CHAPTER 1

INTRODUCTION

1.1 WATER POLLUTION

Water is the basic necessity for the sustenance of life. In the present scenario, millions of people worldwide are suffering due to the unavailability of fresh and clean drinking water. The rapid increase in industrialization, population explosion and unplanned urbanization pollute the environment, especially water. The main reasons for freshwater pollution are the discharge of untreated sanitary and toxic industrial wastes, dumping of industrial effluents, and the runoff from agricultural fields. In particular, the effluents from textile, leather, tannery, galvanizing, electroplating, pigment and dyes, metallurgical and paint industries and other metal processing and refining operations on small and large-scales, contain considerable amounts of toxic metal ions. The presence of heavy metals in wastewater is always a serious environmental problem, because the heavy metals are not biodegradable and they get accumulated in living tissues. The presence of these heavy metals even at very low concentrations in water, would be harmful to human health and aquatic organisms in terms of toxicity and carcinogenicity.

1.1.1 Toxicity of Heavy Metals

Heavy metals in surface and groundwater supplies have been prioritized as major inorganic contaminants of the environment, particularly because of their mobility in aquatic ecosystems, and their toxicity towards
higher forms of life. Their presence even in low concentrations or undetectable quantities, leads to their recalcitrant and consequent persistence in water bodies, exhibiting toxic characteristics. These metals can either be detected in their elemental state, showing that they are not subjected to further biodegradative processes, or can be found in the form of various salt complexes. In either instance, metal ions cannot be mineralized. Apart from environmental issues, the technological aspects of metal recovery and reuse from industrial wastewater, must also be considered.

1.1.2 Effects of Heavy Metals on Human Health

Heavy metals such as lead, copper, cadmium, zinc and nickel are hazardous to human beings. These metals are found naturally in the soil in trace amounts, which pose few problems. When found in higher concentration in particular areas, they are dangerous. The harmful effects of these five heavy metals are as follows:

1.1.2.1 Lead

Lead occurs in water in the divalent state and arises from a number of industrial and mining sources. Lead is widely used in storage batteries, galvanization, petroleum refining, printing and pigment industries, paints, paper and pulp, electrodes in electrochemistry and chemical industries. Lead poisoning is a medical condition caused by increased levels of the lead ions in the human body. Lead interferes with the human metabolism, and is harmful to many organs and tissues including the heart, bones, intestines, kidneys, and the reproductive and nervous systems. It interferes with the development of the nervous system and is therefore particularly toxic to children, causing learning and behavioural disorders. Symptoms include abdominal pain, confusion, headache, anaemia, irritability, and in severe cases, seizures, coma.
and death. According to the Bureau of Indian Standards (BIS), the permissible limit of lead in drinking water is 0.01 mg/L (BIS 1994).

1.1.2.2 Copper

Copper is also one among the heavy metals, and is widely used in many industries including metal cleaning and plating baths, paints and pigments, fertilizer, paper board, wood pulp, printed circuit board production, etc. The effluents from these industries usually contain considerable quantity of copper, which spreads into the environment through soil and water streams, and finally gets accumulated along the food chain causing health hazards. A higher concentration of copper will cause severe mucosal irritation, widespread capillary damage, hepatic and renal damage, and irritation of the central nervous system followed by depression. The maximum recommended concentration of copper in drinking water as stipulated by the BIS is 0.05 mg/L (BIS 1992).

1.1.2.3 Cadmium

Cadmium is a heavy metal, which is regarded as an element of high toxicity. Cadmium ions are not biodegradable and can be accumulated easily in living tissues, and can be readily absorbed into the human body through the food chain. An excessive level of cadmium ions in water can affect biosystems and can pose a threat to human beings. Cadmium toxicity causes adverse health effects such as bone lesions, cancer, lung insufficiency and hypertension. The drinking water guideline value recommended for this element by the BIS is 0.003 mg/L (BIS 1992).

1.1.2.4 Zinc

Zinc is one of the most important heavy metals and it is released into the environment from various natural and anthropogenic activities, such
as acid mine drainage, galvanizing plants, ores and municipal wastewater treatments. Zinc ions are not biodegradable and can get accumulated easily in living tissues. Further they can get readily absorbed into the human body, through the food chain. Higher concentrations of zinc ions can cause hazardous effects in plants and animals. BIS has recommended the maximum permissible limit for zinc in drinking water as 5 mg/L (BIS 1994).

1.1.2.5 Nickel

Nickel is one among the toxic pollutants, and it gets into water from electroplating, refining and welding industries. Excessive amounts of nickel in water can affect biosystems and pose a threat to human beings. Toxicity that is due to nickel causes adverse health effects such as cancer, skin allergy and lung fibrosis. The most important health problems due to nickel and its compounds are allergic dermatitis (nickel itch) and increased incidence of cancers. The BIS requires nickel not to exceed 0.02 mg/L in drinking water (BIS 2003).

1.1.3 Effects of Heavy Metals on Aquatic Organisms

Aquatic organisms are adversely affected by heavy metals in the environment. The toxicity is largely a function of the water chemistry and the sediment composition in the surface water system. The metals are mineralized by microorganisms, which in turn are taken up by plankton and further by aquatic organisms. Finally, the metals which are several times biomagnified are taken up by man during the consumption of fish from the contaminated water.

- Slightly elevated level of metal ions in natural water may cause the following sub-lethal effects in aquatic organisms: histological or morphological changes in tissues.
Changes in physiology, such as suppression of growth and development, poor swimming performance, changes in circulation.

Changes in biochemistry, in particular enzyme activity and blood chemistry.

Changes in behaviour and reproduction cycle.

Metal ions enter the biological systems of aquatic organisms via three main pathways:

a) Free metal ions absorbed through the respiratory surface (e.g., gills) are readily diffused into the blood stream.

b) Free metal ions that are adsorbed onto the body surface are passively diffused into the blood stream.

c) Metals that are sorbed into food and particulates may be ingested or free ions present in water may directly get ingested. For example: Chromium is not known to accumulate in the bodies of fish, but high concentrations of chromium, due to the disposal of metal products in surface waters, can damage the gills of fish that swim near the point of disposal.

It is a known fact that 70-80% of illness in developing countries is due to water contamination, especially for women and children, who are more susceptible to diseases caused by water pollution. Heavy metals such as lead, copper, cadmium, zinc and nickel are among the most common pollutants available in industrial wastewater, as they are used to a greater extent in industries. Hence their removal and recovery from wastewater is important to protect the living environment (Tsekova et al 2010). As a result of the development of advanced analytical techniques and better health monitoring
technologies, the acceptable minimum concentration of these heavy metals is progressively decreasing. As such, stringent regulations have been introduced by many countries with respect to the presence of these heavy metals in water which makes the industries to treat industrial effluents properly before discharging them into the natural water-bodies containing fresh water. Considering the importance of water pollution control, a number of technologies have been developed.

1.2 CONVENTIONAL METHODS FOR METAL ION REMOVAL

It is essential to appraise the quality of water on a continuous basis due to the ever increasing demand for water for municipal and industrial applications. Water treatment process selection is a complex task involving the consideration of many factors which include, the space available for the construction of treatment facilities, the reliability of the process equipment, waste disposal constraints, desired finished water quality, and capital and operating costs. The treatment of wastewater to make it suitable for subsequent use constitutes physical, chemical and biological processes. A number of treatment technologies are available with varying degree of success to remove heavy metals from wastewater. Some of them are chemical precipitation, ion exchange, electro-winning, electro-coagulation, cementation, solvent extraction, evaporation, reverse osmosis and electrodialysis. However, most of them require substantial financial input initially, and their use is restricted because of the operational cost overriding the importance of water pollution control.

1.2.1 Precipitation

Precipitation is the most common method for removing toxic heavy metals upto parts per million levels from water. Some metal salts are
insoluble in water and get precipitated when appropriate anions are added. This process is cost effective, whose efficiency is affected by a low pH and the presence of other salts, and this requires the addition of other chemicals, ultimately leading to the generation of high sludge content, the disposal of which is cost intensive (Gray 1999). Precipitation with lime or bisulphide lacks specificity and is ineffective in the removal of metal ions at a low concentration.

1.2.2 Ion Exchange

Ion exchange is another method used successfully in industries for the removal of heavy metals from effluents. Though it is relatively expensive when compared to other methods, it has the ability to achieve parts per billion levels of clean up while handling a relatively large volume of effluents. An ion exchanger is a resin capable of exchanging either cations or anions from the surrounding materials. Ion exchange resins are available selectively for certain metal ions. The cations are exchanged for H\(^+\) or Na\(^+\). The cation exchange resins are mostly synthetic polymers containing an active ion group, such as the sulphonic acid group (SO\(_3\)H), and other possible groups like carboxylic acid group (-COOH). Natural materials such as zeolites can be used as ion exchange media (Van der Heen 1977). Modified zeolites like zeocarb and chalcarb have a greater affinity for metals like Ni and Pb (Groffman et al 1992). Ahmed et al (1998) reported the removal of cadmium and lead from an aqueous solution by the batch ion exchange with a solid Na-Y zeolite. Inglezakis et al (2005) investigated the effects of competitive cations NH\(_4\)^+, K\(^+\), Ca\(^{2+}\), Na\(^+\), Mg\(^{2+}\) and Li\(^+\) on the ion exchange of heavy metals Pb\(^{2+}\), Fe\(^{3+}\), Cr\(^{3+}\) and Cu\(^{2+}\) on clinoptilolite. The disadvantage of this method is that it cannot handle highly concentrated solutions, as the matrix gets easily fouled by organics and other solids in wastewater. Moreover, ion exchange is non-selective, and is highly sensitive to the pH of the solution.
1.2.3 Electro-winning

Electro-winning is widely used in mining and metallurgical industrial operations for heap leaching and acid mine drainage. It is also used in metal transformation, and electronics and electrical industries for the removal and recovery of metals. Metals like Ag, Au, Cd, Co, Cr, Ni, Pb, Sn and Zn present in the effluents can be recovered by electro-deposition using insoluble anodes (Gray 1999).

1.2.4 Electro-coagulation

Electro-coagulation is also an electrochemical approach, which uses electrical current to remove metals from a solution. This system is also effective in removing suspended solids, dissolved metals, tannins and dyes. The contaminants present in wastewater are maintained in the solution by electrical charges. When these ions and other charged particles are neutralized with ions of opposite electrical charges provided by the electro-coagulation system, they become destabilized and get precipitated in a stable form. Petsriprasit et al (2010) investigated the removal of various heavy metals, including Cu, Cr, Pb and Zn from billet industry wastewater by the electrocoagulation process.

1.2.5 Cementation

Cementation is the displacement of a metal from a solution by a metal higher in the electrochemical series. It offers an attractive possibility for treating any wastewater containing reducible metallic ions. In practice, a considerable spread in the electromotive force between metals is necessary to ensure adequate cementation capability. Due to its low cost and ready availability, scrap iron is the metal that is used often. Cementation is especially suitable for small wastewater flow, because a long contact time is
required. Some common examples of cementation in wastewater treatment include the precipitation of copper from printed etching solutions, and the reduction of Cr(VI) in chromium plating and chromate-inhibited cooling water discharges (Case 1974). The removal and recovery of lead ion by cementation on an iron sphere packed bed has been reported (Angelidis et al 1988, 1989). Lead was replaced by a less toxic metal in a harmless and reusable form.

1.2.6 Solvent Extraction

Liquid-liquid extraction of metals from solutions on a large scale has attained a phenomenal growth in recent years, due to the availability of large number of selective complexing agents (Beszedits 1988). In addition to hydrometallurgical applications, solvent extraction has gained widespread usage for waste reprocessing and effluent treatment. Solvent extraction involves an organic and an aqueous phase. When an aqueous solution containing the metal ion of interest, is mixed with an appropriate organic solvent, the metal ion passes into the organic phase. In order to recover the extracted metal, the organic solvent is contacted with an aqueous solution whose composition is such that the metal is stripped from the organic phase and is re-extracted into the stripping solution. The concentration of the metal in the strip liquor may be increased from 100 to 110 times over that of the original feed solution. Once the metal ion of interest is removed, the organic solvent is recycled either directly or after a fraction of it has been treated to remove the impurities. Di-n-pentyl sulphoxide has been evaluated as an extractant for the removal of Cr(VI), Fe(III), Co(II) and Ni(II) ions from an aqueous solution (Reddy and Sayi 1977). Cerna (1995) investigated the removal of zinc and lead using organophosphoric acid, bis (2-ethylhexyl) phosphoric acid as a solvent in the solvent extraction process. Shah et al (1995) reported that toluene mixed with Di-(2-ethylhexyl) phosphoric acid
removes lead efficiently. The extraction of Cr(VI) ion from an aqueous solutions of 0.1 M ionic strength by a trioctyl methyl ammonium compound, in a mixture of kerosene and xylene, indicates that the extraction of Cr(VI) ion in an acidic aqueous solution is good (Lo and Shiue1998).

1.2.7   Evaporation

In electroplating industries, evaporators are used chiefly to concentrate and recover valuable plating chemicals. Recovery is accomplished by boiling sufficient water from the collected rinse stream to allow the concentrate to be returned to the plating bath. Many of the evaporators in use also permit the recovery of the condensed steam to be recycled as rinse water. Four types of evaporators are used throughout the electroplating industry (USEPA 1979) (i) Rising film evaporators; (ii) Flash evaporators using waste heat; (iii) Submerged tube evaporators and (iv) Atmospheric evaporators. Both capital and operational costs for evaporative recovery systems are high. Chemical and water reuse values must offset these costs, for evaporative recovery to become economically feasible.

1.2.8   Reverse Osmosis and Electro-dialysis

Reverse osmosis and electro-dialysis are two different techniques involving the use of a semi-permeable membrane for the removal and recovery of metal ions from dilute wastewater. Reverse osmosis is a pressure driven membrane process in which a feed stream under pressure is separated into a purified permeate stream and a concentrated stream, by the selective permeation of water through a semi-permeable membrane (Applegate 1984; Gooding 1985). Stiason (1979) and Grampton (1982) investigated the use of reverse osmosis for the recovery of plating chemicals from rinse water as well as the purification of mixed wastewater to allow its reuse. In plating chemical recovery applications, reverse osmosis units separate valuable metal salts
from rinse solutions, yielding a concentrated metal solution, which can be recycled to the plating bath. Reverse osmosis has also been successfully demonstrated for the removal of Cr, Pb, Fe, Ni, Cu and Zn ions from vehicle wash-rack water (Chian 1976).

In electro-dialysis, ion selective membranes (alternation of cation and anion membranes) are fitted between the electrodes in electrolytic cells, and under continuous electrical current the associated ions migrate, causing the removal and recovery of metal ions. The result is that salinity decreases between one pair of membranes and increases between the next pair. Water can pass through several such membranes until the required salinity is achieved (Grebenyuk and Grebenyuk 2002; Chen et al 2007). Mohammadi et al (2004) investigated the removal of lead by electrodialysis.

However, these methods are either expensive or inefficient, when heavy metals exist in low concentrations (Nuhoglu and Malkoc 2009). And also they have several disadvantages that include complete metal ions removal, high reagent and energy requirements and generation of toxic sludge or other waste products that require proper disposal and further treatment. So, it is important to find new treatment methods for removing heavy metals from wastewater. In the present day scenario, adsorption is proven to be one of the simplest and most effective treatment methods for treating wastewater containing heavy metal ions (Ofomaja et al 2010).

1.2.9 Adsorption

The term adsorption refers to the accumulation of a substance at the interface between two phases, such as a solid and a liquid or a solid and a gas. The substance that accumulates at the interface is called ‘adsorbate’ and the solid on which adsorption occurs is the ‘adsorbent’. Although a certain phenomenon associated with adsorption was known in ancient times, the first
set of quantitative studies was reported by C.W. Scheele (1773) on the uptake of gases by charcoal and clays. This was followed by Lowitz’s observations; he used charcoal for the decolourization of a tartaric acid solution. Larvitz (1792) and Kehl (1793) observed a similar phenomenon with vegetable and animal charcoals, respectively. However, the term ‘adsorption’ was proposed by Bois-Reymond but introduced into literature by Kayser. Since then, the adsorption process has been widely used for the removal of solutes from solutions and gases from the atmosphere. At the surface of the solids, there are unbalanced forces of attraction, which are responsible for adsorption. In cases where the adsorption is due to weak van der Waals forces, it is called physical adsorption or physisorption. On the other hand, there may be a chemical bonding between the adsorbent and the adsorbate molecule, and such a type of adsorption is referred to as chemical adsorption or chemisorption.

1.3 COMMERCIAL ADSORBENTS

A number of materials have been extensively investigated as adsorbents in water pollution control. Some of the important ones include silica gel, activated alumina, zeolites, activated carbon, etc.

1.3.1 Silica Gel

Silica gels are classified into three types: regular, intermediate and low density gels. Regular density silica gel is prepared in an acid medium and shows a high surface area (750 m\(^2\)/g). Intermediate and low density silica gels have a low surface area (300-350 and 100-200 m\(^2\)/g, respectively). Silica gel is considered to be a good adsorbent and is used in many industries (Ahmed and Ram 1992; Backhaus et al 2001). Modified forms of silica have also been widely explored for the removal of different pollutants (Moriguchi et al 2005; Saad et al 2008; Wang et al 2009).
1.3.2 Activated Alumina

Activated alumina comprises of a series of non-equilibrium forms of partially hydroxylated alumina oxide, Al₂O₃. In general, a hydrous alumina precursor is heated, and the hydroxyl groups are driven off, leaving a porous solid structure of activated alumina. It has a surface area ranging from 200 to 300 m²/g and is used to remove water from organic liquids, including gasoline, kerosene, oils, aromatic hydrocarbons and many chlorinated hydrocarbons. Activated alumina is receiving renewed attention as an adsorbent and a wealth of information has been published (Ku and Chiou 2002; Kasprzyk-Hordern 2004; Singh and Pant 2004; Naiya et al 2009) on its adsorption characteristics.

1.3.3 Zeolites

Zeolites are aluminosilicates with Si/Al ratios between 1 and infinity. There are 40 natural and over 100 synthetic zeolites. They are also considered as selective adsorbents. Zeolite-based materials are extremely versatile and their main applications include detergent manufacture, water softening resins (i.e. water softeners), catalytic applications in the petroleum industry, separation processes (i.e. molecular sieves) and as adsorbents for water, carbon dioxide and hydrogen sulfide. Various zeolites have been employed for the removal of pollutants (Ellis and Korth 1993; Okolo et al 2000; Metes et al 2004; Motsi et al 2009).

1.3.4 Activated Carbon

Activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment throughout the world. Charcoal, the forerunner of the modern activated carbon has been recognized as the oldest adsorbent known in wastewater treatment. Activated carbon is
produced by a process consisting of raw material dehydration and carbonization followed by activation. The product obtained is known as activated carbon, and generally has a highly porous structure with a large surface area, ranging from 600 to 2000 m$^2$/g. Activated carbon has been found to be a versatile adsorbent, which can remove diverse types of pollutants such as metal ions (Perez-Candela et al. 1995; Gabaldon et al. 1996; Gabaldon et al. 2000; Sanchez-Polo and Rivera-Utrilla 2002), anions (Bao et al. 1999; Huang and Cheng 2008; Mahmudov and Huang 2010), dyes (Pelekani and Snoeyink 2000; Al-Degs et al. 2001; Pereira et al. 2003; Gomez et al. 2007), phenols (Chern and Chien 2002; Haydar et al. 2003; Dabrowski et al. 2005), detergents (Bele et al. 1998; Malhas et al. 2002), pesticides (Foo and Hameed 2010), humic substances (McCreary and Snoeyink 1980; Lee et al. 1983), chlorinated hydrocarbons (Sotelo et al. 2002) and many other chemicals and organisms (Saito 1984; McKay et al. 1985; Najm et al. 1993; Rivera-Utrilla et al. 2003). In spite of the abundant uses of activated carbon, its applications are sometimes restricted due to their high cost. Therefore, researchers are on the look out for low-cost materials for water pollution control, particularly, where the cost factor plays a major role. For quite some time, efforts have been directed towards the development of alternative adsorbents which are efficient and cheap. They can be prepared from a wide variety of raw materials, which are abundant and possess high organic (carbon) content, low inorganic content and can be easily activated (Moreno-Castilla and Rivera-Utrilla 2001).

The preparation of low-cost adsorbents from waste materials has several advantages, mainly of economic and environmental importance. A wide variety of low-cost adsorbents have been prepared from different waste materials including agricultural, industrial and municipal wastes.
1.4 ADSORBENTS FROM AGRICULTURAL WASTES

Agricultural materials, particularly, those containing cellulose, shows potential sorption capacity towards various pollutants. The basic components of the agricultural waste materials include hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch. Agricultural waste materials are cost effective and eco-friendly due to their unique chemical composition, renewable nature, and are a viable option for water and wastewater remediation. Agricultural waste is a rich source for activated carbon production due to its low ash content and reasonable hardness (Ahmedna et al 2000). Therefore, the conversion of agricultural wastes into low-cost adsorbents is a promising alternative to solve environmental problems and to reduce the complexity involved in the preparation of the adsorbents. In the last several decades, various agricultural wastes have been explored as low-cost adsorbents. Some of them include the shells and/or stones of fruits like nuts (Nguyen et al 1995; Ahmadpour and Do 1997; Toles et al 1998), peanuts (Wafwoyo et al 1999), olive wastes (Nyazi et al 2005), almonds (Christopher and Wayne 2002), apricots stones (Soleimani and Kaghazchi 2008) and cherries (Lessier et al 1994); wastes resulting from the production of cereals such as rice (Khalil 1996), maize (Elizalde-Gonzalez et al 2008) and corn (Tsai et al 2001) as well as sugar cane bagasse (Girgis 1994) and coir pith (Namasivayam and Sangeetha 2006). These agricultural waste materials have been used either in their natural form or after certain physical or chemical modifications.

1.4.1 Adsorbents from Rice and Wheat Waste

Rice is the seed of a monocot plant, Oryza sativa. Rice is one of the major crops grown throughout the world. As a cereal grain, it is the most important staple food for a large part of the world’s human population. Consequently, the rice industry produces several by-products, such as rice
husk, rice hull, rice husk/hull ash, rice bran, etc. Wheat (Triticum spp.) is an important staple food, generally used to make flour. Similar to the rice industry, the wheat industry also produces certain by-products, such as wheat bran, wheat husk, etc. whose use as adsorbents, has been explored.

Rice husk has been tested for arsenic removal from water by Nasir et al (1998). The adsorption behaviour of rice husk for the removal of antimony ions from aqueous solutions has been investigated by Khalid et al (2000). The same group of researchers have also studied the removal of Pb(II) and Hg(II) ions using rice husk as an adsorbent (Khalid et al 1998; Khalid et al 1999). The sorption of Cd(II) ion from an aqueous solution by rice husk has been investigated by Kumar and Bandyopadhyay (2006). Rice hull ash has also been explored as an adsorbent for the removal of Pb(II) ion from an aqueous solution by Wang and Lin (2008). Acid-treated (H₃PO₄) rice bran was used as a low-cost sorbent for the removal of nickel by Zafar et al (2007). Wheat bran has been utilized for the removal of Cd(II) ion from wastewater by Singh et al (2006). The adsorption of Pb(II) ion from an aqueous solution on wheat bran has also been reported by Bulut and Baysal (2006).

1.4.2 Adsorbents from Tea and Coffee Waste

Tea is the product of the leaves, leaf buds, and internodes of the Camellia sinensis plant, prepared and cured by various methods. Tea is the most popular drink in the world in terms of its consumption, and the world tea production was 4.73 million tonnes annually in 2008. Waste/spent tea leaves have been investigated as adsorbents by various researchers for the removal of different types of pollutants from water.

Waste tea leaves have been used for the removal of lead, iron, zinc and nickel ions from water by Ahluwalia and Goyal (2005). The adsorption of copper and lead ions onto tea waste from an aqueous solution has also been
studied by Amarasinghe and Williams (2007). Mozumder et al (2008) have investigated the potential of tea-leaves waste for Cr(VI) ion removal from an aqueous solution. The adsorption ability of Turkish tea waste (fibrous) was investigated for the removal of Cu(II) and Cd(II) ions from single (non-competitive) and binary (competitive) aqueous systems by Cay et al (2004). Batch adsorption studies have been carried out for evaluating the suitability of tea factory waste as a low-cost adsorbent for the removal of zinc (Wasewar et al 2009).

Coffee is another most popular beverage known globally. Worldwide, 6.7 million metric tonnes of coffee was produced annually in 1998-2000, and the forecast is a rise to 7 million metric tonnes annually in 2010. Wastes from the coffee industry have been explored as adsorbents for water treatment. The adsorption behaviour of heavy metals on arabica and robusta roasted coffee beans was investigated by Minamisawa et al (2005). Coffee residue has been used as the raw material in the preparation of powder activated carbon by chemical activation with zinc chloride for the sorption of Pb(II) ion from dilute aqueous solutions (Boudrahem et al 2009).

### 1.4.3 Adsorbents from Coconut Waste

Coconut (Cocos nucifera) is highly nutritious and rich in fiber, vitamins and minerals. Coconut palms are grown in more than 80 countries around the world. Coconut wastes such as coir pith, coconut bunch waste, coconut husk, copra meal, male flowers of the coconut tree, etc. have been widely explored as adsorbents for the removal of various pollutants from water. Coir pith waste has been used for the adsorptive removal of Pb(II) ion from an aqueous solution by Kadirvelu and Namasivayam (2000).

Coir pith has also been investigated as an adsorbent for Co(II), Cr(III) and Ni(II) ions adsorption in both single and multi-component systems
by Parab et al (2006). Namasivayam et al (2001) have investigated the use of coir pith as an adsorbent for the adsorption of rhodamine B and acid violet dyes. Coir pith has also been examined for congo red dye removal (Namasivayam and Kavitha 2002). Coconut copra meal, a waste product of coconut oil production, was investigated as a sorbent for cadmium removal from an aqueous solution by Ho and Ofoimaja (2006).

1.4.4 Adsorbents from Peanut or Groundnut Waste

Peanut, or groundnut (Arachis hypogaea), is a species in the legume “bean” family. The world production of 34.43 million metric tonnes of peanuts has been reported during the year 2008–2009. India and China are the world’s largest producers of peanuts. Peanut/groundnut’s husk/hull has been widely used as an adsorbent for the removal of various pollutants from water.

The removal of cadmium and lead ions from an aqueous solution by groundnut husk modified by EDTA, was examined by Okieimen et al (1991). Peanut hull has been converted into an adsorbent by Namasivayam and Periasamy (1993) by treatment with concentrated sulfuric acid. Chamarthy et al (2001) also prepared adsorbents from peanut shell by thermal treatment in the presence of phosphoric acid or citric acid and used it for the adsorption of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) ions. Untreated and silver impregnated groundnut husk carbon were tested for the removal of Cr(VI) ion by Dubey and Gopal (2007). Activated carbon prepared from peanut shell was used for the removal of Pb^{2+} ion from an aqueous solution by Xu and Liu (2008). The use of peanut hulls, for copper and lead removal was studied by Oliveira et al (2009). Zhu et al (2009) have explored the use of peanut hull as an adsorbent for the removal of Cu(II) ion from an aqueous solution.
1.4.5 Adsorbents from Peels of Different Agricultural Products

Peel, also known as skin, is the outer protective layer of a fruit or vegetable, currently gaining wide attention as an adsorbent in water treatment. Peels of different fruits such as, orange, banana, watermelon, cassava, mango, etc. have been used as adsorbents for the removal of different pollutants from water. Orange peel was examined for Ni(II) ion removal from electroplating wastewater by Ajmal et al (2000). The preparation of chemically modified orange peel adsorbents and their sorption behavior for Co(II), Ni(II), Zn(II) and Cd(II) ions have also been studied by Li et al (2008).

Banana peel, a commonly produced fruit waste, was examined as adsorbent for the removal of Cd(II) ion from environmental and industrial wastewater by Memon et al (2008). Activated carbons prepared from waste cassava peel (an agricultural waste from the food processing industry) employing physical and chemical methods have been investigated for their efficiency in the removal of dyes and metal ions from aqueous solutions (Rajeshwarisivaraj et al 2001). The ability of pomelo peel to remove Cd(II) ion from aqueous solutions was investigated by Saikaew et al (2009).

1.4.6 Adsorbents from Shells of Different Agricultural Products

Shells of various agricultural products have also been investigated as adsorbents by different researchers for the removal of toxic pollutants from water. Bael fruit shell was used to prepare activated carbon, and used as an efficient low-cost adsorbent to remove Cr(VI) ion from an aqueous phase (Anandkumar and Mandal 2009). Acid formaldehyde pretreated chestnut shell was used as an adsorbent, and the influence of initial cation concentration, temperature and pH was investigated towards the optimization of Pb^{2+}, Cu^{2+} and Zn^{2+} ions removal from aqueous solutions (Vazquez et al 2009). The sorption of Cu(II) ion onto the chestnut shell using a batch
adsorber has been studied (Yao et al 2010). The potential of shells of hazelnut (Corylus avellana) and almonds (Prunus dulcis) to remove Pb\(^{2+}\) ion from aqueous solutions was investigated by batch experiments (Pehlivan et al 2009).

1.4.7 Adsorbents from Miscellaneous Agricultural Waste

Besides the various agricultural by-products mentioned above, different miscellaneous agricultural wastes have also been investigated as low-cost adsorbents. The utilization of grape bagasse as an adsorbent to remove Cd(II) and Pb(II) ions has been investigated by Farinella et al (2004). The adsorption of iron and manganese either to remove each metal ion singly or both metals as a multi-component system, was studied using maize cob and palm fruit bunch (Nassar et al 2004). The adsorption potential of black gram husk was tested for the removal of Pb, Cd, Zn, Cu and Ni ions from water (Saeed et al 2005). Dried sugar beet pulp was used as a sorbent for the removal of Cu(II) ion from an aqueous solution (Aksu and Isoglu 2005). Sugarcane bagasse was converted into a carbonaceous adsorbent and used for the removal of cadmium and zinc from wastewater (Mohan and Singh 2002).

1.5 ADSORBENTS FROM INDUSTRIAL AND MUNICIPAL WASTES

Widespread industrial activities generate huge amount of solid waste materials as by-products. Some of these materials are being put to use while others find no proper utilization and are dumped elsewhere. Industrial waste materials are available almost free of cost. If these solid wastes could be used as adsorbents, it will provide a two-fold advantage to environmental pollution. Firstly, the volume of waste materials could be partly reduced and secondly, adsorbent if developed from such wastes, can reduce the wastewater treatment cost. In view of the low cost of such adsorbents, it may not be
essential to regenerate the spent materials. Thus, a number of industrial wastes have been investigated with or without treatment as adsorbents for the removal of pollutants from wastewater. Some of them are listed and discussed below.

1.5.1 Adsorbents from Fly Ash

The major solid by-product of thermal power plants based on coal burning, is fly ash. The main uses of fly ash include construction of roads, manufacture of bricks, cement, etc. The high percentage of silica and alumina in fly ash make it a good option for utilization as an inexpensive adsorbent for bulk use. Panday et al (1985) used fly ash without any pretreatment for the removal of Cu$^{2+}$ ions. Sen and Arnab (1987) investigated the potential of fly ash for Hg(II) ion removal. The removal of lead and copper ions from aqueous solutions by fly ash was investigated by Alinnor (2007).

1.5.2 Adsorbents from Steel Industry Waste

Steel industries also produce a number of wastes in large quantities, such as blast furnace slag, dust and sludge, etc. and they have been investigated as adsorbents. Dimitrova (1996) investigated ungranulated blast furnace slag for the removal of Cu$^{2+}$, Ni$^{2+}$, and Zn$^{2+}$ ions from water. Slag columns were utilized by the same worker (Dimitrova 2002) for lead ion removal. Kanel et al (2006) used blast furnace slag for As(III) ion remediation.

1.5.3 Adsorbents from Aluminium Industry Waste

Red mud, a solid waste product of the aluminium industry produced during bauxite processing, was explored as an adsorbent by Lopez

1.5.4 Adsorbents from Fertilizer Industry Waste

The fertilizer industry also produces a number of by-products in large quantities, which cause serious disposal problems and degrade the surrounding environment. Fe(III)/Cr(III) hydroxide, a waste material from the fertilizer industry has been used by Namasivayam and Ranganthan (1993) for the adsorption of Cr(VI) ion from aqueous solutions. Waste carbon slurry, another fertilizer industry waste, was tested to remove Cu\(^{2+}\), Cr\(^{6+}\), Hg\(^{2+}\), and Pb\(^{2+}\) ions from aqueous solutions by Srivastava et al (1989).

1.5.5 Adsorbents from Leather Industry Waste

The feasibility of using leather industry solid waste as an adsorbent for the removal of Cr(VI) and As(V) ions from aqueous media was evaluated by Oliveira et al (2008). Fleshing from animal hides/skins, another waste from the leather industry, is high in protein content. Raw fleshing has been complexed with iron and was used for the removal of Cr(VI) ions (Fathima et al 2005).

1.5.6 Adsorbents from Paper Industry Waste

The paper industry also produces a number of by-products in large quantities, which create serious disposal problems and degrade the surrounding environment. Black liquor, a waste product that originates from the paper industry, was examined for the adsorption of Pb\(^{2+}\) and Zn\(^{2+}\) ions by Srivastava et al (1994).
1.5.7 Adsorbents from Different Types of Industrial Sludge Wastes

Different industries produce sludge as a by-product which has been examined as an adsorbent by various researchers. Chrome sludge, a solid waste material from the electroplating industry, was used as an adsorbent for As(V) ion removal by Lee and Lee (1995). Selvaraj et al (2003) investigated the potential of distillery sludge for Cr(VI) ion removal. Li et al (2004) utilized wine processing sludge as an effective adsorbent for Cr(III) ion removal.

1.5.8 Adsorbents from Miscellaneous Industrial Wastes

Namasivayam and Yamuna (1999) have explored the use of waste biogas residual slurry for Cr(III) ion removal from an aqueous solution. Battery industry waste has been investigated for the removal of some metal ions (Pb, Cu, Cr and Zn) from aqueous solutions by Bhatnagar et al (2007).

Due to the low cost and high availability of these materials, it is not essential to have complicated regeneration processes. Such low cost adsorption methods have attracted many researchers. But most of the times the adsorption capacities of such adsorbents are not large, and hence, the study and exploration of more and more new adsorbents are still under progress. The aim of the present research is to develop inexpensive and effective adsorbents from cashew nut shell, a common agricultural waste, as an alternative to the existing commercial adsorbents.