1. INTRODUCTION

Earth a fragile planet constitutes the atmosphere, lithosphere, hydrosphere and the biosphere. The atmospheric layer consists of a mixture of gases, lithosphere is the landmass, hydrosphere contains all the water that exists on earth and the biosphere is the life zone on earth. All these spheres form the environment. In the recent past, human population has increased to an alarming proportion. Population explosion coupled with careless exploitation of all natural resources has damaged the environment. The concept of 'sustainable' utilization of natural resources adopted in the past is totally non-existent in the society today. Industrial revolution and later the world wars proved to be a disaster not only to man but also to the environment. Deforestation and urbanization have also added to the degradation of the environment. Pollutants are substances with which ecosystems have had no prior evolutionary experience, in terms of kinds or amounts, and so have no mechanisms for dealing with them. From the human perspective, pollutants are substances that adversely affect health, activities, or survival (Starr and Taggart, 1989). Pollution has become a part of our life today. Production and release of chemicals into nature has resulted in health hazards in humans and has proven to be equally deleterious to fauna and flora.

1.1. Air pollution
Air is mainly polluted by oxides of sulphur, oxides of nitrogen, chlorofluorocarbons, photochemical oxidants and suspended particulate matter. Industrial processes produce various gases and smoke, which are let out in to the atmosphere without proper treatment. Factories, power plants and vehicles are main sources of air pollutants. The concentration and dispersion of pollutants at their source in a given time depends upon the climate and topography of the region. Common adverse health effects due to air pollutants are headache, nausea, irritation of eyes, nose and respiratory tract, laboured respiration, bronchitis, dizziness, in extreme cases convulsions, coma and death. Particulate matter such as heavy metals are intrinsically toxic because of their physical or chemical characteristics. Lead that is used as an anti-knocking agent...
in petrol finds its way into the atmosphere through vehicular emissions and is found to be the most prevalent among heavy metals in air. Cadmium, nickel and mercury are also widespread and are known to elicit serious health hazards (Rao, 1998).

1.2. Soil pollution
Soil is the most essential resource on earth. A good fertile soil for agriculture is essential to meet the demands of the growing population. In a healthy ecosystem, soil is a renewable resource. On the other hand, under adverse conditions it may take thousands of years for soil to accumulate 1mm deep! Human activities have led to the decrease in the quality of soil. Industrialization has resulted in large-scale production of solid wastes that are difficult to dispose. Some components of solid wastes such as metals, radioactive substances, synthetic organic chemicals (such as pesticides and solvents) and toxic inorganic materials like arsenic and asbestos are posing threat to soil quality. Availability of land suitable for waste disposal is now scarce. Toxic materials disposed in landfills are causing serious problems due to the leakage of residues resulting in the contamination of ground water, soil, surface waters and finally air. The only way to rectify this kind of pollution is by reducing the production of hazardous wastes and proper treatment of such wastes and packing before disposal (Cunningham and Saigo, 1990).

1.3. Water pollution
Water pollution is any physical, biological, or chemical change in water quality that adversely affects living organisms or makes water unsuitable for desired use. The source of water contamination may be natural or human-induced. The sources of water pollution are classified as point source and non-point source. Sources like factories, sewage treatment plants and underground coalmines that discharge polluting agents from specific locations such as drain pipes or ditches are point sources. On the other hand, non-point sources are scattered where the
discharge in to the water body is not from a specific location e.g. agricultural runoff. Following are the major categories of human-induced water pollutions.

1.3.1. Infectious agents
Disease causing organisms enter the water body through untreated human and animal wastes. Wastes entering the water body from food processing industries or animal slaughterhouses provide a good medium for disease causing microorganisms to multiply.

1.3.2. Toxic organic and inorganic chemicals
Weathering of rocks mobilizes some toxic inorganic chemicals that finally find their way into a lake or ground water through surface runoff. The mobilization of these chemicals is often accelerated by human activities such as mining, processing, using and discarding of minerals. Among such chemicals, metals have received much attention in recent times due to their hazardous and non-degradable nature. The Minamata incidence in Japan in the early 1950's that affected more than 3,500 people who were exposed to methyl mercury through seafood was an eye opener for metal pollution to the world. Similarly, mobilization and concentration of salts result in salinity, which may reach to levels that are toxic to plants. Acid mine drainage results in acidification of surface and ground waters. Organic chemicals such as pesticides, fertilizers and pigments through surface run offs may contaminate surface and even ground waters. Some of these chemicals are highly toxic even at very low concentrations and can also be non-biodegradable.

1.3.3. Radioactive wastes
Construction of nuclear power plants has generated humungous wastes that contain highly hazardous radioactive materials. Most of the industries do not follow the protocol for disposal of hazardous wastes. Radioactive materials find their way into the water body by such thoughtless dumping of wastes from these
industries the consequence of which is serious health problems in people dwelling in that region.

1.3.4. Plant nutrients
Rivers and lakes that have clear water and low productivity are said to be oligotrophic. In contrast, eutrophic lakes are rich in organisms and organic materials. Human activities can greatly accelerate eutrophication. High biological productivity results in algal bloom or thick growth of aquatic plants and high levels of sediment accumulation. Lakes that might exist for thousands of years can be filled in few decades.

1.3.5. Oxygen-demanding wastes
Water quality can be determined by the amount of dissolved oxygen in the water. Water with oxygen content above 8 mg/L will support good aquatic life. Discharge of organic wastes generated by food industries, paper mill, and sewage enhances the growth of decomposers, which utilize oxygen rapidly, and results in high oxygen demand. Oxygen depletion is rapid below the source of pollution in a river, which becomes anaerobic further down stream where only organisms that tolerate anaerobic conditions survive. This totally disturbs the ecological balance of an aquatic environment.

1.3.6. Thermal pollution
Thermal pollution is caused mainly by industrial discharge of heated water directly into rivers and lakes. The main culprits of thermal pollution are thermal power plants, paper mills, metal smelters and food processing industries. This also depletes the oxygen level in the water body.

1.3.7. Metal pollution
Metals are important pollutants in water. In nature, metals occur in sediments and ores in an immobilized form. The multiplicity of industrial, agricultural and anthropogenic activities have enhanced the mobilization of heavy metals above
the rate manageable by biochemical cycles leading to an increased inflow of metal in the environment. Aqueous heavy metal pollution represents an important environmental problem due to its toxic effects and accumulation throughout the food chain (Figueira et al., 2000). Metals find their way into water bodies through various sources some of them being mine drainage, industrial effluents, sewage, agricultural runoff and acid rain. The persistent, non-biodegradable nature of metals contributes to their toxicity.

The toxicity of the metal depends on the concentration of the metal ion and the nature of the organism with which it interacts. Essential metals elicit a toxic response in high concentration. Metals such as mercury, cadmium, chromium and lead are cumulative poisons and are toxic even in low concentrations. Physical, organic and inorganic environmental components can markedly influence the metal availability and toxicity in aquatic and terrestrial environments (Gadd and Griffiths, 1978). The parameters that influence toxicity are temperature, pH, salinity and the presence of other ions (Manivasakam, 1997). Metals inhibit self-purification of rivers. If industrial waste is discharged into sewer, metals precipitate and settle down. Metals cause chromosome aberrations and their deleterious effect manifests in future generations also (Manivasakam, 1997). The commonly occurring metal pollutants from industrial wastewaters are Cr, Pb, Hg, Ni, Cd and Zn.

**Sources and toxicity of metals**

Chromium is one of the most widely used metals in industries. It is mainly used in dyes, electro plating, leather tanning and paints. Cr(VI) is a known carcinogen and mutagen (Suzuki et al., 1992; Llovera et al., 1993; Wang and Shen, 1995).

Lead enters into natural waters from a variety of sources such as storage batteries, lead smelting, tetraethyl lead manufacturing, mining, plating, ammunition, ceramic and glass industries. Lead poisoning in humans results in severe damage of kidney, reproductive system, liver, brain and central nervous system (Manahan, 1984).
Mercury is considered to be one of the most toxic metals found in the environment (Serpone et al., 1988). The major sources of mercury pollution in the aquatic environment are industries such as chloralkali, paint, pulp and paper, oil refining, electrical, rubber processing and fertilizer (Namasivayam and Periyasamy, 1993; Kapoor and Viraraghavan, 1994). Mercury not only affects the central nervous system and chromosomes but also causes impairment of pulmonary functions, chest pain and dyspoea (Berglund and Bertin, 1969; WHO Environmental health criteria, 1991).

Nickel is used in alloy preparation, ceramics, fungicides, pigments and inorganic chemical manufacturing industries. It is also used in nuclear power plants, gas turbine engines, cryogenic containers and pollution abatement equipments (Abbasi and Soni, 1990). Nickel is a potent carcinogen and causes cancer in lungs, nose, stomach and bone. Skin contact with nickel is irritating and results in a very painful disease, nickel itch, which leads to sudden death (Mukherjee, 1986).

Cadmium finds its way in to water bodies through wastewaters from metal plating, battery, paint industries and zinc mining (Tangaromsuk et al., 2002). Cadmium is also used in production of television tube phosphors, alloy preparations and nuclear reactor shields (Perez-Rama et al., 2002). Itai-itai is a well-known disease caused by cadmium poisoning. Effects of acute cadmium poisoning in humans are very serious as it leads to high blood pressure, kidney damage and destruction of testicular tissue and red blood cells (Ranganathan, 1993).

Effluents of electroplating industries, pulp and paper mills, petroleum refineries, fertilizer manufacturing industries and foundries are sources of zinc to the environment. Zinc oxide fumes result in fever and cause irritation of gastrointestinal and respiratory tract (Beliles, 1979).
Certain inorganic and organic compounds such as fluorides, nitrates, carbonates, bicarbonates and chlorides occur in excess in soil sediments due to geological nature, which may mix with groundwater and make it unfit for potable purposes.

A recent report by the geological survey of India listed fluoride red alert areas as regions stretching from Punjab in the north to Tamil Nadu in the south. The bedrock of the Indian peninsula consists of a number of fluoride-bearing minerals such as fluorite, topaz and apatite. When bedrock weathers, fluoride leaches into the water and the soil. Fluoride mainly enters the human body through drinking water and 99% of it combines with bones, as fluoride has affinity for calcium phosphate in bones. Excessive intake of fluoride results in various health hazards such as dental fluorosis, teeth mottling, skeletal fluorosis and deformation of bones (Susheela et al., 1993).

Excessive use of nitrogenous fertilizers in agriculture has been one of the primary sources of high nitrate in groundwater (Schepers et al., 1984). Apart from this, nitrate enters groundwater through mineralization, which is fairly rapid in tropical and subtropical soils (Majumdar and Gupta, 2000). Large amounts of nitrate in drinking water causes a disease called, methemoglobinemia, a blood disorder primarily affecting infants under six months of age. Methemoglobinemia is a condition in which the ability of red blood cells to carry oxygen is reduced that results in blue discoloration of the skin.

Excessive levels of calcium, magnesium, carbonates, bicarbonates and chlorides were recorded in Chiwara Block, Jhunjhunu District, Rajasthan (Singh et al., 2001).

Apart from fluoride and nitrate, aluminium, manganese and iron may also occur in the form of ore. Groundwater from these ore rich areas contains excess of these metals and become non-potable.

Aluminium is widespread throughout nature, air, water, plants and consequently in the food chain. Recent studies have shown that acid rain decreases the pH in
soil, permitting Al mobility through groundwater, which in turn increases its bioavailability and dietary intake. High aluminium content in tissues causes neurodegenerative disorders such as Alzheimer's disease and encephalopathy (Storey and Masters, 1995; Lopez et al., 2000).

Manganese is found in various salts and minerals, frequently in association with iron compounds. It is a vital micronutrient for plants and animals (Barman and Bhattacharyya, 2001). Manganese is found to occur naturally in southern India especially in Salem District of Tamil Nadu where magnasite ore is found (Ramanathan and Mehta, 1981).

Iron is an important element in the human body. It is a component of hemoglobin, myoglobin and many enzymes in the body. The important iron oxide ores are hematite (Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$). The presence of Fe$_2$O$_3$ accounts largely for the red colouration of many rocks and soils. Pyrite (FeS$_2$) occurs as pale yellow crystals with a metallic luster (Holtzclaw, Jr. and Robinson, 1988). Anthropogenically, entry of iron into the environment is mainly through effluents of industries like ink, paint and pharmaceutical products, mining industries, ore processing, electroplating industries, zinc and steel processing plants (Handa et al., 1985). Iron is essential for human health and necessary for proper functioning of the biological system. Deficiency of iron causes anemia. However, excess of iron is toxic to human. Excessive iron intake leads to haemochromatosis resulting in tissue damage due to iron accumulation. Iron is also associated with constipation (Barman and Bhattacharyya, 2001). Initial symptoms of iron toxicity are vomiting, diarrhea, and damage to the intestine. Presence of iron in water makes the water turbid, besides causing staining of plumbing fixtures and laundry. Moreover, iron precipitates in the gills of fishes, which is deleterious to them (Mukhopadhyay and Konar, 1982). In plants, the initial symptoms of iron toxicity are the appearance of necrotic spots on the leaves. In some iron rich, low pH, low manganese soils, interaction between iron and manganese in the soil reduces the manganese uptake by plants resulting in manganese deficiency.
Arsenic is ubiquitous in Earth's crust and ranks 20\textsuperscript{th} among the elements in abundance (Xu \textit{et al.}, 2002). Arsenic is a metalloid element and is found as a main component of several minerals such as arsenopyrite. Arsenic contamination of ground waters is often geological in origin (Pontius \textit{et al.}, 1994; Desesso \textit{et al.}, 1998). The presence of arsenic in ground water above the maximum permissible limits (10-50ppb) has been reported in many parts of the world in the last few years (Rasul \textit{et al.}, 1999). Bangladesh, West Bengal region in India, inner Mongolia region in China, Thai, and Taiwan are facing serious arsenic pollution crisis (Mandal \textit{et al.}, 1996; Dhar \textit{et al.}, 1997; Nickson \textit{et al.}, 1998; Xu \textit{et al.}, 2002). The catastrophic health crisis caused by arsenic poisoning of drinking water in Bangladesh and West Bengal could be the biggest mass poisoning in human history (Sarkar, 1999). Evidences, primarily from Taiwan and Chile, suggest that arsenic in drinking water poses the highest known environment cancer risks (Smith, 1999). The cause for this widespread contamination is still known to be geologic. It is recognized that deep tubewells with about 300m depth are not contaminated with arsenic while shallow tubewells with about 70-100m depth are contaminated above the permissible level (Khan \textit{et al.}, 1999).

The problem of arsenic contamination of ground water is more prominent in the alluvial aquifer of Bengal deltaic plains (BDP). It has affected more than 50 million people in Bangladesh and the neighbouring India. In the aquatic environment, inorganic arsenic exists in +5, and +3 oxidation states. In order of toxicity, the +3 [As (III) as in arsenite] oxidation state is more toxic to humans than +5 [As(V) as in arsenate] (Rasul \textit{et al.}, 1999). Arsenic is a human carcinogen that quietly accumulates in hair, nail, and skin. Common symptoms are de-pigmentation, rashes on palms and soles of feet, which eventually develop to gangrene and cancer. The long-term consumption of drinking water containing around 500 \textmu g/L of arsenic may cause 1 in 10 exposed person to die from arsenic-caused cancers (Smith, 1999). There are innumerable sub clinical cases where people show no physical symptoms, but eventually become sick.
and die. The consequences of human arsenic exposure on pregnancy outcomes and infant development are essentially unknown. These health outcomes will likely prove to be the most sensitive adverse health effects associated with arsenic exposure.

The magnitude of the arsenic calamity of Bangladesh is much more than West Bengal. It is reported that out of 55,000 hand tube-wells that were analyzed from West Bengal only 45 contained arsenic above 1.0 mg/L whereas in Bangladesh, it was 211 out of 12,000 hand tube-wells. In West Bengal, out of the total children examined below 11 years, 1.7% was found to have arsenical skin lesions. Out of the 27 districts where arsenic has been found above 0.05 mg/L, people suffering from arsenic-induced skin lesions such as, melanosis, leucomelanosis, keratosis, hyperkeratosis, dorsum, non-petting edema, gangrene and skin cancer were identified in 25 districts (Biswas et al., 1998).

In West Bengal, out of 31 deep tube-wells (more than 350 feet) installed in Gaighata block in North 24-Parganas District during the last 2 years, 19 that were known to be safe during installation were found to be arsenic contaminated. In many districts of West Bengal and Bangladesh most of the aquifers are unconfined and they run more risk of contamination. Only in the southern part of West Bengal and Bangladesh thick clay barriers are present and may be used for deep tube-wells taking all precautions during installation (Chakraborti, 1999).

Although the cause of widespread arsenic concentrations in ground water of the Bengal delta is a subject of debate, some basic elements of the problem are well established. Of particular importance, from a geochemical standpoint, is the presence of pyrite (an iron-sulfide mineral) and iron oxide in the deltaic sediments. One theory posits that arsenic in ground water results from iron oxide dissolution. A competing theory suggests that pyrite dissolution is the primary source of dissolved arsenic. Arsenic can be released to ground water by desorption from, and dissolution of iron oxide. Many aquifers contain iron oxide
with arsenic as an impurity due to co-precipitation or adsorption. Desorption of arsenic can be promoted by either an increase in pH or the concentration of a competing ion, such as phosphorous. Arsenic also can be released from iron oxide by chemical reduction of the oxide. Deposition of Fe-coated sediment along with organic matter can lead to the dissolution of iron oxide with consequent release of arsenic into ground water. In ground water containing dissolved sulfide, precipitation of arsenic-rich pyrite occurs, resulting in arsenic removal from the water. The rate of sulfide-mineral oxidation is limited by the supply of an oxidizing agent, most commonly molecular oxygen. High nitrate concentrations from agricultural activities also can oxidize sulfide minerals. Human activities that increase the supply of oxygen or another oxidizing agent such as nitrate, to ground water can lead to increased mineral oxidation and, consequently, high arsenic concentrations. A common product of this oxidation is iron oxide with co-precipitated or adsorbed arsenic. Sampling of ground water and deltaic sediments within Bangladesh and West Bengal suggests that these processes may be occurring in the Bengal delta (Welch, 1999).

Significant positive correlations have been noted amongst the total concentrations of Fe, Al, Mn and \( \text{PO}_4 \) with arsenic in these sediments. The total concentration of arsenic leached by sequential leaching was found to be in the range of 116-383 mg/L. Oxalate extraction to understand the relationship of As with the secondary amorphous Fe, Al and Mn phases and organically bound As of the sediments revealed that ferric oxyhydroxides dominated these sediments (Fes\(\text{x} = 264-1233 \text{ mg/kg} \)) as compared to aluminum hydroxides Als\(\text{x} = 27-294 \text{ mg/kg} \) as secondary inorganic mineral phases in these sediments. In the clayey sediments the presence of both Fes\(\text{x} = (933 \text{ mg/kg} \) and Als\(\text{x} = (294 \text{ mg/kg} \) fractions that are complimented by high Sis\(\text{x} (229 \text{ mg/kg} \) at depths indicated the dissolution of secondary aluminosilicates as a potential adsorbent for arsenic. The low concentrations of pyrophosphate extractable Fe, Al, Mn and As suggested that the bulk of the arsenic was bound to the inorganic fractions of Fe, Al and Mn in the sediments.
Hydrochemical characteristics
In West Bengal, groundwater in most cases is found to be Ca-HCO₃ type although Na-HCO₃ type and Na-Cl type water is also found in some areas. Groundwater samples from Nadia District are characterized by elevated pH values, in the range of 7.1 to 7.8 and correspondingly high alkalinity up to 352 mg/L. Concentrations of sulfate (2-12.8 mg/L), phosphate (0.5-3.1 mg/L) and Mn (0.1-0.9 mg/L) are typical characteristics of the groundwater from the Bengal delta plains (BDP). The total concentrations of arsenic was found to be up to 370 μg/L. As(III)/As(V) ratios were generally less than 1.0, but As(III) concentrations were still high, from 15 to 122% of the As(V) concentrations. Concentrations of total iron varied between 1.8-8.8 mg/L and the correlation between the total As and the total Fe was low. Data from discrete aquifer depths however revealed good correlation between total As and total Fe ($r^2$ 0.93) (Bhattacharya et al., 1997, 1998; Ahmed, 1999).

1.3.8. Technologies to treat metal containing waters and wastewaters
Over the years a number of technologies have been developed to remove toxic metal ions from water. Some of the most important technologies among them include, chemical precipitation, cementation, filtration, ion exchange, solvent extraction, electro-deposition, reverse osmosis, xanthate process, evaporation, membrane system, adsorption and phyto-remediation.

1.3.8.1. Physical processes
Precipitation process
Hydroxide precipitation is one of the most widely used technology for different metal bearing effluents such as plating liquid wastes, metal treatment, dilute leach solutions and hydrometallurgical residues (Matis et al., 1998). In this process, pH value of the liquid streams is increased, usually by addition of lime, which costs less, and most of the dissolved ions are precipitated out from the wastewater. But, during application, this method faces certain problems. This method cannot precipitate all the metals. There is no common pH value, where
precipitation of all the metallic ions takes place simultaneously. Following precipitation, some chemical reagents have to be added in order to lower the pH values (Matis and Zouboulis, 1995). The presence of complexing agents like EDTA, NH$_3$ and CN' often depresses precipitation to a great extent. Finally, large volumes of hydroxide sludges are produced, dewatering of which itself is a cumbersome process. The disposal of sludge may also create severe pollution problems due to leaching of toxics into the soil by rainwater. Moreover, some of the metal ions redissolve at higher pH and relatively have high solubility.

An alternative method of heavy metal precipitation is in the form of their respective sulphides, by using specific reagents, such as sodium sulphide, calcium sulphide or iron sulphide (Matis et al., 1998). This method has some advantage over hydroxide precipitation like, less sludge production and low redissolving property of the sulphides. In this process, the influent pH should be adjusted to 7-8 to prevent hydrogen sulphide formation and excess sulphide should be removed by aeration or chemical oxidation (Lazaridis et al., 1992).

Carbonate precipitation is carried out using calcium or sodium carbonate. The treatment at lower pH can be achieved with the carbonate system. In addition, lower volumes of denser sludge can be obtained with relative filtration rates. Barntner and Cichon (1981) have reported that carbonate process is very successful in removing metals when compared to hydroxide precipitation.

**Evaporation**

It is one of the oldest technologies for removal and recovery of chemicals. Single stage or two stage evaporators are used chiefly to concentrate and recover valuable plating chemicals (Groffman et al., 1992). The collected rinse stream is boiled off to remove sufficient water. Many of the evaporators in use also permit the recovery of condensed steam or recycle as rinse water. But this method needs a large area hence, both the capital and operational costs for evaporative recovery systems are high. Chemical recovery and water reuse values must offset these costs for evaporative recovery to become economically feasible.
Cementation
Cementation involves the displacement of electronegative dissolved metal species in aqueous solution to solid electropositive solid metal surface (Ku and Chen, 1992). Cementation is generally applied for small wastewater flows because of the long contact times required. This limits the use of this technology in wide manner. However, the consumption of solid metal as reducing agents and the redox potential of metals are the main limitations of the process (Agarwal, 1988; Agelidis et al., 1988).

Electrodeposition
Electrodeposition is a technique, where some metals are recovered from waste solutions using insoluble anodes. For example, spent solutions resulting from sulphuric acid cleaning of copper may be saturated with copper sulphate in the presence of residual acid. So these are ideal for electrowinning where high quality cathode copper can be electrolytically deposited while free sulphuric acid is regenerated (Dean et al., 1972; Kongsricharoern and Polprasert, 1995).

Ion exchange
This is a stoichiometric and reversible chemical reaction where an ion from a solution is exchanged for a similarly charged ion attached to an immobile solid particle. Each resin has a distinct number of mobile ion sites that set the maximum quantity of exchange per unit of resin. Zeolite is one of the most important materials used as ion exchanger in treatment of industrial wastewaters. Other ion exchangers include modified zeolites like Zeocarb and Chabcarb, which have greater affinity for metals like nickel and lead (Groffman et al., 1992). Natural zeolite and clinoptilolite have high selectivity for the removal of ammonium ions (Hlavay et al., 1982; Gaspard et al., 1983; Komarowski and Yu, 1997). Deans and Dixon (1992) have reported that chelating ion exchanger takes advantage of the three dimensional structure of molecules to chelate and remove ions of a specific size in the presence of other ions. In ion exchange process, the metal can be recovered in a more concentrated form by elution with suitable reagents after separating the loaded resin.
Reverse osmosis
This method uses semi permeable membranes, which basically act as molecular sieves, permitting soluble compounds having various molecular size ranges to pass through their pores. The membranes are generally made up of synthetic organic materials (Dean et al., 1972). This is a pressure driven membrane process, where the feed stream under pressure is separated into a purified permeate stream and a concentrate stream by selective permeation of water through a semipermeable membrane (Applegate, 1984; Gooding, 1985). Membrane has the composites of polyacrylic acid and zirconium oxide deposited on porous stainless steel or ceramic tubes. In plating chemical recovery application, reverse osmosis units separate the metal salts from rinse solutions, resulting in a concentrated metal solution, which can be recycled to the plating bath. Chian (1976) successfully demonstrated the reverse osmosis process for removal of chromium, lead, iron, nickel, copper and zinc from wastewater and acid mine drainage respectively.

1.3.8.2. Chemical processes
Solvent extraction
It is also frequently referred to as liquid-liquid extraction. Solvent extraction involves an organic and an aqueous phase. The aqueous solution containing the metal or metals of interest is mixed with an appropriate organic solvent and the metal passes into the organic phase. In order to recover the extracted metal, the organic solvent is reacted 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. Reddy and Sayi (1997) used di-n-pentyl sulfoxide (DPSO) for the removal of Cr(VI), Cr(III), Co(II) and Ni(II) from aqueous solutions. McDonald and Bajwa (1997) used 25% alamine 336 - xylene as extractant for the recovery of chromium, cadmium and zinc from metal finishing wastewater taken from the Dixie metal finishing plant of Houston, Texas. Stripping agents evaluated includes sulfuric acid, EDTA, and NaOH.
Xanthate process
Xanthate process works like ion exchanger, removing heavy metals from wastewater and replacing them with sodium. Xanthates are synthesized commercially by reaction between starch or cellulose with sodium hydroxide and carbon disulphide. This insoluble starch xanthate (ISX) is commonly used for wastewater treatment by continuous flow operations (Wing, 1978). Treatment with cellulose xanthate of industrial wastewaters containing lead, nickel, copper, chromium and iron resulted in minimum levels of residual metals at pH 6.5-9.5 (Wing et al., 1978). The resultant ISX-metal sludge settles quickly due to the viscous nature of ISX.

1.3.8.3. Biological processes
Though various biological processes are available for wastewater treatment like oxidation ponds, lagoons, activated sludge and trickling filters, these processes are not effective in removal of metal ions. Generally, they are employed for BOD and COD reduction. Only biological process recommended for metal removal is phytoremediation.

Phytoremediation is a technique where the plant system is used to clean up the contaminants and metals from soil and wastewater (Scragg, 1999). The plants must be able to tolerate high levels of metal in their roots and shoots and this is possible by the concentration of the metal in the vacuole or by chelation of the metal (Ortiz et al., 1995). Plants like, Thaspia caerulescens and Cardaminopsis halleri are known to accumulate high amounts of Zn and Cd (Scragg, 1999).

1.3.9. Adsorption
Adsorption is a surface phenomenon. It is bonding between two phases at an interface where accumulation of one phase has occurred. Adsorption occurs on the active site of the solid phase. Active sites that contain same energy potential are said to be homogenous and those with different energy potentials heterogeneous (Manivasakam, 1997).
Adsorbents can be classified as non-polar and polar solids. In non-polar solids, adsorption is mainly a physical process; e.g., activated carbon, while in polar solids, adsorption is a chemical process where the chemical structure of the molecules or the surface is not changed e.g., silica and aluminum oxides.

Activated carbon is the most widely used adsorbent in water treatment units due to its large surface area per unit weight. Although efficient, the preparation of carbon from various materials is an expensive process and therefore unaffordable by small-scale industries.

1.3.9.1. Non-toxic industrial solid wastes as adsorbents

Over the years many workers have used various industrial solid wastes as adsorbents. Pandey and co-workers (1986a) tried a range of mixed low-cost mineral adsorbents for the removal of Cu(II) from industrial wastewaters. Fly ash, an inorganic residue from the combustion of powdered coal, has received much importance as an adsorbent (Ferraiolo et al., 1990; Mohapatra and Rao, 2001). Adsorbents prepared from homogenized blends of fly ash, wollastonite and China clay were used for the removal of Cu(II) from aqueous solutions. Wollastonite and a mixture of fly ash-wollastonite were also used as adsorbents for removal of dyes from textile wastewaters (Khare et al., 1987, 1988). Kumar and co-workers (1987) used fly ash as an adsorbent in removing phenol, cresol and phenol: cresol (1:1) from aqueous solutions and achieved 40, 45 and 45% removal efficiencies respectively. Fly ash has been used successfully in the removal of Cr(VI), Cd(II), Pb(II), Ni(II), Cu(II) and Zn(II) from various industrial wastewaters (Grover and Narayanaswamy, 1982; Yadava et al., 1987; Gashi et al., 1988; Mathur and Rupainwar, 1988; Viswakarma et al., 1989; Viraraghavan and Rao, 1991; Zouboulis and Marros, 1992; Viraraghavan and Dronamraju, 1993). Rio et al. (2002) used fly ash from fluidised bed power plants to remove Pb(II), Cu(II), Cr(III), Ni(II), Zn(II) and Cr(VI) from aqueous solutions. Peikos and Paslawska (1999) experimented fly ash for the removal of fluoride. Cement kiln
dust was used as adsorbent for the removal of some anionic dyes from aqueous solution and effluent liquors (Ibrahim et al., 1998).

Waste slurry generated in fertilizer plants was used as adsorbent in removal of Cr, Hg, Pb, Cu and Mo (Srivastava et al., 1989; Mohan et al., 2001). Charred solid waste obtained from an oxalic acid plant has been used as absorbent in removal of Pb, Hg, Cr, F and dyes (Shukla and Pandey, 1990). Zouboulis and co-workers (1993b) employed industrial solid wastes/byproducts for removal of Cu(II), Pb(II), As(III) and As(V). Waste Fe(III)/Cr(III) hydroxide has been extensively studied for its efficacy to remove metals including Ni(II), Pb(II), Cd(II), Hg(II), As(V), Cu(II), Cr(VI) (Namasivayam and Ranganathan, 1993, 1994a, b, 1995a, b; Namasivayam and Senthilkumar, 1997; 1998; 1999) and for treatment of dairy wastewater (Namasivayam and Ranganathan, 1992). Namasivayam and Yamuna (1995a, b) used waste biogas residual slurry as adsorbent for removal of Pb(II) and Cr(VI).

Looma and Pandey (1995) used blast furnace granulated sludge in removal of Hg(II), Cu(II), Pb(II), and Ni(II). Sorption of Pb(II), Zn(II), Cd(II), Cu(II) and Cr(III) on blast furnace sludge was investigated by Lopez-delgado and his co-workers (1998). Processed solid residue of olive mill products was used to remove Cr(III), Ni(II), Pb(II), Cd(II) and Zn(II) (Gharaibeh et al., 1998). Mameri et al. (2000) used activated carbon prepared from olive mill solid residue for removal of phenolic compounds. Oil palm ash was used as an adsorbent for the removal and recovery of Zn(II) from aqueous solutions (Chu and Hashim, 2002). Lister and Line (2001) investigated the potential utilisation of sewage sludge and paper mill waste for sorption of metals from polluted waterways. Chen et al. (2002) used dried waste activated sludge for Cu(II) removal from simulated wastewater. Chaudhary et al. (2002) reported the use of chromium waste sludge in removal of colour from dye effluent streams.
1.3.9.2. Activated carbon from non-toxic agricultural wastes or by-products as adsorbents

Cellulosic and lingo-cellulosic wastes have long been recognized as starting materials for the preparation of activated carbon. Mackay and Roberts (1982a, b, c) performed a series of investigations for evaluating the specific influence of pyrolysis on the subsequent gasification, yield and microporosity of lignocellulosic chars.

A large variety of nutshells are used in the preparation of granular activated carbon. Carbon prepared from almond shells by acid, steam or carbon dioxide activation (Toles et al., 1997; 2000a, b), cashewnut hull carbon (Vasanthy and Lakshmanaperumalsamy, 1998), pecan shell carbon activated by steam, carbon dioxide, or phosphoric acid (Jhons et al., 1999), peanut shells (Wafwoyo et al., 1999), raw soybean hulls (Flock et al., 1999), oil-palm shells impregnated with potassium hydroxide (Guo and Lua, 2000), modified peanut shells (Chamarthy et al., 2001), pistachio shells, macadamia nutshells, hazel nutshells, black walnut shells, almond nutshells, pecan shells and english walnut shells activated by carbon-di-oxide (Wartelle and Marshall, 2001) and hazelnut shell (Demirbas et al., 2002), were used for the removal of metals and dyes from aqueous solutions and wastewaters.

Rodriguez-Reinoso and his co-workers (1982, 1984) have prepared activated carbons from locally available agricultural by-products like almond shells and olive stones. Apricot stones, lignites and anthracite have been used for removal of Zn(II) and Pb(II) (Ravigorova et al., 1998). Ferro-Garcia et al. (1989) evaluated a range of fruit pith carbons for the specific removal of Zn(II), Cd(II) and Cu(II) from industrial wastewaters. Macchi et al. (1986) used waste tea leaves and coffee powder for mercury removal. Orhan and Buyukgungor (1993) used waste tea, exhausted coffee and walnut shells as adsorbents for the removal of Cr(VI), Cd(II) and Al(III) from waste waters. Waste tea leaf carbon packed in column was used for the removal of Cr(VI) from chromium plating industry waste water (Singh and Lal, 1992). Vaughan et al. (2001) reported the
removal of selected metal ions, Cd, Cu, Pb, Ni and Zn from aqueous solution using modified corncobs. Cr(VI), Ni(II) and Fe(II) removal from electroplating industry wastewater by carbonized maize cob was reported by Selvakumari et al. (2002). Coconut shell has long been known as a precursor for high quality, granular carbons with extensive micropore volume that could be used as an adsorbent (Bansal et al., 1988; Alaerts et al., 1989; Laine et al., 1989; Tam and Antal, 1999). Coconut coir pith was used for the preparation of activated carbon for the removal of toxic ions, dyes and pesticides from wastewaters (Namasivayam and Kadivelu, 1994, 1997a, b, 1998, 1999; Namasivayam et al., 2001; Namasivayam and Kavitha, 2002).

An additional high-volume agricultural waste prevalent in much of the developing world is rice hulls or husks. Battacharya and Venkobachar, (1984) used three low cost adsorbents, bituminous coal, crushed raw coconut shells and rice husk carbon for the removal of Cd(II). Rice husk carbon was used as adsorbent for Cr(VI) removal from industrial wastewater (Srinivasan et al., 1988). Groundnut husk, melon seed husk and thiolated maize cob-meal have been successfully employed for the removal of heavy metals from wastewaters (Okieman and Ohyenkpa, 1989a, b; Okieman et al., 1991). Deflated rice bran, rice straw, soyabean, soyabean hull, sugarcane bagasse, cotton seed hulls, peanut shells and walnut shells have been used for removal of metal ions such as Pb(II), Cu(II), Ni(II), Cd(II) and Zn(II) from wastewaters (Larsen and Schierup, 1981; Suemitsu, 1986; Marshall et al., 1993; Marshall and Champagne, 1995; Marshall and Johns, 1996; Jhons et al., 1998). Banerjee and Mathew (1985) prepared light weight, high quality charcoal chips from jute sticks, a bulk volume agricultural waste, which amounts to 3-4 Mt per year in India. Srinivasan et al. (1988) used tamarind nuts to produce carbon for metal removal. Activated carbon prepared from peanut hull was used for removal of Cr(VI), Cd(II), Pb(II), Ni(II) and Cu(II) (Periyasamy et al., 1991; Periyasamy and Namasivayam, 1994, 1995a, 1995b, 1996). Howlader et al. (1999) prepared activated carbon from Krishnachura fruit (Delonix regia) and castor seed (Ricinus communis). Al-Asheh

1.3.9.3. Biosorbents
Biosorption is an alternative treatment process for the removal of metal ions using biological adsorbents. There have been numerous studies on the sorption of metals from aqueous solutions by microbial biomass (Beveridge, 1986; Volesky, 1986; Volesky and Holan, 1995). Fourest et al. (1994) observed the biosorption of metals by dead mycelial biomasses of Rhizopus arrhizus, Mucor miehei and Penicillium chrysogenum. Kapoor and Viraraghavan (1995) reviewed the fungal biosorption of wide range of metals such as Cu, Zn, Cd, Pb, Fe, Ni, Ag, Th, R and U from metal bearing wastewaters.

Kapoor and Viraraghavan (1997) reported that chemical modification of Aspergillus niger biomass using sodium hydroxide, formaldehyde, dimethyl sulfoxide and detergent resulted in significant improvements in biosorption of Pb, Cd and Cu. But, esterification of carboxyl and methylation of amine groups present in the cell wall significantly decreased the sorption of Pb and Cd. Addour et al. (1999) studied the Zn uptake by Streptomyces rimosus biomass using a packed-bed column. A comparative investigation on the biosorption of Pb by filamentous fungal biomass was done by Lo et al. (1999), which showed Mucor rouxii as a potential biosorbent for Pb removal. Krämer and Meisch (1999) improved the metal-binding ability of Aspergillus niger mycelial waste by chemical modification by introducing additional carboxy groups using oxidation methods or the introduction of the ethyl-di-amino group first by chlorination of A. niger using methyl chloride and subsequent reaction of the product with ethylene di-amine. The metals studied were Cd(II), Co(II), Ni(II) and Zn(II). Yan and Viraraghavan (2000, 2001) studied the effect of pretreatment on the sorption of metals Pb(II), Cd(II), Ni(II) and Zn(II) on Mucor rouxii. Pretreatment with
detergent and alkali improved the biosorption capacity when compared to live biomass whereas acid, CaCl₂ and NaCl pretreatment reduced biosorption. Biosorption sites for Basic blue 9, Acid blue 29, Congo red and Disperse red-1 dyes by Aspergillus niger were investigated by Fu and Viraraghavan (2000, 2002).

Baik et al. (2002) studied the biosorption of metal ions using whole mycelia and selected components of Aspergillus niger, Rhizopus oryzae and Mucor rouxii. The study revealed that binding of Cu, Cd, Ni and Zn was considerably improved by treating the cell wall fraction with 4 M NaOH at 121°C. Chitosan contributed most to the biosorptive capacity; 0.96 mmol Cu was bound by 1 g of the treated mycelium of M. rouxii DSM 1191. Bai and Abraham (2001, 2002) reported the biosorption of Cr(VI) from aqueous solution by native and chemically modified biomass of Rhizopus nigricans. The biomass was modified with alkalis, formaldehyde, acids, alcohols and acetone. The infrared spectroscopic analysis of the native, Cr-bound and the other types of chemically modified biomasses indicated the involvement of amino groups of Rhizopus cell wall in Cr(VI) binding. Koumanova et al. (2002) reported biosorption of Cd, p-chlorophenol (p-CP), 2,4-dichlorophenol (2,4-DCP), 3,5-dichlorophenol (3,5-DCP) and reactive dye from aqueous solutions by Rhizopus oryzae. Dias et al. (2002) studied the removal of metals (Cr, Ni and Fe) from metallurgical effluents, produced by a steel foundry by an Aspergillus terreus strain immobilized in a polyurethane matrix.

Zouboulis et al. (1999) investigated the biosorption of toxic metals from an aqueous mixture containing Zn, Cu and Ni, in the presence of Ca and Na ions (usual co-existing cations in related systems), by industrial biomass samples of different origin which included *Streptomyces rimosus*, *Penicillium chrysogenum*, *Saccharomyces carlsbergensis* and *S. cerevisiae*.

Non-viable yeast biomass was capable of removing more than 99% of Zn(II), Cr(VI) and Cu(II) from electroplating wastewaters and 50-60% of Cr(III) from tannery wastewater (Brady et al., 1994). Brady and Duncan (1994 a, b) reported the accumulation/binding of metal ions by *Saccharomyces cerevisiae*. Volesky and May-Phillips (1995) investigated the biosorption of U, Zn and Cu on live and non-living biomass of *S. cerevisiae*. Dead cells of *S. cerevisiae* removed 40% more U or Zn than corresponding live cultures. The removal of divalent metal ions, Ni(II), Cu(II) and Pb(II) using yeast (*S. cerevisiae*) as carriers in a crossflow microfiltration was investigated by Bayhan et al. (2001). Zetic et al. (2001) studied the uptake of Cr during fermentation process by *S. cerevisiae* biomass. Soares et al. (2002) studied the efficacy of a flocculant strain and a non-flocculant strain of *S. cerevisiae* to adsorb Cu(II). Results revealed that the flocculant strain removed nearly triple the amount of Cu(II) than the non-flocculant strain.

Bacteria are also capable of adsorbing metal ions (Gadd, 1990). Hu and Reeves (1997) studied the ability of *Pseudomonas aeruginosa* to adsorb U. Immobilized bacterial biomass was tested for selective adsorption and recovery of lead, Cu and Cd by Chang and Huang (1998). Chen and Wilson (1997a, b) used genetically engineered *Escherichia coli* that could express Hg(II) transport system and metallothionein for the removal of Hg(II). Chen et al. (1998) observed the removal of Hg(II) by genetically engineered *E. coli* in a hollow fibre bioreactor. Puranik and Paknikar (1999) used *Citrobacter* for biosorption of Pb, Cd and Zn. Accumulation of Zr and Ni by *Citrobacter* sp. was reported by Basnakova and Macaskie (1999). Hao et al. (1999a, b) used genitically engineered *Lactobacillus plantarum* for the uptake of Cd. *Pseudomonas stutzeri*
was tested for its efficacy to adsorb Ni(II) (Ramteke, 2000). Sar and D’Souza (2001) reported biosorption of U by live and lyophilized cells of *Pseudomonas* sp. Lyophilized cells of *Pseudomonas* showed better results than live cells. Lopez *et al.* (2002) made a comparative study between the free and immobilized cells of *Pseudomonas fluorescens* 4F39 to test their efficacy to adsorb Ni(II). Nourbakhsh *et al.* (2002) studied the sorption of Cr(VI), Pb(II) and Cu(II) separately and in combination in batch mode by *Bacillus* sp. Yong *et al.* (2002) reported the Pd uptake by resting cell suspensions of *Desulfovibrio desulfuricans*. Kannan and Ramteke (2002) reported that *Serratia marcescens*, a Gram-negative eubacterium, excreted a pigmented secondary metabolite, prodigiosin, which had additional electronegative sites for metal binding. Srinath *et al.* (2002) studied the biosorption and bioaccumulation of Cr(VI) by some chromate resistant bacteria isolated from tannery effluent.

Many algae were also used as biosorbents for removal of toxic pollutants from wastewaters. Greene *et al.* (1986) and Darnall *et al.* (1986) studied the removal and complexing of gold by algal biomass. Jorge *et al.* (1990) modified the carboxyl groups of *Cyanidium caldarium*, a red alga, with methanol and used it as biosorbent for Cu(II), Al(III) and Au(III) removal in batch technique. Harris and Ramelow (1990) studied the metal binding properties of *Chlorella vulgaris* and *Scenedesmus quadricanda*. Savvaidis (1997) studied the recovery of gold from thiourea solutions using three different microorganisms, *Saccharomyces cerevisiae*, *Spirulina platensis* and *Streptomyces erythraeus*, out of which *Spirulina platensis* showed the maximum affinity and capacity for gold adsorption even at low pH values. Zhao and Duncan (1998, 1999) have reported the removal and recovery of Ni(II) and Cr(VI) from electroplating effluent using *Azolla filiculoides* as adsorbent. Sanyahumbi *et al.* (1998) reported the removal of lead from aqueous solution by *Azolla filiculoides*. Kratochvil and Voleskey (1998) demonstrated the removal/recovery of Cu from ferruginous wastewater using *Sargassum* biomass. Aquatic moss, *Fontinalis antipyretica*, was used for Cu(II) removal (Gonculves and Boaven-Tura, 1998). Williams *et al.* (1998) made a

### 1.3.9.4. Other adsorbents

Apart from the above said adsorbents, many other substrates were also tried as adsorbents for removal of heavy metals and other pollutants. Peat moss is one of the widely used adsorbent. It has been used for the removal of Cr(VI), Hg(II), Cd(II) and diuron (Chaney and Hundemann, 1979; Lee *et al.*, 1995; Sharma and Forster, 1995; Sorensen and Fernqvist, 1996; Prasad *et al.*, 1998). Wollastonite has been used for removal of Cu(II), Fe(II), Pb(II) Ni(II) and Cd(II) (Pandey *et al.*, 1986b; Singh *et al.*, 1988a; Sharma *et al.*, 1988; 1990; Yadhava *et al.*, 1991). Yadava *et al.* (1991) used China clay and wollastonite as adsorbents for the removal of Pb form aqueous solution. Lignite coal was used as adsorbent for Cr(VI) adsorption (Kannan and Vanangamudi, 1991). Bituminous coal was tested for its efficacy to adsorb metals (Singh and Rawat, 1994; 1995). Sivasamy *et al.* (2001) used lignite, fine coke and bituminous coal for defluoridation of water.
Singh et al. (1992) used feldspar for the removal of Cr(VI) from plating industry wastewater. Balkose and Baltacioglu (1992) examined the adsorption capacity of wool fibres for Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) from aqueous solutions. Kinetics of Zn adsorption on charcoal was studied by Mishra and Chaudhury (1994). Biotite mica was used for the adsorption of high molecular weight guar gum (Rath and Subramaniam, 1997). Subha and Anirudhun (1996) used polyacrylamide grafted tin(IV) oxide gel for removal of Pb(II). Ajmal et al. (1998) used saw dust as adsorbent for removal of Cu(II). Raji and Anirudhan (1996, 1998) used saw dust polymerized with polyacrylamide for adsorption of Hg(II) and Cr(VI). Yu et al. (2000) demonstrated the use of saw dust in removal of Cu. Cox et al. (2000) studied the removal of Hg(II) from aqueous solution on a carbonaceous sorbent prepared from flax shive. El-Shafey et al. (2002) also investigated the adsorption capacity of a carbonaceous material produced by treating flax shive with H$_2$SO$_4$ in removing Cd(II), Cu(II), Cr(III), Co(II), Ni(II), Zn(II) and Pb(II) from aqueous solution. Artola et al. (2001) investigated the adsorption efficacy of anaerobically digested sludge for removal of Cu(II).

Zhang et al. (2001) used cetyltrimethylammonium bromide microemulsions for the extraction and recovery of gold. Niu and Volesky (2000, 2001) studied AuCN$_2^-$ biosorption with L-cysteine and chitinous materials such as acid-washed crab-shells, burnt crab-shells, as well as chitin modified by quaternization of amine. Adsorption behaviour of metal ions on imprinted chitosan resin was studied by Tianwei et al. (2001). Ishikawa et al. (2002) studied the uptake and recovery of Au(III) from electroplating wastes using eggshell membrane. Shekinah et al. (2002) reported the adsorption of Pb(II) from aqueous solution by activated carbon prepared from Eichhornia. Bone powder prepared from animal bones and plant powder prepared from the roots of Nile rose plant (Eichhornia speciosa) were tested for their adsorption efficacy to remove Zn and F from industrial wastewaters (Abdel-Halim et al., 2003). Kara et al. (2003) studied the adsorption capacity of sepiolite to remove Co(II) from aqueous solution.

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Oxides of manganese and iron (McKenzie, 1980), aluminium and iron oxide minerals (Goldberg, 1986), lignin (Verma et al., 1990), chemisorption filters (Jubinka et al., 1992), biopolymers (Deans and Dixon, 1992), EDTA coated activated carbon (Lu and Subramanian, 1993), activated charcoal cloth (Jayson et al., 1993), Ganga sand (Vaishya and Agarwal, 1993), pyrite and dolomite (Zouboulis et al., 1993b), porous chitosan chelating resin (Kawamura et al., 1993), natural clay (Hawash et al., 1994), pyrite fines (Zouboulis et al., 1995), raw charcoal obtained from reeds (Khalfaoui et al., 1995), humus-kaolin complexes (Huang and Yang, 1995), hydroxyapatite (Mandjny et al., 1995), silica gel modified with benzimidazole (Fillow et al., 1995), lithuanian glauconite (Smith et al., 1996), iron-oxide coated sand (Benjamin et al., 1996), porous cellulose modified with poly ethyleneimine (Navarro et al., 1996), geothite (Rodda et al., 1996), pyrophyllite (Scheidegger et al., 1996), montmorillonite (Pabalan and Turner, 1997; Turner et al., 1998; Altin et al., 1999a, b), steel wool (Ozer et al., 1997), pressed sludge cake (pulp mill waste), coal dust, pyrolysed tyre, sugar beet pulp, leather hide powder (Bousher et al., 1997), colloidal ferric hydroxides (Dario and Ledin, 1997), natural bentonite (Mellah and Chegrouche, 1997), magnetic charcoal (Safarik et al., 1997), exo-polysaccharide (Loaec et al., 1997), modified zeolites (Curkovic et al., 1997), bambaranuts (Said et al., 1997), Fe(III) doped alginate gels (Min and Hering, 1998), heat treated sulphurized activated carbon (Serrano et al., 1998), aluminium-oxide coated sand (Kuan et al., 1998), red mud (Lopez et al., 1998), megadiite (Jeong and Lee, 1998), Cyanex 923 (Alguacil et al., 1998), acid-activated spent bleaching earth (Low et al., 1998), carbonized slash pine bark (Edgehill and Lu, 1998), LIX 54 (Alguacil and Alonso, 1999), compost derived from household waste (Grimes et al., 1999), purified soybean peroxidase and raw soybean hulls (Flock et al., 1999), poly (acryl-amino-phosphonic) – type chelating fiber (Liu et al., 1999), *Eucalyptus globulus* and peach stone-activated carbons (Bello et al., 1999), synthetic and natural aliphatic compounds (Diez et al., 1999), natural and activated bentonite (González-Pradas et al., 1999), immobilised persimmon tannin (Nakajima and Sakaguchi, 2000), modified silica impregnated with LIX 84 (Kim and Yi, 1999;
2000), LIX 622 (oxime derivative) (Sastre et al., 2000), cork and yohimbe bark wastes (Villaescusa et al., 2000), polystyrene resins (Douliya et al., 2001), macroporous resins (Tangzhigang et al., 2001), crab shell (Kim and Park, 2001), eggshell membranes (Koumanova et al., 2002), polymeric Fe- and Al-modified clays (Cooper et al., 2002), waste tyre rubber (Knocke and Hemphil, 1981; Miguel et al., 2002) and compost (Tsui et al., 2003) are few examples of adsorbents that have been used in the removal of heavy metals and other pollutants from wastewaters.

1.3.10. Technologies to treat arsenic pollution

In terms of low-cost remediation techniques for safe drinking water supply, four major options are suggested. They are,

i) Auto-attenuation

ii) Use of geological materials as natural adsorbents

iii) Use of low cost industrial and agricultural wastes as adsorbents

iv) Use of biosorbents

Auto-attenuation is one of the most convenient methods to remediate groundwater. The principle is to allow the groundwater collected from wells to stand for a specific period of time. Dissolved iron, present in groundwater is readily oxidized and precipitates as Fe(III). The auto-oxidation of Fe(II) to Fe(III) generates a favorable substrate with surface reactive sites for adsorption of both uncharged As(III), as well as anionic As(V) species.

Laterite has been tested as an adsorbent and proved to be a promising low-cost remedial technique to safeguard drinking water (Larsson et al., 1998). Laterite, a red-colored vesicular clayey residue occurs abundantly in tropical regions. The major components of laterite are hydrous oxides of iron- and aluminum, with minor proportions of manganese and titanium. Laterite is an acidic soil with a typical pH between 4-5. Both hydrous iron and aluminum oxide components in
laterite have a pH$_{zpc}$ at 8.5-8.6 (Anderson et al., 1976; Kinniburgh et al., 1976). Under natural conditions, they are characterized by a net positive surface charge, and thus have the capacity to adsorb several anionic contaminants at a wide pH range (Pierce and Moore, 1982; Wilkie and Hering, 1996). Laterite could either be used in a filter column or directly mixed with water in the water vessel where the soil particles would act as adsorbent during sedimentation. The results of the adsorption batch experiments on high-As groundwater from Ghetugachi village, Chakdaha in Nadia District, West Bengal indicate that laterite is an effective filter medium, notably for those in which arsenate dominates over arsenite.

Nenov et al. (1993) used ferrous sulphate for the removal of As(III) from aqueous solutions. Flotation process was also employed, which selectively removed surface active or hydrophobic compounds and solids from aqueous solutions. Low concentrations of As(III) ($\leq$10 mg/L) was removed by bubbling gas through the solution. Matis et al. (1997) studied the flotation removal of As(V) onto goethite.

Activated alumina, activated bauxite, activated carbon and activated carbon impregnated with Ag$^+$ were experimented for adsorption of As(III) and As(V) from aqueous solutions (Gupta and Chen, 1978; Rajakovic and Mitrovic, 1992). Krishnan et al. (1987) investigated the efficacy of amorphous iron-hydroxide and cattails to adsorb As(III). Sen and De (1987) investigated the adsorption of As(III) onto coal fly ash; haematite was also tested for As(III) adsorption (Singh et al., 1988b). Vaishya and Agarwal (1993) studied the efficiency of Ganga sand to adsorb As(III). Zouboulis et al. (1993b) investigated the removal of As(III) and As(V) from dilute solutions by pyrite fines. Adsorption of As(III) and As(V) on to Al$_2$O$_3$/Fe(OH)$_3$ was studied by Hodi et al. (1995). Alumina, Y(III) impregnated alumina, La(III) impregnated alumina and La(III) impregnated silica gel were also tested for adsorption of As(V) (Wasay et al., 1996a, b, c). The adsorption isotherm of arsenic(III) on copper impregnated active carbon from coconut husk was studied by Manju et al. (1998). Senthilkumar (1998) reported the adsorption of As(III) and As(V) onto Fe(III)/Cr(III) hydroxide waste. Matis et al. (1999)
studied sorption of As(V) by goethite particles and their flocculation. Lanthanum impregnated sawdust carbon was tested for its efficacy to adsorb As(III) (Raji and Anirudhan, 1999). Some natural solids including, natural zeolites, volcanic stone and the cactaceous powder were used as adsorbents to remove As(III), As(V), dimethylarsinic acid (DMA) and phenylarsonic acid (PHA) (Elizalde-Gonzalez et al., 2001). Altundogan et al. (2002) investigated the sorption of As(V) onto raw red mud and activated red mud at 25°C and 70°C. Lenoble et al. (2002) reported arsenic adsorption by pillared clays and iron oxides.

In many affected areas of West Bengal and Bangladesh, villagers do not have access to any secondary source of arsenic-free water. Surface water treatment and subsequent distribution of treated water in such remote areas will be extremely complex and cost-wise prohibitive. Installing operationally simple low-cost arsenic removal units at the existing wells is practically the only way-out to ensure a supply of safe drinking water. To this end, through a grant from the Water for People (WFP) in Denver, CO, to Bengal Engineering College in Howrah, West Bengal, four wellhead arsenic removal units were installed in the villages of North-24-Parganas during 1997 and 1998. In these units, activated alumina has been used as the adsorbent for the removal of soluble arsenic (Gupta, 1999).

Another process is Arsenic Remediation Technology (AsRT), which uses common materials such as zero-valent iron and sand, to remove arsenic to levels below 1 ppb. After completing successful laboratory scale tests at the University of Connecticut, a two-year pilot demonstration was conducted at the Winthrop Superfund Site in Maine. Nine months of operation resulted in lowering of the influent As(III) concentration from about 350 ppb to less than 1 ppb in groundwater (Lackovic et al., 1999).

Bijoypur clay from Mymensingh and processed cellulosic materials like delignified jute, bleached sawdust and pulped newspaper were found to adsorb both As(III)
and As(V) in solutions acidified with vinegar or hydrochloric acid. Iron(III) hydroxide coated newspaper pulp and adsorption filters coagulated arsenic most. The material showed potential for use in small-scale home treatment units. The sludge was regenerated by sodium hydroxide elution (Khair et al., 1999).

Ahmed et al. (1999) developed a mitigation technology, adding a floc forming composition to the contaminated water followed by filtration through a specially formulated filter bed, for the removal of soluble arsenic from tube well water. The cost of the treatment comes about $30 for 600 liters of water.

Ghimire et al. (2002) used untreated and FeCl₃ pretreated orange juice residue for As(III) removal and observed that the As(III) removal was high in the FeCl₃ treated orange juice residue than the untreated orange juice residue. Murugesan (2002) studied the biosorptive capacity of live and pretreated biomass of tea fungus to remove As(III) and As(V) from aqueous solutions and groundwater. Xu et al. (2002) used aluminum loaded shirasu-zeolite for the removal of As(V) from drinking water. DeMarco et al. (2003) studied the removal of As(III) and As(V) by a polymeric/inorganic hybrid sorbent. Iron oxide coated sand was used as adsorbent for arsenic removal from drinking water (Thirunavukkarasu et al., 2003).

Katsoyiannis et al. (2002) reported the removal of As(III) from groundwaters using fixed-bed upflow bioreactors. Mokashi and Paknikar (2002) used Mycobacterium lacticum, a As(III) oxidizing bacterium, to develop a microbially assisted process for the removal of arsenic from contaminated groundwater. They observed that the oxidation of groundwater As(III) by a column immobilized with Mycobacterium lacticum, followed by adsorption using activated carbon, could be an efficient method to remove As(III). Penicillium purpurogenum biomass was used as adsorbent for the removal of arsenic from solution (Say et al., 2003).
Biosorbents have numerous advantages over chemical adsorbents. Use of biosorbents for metal removal is considered to be a cost effective technique, particularly when the waste biomass from fermentation industry, sewage sludge etc. are used as adsorbents. Fungal biosorbents especially, are highly effective in metal removal due to their large surface area than other microbes. Moreover, the adsorbent and the adsorbate can be easily recovered after the adsorption process. As biosorbents are easily biodegradable, this technology is considered to be eco-friendly.