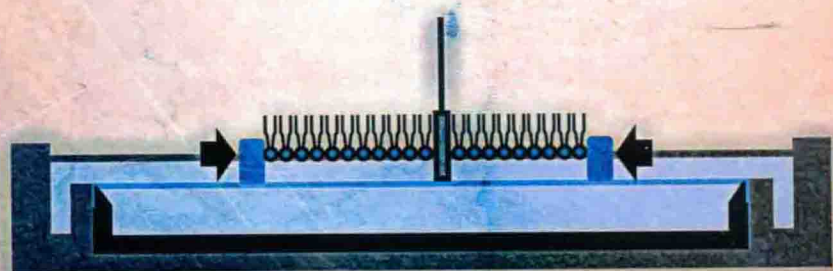


Chemical Engineering Methods and Technology

LANGMUIR MONOLAYERS in Thin Film Technology



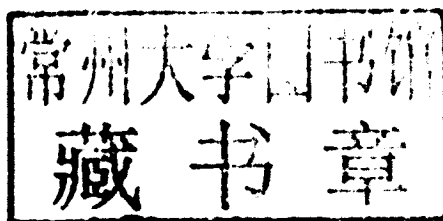
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CHEMICAL ENGINEERING METHODS AND TECHNOLOGY

LANGMUIR MONOLAYERS IN THIN FILM TECHNOLOGY

JENNIFER A. SHERWIN
EDITOR



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CHEMICAL ENGINEERING METHODS AND TECHNOLOGY

**LANGMUIR MONOLAYERS IN THIN
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PREFACE

The Langmuir-Blodgett (LB) technique for the preparation of ultrathin films of various organic, metallorganic, and polymeric compounds play an increasingly important role as a means of organizing molecular materials at the microscopic level. The LB technique has many potential applications in molecular electronics, nonlinear optics and conducting thin films. This book presents current research from across the globe in the study of Langmuir Monolayers, including the study of thermotropic liquid crystals and binary mixtures of dichroic azo dye/liquid crystal in Langmuir and Langmuir-Blodgett films; proteo-lipidic nanostructures generated via the Langmuir-Blodgett film method; Langmuir Monolayers in biosensors; as well as adsorptive characteristics of bovine serum albumin onto cationic Langmuir Monolayers of sulfonated poly-grafted cellulose.

Chapter 1 - In this article, various adsorption isotherm models, kinetic models, adsorption thermodynamics and the technical viability of carbons made from different biomaterials and different types of naturally occurring clays for heavy metals removal by adsorption from contaminated water has been reviewed. Natural clays and carbons prepared from waste plant products can be employed for heavy metals removal from aqueous solutions and disposed of with little cost. Modification of these materials can also improve their adsorption capacity. In this review, an extensive literature survey from the past decade on the heavy metals removal characteristics of clays and carbons has been compiled to provide a summary. It is evident from this literature survey that carbons made from biomaterials and clays have demonstrated outstanding removal capabilities for certain metal ions. Some of the highest adsorption capacities reported are: for Cd(II), 180 mg/g by bean husk (*Phaseolus vulgaris*) carbon; for Cr(VI), 120.48 mg/g by date palm seed wastes carbon; for Pb(II), 279.92 mg/g by carbon made from *Euphorbia rigida*; for Hg(II), 151.5 mg/g by ZnCl₂ activated walnut shells carbon; for Cr(III), 117.5 mg/g by Smectite clay with a small proportion of kaolinite; for Cd(II), 74.07 mg/g by petra clay; for Cu(II), 105.38 mg/g by modified Unye clay; for Pb(II), 104.28 mg/g by natural palygorskite clay; for Cu(II), 909 mg/g by Saudi bentonite. It is important to note that the adsorption capacities of the adsorbents presented in this paper vary, depending on the experimental conditions, characteristics of the individual adsorbent, the extent of chemical modifications, and the concentration of adsorbate.

Chapter 2 - In this review articles the results of the study of thermotropic liquid crystals and of binary mixtures of dichroic azo dye/liquid crystal in Langmuir and Langmuir-Blodgett films are presented. The liquid crystals of rod-like shape from various homologous series and nine azo dyes with different molecular structure as well as different values and directions of

the dipole moment were chosen. It was found that the liquid crystals with the terminal isothiocyanato (–NCS) group are not able to form a compressible monolayer at the water surface. Very short and very long alkyl or alkoxy chains attached to the rigid molecular core also hinder the creation of the stable film. Azo dyes cannot form the Langmuir film themselves; therefore, the liquid crystals 4-*n*-octyl-4'-cyanobiphenyl (8CB) and *trans*-4-*n*-octyl(4'-cyanophenyl)-hexane (8PCH) were used as supporting matrices. The Langmuir films were characterized by the surface pressure-area and surface potential-area isotherms and by Brewster angle microscopy (BAM). The analysis of the isotherms and BAM images of liquid crystals indicated that the organization of the mesogenic molecules at the air-water interface is dependent on their structure and to some extent reflects their ability to form an appropriate mesophase in the bulk. For the binary azo dye/8CB mixtures the miscibility of two components as well as the organization and the packing of molecules at the water surface were determined. The absorption spectra by using natural and linearly polarized light were recorded for both Langmuir and Langmuir-Blodgett films. Information about spectral properties of ultra-thin layers and ability of dye and liquid crystal molecules to form self-aggregates was obtained. The polarized absorption spectra allowed one to determine the alignment of molecules on the quartz surface.

Chapter 3 - Recently, much of the emphasis in biotechnology has been on producing nanosystems and nanodevices for a vast range of medical applications, including nanoelectronic biosensors, drug delivery systems, and diagnostic and imaging techniques, to name a few. This chapter reviews the potentially useful creation of proteo-lipidic nanostructures generated via the Langmuir-Blodgett (LB) film method, and their direct characterization by atomic force microscopy (AFM). Following the introductory sections, a brief overview on LB film fabrication on surfaces suitable for AFM will be presented, LB films containing proteins, lipids, and biocompatible amphiphilic molecules will be described, and how they have been studied using various AFM imaging modes. We aim to highlight recent developments that illustrate the unique capability of AFM in elucidating nanometer scale organization and the physicochemical properties of artificially engineered biological membranes through the Langmuir-Blodgett method; as it could potentially open a new pathway toward the development of self-organized nanostructures of technological significance.

Chapter 4 - In recent years, the Langmuir-Blodgett (LB) technique for the preparation of ultrathin films of various organic, metallorganic, and polymeric compounds plays an increasingly important role as a means of organizing molecular materials at the microscopic level. The LB technique has many potential applications in molecular electronics, nonlinear optics and conducting thin films. The most important advantage of this method is that the characteristic of the film can be varied by changing various LB parameters, namely, surface pressure of lifting, temperature, barrier speed, dipping speed, molar composition, etc. So it is important to study different molecules having various chromophores with interesting photophysical and electrical properties, confined in the restricted geometry of the LB films to fabricate various molecular electronic devices and also to realize the basic physicochemical processes involved at the mono and multilayer films [1].

Chapter 5 - Investigation on adsorption behaviour of Bovine Serum Albumin (BSA) on polymeric adsorbent materials is critical for many analytical and biomedical applications. In the present study a novel adsorbent poly(glycidylmethacrylate)-grafted-cellulose having sulfonate functional groups (PGMA-g-Cell-SO₃H) was prepared by graft copolymerization of

glycidylmethacrylate (GMA) onto cellulose in the presence of ethyleneglycoldimethacrylate as crosslinker using α,α -azobisisobutyronitrile as initiator followed by the introduction of sulfonic acid groups through ring opening reaction of the epoxide groups of the grafted GMA with sodium sulfite–isopropanol–water mixture. The original and the modified materials were characterized by means of FTIR, SEM, XRD and BET analysis. Adsorption characteristics of BSA onto PGMA-g-Cell-SO₃H were investigated under different optimized conditions of pH, contact time, initial BSA concentration, adsorbent dose and temperature. The maximum value of BSA adsorption was found to be 49.95 and 72.07 mg/g for an initial concentration of 100 and 150 mg/L, respectively at pH 4.5. Kinetic studies showed that the equilibrium conditions were achieved within 3 h. The kinetic data obtained at different concentrations and temperatures were analyzed using a pseudo-first-order and pseudo-second-order equation. The adsorption process followed pseudo-second-order kinetics. The experimental kinetic data were correlated by the external mass transfer and intraparticle mass transfer diffusion models. The intraparticle mass transfer diffusion model gave a better fit to the experimental data. Experimentally obtained isotherms were evaluated with reference to Langmuir, Freundlich and Sips equations. The isotherm data were best modelled by the Langmuir isotherm equation and the maximum monolayer adsorption capacity was found to be 124.85 mg/g at 30 °C. Thermodynamic study revealed an endothermic adsorption process. The negative ΔG° values indicate feasible and spontaneous adsorption of BSA onto PGMA-g-Cell-SO₃H. The positive and small value of enthalpy change ΔH° (9.50 kJ/mol) indicates the endothermic nature of adsorption primarily through weak physical forces between adsorbent and adsorbate. The positive and small value of entropy change, ΔS° (185.52 J/mol/K) indicates that the order less nature of adsorption system increases with adsorption of BSA onto adsorbent surface. Also at all temperatures $\Delta H^\circ < T \Delta S^\circ$, indicating that the BSA adsorption onto PGMA-g-Cell-SO₃H is dominated by entropic rather than enthalpic changes. The values of isosteric heat of adsorption computed from linear isotherms remained almost constant (~ 26.45 kJ/mol) with different surface loadings suggest that the surface of PGMA-g-Cell-SO₃H is energetically more or less homogeneous and the lateral interactions between adsorbed BSA ions do not exist. Adsorbed BSA was eluted completely by 0.2 M CH₃COOH solution. Results obtained from repeated adsorption/desorption process showed that PGMA-g-Cell-SO₃H can be used for the adsorption of BSA from various aqueous solutions.

Chapter 6 - The utilization of the Langmuir-Blodgett (LB) technology for the fabrication of engineered supramolecular thin films has received an exceptional development in these last years due to possibility of different applications in materials science ranging from nanotechnology to biosensors. The materials fabricated by LB technology provide an accurate control of the order at the molecular level. The main objective of this chapter is to give an overview of the electrochemical properties of a particular class of polymeric thin films such as conducting polymers and ionomer polymers and describe the potentialities of some recent electrochemical technique for nanotechnological applications mainly scanning electrochemical technique (SECM) and SECM combined to Langmuir trough.

CONTENTS

Preface		vii
Chapter 1	Carbons and Clays for Heavy Metals Removal – A Review of Latest Literature <i>John U. Kennedy Oubagaranadin and Z.V.P. Murthy</i>	1
Chapter 2	Molecular Organization of Thermotropic Liquid Crystals and Their Mixtures with Azo Dyes in Langmuir and Langmuir-Blodgett Films <i>Danuta Bauman, Anna Modlińska, and Krzysztof Inglot</i>	51
Chapter 3	Atomic Force Microscopy Characterization of Lipid/ Protein Nanostructures Formed in Langmuir-Blodgett Films <i>Yih Horng Tan and Keith J. Stine</i>	101
Chapter 4	Langmuir Monolayers in Biosensors <i>Jadwiga Soloducho and Joanna Cabaj</i>	131
Chapter 5	Adsorptive Characteristics of Bovine Serum Albumin onto Cationic Langmuir Monolayers of Sulfonated Poly (Glycidylmethacrylate)- Grafted Cellulose: Mass Transfer Analysis, Isotherm Modeling and Thermodynamics <i>T. S. Anirudhan and P. Senan</i>	151
Chapter 6	Electrochemistry of Polymeric Thin Films Prepared by Langmuir-Blodgett Technique <i>Paolo Bertoncello</i>	177
Index		201

Chapter 1

CARBONS AND CLAYS FOR HEAVY METALS REMOVAL – A REVIEW OF LATEST LITERATURE

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ABSTRACT

In this article, various adsorption isotherm models, kinetic models, adsorption thermodynamics and the technical viability of carbons made from different biomaterials and different types of naturally occurring clays for heavy metals removal by adsorption from contaminated water has been reviewed. Natural clays and carbons prepared from waste plant products can be employed for heavy metals removal from aqueous solutions and disposed of with little cost. Modification of these materials can also improve their adsorption capacity. In this review, an extensive literature survey from the past decade on the heavy metals removal characteristics of clays and carbons has been compiled to provide a summary. It is evident from this literature survey that carbons made from biomaterials and clays have demonstrated outstanding removal capabilities for certain metal ions. Some of the highest adsorption capacities reported are: for Cd(II), 180 mg/g by bean husk (*Phaseolus vulgaris*) carbon; for Cr(VI), 120.48 mg/g by date palm seed wastes carbon; for Pb(II), 279.92 mg/g by carbon made from *Euphorbia rigida*; for Hg(II), 151.5 mg/g by ZnCl₂ activated walnut shells carbon; for Cr(III), 117.5 mg/g by Smectite clay with a small proportion of kaolinite; for Cd(II), 74.07 mg/g by petra clay; for Cu(II), 105.38 mg/g by modified Unye clay; for Pb(II), 104.28 mg/g by natural palygorskite clay; for Cu(II), 909 mg/g by Saudi bentonite. It is important to note that the adsorption capacities of the adsorbents presented in this paper vary, depending on the experimental conditions, characteristics of the individual adsorbent, the extent of chemical modifications, and the concentration of adsorbate.

1. INTRODUCTION

Heavy metals in the environment are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Eleven metals, viz., Pb, Cr, Hg, U, Se, Zn, As, Cd, Co, Cu and Ni, out of 20 classified metals as toxic, are emitted into environment in quantities that pose risks to human health (Kortenkamp et al., 1996). It is known that adsorption is cost effective and efficient in heavy metals removal from solutions.

Application of carbons made from plant species and naturally occurring inorganic materials (clays) in heavy metals removal from various industrial effluents or water resources have been reported. Adsorption with clays has become an alternative to traditional methods of industrial wastewater treatment and it is relatively inexpensive, non-hazardous, and may permit recovery of the metals from the adsorbing mass.

Adsorbent carbons and clays are different in nature. A pure carbon surface is considered to be non-polar, but in actuality some carbon-oxygen complexes C_xO , CO_x and C_xO_2 are usually present. When a metal ion is present in solution, surface complexes may be formed by ion exchange between H^+ functional groups and metal ions in solution. Such mechanism is consistent with those proposed in earlier investigations (Namasivayam and Periasamy, 1993; Namasivayam and Kadirvelu, 1999). As metal ions are adsorbed onto the carbon, more hydrogen ions are released from the carbon into solution. The hydrogen ion sources are most likely the carboxylic, phenolic, sulfonic and lactonic groups in the carbon. These groups are generally considered to be responsible for cation exchange capacity of carbons (Kadirvelu et al., 2000).

Clays are basically aluminosilicate minerals containing sodium, potassium and calcium, in which magnesium and iron may be substituted for aluminium. The ion-exchange capacity of clays depends on the frame work of Si/Al ratio and decreases as the Si/Al ratio increases. The clays carry a net negative charge due to the broken bonds around the edges of the silica-alumina units that would give rise to unsatisfied charges, which would be balanced by the adsorbed cations. Substitutions within the lattice structure of trivalent aluminum for quadrivalent silicon in the tetrahedral sheet and of ions of lower valence, particularly magnesium for trivalent aluminum in the octahedral sheet, result in unbalanced charges in the structural units of clay minerals (Pehlivan et al., 2006).

The process of adsorption is well explained by the well-known two-parameter Freundlich and Langmuir isotherms. However there are a number of other two-parameter, three-parameter and four-parameter models that can explain the adsorption equilibrium data better. Similarly kinetics of adsorption can be represented by a number of rate models. This article provides a collection of these models for the testing of adsorption equilibrium and kinetics data, and an overview of carbons made from bio-materials and clays for heavy metal removal from aqueous solutions based on recent publications (past decade).

2. ADSORPTION ISOTHERMS, KINETICS AND THERMODYNAMICS

2.1. Adsorption Isotherms

Adsorption is a surface process that leads to transfer of molecules from a fluid bulk to solid surface. This can occur because of physical forces or by chemical bonds. In most of the

cases, this process is described at the equilibrium by means of some equations that quantify the amount of substance attached on the surface given the concentration in the fluid. These equations are called isotherms because of the dependence of their parameters on the temperature, which is one of the most important factors affecting the adsorption. The uptake capacity of an adsorbent at equilibrium is given by:

$$q_e = \frac{(C_0 - C_e)}{m/V} \quad (2.1)$$

where, C_0 and C_e are the initial and equilibrium concentration of the adsorbate (mg/L), m is mass of the adsorbent (g) and V is the volume of the solution (L). A brief description of various adsorption isotherm models used by researchers is given below.

2.1.1. Henry Isotherm

Henry's law is basically a one parameter model and has been applied in many cases (Ho, 2004a). It has the form of equation of a straight line with no intercept. This model normally does not represent the adsorption equilibrium data due to the unavailability of adsorption data in the lower range of metal concentration. In liquid-phase adsorption, the equilibrium adsorption data are normally obtained at higher equilibrium concentrations, where the adsorbent surface is almost at the edge of saturation. High concentrations may suggest the applicability of a model having a linear relationship between q_e and C_e at the latter part of the equilibrium isotherm curve. This requisite may be partially fulfilled using Henry's law equation with an intercept. The addition of a constant term in Henry's law provides the model to integrate the basic characteristics of the equilibrium isotherm curve at the high concentration range. Henry's law is given as:

$$q_e = K_H C_e + b \quad (2.2)$$

where, K_H and b are model constants. This model can be applied for high effluent concentration.

2.1.2. Freundlich Isotherm

The Freundlich isotherm (Freundlich, 1907) habitually gives a better fit particularly for adsorption from liquids and can be expressed as:

$$q_e = K_F C_e^{1/n} \quad (2.3)$$

In this model, the mechanism and the rate of adsorption are functions of the constants n and K_F (L/g). For a good adsorbent, $1 < n < 10$, and a higher value of n indicates better adsorption and formation of rather strong bond between the adsorbate and adsorbent (Treybal, 1981). It is a simple expression and shows no leveling.

2.1.3. Langmuir Isotherm

The Langmuir (1916, 1917, 1918) model assumes uniform energies of sorption onto the surface and no transmigration of adsorbate in the plane of the surface. The Langmuir equation may be written as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2.4)$$

In this model, q_m (mg/g) is the amount of adsorption corresponding to complete monolayer coverage, i.e., the maximum adsorption capacity and K_L (L/mg) is the Langmuir constant. It is also a simple expression with interpretable parameters and applicable for monolayer adsorption. For Langmuir type adsorption process, to determine if the adsorption is favorable or not, a dimensionless separation factor, R_L , is defined (Hall et al., 1966) as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (2.5)$$

If $R_L > 1$, the isotherm is unfavorable

$R_L = 1$, the isotherm is linear

$0 < R_L < 1$, the isotherm is favorable

2.1.4. Dubinin-Radushkevich Isotherm

The Dubinin-Radushkevich (D-R) adsorption isotherm (Dubinin and Radushkevich, 1966) is given as:

$$q_e = q_m \exp(-D\varepsilon^2) \quad (2.6)$$

here, ε (known as Polanyi potential) is given as (Rosene and Manes, 1977):

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (2.7)$$

where, R is the gas constant, T is temperature and the constant D (mol^2/kJ^2) given by the following Eq. (2.8), in terms of the mean free energy E (kJ/mol) of sorption per molecule of adsorbate. When the molecule is transferred to the surface of the solid from infinity in the solution, E is given by:

$$E = \frac{1}{\sqrt{2D}} \quad (2.8)$$

This isotherm is temperature independent and suitable for porous adsorbents.

2.1.5. Temkin Isotherm

The derivation of the Temkin isotherm (Temkin and Pyzhev, 1940) assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm equation assumes that the heat of sorption of all the molecules in the layer decreases linearly with coverage due to sorbent-sorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. The Temkin isotherm has generally been applied in the following form:

$$q_e = B \ln(K_T C_e) \quad (2.9)$$

$$\text{where } B = \frac{RT}{-\Delta H^o} \quad (2.10)$$

Here, B is related to the heat of sorption (J/mol), R the gas constant (8.314 J/mol/K) and T the absolute temperature (K) and K_T (L/mg) is the equilibrium binding constant corresponding to the maximum binding energy.

2.1.6. Harkins-Jura Isotherm

The Harkins-Jura adsorption isotherm can be expressed as (Başar, 2006):

$$q_e = \sqrt{\frac{P_1}{P_2 - \log C_e}} \quad (2.11)$$

where, P_1 and P_2 are isotherm constants. This model accounts to multi-layer sorption and can be explained with the existence of a heterogeneous pore distribution.

2.1.7. Halsey and Henderson Isotherms

The Halsey isotherm (Halsey, 1948) and Henderson isotherm (Henderson, 1952) models explains multilayer sorption. They are generally applied in the following forms, respectively:

$$q_e = \exp\left(\frac{\ln P_3 - \ln C_e}{P_4}\right) \quad (2.12)$$

$$q_e = \left(\frac{-\ln(1 - C_e)}{P_5}\right)^{1/P_6} \quad (2.13)$$

where P_3 , P_4 , P_5 and P_6 are isotherm constants.

2.1.8. Brunauer-Emmet-Teller Isotherm

The Brunauer-Emmet-Teller (BET) isotherm (Brunauer et al., 1938) is an S-shaped isotherm, given as:

$$q_e = \frac{q_m k C_e}{(C_0 - C_e)[1 + (k - 1)(C_e / C_0)]} \quad (2.14)$$

The constant k is large as compared to unity and, therefore, the isotherm consists of two regions, i.e. low and high concentration regions. This isotherm is applicable for multilayer adsorption.

2.1.9. Redlich-Peterson Isotherm

Redlich-Peterson sorption isotherm (Redlich and Peterson, 1959) is an empirical isotherm incorporating three parameters. It combines elements from both the Langmuir and Freundlich equations, and the mechanism of sorption is a hybrid and does not follow ideal monolayer sorption. This model is given as:

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^\beta} \quad (2.15)$$

Here K_{RP} is Redlich-Peterson isotherm constant (L/g), a_{RP} is also a constant (L/mg)^{1/β} and β is an exponent that lies between 0 and 1. For $\beta = 1$, Eq. (2.15) reduces to Langmuir equation and for $\beta = 0$, it reduces to Henry's equation. This three-parameter model approaches the Freundlich model at high concentrations and is in agreement with the low concentration limit of the Langmuir equation.

2.1.10. Sips Isotherm

Recognizing the problem of the continuing increase in the adsorbed amount with an increase in concentration in the Freundlich equation, Sips (1948) proposed an equation similar in form to the Freundlich equation, but it has a finite limit when the concentration is sufficiently high. Sips isotherm has the following form:

$$q_e = \frac{q_m (K_S C_e)^\gamma}{1 + (K_S C_e)^\gamma} \quad (2.16)$$

where, q_m is the maximum adsorption capacity (mg/g), K_S is the Sips isotherm constant (L/g) and γ is the model exponent. At low sorbate concentrations, Sips equation reduces to the Freundlich isotherm. At high sorbate concentrations, Sips model predicts monolayer sorption capacity and distinctiveness of the Langmuir isotherm.

2.1.11. Radke-Prausnitz Isotherm

The Radke-Prausnitz isotherm model (Radke and Prausnitz, 1972) can be expressed as:

$$q_e = \frac{q_m K_{rp} C_e}{(1 + K_{rp} C_e)^\alpha} \quad (2.17)$$

where, K_{rp} is Radke-Prausnitz model constant and α the model exponent. It represents the Langmuir model for $\alpha = 1$ and Henry's model for $\alpha = 0$.

2.1.12. Tóth Isotherm

Tóth (2000) has modified the Langmuir equation to reduce the error between experimental data and predicted values of equilibrium adsorption data. The application of this equation is best suited to multi-layer adsorption similar to BET isotherm which is a special type of Langmuir isotherm and has very restrictive validity. The Tóth model can be represented as:

$$q_e = \frac{q_m K_{Th} C_e}{[1 + (K_{Th} C_e)^\delta]^{1/\delta}} \quad (2.18)$$

where K_{Th} is the Tóth model constant and δ is the model exponent. For $\delta = 1$, this isotherm reduces to the Langmuir adsorption isotherm.

2.1.13. Fritz–Schluender Isotherm (3-Parameter)

The Fritz–Schluender equation (Fritz and Schluender, 1974) has the following form:

$$q_e = \frac{q_m K_{FS} C_e}{1 + q_m C_e^\lambda} \quad (2.19)$$

where K_{FS} the Fritz-Schluender equilibrium constant (L/mg), and λ is the Fritz–Schlunder model exponent.

2.1.14. Fritz–Schluender Isotherm (4-Parameter)

Fritz–Schluender (Fritz and Schluender, 1974) proposed an empirical relation with four parameters to describe equilibrium data and it is Langmuir-Freundlich type of equation.

$$q_e = \frac{J C_e^K}{1 + L C_e^M} \quad (2.20)$$

where J and L are the Fritz–Schluender parameters, and K and M are the Fritz–Schluender equation exponents. At high liquid-phase concentrations of the adsorbate, Eq.(2.20) reduces to the Freundlich equation and for $K = M = 1$, Eq. (2.20) reduces to the Langmuir equation.

2.1.15. Extended Langmuir Isotherm

Originally, the Langmuir model was intended for monolayer adsorption with no interaction between adsorbed molecules. Thus, its ability to correlate experimental data is

limited. The extended Langmuir model (Yao, 2000) is a modified three-parameter version of the Langmuir model, which can provide better fit to the experimental data (Hall et al., 1966).

$$q_e = \frac{q_m K_{EL} C_e}{(1 + K_{EL} C_e + k_{EL} \sqrt{K_{EL} C_e})} \quad (2.21)$$

where, K_{EL} (L/mg) and k_{EL} (dimensionless) are model parameters. The constant K_{EL} of the model is a coefficient attributed to the affinity between the adsorbent and adsorbate.

2.1.16. Competitive Langmuir Isotherm

The difficulties in describing the adsorption of metal ions from wastewater resulted from the presence of several different ions, causing interference and competition on adsorption sites. Therefore, for a wastewater containing two different metal ions, the competitive Langmuir model for two competing ions, can be used in order to express the relationships between the quantity of the first component adsorbed and the concentration of the second component (Ho and McKay, 2000). The model can be expressed as:

$$q_{e,i} = \frac{q_{m,i} K_i C_{e,i}}{1 + K_i C_{e,i} + K_j C_{e,j}} \quad (2.22)$$

where, K_i and K_j are model parameters, and the subscripts i and j indicate two different metal ions.

2.2. Adsorption Kinetics

Two vital evaluation elements for an adsorption process operation unit are the mechanism and the reaction rate. Solute uptake rate determines the residence time required for completing the adsorption and can be enumerated from kinetic analysis. Numerous attempts were made in formulating a general expression to describe the kinetics of adsorption on solid surfaces for the liquid-solid adsorption system. In 1898, Lagergren presented the pseudo-first-order rate equation for the adsorption of oxalic acid and malonic acid onto charcoal (Lagergren, 1898; Ho, 2004b). Lagergren's kinetics equation may have been the first one in describing the adsorption of liquid-solid systems based on solid capacity.

The two kinetic models, namely pseudo-first-order (Lagergren, 1898; Ho, 2004b) and pseudo-second-order (Ho and McKay, 1999) equations have been widely used to describe adsorption data obtained under non-equilibrium conditions. In most of the adsorption kinetic studies, both pseudo-first-order and pseudo-second-order kinetic equations have been commonly employed parallelly and one is often claimed to be better than another according to marginal difference in correlation coefficient. As noted by Rudzinski and Plazinski (2006), in the past decades no attempts were made to clearly explain the theoretical origins of these two equations, i.e., current understanding of adsorption kinetics is much less than theoretical description of adsorption equilibrium. A brief description of various kinetic models is given below.