CHAPTER 1

INTRODUCTION
1 INTRODUCTION

Water is essential to all forms of life. Irrespective of origin, it always contains a complex mixture of organic and inorganic substances most of which are of natural origin resulting from the complex interaction between water, soil and underlying geological strata and from complex biological and microbiological processes occurring in soil and water. Suspended and colloidal mineral matter, eroded soil, decaying vegetation and living micro-organisms are also frequently found.

In water, meant for drinking purposes, the total organic content, represented as total organic carbon, is usually not greater than 5 mg/L and many of the individual substances are of anthropogenic origin. The dissolved inorganics, mostly bicarbonates, chlorides and sulphates of calcium and magnesium with lower concentrations of sodium and potassium ions, usually range between 50-500 mg/L, although its concentration may go as high as 1500 mg/L in some arid regions.

The inorganic minerals which are present in water can be classified into three categories: (i) Minerals needed daily in large quantities include sodium, calcium, magnesium and potassium, (ii) Elements needed in smaller quantities include iron, copper, cobalt, manganese, zinc, molybdenum and fluoride and (iii) Mineral elements which are toxic even at low concentrations include beryllium, bismuth, cadmium, lead, arsenic, mercury and silver and these heavy metals can exert toxic effects because human beings have no natural defence against them.

Increasing environmental pollution from industrial wastewaters in the world, particularly in developing countries is of major concern. The rapid growth of industries especially of chemicals and allied products has resulted in the production and use of substances some of which are health hazards. A significant amount of these compounds also get released into the environment, affecting the flora and fauna. The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in aquatic environment. Mine drainage, domestic effluents, agricultural run off, acid rain etc., have all contributed to some extent to the metal loads in the water bodies [1].
Large-scale extraction of metals present hazardous waste management problems worldwide. Predictions show that by the year 2000 mining will have directly disturbed about 2,40,000 km$^2$ of the earth's surface. High concentrations of Cu, Zn, Cd, Pb and As in rivers resulting from metal extraction have adversely affected fisheries in more than 21,000 km of rivers [2]. The heavy metals are of special concern because they are non-degradable. The metals of most immediate concern are: Hg, Pb, Cd, Cr, Zn, Cu, Ni, Mn, Fe and Co. These metals are widely distributed in materials which make up the earth's surface [3].

The extent of heavy metals contamination of water environment has now been identified to be responsible for various occupational and corporate diseases, death and destruction of flora and fauna apart from their effect on cultural and aesthetic aspects of civilization. As it has become cognisant that man and technology are inseparable parts of modern civilization, in order that technological advances make minimum impact on the biosphere, it has become necessary to take adequate steps for controlling the levels of heavy metals from polluted water bodies so that their lethal effects are not felt by the exposed population. The heavy metals examined in the thesis are Hg, Pb, Cd, Ni and Cu. The advances made on the treatement of water and wastewater containing these ions can be best appreciated in the light of a brief account of their toxicity and source.

1.1 Toxicity of heavy metals

The toxicity of heavy metals depends on the concentration of the metal ion and the nature of organism with which it interacts. Temperature, pH and presence of complexing agents also affect the toxicity of metal ions. It is evident that a toxic substance may influence the biota if its concentration in the environment is over a certain level. Indeed, some heavy metals, dangerous at high concentrations, are essential to the biota at low concentrations. Unfortunately, it is often difficult to establish the level.

Mercury: Mercury causes damage to the central nervous system and chromosomes, impairment of pulmonary function and kidney, chest pain and dyspnoea [4-6]. The harmful effects of organic
mercury, particularly the alkyl compounds, include the contamination of fish in Minamata Bay, Japan [7, 8]. The biochemical kinetics of mercury methylation in water under naturally occurring conditions of pH and temperature have confirmed that inorganic mercury could be easily converted into the more toxic organic mercury by certain micro-organisms [9].

**Lead**: The toxicity and deleterious effects of lead are well documented. Lead has been recognized for centuries as a cumulative poison [10]. The Federal centres for Disease control in the USA consider a blood level exceeding 300 μg/L to be excessive. Health studies done in Poland during the past two years have linked elevated levels of lead in the environment with retardation and learning disabilities of children [11]. Acute lead poisoning in humans causes severe destruction in kidney, reproductive system, liver, brain and central nervous system. Mild lead poisoning causes anaemia. The victim may have headache and sore muscles and may generally feel fatigue and irritable [12-14]. Lead is also toxic to aquatic organisms. Fish avoid water containing 0.3 mg/L lead and above 1 mg/L, lead is lethal [15]. The concentration of lead in water below the WHO standard (50 μg/L) cannot be considered as a serious source of lead intake [16].

**Cadmium**: The "itai-itai" disease around Jintsu river in Japan was probably due to the transport of cadmium containing suspended particles to the paddy soil on irrigation with the river water. The first symptoms of chronic cadmium poisoning occur in the tubular system of kidney. The critical level is about 200 mg/kg. The normal value for the present population is about 10-20 mg/kg [17]. Shellfish can accumulate cadmium from bottom sediments but fish does not. Some plant species also have sensitivity to cadmium and has shown phytotoxic effects [18]. The no-effect level of cadmium administered at a single oral dose to adults has been estimated at 3 mg and the lethal doses from 350-8900 mg [19]. The harmful effects of cadmium in humans include a number of acute and chronic disorders such as renal damage, emphysema, hypertension and testicular atrophy [20]. Cadmium may replace zinc in some enzymes, thereby altering the stereostructure of the enzyme and impairing its catalytic activity [21]. Small amounts of cadmium (II) are believed to be harmful to man, having been
associated with hypertensive diseases [22] and the International Agency for Research on Cancer classified cadmium among chemicals which are probably carcinogenic to man [23].

**Nickel**: Dermatitis (nickel itch) is the most frequent effect of exposure to nickel, such as in coins and costume jewelry. Nickel carbonyl \([\text{Ni(CO)}_4]\) has been estimated to be lethal in humans at atmospheric exposures of 30 ppm for 30 minutes [24]. The mechanism of toxic action of nickel is its capacity to inhibit oxidative enzyme systems within the body. The main storage depots of nickel are the spinal cord, brain, lungs and heart, with lesser amounts widely distributed throughout the organ system. Acute poisoning causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness [25]. Nickel concentrations in soil in the range 20-40 \(\mu\text{g/L}\) is reported to be toxic to beans and maize [26]. Vymazal [27] studied the toxicity of nickel (II) and found to be harmful to fish and algae. Heale and Ormrod [28] have found retarded growth of maple dogwood, honeysuckle and pine by the application of nickel at 20 mg/L. Seed germination, plant growth, root nodulation and reproductivity of lentil plants were adversely affected by nickel (II) treatments particularly in high concentrations [29].

**Copper**: The adult human ingests about 2-5 mg of copper per day, about 30% of which is absorbed. Both the uptake and excretion of copper are highly regulated by the body since excess copper is toxic. Copper has been reported to cause neurotoxicity commonly known as "Wilson's disease" due to the deposition of copper in the lenticular nucleus of the brain and liver, leading to neurological problems and liver and kidney failure [30, 31]. Human serum albumin has one specific copper (II) binding site. Copper bound to albumin is considered to be the transport form of copper (II) in blood [32]. Eating liver or shellfish such as oysters, provides our sources of copper. Excess copper if not excreted may be found deposited in the eyes. It has long been known that copper salts are poisonous to lower organisms and so they are used as a fungicide to destroy algae [33]. Copper is highly toxic to most aquatic plants and its toxicity is generally manifested as a general chlorosis and stunting of
growth [34]. Copper is also toxic to fish but toxication depends upon other parameters like alkalinity, pH, hardness and many organic compounds frequently present in water [35,36].

1.2 Sources of heavy metal pollution

Most of the mercury produced is consumed by the chloralkali industry. Mercuric chloride and sulphate find use as catalysts in the production of polyvinyl chloride and polyvinyl acetate [5]. Elemental mercury finds widespread use in fluorescent and discharge lamps, thermometers, batteries and electrical control instruments. paint, pharmaceutical, paper and pulp industries also use mercury compounds. Most of the mercury used finds its way into the environment and it has been reported that about 0.1-0.2 kg of mercury is lost into the environment by chloralkali plant for every tonne of chlorine produced [37].

Lead occurs as a variety of ores, the most important of which is galena, with cerussite and anglestie being of secondary importance. Anthropogenic sources of lead in the environment from the production of lead can be associated with (a) mining-milling operations, which include grinding, concentrating and transportation of the ore, as well as disposal of the tailings and mine and mill wastewater and (b) the smelter-refininery process and problems associated with concentrate hauling, storage, sintering, refining, atmospheric discharges and blowing dust [14]. In 1975, there was an estimated total of 19,225 tonnes of lead emitted to the atmosphere from stationary sources. Of this total, 400 tonnes were from primary lead smelting and 755 tonnes were from secondary lead smelting, representing 2.1 and 3.9%, respectively, of the total lead were emissions from stationary sources. In 1975, 1,42,000 tonnes of lead were emitted from mobile sources through the combustion of gasoline [38]. In addition lead is generated in the effluents from the production of television picture tubes, storage batteries, pigments, petroleum, fuels, photographic materials and explosives. Printing, glass industrial operations and inorganic chemicals manufacturing industries are also main sources of lead pollution [39, 40].

About one half of all cadmium produced is reported to find its way for plating purposes. The discharge of liquid wastes from these operaions can lead to seepage of cadmium resulting in the
contamination of the ground water. Cadmium concentrations ranging from 0.01 to 3.2 mg/L have been reported in such situations [41]. Discharges from pigment plants, battery and fertilizer industries are the other major sources of cadmium in the aquatic environment. Cadmium is also used to some extent in the production of television picture tubes, fungicides, rubber curing agents and nuclear reactor shields and rods [42, 43].

Nickel has excellent corrosion resistance property and is used for alloy preparation. It is also frequently used as catalyst in plating plant, zinc base casting industries and storage batteries. Lesser quantities of nickel are used as a gasoline additive and in ceramics, fungicides, pigment and in inorganic chemicals manufacturing industries. The current users of nickel include nuclear power plants, gas turbine engines, cryogenic containers and pollution abatement equipments. Nickel from the effluents of the above industries contaminates water sources [21, 44].

Elevated environmental level of copper may come from variety of sources, such as metal cleaning and plating baths, paper and pulp, petroleum refining and fertilizer industries [35]. Other sources include discharges from basic steel works and non-ferrous metals, motor vehicles and aircraft-plating industries [3]. Discharges from the printed circuit board also contribute to copper in the water environment [45].

Effluents from the above industries containing heavy metals, which are let out into inland surface waters or onto land, percolate through soil and contaminate ground water systems. The ubiquitous nature of heavy metals, their extreme toxicity even in trace quantities, their tendency for bioaccumulation in the food chain and the strict environmental regulations related to heavy metals discharges make it necessary to develop schemes for the removal of heavy metals from wastewaters.

1.3 Effluent limitations

The permissible limits (mg/L) of the metals for discharge of wastewaters are given in the following table:
chemical precipitation of heavy metals as their hydroxides using lime or sodium hydroxide is widely used. Lime is generally favoured for precipitation purposes due to the low cost of the precipitant, ease of pH control in the range 8.0-10.0 and the presence of excess lime also serves as an adsorbent for the removal of metal ions [48]. The efficiency of the process depends on a number of factors, which include the ease of hydrolysis of the metal ion, nature of the oxidation state, pH, presence of complex forming ions, standing time, degree of agitation and settling and filtering characteristics of the precipitate. Chlorination is sometimes required to breakdown the organo-
metallic compounds prior to precipitation. Flocculating agents are frequently added to aid settling of
the precipitate. The method has been used for the removal of iron, copper, zinc, tin, cadmium and
nickel from the effluents of metal finishing industries [49] and for the removal of iron and aluminium
in sewage water [50]. Sorg et al. [48] evaluated the use of lime for the removal of lead and cadmium
from water and wastewaters and concluded that the effluent after treatment meets the requirements
prescribed by EPA.

Limitations of hydroxide precipitation method include the following: Difference between
metals in the optimum pH for hydroxide formation may lead to problems in the treatment of effluents
containing combined metal ions. Complexation of metals with organic matter or cyanide may
produce soluble metal chelates even at high pH. Variability in metal hydroxide solubility at a fixed pH
is another drawback. The amphoteric nature of some metals leads to problems of potential
resolubilization.

1.4.2 Carbonate precipitation

Carbonate precipitation of metals by using calcium or sodium carbonate is very limited. Patterson et al. [51] reported improved results using carbonate precipitation for cadmium (II) and
lead (II) from electroplating effluents. When the pH of the solutions were brought to 7.5, residual
concentration of lead (II) and cadmium (II) were 0.60 and 0.25 mg/L, respectively. Brantner [52]
compared pilot plant tests of carbonate precipitation with hydroxide precipitation of cadmium from
an electric arc furnace blowdown. At a sodium carbonate dosage of 650 mg/L and a pH ranging from
8.3 to 8.7, the total cadmium concentration was reduced from 1.37 mg/L down to 0.14 mg/L in
clarified effluent. Soluble cadmium concentration was reduced from 0.79 mg/L down to 0.1 mg/L
and in another test from 1.2 mg/L down to 0.04 mg/L.

With hydroxide precipitation comparable results could be obtained only at pH 10.5. Apart
from lower pH of precipitation, the relative filtration rates of carbonate precipitates were found to be
approximately twice that of hydroxide precipitation.
1.4.3 Sulphide precipitation

Since most of the heavy metals form stable sulphides, excellent metal removals can be attained by sulphide precipitation. Treatment with sulphide is most advantageous when used as a polishing step after conventional hydroxide precipitation or when very high metal removals are required.

Two approaches are available for precipitation of sulphides. They are soluble sulphide precipitation (SSP) and insoluble sulphide precipitation (ISP). The former uses water soluble sodium sulphide as reagent while in the latter, the slightly soluble ferrous sulphide slurry finds use. In the case of ferrous sulphide, though large quantities of sludge are generated, it is advantageous in the sense that the process does not result in the evolution of hydrogen sulphide. The SSP process, on the other hand, is rapid but results in particulate fines which are difficult to separate.

The advantage of sulphide precipitation is that the solubility of metal sulphide is generally low, resulting in a higher efficiency [53]. In the sulphide precipitation method, the metal level is reduced to 0.01 mg/L for cadmium, copper and zinc and 0.05 mg/L for chromium and nickel [39]. Mercury containing-wastewaters have been treated using sodium sulphide in the pH range of 6.0-10.0 using ferric hydroxide as the collector [54]. The residual concentration of mercury in the treated water was less than 0.06 mg/L. According to Whang et al. [55] metal sulphide exhibits better thickening properties and dewatering ability than metal hydroxide sludge from the hydroxide precipitation process. In addition, metal sulphide sludge is three times less subjected to leaching at pH 5.0 compared to hydroxide sludge and therefore final disposal is easier and safer.

The process technology for metal sulphide precipitation is similar to that used for hydroxide precipitation, with reaction tank, flocculation unit, settlement tank and filtration of fines. The influent pH should be adjusted to 7.0-8.0 to prevent hydrogen sulphide formation and excess sulphide should be removed from the effluent by aeration or chemical oxidation [56].

1.4.4 Ferrite coprecipitation

This process is based on the production of insoluble ferromagnetic oxides or ferrites, which may be removed from the effluents magnetically or by filtration [39]. This treatment is carried out by
adding a ferrous salt to the wastewater followed by neutralization to form a heavy metal ferrous hydroxide precipitate. This precipitate is then oxidised by aeration to form a ferrite coprecipitate. Preliminary information has indicated fairly high removal levels for many metal ions.

1.4.5 Chemical reduction

Reduction of hexavalent chromium can be accomplished with electrochemical units. The electrochemical chromium reduction process uses consumable iron electrodes and an electrical current to generate ferrous ions that react with hexavalent chromium to give trivalent chromium [57] as follows:

\[ 3 \text{Fe}^{2+} + \text{CrO}_4^{2-} + 4\text{H}_2\text{O} \rightarrow 3 \text{Fe}^{3+} + \text{Cr}^{3+} + 8\text{OH}^- \]  

Another example of the application of reduction process is the use of sodium borohydride, which has been considered effective for the removal of mercury, cadmium, lead, silver and gold [39].

1.4.6 Xanthate process

Insoluble starch xanthate (ISX) is made from commercial crosslinked starch by reacting it with sodium hydroxide and carbondisulphide. To give product stability and to improve the sludge settling rate, magnesium sulphate is also added. ISX works like an ion exchanger, removing the heavy metals from the wastewater and replacing them with sodium and magnesium. Average capacity is 1.1–1.5 meq of metal ion per gram of ISX [58].

ISX is most commonly used by adding it to the wastewater as a slurry for continuous flow operations or in the solid form for batch treatments. It should be added to the effluent at pH \( \geq 3.0 \). Then the pH should be allowed to rise above 7.0 for optimum metal removal [59]. Residual metal ion level below 50 \( \mu \text{g/L} \) have been reported [60, 61]. The effectiveness of soluble starch xanthate (SSX) for removal of cadmium (II), chromium (VI) and copper (II) and insoluble starch xanthate (ISX) for chromium (VI) and copper (II) have been evaluated under different aqueous phase conditions. Insoluble starch xanthate had better binding capacity for metals. The binding capacity of SSX and
ISX, respectively, for different metal ions follows the sequence Cr(VI) > Cu(II) > Cd(II) and Cr(VI) > Cu(II) [62].

1.4.7 Cementation

Cementation is the displacement of a metal from solution by a metal higher in the electromotive 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. Because of its low cost and ready availability, scrap iron is the sacrificial metal used often. Cementation is especially suitable for small wastewater flows because a long contact time is required. Some common examples to cementation in wastewater treatment include the precipitation of silver from photoprocessing discharges, the precipitation of copper from printed etching solutions and the reduction of Cr(VI) in chromium plating and chrome-inhibited cooling water discharges [63]. Removal and recovery of lead ion by cementing on iron sphere packed bed has been reported [64, 65]. Lead was replaced by a less toxic metal in a harmless and reusable form.

1.4.8 Solvent extraction

Liquid-liquid extraction (also frequently referred to as solvent extraction) of metals from solutions on a large scale has experienced a phenomenal growth in recent years due to the introduction of selective complexing agents [66]. 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. The aqueous solution containing the metal or metals of interest is mixed intimately with the appropriate organic solvent and the metal 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 reextracted into the stripping solution. The concentration of the metal in the strip liquor may be increased, often 10 to 100 times over that of the original feed solution. Once the
metal of interest has been removed, the organic solvent is recycled either directly or after a fraction of it has been treated to remove impurities.

The classification of different extractions available is based on reaction type and includes inert extractants, solvating extractants, acidic extractants, chelating extractants and ionic extractants [67]. Reddy and Sayi [68] have evaluated di-n-pentyl sulfoxide as extractant for the removal of Cr$^{6+}$, Cr$^{3+}$, Co$^{2+}$ and Ni$^{2+}$ from aqueous solutions. McDonald and Bajwa [69] have found a 25% Alamine 336-xylene solution to be the most effective solvent for the recovery of chromium, cadmium and zinc from metal finishing wastewater taken from the Dixie Metal Finishing Plant of Houston, Texas; the three metals could be extracted selectively or simultaneously. Stripping agents evaluated included sulphuric acid, EDTA and sodium hydroxide. When 4M sodium hydroxide was used for stripping, more than 99.5% recovery of the three metals was attained, and the regenerated solvent could be recycled and reused without any loss of extraction efficiency. Peterson et al. [70] investigated the use of liquid ion exchangers for the removal of cadmium (II) from electroplating wastes using kerosene as the solvent and concluded that the cost of treatment was only half that of lime precipitation method. Knocke et al.[71] investigated the extraction of chromium (III), cadmium (II), copper (II), nickel (II) and zinc (II) from solution containing 100 mg/L of each ion with 0.5 M solution of 8-hydroxy quinoline into chloroform. At pH 5.4, 99% of the cadmium (II) was reported to have extracted into the chloroform layer. Back titration with dilute hydrochloric acid solution showed that at pH 2.0, 79% of the cadmium could be stripped into aqueous phase. The extraction of nickel (II) into chloroform was 95% at pH 2.0, while the extraction of chromium (III) was poor at all pH conditions.

1.4.9 Membrane process

Important examples of membrane process applicable to inorganic wastewater treatment include reverse osmosis and electrodialysis [72]. The removal of solute by forcing the solvent alone to flow through a membrane by applying a pressure greater than the osmotic pressure of the solution
forms the basis of reverse osmosis. The membrane meant for this purpose should possess a high permeability for water over a wide pH range even at moderate pressure.

Electrodialysis unit consists of a number of chambers made up of alternate cation and anion exchange membranes with electrodes in the end compartments. The arrangement of alternate anionic and cationic membranes permit the transfer of only one type of ion through one membrane so that the solution in every second chamber become more concentrated while those in the other chambers become more dilute.

Cellulose acetate membranes and polyamide membranes which are useful over the pH range 4.0-5.0 and 3.0-6.0, respectively, are widely used. Mixon [73] examined the use of cellulose acetate membrane for the removal of lead (II) and cadmium (II) by reverse osmosis. More than 90% and 98% cadmium (II) were removed from waters containing cadmium (II) at 0.1 and 0.98 mg/L, respectively. In the case of lead (II) more than 99.5% removal was achieved from water containing 0.95 mg/L of lead (II). Hindin et al. [74], however, was able to achieve only 70% removal of cadmium (II) from water containing 0.95 and 9.5 mg/L of cadmium (II) using cellulose acetate membrane. Thin film composite resins containing both cellulose acetate and polyamide des were reported to permit the metal ion removal at low pressures with high water flux and over a wide pH range of 2.0-12.0 [75, 76]. It was reported that membranes containing quaternised polyethyleneamine possessed good selectivity of lead (II) and cadmium (II) and polythiourea membranes were effective for binding mercury (II) present in wastewaters [77].

Sorg et al. [48] reviewed the methods available for the removal of lead (II) and cadmium (II) from drinking water and wastewater. They concluded that though very little information was found in literature for lead (II) and cadmium (II) removal from water by electrodialysis, this technique would be as effective as reverse osmosis for the removal of these metal ions. The application of membrane process described is limited due to pretreatment requirements, primarily, for the removal of suspended solids. The methods are expensive and sophisticated, requiring a higher level of technical expertise to operate.
1.4.10 Electrodeposition

Some metals found in waste solutions can be recovered by electrodeposition techniques 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. These are ideal for electrowinning where high quality cathode copper can be electrolytically deposited while free sulphuric acid is regenerated [3].

1.4.11 Evaporation

In the electroplating industry, evaporators are used chiefly to concentrate and recover valuable plating chemicals. Recovery is accomplished by boiling off 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 for recycle as rinse water. Four types of evaporators are used throughout the electroplating industry [78]. They are (i) rinsing 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 recovery and water reuse value must offset these costs for evaporative recovery to become economically feasible. A closed loop system design for rinse and plating is most attractive.

1.4.12 Ion exchange

Ion exchange is a reversible process which facilitates the removal of anionic or cationic constituents present in water by exchange with ions of the resin. When the resin bed becomes saturated, they are regenerated using acid or alkali.

Ion exchange resins are available selectively for certain metal ions. The cations are exchanged for $\text{H}^+$ or $\text{Na}^+$. The cation exchange resins are mostly synthetic polymers containing an active ion group such as $\text{-SO}_3\text{H}$. The natural materials such as zeolites can be used as ion exchange media [79]. The modified zeolites like zeocarb and chabcarb have greater affinity for metals like nickel and lead [11]. The limitations on the use of ion exchange for inorganic effluent treatment are primarily
high cost and the requirements for appropriate pretreatment systems. Ion exchange is capable of producing metal ion concentrations to parts per million levels. However, in the presence of large quantities of competing mono and divalent ions such as sodium and calcium, ion exchange is almost totally ineffective.

As opposed to simple ion exchange, chelation ion exchange takes advantage of the three dimensional structure of molecules to chelate and remove ions of a specific size in the presence of large quantities of other ions [80]. Some of the best chelation ion exchange materials are biopolymers like cellulosics, alginates, carrageenans, lignins, proteins and chitin derivatives. Among the derivatives, the hydroxamic acid derivatives of biopolymers were the most efficient at removing lead (II) and copper (II). Chelation ion exchange materials have higher associated production costs. Selective ion exchangers containing functional groups such as imminodiacetate, aminophosphoric acid and thiol are commercially used for the recovery of toxic and precious metals from aqueous and non-aqueous solution and radionuclids from liquid nuclear fluids [81].

1.4.13 Ion flotation

Separation of ions from aqueous solutions by flotation is based on the production of foam by surface active agents with charge opposite to that of ion to be concentrated. Air or nitrogen is introduced into the solution to cause frothing. The frothing produces foam which separates as a scum containing the ion as concentrate.

Thackston et al. [82] have described a method for the treatment of lead bearing wastes by adsorbing on ferric hydroxide in the presence of lauryl sulphate as collector. They reported that in continuous flow studies, the residual concentration of lead (II) can be brought down to as low as 0.15 mg/L over the pH range 5.0-6.5 from an initial concentration of 5 mg/L. Mukai et al. [83] investigated ferric hydroxide for the removal of cadmium (II) and mercury (II) from solutions containing 1 mg/L of each ion using sodium oleate as the collector. The cadmium (II) concentration was found to be less than 0.05 mg/L over the pH range 8.0-10.0. Mercury (II) was recovered to the
extent of 98% over the pH range 8.0-9.0; the residual concentration of mercury (II) in the tailing solution being 0.03 mg/L.

1.4.14 Adsorption

This is one of the most widely used methods for wastewater treatments. Adsorption involves accumulation of substances at solid-liquid interface. A liquid surface in contact with a solution has a tendency to accumulate a surface layer of soluble molecules because of the imbalance of surface forces and adsorption takes place. The adsorption results in the formation of a molecular layer of the adsorbate on the surface [84].

Activated carbon adsorption in both the granular and powdered form is one of the most popular physico-chemical treatments for the removal of dissolved organics from wastewaters. Since activated carbon also possesses an affinity for heavy metals considerable attention has been focused on the use of carbon for the removal of hexavalent chromium, complexed cyanides and metals present in various other forms from wastewaters. The use of activated carbon for the adsorption of heavy metals was first presented in 1929 by Watonabe Ogawa [85].

Activated carbon treatment generally provides a simple method of operation and has been used for both vapour phase and liquid phase applications, especially for the removal of noxious gases and organics. For both vapour and liquid phase applications, the carbon is expected to have large surface area and high pore volume for the removal of contaminants. For liquid phase the carbon, in addition, must have sufficient hardness or abrasion resistance. Hardness is particularly important for regenerable carbons as it should undergo alternate cycles of exhaustion and reactivation with minimum physical loss.

Though both pulverised and granular carbons have been used for treatment of liquids, granular carbon is extensively used in a column system. The reason being,

i) More efficient use of the adsorptive capacity of the carbon can be obtained.
ii) Column treatment permits continuous operation and provides the flexibility necessary to cope with overloads and to blend effluents to maintain uniform quality. The granular activated carbon is used in the form of fixed beds for continuous treatment, where the water is contacted with carbon. The continuous flow through the carbon bed results in maximum utilization of the carbon adsorption capacity. The carbon in the column acts like a series of layers with each layer in contact with fresh solutions of constant solute concentration. This results in maximum loading of the carbon at constant solute concentration in contrast to continuously declining solute concentration in batch processes.

iii) Granular carbon can be thermally reactivated for reuse, which eliminates the waste disposal problems associated with pulverised carbon.

Batch type processes use pulverised carbon and may be considered advantageous in situations where the temperatures and pressures required for wastewater treatment in column systems impractical. Generally, the use of powdered activated carbon is adaptable when the contaminant levels in the effluent are low.

Huang and Bowers [86] found that the reduction and adsorption occurred simultaneously when the kinetics of Cr(VI) removal onto Filtrasorb 400 activated carbon were examined in batch experiments. Maximum Cr(VI) adsorptive capacity occurred at pH 2.5 and decreased rapidly between 2.5 and 7.1, largely due to the decreasing electrostatic attraction between the positively charged carbon surface and the anionic hexavalent chromium in solution. At pH < 2.5, Cr(VI) adsorptive capacity decreased due to the rapid reduction of hexavalent chromium species and the subsequent dominance of the cationic trivalent chromium species at low pH. Yusci et al. [87] have employed activated carbon to remove iron (III) from wastewaters. Granular activated carbon fixed bed adsorbers was used for removing soluble and insoluble lead from drinking water. It was possible to reduce lead concentrations in drinking water to less than 15 ppb with a properly designed fixed bed operated at the recommended pH range of 6.5-8.5. Carbon type, particle size distribution, solution pH, contact time of water with carbon and presence of other metals affect adsorption [88]. Netzer and Hughes [89] and Corapcioglu and Huang [90] have used activated carbon to remove heavy
metals Cu(II), Pb(II) and Co(II) from wastewaters. Cadmium adsorption on activated carbon was studied by Huang and Wirth [91]. Logsdon and Symons [92] observed that 80% of inorganic and organic mercury could be removed using granular activated carbon. Maruyama et al. [93] conducted a pilot plant test for the removal of 0.5 mg/L of Hg(II) from wastewater using a high lime process that consists of flash mixing, flocculation and granular activated carbon filtration and reported a removal efficiency of 70%. Theim and O'Connor [94] evaluated several varieties of activated carbon samples derived from lignite for the removal of inorganic and organic Hg(II) at 0.01 mg/L from simulated drinking water and showed that at a 100 mg/L dosage of carbon nearly 50% of both inorganic and organic mercury were removed in the pH range 7.0-9.0. Humenick and Schnoor [95] reported that the capacity of the powdered activated carbon, Filtrasorb-300, to remove 90% of inorganic mercury (10 mg/L) was nearly 10 times higher at pH 4.0 than at pH 10.0. Considerable reduction in the concentration of inorganic mercury was obtained when the conventional coagulation treatment was combined with activated carbon [92, 96]. Granular activated carbon [97] was used for removal of Hg(II) (10 μg/L) from drinking water down to < 1 μg/L. The percent removal was maximum at pH 7.0. It was also recently used to adsorb low levels of Pb(II) [98]. Eventhough activated carbon has been successfully used in the treatment of heavy metal-containing wastewater, the cost of the adsorbent prohibits its application in the wastewater treatment. Several commercially available aluminosilicates were able to remove metals from wastewaters [99]. Activated silica was used for the removal of Cu(II) from aqueous solution [100].

1.5 Nonconventional adsorbents for the treatment of heavy metals-containing wastewater

The need for effective and economic removal of toxic or valuable heavy metals from sewage, industrial and mining wastewaters resulted in a search for unconventional methods and materials. Various industrial solid wastes, agricultural by-products and discards and similar products have adsorption affinity for heavy metals. They are not only readily available but also inexpensive. Pollard et al. [101] and Namasivayam [102] have recently reviewed the literature on non-conventional adsorbents for the removal of dyes and heavy metals from wastewaters. Peat, clay, soil and
agricultural wastes have also been tested with varying degrees of success for removing metals from wastewaters.

1.5.1 Industrial wastes/by-products as adsorbents

Utilization of coal ash in water pollution control has been recently reviewed by Viraraghavan and Dronamraju [103]. Fly ash was used for the removal of Cr(VI) [104, 105], Cd(II) [105, 106], Pb(II) [107], Ni(II) [108] and mercury (II) [109]. The monolayer adsorption capacities for Cr(VI), Cd(II) and Ni(II) were found to be 2.2, 34.0 and 0.293 mg/g, respectively. The adsorption of Cr(VI) and Cd(II) on flyash was exothermic and maximum adsorption was observed at pH 2.0 and 7.5, respectively. Endothermic adsorption was observed for Ni(II) and maximum adsorption was at pH 8.5. The optimum pH for mercury was found to be between 5.0 and 5.5. Fly ash samples obtained from three Texas power plants fuelled with lignite coal were used to remove heavy metals including Cr(VI) from 100 mg/L solutions in a study conducted at the University of Texas [110]. Although metal removals of about 99% were obtained under most of the conditions studied, large amounts of fly ash were required. Studies by Gashi et al. [111] showed that fly ash had good adsorptive properties of removal of Pb, Zn, Cd and Cu from effluents of battery industry, fertilizer industry and zinc electrolysis and sulphuric acid production industry. Removal efficiencies were greater than 70%. Adsorption studies carried out to estimate heavy metal removal using fly ash on wastewater at Varanasi, India showed that removal was in the following order: Pb > Zn > Cu > Cr > Cd > Co > Ni > Mn [112]. Adsorption of Cu(II), Ni(II), Cd(II), Pb(II), Zn(II) and Ag(I) on fly ash was investigated by Weng and Huang [113] and they found that the process was spontaneous and endothermic. The ability of a homogeneous mixture of fly ash and wollastonite (1:1) to remove Cr(VI) from aqueous solution by adsorption was investigated by Panday et al. [114]. The Langmuir adsorption capacity (2.9 mg/g) was better than that of fly ash alone (2.2 mg/g) [103]. Maximum removal was observed at pH 2.0 and 30°C. Panday et al. [115] studied the adsorption of Cr(VI) on fly ash-china clay. Charred waste, obtained on the treatment of a tree bark (Terminalia tomentosa) for the manufacture of oxalic acid plant, has been identified as a good adsorbent for the removal of
Pb(II), Hg(II), Cr(VI), F− and dyes [116]. The bottom ash from thermal power plant was also used for the removal of Cu(II), Pb(II) [117] and Cr(VI) [118] from wastewaters. Removal of some toxic metal ions such as Hg(II), Cu(II), Pb(II) and Zn(II) using steel plant granulated slag was recently studied by Looma and Panday [119].

Lee et al. [120] have studied the adsorption of chromium (VI) from aqueous solution using activated sludge and powdered activated carbon. Namasivayam and Ranganathan have made detailed studies on the application of waste Fe(III)/Cr(III) hydroxide sludge from a fertilizer industry for the adsorption of heavy metals such as Cr(VI) [121], Fe(II) [122], Pb(II) [123], Cd(II) [124] and Ni(II) [125] from aqueous solution and industrial wastewaters. Batch mode and fixed-bed studies were also carried out. Adsorption was endothermic and increased with increase of pH for Fe(II), Pb(II), Ni(II) and Cd(II) and increased with decrease of pH for Cr(VI). Langmuir adsorption capacity for Cr(VI), Fe(II), Pb(II), Ni(II) and Cd(II) were found to be 1.43, 34.48, 126.58, 21.00 and 40.49 mg/g, respectively, at 29 °C.

1.5.2 Agricultural wastes/by-products as adsorbents

Many agricultural by-products such as tree bark for mercuric chloride [126], peanut skin for cupric ion [127], walnut expellor meal, wheat flour waste, sugar cane bagasse for Hg(II) [128], waste tea, turkish coffee, exhausted coffee, nut shell and walnut shell for Cr(VI) [129] have been employed for adsorption studies. Alves et al. [130] have used pinus sylvestris bark as an adsorbent for the removal of Cr(III) from aqueous solutions. Bark concentrations of 1 and 2 g/L were used and chromium removal of ≥ 90% were achieved in the pH range of 4.5-5.0. Agricultural wastes such as rice husk [131], crushed coconut shell [132] have been used for the removal of Cr(VI) and maximum removal of Cr(VI) was observed at lower pH values. Prakash and Chand [133] have investigated saw dust as adsorbent for the removal of Cr(VI) and found that it was effective at low pH. Four organic wastes such as saw dust, sugar beet pulp, sugarcane bagasse and maize cob have been tested as potential adsorbents for Cr(VI) [134]. Best results were achieved at pH 1.5-3.0. Rice straw (oryza stativa) has been found to be effective for the removal of Cr(VI) from aqueous solution [135, 136].
The adsorption process was fully pH dependent at room temperature and the percent adsorption of Cr(VI) varied widely from 100% at low pH of 1.0-3.0 to 60-70% at pH 4.0-12.0. Waste banana pith was found to be capable of removing heavy metals from wastewaters [102].

The low cost biological sorbents from agricultural waste materials like natural compost, irish peat, peanut shell, walnut, shell, bone, biomass such as Aspergillus terreus and Mucar ramanniamus and activated carbon, respectively, were found to remove 92.0, 88.0, 68.0, 46.3, 92.6, 77.3, 95.0 and 64.3% Cd(II) from a solution of 100 mg/L Cd(II) [137]. Maranon and Sastre [138] used agricultural waste from apple-juice processing and cider production to remove and recover Cu(II), Zn(II) and Ni(II) ions from aqueous solutions. Cellulosic materials of tropical origin, bambara nuts and rice husks were also studied recently for the adsorption of Cu(II) and Ni(II). Copper (II) had a greater adsorptivity than Ni(II) [139].

Biopolymers which are of low cost were also used for adsorption of metal ions from aqueous solution. Waste biomass like excess sludge from activated sludge unit, Ganoderma lucidum- a wood rotting fungus and Aspergillus niger from fermentation industry have been used for the removal of Cr(VI) and Cu(II) [140] and hair for adsorption of Cr(VI) [131]. One of the major components of crustacean shells, namely chitin and its deacetylated derivative chitosan have been employed as adsorbents for a number of heavy metals [141]. Coughlin et al. [142] examined chitosan for the purification of electroplating wastewater containing Cu, Ni and Cr. Peat moss, a complex material containing lignin and cellulose as major constituents has been found to be effective for the treatment of wastewaters containing heavy metals such as Hg, Cd, Zn, Cu, Fe, Ni, Cr(VI), Cr(III), Pb and Sb [46]. Sphagnum peat and saw dust have been used for the removal of individual and combined metal ions Al³⁺, Zn²⁺, Fe²⁺, Ni²⁺, Cd²⁺, Na⁺, Mn²⁺, Ca²⁺ and Mg²⁺ from water [143]. Sphagnum peat retained more metals by binding than saw dust. Peat moss was used by Chaney and Hundemann [144] to remove cadmium down to < 3 µg/L from wastewaters by column studies. Abbasi and Nipaney [145] have recently studied Salvina molesta (Mitchell) as a bioagent for treating wastewaters containing 1-100 mg/L of Ni(II), Cu(II), Cr(VI), Mo(VI), Cd(II) and Hg(II).
Latif and Jaafar [146] have examined oil palm fibre and coconut husk for the adsorption of heavy metal ions such as Cu(II), Zn(II) and Pb(II). The efficiency of barley straw for the adsorption of heavy metals improved by 10-90% when mixed with calcium carbonate [147]. The adsorption capacity for Zn, Cu, Ni and Pb ranged from 4.3 to 15.2 mg/g of straw, from 6.2 to 19.5 mg/g of activated carbon and from 1.3 to 5.0 mg/g of pine dust. Green algae and ground rice hulls have been recently applied for the adsorption of heavy metals [148]. Kumar and Dara have prepared polymerized onion skin [149] and bark [150] with formaldehyde and employed them for the removal of Cu(II), Cd(II), Zn(II), Ni(II), Hg(II) and Pb(II) from aqueous solutions. Okieimen and coworkers have modified the groundnut husk [151], cellulosic materials [152] and melon seed husks [153] with EDTA to improve the adsorption capacity for the removal of heavy metals from aqueous solutions. Randall et al. reported the quantitative removal of Ag+, Cd2+, Cu2+, Hg2+, Pb2+ and Zn2+ when contacted with formaldehyde-treated peanut skin [154]. Adsorption of Zn(II), Cu(II) and Pb(II) on chemically modified Pinus pinaster bark (pretreated with acidified formaldehyde solution) have been reported by Vazquez et al. [155]. The $k_f$ and $n$ values for Zn(II), Cu(II) and Pb(II) were reported to be 0.26 and 1.724, 0.57 and 2.326 and 1.40 and 3.704, respectively. Krishnan et al. [156] have investigated hair and cattails (Typha plant) for the adsorption of Cd(II), Pb(II) and Hg(II). Adsorption capacities varied from 1-27 mg of metal per gram of adsorbent. Calymperes delessertii besch, a biosorbent, has been used for the adsorption of Cd(II) [42], Pb(II) and Cu(II) [157] from wastewaters. Muzzarelli and Rocchetti [141] have studied the adsorption of Cd, Pb, Ni and Cu from aqueous solutions by chemically modified chitin. Moo et al. [158] have found that the adsorption of metals by peat was found to be maximum at pH 5.0 and 5 g of peat adsorbed 95% of Pb, 95% of Cu, 70% of Sn and 45% of Cr(VI) from 100 mL synthetic samples containing 100 mg/L metal ion. Metal containing dye house wastewaters treated with peat reduced the concentrations of heavy metals such as Cd, Cu, Fe, Pb, Ni, Zn, Hg, Cr(VI) and Cr(III) by about 99% [159]. Brady et al. [160] have recently reported the use of non-viable yeast biomass for the removal of heavy metal ions [Fe(III), Cu(II), Cr(III), Hg(II), Pb(II), Cd(II), Co(II), Ag(I), Ni(II) and Fe(II)]. Accumulation within the heavy metal group was selective [Cu(II) > Cr(III) > Cd(II) and Cu(II) > Pb(II) > Ni(II)]. Bisorption
to the granular biomass was rapid. Above 99% of zinc, chromium and copper from electroplating wastewaters and 50-60% of chromium from tannery wastewater have been achieved. Cellulosic material dyed with monochloro triazine type reactive dyes was able to remove up to 80% Cu(NO₃)₂ compared to 41% with cotton fibres [161].

Carbonized agricultural wastes have also been used for the removal of metal ions from wastewaters. Activated carbons derived from rice husk [162] and groundnut husk [163] have been used for the treatment of Cr(VI) containing wastewaters. The adsorption capacity of coconut shell carbon for the removal of Cd(II) and Pb(II), respectively, from aqueous solutions was reported to be 119 and 275 mg/g as against 7.3 and 14.3 mg/g for a commercial activated carbon [164]. Carbonized coir pith waste was also found to be effective for the removal of heavy metals [102]. Srivastava et al. [165] have reported the use of a carbonaceous material developed from the waste slurry generated in local fertilizer plants for the removal of heavy metal ions such as Cu(II), Cr(VI), Hg(II), Mo(VI), Cd(II), Zn(II), Ni(II), Co(II) and Pb(II). The optimum pH for the maximum uptake of Cd(II), Cu(II) and Mo(VI) was about 6.0, for Cr(VI) and Hg(II) at 2.0 and for Pb(II) at 4.0-6.0.

1.5.3 Miscellaneous

Activated sludge was used for the adsorption of Cr(VI) [120] and Ni(II) [166]. Wollastonite has been used for the removal of Cu(II) [167], Fe(II) [168], Pb(II) [169], Ni(II) [170] and Cd(II) [171] from wastewaters. China clay was used for the adsorption of Fe(II) [172] and Pb(II) [169] from wastewaters.

Inorganic sorbents like oxides and hydrous oxides of iron has been used for removal of heavy metals. Iron hydroxide was used for the quantitative removal of Cr(VI) at pH 5.0 [173]. Forbes et al. [174] examined the adsorption of Cd, Co, Cu, Pb and Zn onto goethite. Adsorption kinetics of Cd onto goethite has been investigated as a function of both solution concentration and temperature [175]. The influence of NTA on the elimination of dissolved Cu, Zn, Cd and Pb ions by coprecipitation with ferric hydroxide was investigated by Frimmel and Geywitz [176]. Conditional distribution coefficients show the order Cd < Zn < Cu < Pb for increasing interaction of the metals.
with the ferric hydroxide. The presence of NTA decreased the efficiency of the metal elimination. The iron hydroxide coated magnetite and uncoated magnetite were able to remove Cr(VI) and Zn(II) > 90% through one adsorption/desorption cycle [177]. Coated magnetite was more efficient than the uncoated. Ferric oxide was used for adsorption of Fe(II) [178] and Pb(II), Cu(II) and Cd(II) [179]. The iron oxide was also used for the effective removal of Cd(II) from wastewater in the presence of phosphate at different pH values [180] and in the presence of alkaline earth metals [181]. Manganic oxide was employed for the removal of Fe(II) [182] and serpentine mineral [183] for the adsorption of Fe(II) Mn(II), Cu(II), As(III), Pb(II) and Cd(II). Effects of Cl\(^-\), SO\(_4\)\(^{2-}\), S\(_2\)O\(_3\)\(^{2-}\) on the adsorption of Cd(II) by oxide surfaces, Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\). H\(_2\)O were studied by Benjamin and Leckie [184]. Aluminium oxide has been used for the removal of Cr(VI) from aqueous solution [185]. Netzer et al. [186] reported > 99.5% metal removal when aqueous solutions of Cd, Cr, Co, Cu, Fe, Pb, Hg, Ag, Ni and Zn were treated by a combination of lime and shredded automobile tyres. The adsorption of Cd(II) by the soils [187] and its constituents such as montmorillonite and kaolinite [188] were studied. The Cd retention was not only influenced by aqueous chemistry of Cd but also the surface chemistry of the adsorbent. The mixtures of clay-cellulose and illite-humic acid were investigated for the adsorption of Pb(II) and Cd(II) [189]. The sorption increased over the pH range 3.0-6.0. Soldatini et al. [190, 191] investigated the adsorption capacity of soil materials for Pb(II). Farid [192] studied the adsorption of heavy metals by soil. Khan and Iqbal [193] examined the adsorption of Pb(II), Cu(II) and Zn(II) from aqueous solution by Ca-saturated illite. The removal of Hg(II) by tannins in agricultural residues in the presence of large excess of other metal cations Ca, Fe(III), Co, Ni, Cu, Zn or Cd occurring in the wastewaters appeared to be rather specific [194]. It was explained that this selectivity was due to the unusually high potential for the reduction of Hg(II) (Hg = Hg(II) + 2e\(^-\); E\(_0\) = -0.86) as compared to most metals. Zouboulis et al. have reported that the mineral samples-pyrite and dolomite can be effectively used for the quantitative removal of Cu, Pb and As [195]. Mercury (II) sorption by waste rubber in the pH range 5.5-6.0 has been reported by Knocke and Hemphill [196]. Mercury (II) adsorption by bentonite clay in the pH range 4.5-5.5 has been reported by Newton et al. [197]. Kaneko reported that the surface modification of the preoxidized activated
carbon fibres with \( \alpha \)-FeOOH significantly improves both the rate and capacity of Hg(II) adsorption in spite of smaller surface area [198]. The adsorption of mercury (II) acetate from aqueous solution onto an activated charcoal cloth has been studied and found that the adsorption capacities of activated charcoal cloth shaken in mercury (II) acetate solution could reach \( 2 \times 10^{-3} \) moles per gram at pH 5.5 [199]. Huang and Blankenship [200] studied the removal of Hg(II) from dilute aqueous solution by eleven different brands of commercial activated carbon and indicated that maximum Hg(II) removal occurs at pH 4.0-5.0 regardless of the carbon type.

### 1.6 Fixed bed studies

Adsorption capacities obtained from batch mode studies are useful in providing information on the effectiveness of adsorbents. Adsorption isotherms derived from batch mode studies have been used traditionally for preliminary tests before running more costly column tests. Isotherms, however, cannot give accurate scale-up data for a number of reasons [201]: (i) Adsorption in a flow column is not at equilibrium, (ii) The adsorbent would not become totally exhausted in a commercial process before regeneration, (iii) Uneven flow pattern throughout the column would result in incomplete exhaustion of the bed and (iv) The effects of adsorbent recycling and regeneration cannot predict chemical or biological changes occurring in the adsorber.

Batch type processes are also usually limited to the treatment of small volumes of effluent, whereas fixed bed flow systems provide the most practical application of the adsorption process in waste treatment [84]. The reasons for this are: (i) A subsequent adsorbent separation step is not required, (ii) Higher removals in equilibrium with the influent concentration rather than the effluent concentration can be approached and (iii) A greater flexibility of operation can be attained. Consequently, it is necessary to carry out flow tests using columns prior to obtaining design models. The normal criterion in designing adsorption columns is to predict the life time of the bed before regeneration becomes necessary. Also, to investigate the influence of hydrodynamic parameters on the processes observed in batch systems, the same adsorbent is subjected to the continuous flow studies. All existing models are based on determining breakthrough curves for a specific systems and
the influence of varying the bed height has been studied. One model termed the Bed-Depth-Service-Time (BDST) Model [202] is a modified form of an earlier theory [203] and states that the service time of a column is given by the following equation:

\[ t = \frac{N_0}{(C_0 u) [H - \{u / (k_a N_0)\} \times \log \{(C_0/C_t) - 1\}]} \]  

\[ C_0 t = \left(\frac{N_0}{u}\right) H - \left[\frac{1}{k_a}\right] \times \log \{(C_0/C_t) - 1\} \]  

where:
- \( t \) = service time to breakthrough, min
- \( N_0 \) = adsorption capacity, mg/L of adsorbent bed
- \( C_0 \) = influent concentration, mg/L
- \( u \) = linear flow rate, mL/min
- \( H \) = depth of bed, cm
- \( k_a \) = rate constant of adsorption, L/min/mg
- \( C_t \) = effluent concentration at time \( t \), mg/L

By plotting \( C_0 t \) vs \( \log_e\{(C_0/C_t) - 1\} \) at fixed value of \( C_0 \), \( H \) or \( u \) and at different values of \( C_t \) from experimental data, \( k_a \) and \( N_0 \) can be evaluated from the slope and intercept of the graph, respectively.

Kumar and Dara [149] reported that the column of polymerized onion skin (10 g) with 16 cm height and 3 mL/min flow rate almost quantitatively removed the metal ions Cu(II) (40 mg/L), Pb(II) (220 mg/L), Zn(II) (100 mg/L), Cd(II) (130 mg/L) and Ni(II) (100 mg/L) for 1 L aqueous solution. Singh et al. [204] have reported by the removal of Cr(VI) by column studies using feldspar. The breakthrough curve was traditional sigmoidal shape with an adsorption capacity of 5.93 x 10^{-2} mg/L. Granular activated carbon was used as a fixed bed adsorber for the effective removal of lead from drinking water [88]. Fixed-bed studies on the removal of Cd(II) by a moss calymperes delessertii, Besch have been reported by Low and Lee [42]. Effects of bed height and flow rate have been studied. Column of chemisorption filters made up of activated carbon and carbon activated with Cu(II) (11.5 g, flow rate 600 mL/h) was able to remove As(V) completely from a solution of 6.65 x 10^{-4} M [205]. Combination of peat moss (200 g) and calcium carbonate (20 g) in a column of 67 cm
long, internal diameter 4.9 cm, adsorbed Cd(II) almost completely from 1 L solution of 100 mg/L [158]. Biomass like tomato and tobacco roots immobilized into gels by carrageenan has been recently used to remove Sr completely from 25 mL aqueous solution of 10 mg/L in a column of 9 mL capacity of 0.5 mL/min flow rate [206]. Complete removal of Cd(II) (100 mg/L) from 5.0 L solution and Pb(II) (200 mg/L) from 5.6 L solution by coconut shell carbon of 2.5 cm diameter and height 7 cm has been reported by Arulanantham et al. [164]. Larsen and Schierup [147] used straw as fixed bed adsorbent for the removal of metals such as Zn, Cu, Pb, Ni and Cd. The efficiency of the straw was improved by 10-90% when mixed with CaCO3. Apple wastes [138] and melon seed moss [153] were also used for the removal of Cu, Zn and Ni from aqueous solutions using fixed bed.