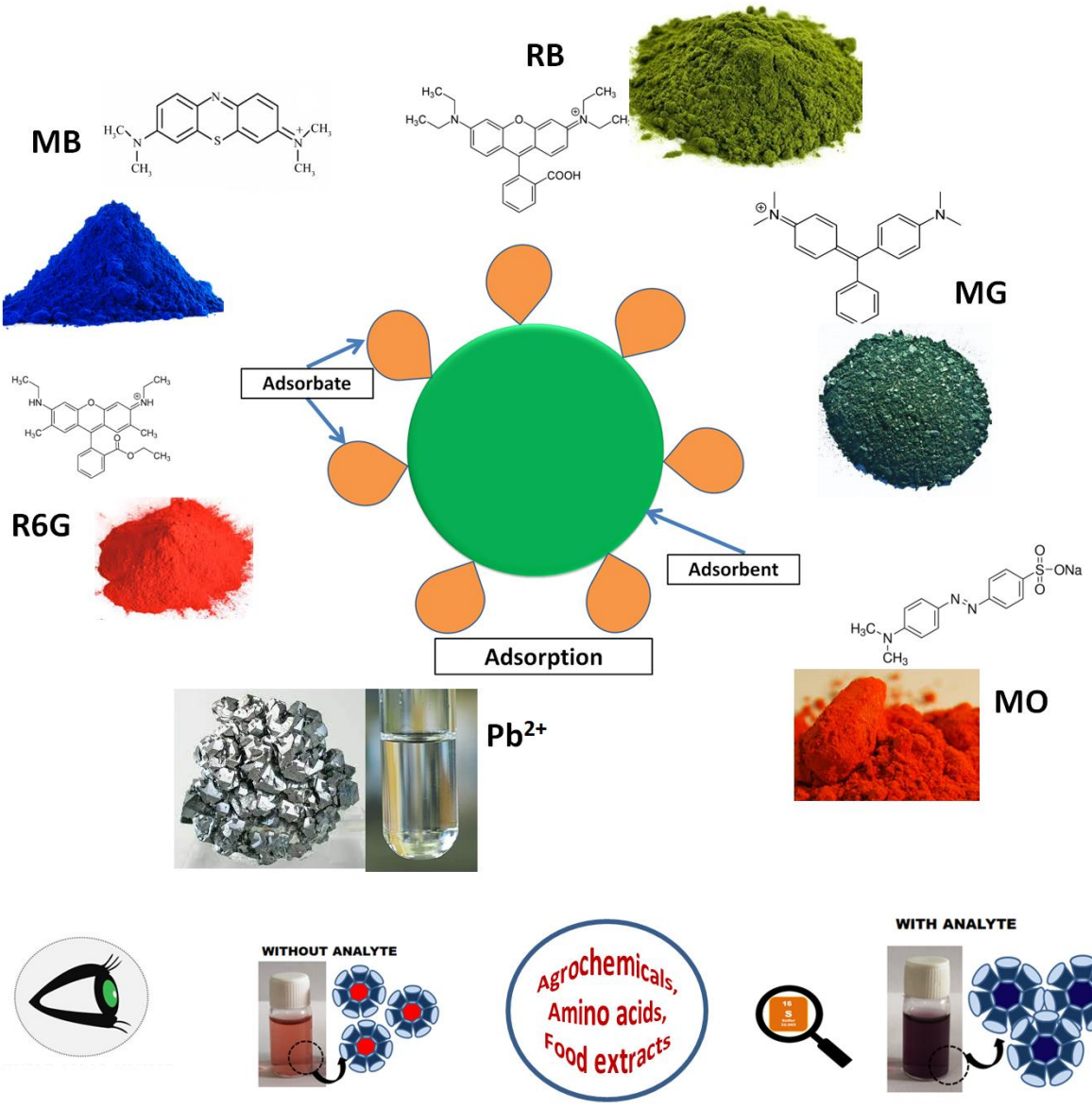
Chapter I

Introduction



1. Introduction

The industrial development, increasing population and rapid destruction of resources leads to increasing pollution load in environment[1]. The pollutants released from chemical industries such as textiles, paper, tanneries, electroplating, color photography, printing, dye, and food industries etc. produces large amount of organic and inorganic contaminants. These contamination loads affect the environment adversely by posing severe threat to agriculture, water, soil, food chain and ultimately the human beings [2]. In recent decades the serious global changes arising due to increasing average temperature and changing climatic conditions have been linked by the accumulation and deposition of several pollutants in environment[3]. Several pathways input fluoride in water and its enhancing concentration makes water unfit and undesirable for drinking purposes. The availability of fluoride in groundwater is due to fluoride bearing aquifers, geological factors, ion-exchange reaction, and rate of weathering and leaching of subsurface contaminants[4]. Heavy metals like tin, lead, nickel etc. are released from printed circuit board (PCB) manufacturing centers in considerable quantity. Cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium etc. heavy metals are produced by electroplating, conversion-coating, anodizing-cleaning, electrolysis depositions, milling and etching industries. Chromate copper-arsenate wood treatment utilized in wood processing industries release arsenic containing wastes. The aquatic organisms are unfavorably affected by presence of heavy metals in environment. Water chemistry and ingredient deposited in surface water reflects its toxicity. Microorganisms mineralize metals and taken up by planktons and enter into the phase of biomagnification passing towards higher trophic levels of ecosystem affecting the aquatic organisms physiologically and morphologically. Heavy metals adversely affect the human health including impairment in growth development, nervous system disorders etc. auto immune disorders like rheumatoid, arthritis, kidney diseases etc are caused by mercury and lead[5]. Precisely in developing countries environmental protection and remediation of water, air and soil pollution are of special concern around the world. Unfortunately, the elimination of pollutants from environment remains a challenge when considering four general points, efficiency, recyclability, environmental benign and cost. Several approaches have been considered for the elimination of environmental pollutants like adsorption, irradiation and membrane processes, oxidation, photodegradation, ozonation, ionic exchange, electrocoagulation, and coagulation–flocculation and other methods. Among other mentioned methods, adsorption is considered as

most appropriate, convenient, easy to operate and cost-effective technique for effluent treatment methods [6].

1.1.Organic Pollutants

Organic pollution term has been originated from urban run-off, domestic sewage, agricultural wastewater and industrial effluents containing large amount of organic compounds. Several organic pollutants present in environment primarily due to anthropogenic activities are phenols, hydrocarbons, fertilizers, biphenyls, pesticides, oil, detergents, grease, dyes, pharmaceuticals, PAHs and many more has been reported so far[7]. The degradation process of organic contaminants consumes dissolved oxygen of water body in a greater extent than it can be replenished therefore, depleting oxygen content and causing adverse impact on aquatic flora and fauna. Organic pollutants containing wastewater have huge amount of suspended solids that reduces light penetration ultimately affecting the photosynthetic activity and altering the characteristic of water body[8]. Persistent organic pollutants are group of toxic organic pollutants that causes severe environmental problems due to their persistence, toxicity and ability to transport up to a longer range[9]. Recently, uncontrolled exploitation of various natural resources like water, soil etc. introduces many organic pollutants in environment. Other than elevated green house gases like CO_2, NO_x, SO_2; load of organic pollutants are also contributed by anthropogenic activities such as discharging household sludge, rapid urbanization, utilization of chemical pesticides in agriculture and so on[10]. The presence of these pollutants into the natural environment adversely affects the natural quality and hygiene. Currently, the methods incorporated for removal of organic pollutants are chemical oxidation, microbial degradation, coagulation-flocculation, adsorption, incineration, deep-well injection, irradiation and solvent extraction[11].

1.2.Inorganic Pollutants

Several water quality parameters have been listed by Environmental Protection Agency (EPA) of United States in order to quantify the quality of water. The list contains some inorganic materials like barium, arsenic, boron, chloride, calcium, cobalt, lead, chromium, fluoride, iron, nickel, mercury, potassium, magnesium, silica, silver, sulfide, tin, uranium, zinc, vanadium and many more. The elemental forms of these materials or in combination with different compounds are

considered as inorganic pollutants after exceeding the permissible limits. Aquatic systems are being polluted by higher concentration of heavy metals as well as other inorganic pollutants like mineral acids, trace elements, inorganic salts, sulfates, metals, metal complexes, cyanides etc. in an alarming rate[12]. The pollutants are commonly chemicals of mineral origin and their existence are due to geogenic activities, while industrial activities, domestic and agricultural wastes elevated their level and mobility in environment[13]. Anthropogenic activities such as manufacturing, handling, storing and disposing of chemicals introduces inorganic pollutants in environment. Other than industries several domestic discharges are also contaminated with inorganic pollutants having chemicals utilized for cleaning and washing of tiles, floors and garments. Heavy metals are the most significant category of inorganic pollutants as it raises lots of concern due to their non-degradable nature and bioaccumulation property[14]. They can easily accumulate in food chain and enter in human body causing several health disorders such as high blood pressure, kidney damage, destruction of red blood cells, anaemia, nervous disorders etc. Methods like coagulation, chemical precipitation, ion exchange, membrane process, adsorption and electrochemical deposition has been reported so far for removal of inorganic pollutants[15].

1.2.1. Lead

Main sources of lead in wastewater includes battery manufacturing, soldering materials, glass industries, ceramic industries, steel-iron industries, printing and pigment, metal plating and finishing manufacturing[16]. Lead is also one of the commonly existing ions in industrial wastewater, agricultural wastewater and acidic leachate of landfill sites. The advancement of lead batteries over lithium batteries might lead to higher production as well as consumption of toxic lead metals. Consequently, leading to enhanced lead contaminated discharge and polluting environment[17]. Lead intake could be harmful for livings things as well as humans. Their long term high level intake may cause severe disorders like convulsions, nausea, coma, cancer, renal failure as well as sharp effect on intelligence and metabolism. Many techniques have been reported so far to eliminate lead ions from wastewater like reverse osmosis, membrane filtration, flocculation, adsorption, ion exchange, cloud point extraction and coprecipitation[18]. The detail discussion of adsorption of lead has been shown in Chapter V (B).

1.3.Dyes

Discharges of large quantity of colored effluents are major concern of industries like textile, plastic, paper, leather and ink manufacturing. The direct discharge of dyes loaded effluent without prior treatment are hazardous for organisms and adversely affect the ecosystem[19]. These colored compounds blocks light penetration that decreases the photosynthetic activity of aquatic plants ultimately hindering their growth and development[20]. Some dyes become persistent in environment as they are difficult to degrade because of complex aromatic structure. They can adversely affect human beings due to their carcinogenic and mutagenic nature causing kidney problems, affecting central nervous system and reproductive system[21]. Therefore, by considering their harmful effects, the dyes should be eliminated from contaminated water before discharging into natural system to maintain their aesthetic nature and functioning. The below discussed dyes have been utilized in experimental studies of thesis.

1.3.1. Methylene Blue

Methylene blue is a commonly used cationic dye among other dyes of its category, generally utilized for dyeing silk, cotton and wood. Although not utterly hazardous but it does cause some negative effects being in contact with humans[22]. This thiazine dye is also utilized in various clinical settings for identification of anatomic and pathologic structures[23]. On acute exposure, methylene blue may cause several disorders in humans like shock, vomiting, increasing heart rate, jaundice, cyanosis, Heinz body formation, tissue necrosis and chronic exposure may cause skin irritation, burning sensation, coldness, skin discoloration, redness or dryness etc. whereas ingestion of methylene blue may result in irritation of lips, gastrointestinal irritation, discoloration of oral mucosa and so on [24,25]. Therefore, removal of methylene blue from wastewater before discharging into natural environment is of prime concern.

1.3.2. Malachite Green

Malachite green is a cationic dye that has been primarily utilized in dyeing wool, jute, silk, leather, paper, distilleries, acrylic industries, food coloring agents, food additives and many more. It is extensively used against fungal and protozoan infections as well as in aquaculture and fish industries[26]. The toxicological symptoms of malachite green comprise pregnancy disorders, pleural infections, developmental abnormalities, carcinogenic nature as well as oral-nasal

inflammation. Malachite green induced chromosomal disorders may result in multi-organ tissue damage and its residual products are also toxic in nature. Rapid breathing, eye burns, excess sweating, gastrointestinal irritation, teratogenesis, mutagenesis, reduced fertility and respiratory toxicity are some of the reported side effects caused by malachite green dye[27]. This dye is difficult to fade out in light exposure and water due to its complicate chemical structure.

1.3.3. Methyl Orange

Methyl orange, is a type of p-amino- azobenzene (p-AAB) dye that is anionic in nature. This dye is broadly utilized in textile and dyeing industries as well as in chemical experiments as acid-base indicator. Their aqueous solution is poisonous in nature and cause irritation of eyes, skin and respiratory tract [28]. It has been also utilized for detection of microorganisms, dental materials, paints, treating dermatological diseases and pharmaceuticals[29]. Since conventional degradation of methyl orange is not easy therefore, their removal from textile effluent is a major concern.

1.3.4. Rhodamine 6 G

Rhodamine 6G, is a monocationic xanthene dye that has been broadly used in textile industry as colorant. It is water soluble dye of dark reddish-purple color with non-volatile nature. It has been used in research laboratories of biochemistry as diagnostic tool in detection of antigen in liquid sample. In biotechnology field, it is also utilized for fluorescence microscopy and fluorescence correlation spectroscopy[30]. It can cause carcinogenic and neurotoxic effect as well as chronic and reproductive toxicity in human beings and other animals[31].

1.3.5. Rhodamine B

Rhodamine B is highly water soluble organic chloride salt of xanthenes class dye imparting basic red color. This is broadly used textile industries colorant and food stuffs. They are well known water tracer fluorescent to determine flow rate and flow direction[32]. It is broadly recognised color effluent that becomes difficult to remove due to its toxic component, color constituent and biological/chemical oxygen demand. They can cause carcinogenic effect and on ingestion might be responsible for irritation of nose, eyes, tongue, skin, gastrointestinal tract and reproductive damages. It critically affects the photosynthetic activity by hindering the sunlight penetration in water body.

1.4.Adsorption

In order to eliminate inorganic and organic pollutants from wastewater, several effective techniques have gathered significant attention. Several methods have been reported for treatment of wastewater out of which adsorption process using solid adsorbents has been considered as most convenient and effective method. This method has various advantage over other convenient methods in terms of cost-effectiveness, simple and facile designing, ease of operation, reusability, less chemical consumption and waste generation[33]. This process is based on surface phenomenon with general mechanism to eliminate organic and inorganic pollutants. In this process, the liquid adsorbate and solid adsorbent with highly porous surface structure comes in contact with each other and solid-liquid intermolecular force of attraction transfer adsorbate molecules on adsorbent surface. The accumulation of adsorbate on the surface of adsorbent is termed as adsorption that defines the basis of separation using adsorption technology[34]. It has been considered as one of the most economic and effective method that may be utilized for removal of organic and inorganic pollutants. The adsorption process has been investigated in detail using various hybrid adsorbent systems for elimination of organic and inorganic pollutants as well as adsorption parameters such as concentration variation, dosage variation, pH and temperature variation has been studied.

1.5.Adsorbents

The adsorption process occurs at solid-liquid interface, where the contaminant being adsorbed is known as adsorbate whereas the adsorbing phase is termed as adsorbent[35]. Availability of broad range of adsorbents simplifies the process of adsorption and helps in better wastewater treatment. The different types of adsorbents are used for different types of pollutants. Initially, activated carbon was used as adsorbent system for removal of contaminants from wastewater that was replaced by various cost-effective adsorbents[36]. Since, the adsorption process is restricted on the basis of adsorption capacity therefore, several surface functionalization process could modify the native adsorbent with active sites for pollutant removal. The adsorbent is generally characterized on the basis of its adsorption capability that depends on preparation condition. Different types of novel hybrid adsorbents used in this thesis have been discussed below.

1.5.1. Magnetic Nanoadsorbents

The nanoparticles have size of approximately 1-100nm that causes potential impact on various scientific fields such as electronics, chemistry, medicine, material sciences and biology[37]. The unique characteristic of nanomaterials like small size, specific surface area, high reactivity etc. helps in synthesis of new high-tech nanoadsorbents. These nanoadsorbents exhibit faster remediation as well as better removal efficiency in comparison to traditional materials. Carbon nanotubes (CNTs), metal oxides and graphene are some categories of nanoadsorbents[38]. Magnetic nanoadsorbents are economical and magnetic decantation helps in easy separation of adsorbent with adsorbate molecules[39]. The unique property of iron-oxide nanoparticles and special magnetic property proved advantageous for synthesis of hybrid nanoadsobents in order to eliminate organic pollutants. Iron oxide nanoparticles properties were enhanced by addition of natural cyclic oligosaccharide, β-cylodextrin with hydrophilic outer and hydrophobic inner cavity. The system was utilized for removal of hydrophilic and hydrophobic dyes that has been thoroughly discussed in Chapter II.

1.5.1.1.Cyclodextrins

Cyclodextrins are synthetic cage molecules of toroidal shape produced after enzymatic degradation of starch and consist of glucose units connected by α-1,4-glycosidic linkages and several hydroxyl groups with a stable inner hydrophobic cavity and outer hydrophilic surface. This unique characteristic of cyclodextrins contributes to the encapsulation of molecules within and adsorption of polar molecules outside. The host-guest relationship may alter the characteristic of the guest molecule whereas outer primary hydroxyl group and inner secondary hydroxyl groups, assist in complex formation with hydrophobic organic pollutants. Cycloheptaamylose, i.e. β-cyclodextrin, is the broadly studied cyclodextrin due to the formation of host-guest inclusion complexes with different ions, molecules and polymers. α-cyclodextrins are rigid and difficult to hydrolyze completely, whereas γ- cyclodextrins are resilient and hydrolyzed effortlessly by α-amylases as they are thoroughly soluble and transparent in aqueous solution. The derivative of cyclodextrins could be synthesized via a nucleophilic or electrophilic attack on -OH groups of pure cyclodextrins by thiols, halide ions, azide ions, amines and thiourea functionalities[40].

1.5.2. Hydrogel

The three-dimensional polymeric network possessing ability to absorb huge amount of water within their structure and swell accordingly gives rise to hydrogels. Several macromolecules have ability to form hydrogels such as starch, polysaccharides, alginates, cellulose etc. have been reported. These are also beneficial in terms of renewable nature, wide availability and low-cost[41]. Hydrogels have significant applications in tissue engineering and artificial muscle as biomaterials. The properties of hydrogels were reinforced with the help of crosslinking by chemical agents or physical methods[42]. The hydrophilic groups like –COOH, -OH, -CONH, -SO_3H and –$CONH_2$ containing macromolecules helps in formation of hydrogels. These groups are either grafted or embedded in the polymeric backbone of macromolecules. Hydrogels could be successfully prepared by using natural or synthetic polymers[43]. The fermentation of sucrose-rich media produces dextran at industrial level. These are the bacterial polysaccharides containing D-glucopyranose[44]. Dextran is a versatile and biocompatible polysaccharide that has been modified in presence of hexamethylene diisocyante for the synthesis of hydrogel, discussed in detail in Chapter III. The synthesized hydrogel was utilized for removal of cationic and anionic dyes as well as valorization of silver adsorbed hydrogel as catalyst demonstration photocatalytic activity in reduction of nitrophenols.

1.5.2.1.Dextran

Lactic acid bacteria i.e. *Leuconostoc mesenteroides* produces one of the most flexible, water soluble, biodegradable and biocompatible exopolysaccharide known as Dextran[45]. It is usually synthesized with products containing sucrose like molasses, sugarcane and sugar beet. The molecular weight and yield of dextran was influenced by processing parameters such as sucrose, temperature, acceptor concentration etc. Reportedly, it was utilized in industrial, pharmaceutical, food, chemical as well as environmental application. The major proportion of dextran is composed of α-1,6-glycosidic linkage and a few branched linkages of α-1,2; α-1,3; and α-1,4. A medium enriched with 15% sucrose synthesize high molecular weight dextrans within optimized conditions[44]. The pendant hydroxyl groups in structure of dextran helps in modifications[46].

1.5.3. Bioadsorbent

Among various materials studied as adsorbent, the low-cost and robust adsorbent is based on polysaccharides. The biomaterials have attracted the attention of researchers as potential bioadsorbent for removal of pollutants from contaminated water body due to their wide-range natural availability, high adsorption efficiency, less expensive, regenerative and environmentally compatible nature. The adsorbents derived from biomass become an alternative to traditional adsorbent system due to their operational flexibility[47]. Several bioadsorbents have been reported so far utilized for elimination organic and inorganic pollutants from wastewater, some of them are egg shell, cabbage waste, olive stone, banana peel, ectodermis of opuntia, fruit peels, *Citrus limetta* peels and many more[48]. These bioadsorbents represents variable adsorption efficiency depending upon the active sites in the form of functional groups on the surface of bioadsorbent majorly hydroxyl, carboxyl and amines[49]. The surface functionalization of bioadsorbent results in modified system with higher adsorption capacity. Considering the point, *Citrus limetta* peels were modified with hexamethylene diisocyante to synthesize bioadsorbent for removal of organic and inorganic pollutants from aqueous solution. Dried marine seaweed (*Fucus vesiculosus*) was also utilized as adsorbent system for removal of organic dyes, thorough discussion has been done in Chapter V (A).

1.6.Sensing

Detection and monitoring of different compounds and elements requires analytical tool such as High performance liquid chromatography, inductively coupled plasma-mass spectroscopy, chromatography, flame atomic absorption spectroscopy, electrophoresis etc. however, these methods are expensive and complicated in context of operation[50]. These techniques could not be utilized for in-situ analysis due to their multi-step and complicated sample preparation, high maintenance cost, time consumption and controlled experimental conditions. Chemosensors have several advantages over conventional sensing systems like sensitivity, non-destructive nature, inexpensive, selectivity, lower detection limit, fast response time and so on. They can be used for on-site detection of compounds without any sophisticated instrument based on optical method. The visual detection of color change can be seen through naked eyes. Therefore, different studies have been reported based on colorimetric sensing of various compounds such as proteins, amino acids, heavy metals, organic molecules etc. [51,52]. The spectrophotometric and colorimetric

detection of compounds based on gold and silver nanoparticles gathers the attention of researchers. The nanoparticles on the basis of degree of aggregation impart certain advantages like rapidness, high sensitivity and simplicity. Hence, the disadvantage of low selectivity can be altered by functionalization of nanoparticles[53]. Therefore, the cyclodextrin crosslinked polymer with pthalic anhydride was used with gold solution to develop stable gold nanoparticles based sensor. The nanosensor was utilized for rapid, colorimetric detection of amino acid (cysteine) and agrochemical (diethyldithiocarbamate), detailed discussion has been done in Chapter IV.

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