Chapter - 1

Introduction
CHAPTER 1

INTRODUCTION

Water is the most versatile inorganic liquid on this planet occurring as a universal solvent and indispensable component of nature holding both biotic and abiotic entities in a complex dynamic and delicate ecological balance. Energy and water are indeed two essential components for propagation of life. Quality of water therefore bears profound significance for conditioning the quality of life and environment. Each human being consumes several litres of fresh water everyday to sustain his or her life. Rapid industrialization, expanding urbanization and population explosion ultimately resulted in environmental degradation.

Scientists all over the world now accept that with industrialization and urbanization there has been a steady destruction of nature. Cities and industries have affected air and water. Industries produce a lot of hazardous wastes and cities produce a lot of garbage. Hazardous waste pollutes the ground water and accumulates. Garbage allows disease-causing agents to proliferate.

1.1 Water pollution

Water pollution is one of the most serious problems faced by the developing and developed countries. Effective management of water resources and control of water pollution are vital for sustainable development and welfare. Industries consume large volumes of water and let out a major part of them from some stage of their manufacturing process with contamination resulting in ecological imbalance. Depending on the type of industry and nature of process, the contaminants in wastewater vary. As industrialization is essential for a nation, industrialization coupled with effective management to control
pollution is inevitable. Industrial, municipal and agricultural wastes mainly cause water pollution. The common pollutants in the industrial wastewater are soluble organics/inorganics, suspended solids, heavy metals, volatile materials, nitrogen, phosphorous, oil and grease.

The soluble organics cause depletion of dissolved oxygen in water and create unpleasant odour and taste. Some important sources of organic pollutants are food processing, dairies, tanneries, and paper and pulp industries. Inorganic substances pollute the surface and ground water by increasing dissolved solid level and make the same unfit for drinking, industrial and agricultural purposes. Suspended solids impair the aquatic life by the way of deposition in water reservoirs. The sludge containing organic solids undergo progressive decomposition resulting in oxygen depletion and production of noxious gases. Presence of nitrogen and phosphorous in the wastewater discharged into water resources will enhance eutrophication and stimulate undesirable algae growth.

1.2 Heavy metals

Heavy metals are elements with atomic number greater than 23 with high density. Survey of various aspects of the environment revealed widespread contamination of air, water and soil by toxic heavy metals [1-3]. Heavy metals are of special concern because they are nondegradable and produce undesirable effects even in extremely minute quantities on human and animal life. The tremendous use of heavy metals over past few decades has inevitably resulted in an increased flux of metallic substances in aquatic environment. The bioavailability of the metals depends on its chemical species in the environment and also its rates of biological uptake [4-10].
High concentrations of copper, zinc, cadmium, arsenic, mercury and lead had affected fisheries in more than 21,000 km of rivers [11]. A variety of industries are responsible for the release of heavy metals into the environment through their wastes. These include mining and metal processing, pigment manufacturing, battery manufacturing, electroplating, printing and photographic industries. The annual toxic metal load added to river Yamuna in India was reported to be 2.59 tonnes of lead and that of chromium was 4.32 tonnes [12]. The major sources of mercury are industries such as chloralkali, paint, electrical, rubber processing and oil refining. About 25,000-150,000 tonnes of gas per year is released from volcanic areas. The burning of fossil fuels releases a further 3000 tonnes per year. Pharmaceuticals, dental applications and precision instruments, fungicides in agriculture and horticulture also contribute heavy metal contamination to the environment.

1.2.1 General effects of heavy metals

Heavy metals are cumulative poisons and affect the aquatic flora. An extremely toxic metal will eliminate the entire aquatic invertebrates until the concentration is reduced below the toxic threshold limit. The exposure of heavy metals to human body can be either through ingestion, inhalation or skin. Infants and foetuses are exposed to metals through breast milk or transplacental transfer. The enhanced level of heavy metals is of concern because of the following reasons:

i. they accumulate in human body,

ii. they create sublethal and chronic effects to organisms even in minute concentrations,

iii. they bring carcinogenic and teratogenic effects in man,

iv. their trace amounts cause phytotoxic and synergistic effects in living organisms,
v. they have a greater affinity to attack sulphur bonds, protein, carboxylic acid and amino group thereby disrupting the cell metabolisms. Concentration of 80 μg/100 g of blood causes brain damage and

vi. they precipitate the mucous secretion of gills in fish. These precipitates occupy the interlameller spaces arresting the movement of gill filaments and block their respiratory tract.

1.3 Effluent limitation

Table 1 gives maximum tolerance limits for industrial effluents discharged into surface water [13]

<table>
<thead>
<tr>
<th>Metal</th>
<th>Limit (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>0.20</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.01</td>
</tr>
<tr>
<td>Copper</td>
<td>3.00</td>
</tr>
<tr>
<td>Lead</td>
<td>0.10</td>
</tr>
<tr>
<td>Cadmium</td>
<td>2.00</td>
</tr>
<tr>
<td>Chromium(VI)</td>
<td>0.10</td>
</tr>
<tr>
<td>Total chromium</td>
<td>2.00</td>
</tr>
<tr>
<td>Nickel</td>
<td>3.00</td>
</tr>
</tbody>
</table>

1.4 Treatment methods

The disposal of untreated effluents, sewage and waste into watercourses pollutes the water and affects the ecosystem. Hence it is necessary to treat the wastewater prior to disposal. A variety of methods have been developed for the removal of organic and inorganic pollutants from water and wastewater. The most common treatment methods are activated sludge process, precipitation method, solvent extraction, cementation, ion
exchange, membrane process, ion flotation, xanthate process, evaporation, coagulation/flocculation, chemical oxidation and reduction and adsorption.

1.4.1 Activated sludge process

It is a biological wastewater treatment method for the removal of biodegradable organics, polychlorinated hydrocarbon, insecticides and herbicides. A mixture of wastewater and microorganism is agitated and aerated. Several authors have reviewed the removal of biodegradable organism by activated sludge process [14-17]. The method works satisfactorily only when the wastewater to be treated is in large volumes.

1.4.2 Precipitation method

In precipitation method, chemicals like caustic soda, hydrated lime, soda ash and sodium sulphide are added to precipitate the metal ion as insoluble hydroxide, carbonate and sulphide [18-24].

The common method for the removal of metals from different metal bearing effluents, such as plating liquid wastes, dilute leach solutions and hydrometallurgical residues is metal precipitation in the form of their hydroxides [25]. In hydroxide precipitation, heavy metals are precipitated as their hydroxides using lime or sodium hydroxide. Lime is generally favoured for precipitation purposes due to its low cost and easy pH control. In addition, presence of excess of lime can serve as adsorbent for the removal of metal ions. This process involves reaction and settlement phases. Toxic metal removal up to 99% has been achieved but it is incapable of removing trace levels of metal ions. The presence of complexing agents depresses precipitation to a great extent and there is no common pH value where precipitation of all the metal ions takes place simultaneously. Following precipitation, chemical reagents have to be added in order to
lower the pH values back to discharging ones [26]. Voluminous hydroxide sludges are produced.

Carbonate precipitation of metals using calcium or sodium carbonate is limited. Patterson et al. reported the removal of lead(II) and cadmium(II) from electroplating using carbonate precipitation [27].

Metal ions are precipitated as insoluble sulphide in sulphide precipitation method. The advantage of this method is the poor solubility of metal sulphide and thereby having higher efficiency in the removal of metal ions. Metal sulphide sludge has better thickening and dewatering ability than hydroxide sludge from hydroxide precipitation method [28]. However, the pH should be adjusted between 7.0-8.0 to prevent hydrogen sulphide formation and excess sulphide should be removed from the effluent by aeration or chemical oxidation [29].

1.4.3 Solvent extraction

Solvent extraction involves an organic and an aqueous phase. Liquid-liquid extraction of metals from solution on a large scale has made a phenomenal growth due to introduction of selective complexing agents. In addition to hydrometallurgical applications, solvent extraction has gained widespread usage for waste reprocessing and effluent treatment. The aqueous solution containing metals of interest is mixed intimately with appropriate organic solvent and metal passes into the organic phase. Metal is recovered by keeping the organic solvent in contact with an aqueous solution whose concentration is such that metal is stripped from organic phase and extracted into the stripping solution. The removal of chromium(III), cobalt(II) and nickel(II) from aqueous solution using di-n-pentyl sulphoxide has been reported in the literature [30]. McDonald
and Bajwa reported the removal of chromium, cadmium and zinc from metal finishing wastewaters [31].

1.4.4 Cementation

It is the displacement of a metal from solution by a metal of higher order in the electrochemical series. Wastewater containing reducible metallic ions is treated by this method. For adequate cementation capability, considerable spread in the electromotive force between metals is necessary. This method is suitable for small wastewater flows because a long contact time is required. Removal and recovery of lead ion by cementation has been reported in the literature [32-34].

1.4.5 Ion exchange

Ion exchange is a reversible process which facilitates the removal of cationic and anionic constituents present in water by exchange with ions of the resin. When the resin bed becomes saturated, they are regenerated using acid or alkali. Selective removal of metal ions is possible with ion exchange resins. The cations are exchanged for H\(^+\) and Na\(^+\). Chelating ion exchanger takes the advantage of the three dimensional structure of molecules to chelate and remove ions of a specific size in the presence of other ions. Natural materials such as zeolites can be used as ion exchange media [35]. Removal of heavy metal ions from dilute solutions using synthetic organic resins, inorganic gels and liquid ion exchangers has been reported. Modified zeolites like zeocarb and chabcarb have greater affinity for nickel and lead. Natural zeolite has been found to have high selectivity for the removal of ammonium ions [36-39].
1.4.6 Membrane process

Reverse osmosis and electrodialysis are important membrane processes applicable to inorganic wastewater treatment. In reverse osmosis, pressure difference is applied to initiate the transport of solvent across a semipermeable membrane [40,41]. Cellulose acetate membrane and polyamide membranes which are useful over the pH range 4.0 to 5.0 and 3.0 to 6.0, respectively are used. Thin film composite resins containing cellulose acetate and polyamides in the removal of metal ions at low pressures and wide pH range of 2.0 to 12.0 have been reported [42,43]. Electrodialysis is ion migration through selective permeable in response to a current applied to electrodes. The methods available for the removal of lead(II) and cadmium(II) from drinking water and wastewater have been reviewed [22]. The application of the membrane process is limited due to pretreatment requirement, primarily for the removal of suspended solids. The methods are expensive and sophisticated requiring a higher level of technical expertise to operate.

1.4.7 Ion flotation

Separation of ions from aqueous solution by flotation is based on the production of foam by surface active agents with charge opposite to that of the 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 concentrate. Thackston *et al.* [44] have reported the treatment of lead bearing wastes by adsorbing on ferric hydroxide in the presence of lauryl sulphate as collector.
1.4.8 Xanthate process

Insoluble starch xanthate (ISX) made from commercial cross-linked starch works like an ion exchanger removing heavy metal from wastewater and replacing them with sodium and magnesium. ISX is added in the form of slurry for continuous flow operations and in the solid form for batch treatment. It should be added to the effluent at pH > 3. Then the pH should be allowed to rise above 7.0 for optimum metal removal. Residual metal ion level below 50 μg/L has been reported [45,46].

1.4.9 Evaporation

Evaporators are mainly used in electroplating industries to concentrate and recover valuable plating chemicals. Four types of evaporators are used in the electroplating industry [47]. They are, rinsing film evaporators, flash evaporators using waste heat, submerged tube evaporators and atmospheric evaporators. Both capital and operational costs for evaporative recovery systems are high.

1.4.10 Coagulation/Flocculation

The colloids do not settle on standing and are not removed by conventional physical treatment process. The stability of a colloid is due to electrostatic forces and neutralisation of this charge is necessary to induce flocculation and precipitation. Coagulation is employed for the removal of waste materials in suspended or colloidal form. The common coagulants used are alum, ferrous sulphate, ferric chloride and lime. Polyelectrolytes act as coagulant aids enhancing coagulation by promoting the growth of large and rapid settling flocs [48].
1.4.11 Chemical oxidation and reduction

Chemical oxidation and reduction are used in the treatment of electroplating rinse waters. Chemical oxidation of wastewater is employed to oxidise pollutants to terminal end products or to intermediate products that are more readily biodegradable or removable by adsorption. Common oxidants are chlorine, ozone, hydrogen peroxide and potassium permanganate.

Chemical reduction is employed for the reduction of heavy metals which cannot be precipitated in their high valence state. A solution of soluble sulphite at pH < 3.0 or sulphur dioxide is used to reduce hexavalent chromium to trivalent state which can be precipitated by alkali [49].

1.4.12 Adsorption

Adsorption is a unique process for the removal of both organics and inorganics from water and wastewater. It is a process by which the concentration of solute is enriched at the surface or interface between two phases. Adsorbates stick to the surfaces in two ways. In physisorption, there is a van der Waals interaction between the adsorbate and the substrate. There is a long range but weak interaction. In chemisorption, the adsorbate sticks to the surface by forming a chemical bond and tends to find sites that maximize their coordination number with adsorbent. Adsorption technique provides reliable results without much cost and working efforts. It is also capable of producing effluent free of suspended solids. Adsorption techniques are applied for the removal of trace inorganics and organics from water and wastewater. Commercial activated carbon, silica and alumina are used as adsorbents. Activated carbon is one of the most popular adsorbents employed for the removal of toxic biodegradable and non-biodegradable
substances from wastewater. Many adsorbents other than activated carbon such as clay minerals, acidic and basic fly ashes, polymeric adsorbents, carbonaceous adsorbents and ion exchange resins have also been used for the removal of contaminants in water and wastewater. The cost effective and economic removal of toxic heavy metals from industrial wastewater can be done with low cost adsorbents. Various industrial solid wastes, agricultural by products and similar products have also been found to have adsorption affinity for heavy metals. They are readily available and also inexpensive.

1.4.13 Industrial wastes

The need for effective and economic removal of toxic or valuable heavy metals from sewage and industrial wastewater resulted in a search for nonconventional methods and materials. Pollard *et al.* and Namasivayam reviewed the literature on nonconventional adsorbents for the removal of dyes and heavy metals from wastewaters [50,51]. Many industrial wastes have been tried for the removal of heavy metals. Namasivayam and Ranganathan studied the adsorption of heavy metals Cr (VI), Fe (II), Pb (II), Cd (II) and Ni (II) [52-56] from aqueous solution and industrial wastewater on Fe (III)/Cr (III) hydroxide sludge obtained from a fertilizer industry. Adsorption was reported to be exothermic 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.

Srivastava *et al.* [57] prepared a carbon from waste slurry generated by a local fertilizer plant and studied the batch and column removal of lead(II) and mercury(II). The removal efficiencies were reported to be 99% for both the metal ions. The breakthrough
capacity of the column for each metal species was found to be higher than the batch capacity.

**Crude oil residue** after activation was found to be effective in the removal of chromium(VI) [58,59]. The use of fly ash for the removal of chromium(VI), lead(II), cadmium(II) and mercury(II) has been reported in the literature [60-67]. Adsorption studies carried out using fly ash in the removal of heavy metals at Varanasi, India by Mathur et al. showed that the removal was in the following order Pb > Zn > Cu > Cr > Cd > Co > Ni > Mn. Heavy metal removal by blast furnace slag was reported by Dimitrova [68]. At low sorbate concentration (5 x 10^{-4} M) 100% removal of Cu^{2+} and Zn^{2+} and 72% removal of Ni^{2+} were reached within 150 mins. In solutions of higher initial concentration (3.5 x 10^{-3} M), the sorption effect under equilibrium conditions was 60% for Cu^{2+}, 46% for Zn^{2+} and 32% for Ni^{2+}.

Recycled iron bearing material obtained in the manufacturing of cast-iron was found to uptake cadmium, zinc and lead. The adsorption capacity of lead was reported to be the highest followed by zinc and cadmium [69]. The adsorption data fitted Freundlich adsorption isotherm. The adsorption of metals increased with increase in pH. Banerjee et al. studied the kinetics of o-xylene on fly ash and reported the activation energy [70]. The adsorption of As (V) on fly ash was also reported by Evan Diamadopoulos et al [71]. The feasibility of solid residue of olive mill products in the removal of lead and zinc was investigated by Gharaibheh et al [72]. Langmuir adsorption capacity (Q_o) for Zn and Pb was reported to be 5.40 and 21.56 mg/g, respectively. Lopez et al. investigated the sorption of lead(II), zinc(II), cadmium(II), copper(II) and chromium(III) on blast furnace sludge [73]. The experimental data were better fitted to
the Langmuir equation than to the Freundlich equation. Since the sludge adsorption capacity and affinity improved with the temperature, the adsorption process was proposed to be endothermic. Charred waste produced during the manufacture of oxalic acid was found to be effective in the removal of toxic ions Pb (II), Hg (II) and Cr (VI) and dyes like methyl red, alizarin red and methyl violet [74]. The bottom ash from thermal power plant was also used for the removal of Cu (II), Pb (II) and Cr (VI) [75, 76]. Looma and Panday studied the removal of metal ions mercury(II), copper(II) and lead(II) [77].

1.4.14 Agricultural waste/biopolymers

Bambaranuts and rice husk were used in the adsorption of nickel and copper ions by Said et al [78]. The sorption data obeyed Freundlich adsorption isotherm. The adsorptivity of Cu (II) ions was reported to be greater than that of Ni (II) ions due to the smaller ionic radius of Cu$^{2+}$. Many agricultural by products such as tree bark, peanut skin, rice straw, paddy husk, sugarcane bagasse and wheat flour waste have been used for the removal of toxic heavy metals [79-81]. Arulananthan et al. studied the adsorption capacity of coconut shell carbon for the removal of Cd (II) and Pb (II) from aqueous solution [82]. The adsorption capacity of the coconut shell carbon for the removal of Cd (II) and Pb (II) was reported to be higher than commercial activated carbon. Okieimen et al. showed a maximum capacity of 40.5 mg/g and 39.4 mg/g at pH 6.8 for Cd (II) and Pb (II) ions using EDTA modified groundnut husks [83]. Namasivayam and Periasamy compared the adsorption capacity of peanut hull carbon with commercial carbon for the removal of Hg (II) and reported that the peanut hull carbon was 7 times more effective than commercial carbon [84]. Many reports showed the effective adsorption of heavy metals from wastewater by agricultural waste or by products such as
walnut expeller meal, peanut skins, wool, rice straw, plumpit shells and sugarcane bagasse [85,86]. In this extensive study, the effect of temperature, complexing agents and accompanying anion on the adsorption of Zn (II), Cd (II) and Cu (II) were studied. The use of waste tea leaves and coffee powder for mercury removal has been reported by Macchi et al [87]. Orhan and Buyukgungor reported waste tea, turkish and exhausted coffee and wallnut shells as adsorbents for the removal Cr (VI), Cd (II) and Al (III) from watewaters [88]. The equilibrium data were correlated both by Langmuir and Freundlich isotherm models.

Polymerised oil palm fibre and coconut husk were used for adsorption of Cu (II), Zn (II) and Pb (II) ions in batch studies. The adsorption followed Langmuir model [89]. The binding of metal ions to biosorbent and application of this phenomenon to waste water treatment were also reported in the literature. Tobin and Roux studied chromium removal using mucor biosorbent and reported the sorption levels of 1.15 and 0.7 mmol/g at pH 4 and 2, respectively [90]. David Kratochvil et al. optimised the removal of copper ions in a column containing sargassam biomass [91]. The removal of 2.3 meq/g of metal cations by sargassam biomass has also been reported by David Kratochvil and Bohumil volesky [92]. Chang et al. investigated the biosorption kinetics of lead, copper and cadmium on inactivated cells and resulting cells of pseudomonas aeruginosa and reported a maximum adsorption capacity of 43 mg/g dry cell for inactivated cell [93]. Recently, adsorption of Cu (II) in aqueous solution by living mycelium pellets of phanerochaete chrysoporum was investigated to study the effect of Cu (II) concentration, pH and organic solvent [94]. The high capacity of Cu (II) uptake was mainly attributed to adsorption of tiny colloids of copper hydroxide formed at pH 6.0 for
100 mg/L concentration of Cu (II) solution. Williams et al. compared the ability of brown seaweed, dealginated seaweed waste, alginate fibre and waste linseed fibre in the removal of metal ions from aqueous solutions. Alginate fibre was found to show the best overall metal ion binding capacity [95]. Many authors [96-101] have reported sorption of metal ions by biomass. Comparative biosorption analysis of cadmium, lead, nickel and zinc by algae has been reported by Klimmek et al. They reported maximum capacity for Pb, Cd, Ni and Zn to be 1.47, 0.37, 0.65 and 0.49 mmol/g of dry biomass, respectively [102]. Column efficiencies of immobilised *mucor rouxii* biomass for the metal ions lead, cadmium, nickel and zinc were reported by Yan and Viraraghavan [103]. Rahmani and Sternberg investigated the removal of lead from water using *lemna minor* [104]. The sorption potential of cowdung for copper was reported by Himesh and Mahadevasamy [105]. The rate of sorption showed spontaneous increase at the beginning and decreased between 30 to 90 seconds and attained equilibrium in 180 seconds. A maximum efficiency of 93.6% was achieved with Cu (II) concentration of 230 mg/L and biosorbent dosage of 60 g/L.

A carbonaceous sorbent prepared from flax shive has been found to have high adsorption capacity for the removal of Hg (II) from aqueous solution. The removal of mercury ions on wet and dry carbon of flax shive followed a first order kinetics with rate constants 0.0359 and 0.0144 h⁻¹ for wet and dry carbon, respectively and the sorption was pH dependent [106]. Biomaterials like cork and yohimbe bark waste have been tried by Villaescusa et al. for the uptake of nickel and copper [107]. The adsorption of both metals was pH dependent and maximum adsorption was found to occur at pH 6-7. High chloride concentrations significantly reduced the metal removal by cork wastes but no
significant effect of chloride on the removal of both the metals by yohimbe bark wastes. Giuseppe Cimino et al. reported the use of hazelnut shell as a biosorbent to remove toxic Cd (II), Zn (II) and Cr (III) and Cr (VI) ions [108]. The sorption experiment data fitted Langmuir isotherm model and at pH 4.0, adsorption capacities for Cd (II), Cr (III) and Zn (II) ions were found to be 5.42, 3.08 and 1.78 g/kg, respectively. The removal of 96% o-cresol by carbon prepared from agricultural waste palm seed has been reported in the literature [109]. The adsorption obeyed first order reversible kinetics. Carbonized coirpith has been found to be efficient in the removal of heavy metals [110]. Hexavalent chromium removal on saw dust was found to be effective at low pH by Selvi et al. [111]. Toles et al. prepared a series of phosphoric acid activated carbons from almond shell and investigated the adsorption properties [112]. The activated carbon prepared by ‘air activation’ method was found to be the best of all carbons studied. Wartelle and Marshall prepared activated carbons from nutshells of seven different sources (pistachio, hazelnut, almond, black walnut, English walnut, macadamia nut and pecan) and studied their physical, chemical and adsorption properties. Granular carbon prepared from *macadamica* nutshell was found to process higher efficiency than other carbon [113]. Activated carbons prepared from *eucalyptus globulus* and peach stone were used in the retention of Cr (VI) and Hg (II). These carbons showed better initial rate retention and retention capacity than the commercial filtrasorb 400-activated carbon [114]. Activated carbons from animal bone [115], wheat stem and babul bark [116], apricot stones, lignites and oxidized anthracite [117] have also been reported.
1.4.15 Miscellaneous

McKay and Porter studied the sorption of divalent cadmium, copper and zinc ions onto peat [118]. The cross linked imprinted chitosan resin has been reported to have good chemical and physical stability by Tianwei et al [119]. Weng et al. studied the removal of Cr (VI) using hydrous concrete particles which had Si, Al, Fe, Ca and Mg as major components [120]. They compared the adsorption free energy of $\text{HCrO}_4^-$ and $\text{CrO}_4^{2-}$ and reported maximum favourable adsorption for $\text{CrO}_4^{2-}$. The competitive adsorption of phosphate and arsenate on goethite was studied both simultaneously and sequentially by Hongsho and Stanforth [121]. In the simultaneous addition, the two anions were reported to be adsorbed equally and in sequential addition the extent of exchange for the first ion depended on equilibrium time before the second ion was introduced. The synthesis of a novel nanocomposite sorbent material, copper ferrocyanide immobilized with a mesoporous ceramic matrix was made by Lin et al [122]. This nanocomposite material was reported to be highly selective for cesium from various high salt and acid solutions.

Commercially available aluminosilicates were able to remove metals from wastewaters [123]. Activated silica was used for the removal of Cu (II) from aqueous solution [124]. Wollastonite was used in the removal of Cu (II), Fe (II), Pb (II), Ni (II) and Cd (II) from wastewater [125-129]. Adsorption of Cd (II), Pb (II) and Cr (VI) on bituminous coal was found to be dependent on contact time, concentration, temperature and pH [130-132]. Kannan and Vanangamudi used lignite coal for Cr (VI) adsorption and found maximum removal at pH 2.0 [133]. Mishra and Chaudhury studied the kinetics of zinc adsorption on charcoal [134]. McKenzie [135] examined the adsorption of Co, Cu, Mn, Pb and Zn on oxides of manganese and iron. Adsorption kinetics of
propyltrimethoxysilane (PTMS) onto polycrystalline iron and aluminium oxide surfaces was investigated using X-ray photoelectron spectroscopy XPS [136]. Adsorption of PTMS on iron reached equilibrium within a few seconds whereas PTMS on aluminium exhibited dramatic time dependence. Thin films of simple organosilane on polycrystalline aluminium and iron oxide substrates were also investigated using XPS [137]. A granular adsorbent consisting of iron oxide was found to remove lead ions from drinking water using both batch and column methods [138]. Results showed the optimum pH for the removal to be between 5 and 7.

Recently, adsorbents from anaerobically digested sludge and sludge from an agri-food industrial wastewater treatment plant have been reported by Calvo et al [139]. The fresh sludges were subjected to three different treatments to determine their methylene blue adsorption properties. The first treatment involved drying, the second involved drying and pyrolysis and the third involved drying and activation. Though activation increased the surface area up to 390 m²/g, the corresponding level of methylene blue adsorbed was not increased. Activated sludges gave methylene blue adsorption below those of the dried sludges.

Adsorbents like modified cellulose [140], natural bentonite [141], linseed straw, pressed sludge cake, coal dust, pyrolysed tyre, sugar beet pulp and leatherhide powder [142], red mud [143], tamarind nut shell activated carbon [144], iron oxide-coated sand [145], heat treated sulphurized activated carbon [146], saw dust [147] and amorphous iron oxyhydroxide [148] were used as adsorbents.

Corncobs modified with citric acid and phosphoric acid were recently reported to adsorb copper, nickel, lead, cadmium and zinc ions by Vaughan et al [149]. The amount
of individual ions adsorbed by corncobs was found to be increased by modification with citric acid and phosphoric acid regardless whether the samples were washed or unwashed.

Activated carbon from *casurina equisetfolia* leaves [150], materials like lignin [151], functionalized formic lignin [152], carbon by contact arc method [153], activated carbons from coconut shell, wood and dust coal [154], montmorillonite illite and kaolin [155], soils [156], inorganic and biological sorbents [157], activated carbon fibres and granulated activated carbon [158], biowaste from fruit juice industry [159], iron (III) hydroxide [160], peanut hull pellet [161], soyabean hull, cottonseed hulls and macadamia nut hulls [162], functionalized clays [163] and activated carbon digested sludge and coconut husk [164] were also found to act as adsorbents.

Ground discarded tires were reported to adsorb naphthalene, toluene and mercury from water [165]. Adsorption by lignocellulosic anion exchangers from rice hull, sugarcane bagasse and wheat straw [166] and hazelnut carbon [167] have also been investigated. Gaikwad and Vipin Bhardwaj studied the removal of zinc from industrial effluents by fly ash [168]. The removal of Pb (II) was studied by Kim and Park using crab shell [169]. Adsorption of cadmium, zinc, nickel and lead from aqueous solution by *magnifera indica* seed shell was investigated by Mohammed Ajmal *et al.* [170]. The shell was used successfully for the removal of Cd, Zn, Ni and Pb from water. The degree of removal was found to be dependent on initial pH of the solution and the adsorption increased as the pH increased. Jesuia *et al.* reported the removal of Cr (VI) from wastewater by *abiesmoschus esculentus* (lady finger plant). The effect of pH, Cr (VI) concentration, adsorbent dose and contact time were studied in batch experiments. The
removal was reported to be effective at low pH values \cite{171}. Adsorbents from bagasse and coconut jute were studied for the removal of chromium(VI) from aqueous solutions by Shri Chand et al. \cite{172}. The removal was in general more effective at low pH values and low chromium(VI) concentrations. Many authors have reported the potential and carbonization of bagasse \cite{173, 174}.

Selvaraj et al. evaluated the adsorption capacity of photofilm sludge in the removal of metal ion \cite{175}. Ash particles from oil palm waste, modified peanut shells, carbon slurry from naphtha based ammonia plant and amidoximated cellulose were also tried on the adsorption of heavy metals \cite{176-178}.

1.5 Fixed bed studies

Effectiveness of the adsorbent is provided by batch mode studies. Adsorption capacities obtained from batch mode experiments are considered to be preliminary tests before conducting more costly column tests. Isotherms do not give accurate data for practical applications due to a number of reasons \cite{179}. Adsorption in a flow column is not at equilibrium and the adsorbent would not become totally exhausted in a commercial process before regeneration. Batch mode studies are limited to the treatment of small volumes of effluent whereas fixed bed studies are useful in the practical application of the adsorption process in wastewater treatment. The normal criterion in designing a fixed bed column is to predict the lifetime of the bed before regeneration. All existing models aim to determine the breakthrough curves for specific system.
Bed-Depth-Service-Time (BDST) model [180] is given by the following equation

\[
C_o t = \frac{N_o}{u} - \frac{1}{k_a} \left[ \ln \left( \frac{C_o}{C_i} - 1 \right) \right]
\]  

--- (1)

where

- \( t \) - service time to breakthrough (min),
- \( N_o \) - adsorption capacity (mg/L),
- \( C_o \) - influent concentration (mg/L),
- \( C_i \) - effluent concentration (mg/L),
- \( u \) - is linear flow rate (mL/min) and
- \( k_a \) - is rate constant of adsorption (L/mg/min).

By plotting \( C_o t \) vs ln[(\( C_o/C_i \)-1) at fixed value of \( C_o \) and different values of \( C_i \), \( k_a \) and \( N_o \), can be evaluated from the slope and intercept of the graph.

Singh et al. reported the removal of Cr (VI) by column studies using feldspar. The breakthrough curve was traditional sigmoid shape with adsorption capacity of 5.93 x 10^{-2} mg/L [181]. Reed and Arunachalam investigated the removal of lead and cadmium from aqueous waste stream using granular activated carbon. Granular activated carbon columns were used to treat metal bearing wastewater. The parameters influenced the column were found to be the influent characteristics and pH of the column. The columns were regenerated using 0.1 N HNO₃ and NaOH [182]. Kumar and Dara reported the removal of Cu (II), Pb (II), Zn (II), Cd (II) and Ni (II) ions using column of polymerised onion skin [80]. Arulanantham et al. investigated the removal of Cd (II) and Pb (II) ions using a column of height 7 cm and diameter 2.5 cm [82]. Fixed bed studies with apple wastes and melon seed moss were also reported in the literature [183, 184].
The adsorption of uranium(VI) and lead(II) on fixed bed of silica gel was investigated at initial pH 5.15 and an initial concentration of 0.5 mM and 0.1 mM, respectively by Tran and Roddick [185]. Low and Lee reported both batch mode and column experiments with moss calymperes decesperii besch. Hutchin model was applied to calculate $t_{1/2}$ at breakthrough volume $C/C_0 = 0.5$ [186].

1.6 Scope of the present work

The tools shaped the modern world not only depleted the wealth of nature but also created environmental degradation. The problem of water pollution due to heavy metals and its impact on environmental health is currently the focus of international attention. The cost effective removal of toxic metal ions from wastewater is an important and widely studied research area. Many techniques have been developed in recent years to remove toxic metal ions from wastewater. In choosing a wastewater treatment technology, factors like nature of the pollutants, permissible limits and economy of the treatment method have to be considered. Among various methods available, adsorption appears to have the least adverse effects. Its flexibility and dependability with good performance make it attractive. Even though the adsorption using activated carbon appears to have least adverse effects and can treat wastewater to suitable for reuse, the manufacturing and regeneration cost of activated carbon may be high. The search for efficient, cost effective option for treating metal bearing waste has intensified in recent years in the light of increasingly stringent discharge limits. Low cost alternatives to active carbon from a range of carbonaceous and mineral precursors were developed. The use of waste material from industries for the removal of metal ions reduces the treatment cost
and also provides a solution for the solid waste management of the industries which
dump the waste in the land.

In developing countries like India, industries cannot afford to use conventional
wastewater treatment methods due to their high cost. Agricultural and industrial solid
waste can be used and recycled as non-conventional adsorbents, if they are non toxic.

In the present study, distillery sludge has been tried as an adsorbent for the
removal of heavy metal ions from wastewater. The sludge does not contain any toxic
substance. It contains mainly organic cellulose and lignin. A huge amount of the sludge is
being accumulated in several industries.

The objective of this research work is to explore the adsorption capacities and
adsorption kinetics of the sludge for the uptake of heavy metal ions such as
crchromium(VI), copper(II), lead(II) and nickel(II). The study includes batch mode and
fixed bed studies. The abundance and easy availability makes distillery sludge a strong
candidature to remove heavy metals from water and wastewater.