CHAPTER 2

LITERATURE REVIEW AND SCOPE OF THE PRESENT STUDY

2.1 LITERATURE REVIEW

Liquid phase adsorption technique is one of the most popular methods for the removal of pollutant from wastewater since proper design of the adsorption process will produce a high-quality treated effluent. This process provides an attractive alternative for the treatment of contaminated water, especially if the sorbent is less expensive. Adsorption is a well-known equilibrium separation process and an effective method for the decontamination application due to less cost, flexibility and simplicity of design, ease of operation and insensitive to toxic pollutants (Crini et al 2006; Dabrowski 2001).

To achieve an economically effective treatment of metal contaminated wastewater, various low cost materials have been investigated worldwide. In recent years, the search for the low cost adsorbent that have metal binding capacities has intensified. Several investigators have identified and used novel adsorbents for the metal ion removal in wastewater treatment, which are complied and discussed in this chapter. Various methods of adsorption on various adsorbents are described and the advantages and disadvantages of their use in metal ion removal for wastewater treatment discussed and their efficacies are compared. The adsorbents used in wastewater treatment process for the removal of metal ion are broadly
classified as commercial and activated carbon from solid wastes, biosorbents, Agriculture solid wastes, natural materials like zeolite and clay etc.

2.2 WASTE MATERIALS FROM AGRICULTURE AND INDUSTRY

Waste material locally available in large quantities such as agriculture wastes and industrial byproducts can be utilized as low cost adsorbents, which can be used as an adsorbent for water purification, helping industries to reduce the cost of waste disposal and hence providing a potential application.

2.2.1 Agriculture Waste

Agriculture waste is one of the rich sources for low cost adsorbent besides natural materials, due to abundant availability, like Orange peel, Rice husk (Ajmal et al 2000) Pecan shell (Shawabkeh et al 2006), Orange peel Parthenium (Kadirvelu et al 2001a), Coirpith (Kadirvelu et al 2002), Banana peel (Annadurai et al 2002), Hazelnut shell (Demirbas et al 2002; Kobya et al 2004), Cocoa shell (Meunier et al 2003; Bable et al 2004), Almon husk (Hasar et al 2003), Soyabean hull (Marshall et al 1999) and Turkish fly ash (Bayat et al 2002) etc. Agricultural wastes are utilized for the removal of heavy metal by adsorption. This process can be costly due to energy and chemical consumption (Bailey et al 1999).

2.2.2 Industrial byproduct

Several studies have been conducted on the potential of industrial byproducts for metal removal, due to their low cost and local availability. They are used for heavy metal removal for Activated slags, Steel slags, iron
slags (Feng 2004), Hydrous titanium oxide (Ghosh 2003), Seyitomer (Rao 2002), Afsin-Elbistain (Bayat et al 2002), Bagasse, Magnetite (Ortiz 2001), Red mud (Zoubulis 1995) and Fly ash (Pedersen 2003).

2.3 COMMERCIAL AND ACTIVATED CARBON FROM SOLID WASTE

Commercial and activated carbons are usually derived from natural carbonaceous material such as wood, coconut shell, lignite or coal. In general, almost any carbonaceous material may be used as a precursor for the preparation of carbon adsorbents. A wide variety of carbons have been prepared from agriculture waste such as rice hull (Gupta 2009; Naiya 2009), coirpith carbon (Kadirvelu 2001b) Peanut hull carbon, Granular activated carbon (Liyan 2009; Sharma 1996; Periyasamy 1995, 1996), Soyabean hull, cotton seed hulls, NaOH treated rice hull carbon (Marshall 1999), commercial activated carbon, charcoal, coconutshell, modified activated carbon (Monser 2002; Choi 2009) and hazelnut shell activated carbon (Demirbas 2002) etc. Activated carbon adsorption is considered particularly competitive and effective for the removal of heavy metal ions trace quantities. However the use of activated carbon is not suitable in developing countries due to the high costs associated with production and regeneration of spent carbon (Panday1985).

2.4 BIOSORBENT

The accumulation and concentration of pollutants from aqueous solution by the use of biological materials is termed as biosorption. In this instance, biological materials, such as chitosan, chitin, peat moss, yeast, fungi or bacterial biomass, are used as sorbent to concentrate and remove heavy metal ion from aqueous solutions.
2.4.1 Chitosan

Among various biosorbents, chitin is the second most abundant natural biopolymer after cellulose. However, more important than chitin is chitosan, which has a molecular structure similar to cellulose. Presently, chitosan is attracting an increasing amount of research interest, as it is an effective scavenger for heavy metals. The removal of heavy metal ion for chitosan and chemically activated chitosan is given below (Chen et al 2009; Bable et al 2004; Juang et al 2000). They are epichlorohydrin and ethylene glycol diglycidyl ether, Non-cross linked chitosan and cross linked chitosan (Schmuhl et al 2001) Chitosan (Annachhatre et al 1996), Chitosan beads (Hsien et al 1998), Cross linked chitosan with glutaraldehyde (Guibal et al 1998) chitosan (Bable et al 2004). Overall, the results mentioned previously indicate that chitosan is a good adsorbent for all heavy metals. It is widely known that the excellent adsorption behaviors of chitosan for heavy metal removal is attributed to (i) high hydrophilicity of chitosan due to large number of hydroxyl groups, (ii) large number of primary amino group with high activity and (iii) flexibility structure of polymer chain of chitosan making suitable configuration for adsorption of metal ions.

2.4.2 Biomass

Biomass has a high potential as a sorbent due to its physiochemical characteristics. The use of biomass for wastewater treatment is increasing because of its availability in large quantities and at low cost. The major advantage of biosorption technology is its effectiveness in reducing the concentration of heavy metal ions. Biomass is especially useful when heavy metal ion is very toxic. Biomass adsorption is effective when conditions are not always favourable for the growth and the maintenance of the microbial population.
The phenomena of biosorption has been described in a wide range of living biomass like algae (Kola 2005), bacteria (Ozturk 2004; Chang 1997), yeast (Zhang 1998) fungi (Matheickal 1997) moss (Low 1991), aquatic plant (Schneider 1995) and waste biomass (Akar 2009). The investigations have shown that the biosorption of heavy metal cations by microorganism is a rapid and reversible reaction and is not necessarily mediated by metabolic processes. In general, it is observed that the heavy metal biosorption capacity depends on the type of biomass and the reaction may be selective for certain cations. The biosorption of marine algae Sargassum, pandina, Ulva, Palmaria palmate and Gracillaria species has been studied for removal of Cu, Pb, Zn, Cd and Ni from aqueous solution (Holam1993).

2.4.3 Peat moss

Peat moss is a complex soil material containing organic matter in various stages of decomposition. Peat moss is a natural substance widely formed and abundant, which has large surface area and highly porous so that it can be used to bind heavy metals. The constituents especially lignin and humic acid, bear polar functional groups, such as alcohols, aldehyde, ketones, carboxylic acids, phenolic hydroxide and ethers that can be involved in chemical bonding. It was observed that peat moss plays as important role in treatment of metal-bearing industrial effluent such as Cu$^{2+}$, Cd$^{2+}$, Zn$^{2+}$ and Ni$^{2+}$ using eutrophic and oligotrophic peat. Eutrophic peat is poor in cellulose, but rich in humic acidic than oligotrophic peat and contain more organic matter. Both peats contain about 85% of humic acid and 15% of fluvic acid. The adsorption capacity for different metals by Eutropic peat Oligotrophic peat (Chen et al 1990) and Sphagnum peat moss (Sharma et al 1994) have been analyzed.
2.5  NATURAL MATERIAL

2.5.1  Clay

Clay represents a layered structure of alumino-silicate minerals with structure of a tetrahedral (Si centre) and octahedral (Al centre). There are different classes of clays Montmorillonite, kaolinite, Bentonite, Diatomite, Perlite, Vermiculite, Gluconite and Wollastonite. Clay material has high surface area, layered structure and high porosity. Also, they possess a negative charge and hence have the capacity to adsorb positively charged materials. Clay material is valuable for its tendency to absorb water in interlayer sites. The removal of heavy metal ion from clay material by Moroccan clay (Saffaj 2004), Natural zeolite (Inglezakis 1989), Na-montmorillonite (Abollino 2003), mesoporous silica (Aguado 2009; Stylianou 2007), Clinoptilolite (Mendoza 2006; Cedillo 2009) Kaolin and ball clay (Chantawong 2003), clay (Vengris 2001), surfactant-modified montmorillonite (Lin 2002), Kaolin (Arias 2002; Bable 2003; Chatawang 2003), vermiculites (Ayuso 2003), kaolinite (Yavuz 2003), Lithuanian Gluconite (Smith 1996) have been studied. Compared to that of adsorbents derived from agriculture waste, the price of those originating from natural materials is relatively higher, making them not competitive enough for commercial application.

2.5.2  Zeolites

Natural zeolites are the most important cation exchangers that exhibit high ion exchange capacity, selectivity and compatibility with the natural environment. Among minerals that possess sorbent properties, zeolites appear as most promising for water purification. Zeolite, an alumino-silicate tetrahedron connected with oxygen atom, has charge-balance the negative charge localized on the aluminosilicate framework (Keane et al 1998). The
discovery of natural zeolite deposits has lead to an increasing use of these minerals for the purpose of eliminating or at least reducing many long standing pollution problems. The removal of heavy metal ion by zeolite material (Babel et al 2003; Aguado et al 2009; Peric 2004; Arias 2002; Wingenefelder 2005; Kurniawan et al 2006; Ayuso 2003; Ahmed 1998; Kocaoba 2007; Ferreira 2009), zeolite-Y, ZSM-5 and β (Panneerselvam et al 2008, 2009a; 2009b) etc has been studied and the removal efficiency of the heavy metals by zeolite is higher than other adsorbents. Zeolite is a suitable adsorbent for the separation and purification in water technology.

A wide range of low cost adsorbents has been studied worldwide for heavy metal removal. It is evident from literature survey that inexpensive and locally available material could be used instead of commercial zeolite. To improve removal efficiencies and adsorption capacities, chemical modification of low cost is done.

In spite of the scarcity of consistent cost information, low cost adsorbents for wastewater treatment application are strongly recommended due to their local availability, technical feasibility, engineering applicability, and cost effectiveness. Low-cost adsorbents such as zeolite, clay, chitosan, waste slurry and lignine perform well in removing heavy metals, so these materials can be adopted and widely used in industries not only to minimize cost but also to improve wastewater quality.

If the alternative adsorbents mentioned previously are found to have high efficiency for heavy metal removal, not only industries, but also the living organism and the surrounding environment will also benefit from the potential toxicity due to heavy metal. Thus, the use of low cost adsorbent may
contribute to the sustainability of the surrounding environment. Undoubtedly low cost adsorbent offer a lot of benefits for commercial purpose in the future.

2.6 SCOPE OF THE PRESENT STUDY

The above literature review indicates that different forms of phosphoric acid modified zeolites can be used for the removal of cationic heavy metal pollutants present in the industrial effluents. Recently a systematic investigation has been carried out to evaluate the performance of locally available synthetic zeolites for removal of caesium, strontium and thorium from aqueous solution. Undoubtedly, such low cost adsorbents offer a lot of promising benefits for their commercial use in the future. Although zeolites have been largely exploited for adsorption application, the phosphoric acid forms have not been exploited for removal of heavy metal ion from aqueous solution. Three zeolites viz., Y, ZSM-5 and β each possessing different structure, were procured and characterized with respect to relevant parameters. They were subjected to a detailed study in batch experiment, for the evaluation of their performance towards removal of the heavy metal ions. Further, the uptake of hydrolysable was taken for different cationic ions by zeolites. Zeolite loaded with heavy metal ions on being subjected to hydrothermal treatment, the phosphoric acid modified zeolites were evaluated for further uptake of heavy metal ions. In the present study we have planned to use phosphoric acid modified H-ZSM-5, H-Y and H-β zeolites for removal of heavy metal ions from water. Accordingly, the scope of the present investigation are as follows.
The major objectives of the present investigation are

- To convert the H form of Y, ZSM-5 and β zeolites to their sodium form using aqueous NaHCO₃ solution.
- To modify H form of Y, ZSM-5 and β zeolites with phosphoric acid.
- To characterize the modified zeolites by X-ray diffraction analysis (XRD).
- To measure surface area of the modified zeolites by Brauner Emmett and Teller (BET) surface area analyzers.
- To analyse the morphology of the modified zeolites using Scanning Electron Microscope (SEM) images.
- To carry out adsorption studies of modified zeolites with different synthetic metal ion solutions.
- To study effect of pH on the percentage of metal ions removal.
- To study the effect of adsorbent dosage on the percentage removal of metal ions.
- To study effect of contact time on the percentage removal of metal ions.
- To study effect of temperature at which maximum percentage removal of metal ions takes place.
- To evaluate the applicability of Langmuir and Freundlich isotherm for the adsorption of metal ions.
- To evaluate the adsorption mechanism, by fitting the kinetic data with the pseudo-first order, pseudo-second order and intraparticle diffusion models.
- To calculate thermodynamic parameters such as free energy, entropy and enthalpy.
- To check the efficiency of modified zeolites with real industrial electroplating effluents.
- To compare the performance of the modified zeolites with the unmodified commercial zeolites.

In this study different zeolites (Y, β and ZSM-5) were modified with phosphoric acid. The exchangeable protons in them were replaced by Na$^+$ ions using a mild base like NaHCO$_3$. Such modified zeolites were tested for sorption of heavy metal ions from aqueous solution and to also examine the kinetics of sorption and other parameters involved.