

CHAPTER TWO

LITERATURE REVIEW

2.1 Theory of adsorption

Adsorption is the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface. The adsorption process occurs at an interface between any two phases, such as, liquid-liquid, liquid-gas, liquid-solid, or gas-solid interfaces. The probability of adsorption occurring from the precursor state is dependent on the adsorbate's proximity to other adsorbate molecules that have already been adsorbed. The liquid-solid interface of interest in water and wastewater treatment. The adsorption of various substances on solids is due to the increased free surface energy of solids to their extensive surface. According to the second law of thermodynamics, this energy must be reduced. This is achieved by reduced the surface tension via the capture of extrinsic substance. From external surface of solids and liquids as well as from the internal surface of porous solid or liquids adsorption is one of the most widely used methods for potable and wastewater treatment by adsorption method most of the heavy metals are efficiently removed depending on the type of bonding involved, adsorption can be classified as follows:

2.1.1 Physisorption

Physisorption, also called physical adsorption, is a process in which the electronic structure of the atom or molecule is barely perturbed upon adsorption. The weak bonding of physisorption is due to the induced dipole moment of a nonpolar adsorbate interacting with its own image charge in the polarizable solid. Physisorption or physical adsorption occurs as result of energy differences and/or electrical attractive weak forces such as the (Van der Waals forces), the adsorbate molecules (liquid contamination) are physically attached to the adsorbent molecules (solid surface). The reversibility of physisorption is dependent on the attractive forces between adsorbate and

adsorbent. If these forces are weak, desorption is readily effected. The high temperature of adsorption for physisorption is at most a few kcal/mole and therefore this type of adsorption is stable only at temperature below 150°C.

2.1.2 Chemisorption

Chemisorption is a sub-class of **adsorption**, driven by a chemical reaction occurring at the exposed surface. A new chemical species is generated at the adsorbent surface. The strong interaction between the adsorbate and the substrate surface creates new types of electronic bonds - ionic or covalent, depending on the reactive chemical species involved. Unlike physisorption, this procedure is one molecule thick and irreversible because energy is released to form the new chemical compound at the surface of the adsorbent and energy would be necessary to reverse the process.

Both processes take place when the molecules in the liquid phase are attached to the surface of solid as a result of the attractive forces at the adsorbent, overcoming the kinetic energy of the adsorbate molecules. The substance that is being removed from liquid phase at the interface is call adsorbate or sorbent. The adsorbent or sorbate is the solid, liquid or gas phase onto which the adsorbate accumulate, as show in (Figure 2.1).

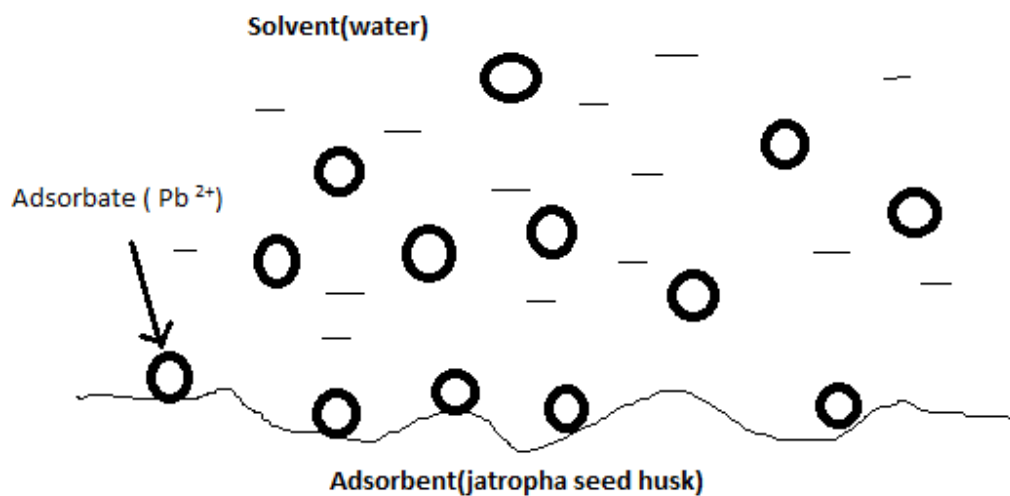


Figure.2.1: Mechanism of adsorption process

In general, adsorption is the accumulation of molecules from a solvent onto the interior and exterior (i.e. pore) surface of the adsorbent.

The surface phenomenon is a manifestation of complicated interactions among three components involves, i.e. the jatropha seed husk, the lead(II) and the solvent (Figure 2.2) shows a schematic for the three components in adsorption model and their interactions. Normally, the affinity between the jatropha seed husk and the lead(II) is main interaction force controlling adsorption. However, the affinity between the jatropha seed husk and the solvent (i.e. solubility) can also play a main role in adsorption.

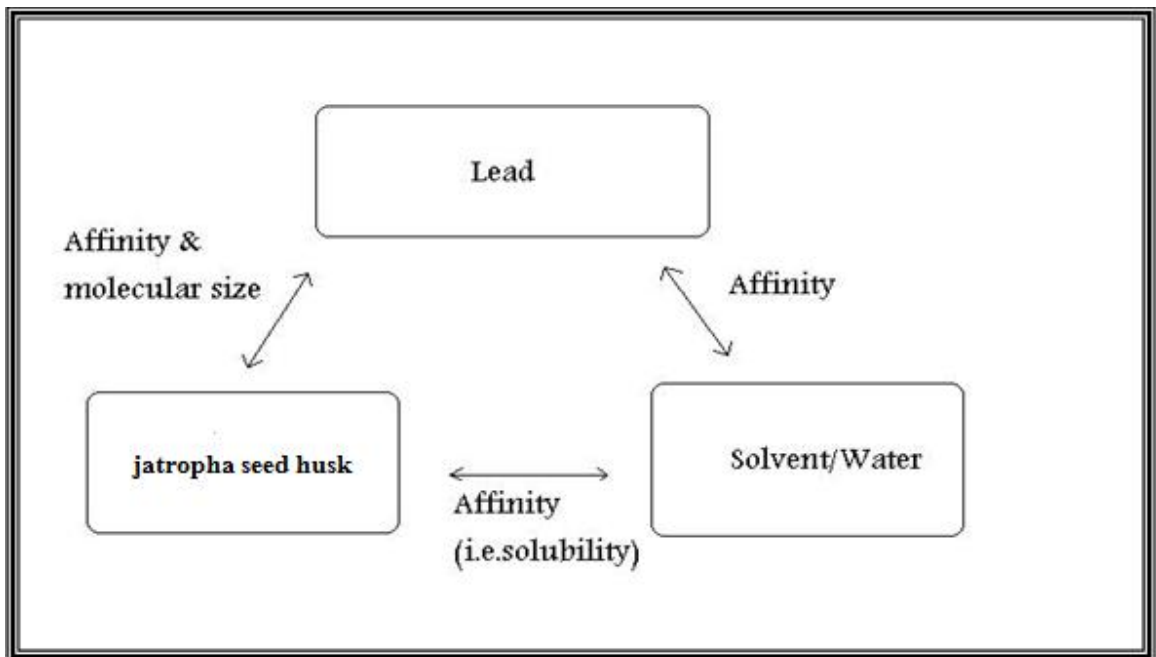


Figure.2.2: Schematic representation of adsorbate-adsorbent-solvent relationship.

2.2 There are eight factors that effect an adsorption:

1. Nature of the adsorbate
2. Nature and surface area of the adsorbent
3. Specificity of the reaction
4. Characteristics of the reaction
5. Specific area of the adsorbent
6. Activation of adsorbent
7. Enthalpy of adsorption
8. The residence time of the system.

2.3 Impact of lead on aquatic ecosystems

The unique physical properties of lead, counting low melting point, malleability, corrosion resistance and high density have led its use in a wide variety of industries and trade and consequently increased the potential of lead exposure in many occupations. Some of the Workplace at the risk of lead exposure include Auto repairers, Battery manufacturers, Bridge reconstruction workers, Firing range instructor, Construction workers, Gas station attendants (past exposures), Lead manufacturing industry employees, Glass manufacturers, Lead mining workers. Lead refining workers, Lead smelter workers, Plastic manufacturers, Plumbers, pipe fitters, Printers, Police officers, Rubber product manufacturers, Shipbuilders and Steel welders or cutters.

Existence of lead in natural waters is greatly dependent on the atmosphere and earth surface that they are in direct contact (HMSO/1974). The major sources of lead in aquatic ecosystem including the ocean are domestic wastewater effluent, coal burning power plants, non-ferrous metal smelters, iron and steel plants and dumping of sewage sludge (Nriagu and Pacyna, 1988). (Leland et al. (1973) demonstrated that urban runoff and disposal of treated wastewaters had an adverse effect on a river ecosystem. They found acid extractable lead in river sediments in urban and rural drainage areas varied from 10 to 388 ppm respectively and that fishes were generally absent from urban drainage waters.

Pringle et al. (1968) demonstrated that oyster, *Crassostrea virginica*, could accumulate lead in concentrations of several hundreds to several thousand times greater than concentrations in seawater. Lead accumulating ability of shell fish thus made them very useful as a means of monitoring lead pollution (Navrot et al., 1974). Schultz-Balds (1972) found that absorption and accumulation of lead by shell fish produced lethal and chronic effects even at 0.5 ppm in aqueous solution.

Other smaller aquatic organisms also have ability to accumulate lead from their food as well as from their surrounding medium and these may attain lethal concentrations. Aubert et al, (1975) determined that the toxic threshold of $Pb(NO_3)_2$ in sea water for the aquatic worm *Nereis diversicoZour* was 8.3 ppm for eight days. Brown and Ahsanullah (1971) also found that 50% mortality was reached in a group of 50 *Ophyotrocha Zabronica* maintained in sea water containing 1 ppm lead in about 600 hours. They also reported a linear relationship between lead concentration in sea water and the time required for 50% mortality in groups of 50 brine shrimp (*Artenia salina*).

Drifineyer and Odum (1975) reported that fish taken from control marsh harbor contained significantly lower levels of lead (0.2-0.6 ppm) than fish from a marsh receiving dredge soil from a polluted industrialized harbor (4.5 ppm). Carpenter (1925) showed that acute lead toxicity resulted in production of copious amounts of fish epidermal mucus which interfered with the gills and caused death by asphyxia. National Research Council Canada (1978) reported that under conditions of low pH and low water hardness, insoluble lead compounds can release Pb^{2+} to levels toxic to fish.

2.4 Treatment methods for heavy metal removal

The attendance of large quantities of toxic metals such as zinc, lead, cadmium, and mercury or others, poses severe health risks to humans, and this threat puts the scientific community under pressure to develop new methods to detect and eliminate toxic contaminants from wastewaters in efficient and economically viable ways. The term adsorption is the process of accumulation substances that are in solution on a suitable interface. Another definition was a mass transfer operation in that a constituent in the liquid phase is transferred to the solid phase.

2.4.1 Modified jatropha seed husk adsorption:

Modified jatropha seed husk (carbon) is the main adsorbent that can be used as an adsorbent for the removal of toxic pollutants from wastewater. The raw material for the carbon, namely, jatropha seed husk is disposed as waste in the bio-diesel production industries and the new activated carbons developed from the agricultural waste material can be used for the economic removal of dyes, organics and toxic ions from waters. Approximate calculations show that the cost of the Jatropha seed husk carbon is \$0.50 per kg, while that of the commercial carbon is \$3.00 per kg. Addition of chemical activants would increase the cost of Jatropha seed husk carbon only by 5–10%. This may be due to making them easy to be processed into adsorbents.

Table 2.1. Removal of anions, heavy metals, organics and dyes using jatropha seed husk carbon in comparison with coir pith carbon in the presence (ZnCPC) and absence (CPC) of ZnCl₂ activation (Namasivayam and Sangeetha, 2006).

Adsorbate	Jatropha seed husk carbon		ZnCPC/COC	% Removal	
	Adsorbent dose (mg/50ml)	%Removal	Adsorption dose (mg/50ml)	ZnCPC	CPC
Nitrate	500	64	400	95	MI
Phosphate	500	92	450	91	MI
Thocyanate	500	16	250	100	MI
Selenite	300	45	600	74	MI
Chlromium(VI)	300	61	50	99	18
Nickel(II)	50	97	600	41	58
Vandum(V)	200	30	250	99	MI
2-Chlorophenol	300	60	50	99	67
Bisphenol	300	68	50	97	57
Acid brilliant blue	300	89	200	99	92
Acid violet	200	82	200	99	92
Congo red	300	63	200	93	79
Direct red 12B	300	75	200	99	62
Methylene blue	300	83	50	100	50
Procion orange	1000	45	200	97	42

2.4.2 Use of activated carbon for the removal of lead

Tan and Teo (1985) studied the combined effect of initial concentration and carbon dosage on the adsorption isotherm of chromium and lead onto activated carbon. They found that the Langmuir and Freundlich equations were unable to adequately describe the observed isotherm under combined influence of carbon dosage and initial adsorption concentration and this had to be modified. The activated carbons used were pre-conditioned by soaking in 6N HCl solution for twenty four hours and washed after that soaked in deionized water for 24 h before it was oven dried at 103°C. The contact times for the adsorption studies were three days. They concluded from their studies that adsorption of chromium and lead by activated carbon showed significant dependency on pH, initial adsorbate concentration and carbon dosage.

The adsorption of copper, lead and cobalt by carbon studied by Netzer and Hughes (1984). They used 10 mg/L from an initial concentration for each metal to evaluate and optimize process variables like time, pH, carbon type, time, equilibrium and carbon dosage. They found that when two or three metals were present in solution the required time for complete adsorption was affected by the ratio of metal species to adsorption sites and there seemed to be a competition for adsorption sites. The presence of other metals like copper or cobalt are cause hinder lead adsorption with copper having a greater hindrance effect on lead than cobalt. Also approximately twice as much lead was removed than copper and 10 times more lead was removed than cobalt. An optimum pH of 4 was obtained for the two metals.

Lee et al. (1998) studied the removal of lead in a fixed bed column packed with crab shell and activated carbon. They found that the addition of 1 g crab shell to a column packed with log of activated carbon lengthened breakthrough time from 380 bed volumes to 1500 bed volumes. This was attributed to the increases in CO_3^{2-} and OH^- ions available for bonding

of lead. The stock solution used had concentrations from 10 to 50 mg/L, when the influent lead concentration increased from 10 to 50 mg/L, the lead uptake doubled from 31.4 mgPb/g packing material to 62.7 mgPb/g packing material and pH was fixed at 3 to minimize concentration of lead. The major mechanism for lead removal was through dissolution of CaCO_3 in the crab shell followed by precipitation of lead in the form of $\text{Pb}(\text{CO}_3)_2\text{OH}_2$.

Reed and Aunachalan (1994) studied the removal of cadmium and lead from metal bearing wastewaters containing cadmium and lead using granular activated carbon columns. Three synthetic wastewaters were simulated containing combinations of 10 and 50 mg/L concentrations of cadmium and lead, organic compounds and acetic acid. Column pH was a critical parameter for the column performance, there was significant increase in effluent metal concentrations with increasing pH. The granular activated carbon (GAC) was successfully regenerated by rinsing with 1L (\approx 8 bed volume) of 0.1 HNO_3 , and the column performance was not adversely affected by the regeneration. The use of regeneration procedure for virgin carbon was recommended by the authors to enhance column performance since it increases pore liquid precipitation and OH^- available for surface, increases sites available for adsorption and also increases carbon pH.

Taylor and Kuennen (1994) studied removal of soluble and insoluble lead from drinking water using a fixed bed adsorber (FBA), point of use (POU), granular activate carbon (GAC). The setup was composed of a pressed carbon block with five stages of filtration and a rated life of 500 gallons. The first two were made of non woven materials to remove large particles, the next two stages of carbon filtration consisted of first a coarse GAC followed by a fine GAC, and the final stage is a porous plastic made of sintered polyolefin. It was demonstrated that the setup adequately removed both soluble and insoluble lead

from drinking water. They found from temperature studies that mechanisms other than adsorption such as precipitation on carbon surface and hydrogen bonding are also involved in the removal of lead. They also found that different carbons had a wide range of lead adsorption capacities and that adsorption also different significantly with the pH of the water.

Wilczak and Keinath (1993) studied the kinetics of sorption and desorption of lead(II) and copper (II) on activated carbon. It was found that the sorption of lead(II) and copper(II) on activated carbon consisted of a rapid initial uptake followed by a slow approach to equilibrium which spanned over a time of several weeks. They found that sorption of lead and copper ions on activated carbon were fully reversible.

2.4.3 Use of peat for the removal of lead

Peat can be described as a naturally occurring highly organic substance derived primarily from plant materials, in generally peat occurs in wet areas where there is a deficiency of oxygen thereby promoting the accumulation of plant substance over its decomposition. Peat is a complex material consisting predominantly of cellulose and lignin (Coupai and Lalacette, 1976). These constituents, especially lignin, bear polar functional groups such as acids, alcohols, ketones, aldehydes, and phenolic residue which may involved in chemical bonding and complexation roles through metal ion fixation from solutions (Coupal and Lalancette, 1976).

The use of peat in wastewater treatment has been widely studied and it has been proven that peat is an useful adsorbent to removal of heavy metals from wastewater. Peat has a natural capacity for exchange adsorption with heavy metals such as lead, cadmium, chromium, nickel, copper and zinc. Exchange adsorption takes set as a result of either solvent

motivated force, which relates to surface tension, or adsorbent motivated force which combines physical interaction and chemical electrostatics between adsorbate and adsorbing surface. Adsorption is generally driven via the two forces (Weber and DiGiano, 1996). Peat strongly adsorbs various metal cations using their phenolic, hydroxylic and carboxylic functional group (Smith et al., 1977; Wolf et al., 1972).

Bunzl et al. (1976) studied the desorption and adsorption of calcium, copper, cadmium, zinc and lead on peat. The peat was pre-treated by washing with 1M HCl and then rinsed with deionized water. 1.00 g of wet peat samples was then added to 200 mL of deionized water and moved for some hours to establish the bulge equilibrium of the peat particles. The metal solution was then added to adsorption study. This was followed by decant of the supernatant which was replaced with 200 mL of dilute HNO₃. They found from their studies that in the pH range of 3.5 to 4.5, the selective arrange of metal adsorption by peat was Pb > Cu > Cd =S Zn > Ca. An initial increase in metal ion desorption rate was observed which consequently decreased and followed a selective order similar to that of the adsorption.

Zhipei et al. (1984) conducted a study on the removal of coromium, cadmium, zinc, nickel and lead from wastewater using some Chinese peats with particle size ranging from 18 to 40 mesh sieves. 0.125 g of peat was mixed with 25 mL of heavy metal solutions, rough for two hours and allowed to resolve for seventy-two hours at room temperature. They found from their studies that the efficiency of heavy metal ion removal with a variety of peats was related to property and composition of peat samples as well as the adsorbed ion. They also found that the equilibrium time was not dependent for particle size. The desorption studies indicated that lead, nickel, zinc and cadmium could not be desorbed by refluxing with hot water but could be desorbed using 1M nitric (HNO₃) or hydrochloric (HCl) acids.

Coupal and Lalancette (1976) studied the treatment of wastewater containing cadmium, zinc, mercury, copper, iron, nickel, chromium(VI), lead, silver and cyanide, by circulating the wastewater over a mat of peat. Heavy metal concentrations were initially reduced to the level of 1 mg/L by increasing pH which resulted in precipitation of metals as hydroxides and sulfide. The precipitates were allowed to settle and the supernatant was then circulated through the mat of peat where greater part of the remaining metal ions which were in form of suspended hydroxide and sulfide were then removed by adsorption to the surface of the mat of peat. The remaining metal ions were more removed by chemisorption onto the peat mat. The sewage metal concentration after the treatment fell below limits specified by the United States Environmental Protection Agency (US EPA).

Ho and McKay (1999) studied the kinetics of lead (II) sorption on to peat based on the assumption of pseudo-second order mechanism and taking prominent cognisance of chemisorption. They developed a pseudo-second order model to guess the sorption rate stable, equilibrium capacity initial sorption and initial sorption.

Effects of initial concentration, particle size and temperature were investigated. From their study the rate constant decreased non-linearly with increasing initial concentration, and increased with decreasing particle size and increased with increasing temperature.

McLellan and Rock (1988) investigated the removal of copper, chromium, lead and cadmium from landfill leachate with peat at a contact time of 1 and 24 h. They observed that adsorption of metals increased with increasing longer contact time and concentration. They also found that metal interaction played an significant role in the adsorption of metal from leachate, with a variety of metals competing for adsorption sites on the peat. The desorption studies discovered a substantial final disposal problem as the application of deionized water to the peat after 76 days of operation showed that approximately 50 % of

the adsorbed metal leached back into the solution. They thus concluded that ultimate disposal of the exhausted peat would require considerable attention and minimization of water infiltration to the final disposal site would be of pertinent importance to control leaching of metals.

2.5 Adsorption kinetics and equilibrium

Evaluation of metal adsorption by *Jatropha* seed husk modified as a unit operation often focus on two important physico-chemical aspects of the process, i.e. equilibrium and adsorption kinetics

2.5.1 Adsorption isotherms models

Adsorption isotherm is relationship between the concentration of a substance and a amount adsorbed (Ahmed et al, 2007). It is the most important information, which explains how the adsorbate molecules distribute between the adsorbent and the solution (Hsan et al, 2008).

Adsorption equilibrium is established when a certain amount of metallic species sequestered and bound by a solid phase which is in dynamic balance with remaining dissolved metal in the solution. The equilibrium adsorption isotherms are one of the most useful data to understand the mechanism of the adsorption.

The isotherm plot is a graphical expression that represents metal adsorption by the adsorbent against the residual metal concentration in the contact solution.

When a metal solution is contacted with *Jatropha* seed husk modified cells, metal ions may collide with the cell surface and result in several incidences; they are as follows:

- i. The metal ion may rebound from the surface.

ii. The metal ions may be adsorbed and the solid phase may referentially concentrate specific metal ion species from solution onto its surface.

iii. Reaction may take place between the incoming cation and functional group on the solid surface.

Several isotherm equations have been for the equilibrium modeling of adsorption systems, but two important isotherms are chosen in this study, which are namely the Freundlich and Langmuir adsorption isotherms were applied to describe the equilibrium relationships between adsorbent and adsorbate in solution. Adsorption equilibrium is established when the concentration of sorbate in the bulk solution is dynamic balance with that of the interface (Ho et al, 2000).

2.5.1.1 Langmuir adsorption isotherm

The Langmuir adsorption isotherm is derived from consideration based upon an assumption of maximum monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies of adsorption with no transmigration of adsorbate in the plane of the surface. The linearized Langmuir isotherm equation is represented by the following (Langmuir, 1918):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{bq_{\max}} \quad \mathbf{LLL} \quad (2.1)$$

where,

q_e is the amount of adsorbate adsorbed per unit weight of adsorbent (g/mg).

q_{\max} the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg/g)

b is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g)

C_e = Concentration of adsorbate in solution at equilibrium (mg/L).

The plots of C_e/q_e vs. C_e for the adsorption of lead(II) ions onto adsorbent give a straight

line of the slope, $\frac{1}{q_{\max}}$, and the intercept $\frac{1}{bq_{\max}}$.

Hall et al (1966) introduced a dimensionless equilibrium term R_L , also known as the separation factor to express the Langmuir constant b . The significance of the R_L term is based upon an initial assumption of the applicability of the given data to Langmuir isotherm model, beyond which the value of R provides important information about the nature of the adsorption isotherm (see Table 4.5)

Table 2.2 : Use of separation factor R_L in obtaining information about the nature of adsorption (Hall et al., 1966).

Value of R_L	Information about the adsorption
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorably
$R_L = 0$	Irreversible

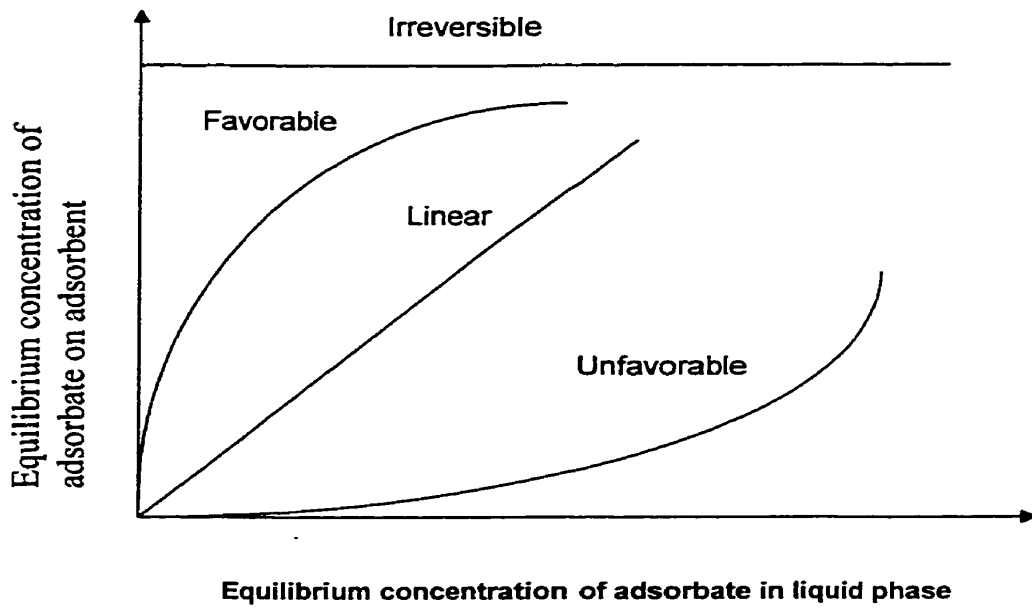


Figure (2.3) various curves that can be used to determine the shape of an isotherm from information in Table 2.1.

2.5.1.2 Freundlich isotherm

The Freundlich isotherm (M.O Zacar, 2005; A.S.O Zacar, 2004) is often used for heterogeneous surface energy systems. The Freundlich equation can be writing as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \mathbf{LLL} \quad (2.2)$$

where

q_e is the amount of an adsorbate adsorbed at equilibrium contact time (mg/g).

C_e is the concentration at equilibrium contact time (mg/g)

$1/n$ is an empirical parameter relating the adsorption intensity (which varies with the heterogeneity of the material).

K_F is a constant relating the adsorption capacity (Freundlich constants)

Freundlich equation suggests that the stronger binding strength decreases with increasing degree of the site occupation (Hameed, 2007)

The values of the $1/n$ and K_F can be obtained from the slope and intercept of the linear plot of $\log q_e$ versus $\log C_e$ respectively. If the value for the $1/n$ is between 0 and 1, this indicates that the adsorption is favorable (Atun et al, 2003)

2.6 Adsorption kinetic

Numerous simplified kinetic models including the pseudo-first-order equation and pseudo-second-order equation models are used to test the experimental data to examine the mechanism of adsorption processes.

2.6.1 Pseudo-first-order kinetic model

Lagergren (1898) developed the first model for adsorption kinetics based on the first order reaction rate and has the form:

$$\frac{dq_t}{dt} = K_L (q_e - q_t) \quad (2.3)$$

After defined integration by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ equation (2.3) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{K_L}{2.303} t \quad (2.4)$$

where,

K_L is the Lagergren rate constant for adsorption (h^{-1}).

q_e is the amount of metal ion adsorbed at equilibrium (mg/g);

q_t is the amount of metal ion adsorbed (mg/g at any given time t (h)).

The values of amount of the adsorbate adsorbed at equilibrium, q_e and the pseudo-first-order rate and constant K_1 are obtained from intercept and the slope of the plot of $\log(q_e - q_t)$ versus t , respectively. If the correlation coefficients for the first-order kinetic model were low at all the studied concentrations indicates that Lagergren's equation is not suitable for the experimental data of the adsorption process.

2.6.2 Pseudo-second-order-kinetic model

The adsorption kinetics data can be analyzed by using Ho and McKay's pseudo-second-order kinetic model (Ho et al, 1999). This model is based on the assumption that the rate of sorption is proportional to the square of the number of unoccupied sites. Its mathematical formula is given as:

$$\frac{q_e}{q_t} = \frac{1}{k_2(q_e)^2} + \frac{1}{q_e} t \quad (2.5)$$

q_e and the pseudo-first-order rate and constant K_2 are obtained from slope and the intercept of the plot of $\log t/q_t$ versus t , respectively. If the correlation coefficient for the pseudo-second-order model has high value. These facts suggest that the pseudo-second-order mechanism is predominant and that chemisorption might be the rate-limiting step that controls the adsorption process (Ho and McKay, 1999; McKay and Ho, 1999)