CHAPTER 1

INTRODUCTION
Chapter 1

Present day environmental pollution problem is the most horrible ecological crisis since the civilization on earth. Just before last century, environment was pure, undisturbed and hospitable for man to live. Environmental pollution may be defined as, “the unfavourable alternation of surrounding environment, wholly or largely due to byproducts of man’s activity, through direct or indirect effects of changes in energy patterns, radiation levels, chemical and physical constitution or abundance of organisms”. These changes may affect human being directly or indirectly through water supplies, agricultural or biological products, physical objects or possessions or opportunities for recreation and appreciation of nature [1].

1.1 WATER POLLUTION

Increasing industrialization, uncontrolled use and exploitation of natural resources during the last several decades have caused major devastation and degradation of the Earth. Throughout history, the quality of drinking water has been a factor in determining human welfare. In some areas, the quality of water is subject to a number of chemical threats. There are many possible sources of chemical contamination. Since World War II there has been a tremendous growth in the manufacture and use of synthetic chemicals. Many of the chemicals have contaminated water supplies [2].

The industrial revolution resulted in an improving lifestyle, raising the standard of living of people, but also resulted in an indiscriminate exploitation of natural resources. Human activities have put a considerable pressure on the availability of basic human necessities such as clean water and air. Waste water from various industries, municipal corporations, urban and rural runoff, coupled with the increasing use of various chemicals, surfactants, fertilizers, pesticides and herbicides in agriculture and the decomposition of vegetable and animal matter discharge varying amounts of these and other chemicals into ground and surface water, making it unfit for human and animal consumption. With the rapid development of chemical, polymer, their processing, and petroleum processing industries, there is a rapid increase in the amount and the
variety of chemicals that are thrown into waters. This increase is attaining hazardous conditions, especially in big cities where the population is large, the demand for water is very high, and chemical industries and other industries are developing at a faster rate. Some of the organic and inorganic compounds, when present in water are toxic, carcinogenic and mutagenic, and cause several ailments in humans. Pollution in general and water pollution in particular has attracted the attention of scientific workers the world over [3].

Among the inorganic contaminants of the river water, heavy metals are getting importance for their non-degradable nature and often accumulate through tropic level causing a deleterious biological effect. Anthropogenic activities like mining, ultimate disposal of treated and untreated waste effluents containing toxic metals as well as metal chelates from different industries, e.g. tannery, steel plants, battery industries, thermal power plants etc. and also the indiscriminate use of heavy metal containing fertilizers and pesticides in agriculture resulted in deterioration of water quality rendering serious environmental problems posing threat on human beings and sustaining aquatic biodiversity [4]. The discharge of heavy metals into water sources is a serious pollution problem which may affect the quality of water supply. Increasing concentrations of these metals in the water constitute a severe health hazard mainly due to their nondegradability and toxicity [5].

Out of a number of industries, the textile industry is a major source of colored effluent discharge to water bodies [6]. Effluents from dyeing and finishing processes of the textile industry are known to add a number of pollutants like dissolved and suspended solids, heavy metals, and a large amount of surfactants and colors to the water sources. Dyes have been reported to be toxic, carcinogenic, and mutagenic. The colored water contains –C=C– bonds and –N=N– bonds, and heterocyclic and aromatic rings occur at the time of reduction of the cleavage of these groups [7]. Dyes are generally nondegradable and constitute a problematic group of pollutants. Dyes are harmful to flora and fauna. In addition to a number of adverse effects, colored water are aesthetically unacceptable to people. Colored waters also inhibit solar
radiation into the water sources and result in a reduced extent of photosynthesis [8].

1.2 HEAVY METAL POLLUTION

Heavy metals are toxic to aquatic flora, animals and human beings even at relatively low concentrations. Numerous metals such as As(III) and As(V), Cr(III) and Cr(VI), Cu(II), Pb(II), Mn(II), Hg(II), Cd(II) etc. are known to be significantly toxic [9]. Heavy metals contamination of water is a serious threat to the global ecosystem. Some of them (such as: Cd(II), Cr(VI), Hg(II) etc.) are capable of being assimilated, stored and concentrated by organisms. Heavy metals do not degrade into harmless end products in the metabolism and they are accumulated in the food chain, water–plants–animals–humans, thereby posing the greatest threat to the living organisms. They can cause very toxic effect and it may in turn result in serious problem. Most of the trace elements are transition metals with variable oxidation states and coordination numbers. These metals form complexes with organic substances in the environment thereby increasing their mobility in the biota and manifest toxic effects [10].

1.2 a) Source of heavy metals pollution

Now days, various metals are discharged into the water bodies. The sources of heavy metals are associated with human activities. In case of chromium, this is usually found in industrial sewage, the most usual and important sources of which come from the electroplating, leather tanning and textile industries [11]. Cadmium is introduced into water from smelting, metal plating, cadmium–nickel batteries, phosphate fertilizers, mining, pigments, stabilizers, alloy industries and sewage sludge [12]. Lead is the one of such highly toxic element that is found both naturally and as introduced contaminant in the environment. Process industries, such as acid battery manufacturing, metal plating and finishing, ammunition manufacturing, tetraethyl lead manufacturing and ceramic and glass industries are the major sources of lead pollution [13]. Arsenic is a commonly occurring toxic metal in natural
ecosystem. Its presence in natural water may originate from geochemical reactions, industrial waste discharges, or agricultural use of arsenical pesticides [14, 15]. Nickel is also a common toxic pollutant. It is a naturally occurring as hard, silvery-white metal. Its widespread industrial applications such as in nickel plating and making of steel, coins, jewellery, batteries and heat exchangers have resulted in its presence in many industrial effluents [16]. Sources of introduction of mercury in environment are volcanic activity, weathering of rocks, water movements, biological processes, combustion of fossil fuels (specially coal), electricity and power generating stations, mining, manufacture of cement, pesticides, medical equipments etc. [17, 18].

1.2 b) Effect of heavy metals on human being

There are various severe, acute, chronic as well as carcinogenic health threats arises due to introduction of heavy metals into human body by any chain. The effluent from the various industries can contain hexavalent chromium, at concentrations ranging from tenths to hundreds of mg/dm³. Cr(VI) is considered by the International Agency for Research on Cancer (IARC) (1982) as a powerful carcinogenic agent that modifies the DNA transcription process causing important chromosomic aberrations [19]. On the other hand, the presence of Cr(VI) in water causes important environmental problems and the National Institute for Occupational Safety and Health (NIOSH) recommends that the levels of Cr(VI) in water should be reduced to $10^{-3}$ mg/m³ [11].

Long-term exposure to cadmium can cause damage to the kidney, liver, bone and blood. Therefore, cadmium should be removed from waste streams before discharge into the environment. 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 0.05 mg/dm³. Arsenic is known to be carcinogenic. It has also been
suspected as a causal factor for Haff’s disease. Acute and chronic arsenic poisoning from consumption of arsenic contaminated drinking water has been reported. In most countries, the arsenic level of water is limited to the value of 0.05 mg/dm³ [20].

A number of nickel-related effects, including renal and reproductive effects, have occasionally been reported, the main effects noted in humans are respiratory and dermal. Long-term exposures to some nickel compounds have been associated with excess lung and nasal sinus cancers. Respiratory toxicity due to soluble nickel exposures may have enhanced the induction of tumors by less soluble nickel compounds or other inhalation carcinogens. In Germany, 0.5 mg/dm³ level is the current maximum allowable concentration for water-insoluble forms of nickel [16]. Elemental and methylmercury are toxic to the central and peripheral nervous system. Neurological symptoms include mental retardation, seizures, vision and hearing loss, delayed development, language disorders and memory loss. The inhalation of mercury vapor can produce harmful effects on the nervous, digestive and immune systems, lungs and kidney, and may be fatal. The inorganic salts of mercury are corrosive to the skin, eyes and gastrointestinal tract [21]. The tolerance limit for Hg (II) for discharge into inland surface waters is 10 µg/dm³ and for drinking water, 1µg/dm³ [22].

1.3 DYES POLLUTION

The analysis of a product which is to be marketed nowadays requires the identification of its technical and application properties as well as comprehensive toxicological and ecological considerations and the dyes are no exception [23]. For industrial liquid effluents, color is the first indication of water pollution. At present, more than 10,000 dyes have been effectively commercialized [24]. The evaluation and knowledge of physical, chemical, toxicological and ecological properties of a dye is essential in order to assess its influence on the environment and to estimate whether or not a given product presents a potential hazard.
The dyeing industries discharge in the environment large volume of strongly colored effluents that are heavily loaded with pollutants and highly concentrated in salts. After reviewing the characteristics of these effluents, Hessel et al. [25] compared the current legislation on the dyeing industry emission. They examined more closely the discharge legislation, first in France and then in other countries around the world. Considering six of the most representative parameters (color, BOD, COD, suspended solids, salinity, detergents and oil and grease) it was shown how different the applied constraints are in different countries. The industrial dumping of effluents containing dyes not only marks the natural aspect of the rivers but also perturbs the aquatic life interfering in the transmission of sunlight and thus reducing the action of photosynthesis because some dyes and their degradation products are highly toxic and even carcinogenic [26].

1.3 a) Source of dyes pollution

Waste water from textile, cosmetics, printing, dyeing, food coloring, paper-making industries are contaminated by dyes. The organic dyes discharged (12%) from such industries are the main sources for polluting surface water, ground water and soil. Methylene blue dye has wide applications, which include paper coloring, cotton or wool dyeing, and coating for paper stock. Malachite green is a common dye for dyeing wool, silk, leather, cotton, jute and fungicide, ectoparasiticide in aquaculture, fisheries and also in manufacturing of paints and printing inks [27-30].

1.3 b) Effect of dyes on human being

Dyes in general are not readily biodegradable. Dermatologists have reported cases of skin reactions suspected to be caused by textile dyes. There is evidence that some reactive dyes cause contact dermatitis, allergic conjunctivitis, rhinitis, occupational asthma, or other allergic reactions in textile workers. The reason is believed to be the capability of reactive dyes to combine with Human Serum Albumin (HSA) to give a dye-HSA conjugate.
which acts as an antigen. The antigen in turn gives rise to specific Immunoglobulin E (IgE) antibodies and, through the release of intermediates such as histamine, produces allergic reactions. Some dyes exhibit a mutagenic potential. The Ames test is commonly used as a first screening for the prediction of mutagenicity of a substance. The reductive enzymatic cleavage of the azo bond occurring in mammals is simulated by this test. The possible release of the aromatic amines, which are carcinogenic in rodents and subsequent metabolic activation in the organism, is assumed to be the reason for the carcinogenic effect of some members of dye in animal testing. These findings support the conclusion that dyes which could be metabolized to a carcinogenic aromatic amine should be considered to be carcinogenic [23].

In case of methylene blue dye, the colored effluents are having various harmful effects on living things. Once inhaled, it can cause heart beat rate increasing, nausea and vomiting. If the amount of intake is large, severe symptoms such as difficulties in breathing, mental confusion, and methemoglobinemia like syndromes may take place [31]. The release of colored waste water introduces the potential danger of bioaccumulation, which may eventually affect man through the food chain.

Malachite green (MG), though it effectively controls the infection of bacteria, protozoans, cestodes, trematodes, nematodes and crustaceans in aquaculture, MG was found to cause muscle glycogenolysis, impairs protein synthesis, severe damage to gills and degenerative changes in fishes. However, MG is also dangerous and highly cytotoxic to mammalian cells which act as a liver tumor enhancing agent. The dye MG is harmful to symbiotic bacteria present in water. MG blocks out sunlight penetration [32]. Though the use of this dye has been banned in several countries and not approved by US Food and Drug Administration, it is still being used in many parts of the world due to its low cost, ready availability and efficacy and lack of a proper alternative [30, 33]. Recently, the Minimum National Standards (MINAS) have been developed for different industries by Central Pollution Control Board, New Delhi (India). Accordingly, industries have been required to reduce the
pollution load including decolourization of their effluents before disposal into surface waters, municipal sewage system or on land [34].

1.4 NEED FOR THE REMOVAL OF HEAVY METALS AND DYSES

Continuous discharge of industrial, domestic and agricultural wastes in rivers and lakes causes deposit of pollutants in sediments. Such pollutants include heavy metals, as well as other pollutant like dyes and other organic compounds, which endanger public health after being incorporated in food chain. Heavy metals and dyes cannot be destroyed through biological degradation, as is the case with most organic pollutants [9]. Incidence of heavy metal accumulation in fish, oysters, mussels, sediments and other components of aquatic ecosystems have been reported, such as very well known Minamata disease (Japan).

Excessive amounts of some heavy metals can be toxic through direct action of the metal or through their inorganic salts or via organic compounds from which the metal can become easily detached or introduced into the cell. A large number of physical and chemical wastes find their way into the aquatic environment and the pollutants are absorbed by fine grained organic particles that end up in the bottom deposits. Heavy metals are serious pollutants of the aquatic environment with deleterious effects on aquatic fauna. These metals are toxic to aquatic life at low concentration particularly in soft water environment. The metals may be accumulated from water to higher levels in fish tissue. Fish can accumulate high concentrations of metals present in the water or in their food, thus increasing the concentration of toxic compounds found in the food chain. Essentially, fishes assimilate these heavy metals through ingestion of suspended particulates, food materials and/or by constant ion exchange process of dissolved metals across lipophilic membranes like the gills, adsorption of dissolved metals on tissue and membrane surfaces. The progressive and irreversible accumulation of these metals in various organs of marine creatures ultimately leads to metal related diseases in the long run because of their toxicity, thereby endangering the aquatic biota and other organisms [35].
The presence of small amount of dyes (less than 1 ppm) is highly visible and undesirable. Dyeing industry effluents are one of the most problematic waste water to be treated not only for their high chemical oxygen demand, but also for high biological oxygen demand, suspended solids, turbidity, toxic constituents and for colour, which is the first contaminant discernible by the human eye. Dyes may affect the photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to some aquatic life due to the presence of aromatics, metals, etc. in them [34].

Research and development, therefore focuses on sector-specific methods and technologies to remove colour and heavy metals from different kinds of waste streams. In view of the above toxicological effects of heavy metals and dye on environment, animals and human beings, it becomes imperative to treat these toxic compounds in waste water effluents before they are discharged into water bodies.

1.5 CONVENIENT ROUTES FOR THE TREATMENT OF HEAVY METALS AND DYED FROM AQUEOUS SOLUTION

There are various methods developed to remove the heavy metal as well as the dyes from the aqueous solutions and waste water. 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.

1.5.1 Chemical precipitation

Chemical precipitation involves the addition of chemicals to alter the physical state of dissolved and suspended solids and facilitate their removal by sedimentation. Chemical precipitation is employed for most of the metals. Common types of precipitates include hydroxides (OH\textsuperscript{-}) and sulfides (S\textsuperscript{2-}). Metals are precipitated commonly as metal hydroxides through the addition of
lime or caustic to a pH of minimum solubility. The conceptual mechanism of heavy metal removal by chemical precipitation is:

\[
M^{2+} + 2(OH)^{-} \leftrightarrow M(OH)_{2} \downarrow
\]

However, this method is inappropriate for large solution volumes with very low concentrations of metal ions. Precipitating hydroxides of the metals with lime and soda (NaOH) are used in removal of heavy metals. In spite of its advantages, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. Other drawbacks are excessive sludge production that requires further treatment, the increasing cost of sludge disposal, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal [36-38].

1.5.2 Coagulation–flocculation

Coagulation is a phenomenon in which the charged particles in colloidal suspension are neutralized by mutual collision with counter ions and are agglomerated, followed by sedimentation. The coagulants are added in the form of suitable chemical substances. It is generally accepted that coagulation occurs primarily by reduction of the net surface charge to a point where the colloidal particles, previously stabilized by electrostatic repulsion, can approach closely enough by van der Waal’s forces to hold them together and allow aggregation. The reduction of the surface charge is a consequence of the decrease of the repulsive potential of the electrical double layer by the presence of an electrolyte with an opposite charge [39]. There are number of different compounds, known as chemical coagulants, that react with suspended matter to form flocs-alum [aluminium sulphate, \(Al_{2}(SO_{4})_{3}.12H_{2}O\)], iron as ferrous sulphate, \(FeSO_{4}.7H_{2}O\), ferric sulphate [\(Fe_{2}(SO_{4})_{3}\)], ferric chloride (FeCl₃) etc. In recent years, a number of synthetic high molecular weight, water soluble
polymers have been developed for this purpose, one example being Calgon Corporation’s polydiallyldimethyl ammonium chloride [1].

1.5.3 Ion exchange

Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex. In most cases, the term is used to denote the processes of purification, separation, and decontamination of aqueous and other ion-containing solutions with solid polymeric or mineralic ion exchangers. Typical ion exchangers are ion exchange resins (functionalized porous or gel polymer), zeolites, montmorillonite, clay and soil humus. Ion exchangers are either cation exchangers that exchange positively charged ions (cations) or anion exchangers that exchange negatively charged ions (anions). There are also amphoteric exchangers that are able to exchange both cations and anions simultaneously. However, the simultaneous exchange of cations and anions can be more efficiently performed in mixed beds that contain a mixture of anion and cation exchange resins or passing the treated solution through several different ion exchange materials. Ion exchangers can be unselective or have binding preferences for certain ions or classes of ions depending on their chemical structure. This depends on the size of the ions, their charge and their structure [40].

Ion exchange has difficulty in removing heavy metal concentrations below about 10 parts per billion (ppb) on a commercial scale. Another difficulty is in the consumption of the removal medium, hydroxide ions or available ion exchange sites, by common but innocuous metals such as calcium, iron and like. While this is easy to monitor and correct for hydroxide precipitation and it is much more difficult for ion exchange processes [41].

1.5.4 Solvent extraction

Liquid-liquid extraction, also known as solvent extraction and partitioning, is a method to separate compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic
Chapter 1

removal of dyes and heavy toxic metals with adsorption technique using low cost adsorbents

solvent. It is an extraction of a substance from one liquid phase into another liquid phase. Liquid-liquid extraction is a basic technique in chemical laboratories, where it is performed using a separating funnel. This type of process is commonly performed after a chemical reaction as a part of the workup.

In other words, this is the separation of a substance from a mixture by preferentially dissolving that substance in a suitable solvent. By this process, a soluble compound is usually separated from an insoluble compound. Solvent extraction is used in nuclear reprocessing, ore processing, the production of fine organic compounds, the processing of perfumes and other industries.

Liquid-liquid extraction is also possible in non-aqueous systems. In a system consisting of a molten metal in contact with molten salt, the metals can be extracted from one phase to the other. This is related to a mercury electrode where a metal can be reduced, the metal will often then dissolve in the mercury to form an amalgam that modifies its electrochemistry greatly. For example, it is possible for sodium cations to be reduced at a mercury cathode to form sodium amalgam, while at an inert electrode (such as platinum) the sodium cations are not reduced. Instead, water is reduced to hydrogen. A detergent or fine solid can be used to stabilize an emulsion or third phase [42, 43].

1.5.5 Membrane technology

Membrane processes are interesting as they reduce the number of unit operations and are now used to obtain effluents without contaminants; they recycle process water and recover valuable products which can be reused in the process itself or in other applications [44].

Membranes have gained an important place in chemical technology and are used in a broad range of applications. The key property that is exploited is the ability of a membrane to control the permeation rate of a chemical species through the membrane. In separation applications, the goal is to allow one component of a mixture to permeate the membrane freely, while hindering permeation of other components. A membrane is nothing more than a discrete,
thin interface that moderates the permeation of chemical species in contact with it. This interface may be molecularly homogeneous, that is, completely uniform in composition and structure, or it may be chemically or physically heterogeneous, for example, containing holes or pores of finite dimensions or consisting of some form of layered structure. A normal filter meets this definition of a membrane, but by convention, the term filter is usually limited to structures that separate particulate suspensions larger than 1 to 10 μm [45].

The four developed industrial membrane separation processes are microfiltration, ultrafiltration, reverse osmosis and electrodialysis. Ultrafiltration and microfiltration are basically similar, in that the mode of separation is molecular sieving through increasingly fine pores. Microfiltration membranes filter colloidal particles and bacteria from 0.1 to 10 μm in diameter. Ultrafiltration membranes can be used to filter dissolved macromolecules such as proteins from solutions. In reverse osmosis membranes, the membrane pores are so small, from 3 to 5 Å in diameter that they are within the range of thermal motion of the polymer chains that form the membrane. The accepted mechanism of transport through these membranes is called the solution-diffusion model. According to this model, solutes permeate the membrane by dissolving in the membrane material and diffusing down a concentration gradient. Separation occurs because of the difference in solubilities and mobilities of different solutes in the membrane [45].

1.5.5 a) Reverse osmosis

Reverse osmosis is based upon the fundamental pursuit for balance. Two fluids containing different concentrations of dissolved solids that come in contact with each other will mix until the concentration is uniform. When these two fluids are separated by a semi permeable membrane (which lets the fluid flow through, while dissolved solids stay behind), a fluid containing a lower concentration will move through the membrane into the fluids containing a higher concentration of dissolved solids. After a while the water level will be higher on one side of the membrane. The difference in height is called the
osmotic pressure. By pursuing pressure upon the fluid column, which exceeds the osmotic pressure, one will get a reversed effect. Fluids are pressed back through the membrane, while dissolved solids stay behind in the column. Using this technique, a larger part of the salt content of the water can be removed. The semi-permeable membrane rejects salts (ions) by a charge phenomena action, the greater the charge, the greater is the rejection [46]. It has drawback that, flow rates are usually limited to a certain gallons/day. Reverse osmosis reduces both the organic and inorganic content of the waste water but some fouling of membranes can still occur as well as this method is not economical as its unit is expensive [1].

1.5.5 b) Microfiltration

Microfiltration (MF) is widely used for the purification of colloid suspensions with particles in the range of 0.1–20 µm. Even distilled water often contains up to 100,000 particles/cm³, but for microelectronics processing this concentration should be less than 500 and in some cases not more than 2 particles/cm³. Thus, MF is useful for purification of very dilute colloidal suspensions [47].

The two principal types of microfiltration membrane filter in use (i) depth filters and (ii) screen filters. Screen filters have small pores in their top surface that collect particles larger than the pore diameter on the surface of the membrane. Depth filters have relatively large pores on the top surface so particles pass to the interior of the membrane. The particles are then captured at constrictions in the membrane pores or by adsorption onto the pore walls. Characterizing the pore size of microfiltration membranes is a problem for manufacturers. Most microfiltration membranes are depth filters. If the membrane pore size was small enough, a point was reached at which no breakthrough of bacteria to the filtrate occurred, no matter how concentrated the challenge solution. This point is taken to be the pore size of the membrane [45]. The major problem during microfiltration is reduction of permeate flux due to concentration polarization and membrane fouling [48].
1.5.5 c) Nanofiltration

Between ultrafiltration and reverse osmosis (RO), pore size of nanofiltration (NF) membranes is typically 1 nm which corresponds to molecular weight cut off (MWCO) of 300–500 Da. NF membranes in contact with aqueous solution are also slightly charged due to dissociation of surface functional groups or adsorption of charge solute. Similar to RO membranes, NF membranes are efficient in the separation of inorganic salts and small organic molecules. The characteristics of NF membranes are lower rejection of monovalent ions, higher rejection of divalent ions and higher flux compared to RO membranes. Due to this reason, NF membranes are now widely applied in food and beverage processing such as demineralization of dairy products, concentration of fruit juice and treatment of wastewater in food industry [49].

Nanofiltration is a kind of pressure-driven process between reverse osmosis and ultrafiltration processes. Because of its advantages such as low operating pressures, high fluxes, high retentions of multivalent salts, low investment and operation costs, this technology is rapidly developed for different applications such as water softening, color removal, chemical oxygen demand (COD) and biological oxygen demand (BOD) reduction. Most of the commercial nanofiltration membranes are thin-film composite (TFC) membrane. The main advantage of TFC membrane is that the membrane properties can be controlled by optimizing the characteristics of the thin selective layer and support. The thin selective layer can be optimized for solute rejection and permeability by controlling the polymerization such as coating time, monomers concentration and curing temperature. Various supports with different porosity, strength and solvent resistance can be selected for preparing TFC membrane. The polysulfone or polyethersulfone ultrafiltration membranes are generally used as support for making thin-film composite nanofiltration membrane [50].
1.5.5 d) Ultrafiltration

Ultrafiltration (UF) is gradually emerging as promising separation tool in many applications across a range of food and beverage industries, including fluid milk, dairy products, juiced fruit and vegetables, wine, sugar and other sweeteners, vegetable oils, and water and wastewater treatments [51]. Ultrafiltration uses a finely porous membrane to separate water and microsolutes from macromolecules and colloids. The average pore diameter of the membrane is in the 10–1000 Å range. Ultrafiltration and microfiltration are related processes—the distinction between the two lie in the pore size of the membrane. Microfiltration membranes have larger pores and are used to separate particles in the 0.1–10 μm range, whereas ultrafiltration is generally considered to be limited to membranes with pore diameters from 10 to 1000 Å.

Regular cleaning is required to maintain the performance of all ultrafiltration membranes. The period of the cleaning cycle can vary from daily for food applications, such as ultrafiltration of whey, to once a month or more for ultrafiltration membranes used as polishing units in ultrapure water systems. The high cost per gallon of permeate produced limits the expansion of ultrafiltration into most large wastewater and industrial process stream applications. The costs are high because membrane fluxes are modest, large amounts of energy is used to circulate the feed solution, to control fouling membrane modules must be cleaned frequently, and membrane lifetimes are short. These are all different aspects of the same problem—membrane fouling. Unfortunately, membrane fouling and gel layer formation are inherent features of ultrafiltration. Vibrating membrane modules have been introduced recently and, although costs are high, their performance is very good [45].

1.5.5 e) Electrodialysis

Electrodialysis (ED) is an electrochemical separation process that employs electrically charged ion exchange membranes with an electrical potential difference as a driving force [52] and it has been widely applied in seawater and brackish water desalination as well as wastewater treatment.
Numerous investigations have been performed to apply electrodialysis technology in other fields, including fermentation broth desalination, metal ion separation and food processing, due to its inherent advantages such as being environmentally friendly, convenience of operation, and low energy consumption [53].

Related electromembrane technologies were subsequently developed by optimizing the membrane stack configuration and operational processes. Examples of these technologies such as, bipolar membrane electrodialysis can be used in the regeneration of acids and bases from inorganic salts and in organic acid production by water splitting in the bipolar membrane interface. In addition, continuous electrodeionization has been used to produce pure and ultrapure water [53].

Fouling of ion exchange membranes is considered to be one of the most important limitations on the design and operation of electrodialysis processes. It is generally accepted that fouling occurs in membrane processes due to deposition of foulants (organic substances, colloidal particles, proteins, etc.). It is accepted that colloidal fouling is caused by the accumulation of colloidal particles on the membrane surface, followed by coagulation. The deposition of silica sol significantly decreases the performance of the pressure-driven membrane processes (ultrafiltration, nanofiltration, and reverse osmosis) by plugging into the pore structures. Electrodialysis performance is also affected by deposition of colloidal particles, which is related to the electrochemical properties of the particles. Colloidal particles having negative charges move toward anion exchange membranes in the electric field during electrodialysis. Then the colloidal particles deposit on the membrane surface due to electrostatic attraction between the positively charged anion exchange membrane and the negatively charged colloidal particles [52].

1.5.6 Advanced oxidation process

Advanced oxidation process (AOP) is a chemical treatment which is designed to remove compounds and carcinogens in water. The water is
analyzed first for its inorganic and organic compounds and then a specific type and amount of reagent is added to the compound to create radicals and then chemically turned the waste water back to pure water. Common reagents include ozone, hydrogen peroxide, and oxygen. The main mechanism of AOPs function is the generation of highly reactive free radicals. The hydroxyl radicals (HO•) are effective in destroying organic chemicals because they are reactive electrophiles (electron preferring) that react rapidly and nonselectively with nearly all electron rich organic compounds. They have an oxidation potential of 2.33 V and exhibit faster rates of oxidation reactions compared to conventional oxidants such as H₂O₂ or KMnO₄. Once generated, the hydroxyl radicals can attack organic chemicals by radical addition, hydrogen abstraction and electron transfer [54, 55].

The AOP procedure is particularly useful for cleaning biologically toxic or non-degradable materials such as aromatics, pesticides, petroleum constituents and volatile organic compounds in waste water. A goal of the waste water purification by means of AOP procedures is the reduction of the chemical contaminants and the toxicity to such an extent that the cleaned waste water may be re-introduced into receiving streams [54, 55].

1.5.6 a) UV/O₃ process

The use of Advanced Oxidation Processes involving the combination of UV-irradiation and oxidants (O₃, H₂O₂) and/or catalyst (Fe²⁺, TiO₂) has become an alternative to electron-beam processing technology as well as to conventional water treatment plants. Hence, comparative studies of photo and radiation induced processes in the absence and presence of ozone are undertaken for the degradation of water pollutants. Another approach to detoxification of water is ozonation. Ozone is a powerful oxidizing agent and hence is used on a technical scale for purification of drinking water as well as wastewater. Ozone may react with solutes either by direct oxidation (O₃ attack takes place at the electron rich site of the solute) or after radiolysis or photolysis, whereby OH radicals are resulting. Although, these radicals react
very rapidly with organic and inorganic solutes, they exhibit little solute selectivity [56].

The UV/O₃ system is an effective method for the oxidation and destruction of organic compounds in water. Basically, aqueous systems saturated with ozone are irradiated with UV light of 253.7 nm. The extinction coefficient of O₃ at 253.7 nm is 3300 L.mol⁻¹.cm⁻¹ which is much higher than that of H₂O₂ (18.6 L.mol⁻¹.cm⁻¹). The decay rate of ozone is about a factor of 1000 times higher than that of H₂O₂.

\[
O_3 + H_2O \rightarrow O_2 + H_2O_2 \quad \text{(in the presence of UV light)}
\]

\[
2 \ O_3 + H_2O_2 \rightarrow 2 \cdot OH + 3 \ O_2
\]

The AOP with UV radiation and ozone is initiated by the photolysis of ozone. The photodecomposition of ozone leads to two hydroxyl radicals which do not act to produce hydrogen peroxide [57].

1.5.6 b) UV/H₂O₂

Photochemical oxidation as a powerful degradation method seems to be very promising for drinking water treatment. By means of photolysis of H₂O₂, the reactive HO• radicals can be formed. It is known that HO radicals are able to oxidize nearly all organic substances. In contrast to UV disinfection, UV/H₂O₂ is based on two major mechanisms: (i) absorption of UV photons which leads to excitation of molecules which may result in breaking of bonds (ii) reaction of organic micro pollutants with hydroxyl radicals that are formed in the reaction between H₂O₂ and UV photons. A major difference between UV disinfection and UV/H₂O₂ oxidation is the applied UV dose. The UV dose is directly related to the energy input which may be up to about 35 times higher for UV/H₂O₂ oxidation (500 – 750 mJ/cm²) than for UV disinfection (20 – 70 mJ/cm²). The higher the energy input the molecular bonds are broken more easily. Since, besides direct photolysis micro pollutants also strongly react with
Chapter 1

the in situ produced hydroxyl radicals in UV/H₂O₂ systems and the level at which by products are formed is much higher than in disinfection systems. The question is whether these levels can be satisfactorily controlled during high quality drinking water production [58].

1.5.7 Biological treatment

Biological treatment of waste water is evaluated as a good treatment for industrial effluents. In waste water treatment, the removal of undesirable organic impurities is achieved through biological treatment with bacteria, involving the stabilization of waste by decomposing them into harmless inorganic solids either by aerobic or anaerobic modes. In aerobic systems oxygen supply in waste water is done through aeration devices. As the oxygen solubility in water is limited, the driving force is small and this necessitates improving the conditions for mass transfer at the interface of air and waste water. In aerobic process, the decomposition rate is more rapid than the anaerobic process, whereas in anaerobic process, longer detention period is required. Hence, the aerobic treatment was accomplished to better performance in the treatment of wastes. It is an economical method for the treatment of concentrated, soluble, non-toxic and organic wastes [59].

1.5.8 Adsorption

Adsorption arises as a result of the unsaturated and unbalanced molecular forces that are present on every solid surface. Thus, when a solid surface is brought into contact with a liquid or gas, there is an interaction between the fields of forces of the surface and that of the liquid or the gas. The solid surface tends to satisfy these residual forces by attracting and retaining on its surface the molecules, atoms, or ions of the gas or liquid. This results in a greater concentration of the gas or liquid in the vicinity of the solid surface than in the bulk gas or vapor phase, despite the nature of the gas or vapor. The process by which this phenomenon is caused is called adsorption phenomenon. “Adsorption is surface phenomenon in which collection or accumulation of
Chapter 1

REMOVAL OF DYES AND HEAVY TOXIC METALS WITH ADSORPTION TECHNIQUE USING LOW COST ADSORBENTS

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 [60]. Adsorption phenomenon is mainly related with two terms adsorbent and adsorbate.

(1) **Adsorbent**: The substance which adsorbs another substance on its surface is called as adsorbent. e.g.- charcoal, coconut shell fibers etc.

(2) **Adsorbate**: The substance which itself get adsorbed on the surface of another substance is called adsorbate. e.g.- heavy elements as Cr, Pb etc.

**1.6 TYPES OF ADSORBENT**

There are many types of adsorbents developed and applied for various applications. Some examples of adsorbents are (I) activated carbon (II) silica gel (III) fly ash (IV) clays (V) zeolites (VI) biosorbents etc.

**1.6.1 Activated carbon**

**1.6.1 a) Historical background of the activated carbons**

The use of carbon extends far back in time that its origin is impossible to determine exactly. The first recorded case dates back to 3750 BC, when both the Egyptians and Sumerians used wood char for the reduction of copper, zinc and tin ores in the manufacture of bronze, and also as a smokeless fuel [61]. The first proof of the medicinal use of carbon was found in Thebes (Greece), in a papyrus document from 1550 BC [62]. Later on, Hippocrates (around 400 BC) recommended that water should be filtered with wood char prior to consumption, in order to eliminate bad taste and odour and to prevent several diseases, including epilepsy, chlorosis and anthrax. Nevertheless, the first reported application of activated carbons as a gas phase adsorbent did not take place until as late as 1793 AD, when Dr. D.M. Kehl applied woodchar in order to mitigate the odours emanating from gangrene. The first application of activated carbon in the industrial sector took place in England in 1794, when it
was used as a decolorizing agent in the sugar industry. This application remained a secret until 1812 (18 years), when the first patent appeared in Great Britain. The first patent for the thermal regeneration of activated carbon dates from 1817, and a continuous process for manufacturing and regenerating bone char were developed in Germany in 1841. At about the same time, activated carbon material, as it is known now a day was discovered by R. Von Ostrejko, who is considered as the father and inventor of activated carbon. In 1910, Wijnberg and Sauer acquired the patent rights, and were the first to apply activated carbons to the sugar industry (Norit White Sugar Company) [63]. The First World War stimulated the development of both the production and application of activated carbons. The use of poisonous gases by the German army against the French, British and Russians on different fronts, posed a severe problem for the allies, and as a consequence, there was an urgent need for gas mask development. From the Second World War the importance of activated carbon was emerged in all applied field and till it is continued [64].

1.6.1 b) Methods of development of activated carbon

It is also called activated charcoal or activated coal is form of carbon that has been processed to make it extremely porous and thus to have very large surface area available near about 800-1500 m²/g for adsorption or chemical reaction. Activated carbon is usually derived from carbonaceous source materials like nut shells, wood and coal. It can be produced by following methods [65]

(I) Physical activation
This generally is done by using one process or combining following two processes.

(i) Carbonization
Materials with high carbon contents are pyrolysed at 873-1173 K in the absence of air.
(ii) Activation/Oxidation

Raw materials or carbonized materials are exposed to oxidizing atmosphere (CO$_2$, O$_2$, steam) at temperature above 523 K, usually in the temperature range of 873-1473 K.

(II) Chemical activation

Impregnation with chemicals such as acids like phosphoric acid, sulphuric acid or bases like KOH, NaOH or salts like zinc chloride followed by carbonization at temperature in the range of 723-1173 K.

1.6.1 c) Classification of activated carbon

Based on their physical characteristics activated carbon adsorbents are classified as,

(I) Powdered activated carbon (PAC)

It is made up of crushed or ground carbon particles, 95–100% of which will pass through a designated sieve 0.297 mm according to the American Water Works Association Standard.

(II) Granular activated carbon (GAC)

It is designated by mesh sizes such as 8 × 20, 20 × 40 or 8 × 30 for liquid-phase applications and 4 × 6, 4 × 8 or 4 × 10 for vapor-phase applications. GAC is used for the removal of toxic organic compounds from ground water, and industrial waste water.

(III) Extruded activated carbon (EAC)

This type of carbon consists of cylindrical shaped activated carbon with diameters from 0.8-45 mm. These are mainly used for gas phase applications.

(IV) Impregnated carbon

Porous carbons containing several types of inorganic impregnates such as an iodine, silver and cations such as Al(III), Mn(II), Zn(II), Fe(III), Li(I) have also been prepared.
Chapter 1

(V) Polymer coated carbon

This is a process by which a porous carbon can be coated with a biocompatible polymer to give smooth and permeable coat without blocking the pores. e.g. Adsorption of patient’s blood to remove toxic substances from blood.

1.6.2 Silica gel

Silica gel is synthetic amorphous silica consisting of a compact network of spherical colloidal silica particles. Its surface area is typically between 300 and 850 m²/g. The predominant pore diameters are in the range 22 to 150 Å. Silica gel is a chemically inert non-toxic, polar and dimensionally stable (<673 K) amorphous form of SiO₂. It is prepared by the reaction between sodium silicates and H₂SO₄ followed by aging, pickling etc.

1.6.3 Fly ash

Fly ash is one of the residues generated in the combustion of coal. It consists of mainly SiO₂, which is present in two forms (a) amorphous-which is rounded and smooth (b) crystalline- which is sharp, pointed and hazardous (Al₂O₃ and Fe₂O₃). Fly ashes are generally highly heterogeneous consisting of mixture of glassy particles with various crystalline phases such as quartz, mullite and various iron oxides. It is presently used in the synthesis of geopolymers and zeolites and also in waste water treatment.

1.6.4 Clays

The major content of clay minerals is metal oxide such as SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO. Depending upon the source there are five main groups of clays 1) Kaolinite 2) Montmorillonite 3) Smectite 4) Illite 5) Chlorite. Montmorillonite is having small size, large surface area and highest cation exchange capacity for the removal of heavy metals from waste water and air purification.
1.6.5 Zeolites

Zeolite molecular sieves are composed of silicon and aluminum and can be natural or manmade minerals. Molecular sieves are crystalline, hydrated aluminosilicates of (most commonly) Na(I), K(I), Ca(II), Mg(II) and others. The alumininosilicate portion of the structure is a three dimensional open framework consisting of a network of AlO$_4$ and SiO$_4$ tetrahedra linked to each other by sharing all of the oxygens.

$$R_{2n}^{n^+}.Al_2O_3. X SiO_2.H_2O$$

Zeolites may be represented by the above empirical formula where $X$ is generally equal to or greater than 2, and $n$ is the cation valence. The zeolite framework contains pore channels and interconnected voids and cavities, which are occupied by cations and water molecules. These cations are generally mobile and can be exchanged. Zeolites have a micro-porous structure. They have an open structure that can accommodate a wide variety of cations. These positive ions are rather loosely held and can be readily exchanged for others in a contact solution. Some common zeolites are analcime, chabazite, heulandite, natrolite, phillipsite and stilbite etc.

1.6.6 Chitosan

Chitosan has a molecular structure similar to cellulose. This material is produced from chitin, which is widely found in the shell of fish and crustaceans. Chitin is the second most abundant natural biopolymer after cellulose. Chitosan is a good adsorbent for all heavy metals.

1.6.7 Peat moss

Peat moss is a complex soil material containing lignin and cellulose as major constituents. It is a widely available natural substance. It has a large surface area (>200 m$^2$/g) and is highly porous.
1.6.8 Biosorbent

Biosorbent is nothing but the dead biomass, which is used as it is or by treatment with reagent as low cost biosorbents. The biological waste, agriculture waste, fruit waste, food waste are used as adsorbent. The results reported in literature show the sorption capacity for biosorbent is more than commercial activated carbon. This may be due the various functional groups that are present on the dead biomass surface. Some biosorbents are cotton stalk, cotton waste and cotton dust [66], beech wood saw dust [26], shells of lentil, wheat, rice [67] etc.

1.7 ADVANTAGES OF ADSORPTION TECHNIQUE OVER OTHER METHODS

There are several methods developed as per very vital issue of potable water is concerned. The methods are having there own advantages as well as disadvantages. If all other methods are taken in consideration, all are good but they are not feasible due to there cost and operation. In case of chemical precipitation, coagulation and flocculation there is high sludge production and handling and disposal are the main problems. They fail for soluble pollutants and running cost is high. Membrane separations is facing problem like high pressures, expensive, incapable of treating large volumes as well as fouling of membrane. Ion-exchange has economic constraints and not effective for disperse dyes as well as non-ionic pollutants. Solvent extraction is having high cost of extractant, appreciable solubility of solvents in water results in high solvent loss and method itself result in pollution. The oxidation is very expensive, difficult to scale up and formation of byproducts is inevitable. The biological treatment is incapable of effectively treating organic waste, removing color and it requires more space.

In comparison with the adsorption, all these processes, requires additional chemicals, which causes environmental pollution, corrosion and the processes are more expensive. Adsorption is the most effective method which has great capacity to produce a high-quality treated effluent. This is useful for
removal of heavy metal, dye and organic pollutants. Selective adsorption, utilizing biological materials, mineral oxides, activated carbon or polymer resins, has generated much excitement among researchers, environmental engineers and scientists. There are many absorbents reported with great capacity as well as the process takes place in very short time.

1.8 HISTORY AND GENERAL PRINCIPLE OF ADSORPTION

The use of activated carbon has ancient history. The term “adsorption” was first used by H. Kayser in 1881. J. W. McBain introduced a similar term in 1909, i.e. “absorption”, to determine an uptake of hydrogen by carbon much slower than adsorption. He proposed the term “sorption” for adsorption and absorption. In 1903, Tswett was the first to study selective adsorption. He investigated the separation of chlorophyll and other plant pigments using silica materials. The technique proposed by Tswett has been called “column solid liquid adsorption chromatography.” However, there was no sound theory that enabled the interpretation of adsorption isotherm data until 1914. Despite the fact that the Freundlich equation was used, there was no theoretical justification for it. It was an empirical equation, proposed actually by van Bemmelen in 1888. However, it is today known as the Freundlich equation, as Freundlich assigned great importance to it and popularized its use. Langmuir was the first to have introduced a clear concept of the monomolecular adsorption on energetically homogeneous surfaces in 1918 and derived the equation based on kinetic studies. The first practical application of adsorption was based on the selective removal of individual components from their mixtures using other substances. The first filter for water treatment was installed in Europe and the United States in 1929 and 1930, respectively. Activated carbon was recognized as an efficient purification and separation material for the synthetic chemical industry in 1940s. By the late 1960s and early 1970s, activated carbon was used in many applications for removing a broad spectrum of synthetic chemicals from water and gases [65].
It is well known that, unbalanced or residual forces act along the surface of a liquid giving rise to surface tension. Such force also exits on the surface of a solid. As a result of these residual forces, the surface of a solid has tendency to attract and retain molecules of other species with which it is brought into contact. As these molecules remain only at the surface and do not go deeper into the bulk, their concentration is more at the surface than in the bulk of the solid. The phenomenon of higher concentration of any molecular species at the surface than in the bulk of a solid is known as adsorption. The forces involved are, evidently intermolecular forces (van der Waal’s forces). The adsorption may form the chemical bond between adsorbate and adsorbent [68].

At the molecular level, adsorption is due to attractive interactions between a adsorbent surface and the species being adsorbed. The magnitude of these interactions covers approximately two orders of magnitude (8–800 kJ/mol), similar to the range of interactions found between atoms and molecules in bulk phases. The types of adsorption are,

1.8 a) Physical adsorption

In physical adsorption (physisorption), no exchange of electrons is observed; rather, intermolecular attractions between favorable energy sites takes place and are therefore independent of the electronic properties of the adsorbent and adsorbate involved. In physical adsorption there is van der Waals interaction between adsorbate and adsorbent. The van der Waals interactions are long range, weak and the energy released when a particle physisorbed is of the magnitude of the enthalpy of condensation. Such small energies can be absorbed as vibrations of the lattice and dissipated as thermal motion and a molecule bouncing across the surface will gradually loose its energy and finely adsorb to it in the process called accommodation. The enthalpy of physisorption can be measured by monitoring the rise in temperature of a sample of known heat capacity and the typical values are in the region of 20 kJ/mol. This small enthalpy change is insufficient to lead to bond breaking, so
a physisorbed molecule retains its identity, although it might be distorted by the presence of the surface.

Physical adsorption is usually observed at low temperature. Physical adsorption equilibrium is very rapid in attainment and is reversible, the adsorbate being removable without change by lowering the pressure [69, 70].

1.8 b) Chemical adsorption

Chemical adsorption (chemisorption) involves an exchange of electrons between specific surface sites (adsorbents) and solute molecules (adsorbates) and as a result a chemical bond is formed. In chemical adsorption, the molecules (or atoms) stick to the surface by forming a chemical (usually covalent) bond and tend to find sites that maximize their co-ordination number with the substrate. The enthalpy of chemisorption is very much greater than that for physisorption and the typical values are in the region of 200 kJ/mol. The distance between the surface and the closest adsorbate is also typically shorter for chemisorption than for physisorption. A chemisorbed molecule may be torn apart at the demand of unsatisfied valencies of the surface which indicates reason why solid surfaces catalyse reactions.

Generally, only a single molecular layer can be adsorbed. Chemical adsorption may be rapid or slow and may occur above and below the critical temperature of the adsorbate [69, 70].

1.9 ADSORPTION FROM SOLUTION

The adsorption of organic and inorganic compounds from their aqueous solutions has been found to be influenced by the presence of carbon-oxygen surface groups. The adsorption, although determined by surface area of the carbon, was strongly influenced by the presence of acidic surface oxides. The adsorption of cationic dyes increased with the increase in the amount of surface oxygen group on oxidation of the carbons and decreased when these surface oxides were removed on evacuation. In the case of anionic dyes, the adsorption decreased on oxidation, the extent of decrease depends upon the increase in the
amount of acidic surface groups. The adsorption of several metal cations such as Cr(III), Cr(VI), Co(II), Cu(II) and Ni(II) on several activated carbons have different surface areas and associated with varying amounts of carbon-oxygen surface groups. The adsorption could not be related to surface area alone, but also depend upon the amount of the surface oxygen groups and more so on the acidic oxygen groups. The adsorption of these cations increased on oxidation and decreased on degassing. The increase in adsorption on oxidation has been attributed to the creation of acidic surface groups that ionize in water to produce H⁺ ions, which are directed toward the liquid phase, leaving the carbon surface with negative sites on which the adsorption of metal cations could take place. When these negative sites are eliminated on degassing, the carbon surface loses its tendency to adsorb cations [3].

In general adsorption of solutes from solutions can occur on various solids to different extents, which is the same as for gases. It may in general be traced to two effects:

(i) Due to decrease in the interfacial tension through adsorption of a solute, and

(ii) Due to solid surface acquiring electrostatic charge in a solvent. This charged surface of adsorbent then attaches oppositely charged ions from the solution.

This type of adsorption is of three types [60]:

1.9. a) Positive adsorption:

In this type, solute alone is adsorbed and the concentration of the solution gets decreased. An interesting example is that, when activated charcoal is kept in contact with the dilute solution of acetic acid, a part of acid is adsorbed by the charcoal and the concentration of the acid decreases.

1.9. b) Negative adsorption:

In this type, the solvent is adsorbed and the concentration of the solution is increased and an interesting example is that when blood charcoal is added to potassium chloride solution, the concentration of the solution gets increased. This type of adsorption is not very common.
1.9. c) Electrostatic adsorption:

Many solids are known which on coming in contact with water acquire an electrostatic charge. This may be positive due to the attachment of $\text{H}^+$ ions or negative due to the attached $\text{OH}^-$ ions to the surface of solid. These acquired charges on the surface will have the tendency to attract oppositely charged ions of solutes from the solutions. This is termed as electrostatic adsorption and, if possible, would occur over and above mechanical adsorption. The example of electrostatic adsorption is silica powder which acquires a negative charge on coming in contact with water. If this silica powder having negative charge is shaken with positively charged ferric hydroxide sol and then filtered, the filtrate will be colourless, illustrating the phenomenon of electrostatic adsorption.

1.10 FACTORS AFFECTING THE ADSORPTION

The phenomenon of adsorption of gases by solids depends upon the following factors [60],

1.10. a) Nature of the adsorbent and adsorbate

The amount of the gas adsorbed depends upon the nature of the adsorbent and the gas (adsorbate) which is to be adsorbed.

As the critical temperature of the easily liquefiable gases are more than the permanent gases, it follows that higher the critical temperature of the gas (adsorbate), the greater the extent of adsorption.

1.10. b) Surface area of the adsorbent

The extent of adsorption of gases by solids depends upon the exposed surface area of the adsorbent. It is well known that larger the surface area of adsorbent, the larger will be the extent of adsorption under the given conditions of temperature and pressure. It is for this reason that silica gel and charcoal obtained from different animal and vegetable sources become activated because they possess a porous structure and thereby render a larger surface.
1.10. c) The partial pressure of the gas in the phase

For a given gas and a given adsorbent, the extent of adsorption depends on the pressure of the gas. Adsorption of a gas is followed by decrease of pressure. Therefore, in accordance with Le Châtelier’s principle, the magnitude of adsorption decreases with the decrease in pressure and vice-versa. The variation of adsorption with pressure at constant temperature is expressed by a curve known as adsorption isotherm.

1.10. d) Effect of temperature

For a given adsorbate and adsorbent, the extent of adsorption depends upon the temperature of the experiment. As discussed earlier, adsorption usually takes place with the evolution of heat. Therefore, according to Le Chaterlier’s principle, the decrease in temperature will increase the adsorption and vice-versa.

1.11 GENERAL APPLICATIONS OF ADSORPTION [3, 60, 68]

1) In the gas mask, activated carbon has been used since World War I to adsorb the toxic gases.

2) Softening of hard water is achieved with adsorption technique. The removal of minerals as well as salts from water and the heavy metals is also possible with this method.

3) The adsorptive force of silica gel and alumina for water is very great. It, therefore, acts as a good drying agent to control the humidity.

4) Activated carbon adsorption from liquid phase has found wide applications in several areas of food production and processing industries. The activated carbons remove undesirable odors, colors, and unwanted components of the solution, and improve the quality and consumability of the food material.

5) The adsorption phenomenon is used in distilleries for refining neutral spirits and rectified spirits.

6) Activated carbons used in the preparation of different wines must conform to special requirements.
7) For decolorization of oils and fats, activated carbon is not used alone but always in combination with certain bleaching clays.

8) The manufacturing of white sugar by decolorization of sugar solutions by adsorption on wood charcoal was first reported from a London refinery.

9) One of the oldest and the most widespread applications of activated carbon adsorption is the decolorization of organic components. During the processing of organic compounds, several types of polymeric impurities impart dark color and bring about serious technological problems, particularly during crystallization. This application is used in chemical and pharmaceutical industries.

10) The wood charcoal could also be used for the recovery of gold from cyanide leaches liquors by adsorption. The activated carbons have high selectivity for gold and silver in the presence of large concentrations of base metals such as copper, iron, nickel, cobalt, antimony and their availability in abundance.

11) After the electroplating process, the effluent contains organic impurities, such as emulsified oils and fats, residues of lacquers, decomposition products of wetting agents and brighteners and many other impurities from the soluble and emulsified substances, the activated carbon treatment is most advantageous during this.

12) Gasoline contains several types of sulfur compounds, including mercaptans. These compounds can be removed from gasoline using activated carbons impregnated with sodium hydroxide.

13) The recovery of organic solvents and the removal of certain volatile organic compounds from industrial waste gases is one of the important and largest gas phase application of active carbons.

14) Adsorption also plays an important role in heterogeneous catalysis, e.g. the role of finely divided iron in the manufacture of ammonia and that of finely divided nickel in the hydrogenation of oils.
1.12 PRESENT WORK

In the present work, we have developed the low cost adsorbent from the easily and abundantly available material and in very simple manner. As the adsorption is concerned the activated carbon is most applied adsorbent in various applications. As the commercial activated carbon is expensive, we have developed the low-priced and effective adsorbent from wood apple shell, coconut shell, mahogany fruit shell and used to apply to remove the heavy metals and dyes from the aqueous solution.

Wood apple shell activated carbon has been prepared with help of sulphuric acid and made porous by heating at 573 K in muffle furnace. The developed adsorbent was characterized by FTIR, SEM and C, H, N, S Elemental analyzer and other properties were also investigated. The developed adsorbent was used to remove heavy metal ions Cr(VI) and Cd(II) from aqueous solution. The removal of Cr(VI) ions with an initial concentration of 90 mg/g was found to be 98.05% after shaking for 180 min at 140 rpm at constant temperature. In case of Cd(II) ion, the different operational parameters observed during the process of investigations reveal that the contact time, initial concentration, adsorbent mass, pH of solution, stirring speed and temperature govern the overall process of sorption. It can be efficiently used to remove 98.80% cadmium ions from aqueous solution.

For both of the metal ions, the increase in the adsorption capacity was observed with increasing temperature which showed that the adsorption process was chemical in nature, being feasible, spontaneous and endothermic as confirmed by the evaluation of the relevant thermodynamic parameters, viz. $\Delta H^0$, $\Delta G^0$ and $\Delta S^0$. For both metal ions, the experimental data for the adsorption process was well fitted by the Langmuir adsorption isotherm model relative to the fit of the Freundlich adsorption model. The Langmuir adsorption capacity was determined as 13.74 mg/g for Cr(VI) adsorption while Langmuir fits better than Freundlich isotherm with 28.33 mg/g maximum adsorption capacity in case of Cd(II). Kinetic pseudo-first order model was followed by this adsorption study.
Another adsorbent was developed from coconut shell by same manner and characterized also in the same way; it was applied to adsorb the bismuth from aqueous solution. This developed activated carbon is has the high capacity to adsorb Bi(III) ions from aqueous solution with amount adsorbed from 17.62 mg/g to 53.47 mg/g as per increase in the initial concentration up to 1000 mg/dm³. All adsorptions were carried out in acidic pH. The required period was only 4 h. The removal percentage was significant i.e. 98.62%. The models of adsorption like Langmuir and Freundlich are also studied, amongst them Langmuir equation shows more applicability to the experimental data than Freundlich isotherm. The rate of adsorption was also investigated with kinetic study and it was found that the experimental data fits better in pseudo-second order than pseudo first order. The adsorption study was feasible, spontaneous and endothermic, which was confirmed by the evaluation of thermodynamic parameters as standard free energy change ($\Delta G^\circ$), standard enthalpy change ($\Delta H^\circ$), and standard entropy change ($\Delta S^\circ$) successfully.

We have introduced a new adsorbent Mahogany fruit shell. It was also characterized as like above adsorbents. This adsorption study has been carried out with inexpensive adsorbent, to determine the parameters like, pH, agitation period, speed, initial concentration etc. as well as the isotherm, kinetic and thermodynamic models were applied to remove methylene blue (MB) dye. The removal of MB was possible by this adsorbent up to 99.05% in 100 mg/dm³ concentration of the dye. The study was evaluated with isotherm models among them, Langmuir adsorption was fitted better with its capacity correlated with calculated value. The kinetic study has been shown the pseudo second order is more suitable for this study. The process is endothermic and spontaneous, and evaluated the thermodynamic parameters such as $\Delta H^\circ$, $\Delta G^\circ$ and $\Delta S^\circ$.

Wood apple shell (WAS), a fruit and food solid waste, was successfully utilized as a low cost alternative adsorbent for the removal of hazardous dye Malachite green (MG). It was also characterized as like all earlier adsorbents. The removal of MG with initial concentration 100 mg/dm³ at pH 8-10 was found to be 98.87% in 3.30 h by shaking at 150 rpm and at constant
temperature. The adsorption equilibrium data is in good agreement with the Langmuir isotherm model. The adsorption kinetics followed pseudo first order kinetic equation for sorption of MG onto WAS. Thermodynamic studies demonstrate the spontaneous and endothermic nature of biosorption process due to negative values of free energy change and positive value of enthalpy change, respectively.

References


[44] N. Saffaj, H. Loukili, S. A.Younssi, A. Albizane, M. Bouhria, M. Persin, A. Larbot, Filtration of solution containing heavy metals and dyes by
Chapter 1


