Chapter 2

Literature Survey and basic concepts

2.1 INTRODUCTION

Due to globalization, there is a huge growth of industries worldwide, like dyeing, battery manufacturing, electroplating, mining operations, glass manufacturing, paper manufacturing and chemical manufacturing, which are the major source of metallic pollutants (Nriagio et al., 1988). The industries are contributing not only metal pollutants but also polluting the air and soil. Toxic gases such as (NOx, SOx, NH3 and CO) are released to the atmosphere from such industries. Metallic pollutants such as heavy metal ions and dyes waste coming from these industries are directly or indirectly discharged into the environment in huge quantity, specifically in the developing countries. Heavy metals such as lead, cadmium, arsenic, chromium and copper are continuously used by the industries and these heavy metals are non-biodegradable and will exist long in the environment. So many metal ions are toxic and have ease tendency to accumulate into the living organisms including human beings. Even at very low concentrations, these are very harmful to the living species (Srivastava et al., 2008). Based on the reasons mentioned above, these industrial pollutants should be treated prior to their discharge into the environment.

According to the Unites States Environmental Protection Agency (EPA), there are some standards in the mean of Maximum Contamination Levels (MCLs) for the drinking water quality. The limit of contamination levels is expressed in milligrams per liter (mg/L) or parts per million (ppm). Based on the several examining tests EPA have determined the maximum contamination level for each metal ions. The adverse effects on human being by toxic heavy metal ions contamination levels are shown in the following Table 2.1.

Metal toxicity is the major phenomenon affecting various doses of life. There are certain metals, which become toxic as they form poisonous soluble compounds, whereas some metals have no biological role and hence cause toxicity. For instance, lead in any
quantity may have negative health effects and often even lighter metals could also be toxic like beryllium and iron and other trace elements high doses.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Heavy Metal ions</th>
<th>MCL (mg/L)²</th>
<th>Health Effects</th>
<th>Sources of Contamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Lead</td>
<td>0.015</td>
<td>Kidney problems for adults and physical mental development delays in infants and children’s</td>
<td>Erosion of natural deposits and corrosion of household plumbing systems</td>
</tr>
<tr>
<td>2.</td>
<td>Cadmium</td>
<td>0.005</td>
<td>Kidney damage</td>
<td>Discharge of waste water from metal refineries, waste batteries, paints and erosion of natural deposits</td>
</tr>
<tr>
<td>3.</td>
<td>Chromium (total)</td>
<td>0.1</td>
<td>Allergic dermatitis</td>
<td>Discharge from steel, pulp mills and erosion of natural deposits</td>
</tr>
<tr>
<td>4.</td>
<td>Mercury</td>
<td>0.002</td>
<td>Kidney damage</td>
<td>Discharge from refineries and factories, runoff from landfills and croplands and erosion of natural deposits</td>
</tr>
<tr>
<td>5.</td>
<td>Arsenic</td>
<td>0.010</td>
<td>Skin damage or problems with circulatory systems, and may have increased risk of getting cancer</td>
<td>Erosion of natural deposits; runoff from orchards, runoff from glass and electronics production wastes</td>
</tr>
<tr>
<td>6.</td>
<td>Copper</td>
<td>1.3</td>
<td>Liver and kidney damage</td>
<td>Corrosion of household plumbing systems and erosion of natural deposits.</td>
</tr>
<tr>
<td>7.</td>
<td>Antimony</td>
<td>0.006</td>
<td>Increase in blood cholesterol; decrease in blood</td>
<td>Discharge from petroleum refineries; fire retardants; ceramics; electronics; solder</td>
</tr>
</tbody>
</table>

Table 2.1. Heavy metal ions with their maximum contamination levels

Toxic metals interfere with the metabolic process of the body to cause illness. While most of the metals are toxic, some elements are essential like bismuth and have a less toxicity. In general, toxic metals include cadmium, lead, mercury, radioactive metals along with metalloids like arsenic and polonium. Radioactive metals have both radiological toxicity and chemical toxicity. Metals in a particular oxidation state is
hazardous to human like chromium (III) is an essential trace element, but chromium (VI) is a carcinogen. Solubility is yet another factor leading to toxicity and insoluble compounds as well as the metallic forms often exhibit negligible toxicity. Organometallics such as methyl mercury and tetraethyl lead, can also be extremely toxic.

Decontamination for toxic metals is different from organic toxins as toxic metals are elements and hence cannot be destroyed. In this view, it has to be made insoluble by the use of chelating agents or could be diluted into a large reservoir, like ocean as immediate toxicity is a function of concentration rather than amount. But bioaccumulation has the potential to reverse this. Toxic metals can bioaccumulate in the body and in the food chain. Therefore, a common characteristic of toxic metals is the chronic nature of their toxicity. This is particularly notable with radioactive heavy metals such as radium, which imitates calcium to the point of being incorporated into human bone, although similar health implications are found in lead or mercury poisoning. The exceptions to this are barium and aluminum, which can be removed efficiently by the kidneys.

Lead is one of the most toxic heavy metal ions, which have easy accumulation into the living species even at low concentrations. This metal ion can cause the damage of kidney, central nervous system and some parts of human body. The symptoms from this metal ion are headache, anemia, dizziness, weakness of muscles and insomnia (Naseem et al., 2001). Lead interferes with a lot of body processes and is toxic to many organs and tissues like heart, bones, intestines, kidneys, reproductive and nervous systems. It disturbs the development of the nervous system and is therefore particularly toxic to children, causing permanent learning, behavior disorders and other symptoms include abdominal pain, confusion, headache, anemia, irritability, and in severe cases seizures, coma, and death. Lead exposure is from various sources like contaminated air, water, soil, food, and consumer products. Occupational exposure is a common cause of lead poisoning in adults. According to estimates made by the National Institute of Occupational Safety and Health (NIOSH), a huge population of more than 3 million workers in the United States is exposed to lead in the workplace. It’s not only from industries, but even at homes, children are prone to lead poisoning from lead paint lead dust from moveable window
frames with lead paints. It could be prevented from individual efforts (e.g. removing lead-containing items such as piping or blinds from the home) to nationwide policies (e.g. laws that ban lead in products, reduce allowable levels in water or soil, or provide for cleanup and mitigation of contaminated soil, etc.).

Lead poisoning causes a variety of symptoms and signs depending on the individual and the duration of lead exposure. It generally takes weeks to show up the symptoms as lead builds up in the body during a chronic exposure. Symptoms from exposure to organic lead, is probably more toxic than inorganic lead due to its lipid solubility. The latter predominantly affect the central nervous system like insomnia, delirium, cognitive deficits, tremor, hallucinations, and convulsions. Symptoms generally vary in adults and children with the main symptoms in adults being headache, abdominal pain, memory loss, kidney failure, male reproductive problems, weakness, pain, or tingling in the extremities. Early symptoms in adults are generally nonspecific, which includes depression, intermittent abdominal pain, nausea, loss of appetite, diarrhea, constipation, and muscle pain and apart from these, an unusual taste in the mouth with and personality changes is also seen.

Cadmium is yet another heavy metal ion classified by the U.S. Environmental Protection Agency as a carcinogen. Cadmium is an extremely toxic metal found in industrial workplaces and is used extensively in electroplating, although the nature of the operation does not generally lead to overexposures. Cadmium is also found in some industrial paints and may represent a hazard when sprayed. Cadmium is also present in the manufacturing of some types of batteries. Cadmium poisoning causes the disfunctioning of kidney and a higher concentration will be fatal to humans. Symptoms will show up only after few hours of exposure, like cough, dryness, irritation of the nose and throat, headache, dizziness, weakness, fever, chills, and chest pain. Inhalation of cadmium-laden dust leads to respiratory tract and kidney problems and ingestion of the same leads to immediate poisoning and damage to the liver and the kidneys. Apart from elemental cadmium, compounds containing cadmium are also carcinogenic.

Chromium exists in two states where in Cr(III) ions are less toxic than Cr(VI) state. The effect by Cr(VI) to human bodies varies from simple skin irritation to lung
carcinoma with various other effects (Khezami et al., 2005). In the body, chromium(VI) is reduced to chromium(III) already in the blood before it enters the cells and the chromium(III) is excreted from the body. The chromate ion is transferred into the cell by a transport mechanism, through which also sulfate and phosphate ions enter the cell. The acute toxicity of chromium(VI) is due to its strong oxidational properties. When it reaches the blood stream, it causes damages to various parts of the body like kidneys, liver and blood cells via oxidation process and as a consequence hemolysis, renal and liver failure results. Chromates are used in various manufacturing units like leather products, paints, cement, mortar and anti-corrosives. Contact with products containing chromates can lead to allergic contact dermatitis and irritant dermatitis, resulting in ulceration of the skin, sometimes referred to as "chrome ulcers". This condition is often found in workers that have been exposed to strong chromate solutions in electroplating, tanning and chrome-producing manufacturers.

Copper has less effect on the human beings and will do essential work in the animal metabolism, but over dosage will lead to severe problems to both human and animals such as cramps, vomiting and convulsions or some time leading to death (Paulino et al., 2006). Hence there are numerous techniques established for the removal of toxic metal ions in the view of supplying safe water to all living organisms.

2.2 TREATMENT OF HEAVY METALS FROM WASTEWATER

There are many techniques for treatment of heavy metal ions from the waste water, with its own pros and cons, and the same has been detailed below.

2.2.1 PRECIPITATION TECHNIQUES

Among these chemical precipitation techniques, conventional processes include sulfide and hydroxide precipitation. Most of the industries widely used process is chemical precipitation, as it is cost effective, simple to use and ease of operation (Ku et al., 2001). In this process, heavy metal ions adsorb on the chemical to form the insoluble precipitates. The resultant precipitates were then separated by filtration or sedimentation process to get the treated water for further usage.
2.2.1.1 Hydroxide precipitation

Hydroxide precipitation is the most widely used process in chemical precipitation, as it is easy to control the pH, cost effective and simple to operate (Huisman et al., 2006). The solubilities of the various metal hydroxides are optimized in the pH range of 8.0 - 11.0. The metal hydroxides can be removed by flocculation and sedimentation. Lime is one of the hydroxide precipitation preferred mostly by the industries, due to its low cost and easy to separate. Cu(II) and Cr(VI) ions removal has been reported using hydroxide precipitation process (Mirbagheri et al., 2005). Cr(VI) was converted to Cr(III) using ferrous sulfate and a maximum precipitation of Cr(III) occurred at pH 8.7 whereas the concentration of chromate was reduced from 30 to 0.01 mg/L. The cupro-ammonia complex was reduced by aeration and a pH of 12 was found optimum pH for maximum copper precipitation. Here, the concentration of copper was reduced from 48.51 to 0.694 mg/L. To enhance lime precipitation, fly ash was used as a seed material (Chen et al., 2009). This process of fly ash - lime carbonation increased the particle size of the precipitate and hence the efficiency was enhanced.

The concentrations of chromium, copper, lead and zinc in effluents can be reduced from an initial concentration of 100.0 mg/L to 0.08, 0.14, 0.03 and 0.45 mg/L, respectively. In hydroxide precipitation process, the addition of coagulants such as alum, iron salts, and organic polymers can enhance the removal of heavy metals from wastewater. Chemical coagulation and precipitation by lime were used to treat synthetic wastewater consisting of Zn, Cd, Mn and Mg at a concentration of 450, 150, 1085 and 3154 mg/L, respectively (Charernpanyarak L. 1999). It was found that the optimum pH was more than 9.5 and the treated wastewater could meet the waste water standard of the ministry of industry. Moreover, if coagulant was added, the residual concentration of heavy metal can be decreased further.

Though this method is widely used, it has few limitations like the process generates large volumes of low density sludge and such sludge will generate dewatering and disposal problems (Kongsricharoern et al., 1995). In addition, the metal hydroxides are amphoteric, and hence the mixed metals will be problematic as the ideal pH for one
metal may put another metal back into the solution. The last issue of this process is that the presence of complexing agents will inhibit metal hydroxide precipitation.

2.2.1.2 Sulfide precipitation

Sulfide precipitation is an effective process especially for the treatment of toxic heavy metals ions. The major advantage of using this process is that the solubilities of the metal sulfide precipitates are lower than hydroxide precipitates and it is not amphoteric. In view of this, sulfide precipitation process can remove a large amount of metals over a broad pH range as compared with the hydroxide precipitation. Metal sulfide sludges also exhibit better thickening and dewatering characteristics than the corresponding metal hydroxide sludges. Reports exist on the use of synthetic iron sulfide to remove Cu$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$ (Ozverdi et al., 2006). Though this is a good method, there are potential threats in the use of sulfide precipitation process as heavy metal ions often in acidic conditions and sulfide precipitants in acidic conditions can result in the evolution of toxic H$_2$S fumes. In view of this, it is imperative that this process be performed in a neutral or basic medium. Also, metal sulfide precipitation forms colloidal precipitate, which could lead to certain separation problems in either settling or filtration processes.

Ion-exchange processes have been used in combination with chemical precipitation for the removal of nickel from wastewater streams (Papadopoulos et al., 2004). Results show that the individual application of ion exchange removed nickel up to 74.8%, while using the combination of ion exchange and precipitation processes, a higher removal from 94.2% to 98.3% was obtained. Besides these, treating acid mine water by the precipitation of heavy metals with lime and sulfides, followed by ion exchange have been reported (Feng et al., 2000).

2.3 ION EXCHANGE

Ion-exchange processes is yet another established method for the removal of heavy metal ions from wastewater due to their advantages like high treatment capacity, high removal efficiency and fast kinetics (Kang et al., 2004). Ion-exchange resin, either synthetic or natural solid resin, has the specific ability to exchange its cations with metals in the wastewater. Synthetic resins are the commonly used ion-exchange processes,
which are effective to nearly remove the heavy metals from the solution (Alyuz et al., 2009).

2.4 ADSORPTION

Adsorption is a surface phenomenon used mainly for the removal of organic and inorganic pollutants, wherein absorbableolute in solution comes into contact with a solid porous adsorbent and the liquid-solid intermolecular forces of attraction causes the solute molecules from the solution to get adsorbed on the solid adsorbent. The solute remaining on the solid in an adsorption processes is called adsorbate, whereas, the solid on which it gets adsorbed called as an adsorbent and the whole process is called as adsorption process. As the adsorbed phase composition is different from that of the bulk phase, this difference becomes the driving force for separation by adsorption technology.

In a bulk material, all the bonding involved like ionic, covalent, or metallic of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbate. The exact nature of bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak Vander wal forces) or chemisorption (characteristic of covalent bonding) and could also occur due to electrostatic attraction. Of all the reported techniques for water purification, adsorption is one of the most effective and low cost technique for heavy metal ion treatment. It offers ease of operation, high efficiency and easy to design. In addition, as adsorption is sometimes reversible, adsorbents can be regenerated by a suitable desorption process. Thus much of the focus is laid on adsorption processes for the removal of various pollutants from aqueous water.

2.4.1 BATCH MODE ADSORPTION

Adsorption parameters were carried out using batch mode processes in an orbital shaker at 250 rpm in 100 mL conical flasks containing 20 mg/L metal ion. The adsorption parameters, like initial metal ion concentration (10-70 mg/L), pH (2-8), and temperature (27°- 47°C) were studied. During the experiment each parameter was kept constant. For measuring contact time, 0.025 g/L adsorbent containing 100 ml of deionized water and
20 mg/L of metal ion were taken in a 250 ml conical flask and were shaken in an orbital shaker at 250 rpm and 37°C. After every 20 min, the conical flask was removed from the shaker, centrifuged and filtered using 0.22 μm cellulose nitrate membranes. The obtained filtrates were analyzed using AAS analysis.

2.4.2 ADSORPTION PARAMETERS

To explore the adsorption behavior of the composite, batch mode adsorption was carried out as explained in the previous section 2.4.1. The adsorption percentage and loading capacity of metal ions were calculated as follows:

\[
\text{Adsorption} \% = \frac{C_i - C_f}{C_i} \times 100
\]  

(1)

\[
q_e = \frac{\nu(C_i - C_e)}{W}
\]

(2)

where \( C_i \) and \( C_f \) being the initial and final metal ion concentration; \( q_e \) and \( C_e \) are equilibrium adsorption capacity and concentration of the metal ions at equilibrium; \( \nu \) is the volume of metal ion solution (L) and \( W \) is the weight of adsorbent in grams.

2.4.3 ADSORPTION Isotherm Models

2.4.3.1 Langmuir Adsorption Isotherm

This describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Based upon these assumptions, Langmuir represented the following equation (Kizilkaya et al., 2011):

\[
q_e = \frac{q_mC_eK_d}{1 + K_d}
\]

(3)

The above equation can be transformed into a linear form as follows
\[
\frac{c_e}{q_e} = \frac{1}{k_d q_m} + \frac{1}{q_m} C_e
\]  
(4)

where, \(C_e\) (mg/L) is the equilibrium concentration of ion in the solution, \(q_e\) (mg/g) is the adsorption capacity at equilibrium, \(q_m\) (mg/g) is the maximum adsorption capacity and \(K_d\) (L/mg) is the effective dissociation constant that relates the affinity binding site. The values of \(q_m\) and \(K_d\) are obtained from the intercept and the slope of the linear plot of \(C_e/q_e\) vs \(C_e\).

### 2.4.3.2 Freundlich Adsorption Isotherm

Freundlich isotherm equation is an empirical relationship, where it is assumed that the adsorption energy of ion binding to a site on an adsorbent depends on whether or not the adjacent sites are already occupied. This isotherm can be described as following equation (Yang et al., 2011):

\[
q_e = K_F C_e^n
\]  
(5)

The above equation can be transformed into a linear equation form as follows:

\[
\ln q_e = \ln K_F + 1/n \ln C_e
\]  
(6)

where, \(K_F\) and \(n\) are physical constants of Freundlich adsorption isotherm. Also, \(K_F\) and \(n\) are indicators of adsorption capacity and adsorption intensity, respectively. The slope and intercept of linear Freundlich equation are equal to \(1/n\) and \(\ln K_F\), respectively.

### 2.4.4 ADSORPTION KINETIC MODELS

To know the performance and mechanisms of adsorption, kinetics and thermodynamics will play a major role. Kinetic model will give the rate of reaction or rate of adsorption on to the adsorbents. From the kinetic analysis, the solute uptake rate, which determines the residence time required for completion of adsorption reaction, may be established.

Presently, reaction models have been widely developed to describe the kinetic process of adsorption (Huang et al., 2008; Tan et al., 2008); however, there still exist
some problems. For example, pseudo-second-order rate equation based on chemical adsorption was unsuitably employed to describe organic pollutants adsorption onto several non-polar polymeric adsorbents.

2.4.4.1 Pseudo-first-order rate equation

A first-order rate equation was described by (Lagergren 1898) the kinetic process of liquid-solid phase adsorption of oxalic acid and malonic acid onto charcoal, which is believed to be the earliest model pertaining to the adsorption rate based on the adsorption capacity. It can be presented as follows:

\[
\frac{dq_t}{dt} = K_1(q_e - q_t) \tag{7}
\]

where \(q_e\) and \(q_t\) (mg/g) are the adsorption capacities at equilibrium and time t (min), respectively. \(k_1\) (min\(^{-1}\)) is the pseudo-first-order rate constant for the kinetic model. Integrating Eq.(7) with the boundary conditions of \(q_t = 0\) at \(t = 0\) and \(q_t = q_e\) at \(t = t\), yields (Ho, 2004) which can be rearranged to:

\[
\ln\left(\frac{q_e}{q_e - q_t}\right) = K_1t \tag{8}
\]

The above equation can be transformed into a linear equation form as follows,

\[
\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \tag{9}
\]

To distinguish kinetic equations based on adsorption capacity from solution concentration, Lagergren’s first order rate equation has been called pseudo-first-order (Ho and McKay, 1998).

2.4.4.2 Pseudo-second-order rate equation

The driving force, \((q_e - q_t)\), is proportional to the available fraction of active sites (Ho, 2006). Then, it yields

\[
\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{10}
\]
The above equation can rearranged as follows

$$\frac{dq_t}{(q_e - q_t)^2} = K_2 dt$$  \hspace{1cm} (11)

Integrating Eq. (11) with the boundary conditions of $q_t = 0$ at $t=0$ and $q_t=q_e$ at $t=t$, yields

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K_2 t$$  \hspace{1cm} (12)

which can be rearranged as follows

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$  \hspace{1cm} (13)

where $V_o$ (mg/(g·min)) means the initial adsorption rate, and the constants can be determined experimentally by plotting of $t/q_t$ against $t$.

Similarly, Ho’s second-order rate equation is called pseudo-second-order rate equation to distinguish kinetic equations based on adsorption capacity from concentration of solution (Ho, 2006). This equation has been successfully applied to the adsorption of metal ions, dyes, herbicides, oils, and organic substances from aqueous solutions (Hameed, 2008).

**2.4.5 ADSORPTION THERMODYNAMICS**

Thermodynamic parameters provide additional in-depth information regarding the inherent energetic changes involved during adsorption. Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. Gibb’s free energy change, $\Delta G^\circ$, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if $\Delta G^\circ$ has a negative value.

The thermodynamic parameters of Gibb’s free energy change, $\Delta G^\circ$, enthalpy change, $\Delta H^\circ$, and entropy change, $\Delta S^\circ$, for the adsorption processes are calculated using the following equations:

$$\Delta G^\circ = -RT \ln K_o$$  \hspace{1cm} (14)
\[ RT \ln K_o = T \Delta S^o - \Delta H^o \]  \hspace{1cm} (15)

\[ \ln K_o = - \frac{\Delta H^o}{R} \frac{1}{T} + \frac{\Delta S^o}{R} \]  \hspace{1cm} (16)

where \( R \) is universal gas constant (8.314 J mol\(^{-1}\)K\(^{-1}\)), \( T \) is the absolute temperature in K, and \( \Delta H^o, \Delta S^o \& \Delta G^o \) are the changes in enthalpy (J/mol), entropy (J/mol/K) and Gibb’s free energy (J/mol) respectively.

The negative value of \( \Delta G^o \) suggests the adsorption is spontaneous and feasible and the negative value of \( \Delta H^o \) suggests that the adsorption is exothermic in nature. The positive value of \( \Delta S^o \) suggests that some structural changes occur on the adsorbent, and the randomness at the solid/liquid interface in the adsorption system increases during the adsorption process.

2.5 ADSORBENTS FOR THE REMOVAL OF HEAVY METAL IONS

2.5.1 ROLE OF NANOMATERIALS

At present there are number of available literature for the adsorption of heavy metal ions from aqueous solution. Activated carbon is one of the material which has been used as a commercial adsorbent. It is having good adsorption of metal ions but the cost is very high and hence there is a search for alternatives to activated carbon. The role of low cost nanomaterials has becoming very attractive due to its effective adsorption and ease of preparation. So the removal of metal pollutants from waste water and as well as industrial effluents using nanomaterials is becoming the fascinating area for the environmental researches. Nanotechnology has diverse applications in various domains but recently its application in wastewater treatment has emerged as a fast-developing, fascinating area of interest.

Nanotechnology is growth of materials at the nanoscale and at nanoscale, where materials show unique characteristics with enhanced surface area and ‘surface area to volume’ ratio (Mamalis 2007). Such characteristics improve the adsorption capacity of the nanoparticles. Apart from the large surface area, they show unique characteristics like
high catalytic potential and high reactivity, which make them better adsorbing materials than usual materials. As these materials have large surface area, nanoparticles have a greater number of active sites for interaction with different chemical species (Khaleel et al., 1999; Li et al., 2006; Hristovski et al., 2007). Such high surface area nanomaterials are being widely used as alternative materials for water purification (Li et al., 2006a; Zhang 2003; Tratnyek et al., 2006; Ngomsik et al., 2005; Vaseashta et al., 2007).

2.5.1.1 Activated Carbon

For the removal of heavy metal ions, the widely used adsorbent is activated carbon (AC). Due to its large mesopores and micropores volumes and having high surface area, activated carbon derives much importance for treating water pollution. A large number of researchers are studying the use of AC for removing heavy metals (Jusoh et al., 2007; Kang et al., 2004). Through activated carbon is a good adsorbent for removal of heavy metal ions, the depleted source of activated carbon is increasing day by day. To overcome these types of problems and to increase the adsorption efficiency doping or additives to activated carbon is necessary. Various additives have been used like alginate (Park et al., 2007), tannic acid (Ucer et al., 2006), magnesium (Yanagisawa et al., 2010), surfactants (Ahn et al., 2009) and AC composite, which are effective adsorbents for heavy metals. Activated carbon extracted from eucalyptus bark have been used for the sorption of Cu$^{2+}$ and Pb$^{2+}$ (Kongsuwan et al., 2009) with a maximum sorption capacities for Cu$^{2+}$ and Pb$^{2+}$ being 0.45 and 0.53 mmol/g. Poultry litter derived AC for treating heavy metal-contaminated water was explored (Guo et al., 2010). Results reveal that poultry litter-based AC possessed significantly higher adsorption affinity and capacity for heavy metals than commercial AC derived from bituminous coal and coconut shell. Thus there is a need of low cost adsorbents with high efficiency for the removal of heavy metal ions.

2.5.1.2 Low Cost adsorbents

Searching for low-cost and easily available adsorbents to remove heavy metal ions have become a main research focus. To date, hundreds of studies on the use of low-cost adsorbents have been published. Agricultural wastes, industrial byproducts, wastes and natural substances have been studied as adsorbents for the heavy metal wastewater
treatment. Several reviews are available that discuss the use of low-cost adsorbents for the treatment of heavy metals contained wastewater. The adsorption of few heavy metals on natural and modified kaolinite and montmorillonite has been reported (Bhattacharyya and Gupta 2008). Agricultural waste material has been reported as a potential adsorbent for sequestering heavy metal ions from aqueous solutions (Sud et al., 2008). The removal of heavy metal ions from wastewater by chemically modified plant wastes have been used as adsorbents (Wan and Hanafiah 2008; Babel and Kurniawan 2003).

Researchers investigated industrial by-products such as lignin (Betancur et al., 2009), diatomite (Sheng et al., 2009), clino-pyrrhotite (Lu et al., 2006), aragonite shells (Kohler et al., 2007), natural zeolites (Apiratikul et al., 2008), clay (Al-Jilil et al., 2009), kaolinite (Gu and Evans 2008) and peat (Liu et al., 2008), etc. for the removal of heavy metal ions. The kaolinite clay obtained from Longyan, China was tested to remove heavy metal ions such as Pb(II), Cd(II), Ni(II) and Cu(II) from wastewater (Jiang et al., 2010). The uptake is rapid with a maximum adsorption being observed within 30 min. Kaolinite clay was used for removing metal ions from real wastewater containing Pb (II), where its concentration was reduced from 160.00 mg/L to 8.00 mg/L. Zinc and copper removal from aqueous solutions were reported using brine sediments, sawdust and a mixture of both materials (Agoubordea et al., 2009). A maximum adsorption capacity was found to be 4.85, 2.58 and 5.59 mg/g for zinc and 4.69, 2.31 and 4.33 mg/g for copper, respectively.

2.5.1.3 Metal oxides

Of the various adsorbents used for water purification, nanosized metal oxides (NMOs), nanosized ferric oxides, manganese oxides, aluminum oxides, titanium oxides, magnesium oxides and cerium oxides, are the promising adsorbents for heavy metals removal from aqueous systems (Vanbenschoten et al., 1994; Coston et al., 1995; Agrawal et al., 2006). Such superior performance is due to their large surface areas and high activities caused by the size quantization effect (El-Sayed 2001).
<table>
<thead>
<tr>
<th>S.No</th>
<th>Adsorbent</th>
<th>Adsorbate</th>
<th>Temp</th>
<th>$q_m$(mg/g)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Goethite</td>
<td>Cu(II)</td>
<td>25±0.1°C</td>
<td>149.25</td>
<td>Grossl et al., 1994</td>
</tr>
<tr>
<td></td>
<td>(α-FeOOH)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Hematite</td>
<td>Cu(II)</td>
<td>25±0.1°C</td>
<td>84.46</td>
<td>Chen and Li 2010</td>
</tr>
<tr>
<td></td>
<td>(α-Fe$_2$O$_3$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>γ-Fe$_2$O$_3$</td>
<td>Cu(II)</td>
<td>25±0.1°C</td>
<td>26.8</td>
<td>Hu et al., 2006</td>
</tr>
<tr>
<td>4.</td>
<td>ZnO</td>
<td>Pb(II)</td>
<td>28±0.1°C</td>
<td>6.7</td>
<td>Ma et al., 2010</td>
</tr>
<tr>
<td>5.</td>
<td>CeO$_2$</td>
<td>Pb(II)</td>
<td>28±0.1°C</td>
<td>9.2</td>
<td>Cao et al., 2010</td>
</tr>
<tr>
<td>6.</td>
<td>TiO$_2$</td>
<td>Pb(II)</td>
<td>25±0.1°C</td>
<td>401.14</td>
<td>Engates and Shipley 2011</td>
</tr>
<tr>
<td>7.</td>
<td>Modified</td>
<td>Pb(II) and</td>
<td>25±0.1°C</td>
<td>100 and 83.33</td>
<td>Afkhami et al., 2010</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$</td>
<td>Cd(II)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2 Adsorption capacities of heavy metal ions onto metal oxides

Reports suggest that many NMOs are favorable for the sorption of heavy metals in terms of high capacity and selectivity, which would result in the removal of toxic metals to meet increasingly strict regulations (Deliyanni et al., 2009). But as the size of the metal oxides reduces from micrometer to nanometer levels, due to the increased surface to volume ratio and surface energy, it inevitably leads to their poor stability. In this view, NMOs are prone to agglomeration due to Van der Waals forces or other interactions (Pradeep and Anshup 2009), and the high capacity and selectivity of NMOs would be greatly decreased or even lost. Moreover, NMOs are unusable in fixed beds or any other flow through systems because of the excessive pressure drops (or the difficult separation from aqueous systems) and poor mechanical strength. To improve the applicability of NMOs in real wastewater treatment, they were then impregnated into porous supports of large size to obtain composite adsorbents (Pan et al., 2009). The
widely used porous supports include activated carbon, natural materials, synthetic polymeric hosts, etc. Besides traditional NMOs, magnetic NMOs have attracted increasing attentions as they can be easily separated from water under a magnetic field (Mandavian et al., 2010). Also, magnetic NMOs-based composite adsorbents allowed easy isolation from aqueous solutions for recycling or regeneration (Zhao et al., 2011). Such facile separation is essential to improve the operation efficiency and reduce the cost during water/wastewater treatment.

Since there are so many types of NMOs employed for heavy metal removal, comparison of their capacity is necessary. The operating conditions, like the solution chemistry (pH, ionic strength and ion types), temperature, experimental form (batch or column runs) are quite different from each other. Here, a simple comparison on some typical NMOs for metal removal has been made. (Table 2.2).

2.5.1.4 Metal oxides supports

NMOs provide an effective and specific adsorption towards heavy metals. Nevertheless, they are usually present as fine or ultrafine particles, which often lead to problems such as activity loss due to agglomeration, difficult separation, and excessive pressure drops when applied in flow-through systems (Cumbal and Sengupta 2005). An effective approach to overcome these technical bottlenecks is to fabricate hybrid adsorbents by impregnating or coating NMOs particles into/onto porous supports of larger size (Chen et al., 2007; Hansen et al., 2001). The widely used supports include natural hosts such as bentonite (Eren 2009; Eren et al., 2010), sand (Lee et al., 2010), and metallic oxide materials such as Al₂O₃ membrane (Zhang et al., 2006), porous manganese oxide complex (Otsu et al., 2005), and synthetic polymer hosts such as cross-linked ion-exchange resins (Pan et al., 2010; Su et al., 2009; Wan et al., 2010). Some host-supported NMOs for heavy metal removal are summarized in Table 2.3.
<table>
<thead>
<tr>
<th>S.No</th>
<th>Metal oxide</th>
<th>Support material</th>
<th>Adsorbents</th>
<th>q_m (mg/g)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Iron oxide</td>
<td>Treated municipal sewage sludge</td>
<td>Pb(II) &amp; Cd(II)</td>
<td>42.4 &amp; 14.7</td>
<td>Babel and Kurniawan 2003</td>
</tr>
<tr>
<td>2.</td>
<td>Fe₃O₄</td>
<td>Cyclodextrin</td>
<td>Cu(II)</td>
<td>47.2</td>
<td>Badruddoza et al., 2011</td>
</tr>
<tr>
<td>3.</td>
<td>Fe₂O₃</td>
<td>Sepiolite</td>
<td>Ni(II)</td>
<td>18.30</td>
<td>Lazarevic et al., 2010</td>
</tr>
<tr>
<td>4.</td>
<td>MgO</td>
<td>Diatomite</td>
<td>Pb(II) &amp; Cd(II)</td>
<td>99.0 &amp; 27.86</td>
<td>Khraisheh et al., 2004</td>
</tr>
<tr>
<td>5.</td>
<td>ZnO</td>
<td>Activated carbon</td>
<td>Pb(II)</td>
<td>100%</td>
<td>Kikuchi et al., 2006</td>
</tr>
</tbody>
</table>

Table 2.3 Metal oxide support materials for removal of heavy metal ions.

Metal oxides are explored as highly efficient adsorbents for heavy metal removal from water/wastewater. They exhibit various advantages such as fast kinetics, high capacity, and preferable sorption toward heavy metals in water and wastewater. Nevertheless, to further promote the practical application of metal oxides in abatement of heavy metal pollution, there still exist some technical bottlenecks to be solved. For instance, when applied in aqueous solution, metal oxides tend to aggregate into large-size particles and their capacity loss seems inevitable. In addition, the way to efficiently separate the exhausted metal oxides from water/wastewater still remains an interesting but a challenging task. As for column operation, the excessive pressure drop caused by metal oxides should also be considered.
Fortunately, fabrication of new metal oxides based composite adsorbents seems to be an effective approach to respond to all the above technical problems. However, it is still in the infant stage, and various issues need to be solved concerning the development of more facile processes to obtain the composite adsorbents, the answer to the interplay between the hosts and the supported metal oxides, the long-term performance of the composite adsorbents, as well as their field application in heavy metal contaminated water treatment.

2.5.2 CARBON BASED NANOMATERIALS

Of the various nanomaterials based adsorbents, carbon based materials have been probed as superior adsorbents for the removal of organics and heavy metal ions with high efficiency. Since the discovery of carbon nanotubes (CNTs) and fullerene, these materials have been extensively used as effective adsorbents but its large scale application is limited on economic grounds and hence designing adsorbent at a lower cost is a great challenge. Multiwalled carbon nanotube shows good removal efficiency of inorganic metal ions with the help of magnetic nanomaterials.

2.5.2.1 Role of Carbon nanotubes

Removal of the contaminants relies on the sorption behavior of a sorbent. CNTs, with their high surface active site to volume ratio and controlled pore size distribution, have an exceptional sorption capability and high sorption efficiency compared to conventional granular and powder activated carbon, which have intrinsic limitations like surface active sites and the activation energy of sorption. Extensive studies found that the adsorption capacity of CNTs depends on both the surface functional groups and the nature of the sorbate. For instance, the amounts of surface acidity (carboxylic, lactonic and phenolic groups) favor the adsorption of polar compounds (Rao et al., 2007). On the other hand, the un-functionalized CNT surface proved to have higher adsorption capacity towards non-polar compounds such as polycyclic aromatic hydrocarbons (Yang et al., 2006; Wang et al., 2008). The sorption behaviors of CNTs mainly involve chemical interaction for polar compounds and physical interaction for non-polar compounds, as given in Table 2.4.
Sorption capacity of CNTs is effective over a broad pH range. Particularly, an optimum performance was reported in the pH range of 7 to 10. Other than this pH range, ionization and competition between ionic species could occur (Stafiej et al., 2008). Although CNTs are more expensive compared to conventional activated carbon, their sorption and desorption cycles are more efficient.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Adsorbents</th>
<th>Metal ions</th>
<th>q_m (mg/g)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CNTs</td>
<td>Pb^{2+}</td>
<td>17.44 at pH-7.0</td>
<td>Li et al., 2002</td>
</tr>
<tr>
<td>2.</td>
<td>CNTs (HNO_3)</td>
<td>Pb^{2+}</td>
<td>49.95 at pH-7.0</td>
<td>Li et al., 2002</td>
</tr>
<tr>
<td>3.</td>
<td>MWCNTs</td>
<td>Ni^{2+}</td>
<td>7.53 at pH-7.0</td>
<td>Lu et al., 2006</td>
</tr>
<tr>
<td>4.</td>
<td>SWCNTs</td>
<td>Ni^{2+}</td>
<td>9.22 at pH-7.0</td>
<td>Lu et al., 2006</td>
</tr>
<tr>
<td>5.</td>
<td>MWCNTs (HNO_3)</td>
<td>Pb^{2+}</td>
<td>97.08 at pH-5.0</td>
<td>Li et al., 2003</td>
</tr>
<tr>
<td>6.</td>
<td>GAC</td>
<td>Pb^{2+}</td>
<td>29.44 at pH-5.0</td>
<td>Goel et al., 2005</td>
</tr>
</tbody>
</table>

Table 2.4 Heavy metal ions adsorption onto carbon nanotubes

2.5.2.2 Role of graphene materials

Due to the less adsorption onto CNTs, research has been recently focused on another allotropy of carbon, which is graphene. Graphene is a substitute for CNT and an ideal material for water treatment. Graphene based materials serve as efficient adsorbent due to their large specific surface area and electron rich environment.

Flower-like TiO_2 on GO hybrid (GO–TiO_2) has been applied for the removal of Zn^{2+}, Cd^{2+} and Pb^{2+} ions from water. The adsorption capacities of the GO–TiO_2 hybrid reached 88.9 mg/g for Zn^{2+}, 72.8 mg/g for Cd^{2+}, and 65.6 mg/g for Pb^{2+}, respectively, at pH 5.6, which are higher than either GO or TiO_2 and as shown in Table 2.5.
<table>
<thead>
<tr>
<th>S.No</th>
<th>Adsorbent</th>
<th>Adsorbate</th>
<th>$q_m$ (mg/g)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>GO</td>
<td>Pb(II)</td>
<td>35.6</td>
<td>Lee et al., 2012</td>
</tr>
<tr>
<td>2.</td>
<td>TiO$_2$/GO</td>
<td>Pb(II)</td>
<td>65.6</td>
<td>Lee et al., 2012</td>
</tr>
<tr>
<td>3.</td>
<td>GO-EDTA</td>
<td>Pb(II)</td>
<td>479</td>
<td>Madadrang et al., 2012</td>
</tr>
<tr>
<td>4.</td>
<td>GNs</td>
<td>Pb(II)</td>
<td>22.4</td>
<td>Huang et al., 2011</td>
</tr>
<tr>
<td>5.</td>
<td>GNs - 500</td>
<td>Pb(II)</td>
<td>35.2</td>
<td>Huang et al., 2011</td>
</tr>
<tr>
<td>6.</td>
<td>SiO$_2$-GNs</td>
<td>Pb(II)</td>
<td>113.6</td>
<td>Hao et al., 2012</td>
</tr>
<tr>
<td>7.</td>
<td>MnO$_2$/GNs</td>
<td>Hg (II)</td>
<td>10.8</td>
<td>Sreeprasad et al., 2011</td>
</tr>
</tbody>
</table>

Table 2.5 Graphene based nanocomposites for removal of heavy metal ions

2.5.2.3 Graphene based magnetic composites

Recently, magnetic adsorbents have attracted intensive interest in water treatment due to its easy separation and collection using a magnet. Incorporation of magnetic particles with GO or GNs offer an effective approach to overcome the separation problems associated with graphene. At the same time, loading of the magnetite nanoparticles can avoid or decrease the possibility of serious agglomeration and restacking of the graphene sheets, and consequently provide a higher available surface area and enhancement of adsorption capacity (Sun et al., 2011). A magnetite Fe$_3$O$_4$/GO composite (M/GO) for the removal of Co$^{2+}$ from aqueous solutions and investigated adsorption kinetics, equilibrium and thermodynamics. M/GO was found to have higher adsorption than that on Fe$_3$O$_4$ and can be separated and recovered by magnetic separation after adsorption (Liu et al., 2011).