milk at level of 1g/L [81]. Therefore, it is considered as bifidogenic factors in fermented milk products and baby foods. GOS consist of number of β1-6 linked galactosyl residues bound to a terminal glucose unit via α1-4 linkage [82], that make GOS utilized by some probiotics (stimulating their growth) depend on their enzymes and especially Lactobacillus group [83]. GOS can be used in food contributing to both thicknessand mouth-feel, sweeteners as it sweetness is 35% of sucrose and source for fiber. They have calorie value of 1.7Kcal/g [84].

Fructooligosaccharides

Fructo-oligosaccharides (FOS) and Inulin are the most classified asbifidogenic oligosaccharides in productions. Fructooligosacchrides (FOS) contains between 2- 4 of β (2→1) linked fructose units linked to the terminal α-D-glucose residue. The natural way of FOS productions is by enzyme hydrolysis of Inulin (Figure 2). Therefore, there is no difference from the chemical view between inulin and FOS, but the DP for FOS is between 2-10 units with an average of 4 [85].

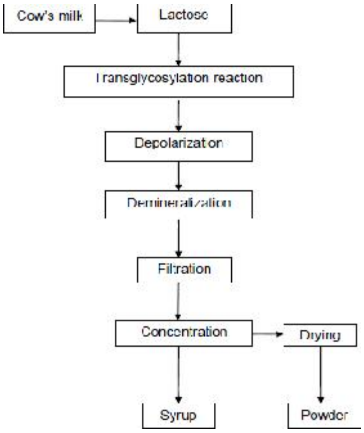

Figure 1: Production of galactooligosaccharide from cows‘ milk’

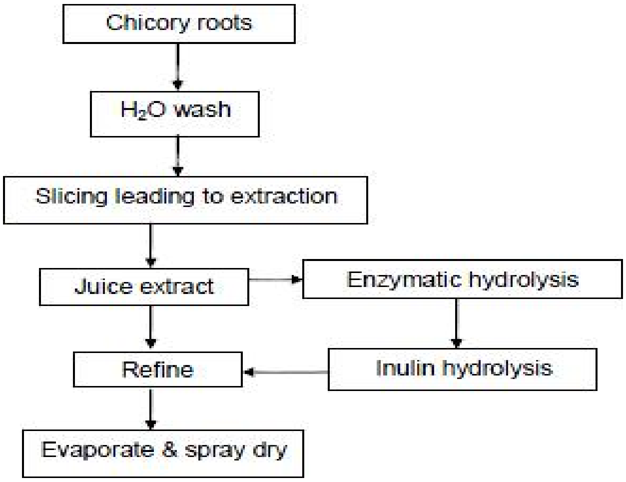

Figure 2: Inulin and oligofructose manufacturing process

Oligofructose is more soluble than sucrose and Inulin, provides 30-50% of the sweetness of table sugar. It is considered to be low-calorie ingredients which around 1.5 Kcal/g. Inulin and FOS are widely found in nature and manufactured by companies such as Orafti, Sensus and Cosucra. A lot of scientific studies *in-vivo* have shown that FOS (RAFTILOSE® P95) andInulin (RAFTILINE® ST) from ORAFTI have bifidogenic effect on host; When consumed at a dose of 5g/day for oligofructose and ≤ 8 g/day for inulin, they significantly modify the composition of the intestinal (faecal) flora, selectively increasing the numbers of Bifidobacteria and reducing the harmful bacteria [86,87,88,89,90, 91](Figure 3).Food for Specified Health Use (FOSHU) is unique system in Japan for approving ingredients/foods with a functional claim [93, 94]. Prebiotic containing foods are most common in this category because the most FOSHU food designed for the gastrointestinal health benefits. The survival of probiotics including *L. acidophilus*, *L. Casei* and *Bifidobacterium spp*. was improved by adding of FOS (P95, from ORAFTI) at 1.5% w/v to yogurt containing these microorganisms[95].

Inulin and oligofructose have found to improve the bioavailability of minerals such as calcium, magnesium and iron and they increase the absorption of calcium and magnesium in the large intestine [96, 97]. Use oligofructose in the diet by 15g/day produce substantial changes in the intestinal microflora and increase the faecal bifidobacteria count and reduce the potential pathogens such as *Clostridium, E. coli*. It has found that symbiotic supplements of Oligofructose and *L.rhamnosus* and *B. animalis* subsp. *Lactis* improved the immune responses and stopped colon tumors. Prebiotics have shown resistance to gastrointestinal infection because of their stimulatory effect on *Bifidobacterium* spp., which produces several anti- pathogenic mechanisms[98].

Although prebiotics can help to increase the beneficial bacteria in the gastrointestinal tract, a general increase in the beneficial bacterial population may however not necessarily contribute to increased health effects, as it is strain related.

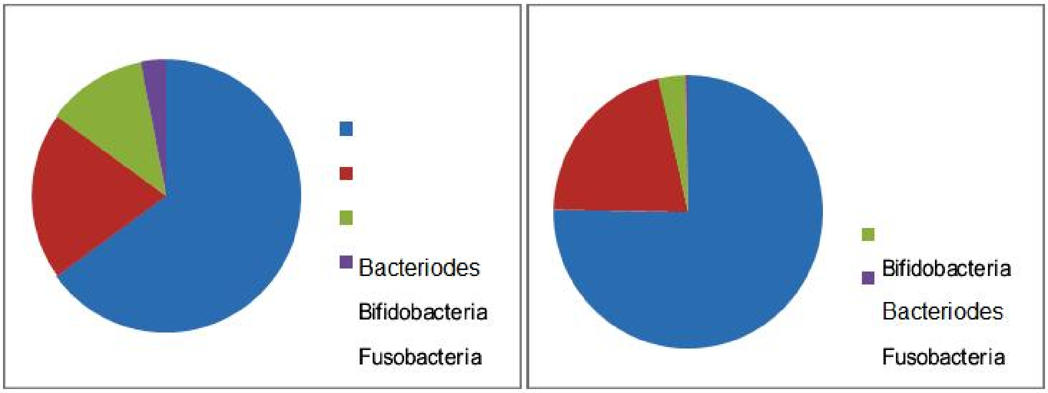

Figure 3: Increase in *Bifidobacteria* after intake of 15g/day of inulin (92. Adapted from Gibson *et al.*, 1995

Biochemical study of the fermentation process of bifidobacteria in milk

The common result of the bacterial fermentation process is lactate. It is referred to the bacteria, which produce lactate in their fermentation as Lactic Acid Bacteria (LAB). Some of these organisms require very complex nutrition, which is related to their environments such as plant, milk and intestinal of animals or humans. Lactic Acid Bacteria are strictly fermentative and some are oxygen tolerant, such as *Streptococcus*. Others are obligate anaerobes such as *Bifidobacteria* spp. but some can tolerant oxygen in the presence of carbon dioxide (CO_2) [99]. Bifidobacteria naturally inhabitants thegut of animals and humans and their sensitive to oxygen is strain related and the less sensitive strain appears to possess weak catalase activity that removes H_2O_2. Hydrogen peroxide inactivates Fructos-6-phosphate phosphoketolase F6PPK [99], a key enzyme of bifidobacteria in carbohydrate metabolism [100,101]. Bifidobacteria do not produce CO_2, Butyric or propionic acid [102]. Their optimum growth temperature is 37 °C to 43 °C, and the optimum pH is 6.5 to 7.0 [103]. Bifidobacteria also produce thiamine, riboflavin, and vitamin B and K [104,105,106,107**]**. These genera are also unique by producing the lactic acid in the form L (+)- lactic acid that easier to metabolize by infants in compare with the D (-)- lactic acid form which produced by *L. acidophilus* and *L. bulgaricus* [108]. There are three pathways has been suggested for the fermentation process of LAB of the carbohydrates tolactate.

The homofermentative pathway, which yields 2 mol of lactate per mol of glucose:
Homofermentative pathway

Glucose ⟶ Lactate

Theheterofermentative,whichyields1molofeachlactate,ethanol,andCO$_2$permolofglucose:
Heterofermentative pathway

Glucose ⟶ Lactate + Ethanol + CO_2

The bifidum pathway, which yields acetate and lactate in ratio of 3 to 2 respectively:

Bifidum pathway ⟶ Glucose + 2 lactate + 3 acetate

Bifidobacteria metabolized carbohydrate as main carbon source is through fructose-6-phosphate shunt by using Fructos-6-phosphate phosphoketolase (F6PPK), which is distinguishing bifidobacteria from *lactobacilli*. This pathway produces L (+) lactic acid and acetic acid in ratio 3:2, some species produce formic acid and ethanol aswell. Bifidobacteria utilize lactose, galactose and fructose beside glucose, and has the ability to metabolize oligosaccharides beside the simple sugars such as Inulin, FOS etc. This ability is strain related, for example it has found that *Bifidobacterium Lactis* Bb12 possessed the enzymes required to utilize somekind of sugar such as raffinose family and lactose which are unable to metabolism by other strain of bifidobacteria [109]. These enzymes which were found in most strains of bifidobacteria and not found in the lactic acid bacteria [110], *Bifidobacterium Lactis* Bb12 were found to possess the highest activity of such like enzymes which found with low activity in other strains, these enzymes such as β–glucosidase, α–glucosidase, Dglucosaminidase and *β*–galactosidase, which are very important in the fermentation process with bifidobacteria [111,109]. *Bifidobacterium Lactis* Bb12 has the ability to grow faster in milk because of possessing the highest activity of leucine aminopeptidase to help the hydrolysis ofmilkproteins,whichstimulatetheirgrowth[110,109].

CONCLUSION

Probiotics are bacteria, often called "good bacteria," found mainly in milk-based products. These products include yogurt, fermented, unfermented milk and other cultured milk products. However, in the case with fermented milk products, many times the probiotics are added after the fermentation process. While the full benefits of probiotics have not been fully explored, there are still many professionals who advocate for theiruse.

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CHAPTER: 17

A REVIEW ON SUPERHYDROPHOBICITY AND ITS MECHANISM ON DIFFERENT TEXTURE BY USING TIO$_2$ NANO STRUCTURE

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ABSTRACT

Super hydrophobicity which is a crucial and important state of the anti-wetting surface is getting much attention in the fundamental research and advanced industrial area. As the surfaces with high surface area and low surface energy are the main components to obtain super hydrophobic surfaces, nano structured materials are of great interest to attain super hydrophobicity. From different metal and non metaloxides nanostructures, TiO2 nanostructures are used in current scenario because of its high photo catalytic activity. In this present review we are going to discuss the recent trend and modification in TiO2 nanostructured based super hydrophobic surfaces of different type of materials. Further the application potential of the artificial super hydrophobic surfaces such as self-cleaning; water/oil separation and anti-fogging etc, will be discussed. In the ending, the exertion and different prospects of this fast developing field will also be concisely purposed.

Keywords: TiO$_2$ nanostructure, super hydrophobicity, Young state, wenzel state, cassie state, glass and metal surface & Application as self-cleaning agent, oil-water implant, anti-fogging, anti-icing etc.

INTRODUCTION

TiO$_2$ Nanostructured based functional materials and their application have received remarkable growing interest in various fields of science and technology.[1] In the past decades, one dimensional (1D) TiO2 nanostructures (nanorods, nanobelts, nanowires, nanotubes)were well investigated due to large surface area, ion exchange & photoelectrocatalytic activity as well as their biocompatibility.[2][3]Various strategies including hydrothermal, electro chemical an odicoxidation and template-assisted methods have been reported for the synthesis of different types of 1DTiO$_2$ nanomaterials.[4] Each strategy has its advantages and unique structural features comparison to other. Due to their specific physical and chemical properties, 1D TiO$_2$ nanomaterials are very fascinating individuals for many potential applications such as solar cells, lithium-ionbatteries, pollutant photo degradation, water splitting and antiwetting properties.[5]

In the last two decades, super-antiwetting surfaces are getting much more attention in both fundamental research as well as industrial application.[6][7]Super antiwetting surfaces such as super hydrophobic, superoleophobic and superamphiphobic due to their broad application in various fields like anti-contamination, anti-icing, emulsion separation, corrosion resistance and water-oil separation are well elaborated.[8][9]Amongall the anti-wetting surfaces, the super hydrophobic surfaces (where the water contact angle larger than 150º and sliding angle is less than 10º) have good prospects for the application in self cleaning, anti fouling and anti-fogging. Nature provides lots of examples like lotus leaves, rose petals which shows the superhydrophobic property.The self-cleaning property of lotus was found because of its structured roughnes surface in combination with the low surface energy of biological wax. Therefore, rough surface morphology and low surface energy cooperatively are two key aspects for the synthesis of super hydrophobicity of solid surfaces.[10]The current research scenario is mainly emphasizing on the preparation and theoretical designing of super hydrophobic surfaces which is evidenced by several major reviews.[11]In this regards various research groups reported number of research papers for the synthesis of super hydophobhic surfaces with bio-mimicking nanostructures of different type of transition metals and their oxides lke TiO$_2$, ZnO, Fe3O4, CuO, Ag, Au and so on.[12]

Super hydrophobic surfaces are generally fabricated through two strategies, they either modify a rough surface with low surface energy materials or roughen low surface energy surface. In this review article we will discuss the recent progress on the synthesis of different super hydrophobic surfaces such as cotton fabric, glass surface, various metal surfaces etc. based on biocompatible TiO$_2$ nanostructures. Manipulation of the chemical composition and morphology of TiO$_2$ micro/nano-structure generates a unique kind of wettibility and adhesion on TiO$_2$ based surfaces. In this way, monitoring of topography and the scale of micro- and nanostructures of TiO$_2$ based materials one can achieve different contact models which can effectively change the solid liquid adhesion.

Different Wetting States TiO_2-Based Surfaces

Wettability which is a fundamental property of interaction of various solid-liquid surfaces is mainly directed by the surface composition and roughness. The wetting behaviour of various solid surfaces can be defined on the basis of their contact angle with the liquid drops which can be further divided in static contact angle and dynamic sliding angle. Generally, the wettability is defined by the static contact angle where as dynamic sliding angle explains the solid liquid adhesion. In comparison to hydrophobic surface (contact angle is more than 90º) , superhydrophobic surfaces possess a low solid/liquid adhesion(contact angle is more than 150º) and a sliding angle less than 10°. However, the adhesion of solid-liquid surface is well explained using two conventional wetting theories: one is Young' equation [13] which well explains about the adhesion forces for smooth surfaces neglecting the roughness, heterogeneity of chemicals and dissolution while interaction of solid-liquid rough surface specifically explained by Wenzel [14]and Cassie models.[15]This adhesion is accompanying with the specific contact modes at the three phase contact line.

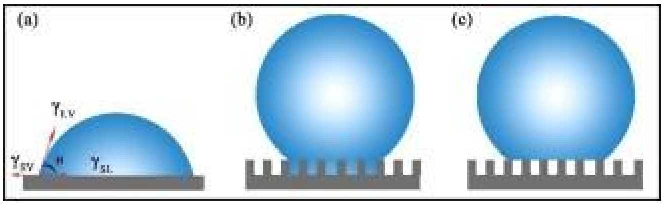

Fig. 1. Schematic illustration of three different wetting states: (a) Young state, (b) Wenzel State, and (c) Cassie state.

In case of young' equation, liquid drops tend to reach a stable state with relatively low energy when comes in contact with a solid surface, and the contact angle is measured at the edge of the droplet. So, the contact angle is an important parameter for checking the surface wettability. In case of wenzel model for the rough surfaces which have comparatively high surface area than the smooth one's, the liquid drop penetrates completely into the cavities. But the wenzel's model was only valid for the homogeneous wetting surfaces. For the heterogeneous wetting regimes Cassie and Baxter purposed aequation which state that the heterogeneous surface are composite of two fractions one is solid-liquid and other is liquid-air fraction. A mixed model of both the wenzel's and Cassie is model was purposed by Marmur[16]which was the model for the intermediate wettability state on the rough surfaces. In General, surfaces in the Wenzel state the surfaces are commonly sticky, while in theCassie–Baxterstatetheyareslippery.Inourdailylife,Cassie–Baxterstatecantransform into Wenzel state under droplet pressure, impact or vibration conditions. In actual, the two models are still challengeable to explain the real situation between liquid droplets and solid surfaces. Moreover, we mainly discuss the mechanism for TiO_2 nanostructured based composites with their unique wetting states and their respective wettability or adhesion, their applicability in practical life.

The mechanism of TiO_2 NP saction in superhydrophobicity

As the superhydrophobic surfaces can be synthesized using the Nano textured structures. However the TiO_2 is hydrophilic in nature, a variety of low surface energy molecules can be used to in combination with TiO_2 to decrease the surface free energy to get the super hydrophobic surfaces. It is well known that the cross linked polymers such as epoxy resin, polyurethane, acrylic resin, polystyrene, phenylene sulfide and polydimethylsiloxane, are a low surface free energy molecules. Various groups used these molecules with TiO_2 nano structures to create super hydrophobic coating. In general, the TiO_2exist with the hydroxyl groups which can bind different surfaces. The low surface energy molecules mostly contain a hydrophobic long carbon chain together with a hydrophilic head which can bind easily with the OH group of TiO_2. In this way the overall coating will work as a micelle formation. And the water repellant part is the long polymer chains. The below figure can show the overall review of the synthesis super hydrophobic coating.

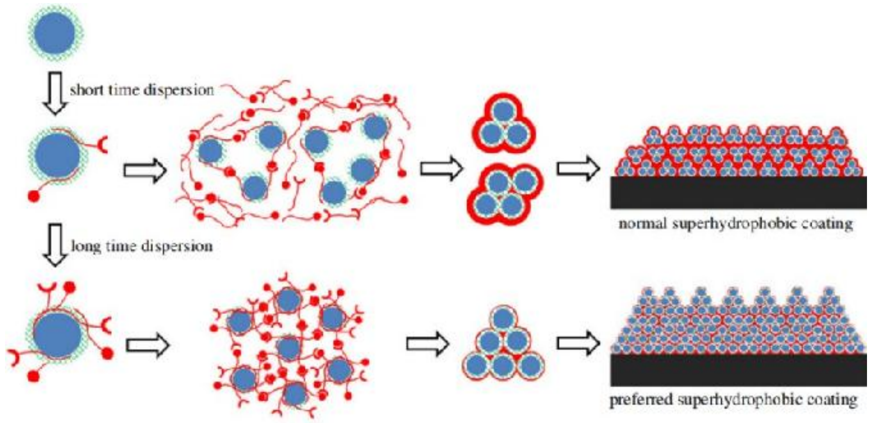

Fig. 2. Formation of Superhydrophobic surface based on TiO2nano-structures with low surface energy molecules.

Current trend in Application of TiO2 superhydrophobicity to different surfaces

TiO2 with its high stability and surface area, low cost and toxicity possess excellent Application in photo catalytic, self-cleaning, anti-corrosion etc. TiO2shows unique electronic and optical properties because of its efficiency for absorbing high energy UV light and decomposes organic molecules. TiO2by itself is hydrophilic in nature. Both these properties in combination lead to the formation of materials whose surfaces can be easily cleaned with light and water fall. TiO2surface scan show superhydrophobicity, provided a TiO2surface which is rough enough and modified with a hydrophobic self-assembled monolayer using low surface energy molecules. Various surfaces like glass, ceramics, polymers, metals and fabric can be made superhydrophobic using TiO2with low surface energy materials. Herein, the latest progress in the preparation of different superhydrophobic materials using TiO2 is explained in brief.

Cotton

Most of the research in the superhydrophobic coating synthesis is conventionalized on cotton fabric because of its real time application in synthetic industry. Currently, In 2019, Furong Tao and co-workers reported a pH-responsive TiO2@SA/CS coating with switchable wettability by simple mixing and dip coating process.[17]The water drop shows bouncing property even after hundred scrubbing cycles with a final contact angle more than 155°(**Fig 3A**). The fabric was also able to separate oil-water mixture. The method was also applicable on sponge and filter paper surfaces (**Fig4A**).In2019, K.Pi& group have reported afacile and easy method for the synthesis of superhydrophobic cotton surface using TiO2in combination with polydimethoxysilane(PDMS).[18]

The cotton fabric was then fabricated and cured with the as prepared superhydrophobic TiO2@PDMS nanoparticles. Water contact angle measurement analysis shows that the fabric shows a contact angle of 156.9°and sliding angle of 6.8° (**Fig 3B**). the coating shows a good stability in different solvents and able show super hydrophobicity in a PH range of 1-14 upto average of twenty laundering cycles(**Fig 3B**). Later on in 2020, same group reported a mild strategy to construct a dual nature (self-cleaning and oil water separation) based superhydrophobic cotton via thiol-ene click reaction.[19]in a typical strategy, the cotton surface was coated with TiO2,3-mercaptopropyl triethoxysilane (MPTS) and polyhedral oligomeric silse squioxanes(POSS) using dip-coating and thiol-eneclick reaction. The modified cotton exhibited superb superhydrophobicity with a WCA of 157.6°, which showed anti-wetting property in both water and air (**Fig 3C**). The surface was also shows high stability at high temperature of 120° and 1-13 pH range (**Fig 4C**).

In early 2019, Ali Nazari prepared a self- cleaning and antimicrobial cotton fabric using tio2 along with green walnut shell dye using dip coating method.[20] The cotton fabric obtained after the coating of TiO2 along with naturaldye was characterized by XRD and FE-SEM technology. The obtained surface showed good photocatalytic activity confirmed by photo degradation of methylene blue dye (**Fig 4D**).

A superhydrophobic coating on cotton fabricis prepared by simple immersion in TiO2 nanoparticles and perfluorodecyltriethoxysilane(PFDTS) solution by A purba Sinhamahapatra and Aditya Kumar.[21]The coating was results in superhydrophobicity property with a water contact angle of 169.3 ± 2.1° and sliding angle of 6.3 ±

2.0°(**Fig 3D**).The coated cotton fabric shows excellent self-cleaning, stain resistance, anti-water absorption, and antibacterial properties (**Fig 3E**).

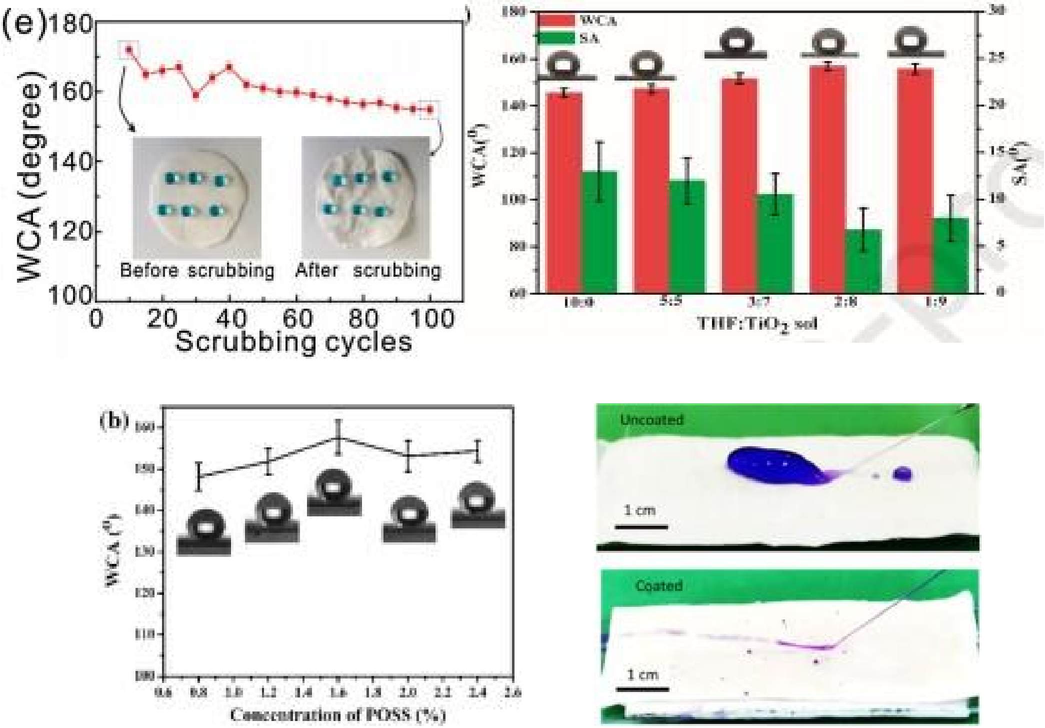

Fig. 3.(A)WCA with scrubbing test**(B)**WCA of cotton surfaces with different mass ration of THF & TiO2 **(C)** WCA changes with the concentration of POSS. **(D)** Optical image of water jet test on uncoated and coated cotton fabric

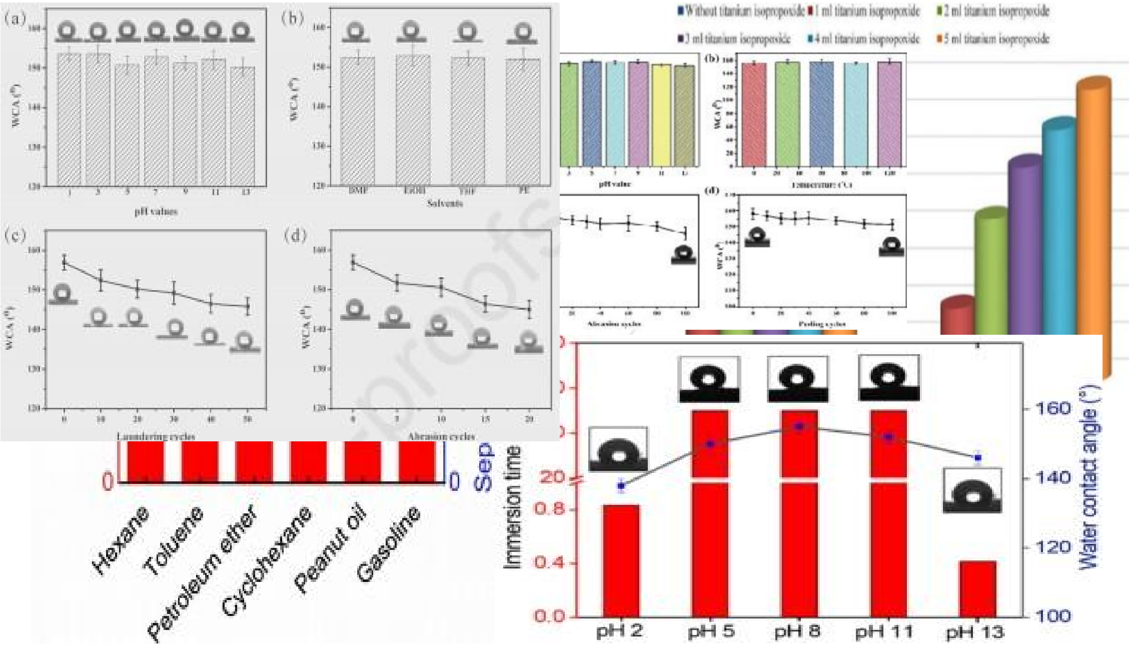

Fig.4.(A) Sepration efficiency for different water oil mixtures **(B)** WCA changes of the SCF with (a) different pH values, (b) various organic solvents, (c) launderingcycles against washing and (d) abrasion cycles.**(C)**WCA changes of the superhydrophobic cotton with (a) pH value, (b) temperature, (c) abrasion test and (d) peeling test **(D)** Photocatalytic activity of titania treated cotton fabric **(E)**retention of superhydrophobicity of coated cotton fabric in diffferent pH solutions

Glass

Glass which is one of the important material that is widely used for the window glasses of buildings, car panes, solar glasses etc.[22]However the dust particles or other pollutants on glass surface causes series of problems. Thus high maintenance cost is required to make it clean. Up to now, various methods have been developed to prepare artificial highly hydrophobic coatings. However, most of these techniques involve high cost and complexity. In the past, various groups already reported the superhydrophobic as well as transparent TiO_2 coating on glass surface to make them useful for real time application in material science. Here the current trend in the synthesis of superhydrophobic glass coating methods are explained. In 2016, Zhiguang Guo & Fuchao Yang successfully developed a facile method for the transparent superhydrophobic nanocoatings based on TiO_2/SiO_2composite gel.[23] The FTO glass substrate was spray coated with TiO_2/SiO_2gel. The superhydrophobicTiO_2/SiO_2composite nanocoatings were endowed (**Fig 5A**) with photo-induced self-cleaning nature and these antifouling coatings (**Fig 6A**) could prolong their servicelife.Inturnof2020,afacile strategy was developed to fabricate transparent ultrahydrophobic glass by Diana Vanda Wellia and co-workers using TiO_2 and octadecyltrichlorosilane (ODTS).[24]

The coating method was first deposition of TiO_2 on glass substrate and then surface modification using ODTS. The contact angle and the sliding angle of the as prepared substrate was observed to be 146º and 7º respectively(**Fig5B**).Apart from this the surfaces shows excellent self- cleaning property(**Fig6B**).

Indecember2019,YanfenHuang and group reported a facile and highly stable super hydrobhobic glass surfaces using a combination of two different nanoparticlesTiO_2/SiO_2in combination with cross linked fluorosilanes.[25]It was found that the synergic use of $TiO_2$and SiO_2 nanoparticles not only increase the roughness of the surfaces but greatly improve the stability of the superhydrophobic coating(**Fig 6C**).The contact angle and the sliding angle of water droplets with the coated glass surface was found to be 166.6° and 3.4° respectively (**Fig 5C**).

Super amphiphobic hybrid coating with excellent mechanical stability and flameretardancy was developed by Zhiguang Guo and group using fluorinated PVT polymer adhesive and highly fluorinated ammonium polyphosphate/TiO_2 (F-APP-TiO_2) particles.[26]the coated surface exhibits excellent super amphiphobicity (**Fig 5D**)due to extremely high F content and good self-cleaning, anticontamination, excellent mechanical durability, flameretardancy and self-recovery property(**Fig6D**).

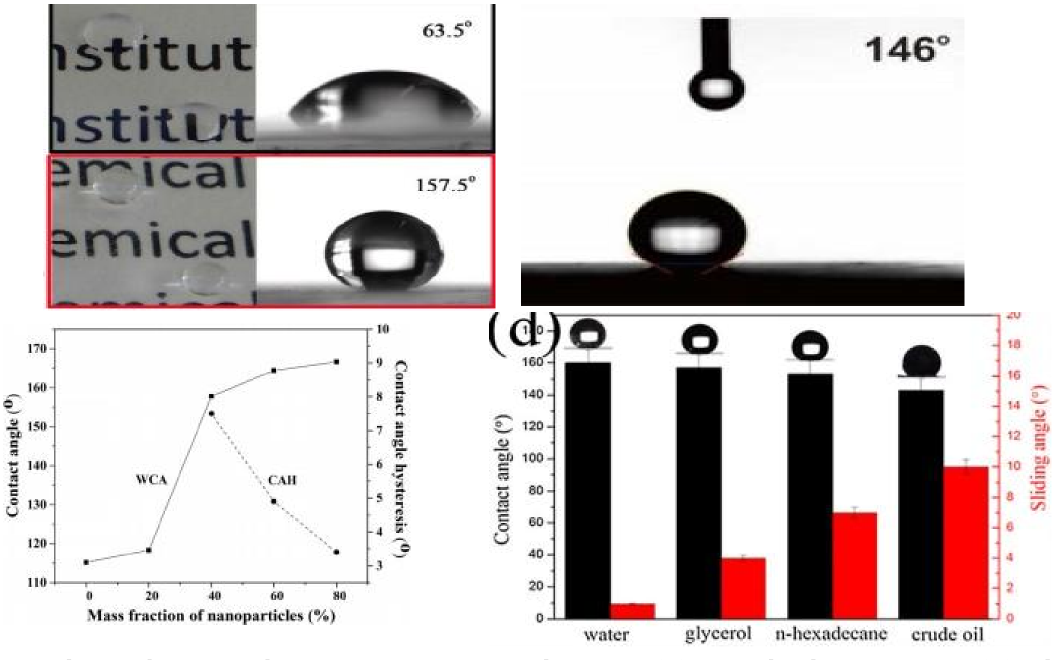

Fig. 5.(A)ITO glass without or with TiO_2/SiO_2 composite gel coatings **(B)** WaterdropletonTNC-O15.**(C)**Relation of mass fraction of total nanoparticles, WCAs and CAH **(D)** Contact angle and sliding angle diagrams of various liquids on sample

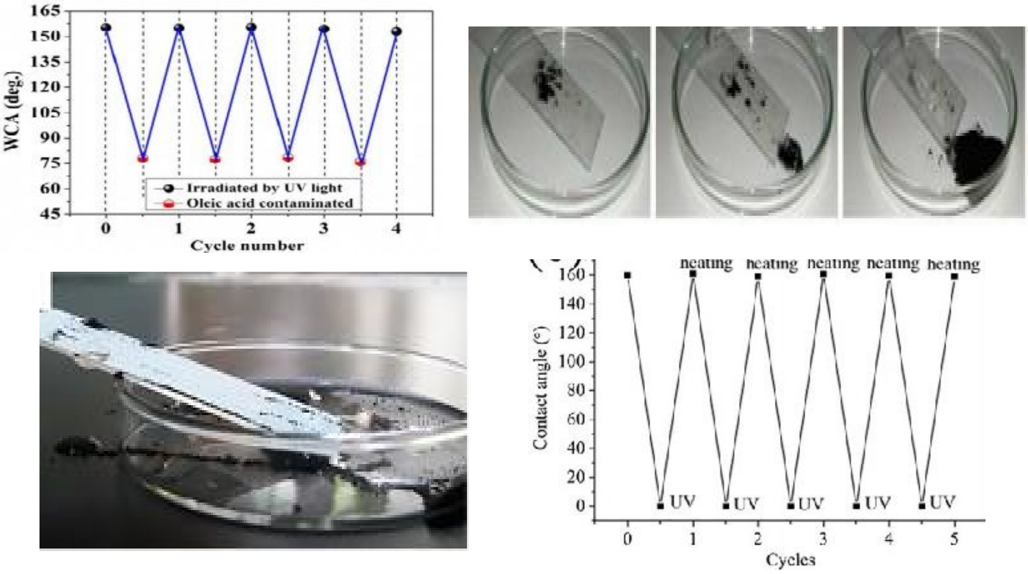

Fig.6.(A) Change in WCA of the surface with UV radiation effect**(B)**Self-cleaning phenomena of TNC- O15. **(C)** Self-cleaning action **(D)** Switchable transition of the coated glass surface between superhydrophobicity and superhydrophilicity in water

Metal surfaces

Jun Wang & co-workers reported a fabrication method for the protection of magnesium alloy using TiO2 and KKC-1(wrinkled silicon dioxide) with stability and photocataly ticproperty.[27] In a typical synthetic method the layered TiO2 prepared by hydrothermal method and wrinkled SiO2 is loaded on TiO2 using electrostatic self-assembly. After modification with stearic acid, the surface shows superhydrophobicity with a contact angle of158°and slidingangle<10°(**Fig7A**).the coating wasstable up to pH range of 1-14 and also thermally stability up to 7 days (**Fig 8A**).

Seyed Masoud Emarati & Mahdi Mozammel established TiO_2 Nanoparticle/ TMPSi(Trimethoxy(propyl)silane) ceramic composite coating for 316L steel by using electrode deposition method.[28]The polarization curve (**Fig 7B**) proved that the superhydrophobic ceramic nanocomposite coatings with water contact angle 168ºand sliding angle of 3.1º (**Fig 8B**) were able to decrease the corrosion rate of bare316L(from 12.180 to 5.621 (μm peryear)).

Song Zhao & his group reported the modified stainless steel with polyaniline(PANI) and TiO2 by nanoclusters using dip-coating method to give mesh surface with Superhydrophobic property.[29]The results shows that PANI/TiO2 modified stainless steel mesh could efficiently and effectively separate different of oil/water mixtures and also exhibit good performance in self cleaning (**Fig 7C**) and anti-corrosion property (**Fig8C**).

Luhong Zhang& group synthesized the TiO2 nanowires coated superhydrophobic stainless steel mesh with the combination of low surface energy material PFDS (1H,1H, 2H, 2H-perflorodecyltriethoxysilane).[30]The coating works with good efficiency up to 250 &is used for the different oil water mixture separation(**Fig7D & 8D**).

Xuelian Gou, and Zhiguang Guo reported a simple method to fabricate Copper mesh using CuO/TiO2and transform the minto super hydrophobic surfaces for the utilization in water harvesting.[31]The surface was coated with a low surface reagent HDTMS (Hexadecyltrimethoxysilane) by pretreatment of surface in presence of UV Ligh t(**Fig7E & 8E**).The obtained surface shows that the sample exposed for 4hUV radiation afforded a high water collection rateod 0.571g $cm^{-2}h^{-1}$.

Gary C.P. Tusi and co workers designed a novel superhydrophobic polyaniline-titaniumoxide (PANI-TiO2) coating and fabricated by (PFTES)1H,1H,2H,2H-perflfluorooctyltriethoxysilane using nano-precipitation method.[32]The developed coating was results to possess high water repellency and better anticorrosion performance than the normal epoxy coatings (**Fig 7F& 8F**).

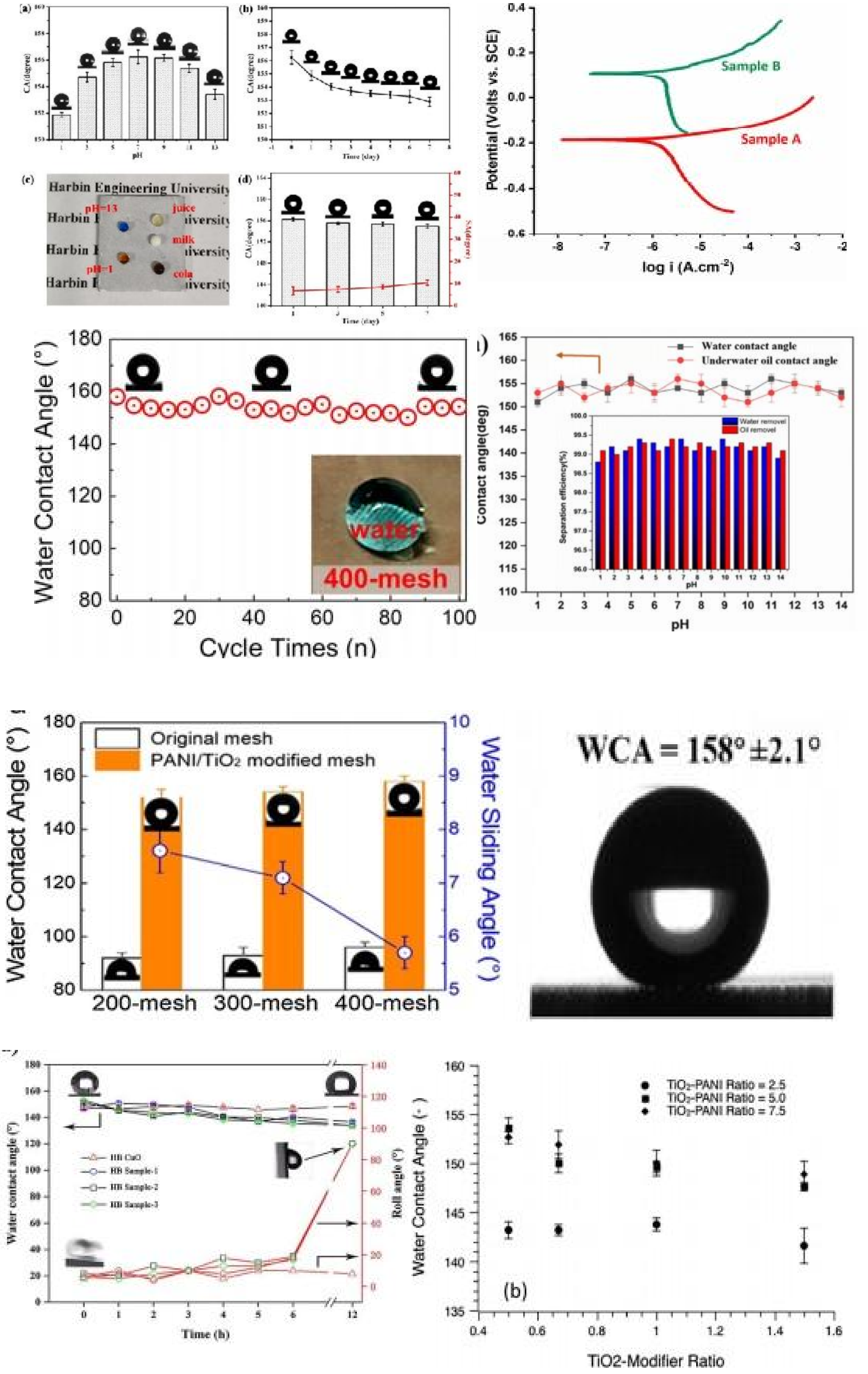

Fig. 7.(A) The contact angles (CA) & slide angles (SA) of samples using diffffferent concentration of KCC-1solution.**(B)** Water drop let on the surface **(C)** WCA of stainless steel meshes before and after modifification **(D)** contact angle of SSM@NWs-PFDS with surface.**(E)**Variation of WCA &RA for

different surfaces with UV irradiation time. **(F)** water contact angles of the coatings with different TiO2 - modifier weight ratios and TiO2-PANI weight ratios

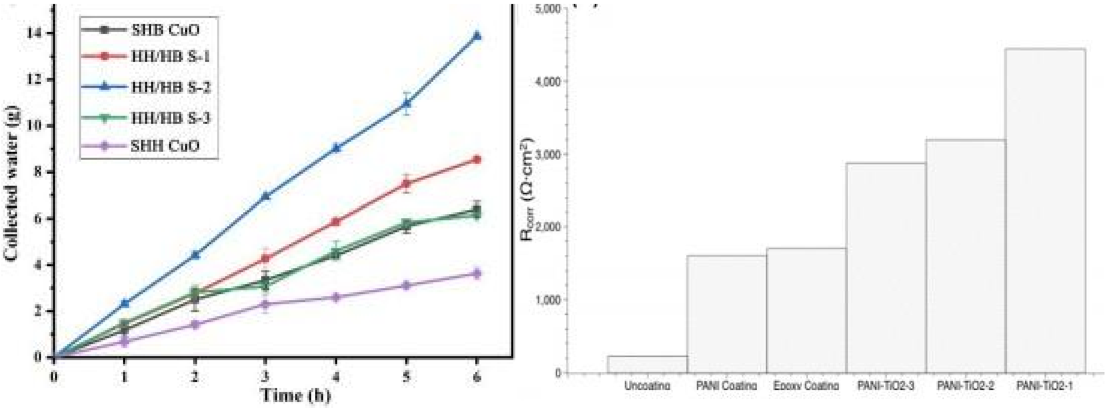

Fig. 8.(A) (a) Influence of pH on the CA of SKTA. (b) CA of SKTA immersed in 3.5 w t% NaCl(c)Droplets of difffferent liquid on the superhydrophobic surface.(d)The CA and SA of SKTA exposed to UV light for difffferent time.**(B)** Potentiodynamic polarization curve of the samples in the corrosion medium. **(C)** WCA after 100 Abrasion cycles **(D)** Influence of solution with different pH. **(E)** Dynamic variation in weight of collected water for different samples **(F)**Corrosion transfer resistance of different samples of PANI/TiO_2.

Application of Superhydrophobic surface

Wetting property of a solid is governed by geometrical and surface structure of solid. Superwetting or anti wetting derived surfaces e.g. superhydrophillic patterned superhydrophobic or superhydrophobic surface with special solid/liquid adhesion have payed more attention. Compare to other nanostructure, TiO2 nanostructured materials has been attracted more attention in research because of they are inexpensive, chemical stable and harmless and have no absorption in visible region. In spite of that TiO2being a ceramic, is very hard and resist corrosion. So, for industrial purpose, it can be a suitable candidate for use as a surface modifying material.

a) Anti-corrosion-Corrosion is one of the biggest problems of the industrial world .As a result of which hundreds of billion dollars is being used to increase research and development for corrosion resistant material. Now days, chromium containing compounds are used as corrosion resistant material but this material provides negative impact on to the environment and human. The synthetic process for making for superhydrophobicity is direct coating on to the surface solid. Recently, various metal surfaces such as Al,Cu, Fe, Ti, Zn ,alloy and steel is used as for making corrosion resistive surface.

M Zhang et. al pod like KCC-1/TiO2 superhydrophobic surface on AZ31 Mg alloy by immersion technique. In other research paper a series of superhydrophobic surface was synthesized by using fluoro alkyl silane modifications.

B) Anti-icing- Accumulation of ice onto the surface of substrate can create difficulties in function of ships, airplanes, highways, power lines etc. Superhydrophobic surface have been employed to develop barrier of wet snow, ice or frost onto the surface. Tourkine et. al investigated the development of water resistance behaviour with delayed deicing ability. Therefore, there are two state which shows superhydrophobic behaviour

(1) Cassie State (2) Wenzel model

The second one state, generates remarkable anti-fogging, large slip and reduced adhesion.

Navedsharifiet.Alsynthesizedtheanti-icingsurfacebytheuseofTiO2.Inthis process

coating sample were prepared in stearic acid solution by suspension plasma spraying TiO2 which shows superhydrophobic behaviour with a contact angle 170 sliding angle 1 and contact angle hysterisis [33]

Karim et al worked to make rough surface by the use of vertically aligned TiO2 nanofillers (VATiO2NPIS). The VATiO2NPIs were coated on Al surface using epoxy resin adhesive during anodization.

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CHAPTER: 18

ROLE OF IRON-PHENOLIC ACID INTERACTION IN COLOUR DEVELOPMENT DURING SUGAR PROCESSING - A REVIEW STUDY

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ABSTRACT

This paper reviews the iron polyphenols interaction which cause to the colour formation during the sugar processing. The chemical structure of various phenolic acid which presents in sugar cane juice are interact with the Fe(III) through chemical reaction or by changing conditions which results in the various colourant formation during sugar formation are described. The uptake of iron by plants depends considerably on the presence of both complexing and reducing reagents. These colour complex impacts on the sugar quality and the effect on the value of the sugar in the market is significant. This study helps in the reduction of colour and provides antioxidants as a by-product during sugar processing.

Keywords: Fe(III), syringic acid, complex, colour formation, activation energy

Introduction

In mass quantity terms colorants in sugar and sugar products are a very small quantity but their impact on sugar quality and the effect on the value of the sugar in the market is significant. Gillet [1] reports that only 17% of the 1% of organic nonsugars in cane juice are colorant components. Colour is one of the most important quality criteria for sugar; the lower the colour value the higher the quality of the sugar. Colour formation also has a negative aspect on final molasses where due to the reaction products formed the assimilable nitrogen reduces and 'unfermentable' are formed [2].

India is known as the original home of sugar and sugarcane. Indian mythology supports the above fact as it contains legends showing the origin of sugarcane[1]. India is the second largest producer of sugarcane next to Brazil. Presently, about 4 million hectares of land is under sugarcane with an average yield of 70 tonnes per hectare. Sugar cane is the significant karif crop in India shown in Fig. 1. India is second greatest producer of sugarcane in whole world and list of ten biggest sugar and sugarcane producing state in India.

Fig.1. sugarcane crop

Table 1.List of ten biggest sugar and sugarcane producing state in India.

S.N.	State	Suger (Lakh Tons)	area sugarcane cultiv-ation in (Lakh Hectares)
1.	Uttarakhand	64.32	1.2
2.	Punjab	66	0.9
3.	Haryana	93.4	1.3
4.	Gujarat	95.3	1.8
5.	Bihar	122	2.6
6.	Andhra Pradesh	149	2.0
7.	Karnataka	346	4.0
8.	Tamil Nadu	375	2.3
9.	Maharashtra	775	9.0
10.	Uttar Pradesh	1,333	21.0

India is the largest single producer of sugar including traditional cane sugar sweeteners, khandsari and gur equivalent to 26 million tonnes raw value followed by Brazil in the second place at 18.5 million tonnes. Sugarcane

(Saccharum afficinarum) is one of the important agro industrial crops in our country [2, 3]. The earliest record on the cultivation of sugarcane in India as available in the Hindu literature is about 3000 years old and the crude sugar was developed by 400 B.C[2]. Over the centuries, sugarcane cultivation methods, area and production have undergone innumerable changes in this country [4]. At present sugar industry is a second largest agro-based industry in India. Among sugar producing plants, sugarcane is responsible for about 70% of the world sugar production; the reaming 30% is coming from sugarbeet, a temperate zone crop. Sugarcane cultivated mainly in tropics though, it is also grown in sub-tropical area in India [5]. Sugarcane crop plays a vital role in the national economy, since; it is one of the most commercial crops for the extraction of sucrose. Sugar industries play a major role in Indian economy. The progress of the rural India is more or less related to progress of sugar mills [6].

The colour of sugar (fig.2) is most important commercial attribute and sugar mills are spending many resources to comply with the market requirements on the colour of their product [7]. When one say “colourant” he means, the material causing the colour [8]. Pure sucrose has no colourant but it appears colourant due to inclusions of a plenty of complex compounds.

Fig.2. Indian sugar

Hence the colourant is the generic term used to cover a variety of components which contributes to the colour of the sugar. The sugar colourants are very extremely complex in nature and not easy to quantify.There can be a variety of sources from where the sugar colourant originates but mainly they can be summarized in two major sources as under [9].

Phenolic compounds in sugarcane juice are partially responsible for its colour [3]. The basic chemistry of iron polyphenol coloured complex formation depends upon the number of phenolic group and their relative positions onto benzene moiety.Iron, the most abundant transition metal, is essential for oxygen transport and many redox reactions. Only slight disturbances to the delicate balance between iron intake and iron loss can push the body into conditions of iron overload or iron deficiency. Phenolic acids are capable of forming Fe(III) complexes and have been generally associated with a negative effect on the absorption of non-haem iron in humans [4, 5]. The caffeic and chlorogenic acids have cis-phenolic groups and are capable of forming chelates with Fe(III). Naringin is also capable of forming a six-membered ring chelate with Fe(III) while quinic, ferulic and sinapic acids do not appear to form such species. The catechol functional group has been identified as a component of many siderophores [6]. Phenolic acids are also of great interest because their redox properties affect the availability of micronutrients to plants [7]. The uptake of iron by plants depends considerably on the presence of both complexing and reducing reagents. Chlorogenic acid is one of the major polyphenol compounds found in numerous plant species [8].The review of the literature [9] revealed that some work has been reported employing a dilute solution of sugar and its allied products with different salts of iron with an object to understand complex formation. Therefore, it was considered necessary to study the influence of redox behaviour of iron-polyphenol interaction on colour development in sugar manufacturing. Reactions between Fe(III) and polyphenol based ligands are also of interest because of the possible role of plant-derived phenolics in mobilisation of iron in acidic soils.[10]. This paper reports the solution structure of the Fe(III) phenolic acids interactions. Because the metal ion coordination resulted in simultaneous deprotonation of the phenolic functions of the aromatic ring, the spectra of the formed metal species resembled those of the anions of the parent molecule, with a bathochromic shift due to the metal ion [17]. The kinetics and mechanism of Fe(III) with various polyphenolic compounds have been investigated [18] and it has been reported that caffeic and chlorogenic acid are generally consistent with the formation of a 1:1 complex that subsequently decays through an electron transfer reaction. However, in the present case, attempt has been made to corroborate the experimental findings by theoretical study of the isolated complex. Objective of the present study, therefore, is to substantiate the mechanistic aspects of the interactions between Fe(III) and phenolic acid employing colour formation in sugar processing.

1.2. Composition of sugar cane juice

Sugarcane juice is an opaque and viscous liquid which is brownish to dark green in colour that is obtained by pressing the cane stalk. Sugarcane juice is an aqueous solution that circulates in the living plants and carrying material required for growth and metabolism. Sugarcane juice is mainly processed in sugar, but the maximum part of the production goes to human consumption as fresh juice or alcohol. Sugarcane juice is an energy-rich food. Sugarcane is an abundant and relatively low-cost agricultural resource, largely produced in tropical and sub-tropical regions of the planet. This raw material contains about 80–85% of water and its dry matter presents an average composition of approximately 30% sucrose and 70% pre-processed lignocellulosic materials [Amalraj, 2008].Pigments are naturally occurring compounds present in sugarcane and other plants. Duringsugarcane crushing, the extracted pigments constitute the juice's non-sugar portion whichultimately impairs the white sugar production process [Diego Matos Favero *et. al.*, 2014].Flavonoids are a critical group for sugar processing since they cause up to 30% of the raw sugar colour when the sugar is produced at pH 7.0. Anthocyanins, which belong to the flavonoids group, produce a red and blue colour respectively in an acid and alkaline medium [Bourzutschky, 2005].

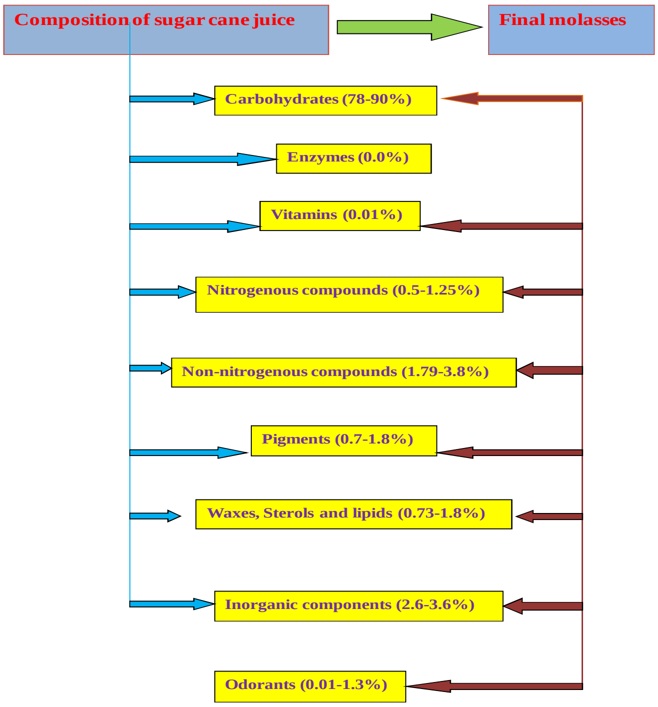


Fig.1. Flowchart showing composition of sugar cane juice

Sugar cane contains phenolic acids, polyphenols, and flavonoids [Parr, A. J.; Bolwell, G. P, 2000; Fuhrman, B.; Aviram, M. 2002; Manach, C.; Mazur, A.; Scalbert, A.2005; Favier, 2005; Moure, 2001; Antolovich, 2000]. These compounds have also been found in sugar products such as syrup or molasses and in the brown sugars themselves [Balasundram, 2006; McGhie, 1993]. Composition of sugarcane (*Saccharum officinarum*) juice were identified and quantified by analytical high-performance liquid chromatography and photodiode array detection, showing the predominance of flavones (apigenin, luteolin and tricin derivatives), among flavonoids, and of hydroxycinnamic, caffeic and sinapic acids among phenolic acids [Joaquim Maur Icico Duarte –Almeida et, *et.al.* 2006].

1.3. Colouring pigments present in Sugar cane juice

The types and amounts of pigments in sugarcane juice are dependent on a number of factors such as the variety and maturity of the raw material, climatic conditions, agricultural practices, time between cutting and processing, thequantity of impurities, soil conditions and grinding types. Sugarcane contains many colourant compounds that could be extracted from its juice [Rupa T R, 2008]. In 1971, a study on sugarcane juice identified chlorogenic acid, cinnamic and flavones as coloured compounds [Farber *et. al.*, 1971]. Those coloured substances (pigments) are derived from plants and can be found in raw sugar after processing [Bourzutschky, 2005]. The presence of a several colourant compounds, such as chlorophylls [Jangpromma *et.al.*,2010; Patil *et. al.*, 2014; Qudsieh *et.al.*, 2002], have been described for agricultural and food chemistry aspects, however, the literature has widely described chlorophylls [Streit *et.al.*, 2005]. Other coloured substances described are anthocyanins, flavonoids

[Li *et. al.*, 2010; Colombo *et.al.*, 2006; Colombo *et. al.*, 2009; Mabry *et. al.*, 1984] and phenolic acids [Duarte-Almeida et.al., 2006; Duarte-Almeida *et. al.*, 2011; Leal *et. al.*, 1994; Santiago *et. al.*, 2009; Singh *et.al.*, 2015]. Sugarcane pigments are mostly chlorophylls, carotenes, xanthophylls and flavonoids. The first three pigments are insoluble in water are easily separated during cane juices clarification [Farber and Carpenter, 1972].

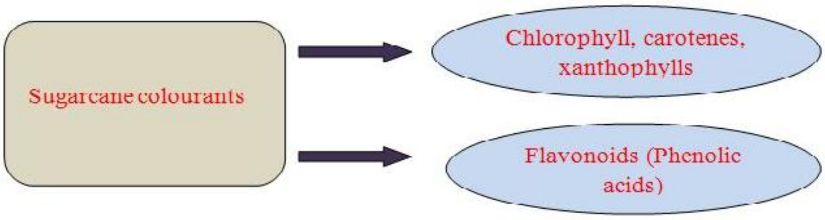


Fig. 2. Classification of colourant present in sugar cane juice

The colour development during the processing

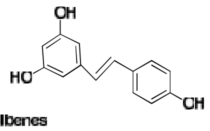
The majority of such colourants is formed from the following two types of chemical reactions:
(i) The colour formed due to the Alkaline Degradation (Hexose Alkaline Degradation Product) and Melanoidins –type material resulting from reaction of amino acids and reducing sugars. These are formed comparatively at low temperature and high pH.
(ii) Caramel type colour products, which are produced by thermal degradation of sucrose and reducing sugars, triggered on high temperature[4, 11].

Phenolic compounds

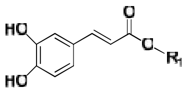
Phenolic compounds are extremely diverse. For example, phenolic diterpenes such as carnosol and rosmanol have been identified in herbs and spices [12] while the main phenolic constituents of soybean are isoavone glycosides [13] plus several phenolic acids including chlorogenic, caffeic acid, syringic and ferulic acids. These same phenolic compounds are found in most fruits and vegetables [14].

- These are Present in plant as Esters. The most common phenolic ester in cane ischlorogenic acid, an ester of caffeic acid with quinic acid Ranges from colourless to yellow [15].
- Phenolic compoundsJuice continue come in contact with metallic iron surfaces and tend to increase intensityof colour due to absorption of iron salts. These form dark coloured polyphenols with Iron inferric state especially in acidic medium [16].
- Melanin is reaction product of amino acids with phenolics as well as very dark enzymaticproducts of phenolics. (Godshall). They have detrimental effect on colour of sugar as theycrystalizes with sugar [17].

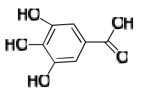
Phenolic compounds (Fig.3 and 4) form one of the main classes of secondary metabolites with a large range of structures and functions, but generally possessing an aromatic ring bearing one or more hydroxy substituents [13].



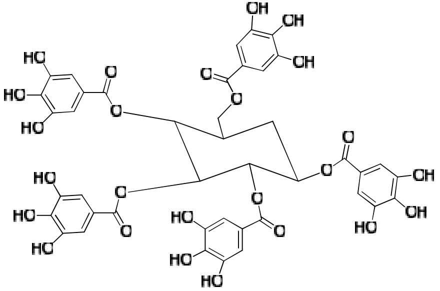
Stilbenes
1, Resveratrol (colorless)



Hydrooxycinnamic acid
2,R1-Quimic acid Chlorogenic acid (Colorless)



Hydroxybenzoic acid
Gallic acid (Colorless)



Gallotanninc
β-pent-O-galloyl-D-glucose (Colorless)

Fig.3. Non flavonoid polyphenols

In particular, a number of compounds, for example, cinnamic acid, elenolic acid, shikimic acid and quinic acid are treated in the present discussion as phenolics because of metabolic considerations although they lack a phenolic group or even an aromatic ring [18]. Plant phenols have been classified into major groupings distinguished by the number of constitutive carbon atoms in conjunction with the structure of the basic phenolic skeleton. The most wide spread and diverse of the phenolics are the favonoids which are built upon C_6-C_3-C_6 flavone skeleton in which the three-carbon bridge between the phenylgroups is commonly cyclised with oxygen [19]. Several classes of flavonoid are differentiated on the degree of unsaturation and degree of oxidation of the three-carbon segment. Phenolic derivatives (benzoic, cinnamic and caffeic acids) are highly reactive and formcoloured complexes with iron by redox reaction [20]. They can also polymerize enzymatically to form colourcomplexes in the early stages of processing before heating [21].

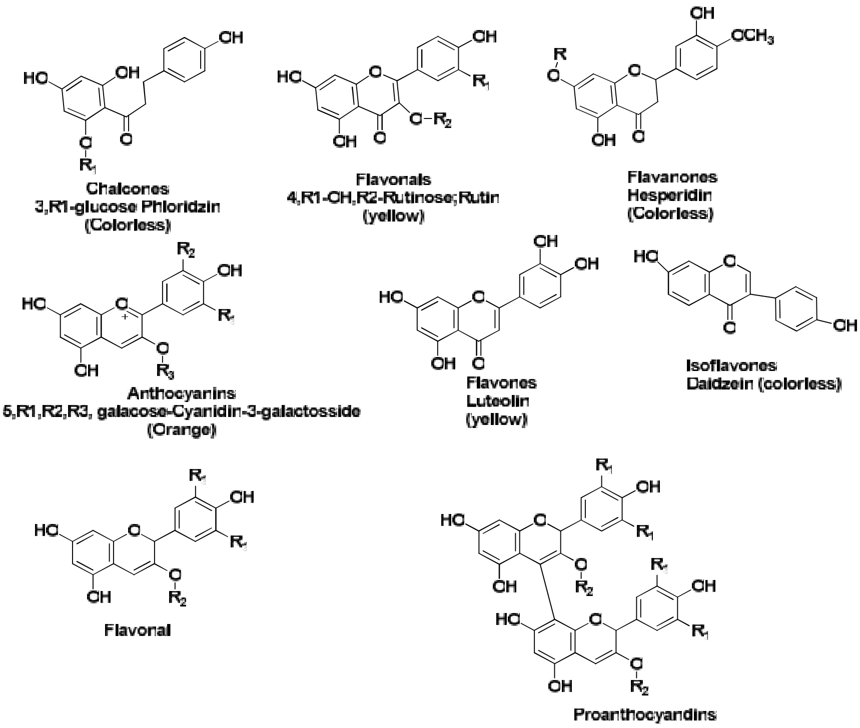


Fig.4. Showing structure of different type of flavonoids polyphenols

Chvatalova et.al, investigated the effect of dietary phenolic acids on the oxidation of Fe2+ caused by molecular oxygen. All phenolic acids bearing 3,4-dihydroxy (catechol) or 3,4,5-trihydroxy (galloyl) moiety formed chelates with ferric iron and significantly increased the rate of Fe^{+2} autoxidation. The carboxylate group and catechol substitution instead of galloyl moiety facilitated the ferrous ion oxidation more effectively. Caffeic acid and protocatechuic acid, the strongest accelerators of Fe^{+2} autoxidation, were able to facilitate autoxidation at concentrations lower than 1% of the initial amount of Fe^{+2}. Therefore chelates of these catecholic acids with iron displayed ferroxidase-like activity. Conversely, when we started from ferric ions, catechols partially formed ferrous ions in the presence of ferrozine. Thus, catecholic acids formed stable chelates with iron, in which ferric ion is the dominant species, but the redox cycling of iron between Fe^{+2} and Fe^{+3} in chelates probably plays a crucial role in the catalysis of ferrous iron autoxidation. Interestingly, 3-hydroxybenzoic acid, 4- hydroxybenzoic acid and vanillic (4-hydroxy-3-methoxybenzoic) acid protected ferrous ions from autoxidation as effectively as ascorbic acid and cysteine. These monophenolic acids, differently from ascorbic acid and cysteine, were not able to reduce ferric ions. Syringic (3,5-dimethoxy-4-hydroxybenzoic) acid did not alter the redox state of iron, only in a large excess over metal, syringic acid slightly inhibited ferrous ions autoxidation and partially reduced ferric ions. Therefore, the effects of syringic acid at high concentration were similar but much lower to those of ascorbic acid and cysteine. The biological importance of ferroxidase-like activity of polyphenols, especially the influence on iron absorption, is also discussed [22].

Wang et.al, were the performed Screening of potential antioxidant activities of water and 70% acetone extracts from ten species of Icelandic seaweeds using three antioxidant assays. Significant differences were observed both in total phenolic contents (TPC) and antioxidant activities of extracts from the various species evaluated using 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activity, oxygen radical absorbance capacity (ORAC) and ferrous ion-chelating ability assays. Acetone extracts from three Fucoid species had the highest TPC and consequently exhibited the strongest radical scavenging activities. High correlation was found between TPC of seaweed extracts and their scavenging capacity against DPPH and peroxyl radicals, indicating an important role of algal polyphenols as chain-breaking antioxidants. However, water extracts generally had higher ferrous ion-chelating activity than 70% acetone extracts and no correlation was found with their TPC, suggesting that other components such as polysaccharides, proteins or peptides in the extracts were more effective chelators of ferrous ions than phenolic compounds [23].

The understanding of redox reaction of iron in cane juice during manufacturing of sugar is qualitatively understood. Iron in aqueous solution is usually present in Fe (III) form. However, it is reduced to Fe (II) state by various known and unknown species present or deliberately added in the cane juice during pre and post clarification [24]. Reducing action of sulphide being relatively non-permanent, the oxidative enzymes may oxidise hydroxyl group of sugar into a series of dark colour compound which are detrimental to sugar quality [25]. The review of literature revealed that some work has been reported employing dilute solution of sugar and its allied products with different salts of iron with an object to understand complex formation. However, the detailed investigation of deliberately added iron in to sugar crystal has not been studied so far [26]. Therefore, it was consider necessary to study the influence of redox behaviour of iron-polyphenol interaction on colour development in sugar manufacturing [27, 28]. Though the polyphenol are present in very minute quantities (60-150 ppm) and cannot be removed completely by convention clarification process. The basic chemistry of iron polyphenol coloured complex formation depends upon the number of phenolic group and their relative positions onto benzene moiety.Iron, the most abundant transition metal in man, is essential for oxygen transport and many redox reactions. Only slight disturbances to the delicate balance between iron intake and iron loss can push the body into conditions of iron overload or iron deficiency. Phenolic acids are capable of forming iron (III) complexes and have been generally associated with a negative effect on the absorption of non-haem iron in humans[26, 28]. The caffeic and chlorogenic acids have cis phenolic groups and are capable of forming chelates with iron (III). Naringin is also capable of forming a six-membered ring chelate with iron (III) while quinic, ferulic and sinapic acids do not appear to form such species. The catechol functional group has been identified as a component of many siderophores [29]. Phenolic acids are also of great interest because their redox properties affect the availability of micronutrients to plants [30]. The uptake of iron by plants depends considerably on the presence of both complexing and reducing reagents. Chlorogenic acid is one of the major polyphenol compounds found in numerous plant species [31].Due to its high sucrose content and low fibre content, sugarcane is one of the important industrial crops of the world. It is principal raw material for the sugar industry as 70% of the world's sugar comes from sugarcane. Besides sugar production, large number of population in the tropics and subtropics relishes its juice, and consume raw cane. In the Indian system of medicine, chewing raw sugarcane is recommended for sound and healthy body. Both the roots and stems of sugarcane are used in Ayurvedic medicine to treat skin and urinary tract infections, as well as for bronchitis, heart conditions, loss of milk production, cough, anaemia, constipation as well as general debility. Some texts advise its use for jaundice and low blood pressure [32]. Phenolic compounds in sugarcane juice are partially responsible for its colour [33] The major flavonoids in sugarcane are flavones, such as naringenin, tricin, apigenin and luteolin derivatives [34]. Tricin has recently been found to interfere with murine gastrointestinal carcinogenesis and may be considered safe enough for clinical development as a cancer chemopreventive agent [35].

In a 1996 report, [36] showed the presence of five antioxidant compounds in a *kokuto* extract, followed by reports, [37] on the isolation of several glycosylated phenolic compounds from the same natural extract. Kokuto is a food product similar to Brazilian rapadura, is highly appreciated as a candy and consisting of a block of raw brown sugar, made from concentrated sugar cane juice. In addition, they [38] found antioxidant activity in different samples of cane brown sugars and proposed various phenolic acids and flavonoids compounds to be at least partially responsible for the observed activity. However, the statistical correlation between phenolics. Content and antioxidant activity was low. Hence, the authors suggested on the possibility of other metabolites to be also involved, possibly, those formed during the sugar production. Thus, although phenolic entities in sugar cane can act as antioxidants, data on its actual polyphenolic composition is scarce and very little is known about its antioxidant activity [26]. Flavonoids are a group of naturally occurring antioxidants and iron chelators, which are widely available in the food we consume, thus their interactions with iron (III) and possible involvement in the absorption of iron are of interest. Flavonoids have been generally associated with a negative effect on the absorption of non-haeme iron in humans [28]. Flavonoids play an important role in the body's antioxidant system. Their ability to reduce the effect of this free radical assault is partly due to their free radical scavenging ability[39] and also due to the fact that they are capable of supplying specific chelators, which are capable of binding any available iron, thus greatly reducing its bioavailability. The antioxidant effect which flavonoids provide arises partly from the specificity of their interaction with iron (III). Reactions between iron (III) and polyphenol based ligands are also of interest because of the possible role of plant-derived phenolics in mobilisation of iron in acidic soils [40]. The astringency (feeling of extreme dryness in the palate) of certain foods and beverages is due to the interactions between polyphenols and proline-rich proteins[41, 42]. Epidemiological studies have shown a relationship between high dietary intakes of phenolics and reduced risk of cardiovascular disease and cancer[43]. Growing evidence suggests that oxidative damage caused by the b-amyloid peptide in the pathogenesis of Alzheimer's disease may be peroxide mediated. Many polyphenols possess stronger neuroprotection against hydrogen peroxide than antioxidant vitamins. Recent reports show that a diet rich in fruit and vegetable juices can significantly reduce the incidence of Alzheimer's disease [44]. Phenolic compounds, commonly referred to as polyphenols, are naturally occurring chemicals present in all plants and thus are part of our diet. They are our largest source of external antioxidants. Over 8000 phenolic structures have been identified that vary structurally from simple molecules to highly polymerized compounds. More than 10 classes of polyphenols have been defined on the basis of chemical structure with the flavonoids being the most common polyphenolic compounds present in plant food [45]. Polyphenols are plant secondary metabolites consisting of hydrolyzable and condensed forms. Tannic acid (TA), which is part of the first group, has a structure consisting of a central carbohydrate (glucose) and 10 galloyl groups. It occurs in the bark and fruits of many plants. Tannic acid and other polyphenols have antimutagenic, anticarcinogenic and antioxidant activities, but the mechanisms involved in these activities are not completely understood. Polyphenols are OH radical scavengers because phenolic groups are excellent nucleophiles and are also able to quench lipid peroxidation, acting as chain break antioxidants [46] Literature survey suggest that in spite extensive data on colour complex formation between polyphenols and iron salts, the detailed investigations of deliberately added ferrous, ferric iron in sugar crystal has not been studied so far. Therefore, it was considered necessary to study the influence of iron-polyphenol interaction on colour development in sugar. It is hoped that such reaction will be truly identical to electron transfer reaction. The result is expected to provide relevant mechanistic information regarding common electron transfer reaction, involving solid, moist and solution phase and which can be extended to other systems of significant importance. The role electron transfer reaction in catalysing colour formation in sugar system where polyphenol play important role in approached which of high technical importance.

The kinetics study of reactions of Fe(III) with phenolic compound

Hynes et.al investigated that The kinetics and mechanisms of the reactions of iron(III) with the hydroxy cinnamic acid based ligands caffeic, chlorogenic, sinapic and ferulic acids and the flavonoid naringin in aqueous solution. The mechanisms for caffeic and chlorogenic acid are generally consistent with the formation of a 1:1 complex that subsequently decays through an electron transfer reaction. On reaction with iron(III), ferulic and sinapic acids undergo an electron transfer without the prior formation of any complex. There was no evidence of electron transfer occurring in the complex formed when iron(III) is reacted with naringin. Rate constants for k1 (formation) and k1 (dissociation) have been evaluated for the complex formation reactions of $[Fe(H2O)_6(OH)]_2$þ with caffeic acid, chlorogenic acid and naringin. Analysis of the kinetic data yielded stability constants, equilibrium constants for protonation of the iron(III) chlorogenic acid complex initially formed, together with the rate constants for complex decomposition through intramolecular electron transfers and in the case of caffeic acid and chlorogenic acid, rate constants for the iron(III) assisted decomposition of the initial complex formed [27].

Kaman Singh and Ajay Kumar were investigated kinetic study on the complexation of syringic acid with Fe(III) was described in aqueous solution at pH 9.0 by experimentally and theoretically. The complexation reaction was found to be a first-order with rate constants for k_1 (formation) $3.67x10^{-2}$ min^{-1}. Additionally the effect of concentration and temperature on the complexation reaction was investigated. The results obtained from each method were correlated with each other and consistency in all methods was observed. The isolated complex was stable at pH 9.0. The apparent activation energy of the complexation reaction was evaluated to be 168 kcal/mol[47].

Gessa et.al were studied the The transfer of several metal ions from the soil to the plant absorbing cells is mediated principally by organic molecules of low molecular weight with complexing and reducing activity, among which caffeic acid (CAF) is particularly important. Here we report the results of a survey which deals with the oxidation of CAF by the Fe(III) ions bound to a polygalacturonate network (Fe(III)-PGA network). The interaction between Fe(III) and CAF was studied by using Fe(III)-PGA networks equilibrated in the 2.4-7.0 pH range by means of kinetic and spectroscopic methods. The reducing power was found to depend on the nature of the Fe(III)-PGA network complexes [48].

Kaman Singh and Ajay Kumar investigated the colour formation study of the complexation of chlorogenic acid with ferric chloride was performed using UV–Vis absorption spectroscopy. The colour complexation reaction was found to be a first-order with rate constants for k_1 (formation) 2.4×10^{-2} min^{-1} for chlorogenic acid. The effect of concentration and temperature on the complexation reaction was also investigated. The apparent activation energy of the complexation reaction was evaluated to be 0.085eV [49].

Chelation properties of polyphenols

Phenolic acids are aromatic secondary plant metabolites broadly distributed throughout the plant kingdom. Phenolic compounds confer unique taste, flavour, and health-promoting properties found in vegetables and fruits [Tomas-Barberan, 2001]. The term “phenolic acids”, in general, designates phenols that possess one carboxylic acid functionality, moreover the reason for including phenolic acids in the family of plant polyphenols lies in the fact that they are bio precursors of polyphenols and, more importantly, they are metabolites of polyphenols. Naturally occurring phenolic acids contain two distinctive carbon frameworks: the hydroxycinnamic and hydroxybenzoic structures. Hydroxycinnamic acid compounds are produced as simple esters with glucose or hydroxy carboxylic acids. Plant phenolic compounds are different in molecular structure, and are characterized by hydroxylated aromatic rings [Mandal, 2010]. Quercetin (3, 30, 40, 5, 7-pentahydroxyflavone) is one of the most common flavonols present in nature that has attracted the attention of many researchers because of its biological and pharmaceutical properties [Cornard, Merlin, 2002]. A multitude of substitution patterns in the two benzene rings (A and B) of the basic structure occur in nature and variations in their heterocyclic rings give rise to flavonols, flavones, catechins, flavanones, anthocyanidins and isoflavones. Over 4000 different naturally occurring flavonoids have been described and this list was still growing. Quercetin ($C_{15}H_{10}O_7$) is a flavonoid of the flavonol type that contains five hydroxyl groups in positions 3, 30, 40, 5, 7 and a carbonyl group in the fourth position. Owing to these features, quercetin easily forms complexes with many metals. A great number of flavonoids, especially flavones, can efficiently chelate metals like Al(III), Fe(II), Fe(III), Cu(II), or Zn(II). Formation of metal complexes play important and multiple roles in biological systems and provide sensitive colour stabilisation mechanisms in vivo in higher plants [Kuntic *et. al.*, 1998; Markovic, *et.al.*, 2009; Panhwar *et. al.*, 2010; Sun *et. al.*,2008]. Quercetin complexing capacity, widely used for elucidating the structure of natural flavonoids, can also contribute to the bioactivity of these compounds, by acting as carriers and regulators of metal concentration [Castro, 2004; Marinic *et.al.*, 2006. Redox reactions are also observed through the change of the oxidation state of the metal, jointly with the oxidation of the flavonoids by the loss of hydrogen [Panhwar *et. al.*, 2010]. In this sense, the use of chelated metals in oxidation process became a promising technology. By definition, chelation requires the presence of two or more atoms on the same molecule capable of metal landing. Oxygen, nitrogen, and sulphur atoms of molecules are most commonly the metal ligands. Chelators in which oxygen atoms serve as the ligand of iron tend to stabilize Fe(III), thus decreasing the reduction potential of the iron [Miller *et.al.*, 1990]. As reported [Bucher *et.al.*, 1983], the autoxidation of some iron chelates produces a powerful oxidant, which is stronger than the hydroxyl radical. For instance, the oxidation of methanol using iron chelates does not directly depend on the hydrogen peroxide used, since is believed that ferryl species are formed during oxidation. These species are able to oxidise high reduction potential compounds as methanol. Other authors suggest the possibility of formation of iron-oxo complexes during the process or a Fe(III)-hydroperoxo complex. Therefore, this simple method could be applied to the degradation of refractory organic compounds such as aromatic compounds, like phenol [Bianchi *et. al.,* 2003]. Caffeic acid is a multifunctional naturally available organic acid substance which plays a significant role in binding metal ions from the natural environment, food substances and beverage such as coca cola, mineral water etc. The ligand has two complexing sites in competition: the catechol group (dihydroxybenzene) and the carboxylic function. Co-workers have been reported the complexation of this compound with different metal ions in aqueous solutions, Al(III) [Cornard *et.al.,* 2004; Cornard *et.al.,* 2006; Khvan *et.al.,*2001], Cu(II), Ni(II), Zn(II) and Co(II) [Khvan *et.al.,* 2001] and Fe(III)[Hynes, 2004]. In addition, the complexation of caffeic acid with polyphenol and aromatic compounds were also investigated by spectroscopic and computational methods to design advanced and controllable carriers of drugs and food components [Gornas *et.al.,* 2009; Mate *et.al.,* 2008]. The redox chemistry of iron plays an important role in the oxygen activation and transfer reactions mediated by a group of polyphenols. Polyphenols are widely found in plants and are present in all plant-derived systems [Deshpande *et.al.,* 1984; Singleton, 1981; Bronco, 2006]. Hydroxy-cinnamates, especially caffeic acid and its derivatives, are widely distributed and their presence in fruit juices is due to their easy extractability. Foods containing polyphenols undergo enzymatic and non-enzymatic browning due to autoxidation reactions [Hees *et.al.,* 1985; Singleton, 1987]. Some polyphenols also have the potential to be used as chelators to modulate physiological reactions involving iron and other transition metals [Blache, Durand, Prost, & Loreau, 2002; Elhabiri, Carrer, Marmolle, Traboulsi, 2006; Haslam, 1996]. Under physiological conditions, iron is constantly bound to maintain its solubility, mainly to proteins (haemoglobin, transferrin, and ferritin), but also to some low molecular weight chelators such as citrate. This non-protein bound iron is called labile iron pool or chelatable iron pool and could be a target to exogenous chelators such as polyphenols [Kakhlon, 2002] but direct experimental evidence for this proposal has been lacking.

Iron-polyphenolic acid complex formation and its role in sugar processing

The entire process of producing refined white sugar, from either sugarcane, is directed toward the removal of extraneous components that adversely affect the final quality of white sugar. Many of these components, while considered extraneous because it is desirable that they are removed, actually are quite normal constituents of the cane or beet plant, examples being soluble cell wall polysaccharides, starch, and other smaller metabolites. Additionally, reactions occur during processing as a result of pH changes, thermal effects and autocatalytic effects, which lead to the formation of polymeric colourant. Extensive research has been performed on the characterisation of sugar colour. Numerous comprehensive reviews have been presented [Riffer, 1988; Clarke *et. al.,* 1985 and Kennedy and Smith, 1976]. There are generally recognised to be four types of colour present in sugar: plant pigments, melanoidins, caramels and alkaline degradation products of fructose (ADF). The last three are factory produced colour pigments. The plant pigments are principally phenolics and flavonoids, which make up about two-thirds of the colour in raw sugar [Smith and Paton, 1985]. The phenolics are generally uncoloured but are oxidised or react with amines or iron to form colourants during processing. Flavonoids are polyphenols that exist in the cane plant and are involved in enzymic browning reactions. Caffeic and chlorogenic acids have cis-phenolic groups and are capable of forming chelates with Fe(III). Naringin is also capable of forming a six-membered ring chelate with Fe(III) while quinic, ferulic and sinapic acids do not appear to form such species. The catechol functional group has been identified as a component of manysiderophores [Albrecht-Gary, 1998]. Phenolic acids are also of great interest because their redox properties affect the availability of micronutrients to plants [Deiana *et.al.,* 1995]. The uptake of iron by plants depends considerably on the presence of both complexing and reducing reagents. Chlorogenic acid is one of the major polyphenol compounds found in numerous plant species [Risch *et.al.,* 1988]. Polyphenols mimic animal iron-binding proteins such as transferrin and protect plants by withholding iron from pathogens. Several studies have shown that beverages containing chlorogenic acid can inhibit the absorption of non-haem iron in man by up to 60% [Hurrell, 1999]. Naringin functions as an antioxidant by chelating iron ions and scavenging peroxyl radicals, whereas it’s OH radical scavenging effect is much less important [Deng, 1997]. The widespread interaction of these phenolic components with metal ions and the implications from a biological viewpoint warrants the investigation of their mechanistic interactions with metals. There have been several studies of the kinetics and mechanisms of the interactions of naturally occurring catechols with Fe(III) with the reactions involving a variety of different mechanisms [Mentasti, 1973; Mentasti, 1973; Mentasti, 1976; Linert *et.al.,* 1993; El-Ayaan *et.al.,* 1997; El-Ayaan *et.al.,* 1998].

Removal of colours/pigments in sugar processing

The presence of coloured impurities in sugar process solutions results from chemical reactions taking place during the production process. The compounds responsible for forming coloured impurities are mainly of polyphenols, they exhibit a negative influence both on the quality and quantity of the sugar produced. Since no specific tests exist to determine the different types of colourants, tests for phenolics, pH sensitivity, molecular weight ranges and distribution inside the crystal or in the syrup layer are the most effective means of determining the fate of colourants in processing. Gel permeation chromatography is an excellent technique for examining the high molecular weight constituents in sugar processing, and diode array detectors and evaporative light scattering detectors are yielding a great deal of information about individual high molecular weight colourants [Bento, 1999]. Adsorption and ionic exchange resins, in either hydrogen or sodium form, are widely employed for softening in the sugar industry. In the chloride form, resins have been used for decolourisation of refined sugar solutions since 1970 [Bento *et.al.,* 1997; Bento *et.al.,* 1998; Bento *et.al.,* 1999]. The resins commonly employed for the decolourisation of refined sugar solutions are anionic, with trimethylammonium groups linked to chloride ions. The resin matrix may be of two types: hydrophobic or acrylic and the colourants retained are different:

- Acrylic resins show low adsorption selectivity and can be regenerated almost completely with sodium chloride solutions [Fries, 1982; Fries, 1991]. Its use is appropriate for high colour cases [Ramm-Schmidt, 1988].
- Polystyrene resins show higher decolourisation efficiencies but its regeneration is more difficult than acrylic resins.

Pigments are widely distributed in the sugarcane plant cell [Singh *et.al.* 2015]. Authors have reported these pigments with colour in sugarcane juice for white sugar production [Tariq, 2014; Alves *et.al.,* 2013; Prati, 2010; Sartori *et.al.,* 2015; Zerban *et.al.,* 1919]. During the clarification process, plant pigments decompose to form polyphenolic compounds with subsequent enzymatic browning [Tariq, 2014;]. Sugar mills in Brazil remove these pigments, as well as other impurities, for the bleaching action of sulphur dioxide during the sulphitation process [Silva *et. al.,* 2015; Ravnö, 2007]. The clarified sugarcane juice as a matterof sugar production is concentrated up to white crystals [Ravnö, 2007; Aguiar *et.al.,* 2015].

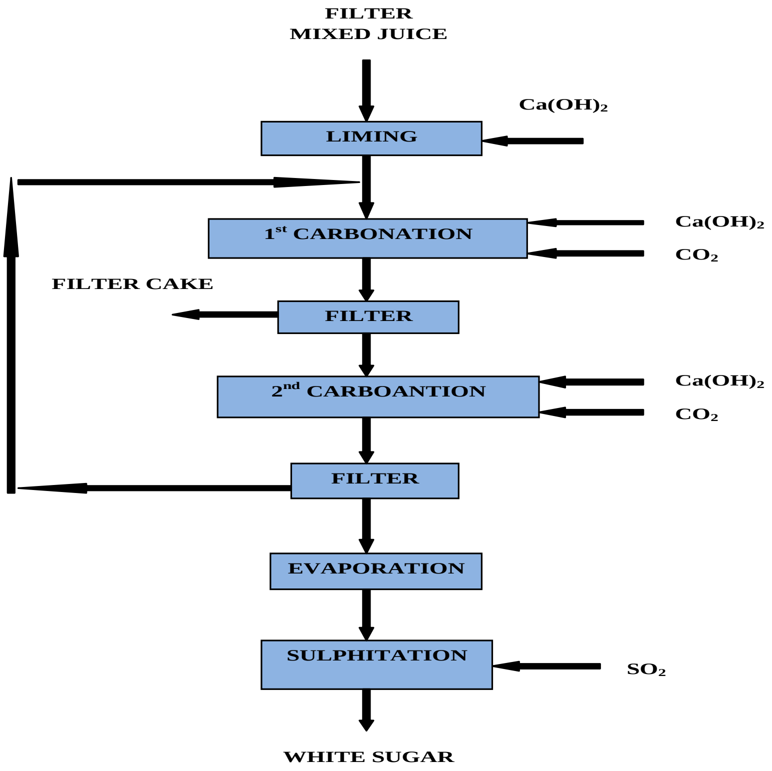


Fig.1.4. Typical flowchart of sugar manufacturing by carbonation process

Chromatography is a versatile technique widely used for the separation of chemical compounds in a suspension or solution [Degani *et.al.,* 1998] and this technique can also be used for separation of pigments from plant extracts [Indriatmoko, 2015]. Chemical compounds can be separated by identification and quantification [Christophoridou et.al., 2005; Ma *et.al.,* 2014]. Adsorption resins have a specific area and pore diameter for rapid diffusion of ions and improved extraction kinetics with an increase in the complexing capacity [Belfer *et.al.,* 1984]. Dowex TM Optipore TM SD-2 has been used in the food industry to remove colour, flavour and odour in sweeteners as it has pore structures to maximize the load, as well as the high mechanical, chemical and thermal capacity [Dow, 2015]. The effect of colour to evaluate the sugar quality without or with different treatments, such as gamma radiation and electron beam has been reported [Aguiar *et.al.,* 2010; Lima, 2015], Fenton-like reaction [Nguyen, 2011], ozone [Aguiar, 2014; Souza-Sartori, 2013] and hydrogen peroxide [Sartori *et. al.,* 2015; Souza-Sartori *et.al.,* 2013; Mandro *et.al.,* 2015]. They evaluated the isolation of pigments in sugarcane juice as potential purification process and isolation system of pigments, which have been associated by antioxidant activities [Aguiar *et. al.,* 2010; Sartori *et. al.,* 2013], by adsorption chromatography column, as described by Lima and Aguiar [Lima and Aguiar, 2015].During the 1970s, Norman Smith (California and Hawaiian Sugar Co.) tried to determinewhether different colourants were harder to remove during refining than others and whether the colourant composition varied between sugars from different sources (Smith, 1972, 1976). He examined the efficiency of colour removal using size exclusion chromatography, attempted to use reverse phase chromatography, followed colourant profiles through the refinery and concluded that colourant material affected the overall colourant removal efficiency through the factory. However, there were a number of problems with this work: the size exclusion columns were inadequate for fractionation of colourants, and the extraction and concentration methods (methanol extraction and adsorption onto a hydrophobic resin) would have altered the colourant composition during the investigation.

Properties of phenolic acids

In recent years there is an increase in the areas related to newer developments in prevention of disease especially the role of flavonoids and phenolic acids as antioxidants moreover flavonoids and phenolic acids components play important roles in the control of different human diseases. Flavonoids and phenolics acids are the most important groups of secondary metabolites and bioactive compounds in plants and good sources of natural antioxidants in human diets [Kim *et. al.*, 2003].Polyphenols are abundant micronutrients in our diet, and evidencefor their role in the prevention of degenerative diseases such ascancer and cardiovascular diseases is emerging. The health effects ofpolyphenols depend on the amount consumed and on their bioavailability. Plants (fruits, vegetables, medicinal herbs, etc.) may contain a wide variety of free radical scavenging molecules, such as phenolic compounds (e.g. phenolic acids, flavonoids, quinones, coumarins, lignans, stilbenes, tannins), nitrogen compounds (alkaloids, amines, betalains), vitamins, terpenoids (including carotenoids), and some other endogenous metabolites, which are rich in antioxidant activity [Larson, 1988; Shahidi and Naczk, 1995; Cotelle *et al.,* 1996; Velioglu *et al.,* 1998; Zheng and Wang, 2001; Cai *et al.,* 2003]. Epidemiological studies have shown that many of these antioxidant compounds possess anti-inflammatory, antiatherosclerotic, antitumor, antimutagenic, anticarcinogenic, antibacterial, or antiviral activities to a greater or lesser extent [Halliwell, 1994; Mitscher *et al.,* 1996; Owen *et al.,* 2000; Sala *et al.,* 2002].

Conclusion

This review paper of sugar colourant composition is appropriate at this point. Colourant may consider as coming from two basic sources: the cane plant and the process. Of the four general types of colourant , the phenolics and flavonoid class comes from the cane plant, where they exist as glycosides attached to sugar residue. Some phenolic are not coloured as they come from the plant, but oxidise or otherwise react (sometimes with amines) to form colourant during process. There is a general update that fast caramalisation catalysed by ion and relationship between polyphenols and uptake of iron is only hypothesis without experimental data on iron polyphenols interaction which can complement the above hypothesis that as and when polyphenols comes in contact with iron is accompanied by colour formation during sugar processing. The review paper revealed that some work has been reported employing a dilute solution of sugar and its allied products with different salts of iron with an object to understand complex formation. Therefore, it was considered necessary to study the influence of redox behaviour of iron-polyphenol interaction on colour development in sugar manufacturing.

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CHAPTER: 19

REDUCTION OF THE CARBON FOOTPRINT FOR THE IMPROVEMENT AND SUSTAINABLE DEVELOPMENT OF ENVIRONMENT

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Abstract

Carbon is the foundation of all life on the earth but its increase in the concentration causing the Ecological imbalance and problems to all living beings. The term carbon footprint is used to calculate the individual carbon emission which includes to the atmosphere every day; this will help us to know the personal and global carbon emissions.By the increase of human activities in the recent years causes lots of carbon emission and in turn increase the global warming, which is harmful to the present, and future of the earth and its living beings.Carbon footprint is a measurement of individual carbon released to the atmosphere and how can we take measure to reduce the emission of carbon to the environment.

Key words: Greenhouse gases, Ecologicalfootprint, carbon dioxide, methane, nitrous oxide, fluorinated gases, life cycle assessment, International Organisation for standardization, greenhouse gas protocol, and greenhouse warming potential.

Introduction

Carbon is a fundamental element of all life on earth, required to form complex molecules like proteins, DNA and RNA which is the fundamental particles in all living beings. This element is also found in atmosphere as carbon dioxide. Carbon helps to regulate the earth's atmosphere like regulating the earth's temperature and carbon is a key ingredient in the food that provides a major source of the energy and to fuel our global economy. Carbon cycle describes the process in which carbon atoms continuously travel from the atmosphere to earth and then back into the atmosphere. On earth most carbon is stored in the form of rocks and sediments. while rest is located in the ocean atmosphere and living beings these are the reservoirs or sinks through which carbon is released back into the atmosphere when organisms die, volcanoes erupt, fireblaze, fossil fuels are Burned and through a variety of other mechanism.

But in in these days human activity increasing the carbon output to the atmosphere also increases, because humans are using fossil fuels and other activities which release carbon to the atmosphere this causing increase in the greenhouse gases in atmosphere which causes global warming.

Carbon footprint is an individual measurement of how much emission of carbon by an individual is releasing to the environment from this we can know how much we are giving out to the atmosphere and how can we reduce it.

Origin of the concept

The term Carbon footprint also known as personal Carbon footprint, it was popularized by a 250 million advertising campaign by the oil and gas company BP in 2005 designed by Ogilvy which was a plan to divert attention from fossil fuel companies to individual consumers.

The concept and the name of the carbon footprint were derived from Ecological footprint which was developed by William E.rees and Matthew Wackernagel in 1990. Where as Ecological footprint reports the comparison to what planet can review and assess the number of Earth's that would be required if everyone in the planet consumes the resource at the same level.

The concept carbon footprint is the total amount of greenhouse gases emission caused by an individual or group of population of organisation and the product expressed as carbon dioxide equivalent, whereas carbon footprint reports that how many tons of carbon dioxide equivalent emissions per year.

Greenhouse gases

A greenhouse gas is a gas that absorbs and emits radiant energy within the thermal infrared range, causing the greenhouse effect

Carbon dioxide is naturally present in the atmosphere as the part of the earth's carbon cycle. Carbon dioxide enters the atmosphere through burning fossil fuels (natural gas and oil) solid waste, trees and some chemical reactions. Carbon dioxide is reduced by the biological carbon cycle where, plant inhaled the carbon dioxide present outside and utilised in the photosynthesis process.

Carbon dioxide is naturally used as warming gas of having global warming potential 1unit although more than half of the carbon dioxide emitted is absorbed by the plants the remaining 20% it will remain in the atmosphere for years

Methane emitted by Natural Sources like natural wetlands .Methane lifetime is much shorter than carbon dioxide but it is more efficient at trapping radiation than carbon dioxide i.e., 25% greater than carbon dioxide.

Methane has atmospheric lifetime of 12 + 3 years and global warming potential of 72 to over a time scale of 20 years. Methane is emitted from energy sector, industry, agriculture, land use and waste management activities.

Nitrous oxide present in the natural Ecological cycle but it is also produced from agriculture sector, industrial sector, fuel combustion, waste management and in the treatment of wastewater. Nitrous oxide has 121 years of atmospheric lifetime.

Fluorinated gases are produced solely from the human activities they are emitted through their use as substitutes for ozone depleting substances(example: refrigerants) and through a variety of industrial process such as aluminium and semiconductor manufacturing many fluorinated gases have very high global warming potential and they also have long atmospheric lifespan.

Hydrofluorocarbons used in refrigerants, aerosols, propellants, foam blowing agents, solvents and fire retardants.

These are developed as a replacement of CFCs newly developed HFOs hydrofluoroolefins are subset of HFCs, and are characterized by short atmospheric lifetimes and lower global warming potential. Perfluorocarbons are produced as a by-product of aluminium production and used in the manufacture of semiconductor. Perfluorocarbons have generally long life and global warming potential near 10000

Sulphur hexafluoride used in Magnesium processing and semiconductor manufacturing and as a tracer gas for leak detection. Sulphur hexafluoride used as a insulating gas in electrical transmission equipment including circuit breaker and global warming potential of sulphur hexafluoride is 22800.

Measurement of carbon footprint

An individual Nations Organisation carbon footprint can be measured by calculating the greenhouse gas emissions assessment.

- a life cycle assessment
- carbon accounting

For calculating personal carbon footprint several free online websites like carbonfootprint calculators exist including a few supported by publicly available Peer- reviewed data and calculations includes University of (California, Berkeley, coal climate network research consortium and carbon story) which asks few questions and based on your answers they estimate the carbon footprints(individual with systematic literature review).

For industrial carbonfootprints use the tool life cycle assessment (LCA) where carbon footprint is also one of many factors considered when assessing the products or services. The international organisation for standardization (IOS) has the Framework for life cycle assessment study and IOS provides a tool for quantifying monitoring, reporting and verifying of greenhouse gas emissions and removals.

Another method is the greenhouse gas protocol -which set standards for tracking greenhouse gases across scope 1, 2 and 3 emissions within the value of chain.

Causes

Direct carbon emissions: Where direct carbon emission comes from the source on the site of action. Example: burning of fuel.

Indirect carbon emissions: Are emissions from sources upstream or downstream from the process.

Upstream

i. transportation of materials
ii. energy used outside of the production
iii. waste produced

Downstream

- end of life process or treatments
- product and waste transportation
- emissions associated with selling the product

National carbon footprints

According to the World Bank in 2017 USA, EU, Australia produces more carbon dioxide metric tons per year.

If we consider a carbon footprint for a person includes mobility (driving, flying etc.) Shelter (electricity, heating, construction etc.) food is most important categories.

The carbon footprint of US household is about 5 times of greater than the Global average.

Carbon footprint of energy consumption

Hydroelectric, wind, and nuclear power produces least amount of carbon dioxide Kilowatt per hour.solar and wind power emits no carbon dioxide during their operation but little of carbon dioxide during construction and maintenance process. Hydropower produces carbon dioxide during initial removal of vegetation and ongoing Methane.In electricity production the generation of CO_2 is equal to half of the world's man made carbon dioxide output chp/dh has the lowest carbon footprint than micro power or heat pumps.

Carbon footprints of transport

- according to LIPASTO's survey average direct admission of airlines
  - Domestic short distance below 463 km 257 g/km CO_2
  - Long distance 113 g/ km CO_2
- Road emissions according to NEDC test cycle in 2013

Passenger cars: 127 g CO_2 /km

Hybrid electric vehicles: 92 g CO_2/ km

Light commercial vehicles (LCV) -175 gram CO_2/ km

- From US EPA (environmental protection agency) Federal Test procedure passenger cars : 200 g/km

Trucks: 280 gram CO2 per km

Combined: 229 g CO2 per kilometre

Several organisations offer footprints calculations for public and corporate use examples like EPA addressed paper, plastic, glass, cans etc. Australia addresses lumber and building materials. Carnegie Mellon University estimated the carbon dioxide footprint of 46 large sectors of eight countries.

Carbon trust work with UK manufacturers on foods, shirts and detergents introducing carbon dioxide label .Carbon trust state they have measured 27000 certifiable product carbonfootprint.

The key way to determine carbon footprint it is to look at the material used to make the item example: Juice carton is made of an aseptic carton, a beer can is made of aluminium and some water bottles either made of glass or plastic. The larger the size, the larger the footprint will be.

Textiles

Carbon footprint of different textiles varies considerably according to a wide range of factors, cotton -8, and nylon 5.43,PET (synthetic fleese)-5.5, wool- 5.48 synthetic fabrics generally have a substantially low carbon footprint than natural ones.

Greenhouse gas is produced natural and human activities

Natural: Decomposition, ocean release and respiration.

Human activities: power plants, residential buildings, transportation, mining, chemical and petrochemical industries.

carbon dioxide is not the most damaging gas because as it uses in the photosynthesis .but Methane released by Coal Oil and natural gas it is very prevalent, it is harmful than carbon dioxide because it traps heat better than carbon dioxide and it is main component in natural gas. Usage natural gas is more harmful. Nitrous oxide release from coal fired powder plants, agricultural and industrial activities, usage of the fluorinated gases causes ozone depletion (substances are refrigerants aerosol propellants form blowing agents solvents and fire retardants).

Reducing carbon footprint

For humans by using 4R can reduce carbon footprint of personal i e., reduce, reuse, recycle and refuse ,by being car free and adopting eco friendly lifestyle one can reduce the personal carbon footprint.

By using public transport and planting the trees in a deforested area reduce carbon footprint and increase their handprint.

By using non-renewable energy sources instead of renewable energy sources can cut off the production of carbon dioxide and other gases produced by the burning of renewable energy.

In 2016, EIA reported that in USA electricity is responsible for 37% of carbon dioxide
emissio

Most powerful industrial climate actions are refrigerant management (90 Billion tons of CO_2emission) from 2017 – 2050. Since refrigerants have thousands times of the warming potential of CO_2.

Land based wind turbines for electricity production (85 billion).

Reduce food waste (71 billion).

Restoring the tropical forests, the cheapest way to reduce is through Energy Efficiency improvements.

Waste heat recovery systems

Insulation for larger buildings and combustion chamber Technology upgrade that is different light sources lower consume lower consumption machines.

Kyoto Protocol defines legally binding targets and timetables for cutting the greenhouse gas emissions of industrialized countries that ratified the Kyoto Protocol.

Carbon dioxide capture and sequestration is a set of Technologies that can reduce carbon dioxide emission from new and existing coal and gas fired power plants industrial process and other stationary source of CO2.

Conclusion

From the above discussion, carbon footprint word is used as a masking agent by the oil and gas companies to mask their emission of harmful products to the environment, as they don't cut off the emission. But they diverted with the idea of carbon footprint, but it is also a useful tool to measure once Carbon release to the environment and by this project world is concentrating the amount of harmful gases releasing to the environment and measures are taking to control and bringing up the innovative ideas to use renewable energy sources as a fuel or energy sources . As carbon footprint made new trend or era on a environment and people interaction but it is also tells individual responsibility towards environment and its balance and How we safeguard our surrounding to the future and maintain the same balance in ecosystem to our future generation and achieve the goal were our future kids are experiencing and enjoying the same nature as we now.

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