CHAPTER 1
Chapter 1

Introduction

Like air, water is one of the essentials for all forms of life. Clean water is vital for the survival of all living organisms. In fact, the reactions that make up life, such as synthesis of proteins and nucleotides occurred in aqueous medium. About one third of the drinking water requirements of the world is met from surface sources like rivers, canals and lakes. But these sources serve as the best sinks for the discharge of domestic as well as industrial wastes. Industrial wastes discharged into water bodies without proper treatment usually contain several objectionable chemicals and cause heavy pollution to water sources. Water pollutants are diverse and varied in nature. They are classified into four broad categories: chemical, physical, physiological and biological. Chemical contaminants include inorganic and organic pollutants. Generally, inorganic pollutants are represented by heavy metals, whereas organic pollutants extend from small molecules such as chloroform to macrocyclic compounds such as dyes.

Heavy metals have been used in a variety of ways for at least two millennia. For example, lead had been used in plumbing, and lead arsenate had been used to control insects in apple orchards. The Romans added lead to wine for improving its taste, and mercury was used as a salve to alleviate teething pain in infants (Eaton and Robertson, 1994; Jarup, 2003). The production and use of heavy metals and related compounds have increased exponentially since the Industrial Revolution. Between 1850 and 1990, production of many metals increased nearly ten-fold, with emissions rising in tandem (Nriagu, 1996). Table 1 lists the key industrial sectors that are likely to have metal-bearing effluent discharge problems and deserve an
especially close scrutiny. Naturally, they are the most likely potential clients for removal of metals from their wastewaters (Volesky, 2001).

Table 1  
Major target industrial sectors

<table>
<thead>
<tr>
<th>Industry</th>
<th>Metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mining operations</td>
<td>Cations: Cu, Zn, Pb, Mn, U, ..</td>
</tr>
<tr>
<td>Electroplating operations</td>
<td>Anions: Cr, As, Se, V, ..</td>
</tr>
<tr>
<td>Metal processing</td>
<td>Cr, Ni, Cd, Zn</td>
</tr>
<tr>
<td>Coal-fired power generation</td>
<td>Cu, Zn, Mn,</td>
</tr>
<tr>
<td>Nuclear industry</td>
<td>Cu, Cd, Mn, Zn, ..</td>
</tr>
<tr>
<td>Special operations</td>
<td>U, Th, Ra, Sr, Eu, Am, Co, ..</td>
</tr>
<tr>
<td></td>
<td>Hg, Au and precious metals</td>
</tr>
</tbody>
</table>

Even though metallic elements are an intrinsic component of the environment, their presence is considered unique in the sense that it is difficult to remove them completely from the environment once they enter into it. They can be carried to places far away from the source by the winds depending on their physical state such as in gaseous form or particulates. The metals are present in all components of the environment – atmosphere, land and aquatic systems. Metallic pollutants are ultimately washed out of the air by rain onto land or the surface of the waterways. Thus, air is also a route for the contamination of the environment. Metals are also added to the environment from domestic sewage discharge, street dust, land runoff and fossil fuel burning.

1.1 Metal Toxicity

Heavy metals are regarded as man’s worst endeavour in his attempt to augment industrial development and are nicknamed as ‘devils in disguise’. One indication of
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their importance relative to other potential hazards is their ranking by the U.S. Agency for Toxic Substances and Disease Registry (ATSDR), which lists all hazards present in toxic waste sites according to their prevalence and the severity of their toxicity (www.atsdr.cdc.gov/mrls.html). It is widely accepted that one billion human beings are currently exposed to elevated concentrations of toxic metals and metalloids in the environment and several million people may be suffering from subclinical metal poisoning (Subramanian, 2002).

The toxicity of these metals has also been documented throughout history: Greek and Roman physicians diagnosed symptoms of acute lead poisoning long before toxicology became a science (Silver and Rothman, 1995). Today, much more is known about the health effects of heavy metals. Exposure to heavy metals has been linked with developmental retardation, various cancers, kidney damage, and even death in some instances of exposure to very high concentrations. Exposure to high levels of mercury, cadmium, and lead has also been associated with the development of autoimmunity, in which the immune system starts to attack its own cells, mistaking them for foreign invaders. Autoimmunity can lead to diseases of the joints and kidneys, such as rheumatoid arthritis, or diseases of the circulatory or central nervous systems.

Since most of the heavy metal salts are soluble in aqueous medium, transport of these toxic materials into organisms is easy. Once entered into the life stream they can interact in biochemical processes, and thus topple the routine life course (Klein, 1996). Toxicity of heavy metals is highly dependent on the concentration, the level of oxidation, the period of retention in living systems and the solubility of compounds. Heavy metal toxicity manifests itself in several forms which include blocking essential functional groups of biomolecules, such as proteins and enzymes, displacing essential metal ions from biomolecules disrupting the integrity of biomembranes, or binding with bioanions to result in a decreased level of
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essential bioanions. Heavy metals form stable complexes with molecules containing donor atoms like N, O or S and thus tend to persist indefinitely. They annihilate large number of enzymes, preventing the normal function of various organs.

1.2 Common Metal Removal Processes

The complex question facing the design engineers and public health officials is: what levels of treatment must be achieved in a given application – beyond those prescribed by discharge permits – to ensure protections of public health and environments. The increased levels of contaminant removal not only enhance the product for reuse but also lesser health risks. The technologies used for the heavy metal removal are listed in Table 2. Some of the conventional techniques are becoming progressively more inadequate in the present context when the emission standards become strict. On the other hand, some of the better technologies are not suitable because of high cost. In addition to being expensive, they are not efficient when the metal concentration is low. Therefore, numerous approaches have been studied to develop cheaper alternatives that are also efficient in treating wastewater with low metal ion concentration.
<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical precipitation, coagulation, flocculation and filtration</td>
<td>Simple, cheap</td>
<td>Applicable only for higher concentrations, separation difficult, not very effective, result in the formation of sludges, handling and disposal problems</td>
</tr>
<tr>
<td>Biodegradation</td>
<td>Economically attractive, publicly acceptable treatment</td>
<td>Slow process, needs optimal favourable environment, Maintenance and nutrition requirements</td>
</tr>
<tr>
<td>Chemical oxidation or reduction</td>
<td>Mineralization, rapid and efficient process</td>
<td>Chemicals required, high energy cost, formation of by-products slow rates</td>
</tr>
<tr>
<td>Electrochemical treatment</td>
<td>Metal recovery, purity</td>
<td>Only for high concentrations, Expensive</td>
</tr>
<tr>
<td>Reverse osmosis, membrane process</td>
<td>Pure effluent for recycle</td>
<td>High pressures, membrane scaling, expensive, incapable of treating large volumes, fouling</td>
</tr>
<tr>
<td>Ion exchange</td>
<td>Effective</td>
<td>Sensitive to particles, expensive resins</td>
</tr>
<tr>
<td>Evaporation</td>
<td>Pure effluent for recycle</td>
<td>Energy intensive, expensive, resulting sludges</td>
</tr>
</tbody>
</table>
1.2.1 Biological treatments

Biological treatment involves biodegradation methods such as fungal decolourisation, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation which are commonly applied to the treatment of organic industrial effluents because many microorganisms such as bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants (McMullan et al., 2001). However, their application is often restricted because of technical constraints. Biological treatment requires a large land area and is constrained by sensitivity towards diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation (Bhattacharyya and Sarma, 2003). This treatment technology is not feasible for the cleanup process of metal-bearing wastewaters.

1.2.2 Chemical methods

Chemical methods include coagulation or flocculation combined with floatation and filtration, precipitation, flocculation with Fe(II)/Ca(OH)\textsubscript{2}, electrofloatation, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes. The conventional process for treating liquid effluents containing metals ions is precipitation–aggregation (coagulation/flocculation)-settling as hydroxides or insoluble salts. However, this method, from a technical point of view, presents certain limitations (Rubio et al., 2002), namely:

- the formation of metal hydroxide is ineffective in dilute metal bearing effluents;
- the hydroxo precipitate tends to re-dissolve, depending on the metal;
• the pH of minimum solubility of hydroxides is different for the various metals present. For example, the minimum solubility for cupric hydroxide occurs at a pH value around 9.5 while for cadmium hydroxide it occurs around 11.0;

• precipitation of metals becomes incomplete when complexing or chelating agents are present;

• volumes of sludge formed are too large and with a high water content; and to destruct or transform or to dispose of the metal-bearing sludges are extremely difficult. Since the sludges are also classified as toxic substances they require special methods for handling – in storing, transportation and disposal;

• filtration may be difficult as a result of the fineness of the precipitates;

• the treatment by coagulation and settling of effluent flow-rates of about 2–4 m³/s is very difficult and costly due to the kinetic and scale problems;

• the precipitation itself cannot reduce the contaminant far enough to meet current water-quality standards;

• chemical techniques are often expensive;

• secondary pollution problem will arise because of the excessive chemical use;

Recently, other emerging techniques, known as advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for pollutant degradation. Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are other problems.
1.2.3 Physical methods

Different physical methods are also widely used, such as membrane-filtration processes (nano filtration, reverse osmosis, electrodialysis) and adsorption techniques. The major disadvantage of the membrane processes is that they have a limited lifetime before membrane fouling occurs and the cost of periodic replacement must thus be included in any analysis of their economic viability. Polyelectrolyte-enhanced ultrafiltration (PEUF) is a novel separation process that can remove low-concentration ionic species from aqueous solution and is particularly effective for multivalent ions (Pookrod et al., 2004). This process includes the addition of water-soluble polymer followed by the ultrafiltration operation. The polymer is a polyelectrolyte of opposite charge to the target ions.

1.3 Adsorption

In accordance with the very abundant literature data, liquid-phase adsorption is one of the most popular methods for the removal of pollutants 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 waters, especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application. Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications.

1.3.1 Adsorption - the pivot role

The vast development in the field of adsorption science and technology has been extended to multi-fold applications such as in the fields of laboratory, research, industry, agriculture, engineering, materials science, environmental protection and is dispersed in tens of thousands of articles, patents and non-published reports.
Many adsorption operations employing solids such as activated carbons and synthetic resins are used widely in industrial applications and for purification of waters and wastewaters.

Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation, versatility of adsorbents and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances. Other main advantages of adsorption process for water treatment include the relatively small amount of inert materials that can be disposed, the possible recovery and release of ingredient chemicals, savings in chemical costs and ability to adjust removal efficiencies to almost any desired minimum national standards by varying the concentration during adsorption steps.

From the early days of using bone char for decolourisation of sugar solutions and other foods to the later implementation of activated carbon for removing nerve gases from the battlefield, to today’s thousands of applications, the adsorption phenomenon has become a useful tool for purification and separation.

1.4 Theoretical Basis of Adsorption

The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate. Adsorption is thus different from absorption, a process in which the material transferred from one phase to another (e.g. liquid) interpenetrates the second phase to form a "solution". The term sorption is a general expression encompassing both processes.

Physical adsorption is caused mainly by van der Waals forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent
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surface. Thus adsorbents are characterized first by surface properties such as surface area and porosity. A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores. Most of the solid adsorbents of great industrial applications possess a complex porous structure that consists of pores of different sizes and shapes. In terms of the experience of adsorption science, total porosity is usually classified into three groups. The micropores are defined as pores of a width not exceeding 2 nm, mesopores are pores of a width between 2 and 50 nm, but macropores represent pores of a width greater than 50 nm. Nowadays, the expression ‘nanopore’ is used to encompass both micropores and mesopores. The size of the micropores determines the accessibility of adsorbate molecules to the internal adsorption surface, so the pore size distribution of micropores is another important property for characterizing adsorptivity of adsorbents (Gregg and Sing, 1982). Materials such as zeolite and carbon molecular sieves can be specifically engineered with precise pore size distributions and hence tuned for a particular separation.

Surface polarity corresponds to affinity with polar substances such as water or alcohols. Polar adsorbents are thus called "hydrophilic". Aluminosilicates such as zeolites, porous alumina, silica gel or silica-alumina are examples of adsorbents of this type. On the other hand, nonpolar adsorbents are generally "hydrophobic". Carbonaceous adsorbents, polymer adsorbents and silicates are typical nonpolar adsorbents. These adsorbents have more affinity with oil or hydrocarbons than water.

The effectiveness of the adsorbent in liquid-phase adsorption is normally assessed by its adsorption capacity which in turn is attributed to many factors. The adsorbate–adsorbent interaction plays an important role as well as that between adsorbate and solvent. Since adsorption is an interfacial phenomenon involving aqueous and solid phases, both the sorbent and sorbate characteristics influence the
process. Factors that affect sorbent characteristics are sorbent structure, surface charge, particle size, porosity and surface area, while the factors influencing sorbate properties include hydrophobicity, water solubility, molecular weight, size and charge. Solution properties such as pH, ionic strength and temperature have an impact on both sorbent and sorbate. Adsorption of solute from solution is greatly influenced by the competition between the solute and the solvent for adsorption sites.

1.4.1 Design of adsorption systems

There are several models of design of adsorption systems depending on the mode of contact of the solid adsorbent and the adsorbate containing solution. According to McKay (1995) the main six types are 1) batch type contact, 2) fixed-bed type process, 3) pulsed bed, 4) steady-state moving beds, 5) fluidized bed and 6) moving mat filters.

Batch type adsorption experiments are carried out through the addition of a measured quantity of adsorbent to a known volume of adsorbate solution in an adsorber. The adsorbate solution and the adsorbent are maintained in contact within the adsorber. The adsorber is partially submerged in a constant temperature flask shaker and the solution within the flask is stirred continuously for a predetermined period. The equilibrium solution is separated from the adsorbent by filtration. But batch type processes are usually limited to the treatment of small volumes of effluent. Although batch laboratory adsorption studies provide useful information on the application of adsorption to the removal of specific waste constituents, continuous column studies provide the most practical application of this process in wastewater treatment. The reason for this is that the high adsorption capacities in equilibrium with the influent concentration rather than the effluent concentration can be achieved. In static mode adsorption studies, the same solution
remains in contact with a given quantity of the adsorbent. The adsorption process continues, however, till equilibrium between the solute concentration in solution, and the solute adsorbed per unit weight of the adsorbent is reached. This equilibrium established is static in nature as it does not change further with time. In dynamic column adsorption, the solution continuously enters and leaves the column so that the complete equilibrium is never established at any stage between the solute in solution and the amount adsorbed. Equilibrium has to be continuously established, as each time, it meets the fresh concentrations, and hence, equilibrium in column mode is termed as dynamic equilibrium.

As fixed-bed reactor is able to treat wastewater in large quantities, it is more preferable than batch reactor in industrial applications (Chen and Wang, 2004). Although it has successfully been applied in the removal of organic contaminants its application for metal waste treatment is not well studied. In order to design and operate fixed-bed reactor for heavy metal removal, an accurate modeling is important, which can be done by solving a series of nonlinear partial differential equations. The calculation is normally very time-consuming and complicated. Hence it is desirable to use simplified, explicit expressions to represent the rate of interphase mass transfer. The assumption of linear driving force was used to simulate organic adsorption (Tien, 1994). However, its application in metal adsorption calculation has not been reported in the literature. Many batch-processing industries now consider that batch adsorption plant is more suitable for their requirements.

Some studies optimize multi-stage batch adsorber systems to be based on minimizing the amount of adsorbent and assuming sufficient residence time allowed for the adsorption system to reach equilibrium or at least 70–80% equilibrium capacity. This approach is suitable for expensive adsorbent such as zeolites, molecular sieves, activated carbon, etc. but optimization based on minimizing the amount of adsorbent, may not always be the main criterion. Due to
size and space limitations on congested industrial sites, the treatment capacity of a batch adsorption plant may be limited. The ability of a batch adsorption plant must then be designed based on the ability of this treatment system to process several batches of process effluent per day rather than using a minimum quantity of adsorbent and utilizing a maximum contact time to achieve equilibrium saturation.

Inspite of the above observations, a majority of the adsorption investigations were conducted in the batch mode (Goel et al., 2005). Usually, the adsorption/desorption equilibrium and kinetics for the metal onto the adsorbent are evaluated in the batch adsorber (Wase et al., 1997; Li et al., 2003). The measured model parameters like adsorption equilibrium parameters and the effective intraparticle diffusivity, kinetic parameters etc., are then used to predict the performance of industrial processes such as chromatography, expanded bed and simulated moving bed. Therefore, modeling separation of metal by the adsorbent in a batch adsorber will be important, which is our objective in the present work.

1.5 Equilibrium Isotherms

The adsorption of a substance from one phase to the surface of another in a specific system leads to a thermodynamically defined distribution of that substance between the phases as the system reaches equilibrium. Sorption equilibria provide fundamental physicochemical data for evaluating the applicability of sorption processes as a unit operation. Sorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the sorbent, at a fixed temperature and pH. Thus an accurate mathematical description of the equilibrium isotherm, preferably based on a correct sorption mechanism, is essential for the effective design of sorption systems and to assess their suitability for application in the field of water pollution control. The cost and performance of a product or the mode of application which are always a concern to
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control process efficiency are understood properly by knowing the sorption capacity and the contact time required for attaining adsorption equilibrium (Ho et al., 2000). Sorption equilibrium is established when the concentration of sorbate in the bulk solution is in dynamic balance with that of the interface.

Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbed and the remaining of the solution. Adsorption isotherms describe how adsorbates interact with adsorbents. They are critical in optimizing the use of adsorbents and fundamentally important in the design of sorption systems. Thus, the correlation of equilibrium data by either theoretical or empirical equations is essential for the practical design and operation of adsorption systems.

1.5.1 Shapes and classifications of isotherms

Isotherm shape can provide quasi-qualitative information on the nature of the solute–surface interaction. The most popular classification of adsorption isotherms of solutes from aqueous solutions has been proposed by Giles et al. (1974a; 1974b). Four characteristic classes (i.e., class S, L, H, C) are identified, based on the configuration of the initial part and curvatures of the isotherm (Figure 1). They distinguished between high affinity H, Langmuir L, constant partition C and sigmoidal-shaped S isotherm classes (Figure 1). To account for plateaus, points of inflection, and maxima, they further distinguished between subgroups in each class shown in rows 1 to 5 of Figure 1. Generally, S isotherms have a concave shape at low concentrations. While both H and L isotherms have a convex shape, the slopes of H isotherms reach high values whereas the slopes of L isotherms remain constant. This indicates that the sorption affinity of H isotherms increases with decreasing concentration. C isotherms are defined by a constant sorption affinity, expressed as straight line plots.
The Langmuir class (L) is the widespread isotherm in the case of adsorption of many species from water, and it is characterized by an initial region, which is concave to the concentration axis. However, the H class (high affinity) results from extremely strong adsorption at very low concentrations giving rise to an apparent intercept on the ordinate. The subgroups relate to the behaviour at higher concentrations. Subgroup 1 shows no plateau, whereas Subgroup 2 is characterized by one plateau. Subgroup 3 has an inflection point due to a change from a plateau to a concave shape. Two plateaus are characteristic of Subgroup 4 isotherms. The unusual behaviour of decrease in amount adsorbed with increase in equilibrium concentration is shown by Group 5. Giles et al. (1974a) used the classification to describe data rather than equations, and they used qualitative criteria lacking mathematical formalism. To apply this classification to isotherm equations, mathematical criteria must be used (Hinz, 2001).

Brunauer and his co-workers have classified physical adsorption isotherms into five characteristic types shown in Figure 2 based on the difference in adsorption behaviour of different gases onto various solid supports (Adamson, 1990; Tien, 1994). Three phenomena may be involved in physical adsorption: monomolecular and multimolecular, adsorption and condensation in pores or capillaries. So the interpretation of adsorption studies can be complicated.
Figure 1
Giles' classification of isotherm shapes

Type I is characterized by a monotonic approach to a limiting adsorption that seemingly corresponds to a complete monolayer. Type II corresponds to multilayer formation. At high concentrations, the adsorbed quantity is divergent; i.e., there is a condensation phenomenon representing a multilayer model. Type III is rare, seems to be characterized by a heat of adsorption equal to or less than the heat of
liquefaction of the adsorbate. Types IV and V reflect capillary condensation phenomenon. The adsorption isotherm of Type IV is the same as that of Type I. The only difference between the two types of isotherms is that the concavity in the case of Type IV is positive at low concentrations. The adsorption isotherm of Type V is similar to that of Type II except the behaviour at low concentrations. The molecules, which are adsorbed at low concentrations, present a sort of dimerization and not a multi-anchorage as could be foreseen for the Type II (Khalfaoui et al., 2003).

The International Union of Pure and Applied Chemistry (IUPAC) gives a different classification of sorption phenomena of gas–solid systems (Sing et al., 1985). This classification is based on physical adsorption of gases measured in porous or on dense solid materials. In addition to different shapes, it takes into account different types of hysteresis loops that are caused by capillary condensation in pores. Type I is characterized by a constant sorption maximum and a convex shape and is equivalent to the L2 and H2 isotherms of Giles’ classification. Type II exhibits an inflection point at which the shape changes from convex to concave similar to the L3 and H3 isotherms. A concave isotherm is classified as Type III and has its equivalent in the S1 isotherm of the Giles’ classification. Type IV has two plateaus and is thus similar to the L4 and H4 isotherms. A concave isotherm with a sorption maximum is referred to as Type V, which is the same as the S2 isotherm. Finally Type VI isotherms belong to the L and H classes with multiple plateaus. The Giles’ classification is more suitable for the general description of sorption isotherms especially when the retention processes are unknown (Hinz, 2001). In the IUPAC recommendations there are six physical adsorption isotherm types, while only five types of isotherms are presented in the Brunauer, Emett and Teller (BET) classifications.
1.6 Equilibrium Approach: Isotherm Models

The preliminary requirement to predict the nature and type of isotherm equation is only possible by the adequate description of sorption data. This involves two
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steps: first, choosing an equation that will describe the data with a given accuracy and second, regression methods to find an optimal parameter set. These two steps are of course not completely independent, because the goodness of fit criteria obtained from parameter estimation often suggests how well an equation describes the data. As yet, no inspectional analysis exists that allows researchers to easily determine the type of isotherm equation that best fits a specific data set.

Owing to these difficulties, empirical design procedures based on adsorption equilibrium conditions have been commonly used to predict the adsorber size and performance. The different parameters and the underlying thermodynamic assumption of these equilibrium models often provide some insights into both the sorption mechanism and the surface properties and affinity of sorbent. The most commonly used equilibrium models are Freundlich, Langmuir, Scatchard, Redlich-Peterson, Dubinin-Radushkevich, Temkin, Toth and Harkins-Jura isotherm models. Among these Freundlich, Langmuir, Scatchard, Temkin and Dubinin-Radushkevich, and Harkins-Jura isotherms are two-parameter equations and Redlich-Peterson and Toth isotherms are three-parameter equations (Table 3).

Freundlich presented the earliest known sorption isotherm equation (Freundlich, 1906). This empirical model can be applied to non ideal sorption on heterogeneous surfaces as well as multilayer sorption. The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. It lacks a fundamental thermodynamic basis since it does not reduce to Henry’s law at low concentrations.

The Langmuir adsorption isotherm assumes that the adsorbed layer is one molecule in thickness and the sites are homogeneous (Langmuir, 1916). The strength of the inter-molecular attractive forces is believed to fall off rapidly with distance. The equilibrium representing the Langmuir isotherm thus confirms the monolayer coverage of solute particles onto sorbent particles and also the
equilibrium curve follows Henry's law at lower initial solute concentrations. Moreover, the Langmuir equation is based on the assumption of a structurally homogeneous adsorbent where all sorption sites are identical and energetically equivalent. Theoretically, the sorbent has a finite capacity for the sorbate. Therefore, a saturation value is reached beyond which no further sorption can take place. The Scatchard isotherm represents intermediate situations, close to the Langmuir model.

Apart from Freundlich and Langmuir isotherm models, the most often-used equilibrium model is Redlich-Peterson model, which incorporates the advantageous significance of both the Freundlich and the Langmuir models (Redlich and Peterson, 1959). Redlich-Peterson isotherm equation represents the equilibrium curve to follow Henry's law and the curve behaviour follows Freundlich isotherm equation at higher initial solute concentrations. Another most commonly used equilibrium model to predict the sorption nature is the Dubinin-Radushkevich model and it is used to calculate the mean free energy of sorption as it is transferred to the surface of solid from infinite distance in the solution. Also the results are mainly used to identify whether chemisorption is involved. If the calculated bonding energy falls between 8 and 16 kJ/mol, it is an indication that chemisorption plays a significant role in the adsorption process. However, at the same time, the Dubinin-Radushkevich equation is known for its incorrect thermodynamic behaviour at two points of the isotherm. This has obviously narrowed somewhat its ability to fit adsorption data and limited its application in thermodynamic analyses of adsorption processes (Jakubov and Mainwaring, 2002).

The dependence of temperature on equilibrium capacity can be identified based on the heat of adsorption value using the Temkin isotherm equation. The Temkin isotherm can be used to describe binding-site heterogeneity (Stumm and Morgan, 1981). Derived from potential theory, Toth isotherm has proven to be
useful in describing sorption in heterogeneous systems. It assumes an asymmetrical quasi-Gaussian energy distribution with a widened left-hand side, i.e., most sites have sorption energy less than the mean value (Ho et al., 2002). The Langmuir, Toth, and Redlich–Peterson isotherm equations can describe L-type isotherm (Hinz, 2001).

**Table 3**  
*Various adsorption isotherm models*

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Mathematical equation</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>[ q_e = \frac{Q^0 b C_e}{1 + b C_e} ] (1.1)</td>
<td>( q_e ) is the amount sorbed, ( C_e ) is the equilibrium concentration, ( Q^0 ) is the monolayer coverage, and ( b ) is a Langmuir constant.</td>
</tr>
<tr>
<td>Freundlich</td>
<td>[ q_e = K_F C_e^{1/n} ] (1.2)</td>
<td>( K_F ) and ( 1/n ) are Freundlich isotherm constants</td>
</tr>
<tr>
<td>Scatchard</td>
<td>[ \frac{q_e}{C_e} = K_S (Q^0_S - q_e) ] (1.3)</td>
<td>( K_S ) and ( Q^0_S ) are Scatchard isotherm constants</td>
</tr>
</tbody>
</table>
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Redlich–Peterson

\[ q_e = \frac{K_R C_e}{(1 + a_R C_e^\beta)} \]  

(1.4)

\( q_e \) is the amount of adsorbed

\( C_e \) is the equilibrium concentration of adsorbate

\( K_R, a_R \) and \( \beta \) are three empirical coefficients. (The value of the exponent \( \beta \) lies between 0 and 1).

Dubinin–Radushkevich

\[ q_e = q_D \exp \left(-B_D \left[ \frac{RT}{n} \ln \left(1 + \frac{1}{C_e}\right) \right]^2 \right) \]  

(1.5)

\( B_D \) and \( q_D \) are Dubinin–Radushkevich isotherm constants

Temkin

\[ q_e = \frac{RT}{b_T} \ln (A_T C_e) \]  

(1.6)

\( A_T \) and \( b_T \) are Temkin isotherm constants

BET

\[ \frac{C_e}{x(C_0 - C_e)} = \frac{1}{x_m k} + \frac{(k-1) C_e}{x_m k C_o} \]  

(1.7)

\( k \) is a constant related to the energy (enthalpy) of adsorption.

Toth

\[ q_e = \frac{K_t C_e}{(a_t + C_e)^{1/t}} \]  

(1.8)

\( t \) is Toth isotherm exponent and \( a_t \) and \( K_t \) are Toth isotherm constants
The main advantages of the equilibrium approach includes reduction of the work load, easier interpretation of experimental data (it does not consider the complex mechanistic part involved before the attainment of equilibrium stage) and interpretation of the nature of adsorption process, as each equilibrium model is possible on a definite mechanical/theoretical assumption. Though a number of models are available, it is the duty of the designer to predict/select the best equilibrium model.

1.7 Surface Complexation Models

An empirical or semi-empirical modeling approach by the use of adsorption isotherms is only applicable to a specific set of conditions such as concentration range, pH and Eh and would consequently be of limited use in modeling the migration of heavy metals or their complexes in groundwater systems (Guclu and Apak, 2003). The interactions of ions with a solid in a suspension are highly dependent on the behaviour of the solid–solution interface (Ordoñez-Regil et al., 2003). The surface develops electrical charges depending on the pH of the suspension. Then, the charged metal ions interact with these surface charges. Molecular-scale information is required to develop mechanistically accurate thermodynamic models of sorption. Therefore, before any sorption experiment, it is necessary to have accurate knowledge of the surface behaviour of the adsorbent in the solution (Goldberg and Johnston, 2001). Descriptions of metal ion adsorption behaviour require knowledge of the mode of bonding of the ions on solid surfaces.

In principle, there are four major models to describe the adsorption of ions onto solid surfaces. They are the Gouy–Chapman–Stern–Grahame model, the ion exchange model, the ion–solvent interaction model and the surface complex formation model (Yiacoumi and Tien, 1995). All these models primarily assume
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that adsorption is the result of a reaction between the ionic species and the ionized surface sites of the adsorbent. Another common feature of these models is the consideration of electrical double layer which is present immediately adjacent to the adsorption surface which develops due to the charges associated with the adsorbent surface and the variation of the ionic solution concentration with the distance from the surface.

In variable charge models, the overall charge at the surface \( \sigma_0 \) is a basic property that can be established by counting the number of the various types of groups and their corresponding charges that are present at the interface. Since the surface oxygen charge is only partially neutralized by protons and partially by the metal ions, the total charge of the surface groups depends on the degree of neutralization coming from the metal ion in the solid as well as on the adsorbed protons. Depending on the solution pH, an excess or a deficiency of protons may be present at the interface, which leads to a positively or negatively charged surface, respectively. This surface charge is compensated by the electrolyte ions in a double layer, normally assumed to be a diffuse double layer (DDL). The concentration of the counter ions increases towards the surface. The co-ion concentration follows the opposite trend. The ions present in the DDL are hydrated and have a finite size, thereby preventing charge neutralization starting directly from the packed and metal hydroxide. The counter and co-ions have a distance of closest approach to the surface. This has led to the formulation of a charge-free layer, called the stern layer. This double-layer picture has been described as the basic stern model.

Unfortunately in contrast to well-defined minerals, natural materials, soils, and waste products are a composite of various mineral phases and natural organic matter that may cause problems in the assessment of surface electrical potentials and other double-layer properties of natural materials are extremely complex rendering the determination of double layer parameters for these materials quite
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difficult. Simplified theoretical treatments of interacting double-layers of dissimilar surfaces suggest that substantially different surface potentials result from the interaction.

Surface complexation models (SCMs) are chemical models that have been used to describe ion adsorption on oxide minerals (Hiemstra and Van Riemsdijk, 1996). Hydroxide and oxide interfaces are characterized by oxygen atoms bound together by metal (M) ions present in the bulk of the solid. The atoms of the oxygen at the interface of (hydr)oxides may in principle bind protons in two consecutive steps, forming $\text{OH}^-$ and $\text{OH}_2^-$ ligands, respectively. The amphoteric behaviour of a surface site corresponds to the following equilibria:

$$
\equiv \text{SOH} + \text{H}^+ \rightleftharpoons \text{SOH}_2^+
$$

(1.9)

$$
\equiv \text{SOH} \rightleftharpoons \text{SO}^- + \text{H}^+
$$

(1.10)

The expressions for the thermodynamic equilibrium constants are

$$
K_1 = \frac{[\text{SOH}_2^+]}{[\text{SOH}][\text{H}^+] \exp \left( \frac{F \psi_0}{RT} \right)}
$$

(1.11)

$$
K_2 = \frac{[\text{SO}^-][\text{H}^+]}{[\text{SOH}] \exp \left( \frac{F \psi_0}{RT} \right)}
$$

(1.12)

where $F$ is the faraday constant, $\psi_0$ the surface electrostatic potential, $R$ the ideal gas constant, and $T$ the temperature expressed in kelvin. Moreover, $K_1$ and $K_2$ are linked together by:

$$
\frac{\log K_1 + \log K_2}{2} = \text{pH}_{\text{pzc}}
$$

(1.13)

where $\text{pH}_{\text{pzc}}$ is the pH point of zero charge.
The basic modes of adsorption assumed by SCM are as follows:

1. The uncomplexed metal ion (M$^{2+}$) binds to the hydrated oxide surface (=SOH) via inner-sphere association (isa), forming a covalently bound surface complex (=SOM$^+$) and releasing protons (H$^+$) from the surface,

\[ M^{2+} + \equiv SOH \leftrightarrow SOM^+ + H^+ \quad (1.14) \]

2. The complexed metal as the anionic MY$^{2-}$ complex binds to the positively charged surface (=SOH$^+$) to yield an essentially electrostatically held (ionic) surface complex (=SOH$^+$ . . . MY$^{2-}$) via outer-sphere association (osa), the process requiring a protonated surface (=SOH$^+$),

\[ MY^{2-} + \equiv SOH^+_2 \leftrightarrow SOH^+_2 \ldots MY^{2-} \quad (1.15) \]

3. The complexed metal as the anionic MY$^{2-}$ complex may also bind to the surface (not necessarily positively charged (=SOH) via outer-sphere association to yield a partly covalently held surface complex (=SOH MY$^{2-}$) by interaction either between the uncoordinated site of a coordinatively unsaturated metal complex and the surface oxygen.

\[ MY^{2-} + \equiv SOH \leftrightarrow SOHMY^{2-} \quad (1.16) \]

1.8 Adsorption Dynamics and Kinetic Models

Eventhough equilibrium analysis is the most important fundamental information required to evaluate the affinity or capacity of a sorbent, this thermodynamic data alone cannot predict the final state of the system from an initial non-equilibrium mode. Therefore it is important to find out how sorption rates depend on factors like, the concentrations of sorbate in solution, temperature, amount and character
of the sorbent. From the kinetic analysis, the solute uptake rate, which determines the residence time required for completion of the sorption reaction, may be established. Several steps can be used to express the mechanism of solute sorption onto a sorbent.

The sorption process can be described by four consecutive steps:

1. transport in the bulk of the solution;
2. diffusion across the liquid film surrounding the sorbent particles;
3. particle diffusion in the liquid contained in the pores and in the sorbate along the pore walls;
4. sorption and desorption within the particle and on the external surface.

To investigate the mechanism of metal sorption and the potential rate controlling steps, such as diffusion mass transport and chemical reaction processes, it is necessary to characterize the main sorption mechanisms. Diffusion processes can be controlled by film/external boundary layer diffusion, diffusion in the liquid-filled pores of adsorbents or surface diffusion of sorbed-soluble molecules that migrate along the surface of the adsorbent. The rate controlling mechanism may be one diffusional mass transfer resistance or a combination of two or three of these processes. Thus any of the four steps described earlier or any combination of the steps may be the rate controlling factor (Choy et al., 2004). However, in a fully mixed agitated tank, mass transport from the bulk solution to the external surface is usually fast. The transport of sorbate from the bulk of the solution to the exterior film surrounding the adsorbent is usually neglected. In addition, the adsorption of sorbate at surface sites (Step 4) is usually rapid. Thus, these processes usually are not considered to be the rate-limiting steps in the sorption process. However, if the adsorbent is a natural material, it will be composed of several thousand different
chemical species that could be involved in a wide range of mechanisms, such as physical adsorption, ion exchange with several organic acids, chelation, lone pair electron sharing, chemical reaction with phenolic hydroxyls or other similar species. Transport in the solution is sometimes rate determining in large-scale field processes. Many experimental sorption systems are designed to eliminate the effect of transport in the solution by rapid mixing so that it does not become rate limiting. To establish the sorption mechanism, knowledge of the rate equations explaining the reaction system is required. A number of equations have been used by various researchers for describing the kinetics of adsorption. These include first-order, second-order and two-constant rate equations.

1.8.1 *Pseudo-first-order forward reaction*

The Lagergren rate equation is considered as the first rate equation for the sorption in liquid/solid systems based on solid capacity (Lagergren, 1898). It is the most widely used rate equation for sorption of a solute from a liquid solution.

\[
\frac{dq_t}{dt} = k_1(q_e - q_t)
\]  \hspace{1cm} (1.17)

where \( k_1 \) is the rate constant of first-order adsorption, \( q_e \) and \( q_t \) denote the amount of adsorption at equilibrium and at time ‘\( t \)’ respectively. Integrating equation (1.17) for boundary condition \( t=0 \) to \( t=t \) and \( q_i=0 \) to \( q_i = q_t \) gives

\[
\log(q_e - q_t) = \log q_e - \frac{k_1t}{2.303}
\]  \hspace{1cm} (1.18)

The equation applicable to experimental results generally differs from a true first-order equation in two ways:
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1. The parameter \( k_i(q_e - q_i) \) does not represent the number of available sites.

2. The parameter \( \log (q_e) \) is an adjustable parameter and often it is not found not equal to the intercept of a plot of \( \log (q_e - q_i) \) against \( t \), whereas in a true first-order equation, \( \log (q_e) \) should be equal to the intercept of a plot of \( (q_e - q_i) \) against \( t \).

In order to fit equation (1.18) to experimental data, the equilibrium sorption capacity, \( q_e \), should be known. In many cases \( q_e \) is unknown, as chemisorption tends to become unmeasurably slow while the amount sorbed is still significantly smaller than the equilibrium amount. In many cases from the literature, the pseudo-first-order equation of Lagergren does not fit well over the range of contact times under investigation (Ho and McKay, 1999; Ho et al., 2000). Furthermore, one has to find some means of extrapolating the experimental data to \( t \) infinity, or treat \( q_e \) as an adjustable parameter to be determined by trial and error. For this reason, it is necessary to use a trial and error solution method to obtain the equilibrium sorption capacity, \( q_e \).

1.8.2 Reversible first-order reaction

A reversible first-order rate expression based on solution concentration has been developed by Bhattacharya and Venkobachar (1984) for the adsorption reaction

\[
A \rightleftharpoons B \tag{1.19}
\]

At equilibrium,

\[
\frac{dC_B}{dt} = - \frac{dC_A}{dt} = C_{A_i} \frac{dX_A}{dt} = k_1C_A - k_2C_B = k_1(C_{A_i} - C_{A_i}X_A) - k_2(C_{B_i} - C_{A_i}X_A) \tag{1.20}
\]
where \( C_B \) is the concentration of adsorbate in the sorbent at any time, \( C_A \) the concentration of the sorbate in solution at any time, \( C_{Ai} \) and \( C_{Bi} \) the initial concentrations of the adsorbate in solution and on the sorbent, respectively, \( X_A \) the fractional conversion of solute material and \( k_1 \) and \( k_2 \) the first-order rate constants. After necessary rearrangements, elimination, factorization and integration of equation (1.20) gives

\[
-\ln \left( 1 - \frac{X_t}{X_e} \right) = k' t 
\]

(1.21)

where \( X_t \) and \( X_e \) are the fractional conversion of the adsorbate at time \( t \) and at equilibrium respectively. A plot of \(-\ln \left( 1 - \frac{X_t}{X_e} \right) \) versus time gives a straight line and from the slope \( k' \) can be obtained. Equation (1.21) may be considered as a pseudo-first-order reversible process.

1.8.3 Second-order reaction

Gosset et al. (1986) proposed a possible mechanism to describe metal removal by peat as per the following equations

\[
P + M \rightleftharpoons PM, \\

\text{with } K^1 = \frac{(PM)}{(P)(M)} = \frac{k_f}{k_r} 
\]

(1.22)

where \( (P) \) is the concentration of peat binding sites (mg/L), \( (PM) \) is the concentration of metal bound to peat (mg/L), and \( (M) \) is the concentration of free metal in solution (mg/L). Based on this equation, Gosset et al. (1986) developed a
technique for obtaining the binding kinetic constant $k_f$. This required the following assumptions:

- the reverse reaction, $k_r$, is negligible;
- the peat metal anion stoichiometry is constant for all experimental conditions and equal to one metal ion per binding site;
- the overall kinetics are limited by the binding reaction itself and not the diffusion of species.

Gosset et al. developed an expression to describe these reactions:

$$ k_f = \frac{1}{(PM)_{\text{lim}} - (M)_{\text{in}}} \ln \left[ \frac{(M)_{\text{in}}}{(PM)_{\text{lim}}} \left( \frac{(PM)_{\text{lim}} - (PM)}{(M)_{\text{lim}} - (PM)} \right) \right]. \quad (1.23) $$

Dzombak and Morel (1986) developed a reversible second-order rate expression for the surface complexation reaction shown in Equation (1.24):

$$ X + C \leftrightarrow XC, \quad (1.24) $$

$$ \frac{d(XC)}{dt} = k_f \frac{X}{k_b} (C) - k_b (XC). \quad (1.25) $$

After including the appropriate mole balance equations for $X_i$ and $C_i$ and algebraic manipulation, Equation (1.25) can be rewritten as:

$$ \frac{d(XC)}{dt} = k_f (XC)^2 - (XC) \left[ k_f (X) + k_f (C) + k_b \right] + k_f (X_i C_i). \quad (1.26) $$

1.8.4 Pseudo-second-order model

For the pseudo-second-order reaction the rate limiting step may be chemical sorption or chemisorption involving valency forces through sharing or the
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exchange of electrons between sorbent and sorbate as covalent forces. Initially, it must be assumed that the sorption follows the Langmuir equation. The pseudo-second-order equation has the following advantages:

- Sorption occurs only on localized sites and involves no interaction between sorbed ions.
- The energy of adsorption is independent of surface coverage.
- Maximum adsorption corresponds to a saturated monolayer of adsorbates on the adsorbent surface.
- The rate of desorption, $k_1$ is negligible in comparison with the rate of adsorption $k$.
- It does not have the problem of assigning an effective sorption capacity; the sorption capacity, rate constant of pseudo-second-order and the initial sorption rate can be determined from the equation without knowing any parameter beforehand.

The rate of pseudo-second-order reaction may be dependent on the amount of metal ions on the surface of the adsorbent and the amount of metal ions sorbed at equilibrium. It means that the rate of reaction is directly proportional to the number of active sites onto the surface of the adsorbent. The rate expression for the pseudo-second-order reaction represented by (Ho and Mckay, 2000; Ho, 2004)

$$\frac{d(S)}{dt} = k_2[(S)_0 - (S)_t]^2$$  \hspace{1cm} (1.27)

where $(S)_t$ is the number of adsorption sites occupied on the adsorbent at time ‘$t$’ and $(S)_0$ is the number of adsorption sites available on the adsorbent. In terms of adsorption quantity, the pseudo-second-order rate equation can be rewritten as

$$\frac{d(q_t)}{dt} = k(q_e - q_t)^2$$  \hspace{1cm} (1.28)
The rate of pseudo-second-order reaction may be dependent on the amount of adsorbate on the surface of the adsorbent and the amount of adsorbate sorbed at equilibrium. The sorption equilibrium, $q_e$ is a function of temperature, initial concentration, the adsorbent dose, and nature of solute–sorbent interaction. The rate expression for the sorption is described by

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

(1.29)

where $k_2$ is the rate constant of sorption (g/mg min), $q_e$ is the amount of adsorbate at equilibrium (mg/g), $q_t$ is the amount of adsorbate on the surface of the sorbent (mg/g) at any time, $t$. Separating the variables in Equation (1.29) gives

$$\frac{dq_t}{(q_e - q_t)^2} = k_2 \, dt$$

(1.30)

Integrating this for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q$, gives

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 \, t$$

(1.31)

which is the integrated rate law for a pseudo-second-order reaction. The above equation can be rearranged to obtain

$$\frac{t}{q_t} = \frac{1}{k_2 \, q_e^2} + \frac{t}{q_e}$$

(1.32)

There is no need to know any parameter beforehand and the equilibrium adsorption density $q_e$ can be calculated from the above equation. In addition, it is more likely to predict the behaviour over the whole range of adsorption and is in agreement with chemical sorption being the rate-controlling step, which may involve valency
forces through sharing or exchange of electrons between the adsorbate and the adsorbent. Much interest was shown by many researchers in interpreting the kinetics of adsorption of various systems by means of the pseudo-second-order kinetic model (Kapoor et al., 1999; Ho and McKay, 2000; Low et al., 2000; Aksu, 2001; Basso et al., 2002).

1.8.5 Elovich equation

An empirical equation of Elovich (Low, 1960) is commonly used for describing the kinetics of adsorption.

\[
\frac{d q_t}{dt} = \alpha \exp(-\beta q)
\]  

(1.33)

where \( q_t \) is the sorption capacity at time \( t \) and \( \alpha \) is the initial adsorption rate (mg/g/min). \( \beta \) is the desorption constant (g/mg) which is related to the extent of surface coverage and the activation energy of the chemisorption (Ho and McKay, 2002).

To simplify the Elovich equation, it is assumed that \( \alpha \beta \gg 1 \) and by applying the boundary condition \( q_t = 0 \) at \( t = 0 \), this equation becomes

\[
q_t = \left( \frac{1}{\beta} \right) \ln(\alpha \beta) + \left( \frac{1}{\beta} \right) \ln t
\]  

(1.34)

Thus, the constants can be obtained from the slope and intercept of the linearized plots of \( q_t \) against \( \ln t \).

\[
q_t = A + \frac{1}{b} \times \ln(t_0 + t)
\]  

(1.35)

where \( A \), and \( t_0 \) are three constants the last of which corresponds to a negative value of \( t \) where the adsorption rate has an infinite value.
According to Aharoni and Ungarish (1976), the Elovich equation usually holds for the results of processes involving the chemisorption of an adsorbate on a sorbent with a heterogeneous surface. According to other authors, however, the Elovich equation cannot be applied unless other processes preceding those which obey such an equation are considered; in the light of this assertion, Taylor and Thon (1952) assumed the presence of a so-called pre-Elovich process of infinite rate starting and ending at $t = 0$. It should be borne in mind that the Elovich equation, in all its forms, is an empirical equation of limited validity.

### 1.8.6 Ion exchange model

Boyd et al. (1947) developed a rate equation, which considered rates of ion exchange sorption in the exchange sorption of ions from aqueous solutions by organic zeolites. For the case of two monovalent ions, the mass law applies to the exchange when written as

$$A^+ + BR \leftrightarrow B^+ + AR \quad (1.36)$$

If $m_{A^+}$ and $m_{B^+}$ denote the concentrations of the ions $A^+$ and $B^+$ in solution, and $n_{AR}$ and $n_{BR}$ the moles of $A^+$ and $B^+$ in the adsorbent, then the net reaction rate can be written as follows:

$$\frac{dn_{AR}}{dt} = k_1 m_A + n_{BR} - k_2 m_B + n_{AB} \quad (1.37)$$

$$= -n_{AR} \left( k_1 m_{A^+} + k_2 m_{B^+} \right) + k_1 m_{A^+} E \quad (1.38)$$

where $k_1$ and $k_2$ are the forward and reverse specific rate constants and $E$ is a constant defined by
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\[ E = n_{AB} + n_{BR} \]  

(1.39)

When the concentrations of \( A^+ \) and \( B^+ \) in solution are kept constant, then, on integration, Equation (1.39) becomes

\[ n_{AR} = \frac{k_1 m_{A^+} E}{k_1 m_{A^+} + k_2 m_{B^+}} \left(1 - e^{-St}\right) = q \]  

(1.40)

where \( q \) is the adsorption capacity at time \( t \), and if

\[ S = k_1 m_{A^+} + k_2 m_{B^+} \]  

(1.41)

and Equation (1.40) can be rewritten as

\[ q_e - q = q_e e^{-St} \]  

(1.42)

where \( q_e \) is the equilibrium capacity. Thus,

\[ \log(1 - F) = -\left(\frac{S}{2.303}\right)t, \]  

(1.43)

where \( F \) is the fractional attainment of equilibrium, \( F = q/q_e \), and \( S \) (min\(^{-1}\)) is a constant. An ion exchange mechanism using the above kinetic equation has been applied by for the adsorption of Pb(II) onto tree fern (Ho, 2004a).

A careful survey of literature reveals that the most used kinetic equation is the pseudo-first-order followed by the pseudo-second-order equation. Azizian (2004) explored the theory of these kinetic models with a view to characterize the influence of reaction conditions on these models and formulated a general kinetic equation. Accordingly it has been stated that at high initial concentration of sorbate the general equation converts to pseudo-first-order model and at lower initial concentration of sorbate it converts to a pseudo-second-order model. According to
him the pseudo-first-order rate constant $k_1$ is a combination of adsorption ($k_a$) and desorption ($k_d$) rate constants which are related by the equation

$$k_1 = k_1 C_0 + k_d$$  \hspace{1cm} (1.44)

1.9 Sorption Diffusion Models

In adsorption processes where ion exchange and ionic bonding are not as prevalent as in chemisorption processes, diffusional mass transport models are extremely important (Ho and McKay, 1998). The diffusion models are usually based on one or more of the following mechanistic steps:

- external mass transport across the boundary layer surrounding the particle;
- diffusional mass transfer within the internal structure of the adsorbent particle by a pore, surface, branched pore or a combination of these mechanisms;
- adsorption at a surface site.

1.9.1 External mass transfer model (film transfer)

The prediction of adsorbate uptake rates by the adsorbent is important for adsorption calculations. For the transport of adsorbates from the bulk of the fluid phase to the interior of a pellet before adsorption takes place, the following mass transfer processes may be present: film mass transfer and intraparticle mass transfer.

The differential mass balance of adsorbate within the adsorbent is assumed to be constant, the effective intraparticle diffusivity $D_i$ is given by the equation

$$D_i \frac{\partial C_r^2}{\partial r^2} + \frac{2}{r} \frac{\partial C_r}{\partial r} - \rho_p \frac{\partial n_r}{\partial t} = \varepsilon_p \frac{\partial C_r}{\partial t}$$  \hspace{1cm} (1.45)
where \( r \) is the radius of the pore, \( t \) is the time, \( C_r \) is the concentration in liquid filled pore at radius \( r \), \( \rho_p \) is the density of the adsorbent particle, \( n \) is the concentration of adsorbed adsorbate at radius \( r \) and \( \varepsilon_p \) is the porosity of the adsorbent. The mass conservation equation for adsorbate in the bulk liquid phase is given by the equation

\[
\frac{dC_t}{dt} = -B_L S_s (C_t - C_s)
\] (1.46)

where \( C_t \) is the concentration in bulk liquid at time \( t \), \( B_L \) is the surface mass transfer coefficient, \( S_s \) is the outer surface of silica particle per unit volume of particle-free slurry and \( C_s \) is the concentration in liquid at outer surface of particle. The boundary and initial conditions of the system are represented by Equations (1.47)–(1.49)

\[
D_t \left( \frac{\partial C_r}{\partial t} \right) = B_L (C_t - C_s)
\] (1.47)

\[
\frac{\partial C_r}{\partial t} = 0 \quad \text{(at } r = 0) \quad (1.48)
\]

\[
C_r = 0 \quad \text{(at } t = 0) \quad (1.49)
\]

The equilibrium conditions are defined by the Langmuir isotherm represented by

\[
q_e = \frac{K_L C_e}{1 + b C_e}
\] (1.50)

where \( K_L \) is the adsorption equilibrium constant and \( b \) is the energy of adsorption (Langmuir constant). From equilibrium considerations, supposing the Langmuir
isotherm applies to the adsorption, \( n_r \) and \( C_r \) are related by the isotherm, which in differential form is predicted by equation

\[
\frac{\partial n_r}{\partial t} = \frac{\partial}{\partial C_r} \left( \frac{K_L C_r}{1 + b C_r} \right) \frac{\partial C_r}{\partial t}
\]  

(1.51)

When intraparticle diffusion is negligible and when the isotherm is linear, an analytical solution for \( C_t \) versus \( t \) is possible and Equations (1.46)-(1.51) can be solved numerically to give equation (1.52)

\[
\frac{C_t}{C_o} = \frac{1}{1 + m K_L} + \frac{m K_L}{1 + m K_L} \exp \left( \frac{1 + m K_L}{m K_L} B_L \right) \cdot S_s \cdot t
\]  

(1.52)

The mass of adsorbent per unit volume of particle-free adsorbate is given by

\[
m = \frac{W}{V}
\]  

(1.53)

where \( W \) is the mass of the adsorbent and \( V \) is the volume of the particle-free solution. The outer surface of the adsorbent per unit volume of particle-free adsorbent is given by

\[
S_s = \frac{6 m}{d_p \rho_p (1 - \varepsilon_p)}
\]  

(1.54)

where \( d_p \) is the particle diameter. As \( t = 0 \), surface mass transfer will be predominant and the two assumptions made in deriving equation (1.52) are valid. Consequently, a plot of \( \ln \left( \frac{C_t}{C_o} - \frac{1}{1 + m K_L} \right) \) versus \( t \) will yield a straight line of
intercept \(\frac{m K_L}{1 + m K_L}\) and slope \(\frac{1 + m K_L}{m K_L} B_L S_s\) at \(t = 0\), from which the surface mass transfer coefficient \(B_L\) can be calculated.

1.9.2 Film diffusion control

Boyd et al. (1947) represented a film diffusion model as follows:

\[
\log(q_m - q_t) = \log(q_m) - \left(\frac{R}{2.303}\right) t
\]  
(1.55)

The above equation is of the same form as Equation (1.18) indicating that differentiating between film diffusion control and pseudo-first-order reaction control will be difficult. However, carrying out a series of sorption studies at different agitation speeds usually demonstrates that film diffusion has a much stronger dependence on agitation. In agitated sorption studies, film diffusion is usually only rate controlling for the first few minutes.

1.9.3 Intraparticle diffusion model (pore diffusion)

In a rapidly stirred batch reactor, the adsorbate species are most probably transported from the solution to the solid phase through intraparticle transport, which is often the rate-limiting step in many adsorption processes. The rate of particle transport through this mechanism is slower than adsorption on the exterior surface site of adsorbent.

For the sorption of the adsorbate in a sphere of radius \(r\), if the diffusion is ficken, the relation between weight uptake and moderate and large sorption time, is

\[
\frac{q_t}{q_m} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -\frac{D_n \pi^2 n^2 t}{r^2} \right)
\]  
(1.56)
where \( q_t \) and \( q_m \) are the weight uptake at time \( t \) and equilibrium respectively. At an early stage \((t \ll t_a)\) the above equation can be simplified to

\[
\frac{q_t}{q_m} = 6 \left( \frac{D}{\pi r^2} \right)^{1/2} t^{1/2}
\]  

(a) plot \( \frac{q_t}{q_m} \) versus \( t^{1/2} \) should yield a straight line having a slope of \( 6 \left( \frac{D}{\pi r^2} \right)^{1/2} \) from which the diffusion coefficient \( D \) can be determined. As \( t \) approaches \( t_\infty \) the above equation can be simplified to

\[
\frac{q_t}{q_m} = 1 - 6 \left( \frac{D}{\pi r^2} \right) \exp \left( - \frac{D_i \pi^2 t}{r^2} \right)
\]  

(b) the natural logarithm of the above equation yields

\[
\ln \left( 1 - \frac{q_t}{q_m} \right) = \ln \frac{6}{\pi^2} + \left( - \frac{D_i \pi^2}{r^2} \right) t
\]  

(a plot of \( \ln \left( 1 - \frac{q_t}{q_m} \right) \) versus \( t \) shall correspond to a line of slope of

\[
- \frac{D_i \pi^2}{r^2}
\]  

from which the diffusion coefficient may be calculated.

Chanda et al. (1983) developed a simple equation for particle diffusion controlled sorption processes as follows:

\[
\ln \left( 1 - \frac{X_t}{X_e} \right) = -k_p t
\]  

(1.60)
where $X_t$ is the fractional conversion of sorbate at time $t$ and $X_e$ is the fractional conversion of sorbate at equilibrium time. This equation has been applied for the sorption of cadmium(II) and lead(II) by modified groundnut husks from aqueous solutions (Okieimen, 1991).

Urano and Tachikawa (1991) developed a model for intraparticle diffusion. The condition for this model is that the adsorption should be very slow and it should not change with the shaking speed. The model is given by

$$\log\left[1 - \left(\frac{q_t}{q_e}\right)^2\right] = -\frac{4\pi^2 D_i t}{2.303 d^2}$$

(1.61)

where $q_t$ and $q_e$ are the amount adsorbed at time $t$ and at equilibrium respectively, $d$ is the diameter of the adsorbent, $D_i$ is the intraparticle diffusion coefficient based on the concentration in solids. The $D_i$ values were found to be in the range of $10^{-12}$ to $10^{-13}$ m$^2$/s.

According to Weber and Morris (1963), for most adsorption processes, the uptake varies almost proportionately with $t^{1.2}$ rather than with the contact time. Plots of amount adsorbed, $q_t$ versus $t^{1.2}$ (Jain and Sharma, 2002) some times follow three phases: a rapid uptake (Phase I); a transition phase (Phase II) and an almost flat phase (Phase III). Phase I, was attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface (bulk diffusion). Phase II, exhibiting additional removal, was attributed to the diffusion of the adsorbate from the surface film into the macro-pores of the adsorbent (pore diffusion or intraparticle diffusion), stimulating further migration of adsorbate from the liquid phase onto the adsorbent surface. Phase III, represents a state of equilibrium. Thus it is inferred that due to the porous nature of the adsorbents, pore diffusion is expected in addition to surface adsorption. According to Weber and Morris if the rate limiting step is intraparticle diffusion, a plot of solute sorbed...
against square root of contact time should yield a straight line passing through the origin. The most widely applied intraparticle diffusion equation for biosorption system is given by Weber and Morris:

\[ q_t = k_p t^{1/2} \]  

(1.62)

where \( k_p \) is the intraparticle diffusion rate constant of transport

1.10 Aim and Scope of the Present Study

In order to maintain and manage the aquatic ecosystem by way of upkeeping the water quality standards, there is a strong need for the recovery of pollutants, by implementing the rule of total reuse of the wastewater components. The elimination of these toxic pollutants from wastewater streams before discharging into the receiving bodies is therefore a fundamental measure for controlling pollution problems and protecting public health. The increasing demand for water for beneficial purposes has forced man to assess and examine water reuse technology more seriously than ever before. The pursuit for a clean environment creates the need to develop industrial wastewater treatment methods with better performance efficiencies than the conventional methods.

The tremendous increase in the use of metals over the past few decades has inevitably resulted in an increased flux of the metal in the aquatic environment. The removal of such hazardous heavy metals as Hg, Pb, Co, Cd, Zn, Ni and Cu from aqueous media has long been a serious environmental issue. Various processes such as carbon adsorption, ion exchange, membrane separation, precipitation and solvent extraction are available for removing the metal ions in wastewaters. However most of these methods are complicated, sophisticated and
the processes are usually either non-selective or expensive for the removal of very dilute metal concentration from the wastewater.

Attention has been focused on various natural solid supports, which are able to remove pollutants from contaminated water at low cost. Numerous adsorbents have been developed for the removal of heavy metals from aqueous solutions which include activated carbons, clays, simple and binary metal oxides, canola meal, bone char, industrial waste Fe(III)/Cr(III) hydroxides, activated sludge, metallurgical slag and red mud etc. (Namasivayam and Ranganathan, 1995; Al-Ashah and Duvnjak, 1996; Thomas and Anirudhan, 1999; Altundogan et al., 2002; Cheung et al., 2002; Kim et al., 2002; Monser and Adhoum, 2002; Kara et al., 2003). Cost is actually an important parameter for comparing the adsorbent materials. According to Bailey et al. (1999), a sorbent can be considered low-cost if it requires little processing, is abundant in nature or is a by-product or waste material from another industry. Certain waste products from industrial and agricultural operations, natural materials and biosorbents represent potentially economical alternative sorbents.

Biosorbents thus offer low operating cost, good efficiency, selectivity and no toxic effect on microorganisms. Many of them have been tested and proposed for metal removal. The utilization of agricultural waste is of great significance in a country like India. The plant residues are cellulosic materials, and have excellent ability to adsorb waste chemicals. Many novel materials have been tested as adsorbents with a twofold objective – to replace activated carbon with cheaper alternatives and to utilize various waste products for the purpose. India, as a developing country has duly recognized the significance of environmental quality control and has initiated large-scale programme to improve, conserve and develop her natural resources. Purification of waters and wastewaters by any methods has in this regard been allowed due importance in view of the environmental pollution problems recently encountered.
The removal of metals by sorbents directly depends on the presence of specific functional groups on the surface. The adsorption capacity is enhanced by the chemical treatment of the adsorbent materials. The thermodynamic and kinetic principles that govern the adsorption of heavy metals from respective solutions onto modified adsorbent surfaces have been the subject of extensive theoretical and experimental studies.

The main objectives of the present study can be summarized as follows:

- The primary objective is to develop novel adsorbents which have fairly good adsorptive power for metal ions and provide regenerability for use in successive cycles in the batch process.
- The study probes the synthetic route way of the adsorbent preparation by ascertaining the important parameters responsible and optimum conditions needed for the maximum yield of the product adsorbents.
- It is further aimed to evaluate the physical and chemical properties of the adsorbents with a view to incorporate mechanistic approach for the adsorption phenomena.
- The present study is designated to assess the effectiveness of the adsorbents developed by surface modification of a commonly available lignocellulosic material banana stalk, in the adsorption, desorption, and retention characteristics of some heavy metal cations such as Pb(II), Co(II), Hg(II), Cd(II) from aqueous solutions.
- The adsorption of Cr(VI) onto amine modified and iron treated lignocellulosics is also aimed at.
- The work also explores the possibility of using a cation exchange resin immobilized by hydrated ferric oxide for the removal of As(III) and As(V) from aqueous solution.
Introduction

- The study incorporates metal adsorption onto the adsorbents over a wide range of pH, initial concentration, adsorbent dose, ionic strength, temperature etc.

- The thermodynamic and kinetic principles that govern the adsorption of toxic substances from respective aqueous solution onto sorbent surface are to be accounted for in the extensive theoretical and experimental studies.

- The present work tests the potential ability of the novel materials synthesized, to sequester the metal ions present in real/simulated wastewaters or groundwater samples with a view to highlight their commercial value and practical applications.

- The study also plans to conduct parallel experiments with commercially available ion-exchangers for the purpose of comparing the adsorption capacities.

- Another objective is to develop mathematical models suitable for prediction of parameters useful in the adsorption technology.

- The study would solve a key challenge to industry and environmental fields and would enable the future growth of adsorption science.