Modeling the Mass-transport Processes in the Sorption of Metal Ions onto Bone Char

by

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This is to certify that I have examined the above PhD thesis and have found that it is complete and satisfactory in all respects, and that any and all revisions required by the thesis examination committee have been made.

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LIST OF PUBLICATIONS

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Modeling the Mass-transport Processes on the Sorption of Metal Ions onto Bone Char

by

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Abstract

This research focuses on the adsorption of cadmium, copper and zinc ions onto bone char. The first part of this research studies the sorption equilibrium of each system. The Langmuir, Langmuir-Freundlich, and binary Langmuir equations are used to correlate the experimental data. The Langmuir and the Langmuir-Freundlich equations are used to incorporate the Ideal Adsorbed Solution Theory to predict the multicomponent data.

The sorption kinetics of metal ions onto bone char was studied using a batch agitation method. Novel film-pore and film-pore-surface diffusion models derived by incorporating a Langmuir-type isotherm equation, shrinking core model and mass balance equation, were used to correlate the experimental data for single component systems. These new diffusion models were applied to different sorption systems to model the effect of initial concentration and mass of sorbent on uptake. The results obtained from these models were comparable to those obtained from the analytical film-pore diffusion model but provide better agreement with the experimental data. The temperature effect was analyzed to verify that the pore diffusion is the primary mass transport mechanism of metal ions.

As the film-pore diffusion model was successfully used to correlate the single component systems, it was extended to incorporate the empirical method or the IAST in the diffusion model to correlate the multicomponent systems. Finally, the IAST-film-pore diffusion is recommended for use in kinetic study for the multicomponent systems.
CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the aquatic environment. These metals are of special concern because they are non-degradable and therefore persistent. A major source of heavy metal pollution in the environment is from industrial and mining wastewaters. As industrialization continues to intensify, industries associated with the use of heavy metals - such as electroplating, metal finishing, foundries and metal works - continue to grow throughout the world. However, many industries, particularly in developing countries, are operated at a small or medium scale, perhaps as a family business within the residential premises of the owner. These units generate considerable amounts of heavy metals, which are in many cases discharged directly into the environment without any facilities for wastewater treatment. This is because the capital investment, turnover and profit for these industries are also small.

In recent years, public awareness has increased with regard to the long term toxic effects of water containing dissolved metal ions. The concentrations of these pollutants must be reduced in order to meet the legislative standards and/or to recover valuable metals from effluents. Consequently improved and innovative methods of wastewater treatment are continuously being developed in simple and economic ways to deal with the requirements of industries. Therefore, the removal of
metal ions from effluents is significant to many industries on an environmental basis, the potential for water reuse and the potential for metal recovery. A number of technologies have been developed over the years to remove metal ions from water. Adsorption is often the most effective method to treat the low concentration pollutants in wastewaters. Therefore, an adsorption system is frequently found in the final stage of a wastewater treatment system to polish the effluent before discharging or recycling.

The most commonly used sorbents to remove metal ions from the effluent are ion exchange resins. Recently, the application of natural sorbent including agricultural products, carbonaceous waste by-product and zeolite has been investigated by a number of researchers. The sorption capacities of some sorbents (i.e. bone char and zeolite) are comparable to ion exchange resins. These sorbents after treatment process may be disposed into the authorized landfill system or may be regenerated for further use in the sorption system depending on the cost of sorbent and the operation cost for the regeneration process. Therefore, the utilization of these sorbents in industrial wastewater treatment may be feasible.

In Hong Kong, all wastewater discharged to foul sewer are required to comply with the Technical Memorandum under section 21 of the Water Pollution Control Ordinance (WPCO, 1993). The minimum allowable discharge concentration limits, which are shown on Table 1.1, are based on the flow rate of are 0.6 mg/L for cadmium, 0.1 mg/L for copper and 0.1 mg/L for zinc.
1.2 THE AIM OF THIS RESEARCH

Sorbent performance is the critical factor in the design and operation of an adsorption system. Bone char is a heterogeneous sorbent which is derived from the calcination of animal bone in the absence of air. This sorbent has been shown demonstrated to remove aluminum ions and iron ions from rural water in a pilot study (Lewis, 1995). Therefore, it is believed that bone char can be used to remove metal ions from wastewaters.

The aim of this research is to study the sorption equilibrium and the sorption mass transport of cadmium, copper and zinc ions onto bone char from aqueous solution. The single component equilibrium data will be substituted into Langmuir, Langmuir-Freundlich and binary Langmuir equation equations. The parameters of the equations will be calculated by computer iteration to minimize the error between the experimental data points to the adsorption equilibrium equations. The best fit single component equilibrium equations will be incorporated into an Ideal Adsorbed Solution Theory (IAST) model to predict the equilibrium behavior of multicomponent systems.

The sorption rates of metal ions on bone char will be investigated by batch contact time studies. The experimental data will be substituted into a number of mass transport models, which are single resistance external mass transfer (Furusawa and Smith, 1973); an analytical film pore diffusion model (Spahn and Schlünder, 1975); a new numerical film-pore diffusion model based on the unreacted shrinking core theory and a new film-pore-surface model based on an extension to the last model, to correlate the sorption rate of metal ions onto bone char. As a result, the best-fit single
component mass transfer model will be used to describe the transport of metal ions onto bone char. To extend the use of the IAST and the film-pore diffusion model in multicomponent systems, the IAST will be incorporated into the film-pore diffusion model. Therefore, this new multicomponent diffusion model will be directly used to correlate the kinetic data without estimating the equilibrium data for multicomponent systems. Based on the sorption capacity and sorption rate of bone char, the effectiveness of bone char in wastewater treatment can be evaluated. The results will be useful in their application to the design of bone char sorption systems.
CHAPTER 2

LITERATURE REVIEW

2.1 CHARACTERIZATION OF BONE CHAR

Bone char, a mixed adsorbent containing around 10% carbon and 90% calcium phosphate is mainly produced from the weathered bones of cattle that have died naturally in India and Argentina (Chen, 1985). The animal bone is heated to form charcoal and bone char is manufactured by at least six companies throughout the world. The supply is more than adequate for the foreseeable future. The price is related to the price and demand for gelatin, which is the principle use of bone. Bone char is mainly used as an adsorbent for the decolorization of cane sugar.

Structurally, the calcium phosphate in bone char is in the hydroxyapatite form (Girgis et al., 1997). Apatites have the formula $\text{Ca}_5(\text{PO}_4)_3\text{X}$ or $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$, where $\text{X}$ can be a $\text{F}^-$ ion (fluorapatite, FAP), $\text{OH}^-$ ion (hydroxyapatite, HAP) or a $\text{Cl}^-$ ion (chlorapatite, ClAP) (Elliott, 1994). Bone charcoal consists of a framework of calcium phosphates and carbonates; it is porous in structure with a great number of minute tubes and channels. The skeleton is lined or coated with carbon in a state of fine subdivision and high activity (Bhargava and Killeadar, 1991). Electron micrographs show a structure very similar to that of the crushed bone (Bennett and Abram, 1967). The amorphous carbon fraction is distributed throughout the whole of the hydroxyapatite structure but mostly exists as a highly active thin film over about 50% of the porous hydroxyapatite surface. This thin carbon film effectively determines the more important adsorbent properties of bone char. It has been shown
that after the decarbonization of bone char it has little or no decolorizing power (Bharagava and Kiledar, 1995), although the hydroxyapatite in bone char retains an adsorption capacity to adsorb calcium salts (Bennett and Abram, 1967) and dissolved salts (Bharagava and Kiledar, 1995). Therefore, bone char can eliminate either organic or inorganic species from their solutions.

2.1.1 Formation of Bone Char

Bone mineral can be described as a heterogeneous compound. The composition of bone mineral varies depending on species, type of bone, diet, etc. The basic elements, which compose the animal bone, are calcium, carbonate, phosphate, hydrogen phosphate and hydroxide (Rey, 1998). The amount of $\text{HPO}_4^{2-}$ and $\text{CO}_3^{2-}$ may vary considerably, however the sum of calcium ions is quite constant in most bone tissues (Rey, 1998). The dihydrogen phosphate ions, $\text{H}_2\text{PO}_4^-$, only form under rather acidic conditions, therefore not normally found in biological systems (Elliott, 1994). As the main component in bone char is calcium hydroxyapatite (CaHAP), the reforming of the chemical structure in bone char happens during the thermal process. Unfortunately, the thermal reformation of calcium phosphate compound to calcium hydroxyapatite in bone char has not been reported. But the formation of CaHAP from calcium phosphates using thermal process was reported.

The forming of the Ca-PO$_4$ bond at high temperature is essentially related to thermal stability. Two ranges of decomposition of apatites and Ca-PO$_4$ compounds can be distinguished (Elliott, 1994; Rey, 1998): a low-temperature irreversible decomposition (150-1000°C) and a high-temperature reversible decomposition (above 1000°C). The first reaction occurring in Ca-PO$_4$ materials is the condensation
of hydrogen phosphate ions HPO$_4^{2-}$. This reaction begins at temperatures as low as 150-300°C in non-stoichiometric hydroxyapatite and other HPO$_4^{-}$ containing compounds:

\[ 2\text{HPO}_4^{2-} \rightarrow \text{P}_2\text{O}_7^{4-} + \text{H}_2\text{O} \quad [2.1.1.1] \]

The P$_2$O$_7^{4-}$ ions in the apatite lattice are believed to remain in a very distorted form. Carbonate ions also begin to decompose at low temperature (300-1000°C) especially in HPO$_4$-containing apatite, probably because of proton transfer and bicarbonate ion decomposition:

\[ 4\text{HPO}_4^{2-} + 2\text{CO}_3^{2-} \rightarrow 4\text{PO}_4^{3-} + 2\text{H}_2\text{O} + 2\text{CO}_2 \quad [2.1.1.2] \]

At higher temperatures (500-1000°C) carbonate ions begin to decompose by themselves:

\[ \text{CO}_3^{2-} \rightarrow \text{CO}_2 + \text{O}^{2-} \quad [2.1.1.3] \]

At about 700°C, pyrophosphate ions react with OH$^{-}$ ions to restore PO$_4^{3-}$ ions:

\[ \text{P}_2\text{O}_7^{4-} + 2\text{OH}^{-} \rightarrow 2\text{PO}_4^{3-} + \text{H}_2\text{O} \quad [2.1.1.4] \]

All these reactions are irreversible. At around 800°C, massive restructuring of the non-stoichiometric hydroxyapatite generally occurs depending essentially on the Ca/P ratio of initial product.

When the atomic Ca/P ratio is between 1.5 and 1.667 β-tricalcium phosphate [Ca$_3$(PO$_4$)$_2$] and stoichiometric hydroxyapatite are formed. When the atomic ratio is higher than 1.667 then CaO and stoichiometric hydroxyapatite are detected. A final reaction may occur at about 850°C, which is the decomposition of OH$^{-}$:

\[ 2\text{OH}^{-} \rightarrow \text{H}_2\text{O} + \text{O}^{2-} \quad [2.1.1.5] \]
This reaction depends on the water partial pressure and is completely reversible. The oxyapatite (i.e. Ca_{10}(PO_{4})_{6}O ) is eventually formed. This compound is very unstable and it cannot exist in a pure form, but only exists as an oxyhydroxyapatite (i.e. Ca_{10}(PO_{4})_{6}OH_{x}O_{1-x/2} ). At temperatures higher than 1200°C apatites may begin to decompose in a reversible manner into tricalcium phosphate and tetracalcium phosphate. This is attributed to the instability of the oxyapatite formed:

\[
\text{Ca}_{10}\text{(PO}_{4}\text{)}_{6}\text{O} \rightarrow 2\text{Ca}_{3}\text{(PO}_{4}\text{)}_{2} + \text{Ca}_{4}\text{(PO}_{4}\text{)}_{2}\text{O } \quad \text{[2.1.1.6]}
\]

At higher temperatures (above 1600°C) a liquid phase is formed. Then CaO is the only solid phase existing. Slow cooling allows these high-temperature phases to react again and restore stoichiometric hydroxyapatite.

From the above description, the animal bone heated at different temperatures generates different chemical compositions. In fact, the production of bone char has been reported at different temperatures. Bhargava and Killedar (1991) reported that the animal bone is carbonized at high temperatures (1000°C – 1600°C) to produce bone char. Abdel Raouf and Daifullah (1997) reported that the bone char could be derived by heating the animal bone at 800°C for 5h. Some researchers just heated the animal bone to 500 – 600°C to produce the bone char to remove fluoride from drinking water at laboratory scale (Christoffersen et al., 1991; Larsen et al., 1993; Phantumvanit and LeGeros, 1997). Therefore, bone char can be derived from different temperature processes and it may contain different types of calcium and phosphate compounds. If animal bone is heated at 800°C, calcium hydroxyapatite should be the major component in bone char.
2.1.2 Crystal Structure of Calcium Hydroxyapatite (CaHAP)

The chemical formula of calcium hydroxyapatite is Ca_{10}(PO_{4})_6(OH)_2 or Ca_5(PO_4)_3(OH). The crystal structure of CaHAP is hexagonal (P6_3/m). At least two kinds of CaHAP structure were reported. According to the International Centre for Diffraction Data, the unit cell parameters for CaHAP (JCPDS, No.72-1243) are a = 0.9432 nm and c = 0.6881 nm. The unit cell parameters for CaHAP (JCPDS, No.09-432) are a = 0.9448 and c = 0.6884 nm. Figure 2.1 shows the structure of CaHAP. Calcium ions occupy two crystallographic sites: Ca(1) on ternary axes at x = 1/3, y = 2/3 and Ca(2) at sites with symmetry m at z = 1/4, z = 3/4. OH⁻ ions are found at z = 0.198, in channels centered on the hexagonal screw-axes. In stoichiometric apatites, here are 4 Ca(1) and 6 Ca(2) sites per unit cell and all are fully occupied (Fedoroff et
al, 1999). Structural refinement showed that, in the apatite, Ca(1) sites are almost entirely occupied, whilst Ca(2) sites are partially occupied.

2.2 STUDY OF THE SORPTION MECHANISM

In recent studies, bone char was used to adsorb the radioisotopes of antimony and europium ions from radioactive wastes (Abdel Raouf and Daifullah, 1997). The authors suggested that chemisorption was the main operating mechanism for $^{152}\text{Eu}^{3+}$ removal with a high and irreversible fixation on bone charcoal from the aqueous solution. The irreversible fixation is due to the cation exchange of metal ions onto hydroxyapatite. In contrast, physical sorption was suggested to be the main mechanism to remove radioactive organic solutions of antimony when loaded from the liquid organic radioactive wastes. Gu and coworkers (1998) found that both bone char and iron impregnated bone char could remove the uranyl ions ($\text{UO}_2^{2+}$) from wastewater. These authors suggested using bone chars to sorb radioactive metal ions from the wastewater because the sorption process is irreversible.

As studies into the sorption of metal ions onto bone char are relatively limited in number, studying the sorption of metal ions onto pure hydroxyapatite may assist to identify the sorption properties of metal ions onto bone char. Suzuki and coworkers (1982, 1985 and 1991) have studied the sorption capacity of metal ions onto CaHAP. In recent work, Suzuki and coworkers (Hatsushika et al., 1999) concluded that the order of cation sorption according to the amount of exchange by the original CaHAP is as follows:

$$\text{Fe}^{2+} >> \text{Pb}^{2+} > \text{Cr}^{3+} > Y^{3+} \geq \text{La}^{3+} > \text{Al}^{3+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+} = \text{Co}^{2+}$$
The authors also proposed that the sorption mechanisms of metal ions onto CaHAP are based on the following reaction mechanisms: (1) Adsorption and ion exchange on the crystal surface; (2) Reconstruction in the crystal lattice. However, these sorption mechanisms are not always true. Ma and coworkers (1994) found that the sorption of lead ions was primarily through a process of the dissolution of apatite, followed by the precipitation of hydrocerussite, Pb₃(CO₃)₂(OH)₂ but the sorption of cadmium and zinc ions by the apatite might include ion exchange, adsorption, absorption, complexation, or coprecipitation of amorphous phases (Chen et al., 1997).

2.2.1 Adsorption of Metal Ions onto Hydroxyapatite

In 1991, Wu and coworkers studied the sorption mechanism of hydrogen ions onto CaHAP using complexation theory. The authors proposed that hydrogen ions were sorbed on phosphate and hydroxyl sites on the CaHAP surface. There are two adsorption sites on the CaHAP surface.

\[ \equiv \text{CaOH} \quad \text{and} \quad \equiv \text{CaPOH} \]

Where \( \equiv \) represented the surface of sorbent. The sorption of hydrogen ions onto CaHAP is based on the following mechanism:

\[ \equiv \text{PO}^- + H^+ = \equiv \text{POH} \quad [2.2.1.1] \]
\[ \equiv \text{CaOH} + H^+ = \equiv \text{CaOH}_2^+ \quad [2.2.1.2] \]

Based on Wu's results, Xu and coworkers (1994) suggested the cadmium and zinc ions form complex onto hydroxyapatite surface.

\[ \equiv \text{POH} + \text{Cd}^{2+} = \equiv \text{POCd}^+ + H^+ \quad [2.2.1.3] \]
\[ \equiv \text{PO}^- + \text{Cd}^{2+} = \equiv \text{POCd}^* \quad [2.2.1.4] \]
\[ \equiv \text{CaOH} + \text{Cd}^{2+} = \equiv \text{CaOCd}^* + H^+ \quad [2.2.1.5] \]
Although Xu and his coworkers suggested the metal ions bind with the phosphate sites and hydroxyl sites on the CaHAP surface, no experimental work has proved that the metal complex form on the CaHAP surface.

In addition, the dissolution-precipitation reaction was reported to remove the cadmium ion onto the CaHAP surface (Fedoroff et al., 1999). Xu and coworkers (1994) suggested that surface complexation and calcium-cadmium co-precipitation were the primary processes in the uptake of cadmium ion by synthetic apatite. Hodson and coworkers (2000) suggested that metal phosphates form by precipitation after calcium phosphate dissolution.

Dissolution:

\[
\text{Ca}_{10}^{}(\text{PO}_4)^{}_6^{}(\text{OH})_2^{}(s) = 10 \text{Ca}^{2+}_{(aq)} + 6 \text{PO}_4^{2-}_{(aq)} + 2\text{OH}^-_{(aq)}
\]

[2.2.1.6]

Precipitation:

\[
10 \text{M}^{2+}_{(aq)} + 6 \text{H}_2\text{PO}_4^{2-}_{(aq)} + 2\text{H}_2\text{O}(_l) = \text{M}_{10}(\text{PO}_4)^{}_6^{}(\text{OH})_2^{}(s) + \text{H}_2\text{O}(_l)
\]

[2.2.1.7]

Where M is metal ion. Therefore, the dissolution-precipitation should be one of the sorption mechanisms for metal ions removal.

2.2.2 Ion Exchange of Metal Ions onto Hydroxyapatite

In the ion-exchange mechanism, several researchers have attempted to identify the sorption paths of metal ions to hydroxyapatite. Madsen (1982) used β-active strontium to trace the sorption path of the metal ion. The author found that the β-active \(^{89}\text{Sr}\) is first adsorbed onto the CaHAP surface, then it diffuses slowly into the crystal interior and finally it substitutes calcium ions through a CaHAP
recrystallization procedure. A more detailed study on the shift of the XRD pattern was suggested by Koutsoukos and Nancollas (1981). The authors incorporated the strontium ions into the CaHAP lattice at different weight percentages and then calculated the change of unit cell parameters of CaHAP. They found that the increase in weight percent of strontium ions in the sample varied linearly with the unit cell parameters of CaHAP. But the morphology of the CaHAP crystal remained unchanged. Koutsoukos (1998) also reviewed the ion exchange of metal ions onto hydroxyapatite. The author proposed that CaHAP undergoes both isoionic and heteroionic substitutions. In the first type, the substituting ion does not interrupt the crystal lattice while in the second, ions in the lattice are exchanged with similar ions present in solutions in contact with CaHAP. Bivalent metal ions with ionic radii close to that of a calcium ion may replace calcium at all positions in the apatite lattice (Elliott, 1994). As the ionic radius of cadmium ion is close to calcium ion, the cadmium can replace the calcium ion from the CaHAP lattice. Suzuki and coworkers (1982) made an observation. If cations have large electronegativity values and radii close to the range 0.9-1.3 Å, the cations are more easily exchange the calcium from CaHAP. Their assumption can explain why copper and zinc ions, which do not have radii close to calcium ion, can exchange the calcium ion from the CaHAP lattice.

In his paper on a summary on the substitution of ions in the CaHAP surface, Tung (1998) suggested that all three ion species (Ca\(^{2+}\), PO\(_4\)\(^{3-}\) and OH\(^-\)) in the structure of apatite can be substituted by various other ions in varying amounts; the replacement of Ca\(^{2+}\) by monovalent ions, Na\(^+\), K\(^+\) and Li\(^+\), divalent ions, Sr\(^{2+}\), Ba\(^{2+}\), Pb\(^{2+}\), Mn\(^{2+}\), Sn\(^{2+}\), Zn\(^{2+}\) and polyvalent ions, Al\(^{3+}\); the replacement of PO\(_4\)\(^{3-}\) by CO\(_3\)\(^{2-}\), HPO\(_4\)\(^{2-}\),
SO$_4^{2-}$, MnO$_4^{-}$, VO$_4^{2-}$, and BO$_3^{3-}$; the replacement of OH$^-$ by F$, \text{Cl}^-$ and CO$_3^{2-}$. Therefore, CaHAP can be used as a cation and an anion exchanger.

2.2.3 Mass Transport of Metal Ions onto Hydroxyapatite

The previous studies used a chemistry based approach to study the sorption capacities of metal ions onto CaHAP. But diffusion models may interpret the sorption rate of metal ions better than the reaction based models. Suzuki and Takeuchi (1994) suggested that the sorptions of cadmium and copper ions on CaHAP are controlled by solid diffusion rather than pore and surface diffusion. The authors used synthetic CaHAP as a sorbent. The metal ions transferring into the sorbent core should penetrate through the solid. Suzuki and Takeuchi (1994) found that the solid diffusivities of Cd$^{2+}$ and Cu$^{2+}$ ions were variable (i.e. $D_{\text{Ca}^{2+}} = 2 \times 10^{-7}$ cm$^2$/s and $D_{\text{Cd}^{2+}} = 1 \times 10^{-7}$ cm$^2$/s at 298.2K). But Fedoroff and coworkers (1999) found that the solid diffusion coefficient of cadmium ions into CaHAP is equal to 2.2$\times$10$^{-20}$ cm$^2$/s at 28$^\circ$C. These results are more persuasive than the approach by Suzuki. This is because the magnitudes of solid diffusion obtaining from Suzuki and Takeuchi (1994) are too large which are close to pore diffusion of metal ions (Yiacoumi and Tien, 1995).

2.3 ADSORPTION EQUILIBRIUM MODELS

In the study of adsorption equilibrium, the experimental data for single component systems will be correlated by equilibrium equations. The best-fit isotherm equation for single component sorption will be determined to incorporate the ideal adsorbed solution theory to predict the sorption capacities for multicomponent systems.
2.3.1 Adsorption Isotherms for Single Component Systems

In the literature survey, only Gu and coworkers (1998) used the Langmuir equation to analyze the sorption of uranyl ions on bone char and iron-impregnated bone char from contaminated groundwater. Although references for the sorption of metal ions onto bone char are limited, the sorption of metal ions on CaHAP can be utilized as a reference base to study the adsorption equilibria. Fuierer and coworkers (1994) used the Langmuir equation to correlate the sorption of zinc and magnesium ions onto CaHAP. Xu and co-workers (1994) suggested the Langmuir equation to interpret the equilibrium data for the sorption of cadmium and zinc ions onto CaHAP. Kanzaki and coworkers (2000) used the Langmuir and Temkin equation to study the inhibitory effect of magnesium and zinc on the crystallization kinetics of CaHAP. All authors using the Langmuir equation know that the sorption of metal ions on bone char does not obey the fundamental assumptions of the Langmuir equation. However, the mathematical fit of the experimental data is the one of the reasons for using the Langmuir equation. The other reasons use the Langmuir equation is that the Langmuir equation can be used to incorporate into the kinetic equation. Hence, the Langmuir equation applied in these sorption systems should be called "Langmuir-type" equation.

2.3.2 The Ideal Adsorbed Solution Theory (IAST)

This method has been applied to predicting the multi-solute adsorption capacity using only data for single-solute adsorption from dilute liquid solution. The original method was proposed by Myers and Prausnitz (1965) for gas-solid systems. Later, Radke and Prausnitz (1972) modified the method for use in liquid-solid adsorption systems.
In the IAST, the equilibrium equation for single components can take any form, which can fit the experimental data best. The Langmuir, Freundlich and Langmuir-Freundlich isotherms are commonly used in the IAST since these equations can be solved by analytical methods to reduce the complexity of the computer program. The success of the calculation of IAST depends on how well the single component data are fitted, especially in the low concentration region.

The IAST has been used for many sorption systems. For instance, McKay and Al-Duri (1988) used the IAST theory by a graphical method to predict the sorption of dyes onto activated carbon. The fitting of the IAST using the Freundlich isotherm could predict better fitting than the Langmuir isotherm. Sheintuch and Rebhun (1988) used the IAST for the sorption of unknown compounds. The equilibrium data of single components could be correlated by the Langmuir and Freundlich equations to predict the sorption capacity of the multicomponent system. Siedel and Gelbin (1988) used the IAST to predict the sorption of p-nitrophenol and p-chloranilin on activated carbon. The authors proposed that the original IAST could not predict the binary systems accurately. After introducing a parameter to account for extrapolation errors in single solution isotherm at very low concentrations, the IAST could predict the binary data very well. As the fitting of single component isotherm data can directly affect the prediction of multicomponent equilibrium, Porter and coworkers (1999) used five different error methods to reduce the fitting deviation of single components for dye adsorption on carbon. The authors concluded that the “best-fit” single-component isotherm did not necessarily result in the “best-fit” IAST model predictions. Reasons for the apparent behaviour were attributed to the liquid phase interaction. Walker and Weatherley (2000) used the IAST in the sorption of acid
dyes on activated carbon. The authors accurately simulated the experimental data with an average deviation of approximately three percent between modeled and experimental data. The above authors used the IAST in the sorption of organic compounds onto various sorbents. This is because the adsorbed solution theory is an "ideal" state. Organic compounds in dilute aqueous solution often do not have large interaction between the sorbate-sorbate and the sorbate-sorbent. However, the interaction between metal ions may be large. Therefore, literature studies on the sorption of metal ions using IAST are rarely found.

Recently, Al-Asheh and coworkers (2000) compared several correlations, namely, extended Langmuir, extended Freundlich, and extended Langmuir-Freundlich equations with IAST for the sorption of metal ions onto pine bark. The fitting of the extended Langmuir-Freundlich equation was the worst but the other methods including the IAST showed reasonably good agreement with the experimental data. Therefore, the IAST can be used to predict the sorption equilibria of multicomponent metal ion systems under certain conditions.

2.4 ADSORPTION KINETIC MODELS

In adsorption systems, the mass transfer of solute or sorbate onto and within the sorbent particle directly affects the adsorption rate. It is important to study the rate at which the solute is removed from aqueous solution in order to apply adsorption by solid particles to industrial uses. There are essentially four stages in the adsorption process:

(1) Transport of sorbate from the bulk of the solution to the exterior film surrounding of the adsorbent.
(2) Movement of sorbate across the liquid film to external surface sites.

(3) Migration of sorbate within the pores of the sorbent.

(4) Sorption of sorbate at internal surface sites.

All these processes may be involved in the control of the sorbate removal rate. 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 as the rate-limiting steps in the sorption process. In fact, the ion exchange of metal ions onto ion exchangers is also considered to be controlled by diffusion (Helfferich, 1995). In most cases, steps (2) and (3) may control the sorption mechanisms, because the mass transport (external and internal) of adsorbate to adsorbent is a relatively slow process.

2.4.1 External Mass Transfer Model

When the sorbent is put into the fully mixed agitated tank, the sorbent is dispersed uniformly throughout the solution. The solution flowing around the sorbent surface forms a liquid film immediately. The thickness of the liquid film will decrease when the agitation speed increases. However, the thickness of the liquid film does not vanish. In the liquid film region, the sorbate transfers to the sorbent surface by molecular diffusion only at a high agitation speed. Figure 2.2 shows the external mass transfer of sorbate onto sorbent surface. Since the sorbate is transported by molecular diffusion, Fick’s first law can be applied to the external mass transport system.
\[
\frac{1}{S_A} N_i = -D_m \frac{dC}{dx} \equiv -D_m \frac{\Delta C}{\Delta x} \quad [2.4.1.1]
\]

Where \( D_m \) is the molecular diffusion of sorbate, \( S_A \) is the external surface area of the sorbent and \( \Delta x \) is the thickness of the liquid film. From equation [2.4.1.1], the external mass transport of the sorbate can be represented by equation [2.4.1.2]:

\[
\frac{1}{S_A} N_i = -\frac{D_m}{\Delta x} (C_i - C_{r,i}) = -k_f (C_i - C_{r,i}) \quad [2.4.1.2]
\]

From equation [2.4.1.2], the external mass transfer coefficient depends on the molecular diffusivity of solution and the thickness of the liquid film. The molecular diffusivity of organic compounds in aqueous solution can be calculated using the Wilke and Chang (1955) method and the molecular diffusivities of electrolyte in aqueous solution can be calculated using Petr Vanýsek methods (Lide and Frederikse, 1994). However, the thickness of the liquid cannot be measured by any instrument, the external mass transfer coefficient can only be determined by correlations based on experimental data.
CHAPTER 2 LITERATURE REVIEW

From equation [2.4.1.2], the external mass transfer coefficient depends on the molecular diffusivity of solution and the thickness of the liquid film. The molecular diffusivity of organic compounds in aqueous solution can be calculated using the Wilke and Chang (1955) method and the molecular diffusivities of electrolyte in aqueous solution can be calculated using Petr Vanýsek methods (Lide and Frederikse, 1994). However, the thickness of the liquid cannot be measured by any instrument, the external mass transfer coefficient can only be determined by correlations based on experimental data.

For the agitated tank, a method to determine the film diffusion coefficient was proposed by Furusawa and Smith (1973) for the sorption of benzene onto activated carbon. Mathews and Weber (1976) directly determined the external mass transfer coefficient from equation [2.4.1.2]. Later, McKay and Allen (1980 & 1983) used the Henry, Langmuir, and Freundlich equations to calculate the external film mass transfer coefficient for the sorption of dyes on peat. Allen and coworkers (1992) applied the Henry equation to the sorption of metal ions onto peat. The mass transfer coefficient was dependent on initial concentration of solution in the system. Tien (1994) proposed to use the Harriot method to determine the external mass transfer coefficient in batch agitation system. The external mass transfer coefficient can be calculated from the Sherwood number, Reynold number and Schmidt number. Therefore, the external mass transfer coefficient is concentration independent. Recently, Carta and coworkers (1999a, 1999b and 2000) based on a chemical potential equation developed a new approximation to calculate the external mass transfer coefficients, which is concentration dependent.
2.4.2 Intraparticle Diffusion Mechanism

The sorption rate for metal ions onto bone char may be controlled by an ion exchange process or a mass transport process. In early studies, the ion exchange process was considered essentially as a chemical reaction best described in terms of rate coefficients and kinetic orders corresponding to the stoichiometry of exchange (Helfferich, 1982). In 1947, Boyd and coworkers studied the sorption rate of metal ions on ion exchange zeolite. The authors argued that the rate of ion exchange increases with decreasing particle size of the ion exchanger and this led to the inescapable conclusion that mass transport rather than an actual reaction must be the rate-controlling mechanism. The authors identified the potentially rate-controlling steps as diffusion in the liquid to the particle surface, diffusion within the particle, and the actual exchange reaction at a fixed site, the slowest of these steps being the bottleneck and therefore limiting the overall rate. These conclusions indicate that ion exchange may also be a mass transport controlled process.
When the sorbate is transferred to the sorbent surface, the sorbate will be transferred along the pore to the sorption sites inside the sorbent. There are three possible mass transfer mechanisms to transport the sorbate from the outer surface of the sorbent to its inner surface. Figure 2.3 shows that the sorbate diffuses along the pore by molecular diffusion. Pore diffusion is one mechanism by which adsorbates move within the pores of the adsorbent before being adsorbed onto the surfaces of the pores. The pore diffusivity is basically proportional to the porosity, tortuosity factor and molecular diffusivity. As a result, the value of pore diffusivity can be predicted from the molecular diffusivity of the adsorbate and the properties of the adsorbent. The dependency of pore diffusivity on temperature can be predicted using a theory similar to that for molecular diffusivity (Lide and Frederikse, 1994; Wilke and Chang, 1955). It should be noted that the pore diffusivity is independent of adsorbate concentration.

Surface diffusion occurs along the pore surface of the adsorbent after initial adsorption has taken place. The driving force for the surface diffusion is the difference in the amount adsorbed on the pore surface (i.e., solid-phase concentration gradient) (Furuya et al., 1996). While pore diffusion is always operating, the importance of surface diffusion is dependent upon the sorptive affinity between the adsorbate and the adsorbent. Experimental results have shown that the value of surface diffusivity may be a function of the solid phase concentration and temperature. At the present time, the numerical value cannot be predicted from thermodynamic theories and must be determined experimentally. Several empirical correlations are available for the calculation of surface diffusivity. These empirical
formulas have limited applications and apply only under the experimental conditions used to derive them.

The relative importance of pore and surface diffusion in adsorption mass transport is dependent upon the adsorbate-adsorbent system used and must be evaluated on a case-by-case basis (Furuya et al., 1996). Intraparticle diffusion is normally characterized by a lumped parameter, the effective pore diffusivity (if pore diffusion is considered as a primary diffusion mechanism and the surface diffusion is lumped into the pore diffusion coefficient) or the effective surface diffusivity (if surface diffusion is considered as primary diffusion mechanism and pore diffusion is lumped into the surface diffusion coefficient). For low-affinity solutes in macroporous sorbents, pore diffusion is usually the dominant intraparticle diffusion mechanism (Furyua et al., 1996). For high-affinity solutes, the surface diffusivity can be higher than the pore diffusivity by orders of magnitude (Ma et al., 1996). But the effective diffusivity should not be larger than the molecular diffusivity, which is physically impossible (Robinson et al., 1994).

Examples of Pore Diffusion Applications

The mathematics required to model adsorption and ion exchange is essentially the same if the ion-exchange process is not rate limiting (Robinson et al., 1994). Therefore, the mass transport model can be directly used for the sorption of metal ions onto bone char. DePaoli and Perona (1996) suggested that pore diffusion is usually assumed to be the rate-controlling intraparticle process (over surface diffusion) if, in a multi-component system, some species should be more strongly adsorbed than other species (i.e. ionic solution).
<table>
<thead>
<tr>
<th>Investigator</th>
<th>System</th>
<th>Sorbate</th>
<th>Sorbent</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bajpai et al. (1974)</td>
<td>Batch</td>
<td>Metal Ions</td>
<td>Ion-Exchange Resin</td>
<td>Numerical</td>
</tr>
<tr>
<td>Spahn &amp; Schlünder (1975)</td>
<td>Batch</td>
<td>Phenylacetic Acid</td>
<td>Activated Carbon</td>
<td>Analytical</td>
</tr>
<tr>
<td>Brauch &amp; Schlünder (1975)</td>
<td>Column</td>
<td>Phenylacetic Acid</td>
<td>Activated Carbon</td>
<td>Analytical</td>
</tr>
<tr>
<td>Seo &amp; Lee (1995)</td>
<td>Batch</td>
<td>Cd²⁺, Cu²⁺ &amp; Zn²⁺ Ions</td>
<td>Hydroxyapatite</td>
<td>Analytical</td>
</tr>
<tr>
<td>Hsien &amp; Rorrer (1997)</td>
<td>Batch</td>
<td>Cd²⁺ Ions</td>
<td>Chitosan Bead</td>
<td>Analytical</td>
</tr>
<tr>
<td>Arévalo et al. (1998)</td>
<td>Batch</td>
<td>Metal Ions</td>
<td>Ion-Exchange Resin</td>
<td>Numerical</td>
</tr>
<tr>
<td>Veglio et al. (1998)</td>
<td>Batch</td>
<td>Cu²⁺ Ions</td>
<td>Biomass Resin</td>
<td>Analytical</td>
</tr>
<tr>
<td>Chiarle et al. (2000)</td>
<td>Column</td>
<td>Hg²⁺ Ions</td>
<td>Chelating resin</td>
<td>Numerical</td>
</tr>
</tbody>
</table>

The pore diffusion model is widely used in the sorption of organic and inorganic sorbates. Spahn and Schlünder (1975) used the shrinking core model (SCM) to correlate the sorption of phenylacetic acid onto activated carbon. Brauch & Schlünder (1975) extended the work to fixed bed adsorption column systems. The
authors developed a pore diffusion model incorporating the SCM to correlate the experimental data. McKay et al. (1983, 1990 and 1995) successfully extended the use of the SCM in the sorption of dyes onto various types of sorbents. Seo and Lee (1995) also used an SCM based method in the sorption of cadmium, copper and zinc ions onto CaHAP in batch systems. The authors used an analytical solution to correlate the batch kinetic data and the Langmuir equation to correlate the sorption equilibrium data. Pore diffusion models have also been used to correlate experimental data for the ion exchange of metal ions into resin. Kataoka and Yoshida (1985) used a macropore diffusion model to correlate the sorption of sodium ions onto resins. Hasnat and Juvekar (1996, 1997a and 1997b) used the shrinking core model to correlate the sorption of metal ions onto resins. Arévalo and coworkers (1998) used ion exchange resin to remove copper and nickel ions from the aqueous solution. The authors successfully used the pore diffusion model to correlate the experimental kinetic data. There are several examples of using pore diffusion models for modeling the sorption of metal ions and a summary of pore diffusion applications is shown in Table 2.1.

Examples of Surface Diffusion Applications

The surface diffusion model has been widely used in the sorption of organic compounds. Crank (1975) summarized analytical and numerical methods into his book to solve diffusion equation. Traegner and Suidan (1989) used the homogeneous surface diffusion model (HSDM) to correlate the sorption of p-nitrophenol on activated carbon. A numerical method was used to solve the partial differential equation to obtain a constant surface diffusivity.
<table>
<thead>
<tr>
<th>Investigator</th>
<th>System</th>
<th>Sorbate</th>
<th>Sorbent</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crank (1975)</td>
<td>Batch</td>
<td>--</td>
<td>--</td>
<td>Analytical &amp; Numerical</td>
</tr>
<tr>
<td>Traegner &amp; Suidan (1989)</td>
<td>Batch</td>
<td>$p$-nitrophenol</td>
<td>Activated Carbon</td>
<td>Numerical</td>
</tr>
<tr>
<td>Miyabe &amp; Suzuki (1992)</td>
<td>Liquid Chromatography</td>
<td>$p$-tert-octylphenol</td>
<td>Silica Gel</td>
<td>Numerical</td>
</tr>
<tr>
<td>Wang &amp; Roy (1993)</td>
<td>Batch</td>
<td>$p$-nitrophenol</td>
<td>Activated Carbon</td>
<td>Semi-analytical</td>
</tr>
<tr>
<td>Axe &amp; Anderson (1997)</td>
<td>Batch</td>
<td>$Cd^{2+}$ &amp; $Sr^{2+}$</td>
<td>Hydrous Ferric Oxide (HFO)</td>
<td>Numerical</td>
</tr>
<tr>
<td>Miyabe &amp; Takeuchi (1997a &amp; b)</td>
<td>Liquid Chromatography</td>
<td>Organic compounds</td>
<td>Sorbents</td>
<td>Numerical</td>
</tr>
<tr>
<td>Trivedi &amp; Axe (2000)</td>
<td>Batch</td>
<td>$Cd^{2+}$ &amp; $Zn^{2+}$</td>
<td>Metal Oxides (HFO, HAO &amp; HMO)</td>
<td>Numerical</td>
</tr>
</tbody>
</table>

Wang and Roy (1993) suggested an approximate semianalytical solution to the HSDM for a batch reactor. The authors used the experimental data from Traegner and Suidan (1989) to evaluate the stability of the model. The results showed only small deviation from the experimental data and reduced the computing time.
Miyahara and Okazaki (1992) used the surface diffusion model to correlate the sorption of nitrobenzene and benzonitrile on activated carbon. The authors proposed that the surface diffusivities of these compounds are concentration dependent. The authors applied the Eyring’s rate theory (Glasstone et al., 1941) to interpret the phenomenon of surface diffusion. Miyabe and Takeuchi (1997a) also used Eyring’s rate theory to explain the mobility of sorbate on the sorbent surface. The use of the surface diffusion model is not restricted to applications of the sorption of organic compounds. Axe and Anderson (1997) used a surface diffusion model to correlate the sorption of cadmium and strontium ions on hydrous ferric oxide (HFO). Later, Trivedi and Axe (2000) used the surface diffusion model to correlate the sorption of cadmium, zinc and strontium ions onto hydrous oxides of aluminum (HAO), iron (HFO), and manganese (HMO). A summary of surface diffusion applications is shown in Table 2.2.

Examples of Parallel Diffusion Applications

Yoshida and coworkers (1991) used the parallel diffusion model for cellulose membrane adsorption to separate dyes from solution. The authors proposed the parallel diffusion process, in which surface diffusion was the primary mechanism. Maekawa et al. (1993) used the parallel diffusion model in the sorption of dye in cellulose membranes. Surface diffusion was the main sorption mechanism and pore diffusion also occurred in the intraparticle diffusion model. Yoshida and coworkers (1994) also used the parallel diffusion model to calculate the effective diffusivity constant. The authors successfully calculated the pore diffusivity and surface diffusivity for the sorption of bovine serum albumin on chitosan. Robinson et al. (1994) used a combined diffusion model for the sorption of metal ions onto zeolite.
<table>
<thead>
<tr>
<th>Investigator</th>
<th>System</th>
<th>Sorbate</th>
<th>Sorbent</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yoshida et al.</td>
<td>Membrane</td>
<td>Sulfonate Dye</td>
<td>Cellulose</td>
<td>Numerical</td>
</tr>
<tr>
<td>(1991)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maekawa et al.</td>
<td>Membrane</td>
<td>Sulfonate Dye</td>
<td>Cellulose</td>
<td>Numerical</td>
</tr>
<tr>
<td>(1993)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yoshida et al.</td>
<td>Batch</td>
<td>Protein (BSA)</td>
<td>Basic</td>
<td>Numerical</td>
</tr>
<tr>
<td>(1994)</td>
<td></td>
<td></td>
<td>Chitosan</td>
<td></td>
</tr>
<tr>
<td>Oscarson</td>
<td>Batch</td>
<td>Multicomponent</td>
<td>Clays</td>
<td>Numerical</td>
</tr>
<tr>
<td>(1994)</td>
<td></td>
<td>Metal Ions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Robinson et al.</td>
<td>Batch</td>
<td>Multicomponent</td>
<td>Chabazite</td>
<td>Numerical</td>
</tr>
<tr>
<td>(1994)</td>
<td></td>
<td>Metal Ions</td>
<td>Zeolite</td>
<td></td>
</tr>
<tr>
<td>Furuya et al.</td>
<td>Batch</td>
<td>Phenolic</td>
<td>Activated</td>
<td>Numerical</td>
</tr>
<tr>
<td>(1996)</td>
<td></td>
<td>Compounds</td>
<td>Carbon</td>
<td></td>
</tr>
<tr>
<td>Hasnat &amp; Juvekar</td>
<td>Batch</td>
<td>Na⁺ &amp; K⁺ Ions</td>
<td>Ion-Exchange</td>
<td>Numerical</td>
</tr>
<tr>
<td>(1996)</td>
<td></td>
<td></td>
<td>Resin</td>
<td></td>
</tr>
<tr>
<td>Ma et al.</td>
<td>Liquid Chromatography</td>
<td>Multicomponent</td>
<td>Column</td>
<td>Numerical</td>
</tr>
<tr>
<td>(1996)</td>
<td></td>
<td>Metal Ions</td>
<td>Packing</td>
<td></td>
</tr>
<tr>
<td>Koh et al.</td>
<td>Packed &amp; Fluidized Bed</td>
<td>L-phenylalanine</td>
<td>Cation-exchange Column</td>
<td>Numerical</td>
</tr>
<tr>
<td>(1998)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yang &amp; Pyle</td>
<td>Batch</td>
<td>Cephalosporin-c</td>
<td>Non-ionic</td>
<td>Graphical</td>
</tr>
<tr>
<td>(1999)</td>
<td></td>
<td></td>
<td>Resin</td>
<td></td>
</tr>
<tr>
<td>Ravindran et al.</td>
<td>Column</td>
<td>Metal Ions</td>
<td>Chelant-Impregnated Activated Carbon</td>
<td>Numerical</td>
</tr>
<tr>
<td>(1999)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The authors suggested that the parallel diffusion model could be used for the heterogeneous sorbent. Hasnat and Juvekar (1996) used the parallel diffusion model to the sorption of metal ions onto resins. Ravindran et al. (1999) compared the pore,
surface and parallel diffusion models for the sorption of toxic metals on chelant-impregnated adsorbent. The authors concluded that the surface diffusion model could correlate the experimental data better than either the pore or parallel diffusion models since the metal ions have a high affinity to the chelant-impregnated surface. A summary of parallel diffusion model is shown in Table 2.3.

2.4.3 Film-Pore Diffusion Model (Shrinking Core Model)

In the previous discussion, Seo and Lee (1995) used the highly rectangular Langmuir equation to correlate the sorption equilibrium of cadmium, copper and zinc ions onto CaHAP. The authors used a film-pore diffusion model (SCM) to correlate the experimental data and determine pore diffusivities of sorption systems. As the sorption of metal ions onto CaHAP may be similar to the sorption of metal ions onto bone char, the use of the film-pore diffusion model in this research may be feasible. The analytical solution (SCM) was derived using the unreacted core model, which was first developed by Yagi and Kunii (Levenspiel, 1972). Yagi and Kunii visualized five steps occurring in succession during reaction.

1. Diffusion of gaseous reactant through the film surrounding the particle to the surface of the solid.
2. Penetration and diffusion through the blanket of ash to the surface of the unreacted core.
3. Reaction of gaseous with solid at this reaction surface.
4. Diffusion of gaseous products through the ash back to the exterior surface of the solid.
5. Diffusion of gaseous products through the gas film back into the main body of fluid.
But some of these steps may not happen during reaction. For example, Steps (4) and (5) do not contribute directly to the resistance to reaction if no gaseous products are formed or if the reaction is irreversible. Spahn and Schlünder (1975) adopted this approach in their pseudoanalytical batch model based on irreversible adsorption. The authors replaced the local solid phase concentration of adsorbate, \( q_{e,r} \), by a hypothetical equilibrium concentration, \( q_h \). Later, McKay (1983) modified the method of solution to avoid graphical differentiation and assumed a constant maximum loading for all conditions (i.e. \( q_h = q_m \)). The analytical solution can be used to correlate the experimental data when the system operating line terminates on the monolayer of the adsorption isotherm. Therefore, the correlation of experimental data using SCM is restricted to high initial concentration of solution or low volume to mass ratio. This method yields more accurate results but it is only applicable to conditions when the system operating line terminates on the isotherm 'plateau'. In Recently, Chen and coworkers (2001) used a Langmuir-type isotherm to incorporate into the shrinking core model to develop a pore-surface diffusion model. The authors assumed that the local solid-phase concentration could be represented by the Langmuir-type isotherm. Therefore, the assumption of hypothetical concentration equilibrium by Spahn and Schlünder is not required in this calculation. This modification of SCM can improve the quality of fitting to experimental data. However, a numerical method must be used to solve the SCM equation and the film diffusion effect was ignored in the calculation.
CHAPTER 3

MATERIAL TESTING AND EXPERIMENTAL METHODS

3.1 SORBATE AND SORBENT MATERIALS

Bone char is derived from animal bone and its surface is dirty and dusty. Therefore, pre-treatment of bone char is necessary to avoid fine powder on the surface, which would increase metal uptake rate by attachment to the dust on the granular bone char. To ensure consistency of the experimental results, all experiments were performed according to the following methods to eliminate experimental errors. In addition, a certain number of experiments were performed in duplicate to ensure consistency in experimental procedures.

3.1.1 Physical and Chemical Properties of Bone Charcoal

The bone char used in this study was Brimac 216, 20/60 mesh supplied by Tate & Lyle Process Technology. The physical and chemical properties of bone char were analyzed by the manufacturer. Table 3.1 shows that the main composition of bone char is calcium hydroxyapatite. The carbon is distributed throughout a porous structure of hydroxyapatite in the bone char. Attempts to relate the performance of the bone char with its B.E.T. area fail because no account is taken of the heterogeneity of the surface. The manufacturer used the adsorption of cetyltrimethylammonium (CTAB) from water to measure the carbon surface area and the adsorption of sodium di-2-ethylhexyl sulfo succinate (Manoxol OT) from water to measure the total surface area (Bennett and Abram, 1967). Although the manufacturer did not use the B.E.T isotherm to measure the surface area of the bone
char, the B.E.T isotherm was used to measure the pore volume distribution in this research.

Table 3.1 Physical and chemical properties of bone char

<table>
<thead>
<tr>
<th>Chemical Composites</th>
<th>Physical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Items</td>
<td>Limits</td>
</tr>
<tr>
<td>Acid Insoluble Ash</td>
<td>3 wt.% max.</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td>7 – 9 wt.%</td>
</tr>
<tr>
<td>Calcium Sulfate</td>
<td>0.1 – 0.2 wt.%</td>
</tr>
<tr>
<td>Carbon Content</td>
<td>9 – 11 wt.%</td>
</tr>
<tr>
<td>Calcium HAP</td>
<td>70 – 76 wt.%</td>
</tr>
<tr>
<td>Iron-as Fe$_2$O$_3$</td>
<td>&lt;0.3 wt.%</td>
</tr>
</tbody>
</table>

(Source: Tate & Lyle Company Limited)

3.1.2 Pretreatment of Sorbent

The bone char was sieved to separate the material into discrete size ranges. In this research, the adsorption properties of 500 – 710 μm particle size bone char were mainly studied. After sieving the char, the adsorbent was rinsed with deionized water. Finally, the adsorbents were dried at 103 – 105 °C for 24 hours and then allowed to cool in the dessicator.

3.1.3 Sorbates

Sulfuric acid is a commonly used acid in industry. Therefore, the wastewater usually contains sulfate ions in solution. In this research, analytical grade cadmium (II) sulfate (3CdSO$_4$·8H$_2$O) and copper (II) sulfate (CuSO$_4$·5H$_2$O) used in the
experiments were supplied by Riedel-de Haën Chemicals. The analytical grade zinc (II) sulfate (ZnSO₄·7H₂O) was supplied by BDH chemicals. Stock solutions of metal ions were prepared using deionized water. All solutions were adjusted to pH = 4.9 ± 0.1 using dilute sulfuric acid. If metal chloride or metal nitrate is used, the sorption capacity and sorption rate of metal ions onto bone char may be different (Suzuki et al., 1991).

3.1.4 Analytical Techniques

The concentrations of metal ion solutions were measured by Inductively Coupled Plasma-Atomic Emission Spectrophotometer (ICP-AES). The samples were diluted five times by deionized water. Therefore, the concentrations of the metal ion solutions should be in the range of 0 to 90 mg/dm³. The calibration standards were prepared using the standard solutions. Three calibration standards (30, 60 and 90 mg/dm³) were prepared for calibrating the machine before measuring. A linear calibration line is obtained after calibration to ensure the accuracy of results. The samples were automatically measured three times in one aspiration. If the standard deviation of test results were greater than one percent, the samples were measured again until the test results fulfilled the analysis requirement.

3.2 SORPTION EQUILIBRIUM ISOTHERMS

The study of adsorption equilibrium isotherms will be separated into three parts to determine:

1. the agitation time to attain the equilibrium for the adsorption.
2. the sorption equilibrium for the single component systems.
(3) the sorption equilibrium for the multicomponent systems.

When the agitation time required for the equilibrium sorption isotherm is determined, the experimental sorption equilibrium isotherms for single and multicomponent systems will be determined according to this limiting contact time. Since the preparation procedures for the single and multicomponent systems are similar, the description for the determination of multicomponent isotherms will not be given.

### 3.2.1 Agitation Time for Sorption Isotherms

As the equilibrium time for the sorption isotherms is unknown initially, the required agitation time must be determined before the equilibrium sorption isotherms can be measured. The highest concentration of metal ion solution to be used in the equilibrium sorption isotherms was used in all of these experiments.

#### Procedure

1. A fixed mass of 0.25 g bone char was added to each test bottle.

2. 0.05 dm$^3$ of the metal ion solution at 6 mmole/dm$^3$ was pipetted into each bottle.

3. The test bottles were placed into the shaker bath and the shaker bath speed was adjusted to provide maximum agitation speed (200 rpm) and to keep at constant temperature (20 ± 2 °C).

4. Each test bottle was removed from the shaker bath at specified time and the metal ion solutions were filtered using polytetrafluoroethene membrane filters.

5. The initial and final concentrations of all solutions were measured using an ICP-AES.
(6) The removal percentages were calculated and plotted against time.

Figure 3.1 shows a plot of the percentage of cadmium ions removed against time. The sorption of metal ions from solution - shown in Figures 3.1-3.3 - was observed to reach equilibrium after 72 hours for all three metal ions. To ensure equilibrium was attained, five days of agitation time were used for all equilibrium experiments.

3.2.2 Adsorption Equilibrium Isotherm

A fixed mass of bone charcoal was weighed into 120ml test bottles. Metal ion solutions were prepared and then pipetted into the test bottles. The initial pH of the solutions was adjusted to $4.9 \pm 0.1$ by the addition of dilute sulfuric acid. The test bottles were put in the shaker bath for five days and were shaken at the maximum shaking rate (200 rpm) to allow the bone charcoal to adsorb the metal ions until the solution reached equilibrium. The initial and final concentrations of the solutions were measured by ICP-AES. These data were used to calculate the adsorption capacity, $q_e$, of the adsorbent. Finally, a diagram of adsorption capacity, $q_e$, against equilibrium concentration, $C_e$, was plotted.

Procedure

Standard metal ion solutions were prepared in the concentration range from 0.1 to 6.0 mmole/dm$^3$ (or mM) and each solution was made up using dilute sulfuric acid and deionized water to adjust the pH at $4.9 \pm 0.1$ in a 200 ml volumetric flask.

(1) 0.25 g of bone char was weighed and put into each plastic bottle.
(2) 50 ml of each solution was pipetted into the test bottle and the bottles were swirled gently to ensure the bone charcoal was wetted and in contact with the metal ion solution.

(3) The bottles were agitated for five days in a thermostatic shaker bath maintained at a temperature of 20 \( \pm \) 2\(^\circ\)C.

(4) The initial and final concentrations of each solution were measured by ICP-AES.

The sorption isotherms of multicomponent systems were also performed using the same method.

Calculation

The amount of metal ion sorbed, \( q_e \), was calculated from:

\[
q_e = \frac{(C_o - C_e)V}{W} \quad [3.2.2.1]
\]

In the batch kinetic study, the sorption capacity at time \( t \), \( q_t \), was calculated by replacing \( C_t \) to \( C_e \) in equation [3.2.2.1].

3.3 BATCH KINETIC STUDIES

These experiments were used to investigate the influence of sorbent mass and initial metal ion concentration on the adsorption rate. An adsorber vessel in a standard batch stirred tank configuration was used in all of the experiments.
3.3.1 Construction of the Adsorption Vessel

A standard tank configuration was used to derive the relative dimensions of the vessel and its components (Furusawa and Smith, 1973). The following relationships hold with respect to the vessel inside diameter, $D_i$ (see Figure 3.4).

\[
\begin{align*}
\text{Height of baffles} &= 0.2 \text{ m} \\
\text{Baffle width} &= 0.075 D_i \\
\text{Height of liquid in the vessel} &= D_i \\
\text{Distance between impeller blade and vessel bottom} &= 0.5 D_i \\
\text{Width of impeller blade} &= 0.1 D_i \\
\text{Impeller diameter} &= 0.5 D_i
\end{align*}
\]

The adsorber vessel used, was a 2 dm$^3$ plastic beaker of internal diameter 0.13 m holding a volume of 1.7 dm$^3$ metal ion solution. Mixing was provided by a six bladed, flat plastic impeller of 0.065 m diameter and blade height of 0.013 m. A Heidolph variable motor was used to drive the impeller using a 0.005 m diameter plastic shaft. Six plastic baffles were evenly spaced around the circumference of the vessel, positioned at 60° intervals and held securely in place on top of the vessel. The purpose of the baffles was to prevent the formation of a vortex and the consequential reduction in relative motion, between liquid and solid particles, and power losses due to air entrainment at the impeller. Polystyrene baffles were 0.2 m long and 0.01 m wide. They were secured in a position slightly away from the vessel wall and the bottom of the tank in order to prevent particle accumulation. Evaporation of liquid was prevented by using a thick polystyrene sheet on top of the vessel.
Figure 3.4  Standard tank configuration for contact time studies.
3.3.2 Kinetic Experiments on Various Metal Ions

The standard condition was fixed at the mass of bone char (8.5 g), at a fixed particle size (500 – 710 μm), a fixed temperature (20 ± 2°C), a fixed pH (4.9 ± 0.1), and a fixed initial concentration of metal ion solution 3 mM (see Table 3.2). Therefore, the effect of initial concentration of metal ion solution on the adsorption rate was studied by varying the initial concentrations of metal ion solution (i.e. 2, 2.5, 3, 4 and 5 mM) and the other conditions were fixed. The effect of sorbent mass, temperature, pH and particle size effects were studied using the same condition as in the previous description.

Table 3.2 The effect of the concentration, mass, temperature, pH and particle size range.

<table>
<thead>
<tr>
<th>Concentration (mM)</th>
<th>Mass (g)</th>
<th>Temperature (°C)</th>
<th>pH</th>
<th>Particle Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>6.5</td>
<td>--</td>
<td>3.0</td>
<td>250 – 355</td>
</tr>
<tr>
<td>2.5</td>
<td>7.5</td>
<td>10</td>
<td>4.0</td>
<td>355 – 500</td>
</tr>
<tr>
<td>3</td>
<td>8.5</td>
<td>20</td>
<td>4.9</td>
<td>500 – 710</td>
</tr>
<tr>
<td>4</td>
<td>9.5</td>
<td>40</td>
<td>--</td>
<td>710 – 1000</td>
</tr>
<tr>
<td>5</td>
<td>10.5</td>
<td>60</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Experimental Error Analysis

The main experimental errors are shown in the following table. Several experiments were repeated to ensure that the experimental values are reproducible.
Table 3.3  Experimental error analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Error Magnitude</th>
<th>Range of Validity</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP-AES Measurements (mg/dm$^3$)</td>
<td>±2 mg/dm$^3$</td>
<td>10 – 90 mg/dm$^3$</td>
</tr>
<tr>
<td></td>
<td>±0.5 mg/dm$^3$</td>
<td>0 – 10 mg/dm$^3$</td>
</tr>
<tr>
<td>Impeller Speed (rpm)</td>
<td>±5 rpm</td>
<td>400 ± 5 rpm</td>
</tr>
<tr>
<td>pH</td>
<td>±0.1</td>
<td>4.9 ± 0.1</td>
</tr>
<tr>
<td>Mass of Sorbent (g)</td>
<td>±0.005 g</td>
<td>0.25 ± 0.005 g</td>
</tr>
<tr>
<td>Time Deviation to Extract Sample (sec)</td>
<td>±15 sec</td>
<td>5 min ± 15 sec</td>
</tr>
</tbody>
</table>

3.4 MATERIAL TESTING

In order to determine the sorption of the metal ion onto bone char, the characterization of materials will be studied to identify the sorption process.

3.4.1 Surface Area of Sorbent

Adsorption isotherm of nitrogen at 77 K was measured by an Omnisorp Coulter 100CX unit to determine the total pore volume and pore size distribution of the prepared catalysts. The BJH method was used to quantify the distribution of the volume of both the mesopores and macropores. In each physisorption analysis, about 0.1 g of the dry sample was degassed at 300°C overnight and put into the sampling bulb. The adsorption process and calculations of both adsorption and desorption isotherms were carried out automatically by the Omnisorp Coulter 100CX unit.
3.4.2 Fourier Transform Infrared Spectroscopy (FT-IR)

The Fourier Transform Infrared Spectroscopy (FT-IR) used is the Bio-Rad Model FTS 6000. The bone char samples were dried and grounded to a powder form. About 2.5 wt% of samples were mixed with the potassium bromide salt and then transferred to the sample cup to measure the IR spectrum. Infrared (IR) spectroscopy relates to the interaction between light and the vibrational motion of the covalent chemical bonding of molecules and the lattice vibrations of ionic crystals. In a modern FT-IR system, IR radiation is introduced to a scanning interferometer, and the output radiation intensity as a function of time, is decoded into frequency and intensity information through a mathematical calculation known as the Fourier transformation. The major components of bone char are hydroxyapatite (phosphates and hydroxyl ions) and calcium carbonate. These compounds are sensitive to the infrared radiation. Therefore, the infrared analysis of bone char may assist to identify the intensity change of function groups on bone char surface after sorption.

3.4.3 Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) can be used not only to examine the surface appearance of the bone char but also to analyze the composition of the bone char surface. The SEM in use was a Philip XL30 with energy dispersive X-ray spectrometer (EDAX) for compositional analysis. The bone char samples before and after sorption experiments were ground using mortar and pestle, uniformly dispersed and fixed to an SEM stub using carbon stick on the aluminum stub. The quantitative and qualitative analyses of elements on the bone char surface were analyzed by the EDAX system.
3.4.4 Powder X-Ray Diffraction

Crystal structure can be determined by powder X-ray diffractometer. The line profile analysis was performed using a Philips powder X-ray diffractometer (Model PW1830, 3kW). Cu Kα (λ = 1.540562 Å) diffracted beam has been used with a scanning step of 0.05° in the range of 10° < 2θ < 60°. The samples before use were ground to a fine powder and then the powder was packed into the window of an aluminum holder. In this research, the bone char samples were analyzed before and after sorption experiments to see whether any crystal structure changes were observable. The precipitation of metal ions to form a new crystal compound can also be determined.
CHAPTER 4

DEVELOPMENT OF MATHEMATICAL MODELS

4.1 ADSORPTION EQUILIBRIUM MODELS

4.1.1 Adsorption Isotherms for Single Component Systems

It is believed that the sorption mechanisms are controlled by both the adsorption of metal ions and the ion exchange effect. Three adsorption equilibrium equations (i.e., Langmuir, bi-Langmuir and Langmuir-Freundlich equation) based on the kinetic theory were selected.

The Langmuir Isotherm

The most simple assumption in adsorption is that the adsorption sites, \( S \), on the surface of a solid (adsorbent) become occupied by an adsorbate from the solution (Stumm, 1992).

\[
S_{(a)} + C_{(aq)} \rightleftharpoons SC_{(s)} \tag{4.1.1.1}
\]

Where \( S \) is the sorption site on sorbent and \( C \) is the sorbate in solution.

Apply the mass law to eqn. [4.1.1.1].

\[
\frac{[SC]}{[S][C]} = K_{eq} = \exp\left(-\frac{\Delta G^o}{RT}\right) \tag{4.1.1.2}
\]

The Gibb’s free energy can be expressed by equation [4.1.1.3].

\[
\Delta G^o = \Delta H^o - T\Delta S^o \tag{4.1.1.3}
\]

Therefore,

\[
K_{eq} = a_L = \exp\left(-\frac{\Delta H^o}{RT}\right) \exp\left(\frac{\Delta S^o}{R}\right) = a_L^o \exp\left(-\frac{\Delta H^o}{RT}\right) \tag{4.1.1.4}
\]
\[ q_e = \frac{q_m a_L C_e}{1 + a_L C_e} \]  

[4.1.1.5]

The conditions for the validity of Langmuir type adsorption equilibrium are (1) thermal equilibrium up to the formation of a monolayer; (2) the energy of adsorption is independent of \( \theta \).

The Langmuir-Freundlich Isotherm

Sips (1948) proposed an equation similar in form to the Langmuir and Freundlich equation in gas sorption and this equation can be used in the liquid sorption (Buffle, 1988). It was assumed that one sorption site adsorbed \( n \) metal ions.

\[ S_{(s)} + n C_{(aq)} \rightleftharpoons S \cdot C_n_{(s)} \]  

[4.1.1.6]

Where \( S \) is the sorption site on sorbent, \( C \) is the sorbate in solution and \( n \) is number of mole of sorbate. When the sorption attains equilibrium, the rate of change of coverage is equal to zero.

\[ \frac{[SC_n]}{[S][C]^n} = \frac{k_{ads}}{k_d} = K_{eq} \]  

[4.1.1.7]

\[ \left[ \frac{\theta}{1-\theta} \right] = K_{eq} C_e^n \]  

[4.1.1.8]

Expanding equation [4.1.1.8], the Langmuir-Freundlich equation can be obtained.

\[ q_e = q_{m,LF} \left[ \left( \frac{1}{K_{eq} C_e^n} \right)^n \right] \] \hspace{1cm} or \hspace{1cm} \[ q_e = q_{m,LF} \left[ \frac{(a_{LF} C_e)^n}{1 + (a_{LF} C_e)^n} \right] \]  

[4.1.1.9]

Where

\[ a_{LF} = a_{L}^{\circ} \exp \left( \frac{-\Delta H^*}{R T} \right) \]  

[4.1.1.10]
If this parameter \( n \) is equivalent to one, equation [4.1.1.9] becomes the Langmuir equation. If \( n \) is not an integer, it implies one sorption site sorbing \( n \) ions. Hence the parameter \( n \) could be regarded as characterizing the system heterogeneity.

The bi-Langmuir Isotherm

The binary Langmuir equation can be used in the sorption of sorbates on homogeneous sites, which contain two types of sorption sites on the sorbent (Stumm, 1992). This equation was used in the sorption of lead (II) and zinc (II) onto goethite (Rodda et al., 1996).

\[
q_e = \frac{q_{m,1}a_{L,1}C_e}{1 + a_{L,1}C_e} + \frac{q_{m,2}a_{L,2}C_e}{1 + a_{L,2}C_e}
\]

Where \( q_{m,1} \) and \( a_{L,1} \) are the saturation capacity and the affinity parameters on the first set of sites, respectively and \( q_{m,2} \) and \( a_{L,2} \) are the analogous parameters on the second set of sites. In this research, the adsorption and ion exchange of metal ions onto bone char are separately correlated by two Langmuir equations. Therefore, the binary Langmuir equation is assumed to use in the adsorption and ion exchange of metal ions onto bone char. The adsorption of metal ions onto bone char surface may include the surface complexation and dissolution-precipitation, etc.

4.1.2 Ideal Adsorbed Solution Theory (IAST)

This method was proposed to dilute liquid adsorption systems by Radke and Prausnitz (1972). The major advantages of the IAST are that it has a sound thermodynamic basis and requires only single component isotherm parameters and system operating conditions to predict the sorption equilibrium for the multi-
component system. The IAS theory is based on the assumption that the adsorbed phase can be treated as an ideal solution of the adsorbed components.

Solution Methodology

The IAST uses several equations to calculate the mole fraction of adsorbed phase concentrations. The use of these equations are shown and discussed.

From the mass balance for each non-volatile component \( i \), the sum of the material in the solid phase and the liquid phase at equilibrium must be equal to its initial solution phase concentration,

\[
C_{e,i} = C_{v,i} + \frac{W}{V} q_{e,i}
\]  

[4.1.2.1]

From the overall mass balance, the sum of the mole in each phase must be exactly equal to unity, i.e. for the solid phase:

\[
\sum_{i=1}^{n} s_i = 1
\]  

[4.1.2.2]

The IAST dictates that the spreading pressure should be constant for each component in a given system:

\[
\pi_1 = \pi_2 = \pi_3 \ldots = \pi_n
\]  

[4.1.2.3]

The best-fit isotherms for the single component systems are used to calculate the spreading pressure, for instance, the Langmuir and Langmuir-Freundlich isotherms may be used. The spreading pressure, \( \pi \), and reduced spreading pressure, \( \Pi \), can be evaluated from equation [4.1.2.5]:

\[
q_{e,i} = \frac{q_{m,i} a_{L,i} C_{e,i}^o}{1 + a_{L,i} C_{e,i}^o}
\]  

[4.1.2.4]
\[ \Pi_i = \frac{\pi_i S_A}{R_t T} \int_0^{C_{e,i}^o} \frac{q_{e,i}^o (C_{e,i}^o)}{C_{e,i}^o} dC_{e,i}^o = q_{m,i} \ln \left( 1 + a_{L,i} C_{e,i}^o \right) \quad [4.1.2.5] \]

or

\[ q_{e,i}^o = \frac{q_{m,i} \left( a_{L,F,i} C_{e,i}^o \right)^{\eta_i}}{1 + \left( a_{L,F,i} C_{e,i}^o \right)^{\eta_i}} \quad [4.1.2.6] \]

\[ \Pi_i = \frac{\pi_i S_A}{R_t T} \int_0^{C_{e,i}^o} \frac{q_{e,i} (C_{e,i}^o)}{C_{e,i}^o} dC_{e,i}^o = \left( \frac{q_{m,i}}{n_i} \right) \ln \left[ 1 + \left( a_{L,F,i} C_{e,i}^o \right)^{\eta_i} \right] \quad [4.1.2.7] \]

Hence, transforming the reduced spreading pressure into those based on single-component data gives the following for one component of a multicomponent system:

\[ C_{o,i}^o = C_{e,i}^o \left[ \left( \frac{W}{V} \sum_{j=1}^{n} \frac{s_j}{q_{e,j}^o} \right) s_i \right] \quad [4.1.2.8] \]

Since

\[ C_{e,i} = C_{e,i}^o s_i \quad [4.1.2.9] \]

\[ q_{e,i} = s_i q_T = s_i \left( \sum_{i=1}^{n} \frac{s_j}{q_{e,j}^o} \right)^{-1} \quad [4.1.2.10] \]

For the Langmuir isotherm, rearranging equations [4.1.2.4] and [4.1.2.5] allows to substitute into equation [4.1.2.8] to obtain the equivalent pure component fluid and adsorbed-phase concentrations at the specified spreading pressure [4.1.2.4]:

\[ C_{e,i}^o = \exp \left( \frac{\Pi}{q_{m,i}} \right) - 1 \quad a_{L,i} \quad [4.1.2.11] \]

Using the Newton-Raphson method will identify values of \( \Pi \) and \( s_i \) that minimize the error between the experimental initial liquid-phase solute concentrations, which are predicted by the IAST.
4.2 MASS TRANSFER MODELING

The study of mass transfer modeling will be divided into two parts. In the first part, the film diffusion coefficients of the sorption systems will be calculated. Several external mass transfer models will be used to determine the external mass transfer coefficient. The second part of the mass transfer study will investigate the intraparticle diffusion process of the sorption systems. The film diffusion coefficients determined from the first part will be substituted into the intraparticle diffusion model to correlate the kinetic data for single component systems and then the work will be extended from single component systems to multicomponent systems.

4.2.1 Single Resistance Models

The film diffusion coefficients can be obtained by two methods. The first method is a correlation method and the second method is a dimensional analysis method. In the correlation method, the experimental data of the sorption system is substituted into the film diffusion equation to calculate the film diffusion coefficient. In the dimensional analysis method, the characterization of the sorbent and sorbate and the terminal velocity of sorbent are used for calculating the film diffusion coefficient. The results from the correlation method and dimensional analysis method will be compared to select the most accurate values for the external film mass transfer coefficients.

Linear Adsorption Isotherm

This model was developed by Furusawa and Smith (1973). The authors studied the adsorption of benzene with activated carbon in an agitation tank. The
experimental data are interpreted by supposing a three-step model: (1) Mass transfer of benzene from bulk liquid to particle; (2) Intraparticle diffusion; (3) Adsorption at internal site. It is assumed that step three is rapid with respect to the first two steps. In fully mixed agitated slurry adsorber, mixing in the liquid phase is rapid. The concentration of sorbate, $C_i$, with respect to time is related to the fluid-particle mass transfer coefficient by the equations.

$$\frac{dC_i}{dt} = -k_j S_A (C_i - C_r)$$  \[4.2.1.1\]

$$C_i = C_o \quad \text{at} \quad t = 0$$  \[4.2.1.2\]

Assuming smooth spherical particles, the surface area for mass transfer to the particles can be obtained from $m_i$, which is defined as the concentration of the adsorbent in the liquid phase.

$$m_i = \frac{W}{V}$$  \[4.2.1.3\]

Thus the surface area for mass transfer is defined.

$$S_A = \frac{6m_i}{d_p \rho_s (1 - \varepsilon_p)}$$  \[4.2.1.4\]

The differential mass balance of metal ions within the particles is, assuming a constant effective intraparticle diffusivity, $D_{eff}$, given by [4.2.1.5].

$$D_{eff} \left\{ \frac{\partial^2 C_r}{\partial r^2} + \frac{2}{r} \frac{\partial C_r}{\partial r} \right\} - \rho_p \frac{\partial q_r}{\partial t} = \varepsilon_p \frac{\partial C_r}{\partial t}$$  \[4.2.1.5\]

$$D_{eff} \left( \frac{\partial C_r}{\partial r} \right)_{r=R} = k_j (C_i - C_r)$$  \[4.2.1.6\]

$$\frac{\partial C_r}{\partial r} = 0 \quad \text{at} \quad r = 0$$  \[4.2.1.7\]

$$C_r = 0 \quad \text{at} \quad t = 0 \quad \text{for} \quad 0 \leq r \leq R$$  \[4.2.1.8\]
Boundary and initial conditions corresponding to the experimental conditions are shown in equations [4.2.1.2], [4.2.1.6], [4.2.1.7] and [4.2.1.8]. Since equilibrium is assumed for adsorption at an interior site, \( q_r \) and \( C_r \) are related by the instantaneous equilibrium expression in equation [4.2.1.9].

\[
\frac{\partial q_r}{\partial t} = \frac{\partial q_r}{\partial C_r} \frac{\partial C_r}{\partial t} = \frac{\partial}{\partial C_r} \left( \frac{K_L C_r}{1 + a_L C_r} \right) \frac{\partial C_r}{\partial t} \quad [4.2.1.9]
\]

When \( 1 \gg a_L C_r \), equation [4.2.1.9] can be simplified. The detailed derivation of the equations is shown in Appendix I. Finally, the film diffusion coefficient can be obtained.

\[
\frac{C}{C_o} = \frac{1}{1 + m_s K_L} + \frac{m_s K_L}{1 + m_s K_L} \exp \left[ -\left( \frac{1 + m_s K_L}{m_s K_L} \right) k_f S_A t \right] \quad [4.2.1.10]
\]

By rearranging, equation [4.2.1.10] becomes the more conventional form shown in equation [4.2.1.11].

\[
\ln \left( \frac{C}{C_o} \left( 1 + m_s K_L \right) \right) = \ln \left( \frac{m_s K_L}{1 + m_s K_L} \right) + \left( \frac{1 + m_s K_L}{m_s K_L} k_f S_A t \right) \quad [4.2.1.11]
\]

As \( t \to 0 \), surface mass transfer will predominate and the two assumptions of negligible intraparticle diffusion and the linear isotherm \( (q_r = K_L C_r) \) are valid, consequently a plot of \( \ln \left( \frac{C}{C_o} \left( 1 + m_s K_L \right) \right) \) versus \( t \) will yield a straight line as \( t \to 0 \) of intercept \( \frac{m_s K_L}{1 + m_s K_L} \) and slope \( \left( \frac{1 + m_s K_L}{m_s K_L} \right) k_f S_A \) at \( t = 0 \) from which the surface mass transfer coefficient \( k_f \) can be obtained.

**Nonlinear Adsorption Isotherm**

The equation methodology and assumptions of film diffusion for the nonlinear adsorption isotherm analysis is similar to the linear adsorption isotherm. It is
assumed that adsorption at an interior site is assumed to occur rapidly in comparison with mass transfer and to be reversible. The manipulation of the mathematical method is shown in Appendix II, and the resultant equation is shown in equation [4.2.1.12] for the Langmuir isotherm.

\[
\frac{d^2C_L}{dt^2} + \left( k_f S_A + \left( \frac{k_f S_A}{m_r K_L} \right) (1 + a_r C_1) + \frac{a_r}{k_f S_A} \frac{dC_L}{dt} \right)^2 \frac{dC_L}{dt} = 0 \quad [4.2.1.12]
\]

The equation [4.2.1.12] must be solved by the numerical method to determine the external mass transfer coefficient.

**Dimensional Analysis**

For liquid adsorption taking place in batch or continuous flow tanks, the liquid phase is often agitated to increase the interphase mass transfer. According to Harriott (Tien, 1994), the interphase mass-transfer coefficient between liquid and suspended particles in an agitated vessel, \( k_f \), and the mass-transfer coefficient of the same particles moving at terminal velocity through the same liquid, \( k_f^* \), may be approximated by the relationship:

\[
\frac{k_f}{k_f^*} \approx 2.0 \quad [4.2.1.13]
\]

To estimate \( k_f^* \), Harriott suggested using the following equation:

\[
\frac{k_f^* d_p}{D_M} = 2.0 + 0.6 \left[ \frac{d_p u_T}{\mu} \right]^{0.5} \left[ \frac{v}{D_M} \right]^{0.33} \quad [4.2.1.14]
\]

The terminal velocity, \( u_T \), may use the correlation of Nienow (Tien, 1994), given as:

\[
u_T = \frac{0.153 g^{0.71} d_p^{1.14} \Delta \rho^{0.77}}{\rho^{0.29} \mu^{0.43}} \quad [4.2.1.15]
\]
where $g$ is the gravitational acceleration (980 cm/s$^2$) and $\Delta \rho = \rho_p + \varepsilon_p \rho$ is the density difference between the wet particle and the liquid density. Furusawa and Smith (1973) compared the correlation of the Harriott method and the single resistance method. The authors concluded that the external mass transfer coefficients obtaining from the single resistance method lied between the ion exchange and dissolution correlations upon Harriott’s data.

4.2.2 Film-Pore Diffusion Model (Analytical Method)

Spahn and Schlünder (1975) developed the film-pore diffusion model based on the unreacted shrinking core mass transfer model by Yagi and Kunii (Levenspiel, 1972). This model assumes that an external and internal mass transfer resistance controls the adsorption rate. Therefore, the adsorption reaction starts at the particle surface forming a reacted zone, which moves inwards with a defined velocity. During the entire reaction time there is an unreacted core, shrinking in size as adsorption proceeds. The mathematical model started with the following assumptions:

1. The adsorbate is transferred within the pores of the bone char particle solely by means of molecular diffusion.

2. Adsorption equilibrium according to the isotherm is presumed between the pore-water and the bone char throughout. In other words, the deposition-rate of the metal ions in the pore water onto the bone char surface is taken to be much higher than their rate of diffusion.

3. The adsorbate concentration in the bone char is independent of that in the pore liquid. Hence, the equilibrium concentration $q_{e,l}(C_{e,l})$ can be replaced by a hypothetical equilibrium concentration, $q_{e,h} = \text{constant}$.
(4) The quantity of adsorbate in the pore water is much lower than that on the bone char per unit volume and can therefore be neglected.

Figure 4.1 shows that the concentration decreases from $C_i$ at bulk to $C_{e,i}$ at the particle surface. This is due to the external resistance measured by $k_f$, the external mass transfer coefficient. $C_{e,i}$ drops further to zero at point $r$ in the particle interior due to the internal resistance measured by $D_{eff}$. The reacted zone moves inwards in a well-defined concentration front with a variable velocity and at all times there is an unreacted core shrinking in size. Therefore, $k_f$ and $D_{eff}$ are the main parameters that describe the profile of a concentration decay curve.

**Calculation of Adsorption Rate**

The adsorption rate of sorbent can be calculated by using the analytical solution of mass transfer equation. The governing equations are as follows:

1. The mass transfer from the external water phase is:

   $$ N_i = k_f 4\pi R^2 \left( C_i - C_{e,i} \right) \quad [4.2.2.1] $$

2. The diffusion in the pore water according to the first Fick law is:

   $$ N_i = \frac{4\pi D_{eff} C_{e,i}}{1/r - 1/R} \quad [4.2.2.2] $$

3. The velocity of the concentration front is obtained from the mass balance on a spherical element:

   $$ N_i = -4\pi r^2 q_{e,b} \rho_r \frac{dr}{dt} \quad [4.2.2.3] $$
(4) The average concentration in the sorbent is given by:

\[ q_t = q_{e,h} \left[ 1 - \left( \frac{r}{R} \right)^3 \right] \]  \hspace{1cm} [4.2.2.4]

Figure 4.2 shows the relationships between the equilibrium concentration \((C_{e,t}, q_{e,t})\) and the bulk concentration \((C_t, q_t)\). By considering these conditions and introducing dimensionless parameters, the adsorption rate for a single particle can be expressed as a function of adsorbate concentration in the water phase \(\xi\), the adsorbent concentration \(\eta\), and of the Biot number \(Bi\). The adsorption rate is represented by equation [4.2.2.5]:

\[ \frac{d\eta}{d\tau} = \frac{3(1-C_e\eta)(1-\eta)^{\frac{1}{3}}}{1-(1-1/Bi)(1-\eta)^{\frac{1}{3}}} \]  \hspace{1cm} [4.2.2.5]

Figure 4.1 Mass transport of sorbate and concentration profile of sorbent.
Figure 4.2  Connection between bulk surface concentrations during adsorption in batch tests.

or in general by:

\[
\frac{d\eta}{d\tau} = \xi f(\eta)Bi
\]  

[4.2.2.6]

Where the dimensionless parameters are defined as

\[
\tau = \frac{C_o}{\rho_p q_{e,h}} \frac{D_{eff} t}{R^2}
\]  

[4.2.2.7]

\[
C_h = \frac{Wq_{e,h}}{VC_o}
\]  

[4.2.2.8]

\[
\eta = \frac{q_i}{q_{e,h}}
\]  

[4.2.2.9]

\[
\xi = \frac{C_i}{C_o}
\]  

[4.2.2.10]

\[
Bi = \frac{K_f R}{D_{eff}}
\]  

[4.2.2.11]
Theoretical Concentration Decay Curve

Batch studies with the equilibrium driving for \( q_{e,t} - q_t \) projecting onto the monolayer can be treated with a "pseudo-irreversible" isotherm approximation.

\[
q_{e,t} - q_t = q_{e,h} - q_t \tag{4.2.2.12}
\]

This allows for the integration of equation [4.2.2.5] to give equation [4.2.2.13]. The detailed derivation of the equations is shown in Appendix III.

\[
\tau = \frac{1}{6C_h} \left\{ \ln\left[ X^3 + a^3 \right]^{(1-\eta)/(1+\eta)} + \ln\left[ X + a \right]^{\eta/(1+\eta)} \right\} - \frac{1}{\sqrt{3aC_h}} \arctan\left( \frac{2X - a}{\sqrt{3a}} \right) \tag{4.2.2.13}
\]

where

\[
X = (1-\eta)^{1/3} \tag{4.2.2.14}
\]

and

\[
a = \left( \frac{1-C_h}{C_h} \right)^{1/3} \tag{4.2.2.15}
\]

The limits for this equation [4.2.2.13] are as follows:

\[
\tau = 0, \quad \eta = 0 \quad \text{and} \quad X = 1
\]

\[
\tau = \tau, \quad \eta = \eta \quad \text{and} \quad X = X
\]

Solving equation [4.2.3.13] with the appropriate boundary conditions, the analytical equation can be obtained (McKay et al., 1995).

\[
\tau = \frac{1}{6C_h} \left\{ \ln\left( \left( \frac{X^3 + a^3}{1+a^3} \right)^{2B-1/a} + \ln\left( \frac{X + a}{1+a} \right)^{\eta/(1+\eta)} \right) \right\} - \frac{1}{\sqrt{3aC_h}} \left\{ \arctan\left( \frac{2-a}{\sqrt{3a}} \right) - \arctan\left( \frac{2X - a}{\sqrt{3a}} \right) \right\} \tag{4.2.2.16}
\]

Therefore by converting dimensionless time \( \tau \) into real time it is possible to compare experimental and theoretical concentration decay curves. The constant effective diffusivity is derived from minimizing the \( SSE_{total} \).

\[
SSE_{total} = \sum_{j=1}^{n} \left\{ \sum_{i=1}^{m} \left[ t_{exp,i} - t_{calc,i} \right]^2 \right\}_j \tag{4.2.2.17}
\]

Where \( m \) is numbers of data points and \( n \) is numbers of experimental data sets.
4.2.3 Film-Pore Diffusion Model (Numerical Method)

The previous section introduced the use of an analytical method to determine the external mass transfer coefficients and the pore diffusion coefficients. The analytical method can provide a good correlation of experimental data when all operating lines terminate on the saturation monolayer (i.e. \( q_{e,t} = q_{e,h} = q_m \)). However, when the operating lines do not terminate on the monolayer of equilibrium isotherm, the hypothetical equilibrium concentration must be assumed to be a certain value before calculation. In order to calculate the effective diffusivity accurately, the hypothetical equilibrium concentration, \( q_{e,h} \), is replaced by the solid phase concentration, \( q_{e,t} \). Since \( q_{e,t} \) is a variable in the equation, the film-pore diffusion model must be solved by a numerical method. The theoretical assumptions of the numerical film-pore diffusion model are similar to the analytical film-pore diffusion model except item (3): The adsorbate concentration in the bone char used the equilibrium concentration, \( q_{e,t} \), which is a function of adsorbate concentration on surface, \( C_{e,t} \).

Calculation of Adsorption Rate

The external mass transfer rate and the first Fick’s law are equivalent to equations [4.2.2.1] and [4.2.2.2]. But the velocity of the concentration front is replaced by equation [4.2.3.1].

\[
N_r = -4\pi r^2 q_{e,t} \rho_p \frac{dr}{dt} \tag{4.2.3.1}
\]

Therefore, the average concentration in the sorbent is given by:

\[
q_t = q_{e,t} \left[ 1 - \left( \frac{r}{R} \right)^3 \right] \tag{4.2.3.2}
\]

The mass balance of the sorbent is given by:
\[ q_t = \left( C_o - C_t \right) \frac{V}{W} \]  \[4.2.3.3\]

Numerical Solution for Concentration Decay Curve

The mass transfer from the bulk solution across the liquid film is equal to intraparticle diffusion of sorbate. Therefore, combining equations [4.2.2.1] and [4.2.2.2] gives the relationship between the concentration of sorbate in bulk solution and the concentration on the sorbent surface:

\[ C_t = \left[ 1 + \frac{D_e r}{k_s R (R - r)} \right] C_{e,t} \quad \text{or} \quad C_t = \psi(r) C_{e,t} \]  \[4.2.3.4\]

The mass balance of solid phase and liquid phase from equations [4.2.3.2], [4.2.3.3] and [4.2.3.4] becomes:

\[ W \left[ q_{e,t} \left( 1 - \left( \frac{r}{R} \right)^3 \right) \right] = V \left( C_o - \psi(r) C_{e,t} \right) \]  \[4.2.3.5\]

The concentration of sorbate on surface at radius \( r \) is equal to \( C_{e,t} \). The Langmuir equation is used to relate equilibrium concentrations on the solid phase surface. Therefore, the solid phase concentration at \( r \) can be represented:

\[ q_{e,t} = \frac{q_m a_l C_o}{1 + a_l C_{e,t}} \]  \[4.2.3.6\]

In the previous model, a rapid analytical solution has been developed by assuming \( q_{e,t} \) is a constant value equal to \( q_{e,h} \). In this model, the tie lines and time dependent values for \( C_{e,t} \) and hence \( q_{e,t} \) can be obtained. Combining eqns. [4.2.3.5] and [4.2.3.6] and putting \( R_m = \left( 1 - \left( \frac{r}{R} \right)^3 \right) \) \( W / V \) the following quadratic equation to be obtained:

\[ a_l \psi C_{e,t}^2 + \left( \lambda + a_l q_m R_m - a_l C_o \right) C_{e,t} - C_o = 0 \]  \[4.2.3.7\]
From the quadratic equation [4.2.3.7], $C_{e,t}$ can then be solved in terms of the shrinking radius (Cheung et al., 2001a, 2001b).

$$C_{e,t}(r) = \frac{-(\psi + a_L q_m R_m - a_L C_o) + \sqrt{(\psi + a_L q_m R_m - a_L C_o)^2 + 4a_L \psi C_o}}{2a_L \psi}$$

[4.2.3.8]

The intraparticle diffusion of sorbate is equal to the velocity of the concentration front. Therefore, combining equations [4.2.2.2] and [4.2.3.1], the rate equation becomes:

$$\frac{\Delta r}{\Delta t} \equiv \frac{dr}{dt} = \frac{D_{eff}(1 + a_L C_{e,t})R}{q_m a_L r(R - r) \rho_p}$$

[4.2.3.9]

or

$$\Delta r = \left(\frac{D_{eff}(1 + a_L C_{e,t})R}{q_m a_L r(R - r) \rho_p}\right) \Delta t$$

[4.2.3.10]

Since $C_{e,t}$ is known as a function of $r$, equations [4.2.3.4], [4.2.3.8] and [4.2.3.10] can be solved for a specified time by a numerical method. The solution scheme proposes that the shrinking core radius can be calculated by equation [4.2.3.11].

$$r^{L+1} = r^L + \Delta r^L$$

[4.2.3.11]

The shrinking core radius $r^L$ and concentration of solution on the surface at time $t'$, $(C_{e,t})^L$, can be calculated using equations [4.2.3.8] and [4.2.3.10], respectively. Therefore, $\Delta r^L$ can be calculated from $(C_{e,t})^L$. The concentration of solution on surface at time $t$ can be obtained by repeating the calculation of $(C_{e,t})^L$ and $r^L$. Since the concentration of solution on the surface cannot be measured, equation [4.2.3.4] will be used to calculate the sorbate concentration in solution. The adjustable parameters in equations [4.2.3.4], [4.2.3.8] and [4.2.3.10] are the film diffusion coefficient, $k_f$, and effective diffusivity, $D_{eff}$. Therefore, the constants $k_f$ and $D_{eff}$ can
be found by minimizing the Sum of Square of Errors, SSE, between the experimental and the theoretical concentration for experimental \( C_i \) values.

\[
SSE_{total} = \sum_{j=1}^{n} \left( \sum_{i=1}^{n} \left[ (C_i)_{exp,j} - (C_i)_{calc,j} \right]^2 \right)_j
\]  \[4.2.3.12\]

### 4.2.4 Film-Pore-Surface Diffusion Model

The rate of internal mass transfer according to Fick's law is:

\[
N_i = D_{eff} \frac{\partial C_{ei}}{\partial r}
\]  \[4.2.4.1\]

In the pore diffusion process, the effective diffusivity, \( D_{eff} \), is equal to the constant pore diffusivity, \( D_p \). Therefore, effective diffusivities in the previous section were assumed to be equal to pore diffusion. That means the metal ions diffuse through the liquid in the pores and adsorb on the sorption sites. However, the correlation of the experimental data is not always very good for some systems. The deviation of theoretical data points may be due to surface diffusion contributing to the effective diffusion. If surface diffusion takes place during adsorption, the effective diffusivity should be considered as a “combined diffusion” parameter.

\[
N_i = D_p \frac{\partial C_{ei}}{\partial r} + \rho_p D_s \frac{\partial q_{es}}{\partial r}
\]  \[4.2.4.2\]

The first term of equation [4.2.4.2] represents the diffusion of sorbate in the pore-liquid. The second term is equal to the surface diffusion of sorbate migration on the pore wall. Equation [4.2.4.2] can be factorized in terms of the radial concentration gradient.

\[
N_i = \left( D_p + \rho_p D_s \frac{\partial q_{es}}{\partial C_{ei}} \right) \frac{\partial C_{ei}}{\partial r}
\]  \[4.2.4.3\]

So, \( D_{eff} \) can be represented by:
\[ D_{\text{eff}} = D_p + \rho_p D_s \frac{\partial q_{e,s}}{\partial C_{e,s}} \]  \hspace{1cm} [4.2.4.4]

Assuming parallel diffusion then, a combined diffusivity can be incorporated into the film-pore diffusion model to become a film-pore-surface diffusion model. However, equation [4.2.4.4] should be rearranged to an algebraic equation format before numerical analysis. The use of the Langmuir isotherm can assist by simplifying the term \( \frac{\partial q_{e,s}}{\partial C_{e,s}} \) because this term is equal to the slope of adsorption isotherm.

\[ \frac{\partial q_{e,s}}{\partial C_{e,s}} = \frac{q_m a_L}{(1 + a_L C_{e,s})^2} \]  \hspace{1cm} [4.2.4.5]

Therefore,

\[ D_{\text{eff}} = D_p + \rho_p D_s \frac{q_m a_L}{(1 + a_L C_{e,s})^2} \]  \hspace{1cm} [4.2.4.6]

In the studies of surface diffusion, Darken (1948) proposed the surface diffusion in terms of chemical potential, which results in equation [4.2.4.7] according to Do (1998):

\[ D_s = D_{so} \left( \frac{d \ln C_{e,s}}{d \ln q_{e,s}} \right) \]  \hspace{1cm} [4.2.4.7]

When the Langmuir equation is used in equation [4.2.4.7], the surface diffusivity can be simplified.

\[ D_s = D_{so} (1 + a_L C_{e,s}) \]  \hspace{1cm} [4.2.4.8]

Therefore, the effective diffusivity can be represented:

\[ D_{\text{eff}} = D_p + \frac{q_m a_L \rho_p D_{so}}{(1 + a_L C_{e,s})} \]  \hspace{1cm} [4.2.4.9]

Equation [4.2.4.9] is substituted into the film-pore diffusion model to generate the film-pore surface diffusion. In the numerical scheme, the only adjustable parameters in the equations are \( D_p \) and \( D_{so} \). Therefore, minimizing the SSEs, between the
experimental and the theoretical concentration values results in obtaining the constants $D_p$ and $D_{so}$.

4.2.5 Mass Transport for the Multicomponent Systems

The film-pore diffusion model can be used to correlate the experimental data for multicomponent systems if the solid phase concentrations on bone char are known. In this research, two methods are used to determine the solid phase concentrations on bone char for multicomponent systems, which are an empirical equation and IAS theory.

Empirical Equation for Solid Phase Concentration (Case I)

When the film and pore diffusion are the main sorption mechanism for the sorption of metal ions onto bone char, the sorption kinetics for the multicomponent systems can be treated as a single component. The calculation of adsorption equations used in this part is similar to section 4.2.3. However, the adsorption isotherms for the sorption of cadmium and zinc ions cannot be fitted by the Langmuir equation. Hence, the empirical equation is used when the Langmuir equation is not fitted. The starting point of this numerical method is assumed that the mass transport rate of metal ions from the bulk solution across the liquid film is equal to the diffusion rate of metal ions to the interior of the particle.

$$C_t = \left[1 + \frac{D_{eff} r}{k_j R(R - r)}\right] C_{s,t} \quad \text{or} \quad C_t = \psi C_{s,t} \quad [4.2.3.4]$$

An empirical equation is used to describe the time dependent surface or tie line concentration at time $t$ on the sorbent surface. It is proposed that the sorption of cadmium and zinc ions on the solid phase can be correlated by the Langmuir
equation. However, parts of sorption sites, which can be correlated by the Henry's law, are displaced by the copper ions. The Henry equation solid phase displacement subtracted from the Langmuir equation becomes the solid phase concentration for cadmium or zinc ions.

\[
q_{e,t} = \frac{q_m a_L C_{e,t}}{1 + a_L C_{e,t}} - H C_{e,t} \tag{4.2.5.1}
\]

Where \(a_L\) is the Langmuir constant and \(q_m\) is the monolayer capacity. Combining eqns. [4.2.3.5] and [4.2.5.1] and substituting \(R_m(r) = \left(1 - \left(\frac{r}{R}\right)^3\right)\frac{W}{V}\) yields the quadratic equation:

\[
\left[ \frac{(q_m a_L - H) C_{e_t} - a_L H C_{e_t}^2}{1 + a_L C_{e_t}} \right] R_m = (C_o - \psi C_{e,t}) \tag{4.2.5.2}
\]

\[
a_L (\psi - H R_m) C_{e,t}^2 - (a_L C_o - (\psi + R_m(q_m a_L - H))) C_{e,t} - C_o = 0 \tag{4.2.5.3}
\]

From the quadratic equation [4.2.5.3], \(C_{e,t}\) can then be obtained in terms of the shrinking core radius.

\[
Dis = (a_L C_o - (\psi + R_m(q_m a_L - H)))^2 + 4 a_L C_o (\psi - H R_m) \tag{4.2.5.4}
\]

\[
C_{e,t}(r) = \frac{(a_L C_o - (\psi + R_m(q_m a_L - H)) + \sqrt{Dis}}{2 a_L (\psi - H R_m)} \tag{4.2.5.5}
\]

Therefore, the equilibrium concentration on solid surface is a function of shrinking core radius. Since \(C_{e,t}\) is known as a function of \(r\), equations [4.2.3.4], [4.2.3.10] and [4.2.5.5] can be solved for a specified time by a numerical method. The solution scheme proposes that the shrinking core radius can be calculated by equation [4.2.3.11].

\[
r_{L+1} = r_L + \Delta r_L \tag{4.2.3.11}
\]

The above numerical scheme can be used to estimate values of the pore diffusivities for the sorption of cadmium and zinc ions for the multicomponent systems.
IAS Theory for Solid Phase Concentration (Case II)

In section 4.1.2, the IAS theory was proposed for use in the prediction of solid phase concentrations at equilibrium. However, the metal ions in the liquid-filled pores may diffuse at different speeds. For the binary kinetic system, there are two reaction fronts moving towards the center of the particle. The solid phase concentration of metal ions $M_1$ and $M_2$ at radius $R - r_2$ can be calculated by the IAST. The solid phase concentration for the faster moving fast metal ions, $M_1$, at radius $r_2 - r_1$ (as shown in Figure 4.3) should be calculated by the single component equation. For the metal ions, $M_1$ and $M_2$, the film and pore diffusion relationships can be derived from equation [4.2.5.6].

$$ (C_i)_i = \psi_i (C_{e,i})_i \quad [4.2.5.6] $$

where $i$ is the metal ion $M_i$.

For the $M_1$ ions, the diffusion in the pore water according to the first Fick’s law is:

$$ N_i,1 = \frac{4\pi D_{p,1} (C_{e,i})_i}{1/r_1 - 1/R} \quad [4.2.5.7] $$

The liquid-phase concentration at radius $R - r_1$ is equivalent to $(C_{e,i})_1$. The velocity of the concentration front is obtained from the mass balance on a spherical element (Arévalo et al., 1998):

$$ N_i,1 = -4\pi r_1^2 \rho_p (q_{e,i})_i \frac{dr_1}{dt} \quad [4.2.5.8] $$

As the $M_1$ is moving faster than $M_2$ in the sorbent, the solid phase concentration $(q_{e,i})_{1^o}$ from $r_2 - r_1$ can be calculated by the Langmuir equation. Therefore, the shrinking core radius $r_1$ can be obtained by solving equations [4.2.5.7] and [4.2.5.8].
Figure 4.3  Mass transport of metal ions $M_1$ and $M_2$ at different speeds in the sorbent.

\[
\frac{dr_1}{dt} = -\frac{D_{p,1} \left( C_{e,1} \right) R}{r_1 \rho_p \left( R - r_1 \right) q_{e,1}}
\]  \[4.2.5.9\]

For the $M_2$ ions, the diffusion in the pore water according to the first Fick’s law is (Arévalo et al., 1998):

\[
N_{1,2} = \frac{4\pi D_{p,2} \left( C_{e,2} \right)}{1/r_2 - 1/R}
\]  \[4.2.5.10\]

The velocity of the concentration front is obtained from the mass balance on a spherical element (Arévalo et al., 1998):

\[
N_{1,2} = -4\pi r_2^2 \rho_p \left( q_{e,2} \right) \frac{dr_2}{dt}
\]  \[4.2.5.11\]

The shrinking core radius $r_2$ can be obtained by solving equations [4.2.5.10] and [4.2.5.11].
\[
\frac{dr_2}{dt} = \frac{D_{p,2} (C_{e,1})_2 R}{r_2 \rho (R - r_2)(q_{e,2})_2} \quad [4.2.5.12]
\]

As the \(M_2\) ions are moving slower than the \(M_1\) ions, part of the \(M_1\) ions on the solid surface are displaced by \(M_2\) at radius \(R - r_2\). The solid phase concentration, \((q_{e,s})_1\) and \((q_{e,s})_2\), and liquid phase concentration, \((C_{e,l})_1\) and \((C_{e,l})_2\), at radius \(R - r_2\) are at local equilibrium. Therefore, the solid phase concentration at \((q_{e,s})_2\) can be calculated by the IAS theory. The total mass balance of metal ions \(M_1\) and \(M_2\) can be calculated by the IAS theory.

\[
q_t = (C_o - C_i) \frac{V}{W} \quad [4.2.3.5]
\]

Therefore, for metal ions \(M_2\) at radius \(R - r_2\), the mass balance is equivalent to equation [4.2.5.13].

\[
C_{N,2} = \psi_2 (C_{e,s})_2 + (q_{e,s})_2 \left( \frac{W}{V} \right) \left( 1 - \left( \frac{r_2}{R} \right)^3 \right) \quad [4.2.5.13]
\]

For the \(M_1\) ions at radius \(R - r_1\), the mass balance is equivalent to equation [4.2.5.14].

\[
C_{N,1} = \psi_1 (C_{e,s})_1 + \left( \frac{W}{V} \right) \left( q_{e,s} \right)_1 \left( 1 - \left( \frac{r_2}{R} \right)^3 \right) + \left( q_{e,s} \right)_1 \left( \left( \frac{r_2}{R} \right)^3 - \left( \frac{r_1}{R} \right)^3 \right) \quad [4.2.5.14]
\]

Where the initial concentration of solution computed by the numerical scheme is represented by \(C_{N,i}\) and the solid phase concentration at radius \(R - r_1\) can be represented by equation [4.2.5.15]. Mijangos and Diaz (1994) used the similar equation to estimate the total solid phase concentration in resin. The authors used the ion exchange capacity to replace \((q_{e,s})_1^o\). The ion exchange capacity of binary systems replace \((q_{e,s})_1\).

\[
(q_t)_1 = (q_{e,s})_1 \left( 1 - \left( \frac{r_2}{R} \right)^3 \right) + (q_{e,s})_1 \left( \left( \frac{r_2}{R} \right)^3 - \left( \frac{r_1}{R} \right)^3 \right) \quad [4.2.5.15]
\]
When the spreading pressure and mole fraction of $M_I$ on solid surface are fixed, the solid phase concentrations and liquid phase concentration at time $t$ can be determined by minimizing the $SSE$ of initial concentration.

$$SSE = \sum_{i=1}^{3} (C_{o,i} - C_{N,i})^2$$  \[4.2.5.16\]

When the liquid phase and solid phase concentration are determined at time $t$. The bulk solution concentration at time $t$, $C_t$, can be calculated from equation [4.2.5.6]. Therefore, the shrinking core radii $r_1$ and $r_2$ can also be determined from equations [4.2.5.9] and [4.2.5.12].
CHAPTER 5

RESULTS AND DISCUSSION

5.1 CHARACTERISATION OF BONE CHAR

In this research, commercial grade bone char was used to remove the metal ions from the wastewater. Although the supplier analyzed and provided data for certain physical and chemical properties of bone char, the other properties of bone char before and after sorption are also of interest to this study.

5.1.1 XRD Pattern of Bovine Bone and Bone Char

Figure 5.1 shows the XRD pattern of powder bovine bone. The calcium and phosphate ions in the bovine bone are arranged in a poorly crystalline apatite form but five main peaks at 26°, 32°, 40°, 47° and 49° can still be identified. Figure 5.2 shows the XRD pattern of bone char and reference peaks of synthetic hydroxyapatite (JCPDS, 72-1243). The XRD pattern of bone char is very similar to the synthetic hydroxyapatite. By comparing Figures 5.1 and 5.2, the five main peaks can be found in both spectrums. Therefore, the calcium and phosphate ions in bone char should predominantly exist in crystal hydroxyapatite form. From the International Centre for Diffraction Data, standards library, the bond lengths of the unit cell of synthetic hydroxyapatite are \( a = 9.418 \, \text{Å} \) and \( c = 6.884 \, \text{Å} \) and the atoms are arranged in a hexagonal lattice structure. In this research, the XRD diffraction data of bone char from Figure 5.2 were substituted into the computer model (Traces – Unitcell) to calculate the bond length of the unit cells. It was found that the unit cell axis lengths are equal to \( a = 9.417 \pm 0.008 \, \text{Å} \) and \( c = 6.857 \pm 0.007 \, \text{Å} \). The short c-axis parameter
might be due to a low Ca/P ratio in biological apatite (Elliott, 1994). The XRD signal of carbon and calcium carbonate are not found in this spectrum. It is believed that the carbon and calcium carbonate in bone char are not in crystal form or the XRD signal is too weak to show this in the spectrum.

5.1.2 Structure of Bone Char

Figure 5.3 shows the surface of bone char under Scanning Electron Microscopy (SEM). There are many straight cylindrical pores evenly distributed on the surface and this pore structure is retained from the original animal bone. Figure 5.4 is a magnification of Figure 5.3 and shows carbon chars of varying sizes randomly is distributed on the CaHAP surface. From the figure, the pore diameters of the sorbent are of the order of 2 μm by observation. According to the classification of pore size as recommended by IUPAC (Do, 1998), these are macropores (d_{pore} > 50nm). A detailed study of the pore size and volume distribution of bone char will be shown and discussed in the next section.

5.1.3 The BET Isotherm

The BET isotherm, used to measure the surface area of sorbent, was proposed by Brunauer, Emmett and Teller (1938). Measurements are commonly made using nitrogen as the sorbate at liquid N\textsubscript{2} temperatures but other small molecules may also be employed, such as helium. The BET surface area of bone char from this study is equivalent to 130 m\textsuperscript{2}/g from the linear plot of BET equation. Figure 5.5 shows the volume of nitrogen adsorbed at 77 K versus reduced pressure. The starting point of the hysteresis loop indicates the start of the capillary condensation mechanism. The hysteresis loop is due to the effect of pore structure on multilayer adsorption and
makes it possible for liquid adsorbate to occur in the pores. The finite pore width places a limit on the extent of multilayer formation before liquid formation occurs. The liquid in a pore will have a highly curved meniscus, which results in a depression of the liquid vapor pressure below its normal value. Adsorption-desorption hysteresis results because pores are filled and emptied by different processes. The desorption curve (ADC) is above the adsorption curve (ABC) because sorbate desorbing from a porous solid at a lower pressure is easier (Anderson and Pratt, 1985). The hysteresis loop shape, classifies the sorbent as type D pore structure which is a tapered slit pore; that is pores with wide bodies and a distribution of narrow necks (Do, 1998). Figure 5.6 shows the pore volume distribution against the pore size of bone char. The pore volume distributions against pore size are separated into two regions. The mean pore diameters after unit conversions are equal to 3.6 nm and 11.2 nm.

5.2 CHARACTERIZATION OF SORBENT SITES

Bone char contains CaHAP surface and carbon surface. The CaHAP surface was reported to adsorb and exchange the metal ions from the solution. Therefore, analyzing the characterization of sorbent can assist in understanding the sorption mechanism of metal ions onto bone char.

5.2.1 XRD Pattern of Bone Char after Adsorption

The sorptions of cadmium, copper and zinc ions from solutions were studied using the batch agitation method. The concentrations of metal ions were prepared at 2, 3, 4 and 5 mM. After the sorption process, the sorbent was separated and dried in the
oven. Then, the crystal structure of the sorbent was analyzed by powder XRD. Figure 5.7 shows the sorption of cadmium ions \((C_o = 5 \text{ mM})\) onto bone char. Two new peaks were observed in Figure 5.7 at 23.5° and 30.3°. The sorption of cadmium ions onto bone char at initial pH = 5 forms a new crystal phase on the sorbent. Chen and coworkers (1997) used CaHAP to remove the cadmium ions and obtained similar results. The authors concluded that no crystalline cadmium phosphates were detected, but otavite \([\text{CdCO}_3]\) forms in the reactions at all pH except for initial pH = 1.1. The main XRD peaks of otavite are at 23.49° and 30.28° (JCPDS, 42-1342), which are similar to the XRD pattern in Figure 5.7. The authors proposed the new crystal formation is based on the following reaction:

\[
\text{Cd}^{2+}_{\text{(aq)}} + \text{HCO}_3^{-}_{\text{(aq)}} \rightarrow \text{CdCO}_3^{(c)} + \text{H}^+_{\text{(aq)}} \quad [5.2.1.1]
\]

Figures 5.8 – 5.10 show the powder XRD spectrum for the sorption of cadmium, copper and zinc ions onto bone char at different initial concentrations. The crystal structures of CaHAP for copper and zinc ions do not show a great change. Figure 5.8 shows a new crystal compound forming on the bone char after the sorption of cadmium ions at different initial concentrations. The sorption of zinc by the apatite does not show any new crystal forming on bone char surface. No crystalline compound besides the original apatite could be identified at the initial pH range of 3.1 – 7.1 (Chen et al, 1997). Also, the XRD spectrums of bone char after sorbing the copper and zinc ions at initial pHs 3.0, 4.0, and 4.8 do not have any new crystalline compounds forming on the bone char surface either. Therefore, the XRD patterns for the sorption of cadmium and zinc ions onto bone char in the present research agreed with Chen and coworkers.
5.2.2 The Effect of pH on the Sorbent

Although bone char is a very effective sorbent in removing the metal ions from wastewater, the pH of wastewater before the adsorption process must be controlled to pH ≈ 5.0 or above to optimize the performance of the sorbent. Figure 5.11 shows the sorption of cadmium ions onto bone char at different initial pHs. Obviously, increasing the hydrogen ions in the solution will decrease sorption capacity of metal ions onto bone char. This phenomenon was found in many sorption systems such as the sorption of metal ions onto peat (Ho et al., 1994) and the sorption of metal ions on resin (Slater, 1991). Many authors have suggested that the competition between hydrogen ions and metal ions causes the decrease in sorption capacity for metal ions. According to the sorption mechanism proposed by Wu et al. (1991) from equations [2.2.1.1] to [2.2.1.3], the CaHAP surface adsorbing hydrogen ions from the solution is one of the reasons to explain the decreasing sorption capacities with decreasing initial pH.

The other reasons to explain the decreasing sorption capacities are due to the solubility of new crystal compounds. Figures 5.12 and 5.13 show that the peak signals of XRD patterns are decreasing when the initial pH of solution decreases. When the bone char is put into the blank solution at pH 3 and 4, no blurring of the XRD peak happens. Although a part of CaHAP dissolves in low pH solution, the CaHAP crystal can still exist after equilibrium. Except calcium ions, no cation in an aqueous phase exchanges with the calcium ions in the lattice of CaHAP. Therefore, the crystal structure of CaHAP can be retained.

\[ \text{Ca}_{10} \text{(PO}_4 \text{)}_6 \text{(OH)}_2 (s) + 2\text{H}^+_{(aq)} \rightleftharpoons 10\text{Ca}^{2+}_{(aq)} + 6\text{PO}_4^{3-}_{(aq)} + 2\text{H}_2\text{O (l)} \]

[5.2.2.1]

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However, the XRD patterns become blurred when the metal ion solutions at low pH are used. These phenomena can be explained by the ion exchange of calcium ions with metal ions. When the calcium ions in the crystal lattice exchange with the metal ions, a new crystal is formed.

\[
\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \text{(s)} + x\text{M}^{2+}\text{(aq)} \rightarrow \text{Ca}_{10-x}\text{M}_x(\text{PO}_4)_6(\text{OH})_2\text{(s)} + x\text{Ca}^{2+}\text{(aq)}
\]

[5.2.2.2]

However, the crystal of new compound is unstable in low pH. As the degree of crystallinity decreases, this results in the XRD signal decreasing. At pH 3, the crystallinity of CaHAP after sorption is similar to bovine bone in Figure 5.1. Therefore, the initial pH of the metal solution should be adjusted to pH 5 or above before the adsorption process commences.

5.2.3 FT-IR study on Bone Char after Adsorption

As the CaHAP contains many functional groups in the crystal lattice, which absorb the infra-red radiation at a specific wavelength, studying the IR spectrum may help to identify the sorption of metal ions onto the specific functional groups. Table 5.1 shows the IR absorbance frequencies of CaHAP, which are summarized from Elliott (1994) and Kazuo (1997).

Figures 5.14 – 5.19 are the sorption of cadmium, copper, and zinc ions onto bone char. Comparing the transmittance signal of the IR spectrum, the concentration effect for the sorption of copper ions is stronger than that of the sorption of cadmium and zinc ions. From Figure 5.16, increasing the sorption of copper ions will decrease the transmittance signal. If the bands at 757 and 670 cm\(^{-1}\) can be found, the CO\(_3^{2-}\) ions will replace OH\(^-\) ions in the lattice (Elliott, 1994). The peak at 757 cm\(^{-1}\) is too weak
to be observed in this figure. The other band at 706 cm\(^{-1}\) decreases when the metal ions increase. It is proposed that is the carbonate band in the calcium carbonate (Kazuo, 1997). Figure 5.17 shows the physical adsorption of carbon dioxide on the sorbent. Cheng (1998) reported that the physical adsorption of carbon dioxide would generate a band at 2347 cm\(^{-1}\). When the CO\(_2\) amount is increased, the 2347 cm\(^{-1}\) band is split into the 2359 and 2344 cm\(^{-1}\) bands. The former band can be assigned to the physisorbed CO\(_2\), and the latter two bands, to CO\(_2\) in the gaseous phase, since the bands of gaseous CO\(_2\) appear at 2360 cm\(^{-1}\) and 2342 cm\(^{-1}\). The FT-IR spectrums for the sorption of cadmium and zinc ions are similar. All band positions in the sorption of cadmium and zinc ions are equivalent to those in the sorption of copper ions. Based on the transmittance of IR spectrums, it can be concluded that higher initial concentrations, result in more metal ions binding with the phosphate ions causing the transmittance to increase.

5.3 ADSORPTION EQUILIBRIUM MODELING

The experimental data of the equilibrium isotherms and sorption rates were analyzed by mathematical models. These models are based on assuming certain adsorption mechanisms and properties. The adsorption equilibrium model will correlate the equilibrium data for the single component systems. Furthermore, the equilibrium model will be used to predict the sorption capacity for the multicomponent systems and to correlate the kinetic data using mass transport models.
Objective Function

The experimental equilibrium isotherm data and mass transfer model equations were substituted into a Microsoft Excel spreadsheet. The equation parameters were determined by minimizing the Sum of the Square of the Errors (SSEs).

$$SSE = \sum (q_{exp,i} - q_{calc,i})^2$$  \hspace{1cm} [5.3.1]

Where $q_{exp}$ is the experimental data of sorption capacity and $q_{calc}$ is the sorption capacity calculated by equilibrium isotherms.

5.3.1 Adsorption Isotherms for Single Component Systems

The experimental data were substituted into different sorption equilibrium models in order to obtain an equation which accurately represents the results and can be used for design purposes. Several sorption equilibrium equations are available for the data analysis. In this study, three isotherm equations, i.e. the Langmuir, Langmuir-Freundlich and bi-Langmuir equations were employed to study the adsorption process.

The Langmuir Isotherm

Figures 5.20 - 5.22 show the sorption of metal ions onto bone char at different temperatures. From these figures, increasing the temperatures of solution will increase the sorption capacities of metal ions. This trend is unusual in conventional adsorption systems and is discussed later. The parameters of the Langmuir isotherm are summarized in Tables 5.2 – 5.4. The use of the Langmuir equation in the sorption of metal ions onto bone char is not realistic if the sorption reaction does not follow equation [4.1.1.1]. Since the Langmuir equation is based on one mole of sorbate to
one mole of sorption site, the heat of adsorption calculated from equation [4.1.1.2] may not be correct.

\[ S_{(s)} + C_{(aq)} \rightleftharpoons SC_{(s)} \]  \[ \text{[4.1.1.1]} \]

However, the Langmuir equation can still be used to correlate the experimental data. Figure 5.21 shows that the distances between the experimental points to the Langmuir equations are less than five percent. Since the Langmuir equation has been widely used in the sorption systems, this equation which is simple and provides a good fit to the experimental data, will be used in the development of the mass transfer model for single component systems.

The Langmuir-Freundlich Isotherm

Figures 5.23 – 5.25 show the correlation of the experimental data by the Langmuir-Freundlich or Sips equation. This equation can also correlate the experimental data very well. It was assumed that one sorption site adsorbs \( n \) metal ions.

\[ S_{(s)} + nC_{(aq)} \rightleftharpoons S \cdot C_{n(s)} \]  \[ \text{[4.1.1.12]} \]

But the sorption mechanism can also be expressed as:

\[ nS_{(s)} + C_{(aq)} \rightleftharpoons S_n \cdot C_{(s)} \]  \[ \text{[5.3.1.1]} \]

The above equation represents that one sorption site can adsorb \( n \) sorbates. Therefore, the Langmuir-Freundlich equation becomes:

\[ q_e = q_{n,LF} \left[ \frac{(a_{LF}C_e)^{\frac{1}{n}}}{1 + (a_{LF}C_e)^{\frac{1}{n}}} \right] \]  \[ \text{[5.3.1.2]} \]

The parameter of the Langmuir-Freundlich equation, \( a_{LF} \), is the affinity constant which is summarized in Tables 5.5 – 5.7:

\[ \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} \]
Since the Langmuir and Langmuir-Freundlich equation can easily be used in the IAST method, these equations and parameters will be used in section 5.3.2.

The bi-Langmuir Isotherm

A heterogeneous surface may be considered to be composed of many homogeneous patches. If the Langmuir equation is assumed to apply to the individual patches, then the overall isotherm expression may be written (Tien, 1994):

\[ q = \frac{q_{m,1} a_{L,1} C}{1 + a_{L,1} C} + \frac{q_{m,2} a_{L,2} C}{1 + a_{L,2} C} + \cdots = \sum_i q_{m,i} a_{L,i} C \]  \[ 5.3.1.3 \]

where \( q_{m,i} \) and \( a_{L,i} \) are the values for the \( i \)th patch,

\[ q_m = \sum_i q_{m,i} \]  \[ 5.3.1.4 \]

\[ a_{L,i} = a_{L,i}^0 \exp\left( -\frac{\Delta H_i^0}{R T} \right) \]  \[ 5.3.1.5 \]

Bone char sorbs the metal ions by sorption and calcium ion exchange. If each type of sorption process can be described by one Langmuir isotherm, the bi-Langmuir equation can be used for these sorption systems. As the calcium ions are exchanged during sorption, the exchanged calcium ions can be measured by ICP-AES. Therefore, one set of the bi-Langmuir parameters was calculated by the ion exchange of metal ions using the following equation:

\[ q_{e,i} = \frac{V}{M} \left( (C_{ca})_{\text{final}} - (C_{ca})_{\text{initial}} \right) \]  \[ 5.3.1.6 \]

The Cation Exchange Capacities (CECs) were plotted against the equilibrium concentration of metal ions. The first set of the bi-Langmuir parameters was determined by using the CEC data to correlate the Langmuir parameters. The other set of the bi-Langmuir parameters were calculated by minimizing the SSE of the bi-
Langmuir equation. Figures 5.27, 5.29 and 5.31 show the sorption of metal ions obtained by correlating the bi-Langmuir equation and the relative CEC of metal ions. The bi-Langmuir constants are shown in Tables 5.8 – 5.13.

Sorption Capacities at Different Temperatures

Figures 5.26 – 5.31 show the cation exchange capacity, the theoretical bi-Langmuir curves and the experimental data. The CEC of cadmium is around thirty percent of the sorption capacities at 20°C. The CECs of copper and zinc ions are around fifty percent of the sorption capacity. Suzuki et al. (1991) and Chen et al. (1997) reported that the metal ion uptake phenomenon on hydroxyapatite was not simply an adsorption effect but rather an ion-exchange process between metal ions and calcium ions. Suzuki and coworkers (1982) proposed that if the cations have large electronegativity values and radii close to 0.9 – 1.3 Å, they are largely removed by the hydroxyapatite. From Table 5.14, the ionic radius of cadmium ions is similar to the calcium ions. Although the ionic radius for copper and zinc ions are not close to 0.9 – 1.3 Å, the strengths of Pauling’s electronegativity of copper and zinc ions are higher than calcium ion. Therefore, cadmium, copper and zinc ions can exchange with calcium ion in the crystal lattice.

In addition, the adsorption process (physical sorption) usually is an exothermic reaction in most cases. Increasing the temperature of solutions usually decreases the sorption capacity of sorbates. However, from Tables 5.2 – 5.13, increasing the temperature of the solution also increased the sorption capacity of metal ions on bone char. The enthalpy, ΔH, is a positive value, which represents the sorption process, undergoes an endothermic reaction. Helfferich (1995) summarized the temperature
effect of ion exchange process that high temperature discourages the ion exchange process which occurs with evolution of heat. Standard enthalpy changes are usually smaller than 2 kcal/mole, though values of up to 10 kcal/mole have been observed in exceptional cases (e.g. neutralization). This phenomenon may be explained by the cation exchange of the CaHAP lattice. In the CaHAP crystal structure, there are two types of calcium sites which are called Ca(1) and Ca(2) sites. Fedoroff et al. (1999) and Mandjiny et al. (1998) identified that there are four Ca(1) and six Ca(2) sites per unit cell occupying the stoichiometric apatites. Fedoroff and coworkers (1999) found that the ion exchange of Cd$^{2+}$ ions in CaHAP only takes place in Ca(2) sites at 18°C and 28°C. When the solution is heated at 75°C, the cadmium ions can occupy both Ca(1) and Ca(2) sites. Obviously, increasing the solution temperature will increase the exchange of metal ions. The Ca(1) sites are almost entirely occupied, whilst the Ca(2) sites are partially occupied. Since the Ca(2) sites are partially occupied (or bonded) in the CaHAP lattice, the ion exchange at the Ca(2) site can easily occur at low temperature. However, the cation can replace the calcium ion in the Ca(1) site in CaHAP lattice when the atom possesses a high energy. As the sorption of metal ions onto bone char involves ion exchange with different sorption sites, the enthalpy parameters in Langmuir, Langmuir-Freundlich and bi-Langmuir isotherms cannot truly represent the heat of sorption. These parameters only represent adjustable constants or apparent heat of sorptions of equilibrium equations.

Table 5.15 show the total sorption capacity, adsorption capacity, cation exchange capacity and calcium metal exchange in solid for the metal ions onto bone char at different temperatures. When the temperature of solution increases, the cation exchange capacity will increase for all sorption systems. The adsorption capacity for
cadmium ions is increased with the temperature. But the adsorption capacities for copper and zinc ions are neither increased with temperature nor decreased with the temperature. At 20°C, less than two weight percent of calcium ions are exchanged from the CaHAP surface. The calcium exchange capacity at different temperatures are calculated and shown in Table 5.15.

**Selection of Adsorption Equilibrium Isotherm**

As discussed before, the sorption capacity of metal ions onto bone char depends on the adsorption and ion exchange of metal ions. The CEC, which depends on the Ca (1) and Ca (2) sites in CaHAP lattice, is controlled by the temperature of solution. Since no adsorption model can fully describe the complex sorption mechanism, the use of the adsorption model is in correlating the experimental data only. Table 5.16 shows the SSEs of Langmuir, Langmuir-Freundlich and bi-Langmuir isotherms for all these sorption systems.

From Table 5.16, the correlation of Langmuir and Langmuir-Freundlich equations are better than the bi-Langmuir equation. Although the bi-Langmuir equation can separate ion exchange and adsorption effects in equation, the SSEs of bi-Langmuir equation are lower than the values of the Langmuir and Langmuir-Freundlich equations. Therefore, the bi-Langmuir equation will not be used to study the sorption equilibrium for multicomponent systems and the mass transport of sorption systems. In fact, many researchers have directly used the Langmuir equation for sorption onto bone char and CaHAP without considering the other sorption isotherms, including the sorption of metal ions onto CaHAP (Hu et al., 1994; Fuierer et al., 1994 and Kanzaki et al., 2000), the sorption of organic compounds onto CaHAP (Fargues et al.,
1998; Misra, 1996 and 1997; and Koutsopoulos and Dalas, 2000) and the sorption of uranium ions onto bone char (Gu et al., 1998). The possible reason may be due to that the Langmuir equation can be used to correlate a rectangular isotherm. In addition, the Langmuir equation is a widely used equilibrium equation. Hence, this equation will be used in the mass transfer modeling section.

**Determining the Maximum Initial Concentration that can be treated to achieve Local Discharge Limit**

The previous section shows that the Langmuir equation can be used to correlate the equilibrium data for the sorption of cadmium, copper and zinc ions onto bone char. When the equilibrium concentration of solution is known, the sorption capacity of sorbent for each metal ion can be calculated by the Langmuir equation. In order to apply bone char in real sorption system, the equilibrium concentration of discharged solution should meet the WPCO discharged limit. To calculate the maximum initial concentration for the metal ion uptake using bone char, the Langmuir and mass balance equation can be used. Therefore, the maximum initial concentration can be calculated by solving the equation [3.2.2.1] and [4.1.1.5]. The mass to volume ratio is fixed at 5, which is used in the section 3.2.1.

\[
C_o = C_e + \left( \frac{W}{V} \right) \left( \frac{q_m a_L C_e}{1 + a_C C_e} \right) \tag{5.3.1.7}
\]

In Hong Kong, the temperatures of wastewater are assumed in the range of 10°C and 40°C. The typical value is assumed at 20°C. The maximum initial concentrations for each metal ion are shown on Table 5.17. If the initial concentration of metal ions solution are controlled based on Table 5.17. The bone char can be used for the removal these ions to meet the legal limits. If the initial concentration is higher than
the maximum initial concentration in Table 5.17, a higher mass of sorbent can be
adjusted to meet the legal limits.

5.3.2 Ideal Adsorbed Solution Theory

The IAST can be used to predict multicomponent adsorption isotherms using
single component equilibrium data. It is based on the assumption that the solution is
ideal, i.e., if there is no adsorbate-adsorbent interaction. In this research, the
Langmuir and Sips equations were used to predict the binary and ternary component
equilibria. From the previous discussion, the quality of the fitting for the Langmuir-
Freundlich equation in single component systems was better than the Langmuir
equation in the sorption of cadmium and copper systems. Comparisons of the
theoretical and experimental data were made to evaluate the deviation of the values.

Figures 5.32 – 5.38 show the sorption of binary metal ions onto bone char. The
sorption capacities for the copper ions in six sorption systems are always higher than
the cadmium and zinc ions and the sorption capacity for the cadmium ions is also
higher than the zinc ions. The possible reason may be due to the selectivity of ion
exchange in multicomponent system. Recently, Lee and Moon (2001) studied the
sorption of metal ions onto natural zeolites. The selectivity of the NaCl-treated
natural zeolite and the chabazite for heavy metals encountered follows the order Cs+
>> Pb²⁺ > Cd²⁺ ≥ Cu²⁺. The result is not matched with ionic radii but fairly coincides
with the reversed order of hydrated ionic radii as Cs⁺ (3.30Å) > Pb²⁺ (4.01 Å) > Cu²⁺
(4.19 Å) > Cd²⁺ (4.26 Å). As zeolite removes the metal ions from solution by ion
adsorption and ion exchange effect, the selectivity properties should be similar to
CaHAP. The selectivity of metal ions onto bone char follows the order Cu²⁺ > Cd²⁺ >
Zn\(^{2+}\). The reversed order of hydrated ionic radii is Cu\(^{2+}\) (4.19 Å) > Cd\(^{2+}\) (4.26 Å) > Zn\(^{2+}\) (4.30 Å) (Table 5.14). This result agrees with Lee and Moon (2001). Hillel explained (1998) more than Lee and Moon regarding the ion exchange properties of clay materials. The smaller the ionic radius and the greater the valence, the more closely and strongly is the ion adsorbed. On the other hand, the greater the ion’s hydration, the farther it is from the adsorbing surface and the weaker its adsorption.

From Figures 5.32 and 5.34, the predictions for the sorption of Cd-Cu and Cu-Zn ions are quite reasonable. Using the Langmuir and the Langmuir-Freundlich isotherms in the IAST are also close to the experimental points. When one of the Langmuir-Freundlich curves is close to the experimental points, the other Langmuir-Freundlich curve deviates from the experimental points. The similar effect can be found in the Langmuir curves. However, Figure 5.33 shows that the IAST cannot accurately predict the experimental data. Both curves are below the experimental data points. The similar effect can be found in Cd-Cu in 3:7 or 7:3 ratio systems. The sorption capacities for these binary systems may be enhanced. The interaction between metal ions and sorbent may be the main factor affecting the quality of prediction. In addition, the unequal mole ratio systems are shown in Figures 5.35 – 5.38. The prediction for the Cd-Cu in the 4:6 or 6:4 ratio systems appears better than the Cd-Cu in the 3:7 or 7:3 ratio systems. The sorption isotherms of copper ions in the multicomponent Langmuir isotherm appear to produce an increasing trend even in low mole ratios.

Figures 5.39 and 5.40 show the sorption of cadmium, copper, and zinc ions at equal mole ratios using the Langmuir and the Langmuir-Freundlich equations.
respectively. The predictions for the sorption of copper and zinc ions are better than for the sorption of cadmium ions. Figures 5.41 and 5.42 show the IAST predictions for the non-equimolar metal ion ratios with copper as the major component using the Langmuir and the Langmuir-Freundlich equation respectively. The predictions for copper and zinc ions are quite reasonable but the prediction for cadmium ions is relatively poor. Figures 5.43 and 5.44 show the prediction of IAST to the experimental points for non-equimolar ratios and in these figures, copper ions is at a low mole ratio. The predictions of cadmium ions using the Langmuir and the Langmuir-Freundlich equations are good. The predictions of zinc ions at low concentrations are good but at high concentration are poor.

The overall performance of the IAST using the Langmuir and the Langmuir-Freundlich equations can provide a reasonable curve fitting to the experimental data. However, the prediction deviates to the experimental data in the non-equimolar ratio systems except Cu-Cd in 6:4 or 4:6 ratio systems. Introducing an interaction factor into the IAST may assist to correlate the correlation of experimental data.
5.4 MASS TRANSFER MODELING

Film diffusion and pore diffusion are important to control the removal rate of sorbate for the sorption system. Film diffusion is usually more important in continuous flow systems, such as fixed beds, whereas in well agitated systems, the boundary layer resistance is usually quite small and pore diffusion should be the rate controlling step (Tien, 1994). This part of the research will focus on the correlation of kinetic data with theoretical mass transfer models. The external mass transfer coefficient will be determined and incorporated into the intraparticle diffusion model to correlate the kinetic data using a film-pore two-resistance model.

5.4.1 External Mass Transfer Models

The external mass transfer coefficient can be directly calculated by the film diffusion equation (Mathews and Weber, 1976).

\[
\frac{dC_t}{dt} = -k_f S_A (C_t - C_s) \tag{4.2.1.1}
\]

This equation can be used to calculate the external mass transfer coefficient when \( t \rightarrow 0 \) and \( C_s \rightarrow 0 \). Then, equation [4.2.1.1] can be integrated to become:

\[
\ln \left( \frac{C_t}{C_o} \right) = -k_f S_A t \tag{5.4.1.1}
\]

An alternative method, which was developed by Furusawa and Smith (1973), calculates the external mass transfer coefficient by incorporating the linear adsorption isotherm into equation [4.2.1.1] to become equation [4.2.1.11]. This equation has been used to calculate the external mass transfer coefficient for many sorption systems (Allen et al., 1992; McKay and Allen, 1983; Furusawa and Smith, 1973). In this research, the external mass transfer coefficients using equation
[4.2.1.11] and equation [5.4.1.1] are compared. Initially, equation [4.2.1.11] is rearranged to equation [5.4.1.2].

\[
\left( \frac{1}{1 + (1/m_s K_L)} \right) \ln \left( \frac{C_t}{C_o} \right) - \frac{1}{m_s K_L} \left( 1 - \left( \frac{C_t}{C_o} \right) \right) = -k_f S_o t \]  

[5.4.1.2]

By plotting \( \left( \frac{1}{1 + (1/m_s K_L)} \right) \ln \left( \frac{C_t}{C_o} \right) - \frac{1}{m_s K_L} \left( 1 - \left( \frac{C_t}{C_o} \right) \right) \) against \( t \), the external mass transfer coefficient can be determined from the slope of the straight line. Plotting the linear equation [5.4.1.2] is easier than plotting equation [4.2.1.11] because the intercept of the straight line must be adjusted to \( \ln \left( \frac{m_s K_L}{1 + m_s K_L} \right) \), while the intercept of equation [5.4.1.2] is equal to zero. This results in an easier determination of the initial gradient (as \( t \to 0 \)). In addition, equation [5.4.1.2] can be converted to equation [5.4.1.1] when:

\[
\frac{1}{m_s K_L} = \left( \frac{V}{m} \right) \left( \frac{1}{q_m a_L} \right) \to 0 \]  

[5.4.1.3]

where \( q_m \) and \( a_L \) are the maximum capacity and the affinity respectively of sorbate to sorbent. These parameters are the intrinsic properties of sorbent to sorbate, which cannot be changed. In equation [5.4.1.3], the \( V/m \) ratio is the only adjustable parameter in this expression. When the mass of sorbent increases, the term \( 1/m_s K_L \) tends to zero. Consider the assumption in equation [4.2.1.9] when \( 1 + a_L C_r = 1 \), equation [4.2.1.11] can be obtained. The conditions \( 1 + a_L C_r = 1 \) and \( 1/m_s K_L \to 0 \) apply to very dilute solution systems or the use of a large mass of sorbent in solution. Therefore, the use of equations [5.4.1.1] and [5.4.1.2] for dilute solution is identical. Figures 5.45 – 5.47 show the plots of the external mass transfer equations. The plots of equations [5.4.1.1] and [5.4.2.2] are very close.
The Harriott equation was developed using dimensional analysis to calculate the external mass transfer coefficient. These coefficients were substituted into the film-pore diffusion model to obtain reasonable intraparticle diffusivities in the next section. Figure 5.48 is the plot of $\text{Sh}/\text{Sc}^{0.33}$ against particle Reynolds number. Increasing the particle sizes will slightly decrease the external mass transfer coefficients in Table 5.18. A similar plot was produced by Harriott who used the equation to calculate the external mass transfer coefficients of ion-exchange resins (Tien, 1994). The external mass transfer coefficient at different particle sizes using Harriott equation were calculated and shown in Table 5.19.

The external mass transfer coefficients using different methods have been calculated and are listed in Tables 5.20 – 5.25. The differences between the linear and nonlinear external mass transfer coefficients are relatively small. The magnitudes of these coefficients, which were calculated by equations [5.4.1.1] and [5.4.1.2], are of the order $10^{-4}$ cm/sec. The external mass transfer coefficients calculated by these methods do vary with the initial concentration of solution and mass of sorbent. From Tables 5.20 – 5.25, increasing the initial concentration of solution increases the external mass transfer rate of sorbates. When the mass of sorbent is increased, the external mass transfer coefficients vary without trend. On the contrary, the external mass transfer coefficients calculated by the Harriott equation are independent of initial concentrations and sorbent masses. The magnitude of the external mass transfer coefficients by the Harriott equation is $10^{-3}$ cm/sec.
As the external mass transfer coefficients obtained from the four methods are different, it is difficult to decide which approach is correct. Therefore, it was decided to substitute these coefficients into the two-resistance film-pore intraparticle diffusion model to determine the ‘best-fit’ method for the sorption systems. When the external mass transfer coefficients from the Harriott equation were substituted into the film-pore diffusion model, the best curves were obtained. However, using the other three coefficients, the experimental data could not be correlated because of their small magnitudes. Similar results were obtained by Allen and coworkers (1997). The authors used the Furusawa and Smith equation to determine the external mass transfer coefficients and Homogeneous Surface Diffusion Model (HSDM) to determine the external mass transfer coefficient. The magnitudes based on the HSDM are $10^{-3}$ cm/sec but using the Furusawa and Smith equation the value is $10^{-4}$ cm/sec. Therefore, the authors used the best-fit external mass transfer coefficient from HSDM.

Further evidence to support this observation can be found from the boundary layer theory. The thickness and properties of the boundary layer film will depend on sorbent particle size, particle density and number of particles per unit volume of solution. This latter property will be negligible for small solids concentrations, as there will be little or no interparticle collisions and subsequent attrition of the boundary layer. In addition, the particle should not be fragment in the agitated adsorber and constant equal agitation should be maintained for all experiments. The critical solution properties are temperature, density and viscosity. Since the metal ion solute concentrations are very low, the solution properties are almost identical to
those of water. At the low initial metal ion concentrations used in this study, there is no effect on solution viscosity or density.

In these film diffusion studies, the discrepancies in the values of the film mass transfer coefficients between the experimental methods and the dimensional analysis method can be explained by the fast external mass transport of sorbates. The first three methods used the experimental data to calculate the film diffusion coefficients. However, the external mass transport of sorbate in these sorption systems may be very fast in comparison with the intraparticle diffusion. The experimental data used to calculate the film mass transfer coefficients may also be in the intraparticle diffusion region. In addition, the single resistance model based on the mass transport of sorbate at the initial stage (as \( t \to 0 \)) only, assumes mass transfer is controlled by the external mass transport of sorbate only, but if the mass transport at the initial stages is also controlled by the film-pore or pore diffusion, equations [4.2.1.12], [5.4.1.1] and [5.4.1.2] are invalid.

In order to prove that intraparticle diffusion may be occurring less than the initial thirty minutes, one experimental data point in the first five minutes is used to calculate the external mass transfer coefficient using equation [5.2.1.2]. The external mass transfer coefficient for the sorption of Cd\(^{2+}\), Cu\(^{2+}\) and Zn\(^{2+}\) ions at 3mM are equivalent to \( 1.03 \times 10^{-3} \), \( 1.65 \times 10^{-3} \), and \( 1.09 \times 10^{-3} \) cm/sec, respectively. The magnitudes of external mass transfer coefficients were increased. If more experimental data points, which are less than 5 minutes, are used, it may obtain a larger external mass transfer coefficient. Therefore, the choice of data points to calculate the external mass transfer coefficient is very important.
In addition, Figure 5.49 shows the sorption capacity of cadmium ions at specified times against the square roots of time. Weber and Morris (1963) stated that if intraparticle diffusion is the rate-controlling factor, uptake of the adsorbate varies proportionately with the square of time. When the linear plots of \( q_t \) vs \( t^{1/2} \) pass through the origin, it appears that the intraparticle diffusion may be the rate-controlling step in the removal of Cd\(^{2+} \) ions (Namasivayam and Ranganathan, 1993; Viraraghavan and Dronamraju, 1993). According to these assumptions, the film mass transfer may be less significant in comparison with the intraparticle diffusion. The sorptions of copper and zinc ions onto bone char have a similar characteristic pattern. Therefore, from Figure 5.49, substituting the experimental data into the film diffusion equation to determine the film diffusion coefficient is invalid. More interesting results are shown on Figure 5.50. When the particle sizes of sorbent decreases, the plot of the square root of time for the smaller particle sizes deviates from the point of origin. In the previous discussion, intraparticle diffusion is the rate-limiting step for whole duration of the sorption system. The film diffusion is not the rate-limiting step but it does exist in the mass transport of sorbate. However, as the radius of the sorbent particle decreases, the mass transport of sorbate inside the sorbent becomes shorter. The film diffusion effect in the metal ion removal rate becomes more and more significant. On the contrary, when the particle size increases, the mass transport distance of metal ions inside the sorbent becomes longer. The film mass transfer effect becomes less significant.
5.4.2 Film-Pore Diffusion Model

In the previous section, the film diffusion coefficient was calculated by the Harriott equation. In this section, the film diffusion coefficient will be used in the film-pore diffusion model to correlate the kinetic data and to calculate the diffusion coefficients. The rate-limiting steps of sorbate will also be determined by substituting the kinetic data into the mass transport model and determining the effective diffusivity of the sorption systems. Furthermore, the effective diffusivity of the multicomponent systems will also be determined using the intraparticle diffusion models.

In the batch kinetic study, the effect of the initial concentrations and the volume to mass ratios for the adsorption isotherms were investigated. Figure 5.51 shows that the equilibrium capacities, $q_e$, change at different initial concentrations and volume to mass ratios, $V/M$. The kinetic data started at an initial concentration, $C_o$ at $t = 0$, and the operating lines can then be plotted terminating on the sorption isotherm, $C_e$ at $t = \infty$. If the removal rate of metal ions is controlled by the pore diffusion, the effective diffusivity is constant at different initial concentrations and volume to mass ratios. If the effective diffusivity is a variable, the intraparticle diffusion may be controlled by the pore-surface diffusion or surface diffusion.

Case I: Analytical Method

The pore diffusivities of the analytical solution [4.2.2.16] were calculated by minimizing the objective function [4.2.2.17] of all sets of experimental data. Figures 5.49 – 5.54 show the analytical solutions compared to the experimental data. As the contact time is a function of concentration of solution, the theoretical time for the
sorption systems are compared to the experimental data. The effect of initial concentration and mass of sorbent for the sorption of cadmium and zinc ions can be correlated by the analytical solution to obtain constant pore diffusivity. However, the analytical solution used in the sorption of copper yields quite poor results. The discrepancy between the experimental and the theoretical data may be due to the assumption of the “pseudo-irreversible” isotherm approximation in equation [4.2.2.12]. Since the equilibrium capacity at time $t$, $q_{e.t}$, is a variable, the hypothetical equilibrium capacity may not be applied to this system.

Case II: Numerical Method

This method was developed by Cheung and coworkers (2001a, 2001b) to calculate the pore diffusivities of the sorption systems. The authors modified the previous work by Chen and his coworkers (2001) who developed the pore-surface model using the fundamental equations of the analytical method. The difference between the numerical and the analytical method is the sorption capacity of each shell layer varying at different surface concentrations. Since the modification of these equations could not be solved by the analytical method, a numerical method was developed to solve the governing equations. The data fitting technique for the numerical method is similar to the analytical method. The pore diffusivities of the numerical solution were calculated by minimizing the objective function, equation [4.2.3.12], of all sets of experimental data. Figures 5.55 - 5.60 show the correlation of the film-pore diffusion model with the kinetic data. The film diffusion coefficients and nine sets of kinetic data were substituted into the film-pore diffusion model to obtain one pore diffusion coefficient. The sorption rate is independent of initial concentration and the mass of sorbent. The film-pore diffusion model can correlate
the kinetic data for the sorption of cadmium and zinc ions very well but the kinetic data for the sorption of the copper ions slightly deviates from the film-pore diffusion model. By comparing the analytical method, the correlation of the numerical method in the sorption of copper ions has been greatly improved.

**Case III: Film-Pore-Surface Diffusion Model**

The mass transport of sorbate inside the sorbent may depend on the pore, surface, and their combined diffusion. The previous section used the film-pore diffusion model and the best-fit constant pore diffusivities for all systems were obtained. This section used the combined diffusion model to correlate the experimental data. Since bone char does not have a micropore region in the pore structure, the pore diffusivity should be the primary mass transport mechanism. However, the surface diffusion may happen in mass transport mechanism. Therefore, a combined diffusion model is considered as the diffusion mechanism of sorbate. The pore and surface diffusivities were obtained by minimizing the objective function [4.2.3.12]. Figures 5.64 – 5.69 show the correlation of the film-pore-surface model. The model prediction of the experimental data for the sorption of copper ions is not good in comparison with the cadmium and zinc ions.

**External and Internal Mass Transport of Sorbate**

The mass transport of metal ions using film-pore diffusion model can be described by equation [4.2.3.4]. When the sorbent was placed into the agitation vessel, the metal ions were transferred from the bulk solution to the internal pores of the sorbent. The metal ions diffuse across the liquid film due to the concentration driving force and after the sorbate reaches the sorbent surface, intraparticle diffusion becomes the
rate-limiting step of the process. Therefore, the film diffusion controls the mass transport of sorbate at the initial stage of the sorption process. However, the rate of the intraparticle diffusion is slower than the film diffusion. The mass transport of sorbate is mainly controlled by the intraparticle diffusion. Hence, equation [4.2.3.4] is used to describe the relationship of film diffusion and intraparticle diffusion.

Figure 5.70 shows that the concentration of bulk solution decreases along the operating line to the equilibrium isotherm. The tie lines can be drawn by connecting the experimental data points \((C_n, q_i)\) to local equilibrium concentrations \((C_{e,i}, q_{e,i})\) at time \(t\). The tie lines change rapidly at the initial stage and then decrease along the equilibrium isotherm. After the first three hours, the tie lines nearly become vertical, which means the concentration of solution at the sorbent surface is nearly equal to the bulk solution (i.e. \(C_i = C_{e,i}\)). Figure 5.71 shows that the concentration of the bulk solution, \(C_i\), decreases rapidly during initial stage of the sorption process. The external mass transfer coefficient and pore diffusivity for the sorption of cadmium ions on bone char are equivalent to \(k_f = 2.4 \times 10^{-3} \text{ cm/sec}\) and \(D_p = 1.14 \times 10^{-6} \text{ cm}^2/\text{sec}\), respectively. The Biot number, \(Bi\), is equivalent to 65. The concentration of solution at the sorbent surface, \(C_{e,i}\), builds up at the same time. The experimental data points of \(C_i\) meet the points \(C_{e,i}\) after 180 minutes. The concentration in the bulk solution is equal to the concentration of solution at the pore surface.

Referring to Figure 5.70, the tie-line liquid phase concentration \(C_{e,i} = 0\) at the beginning of the sorption process when \(t = 0\). The tie line value of \(C_i\) is vertically close to \(C_{e,i}\) after 3 hours. Therefore, the tie-line liquid phase concentration is almost equal to bulk concentration. In order to test the effect of the film diffusion to the
mass transport of sorbate, the sensitivity analyses are performed. The film diffusion coefficient was reduced and the pore diffusivity was kept constant. Therefore, the Biot number was reduced. Figure 5.72 shows the sensitivity analysis of $k_f$ to the film-pore diffusion model. When the film diffusion coefficient decreases, the concentration curves of $C_t$ and $C_{e,t}$ show an increasing separation between the $C_t$ and $C_{e,t}$ curves. The time taken for $C_t$ and $C_{e,t}$ to approach together becomes longer. Therefore, in the present system, the film diffusion has more control over the mass transport process when the values of $k_f$ are decreased to 0.2 $k_f$. The $C_{e,t}$ meets the $C_t$ at equilibrium, which takes just over six hundred minutes to attain in the agitated batch adsorber for $k_f = 0.2 k_f$ actual system. In the extreme case (i.e. 0.05 $k_f$), $C_{e,t}$ will never meet the $C_t$. This means that the film diffusion is controlling the whole mass transport mechanism.

Figure 5.73 shows a sensitivity analysis for $D_{eff}$. It can be seen that the film diffusion of sorbate becomes insignificant when intraparticle diffusion is decreasing as $D_{eff}$ is reduced to 0.1 $D_{eff}$. The Biot number was increased to over 100. Table 5.26 shows the effect of film and pore diffusivities on the Biot number. The Biot number measures the relative resistance contributed by the stagnant film surrounding the particle to the internal diffusion resistance. For most gas phase applications, this number is of the order of 10 to 100, indicating that the internal diffusion resistance is more importance than the film resistance (Do, 1998). Taregner and Suidan (1989) proposed that the Biot number between 1 and 100 indicate that both mass mechanisms are important in liquid phase system. For $\text{Bi} << 1$ external mass transport resistance is the controlling mass transfer step, while for $\text{Bi} >> 100$, Intraparticle
diffusion is the controlling mass transfer mechanism. Therefore, the effect of film diffusion only has a minor effect on the diffusion process.

Comparing the Analytical Model with the Numerical Method

Table 5.27 shows the film mass transfer coefficients and pore diffusivities of the sorption systems. The pore diffusivities for the analytical and numerical method do not have a large change but the quality of fitting for the film-pore diffusion model has been improved.

The molecular diffusivities of metal ions can be calculated by the Petr Vanýsek equation (Lide & Frederikse, 1994).

\[ D_m = \frac{RT}{F^2} \left( \frac{\lambda}{Z} \right) \]  \hspace{1cm} [5.4.2.1]

Using the Petr Vanýsek method to calculate the molecular diffusivities of metal ions in solutions; therefore, the film thickness can be calculated by equation [2.4.1.1]. The calculated film thicknesses are equivalent to \(2.65 \times 10^{-3}\) cm. According to Helfferich (1995), the liquid film thickness is around \(10^{-3}\) to \(10^{-2}\) cm for ion exchangers. Therefore, the calculated values are close to the literature values. The tortuosity factor of sorbent can be calculated from equation [5.4.2.2].

\[ D_p = \left( \frac{\epsilon_p}{\tau_f} \right) D_m \]  \hspace{1cm} [5.4.2.2]

where \(\epsilon_p\) and \(\tau_f\) are intrinsic properties of sorbent, representing its porosity and tortuosity factor. The average tortuosity factor for these three systems is equal to 2.0 ± 0.4. The tortuosity factor for \(\text{Cd}^{2+}\) and \(\text{Zn}^{2+}\) ions is very close. However, the tortuosity factor for \(\text{Cu}^{2+}\) ion is smaller than \(\text{Cd}^{2+}\) and \(\text{Zn}^{2+}\) ions. The possible reason
may be due to that the correlation of copper system is poor than the cadmium and zinc systems.

Seo and Lee (1995) studied the sorption of cadmium, copper and zinc ions onto CaHAP, and determined values for the pore diffusivities of $2.95 \times 10^{-6}$ cm$^2$/s, $2.88 \times 10^{-6}$ cm$^2$/s and $2.77 \times 10^{-6}$ cm$^2$/s, respectively. The discrepancy of pore diffusivities may be due to the difference of pore size distribution of the sorbent. The pore structure of bone char is the intrinsic nature of the animal bone (See Figure 5.6). As the CaHAP is derived from the precipitation of CaHAP, the pore size distribution of bone char may be different to CaHAP. In addition, the porosity and tortuosity factor of these sorbents may also be different. Therefore, the pore diffusivities obtained from Seo and Lee are different to this research.

Comparing the Film-Pore Diffusion Model with the Film-Pore-Surface Diffusion Model

Table 5.28 shows the results of film-pore and film-pore-surface diffusion model. As the effective diffusivities of film-pore-surface model are concentration dependent, the data showed in the table are compared at a fixed initial concentration (i.e. $C_o = 3$ mM). According to the Darken equation (eqn. [4.2.4.7]), the surface diffusivity can be simplified to eqn. [4.2.4.8]. In this equation, the corrected surface diffusivity, $D_{so}$, is a fixed constant. Therefore, the surface diffusivity can be obtained when the $D_{so}$ is calculated.

Comparing the SSEs of three sorption systems, the film-pore-surface model using in the sorption of copper and zinc ions can slightly improve the fitting of the
experimental data. However, the difference of $SSE$s between the film-pore and the film-pore-surface diffusion model for the copper and zinc systems are around four percent. The improvement for the sorption of cadmium ions is around two percent.

From Table 5.28, the surface diffusivities for the sorption systems are greater than the pore diffusivities. However, the changes of the effective diffusivities are relatively small. The main reason why the use of surface diffusion does not improve the fitting of the model is the slope of isotherm. From equation [4.2.4.4], the effective diffusion coefficient is composed of the pore diffusivity, particle density, surface diffusivity and the slope of isotherm. In these sorption systems, the Langmuir isotherm shows a rectangular shape (Figures 5.22 – 5.24). The slopes of the isotherm are very small. Therefore, the slope of the isotherm reduces the magnitude of the surface component in the effective diffusivity. From theoretical consideration, highly rectangular isotherm indicates that the sorption process is likely to be irreversible. The sorbate is favor to rest on the sorption site (irreversible adsorption).

5.4.3 Sorption Rates at Different Temperatures

As the hydrated ionic radius of metal ion is relatively small in comparison with the pore diameter of the sorbent, the sorbate diffuses in the pore by means of molecular diffusion. Therefore, the pore diffusivity in liquid systems is proportional to the mean ionic diffusivity of metal ions. The molecular diffusivity, $D_m$, in equation [5.4.2.1] is a function of temperature. In addition, the molecular diffusivity is independent of the ion concentration in a dilute solution. Therefore, pore diffusivities at different temperatures can be predicted by the numerical film-pore diffusion model and the physical properties of the solution. Since the molecular diffusivity in the
pore-liquid is a function of temperature, an increase in temperature will also increase the diffusion rate of metal ions in the pores.

In order to incorporate the temperature effect into the effective diffusivity, the Stokes-Einstein relationship (Kärger and Ruthven, 1992) was used:

$$\left( \frac{D_m \mu}{T} \right) = \text{Constant} \quad \{5.4.2.2\}$$

Therefore, in an ideal case, the molecular diffusion in a liquid-pore is equal to:

$$D_m(T) = D_{mo} \frac{\mu_o}{\mu} \frac{T}{T_o} \quad \{5.4.2.3\}$$

where $D_{mo}$ and $\mu_o$ are the molecular diffusivity and the viscosity of solution in the pore-liquid respectively at a reference temperature (e.g. $T_o = 293.2$ K). As the viscosity of solution is a function of temperature, the Eyring equation [5.4.2.4] (Bird, 1960) will be used to predict the temperature effect of the solution viscosity.

$$\mu \equiv \frac{\tilde{N}h}{V} \exp(3.8(T_b/T)) \quad \{5.4.2.4\}$$

or

$$\ln \mu = \ln \left( \frac{\tilde{N}h}{V} \right) + \left( \frac{3.8T_b}{T} \right) \quad \{5.4.2.5\}$$

Since this equation is only used to estimate the viscosity of the solvent, the predicted diffusivity is only an approximate value. Combining equations [5.4.2.2] and [5.4.2.4], the effective diffusivity at different temperatures can be expressed by equation [5.4.2.6].

$$D_{ef}(T) \equiv \left( D_{ef} \right)_o \left( \frac{T}{T_o} \right) \exp \left( 3.8T_b \left( \frac{1}{T_o} - \frac{1}{T} \right) \right) \quad \{5.4.2.6\}$$

Where $T_b$ is the boiling point of the liquid. In this research, the boiling point of dilute solution is assumed to be equal to the boiling point of water (i.e. $T = 373.15$ K).
Therefore, equation [5.4.2.6] is used to predict the temperature effect of the experimental data. Figures 5.74 - 5.79 show the temperature effects for all three sorption systems. The best-fit curves were obtained by correlating the experimental data using the film-pore diffusion model. The predictive curves were obtained by incorporating the film-pore diffusion model with equation [5.4.2.6]. The predictions for the sorption of copper and zinc ions are good. Figure 5.77 and 5.79 show difference between error bars and the best-fit diffusivities. The error bar shows ten percent error of the actually value. The predictive curve for some data points are less than ten percent error. Figure 5.76 shows the error bars for the best-fit model. At the high and low temperature of solution, the errors between the experimental data and best-fit curves are less than ten percent at the first four hours. After four hours, the deviations are higher than ten percent. However, the prediction for the sorption of cadmium ions deviates from the best-fit values. The possible reason may be due to the reference effective diffusivity at \( T_o = 293.15 \) K deviate from the actual pore diffusivity. If the effective diffusivity at \( T_o = 283.15 \) K is used as reference, the predictive curve becomes more accurate. As the sorption rate at different temperatures can be predicted by incorporating the expression [5.4.2.6] into the film-diffusion model, it is believe that the sorption mechanism should be controlled by pore diffusion.

5.4.4 Ion Exchange Rates at Different Temperatures

Several sorption mechanisms including ion exchange (Chen et al., 1997), surface complexation (Xu et al. 1994) and dissolution-precipitation (Chen et al., 1997; McGrellis et al., 2001) were reported in the sorption of metal ions onto CaHAP. In this research, all above sorption processes can be classified into two main
mechanisms, which are ion exchange and adsorption. The “ion exchange” process is the calcium ion in CaHAP lattice displaced by metal ions. The “adsorption” process is all possible processes except ion exchange process. Therefore, “sorption” process is composed of ion exchange and adsorption processes. In addition, the adsorption and ion exchange of metal ions only take place on CaHAP surface. No significant research from literature review shows that the carbon surface can adsorb metal ions from solution. Therefore, it is believe that the carbon surface does not have any contribution in the sorption of the metal ions onto bone char.

Figures 5.80 – 5.85 show the ion exchange and adsorption rate of metal ions at different temperatures. From Figure 5.80, the solid lines represent the concentration of calcium ions in solution increasing with time. Fedoroff and coworkers (1999) suggested that the ion exchange ratio of CaHAP for cadmium and calcium ions is one mole to one mole. Therefore, the adsorption rate can be obtained by subtracting the ion exchange rate of cadmium ions from the sorption rate of cadmium ions. From Figures 5.80 and 5.81, the ion exchange rate is slower than the adsorption rate in the first thirty minutes. This is because the metal ions should be adsorbed on the surface first and then the metal ions on the surface undergo ion exchange process with the neighboring calcium sites. If the temperature of the solution is high enough, the metal ions will also exchange with the Ca(1) sites (Fedoroff et al., 1999). As the ion exchange rate at 10 and 20°C in the first ten minutes are slow, the concentration of calcium ions in the solution is near to zero.

From these figures, it may be expected that the sorption rate is controlled by the ion exchange rate. However, this is not the case, because increasing the solution
temperature will also increase the diffusion rate. From the beginning of this research, the ion exchange and adsorption rate are assumed as very fast processes. These processes do not affect the sorption rate if the intraparticle diffusion is the rate-limiting step. A linear plot of sorption capacity at specified time against the square root of time can be obtained (Weber and Morris, 1963). Consider the mass transport of metal ion onto bone char. The metal ion slowly diffuses into the liquid-filled pore from the bulk solution. The metal ion is adsorbed and exchanged from the CaHAP lattice in very fast rate. After the ion exchange process, the calcium ions in liquid-filled pore diffuse out of the sorbent. If the diffusion rate controls the overall sorption rate, the calcium ion diffusing out of the sorbent should be similar to the metal ions diffusing into the sorbent. Therefore, the square root of time plot for the cation exchange capacity (CEC) should be linear.

Figures 5.86 and 5.87 show the CECs of cadmium ion and the adsorption rate against $t^{0.5}$. There are two linear regions in Figure 5.86 and three linear regions in Figure 5.87. In Figure 5.87, the third region at $T = 60^\circ C$ is not a straight line. Referring to Figure 5.81, the adsorption rate at $t = 180$ mins is near to a constant. Therefore, ion exchange is the primary sorption mechanism after 180 minutes at $60^\circ C$. As the diffusion rate controls the ion exchange and adsorption rate, linear plots of $q_t$ against $t^{0.5}$ for ion exchange and adsorption rate can be obtained. Therefore, these results can prove that the intraparticle diffusion rate controls the sorption rate.

5.4.5 Determining the Rate-limiting Step

It was believed that ion exchange is essentially a chemical reaction best described in terms of rate coefficients and kinetic orders corresponding to the stoichiometry of
exchange (Helfferich, 1982). Until 1947, Boyd and coworkers studied the sorption of metal ions using ion exchange resin and zeolite. The authors found that increasing the temperature of solution increases both the reaction and diffusion rates. But, if the mass transport rate of sorbate is not the rate-limiting step of the sorption process, the particle size should not affect the sorption rate. This is because the mass transport rate is very fast and therefore the reaction rate of at the sorption site controlled the overall removal rate. On the contrary, if the mass transport rate of sorbate is the rate-limiting step, the particle size of sorbent affects the removal rate. This is because the larger the particle size, the longer the mass transport distance should be. Figures 5.88 shows the particle size effect for the sorption of metal ions onto bone char. When the particle size increases, the metal ion removal rate will decrease. These results agree with the Boyd’s explanation. The mass transport rate of metal ions is the rate-limiting step for the sorption process.

In this research, the sorption rates were studied using different methods. The rate-limiting step is mainly controlled by the pore diffusion and the film mass transfer has a minor effect on the diffusion at the initial stage. The conclusion is based on the following results.

(1) The \( q_t \) vs \( t^{0.5} \) plots show a straight line. This implies the rate-limiting steps are controlled by the intraparticle diffusion process. The intercept for the large particle sizes intersects the point of origin. Therefore, the film effect less significant for large particle sizes of bone char but becomes significant for small particle sizes (See Figure 5.50).
(2) The $q_i$ vs $t^{0.5}$ plots show a straight line for the ion exchange rate and adsorption rate. This implies the rate-limiting steps are controlled by the intraparticle diffusion process.

(3) The sorption rate decreases when the particle size increases. If the ion exchange rate is the rate-limiting step for the sorption rate of metal ions, the sorption rate should be independent of particle size. Therefore, the sorption rate is controlled by diffusion.

(4) The pore diffusivities at different temperatures can be correlated by the Stokes-Einstein relationship. This infers that the sorbate diffuses along the pore by molecular diffusion. Therefore, considered together with point (3) pore diffusion is the rate-limiting step for this sorption process.

(5) Although surface diffusion may exist in the mass transport process, the sum of the squares of the error did not show a significant improvement. Therefore, the contribution of surface diffusion is quite small or even negligible.

5.4.6 Sorption Kinetics for Multicomponent Systems

The previous section successfully demonstrated the ability of the film-pore diffusion model to correlate the experimental data for single component systems. The mass transfer rate for single component systems appeared to be mainly controlled by pore diffusion. In this section, the mass transfer coefficients for the multicomponent systems will be determined. As the solid phase concentrations of sorbent must be
determined to calculate the liquid phase concentration in sorbent, an empirical method and the IAST are separately used in the calculation of pore diffusivities for multicomponent systems.

**Empirical Equation for Solid Phase Concentration (Case I)**

This method uses single component equations to correlate the multicomponent kinetic data. However, the sorptions of cadmium and zinc ions onto bone char in multicomponent systems may be competed by copper ions. The Langmuir-type equation cannot be used to correlate the sorptions of cadmium and zinc ions in multicomponent systems except the sorption of cadmium ion in Cd-Zn system. Therefore, an empirical equation is used to replace the Langmuir-type equation to obtain better fit for the sorption of cadmium and zinc ions.

Langmuir-type equation: \[ q_{e,i} = \frac{q_m a_i C_{e,i}}{1 + a_i C_{e,i}} \] [4.2.3.6]

Empirical equation: \[ q_{e,i} = \frac{q_m a_i C_{e,i}}{1 + a_i C_{e,i}} - HC_{e,i} \] [4.2.5.1]

The Langmuir-type and the empirical equation are separately used to correlate the experimental data. The empirical method, developed in the present research, utilizes the same equations as in the single component system except for the calculation of the solid phase concentration on the sorbent surface. The most important assumption in the film-pore diffusion model for cadmium and zinc ions sorption is that the solid phase concentration of sorbent at radius \( r \) can be calculated by the empirical equation. Therefore, the solid phase concentration of sorbate is assumed to be at local equilibrium at radius \( r \). As a result, the local equilibrium of the exhausted sorbent is constant irrespective of the radius at a given time. Hence, the pore diffusivity is estimated based on the empirical equation.
Figures 5.89 – 5.91 show the sorption equilibrium isotherms for the single and multicomponent systems. The equilibrium data are better correlated using the Langmuir and empirical equations than the IAS theory. The sorption equilibrium of copper ions in the multicomponent systems is well correlated by the Langmuir-type equation for all systems. In addition, the sorption of cadmium ion in Cd-Zn solution shows a very good Langmuir fit isotherm. Therefore, the Langmuir-type equation will be incorporated into the film-pore diffusion model to correlate the kinetic data in these sorption systems. However, cadmium or zinc ions may be competing with the copper ions in the multicomponent systems, and so the empirical equation has been used to correlate the sorption equilibria for cadmium and zinc ions. The constants for the empirical and Langmuir-type equations are shown in Tables 5.29 – 5.31.

The sorption kinetics of cadmium ions in the binary and ternary systems is shown in Figures 5.92 – 5.97. The concentration effect for the sorption of cadmium ions in Cd-Cu can be correlated very well but the mass effect in Cd-Cu, Cd-Zn and Cd-Cu-Zn systems show some deviation from the experimental data points. Figures 5.98 – 5.103 show the sorption of copper ions from the Cd-Cu, Cu-Zn and Cd-Cu-Zn systems. The film-pore diffusion model, which incorporates the Langmuir-type equation, can correlate the kinetic data for copper systems. From Figures 5.104 – 5.109, the concentration effect for the zinc ions in the Cd-Zn system is good but the other curve fittings for the zinc systems are poor. Table 5.32 shows the pore diffusivities of multicomponent systems. The pore diffusivities of single components are higher than the values of binary and ternary systems.
IAS Theory for Solid Phase Concentration (Case II)

In binary mixtures, there are two reaction fronts moving inside the particle at different speeds, namely, the sorbent two species (binary system) in the outer layer; a single species in the middle layer; and finally the unreacted core of sorbent in the inner layer (see Figure 4.3). As the middle layer of sorbent only contains a single species, the sorption capacity can be predicted from the single component isotherm. The IAS theory is used to predict the solid phase concentration of sorbent at specified radius in the outer layer because multicomponent sorption is taking place in this layer.

Figure 5.110 shows the correlation of kinetic data using the IAST-film-pore diffusion model. The model can correlate the concentration effect for the sorption of cadmium ions from the Cd-Cu solution very well. However, Figure 5.111 shows that the model deviates from the experimental data points for the effect of sorbent mass. The concentration and the sorbent mass effect for the sorption of copper ions from the Cd-Cu solution are shown in Figures 5.112 and 5.113. The correlations of experimental data using the IAST-film-pore are poorer than the Figures 5.98 and 5.99, which use an empirical method in the film-pore diffusion model.

Figure 5.114 shows the sorption of cadmium ions from the Cd-Zn solution. The concentrations at 2.7, 3.1 and 4.1mM can be correlated by the film-pore diffusion model. In high and low concentrations (i.e. $C_o = 2.1$ and 4.8 mM), the concentration-decay curves show deviation to the experimental data points. The film-pore diffusion model can also correlate the sorbent mass effect in Figure 5.115. For the sorption of
zinc ions from the Cd-Zn solution, the concentration and the sorbent mass effects can
be correlated by the film-pore diffusion model. The experimental data points and the
concentration-decay curves of the sorption systems are shown in Figures 5.116 and
5.117.

The correlation of the Cu-Zn system is the worst case among these three binary
systems. Figures 5.118 and 5.119 show the sorption of copper ions onto bone char
from the Cu-Zn system. The correlation at high concentration is better than at low
concentration. Similarly, the concentration decay curves are close to the
experimental data at low sorbent mass. Figures 5.120 and 5.121 show the sorption of
zinc ions from the Cu-Zn solution. Both concentration and sorbent mass effects
cannot be correlated by the IAST-film-pore diffusion model. The pore diffusivities
for these three sorption systems are summarized in Table 5.33. Except the cadmium
ions from the Cd-Cu system, all diffusivities in binary systems are less than the pore
diffusivities in single component systems. But the pore diffusivities obtaining from
the IAST are larger than the empirical method.

As the pore diffusivity for cadmium ions in the Cd-Zn system is lower than zinc
ions, in the numerical calculation, the zinc ions are moving faster than the cadmium
ions inside the sorbent. This implies that only zinc ions exist in the middle layer of
sorbent. In the outer layer of sorbent, the copper and zinc ions co-exist in this region.
A similar result can be found in Cu-Zn system. However, in Cd-Cu system, the
shrinking core radius for cadmium ions is moving faster than the copper ions in the
numerical solution method. This is because the pore diffusivities for cadmium and
copper ions in Cd-Cu are very close. In addition, the sorbent surface is more
favorable to the adsorption of copper ions rather than the cadmium ions. Therefore, the unadsorbed cadmium ions can keep moving in the sorbent. A similar explanation was given by Mijangos and Diaz (1994), who used the ion exchange resins to remove the copper and cobalt ions from aqueous solution.

Arévalo et al. (1997) used ion exchange resin (i.e. resin-Na) to remove cobalt and copper ions from aqueous solution. A shrinking core model was used to correlate the kinetic data for the Co-Cu system. In the calculation of the solid phase concentration, the authors used a mass action law based equation to be incorporated into the pore diffusion model. As the copper ions displaced the cobalt ions in the outer layer of resin, the resin was pre-loaded with the cobalt ions and then the ion exchange experiments with copper ions to calculate the equilibrium constants for Co-Cu system. In comparison with the Arévalo model, the IAST-film-pore diffusion model only requires the single component isotherm parameters. Therefore, the IAST-film-pore diffusion model is easier to calculate the solid phase concentration in binary component layer and more fundamentally correct than the Arévalo model. The pore diffusivities obtained by Arévalo and coworkers (1997) is $1.15 \times 10^{10} \text{ m}^2/\text{s}$ for copper in a single component solution and $8.2 \times 10^{11} \text{ m}^2/\text{s}$ for copper in the Co-Cu solution. The pore diffusivity for copper ion in the binary component is lower than in single component system. Referring to Table 5.33, similar phenomena can be found in Cu-Zn and Cd-Zn system. However, the pore diffusivity for cadmium ion is slightly increased in Cd-Cu system. The increase in pore diffusivity may be due to the fact that the correlation of the binary component system data is poorer than for the single component system.
The pore diffusivity may not always be decreased in multicomponent systems. Evangelista and Berardino (1985) used the Nernst-Planck equation to develop a multicomponent diffusion model for ion exchange resin in fixed bed operation. The pore diffusivities for calcium and magnesium in single component system were equivalent to the values in the binary component systems. Robinson et al. (1994) used the macropore diffusion model to correlate the multicomponent kinetic data for the sorption of Cs, Sr, Ca and Mg on zeolite-Na. The selectivity for the cations is Cs > Sr > Ca > Mg > Na. The pore diffusivities in the binary component system were lower than those in a multicomponent system except for the magnesium ion. Therefore, the pore diffusivity in single component system may not be higher than the value in a multicomponent system.

Discussion of the film-pore diffusion model applied to multicomponent systems.

The previous section utilizes the film-pore diffusion model to correlate the experimental data for multicomponent systems. Two methods, which are the empirical method and the IAS Theory, are introduced to calculate the local equilibrium capacity at radius \( r \). Table 5.34 shows the Sum of the Squares of the Errors (SSEs) of the multicomponent systems. The SSEs based on using the empirical method are lower than for the IAST. This result is expected because the empirical method correlates the experimental data better than the IAST in the sorption equilibrium. As the concentration-decay curve is directly affected by the local equilibrium value at radius \( r \), the empirical equation must provide a good fitting to the kinetic experimental data.
Although the correlation of experimental data using the empirical method is better than the IAST in film-pore diffusion model, the theoretical background of the empirical method to estimate the solid phase concentration is not as fundamentally sound. In addition, the IAST method only required the parameters from single component data to predict the solid phase concentration for binary systems. Therefore, it is recommended to use the IAST in film-pore diffusion to correlate the experimental data providing the IAST equilibrium isotherm predictions give a reasonably good correlation to the experimental equilibrium data.
CONCLUSIONS

Bone char can be used to remove metal ions from aqueous effluent. The sorbent should be used in systems around pH 5 because the crystal structure will dissolve at low pH conditions (i.e. pH 3.0 and pH 4.0). The metal ions are removed both by adsorption as well as ion exchange with the calcium ions from the calcium hydroxyapatite lattice. The IR spectrum shows that the transmittance peaks of phosphate ions increase when higher concentrations of metal ions are sorbed on the surface. This represents the metal ions binding with the phosphate site and provides a shielding to the phosphate site from the metal ion. In addition, the higher the temperature of solution, the greater is the extent of calcium ions exchanged. Hence, based on this research, bone char can be beneficially used at reasonably high solution temperatures (i.e. T = 40 and 60°C).

The equilibrium experimental data can be correlated by the Langmuir, Langmuir-Freundlich and binary Langmuir equations. Based on the Sum of the Squares of the Errors (SSEs), the correlations of experimental data using the Langmuir and the Langmuir-Freundlich equations are better than the new model based on the bi-Langmuir equation even though the bi-Langmuir gives a good representation of the adsorption and ion exchange mechanism. Therefore, the Langmuir and the Langmuir-Freundlich equations were used in IAS theory and modeling to correlate the experimental data in multicomponent systems. The results show that the sorption of metal ions for multicomponent systems can be predicted from the IAS theory with the Langmuir equation or the Langmuir-Freundlich equation for metal ions.
Although the equal molar and unequal molar equilibrium data can generally be predicted by the IAS theory. The results for the mole ratios of 3:7 and 7:3 for the Cd-Cu systems cannot be predicted very well. A possible reason may be interaction between the metal ions affecting the accuracy of calculation without incorporating activity coefficients into the model.

Bone char is a porous material, which does not contain a micropore region in its pore structure. As a hydrated metal ion is relatively small relative to the average pore diameter, it can freely diffuse along the pore to the center of sorbent. Hence, pore diffusion has been considered as a main rate-controlling mechanism and its selection is justified by the results. Before determining the pore diffusivities of the sorption systems, the film mass transfer coefficients were determined using four different methods. Finally, the correlation of Harriott was chosen to determine the film mass transfer coefficients due to the fact that the values obtained from the Mathews & Weber and Furusawa & Smith were too small to use in the film-pore diffusion model. In addition, the plots of square root of time can be extrapolated to the origin of the graph, implying that the external mass transfer across the boundary layer is very rapid; it cannot be accurately determined from the experimental data and only affects the adsorption rate in the very early stages of adsorption.

In this research, new solutions to film-pore and film-pore-surface diffusion models were developed and compared to a previously developed analytical film-pore diffusion model (Spahn and Schlunder, 1975). These two models were used to correlate the experimental kinetic data to determine the pore diffusivities. The SSEs showed that film-pore-surface diffusion is the best-fit model. However, the surface
effect is small and can be neglected because the equilibrium isotherm is almost rectangular—consequently sorption equilibrium is unlikely to be completely reversible. For such isotherms, the contribution by the surface diffusion component is very small (typically < 4%). In addition, pore diffusion is the main mass transfer mechanism, which was proved by the effect of temperature on the sorption process. Therefore, it is proposed that the film-pore model is the most appropriate model for metal ion sorption onto bone char.

The new solution method for the single component film-pore diffusion model was extended to enable the pore diffusivities to be determined for multicomponent systems. The pore diffusivities for multicomponent systems were calculated by incorporating a Langmuir-type equation into the film-pore diffusion model. However, the solid phase concentration for cadmium and zinc ions cannot be determined accurately by the Langmuir-type equation. Therefore, an empirical equation was used instead of the Langmuir-type equation in the film-pore diffusion model. The sorption of copper ions in binary and ternary systems can be correlated very well using the empirical equation. However, the sorption of cadmium and zinc ions does not correlate as well in the binary and ternary systems especially for the effect of sorbent mass. Although the SSEs for the empirical method are lower than the IAST, it is recommended to use the IAST-film-pore diffusion model in the multicomponent system since it does not require binary equilibrium data. In a multicomponent metal ion sorption model by Arévalo (1997), the diffusion model required the equilibrium constant to calculate the solid phase capacities for two moving concentration fronts inside the resin. The Arévalo model was restricted by the need to pre-load one metal ion and then exchange the other metal ion to determine the equilibrium constant for
the binary system. Therefore, extra experimental work is required for this model, which has been overcome in this research using a model based on the IAST and the new solution to the film-pore diffusion model.
RECOMMENDATIONS

The following areas are recommended for further study.

(1) Although the sorption of metal ions on CaHAP is important for the dentist, environmental engineer, biologist, mineralogist, and chemist, the sorption mechanism of metal ions onto CaHAP is not clearly known. Characterizing the Ca(I) and Ca(II) sites in CaHAP lattice may assist in identifying the sorption mechanism of metal ion. This has been done in the case of cadmium using the X-ray line broadening technique for cadmium at varies temperatures (Federoff et al., 1999). This method coupled with other complementary techniques, such as Raman and XPS, could be applied to other metals such as copper and zinc in an attempt characterize these specific sites. From the temperature effect, the energy required for ion exchange with Ca(I) and Ca(II) sites could be determined and would be an important and informative step in characterizing the role of each type of site.

(2) The Ideal Adsorbed Solution Theory has been used to predict the sorption equilibrium for multicomponent systems for the ideal case. It is recommended to introduce an activity coefficient into the IAST for sorption equilibrium and mass transfer model to reduce the deviation for non-ideal systems. The values of the activity coefficients can be obtained
by the method of Pfitzer for metal ions in solution and the method of Wilson for ions in the solid phase (Lee and Moon, 2001).

The chemical regeneration method has been used to regenerate the bone char which is used to remove the color from sugar syrup solutions in sugar production. In case of metal ion sorption, the regeneration of bone char can enable this sorbent to be reused for further metal removal in wastewater treatment systems. It is proposed to test some weak acids (i.e. pHs = 3 or 4) for this purpose to ion exchange metal and dissolve a small amount of the calcium hydroxyapatite which contains the toxic metal ion on the bone char surface. After the acid washed process, bone char particle can be filtered out from the solution. Calcium hydroxide, calcium phosphate and phosphoric acid can then be used to contact the bone char. These two reagents will form precipitate onto the bone char to replenish the lost CaHAP during the acid washing process. The acid leachate will contain metal ions at a high enough concentration for electrolytic recovery and reuse. The treated wastewater can be recirculated for reuse or discharged to receiving waters, now that it has been treated to the legislative effluent discharge limits. An alternative approach to regenerating the bone char would be to strip the metal out using a chelating agent. The problem in this case would be to identify a method to recover the metal from the metal-chelate complex.
Appendix I

Single Resistance Model (Linear Adsorption Isotherm)

The solution of the film diffusion model (Furusawa and Smith, 1973) is derived from equation [4.2.1.1].

\[
\frac{dC_t}{dt} = -k_f S_A (C_t - C_s) \quad [4.2.1.1]
\]

Since \( C_s \to 0 \) as \( C \to C_o \) and \( t \to 0 \) then equation [4.2.1.1] becomes:

\[
\left. \frac{d}{dt} \left( \frac{C_t}{C_o} \right) \right|_{t=0} = -k_f S_A \quad [I-1]
\]

The incremental mass balance on the solid becomes,

\[
m_s \frac{dq_t}{dt} = k_f S_A (C_t - C_s) \quad [I-2]
\]

Differentiating equation [4.2.1.9] for a constant \( K_L \) value,

\[
\frac{dq_t}{dt} = K_L \frac{dC_t}{dt} \text{ at } q_t = 0 \text{ when } t = 0 \quad [I-3]
\]

Combining equation [I-2] and [I-3].

\[
m_s K_L \frac{dC_t}{dt} = k_f S_A (C_t - C_s) \quad [I-4]
\]

Rearranging

\[
\frac{dC_t}{dt} = \frac{k_f S_A}{m_s K_L} (C_t - C_s) \quad [I-5]
\]

Expanding [I-6]

\[
\frac{dC_t}{dt} = -k_f S_A C_t + k_f S_A C_s \quad [I-6]
\]

Differentiating equation [I-6] and substituting equation [I-5]
\[ \frac{d^2 C_i}{dt^2} = -k_f S_A \frac{dC_i}{dt} + k_f S_A \frac{dC_L}{dt} \]  \hspace{1cm} [I-7]

\[ \frac{d^2 C_i}{dt^2} = -k_f S_A \frac{dC_i}{dt} + \frac{k_f S_A^2}{K_L m_s} \left(C_i - C_s\right) \]  \hspace{1cm} [I-8]

Since equation [I-6] becomes,

\[ C_s = C_i + \frac{1}{k_f S_A} \frac{dC_i}{dt} \]  \hspace{1cm} [I-9]

Then substituting,

\[ \frac{d^2 C_i}{dt^2} = -k_f S_A \frac{dC_i}{dt} + \frac{k_f S_A^2}{K_L m_s} \left[C_i - \left(C_i + \frac{1}{k_f S_A} \frac{dC_i}{dt}\right)\right] \]  \hspace{1cm} [I-10]

\[ \frac{d^2 C_i}{dt^2} = -k_f S_A \frac{dC_i}{dt} - \frac{k_f S_A}{K_L m_s} \frac{dC_L}{dt} \]  \hspace{1cm} [I-11]

\[ \frac{d^2 C_i}{dt^2} = -k_f S_A \left(\frac{1 + m_s K_L}{m_s K_L}\right) \frac{dC_i}{dt} \]  \hspace{1cm} [I-12]

\[ \frac{d^2 C_i}{dt^2} + k_f S_A \left(\frac{1 + m_s K_L}{m_s K_L}\right) \frac{dC_i}{dt} = 0 \]  \hspace{1cm} [I-13]

\[ D^2 + k_f S_A \left(\frac{1 + m_s K_L}{m_s K_L}\right) D = 0 \]  \hspace{1cm} [I-14]

\[ D \left[D + k_f S_A \left(\frac{1 + m_s K_L}{m_s K_L}\right)\right] = 0 \]  \hspace{1cm} [I-15]

\[ D = 0 \text{ and } D + k_f S_A \left(\frac{1 + m_s K_L}{m_s K_L}\right) = 0 \]  \hspace{1cm} [I-16]

Representing, in mathematical form, and solving for \( A \) and \( B \),

\[ C_i = A + Be^{\beta t} \]  \hspace{1cm} [I-17]

When \( C_i = C_o \), then \( t = 0 \),

\[ C_o = A + B \]  \hspace{1cm} [I-18]

To determine \( B \),
\[
\frac{dC_t}{dt} = DBe^{Dt}
\]  
[I-19]

\[
\left[\frac{d}{dt} \left(\frac{C_t}{C_o}\right)\right] = \frac{DBe^{Dt}}{C_o}
\]  
[I-20]

At \( t = 0 \),

\[
\left[\frac{d}{dt} \left(\frac{C_t}{C_o}\right)\right] = -k_f S_A
\]  
[I-21]

\[-k_f S_A = \frac{D}{C_o} Be^{Dt} = DB \]
[I-22]

\[
C_o \left[\frac{-k_f S_A}{D}\right] = B
\]  
[I-23]

\[
C_o \left[\frac{m_i K_L}{1 + m_i K_L}\right] = B
\]  
[I-24]

To determine \( A \),

\[
A = C_o - B
\]  
[I-25]

\[
A = C_o - C_o \left(\frac{m_i K_L}{1 + m_i K_L}\right)
\]  
[I-26]

\[
A = C_o \left(\frac{1 + m_i K_L - m_i K_L}{1 + m_i K_L}\right) = \frac{C_o}{1 + m_i K_L}
\]  

Combining and rearranging the equations.

\[
\frac{C_t}{C_o} = \frac{1}{1 + m_i K_L} + \frac{m_i K_L}{1 + m_i K_L} \exp \left[ -\left(\frac{1 + m_i K_L}{m_i K_L}\right) k_f S_A t \right]
\]  
[I-27]
Appendix II

Single Resistance Model (Nonlinear Adsorption Isotherm)

The manipulation of the film diffusion model for nonlinear adsorption isotherms (McKay and Allen, 1983) is similar to the method for the linear adsorption isotherm. The film diffusion is derived from equation [4.2.1.1].

\[
\frac{dC_t}{dt} = -k_f S_A (C_t - C_s)
\]  \hspace{1cm} [4.2.1.1]

From equation [I-2],

\[
m_s \frac{dq_t}{dt} = k_f S_A (C_t - C_s)
\]  \hspace{1cm} [II-1]

The solid phase equation can be expressed:

\[
\frac{\partial q_s}{\partial t} = \frac{\partial q_t}{\partial C_s} \left( \frac{\partial C_s}{\partial t} \right)
\]  \hspace{1cm} [II-2]

The solution of equation [II-1] and [II-2], with [I-8] and [I-9], gives predicted \( C \) versus \( t \) curves for the single-resistance case. For the single resistance model the intraparticle diffusion is neglected. For this single resistance model, \( C_r = C_s \) for any \( r \) and \( q \) is uniform throughout the particle.

For the case of a Langmuir isotherm expression the solution is as follows:

Substituting [II-2] into [II-1]

\[
m_s \frac{dq_t}{dC_s} \left( \frac{dC_s}{dt} \right) = k_f S_A (C_t - C_s)
\]  \hspace{1cm} [II-3]

At \( q_t = 0 \) when \( t = 0 \)

Differentiating the Langmuir expression from [4.1.1.7] with respect to \( C_s \),

\[
\frac{dq_t}{dC_s} = \frac{(1 + a_t C_t)K_e - K_e a_t C_s}{(1 + a_t C_s)^2}
\]  \hspace{1cm} [II-4]
\[
\frac{dq_i}{dC_i} = \frac{K_L}{(1 + a_iC_i)^2} \quad [II-5]
\]

Substituting [II-5] into [II-3]

\[
\frac{m_i K_L}{(1 + a_i C_i)^2} \frac{dC_i}{dt} = k_f S_A (C_i - C_s) \quad [II-6]
\]

Rearranging,

\[
\frac{dC_i}{dt} = \left( \frac{k_f S_A}{m_i K_L} \right) (1 + a_i C_i)^2 (C_i - C_s) \quad [II-7]
\]

Let \( A = k_f S_A / m_i K_L \)

\[
\frac{dC_i}{dt} = A (1 + a_i C_i)^2 (C_i - C_s) \quad [II-8]
\]

Differentiating [4.2.1.1] with respect to time

\[
\frac{d^2 C_i}{dt^2} = -k_f S_A \frac{dC_i}{dt} + k_f S_A \frac{dC_i}{dt} \quad [II-9]
\]

Rearranging,

\[
\frac{d^2 C_i}{dt^2} + k_f S_A \frac{dC_i}{dt} = k_f S_A \frac{dC_i}{dt} \quad [II-10]
\]

Let \( B = k_f S_A \), Combining [II-8] and [II-10]

\[
\frac{d^2 C_i}{dt^2} + B \frac{dC_i}{dt} = A \cdot B (1 + a_i C_i)^2 (C_i - C_s) \quad [II-11]
\]

Substituting [4.2.1.1] into [II-11]

\[
\frac{d^2 C_i}{dt^2} + B \frac{dC_i}{dt} = -A (1 + a_i C_i)^2 \frac{dC_i}{dt} \quad [II-12]
\]

\[
\frac{d^2 C_i}{dt^2} + B \frac{dC_i}{dt} = -A \left( 1 + a_i \left( C_i + \frac{1}{B} \frac{dC_i}{dt} \right) \right)^2 \quad [II-13]
\]

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\[
\frac{d^2 C_i}{dt^2} = \left[ -B - A \left[ 1 + a_L \left( C_i + \frac{1}{B} \frac{dC_i}{dt} \right) \right]^2 \right] \frac{dC_i}{dt} \tag{II-14}
\]

\[
\frac{d^2 C_i}{dt^2} = -\left[ B + A \left( 1 + a_L C_i \right) + \frac{a_L}{B} \left( \frac{dC_i}{dt} \right)^2 \right] \frac{dC_i}{dt} \tag{II-15}
\]

Substituting for \( A \) and \( B \)

\[
\frac{d^2 C_i}{dt^2} + \left( k_f S_A + \left( \frac{k_f S_A}{m_i K_L} \right) \left( 1 + a_L C_i \right) + \frac{a_L}{k_f S_A} \left( \frac{dC_i}{dt} \right)^2 \right) \frac{dC_i}{dt} = 0 \tag{II-16}
\]

Equation [II-16] is an ordinary differential equation, which can be solved numerically.
Appendix III

Film-Pore Diffusion Model (Analytical Method)

The analytical solution (Spahn and Schlünder, 1975) of the film-pore diffusion model is obtained from equation [4.2.2.5].

\[
\frac{d\eta}{d\tau} = \frac{3(1 - C_h\eta)(1 - \eta)^{\frac{1}{3}}}{1 - (1 - 1/B)(1 - \eta)^{\frac{1}{3}}} \quad [4.2.2.5]
\]

By defining

\[
x = (1 - \eta)^{\frac{1}{3}} \quad [\text{III-1}]
\]

\[
x^3 = (1 - \eta) \quad [\text{III-2}]
\]

\[
\eta = 1 - x^3 \quad [\text{III-3}]
\]

\[
B = 1 - \frac{1}{B_i} \quad [\text{III-4}]
\]

Then equation [4.2.2.5] becomes,

\[
-3x^2 \frac{dx}{d\tau} = \frac{3\left[1 - C_h\left(1 - x^3\right)\right]}{1 - Bx} \quad [\text{III-5}]
\]

Rearranging,

\[
d\tau = -\frac{x(1 - Bx)}{\left[1 - C_h\left(1 - x^3\right)\right]}dx
\]

\[
d\tau = \frac{x(1 - Bx)}{C_h\left[\left(1 - C_h\right)/C_h + x^3\right]}dx
\]

Defining \(a^3 = (1 - C_h)/C_h\) then

\[
d\tau = \frac{1}{C_h} \frac{Bx^2 - x}{x^3 + a^3} dx \quad [\text{III-6}]
\]

To obtain the integral \(I_i\) of the equation [III-6].
\[ I_1 = \int d\tau = \frac{1}{C_h} \int \frac{Bx^2 - x}{x^3 + a^3} dx = \frac{B}{C_h} \int \frac{x^2 dx}{(x^3 + a^3)} - \frac{1}{C_h} \int \frac{xdx}{x^3 + a^3} \]

\[ I_1 = \frac{B}{3C_h} \ln|x^3 + a^3| - \frac{1}{C_h} \int \frac{xdx}{x^3 + a^3} \quad \text{[III-7]} \]

Defining the integral \( I_2 \) as:

\[ I_2 = -\frac{1}{C_h} \int \frac{xdx}{x^3 + a^3} \quad \text{[III-8]} \]

Then,

\[ I_1 = \frac{B}{C_h} \ln|x^3 + a^3| - I_2 \quad \text{[III-9]} \]

To evaluate the integral \( I_1 \) it is first necessary to express the term \((x^3 + a^3)\) in partial fractions.

\[ \frac{1}{x^3 + a^3} = \frac{1}{(x + a)(x^2 - ax + a^2)} \quad \text{[III-10]} \]

\[ \frac{1}{(x + a)(x^2 - ax + a^2)} = \frac{A}{x + a} + \frac{Fx + G}{x^2 - ax + a^2} \quad \text{[III-11]} \]

\[ 1 = A(x^2 - ax + a^2) + (Fx + G)(x + a) \]

Hence,

\[ A + F = 0 \]

\[ -Aa + aF + G = 0 \]

\[ a^2A + aG = 1 \]

and

\[ A = \frac{1}{3a^2}, \quad F = -\frac{1}{3a^2}, \quad G = \frac{2}{3a} \]

Substitution of these relationships into equation [III-11],

\[ \frac{1}{x^3 + a^3} = \frac{1}{3a^2(x + a)} + \frac{2a - x}{3a^2(x^2 - ax + a^2)} \]
Thus equation [III-8] becomes,

$$
I_2 = -\frac{1}{C_h} \int \frac{x \, dx}{3a^2(x + a)} - \frac{1}{C_h} \int \frac{(2a - x) \, dx}{3a^2(x^2 - ax + a^2)}
$$

$$
= -\frac{1}{3a^2C_h} \int \frac{x \, dx}{x + a} + \frac{1}{3a^2C_h} \int \frac{(x^2 - 2ax) \, dx}{(x^2 - ax + a^2)}
$$

$$
= -\frac{1}{3a^2C_h} \left[ \ln |x + a| - \int \frac{dx}{x + a} \right] + \frac{1}{3a^2C_h} \left[ \frac{x^2 - ax + a^2}{x^2 - ax + a^2} \right]
$$

$$
= -\frac{1}{3a^2C_h} \ln |x + a| - \frac{1}{3aC_h} \int \frac{(x^2 - 2ax)}{(x^2 - ax + a^2)} \, dx
$$

Defining $I_3$ as:

$$
I_3 = -\frac{1}{3aC_h} \int \frac{(x + a)}{(x^2 - ax + a^2)} \, dx
$$

Then equation [III-9]

$$
I_1 = \frac{B}{3C_h} \ln |x^3 + a^3| + \frac{1}{3aC_h} \ln |x + a| + I_3
$$

Expressing equation [III-14] as:

$$
I_3 = -\frac{1}{6aC_h} \left[ \int \frac{(2x - a)}{(x^2 - ax + a^2)} \, dx + \int \frac{3a}{(x^2 - ax + a^2)} \, dx \right]
$$

$$
= -\frac{1}{6aC_h} \ln |x^2 - ax + a^2| - \frac{1}{2C_h} \left[ \frac{dx}{(x - a/2)^2 + (\sqrt{3}a/2)^2} \right]
$$

$$
= -\frac{1}{6aC_h} \ln |x^2 - ax + a^2| - \frac{1}{2C_h} \frac{1}{\sqrt{3}a/2} \tan^{-1} \left[ \frac{x - a/2}{\sqrt{3}a/2} \right]
$$

$$
I_3 = -\frac{1}{6aC_h} \ln |x^2 - ax + a^2| - \frac{1}{\sqrt{3}aC_h} \tan^{-1} \left[ \frac{2x - a}{\sqrt{3}a} \right]
$$

[III-16]

\[ I_1 = \frac{B}{3C_h} \ln |x^3 + a^3| + \frac{1}{3aC_h} \ln |x + a| - \frac{1}{6aC_h} \ln |x^2 - ax + a^2| - \frac{1}{\sqrt{3aC_h}} \tan^{-1} \left( \frac{2x - a}{\sqrt{3a}} \right) \]

\[ I_1 = \frac{1}{6C_h} \left[ \ln |x^3 + a^3|^{\frac{2B}{a}} + \ln |x + a|^{\frac{3}{a}} - \ln |x^2 - ax + a^2|^{\frac{1}{a}} \right] - \frac{1}{\sqrt{3aC_h}} \tan^{-1} \left( \frac{2x - a}{\sqrt{3a}} \right) \]

\[ I_1 = \frac{1}{6C_h} \left[ \ln |x^3 + a^3|^{\frac{2B-1}{a}} + \ln |x + a|^{\frac{3}{a}} \right] - \frac{1}{\sqrt{3aC_h}} \tan^{-1} \left( \frac{2x - a}{\sqrt{3a}} \right) \]

[III-17]

The limits over which the integral in equation [III-17] is to be are:

When, \( \tau = 0, \eta = 0 \) and \( x = 1 \)

\( \tau = \tau, \eta = \eta \) and \( x = x \)

Thus equation [III-17] becomes,

\[ \left[ \tau \right]_0^\tau = \left[ \frac{1}{6C_h} \left[ \ln |x^3 + a^3|^{\frac{2B-1}{a}} + \ln |x + a|^{\frac{3}{a}} \right] - \frac{1}{\sqrt{3aC_h}} \tan^{-1} \left( \frac{2x - a}{\sqrt{3a}} \right) \right]_1 \]

[III-18]

Hence,

\[ \tau = \left( \frac{1}{6C_h} \left[ \ln |x^3 + a^3|^{\frac{2B-1}{a}} + \ln |x + a|^{\frac{3}{a}} \right] - \frac{1}{\sqrt{3aC_h}} \tan^{-1} \left( \frac{2x - a}{\sqrt{3a}} \right) \right) - \left( \frac{1}{6C_h} \left[ \ln |x^3 + a^3|^{\frac{2B-1}{a}} + \ln |x + a|^{\frac{3}{a}} \right] - \frac{1}{\sqrt{3aC_h}} \tan^{-1} \left( \frac{2x - a}{\sqrt{3a}} \right) \right) \]

\[ \tau = \frac{1}{6C_h} \left[ \ln \left| \frac{x^3 + a^3}{1 + a^3} \right| + \ln \left| \frac{x + a}{1 + a} \right|^{\frac{3}{a}} \right] + \frac{1}{\sqrt{3aC_h}} \left[ \tan^{-1} \left( \frac{2x - a}{\sqrt{3a}} \right) - \tan^{-1} \left( \frac{2x - a}{\sqrt{3a}} \right) \right] \]

[III-19]
# Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_L$</td>
<td>dm$^3$/mg</td>
<td>Langmuir isotherm constant</td>
</tr>
<tr>
<td>$a_{L,i}$</td>
<td>dm$^3$/mg</td>
<td>Binary Langmuir isotherm constant</td>
</tr>
<tr>
<td>$a_{LF}$</td>
<td>dm$^3$/mg</td>
<td>Langmuir-Freundlich isotherm constant</td>
</tr>
<tr>
<td>$Bi$</td>
<td>--</td>
<td>Biot Number, $Bi = \frac{k_f R}{D_{ef}}$</td>
</tr>
<tr>
<td>$C_o$</td>
<td>mg/dm$^3$</td>
<td>Initial liquid-phase concentration</td>
</tr>
<tr>
<td>$C_e$</td>
<td>mg/dm$^3$</td>
<td>Equilibrium liquid-phase concentration</td>
</tr>
<tr>
<td>$C_{e,t}$</td>
<td>mg/dm$^3$</td>
<td>Tie line liquid-phase concentration at particle surface at time $t$</td>
</tr>
<tr>
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<td>Liquid-phase concentration at external sorbent surface.</td>
</tr>
<tr>
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<td>mg/dm$^3$</td>
<td>Liquid-phase concentration at time $t$</td>
</tr>
<tr>
<td>$(C_t)_{exp}$</td>
<td>mg/dm$^3$</td>
<td>Experimental values of liquid-phase concentration at time $t$</td>
</tr>
<tr>
<td>$(C_t)_{cal}$</td>
<td>mg/dm$^3$</td>
<td>Calculated values of liquid phase concentration at time $t$</td>
</tr>
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<td>cm</td>
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</tr>
<tr>
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<td>nm</td>
<td>Diameter of pore</td>
</tr>
<tr>
<td>$D_{ef}$</td>
<td>cm$^2$/s</td>
<td>Effective diffusivity</td>
</tr>
<tr>
<td>$D_m$</td>
<td>cm$^2$/s</td>
<td>Molecular diffusion coefficient of metal ions</td>
</tr>
<tr>
<td>$D_{mo}$</td>
<td>cm$^2$/s</td>
<td>Molecular diffusion coefficient of metal ions at temperature $T_o$</td>
</tr>
<tr>
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<td>Pore diffusion coefficient</td>
</tr>
<tr>
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</tr>
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<td>$D_{so}$</td>
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<td>Corrected surface diffusivity</td>
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<tr>
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<td>--</td>
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<tr>
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<td>g cm$^2$/s</td>
<td>Planck constant</td>
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<td>Length of porous medium (i.e. radius of sorbent)</td>
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<tr>
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<td>Effective length of capillary</td>
</tr>
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<td>$m$</td>
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<td>Number of experimental points</td>
</tr>
<tr>
<td>Symbol</td>
<td>Unit</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td>-------------</td>
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<tr>
<td>$m_s$</td>
<td>g/dm³</td>
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</tr>
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<tr>
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<td>mg/g</td>
<td>Tie line solid-phase concentration at time $t$</td>
</tr>
<tr>
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<td>Hypothetical equilibrium concentration on sorbent surface.</td>
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<td>mg/g</td>
<td>Monolayer capacity of Langmuir equation</td>
</tr>
<tr>
<td>$q_{m,i}$</td>
<td>mg/g</td>
<td>Monolayer capacity of bi-Langmuir equation</td>
</tr>
<tr>
<td>$q_{m,LF}$</td>
<td>mg/g</td>
<td>Monolayer capacity of Langmuir-Freundlich equation</td>
</tr>
<tr>
<td>$q_t$</td>
<td>mg/g</td>
<td>Mean equilibrium solid-phase concentration at time $t$</td>
</tr>
<tr>
<td>$q_T$</td>
<td>mg/g</td>
<td>Total adsorbed phase concentration</td>
</tr>
<tr>
<td>$r$</td>
<td>cm</td>
<td>Radius of concentration front of metal ions penetrating adsorbent</td>
</tr>
<tr>
<td>$R$</td>
<td>cm</td>
<td>Radius of adsorbent particle</td>
</tr>
<tr>
<td>$Re$</td>
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<td>Reynold number, $Re = \left( \frac{\bar{c} \bar{d}_p}{\nu^3} \right)^{1/3}$</td>
</tr>
<tr>
<td>$s$</td>
<td></td>
<td>Mole fraction of sorbate in adsorbed phase</td>
</tr>
<tr>
<td>$S_A$</td>
<td>m²/g</td>
<td>Surface area of sorbent</td>
</tr>
<tr>
<td>$Sc$</td>
<td></td>
<td>Schmidt number, $Sc = \frac{\nu}{D_m}$</td>
</tr>
<tr>
<td>$Sh$</td>
<td></td>
<td>Sherwood number, $Sh = \frac{k_f \bar{d}_p}{D_m}$</td>
</tr>
<tr>
<td>$t$</td>
<td>hrs</td>
<td>Contact time</td>
</tr>
<tr>
<td>$T$</td>
<td>K</td>
<td>Temperature</td>
</tr>
<tr>
<td>$T_b$</td>
<td>K</td>
<td>Boiling point of solvent</td>
</tr>
<tr>
<td>$T_o$</td>
<td>K</td>
<td>Reference temperature</td>
</tr>
<tr>
<td>$V$</td>
<td>dm³</td>
<td>Liquid-phase volume</td>
</tr>
<tr>
<td>$W$</td>
<td>g</td>
<td>Weight of sorbent</td>
</tr>
<tr>
<td>$Z$</td>
<td></td>
<td>The charge on the ion</td>
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### Nomenclature

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<thead>
<tr>
<th>Symbol</th>
<th>--</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$\varepsilon_p$</td>
<td>Porosity</td>
<td>The ratio of pore volume to total volume of sorbent</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Relationship between film and intraparticle diffusion, $\psi = 1 + D_{ap} r / (k_f R (R - r))$</td>
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<tr>
<td>$\lambda$</td>
<td>m$^2$Smol$^{-1}$</td>
<td>Ionic conductivity of ion.</td>
</tr>
<tr>
<td>$\mu$</td>
<td>cp</td>
<td>Viscosity of solvent</td>
</tr>
<tr>
<td>$\mu_o$</td>
<td>Viscosity of solvent at reference temperature $T_o$</td>
<td></td>
</tr>
<tr>
<td>$\rho_p$</td>
<td>g/cm$^3$</td>
<td>Particle density</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>Kcal/mole</td>
<td>Change of Gibbs energy</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>Kcal/mole</td>
<td>Change of enthalpy</td>
</tr>
<tr>
<td>$\Delta x$</td>
<td>cm</td>
<td>Film thickness</td>
</tr>
<tr>
<td>$\Delta S$</td>
<td>Kcal/mole/K</td>
<td>Change of entropy</td>
</tr>
<tr>
<td>$\tilde{N}$</td>
<td>g$^{-1}$mole$^{-1}$</td>
<td>Avogadro's number</td>
</tr>
<tr>
<td>$\tilde{V}$</td>
<td>cm/g/mole</td>
<td>Molar volume of solvent</td>
</tr>
<tr>
<td>$\tau$</td>
<td>--</td>
<td>Dimensionless time</td>
</tr>
<tr>
<td>$\tau_f$</td>
<td>Tortuosity factor, $\tau_f = \left( \frac{L_t}{L} \right)^2$</td>
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### Superscript

<table>
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<th>Superscript</th>
<th>--</th>
<th>Description</th>
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</thead>
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<tr>
<td>$o$</td>
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<td></td>
</tr>
<tr>
<td>$L$</td>
<td>Number of iteration.</td>
<td></td>
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</table>
References


References


Hellferich, F.G., Ion exchange kinetics-evolution of a theory, NATO advanced study institute on mass transfer and kinetics of ion exchange, mass transfer and kinetics of ion exchange (1982: Maratea, Italy).


JCPDS, International centre for diffraction data, PCPDFWIN v2.01, No.09-0432, CaHAP, 1998.
JCPDS, International centre for diffraction data, PCPDFWIN v2.01, No.72-1243, CaHAP, 1998.

JCPDS, International centre for diffraction data, PCPDFWIN v2.01, No.42-1342, CdCO₃, 1998.


References


Namasivayam, C. and Ranganathan, K., Waste Fe(III)/Cr(III) hydroxide as adsorbent for the removal of Cr(VI) from aqueous solution and chromium plating industry wastewater, Environmental Pollution, 82, 255-261, 1993.


Water Pollution Control Ordinance (WPCO), Technical Memorandum, Chapter 358, Section 21, 1993.


Tables and Figures

Table 5.1  Frequencies (cm\(^{-1}\)) and assignments for CaHAP.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(\nu_1)</th>
<th>(\nu_2)</th>
<th>(\nu_3)</th>
<th>(\nu_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-O</td>
<td>O-P-O</td>
<td>P-O</td>
<td>O-P-O</td>
<td></td>
</tr>
<tr>
<td>symmetric stretch</td>
<td>bend</td>
<td>antisymmetric</td>
<td>bend</td>
<td></td>
</tr>
<tr>
<td>[PO(<em>4^{3-})] ions in Ca(</em>{10}(PO_4)_{8}(OH)_2)</td>
<td>962</td>
<td>462, 474</td>
<td>1046, 1087</td>
<td>571, 601</td>
</tr>
</tbody>
</table>

Table 5.2  The parameters of the Langmuir equation for the sorption of cadmium ions onto bone char at different temperatures.

<table>
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<tr>
<th></th>
<th>T = 10(^{\circ})C</th>
<th>T = 20(^{\circ})C</th>
<th>T = 40(^{\circ})C</th>
<th>T = 60(^{\circ})C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_L =)</td>
<td>157.807</td>
<td>157.812</td>
<td>157.821</td>
<td>157.828</td>
</tr>
<tr>
<td>(K_L =)</td>
<td>59.699</td>
<td>75.354</td>
<td>116.154</td>
<td>135.884</td>
</tr>
<tr>
<td>(q_m =)</td>
<td>0.378</td>
<td>0.477</td>
<td>0.736</td>
<td>0.861</td>
</tr>
<tr>
<td>(\Delta G =)</td>
<td>-7.063</td>
<td>-7.333</td>
<td>-7.874</td>
<td>-8.418</td>
</tr>
<tr>
<td>(\Delta H =)</td>
<td>0.506</td>
<td>0.506</td>
<td>0.506</td>
<td>0.506</td>
</tr>
<tr>
<td>(\Delta S =)</td>
<td>0.028</td>
<td>0.028</td>
<td>0.028</td>
<td>0.028</td>
</tr>
</tbody>
</table>

Table 5.3  The parameters of the Langmuir equation for the sorption of copper ions onto bone char at different temperatures.

<table>
<thead>
<tr>
<th></th>
<th>T = 10(^{\circ})C</th>
<th>T = 20(^{\circ})C</th>
<th>T = 40(^{\circ})C</th>
<th>T = 60(^{\circ})C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_L =)</td>
<td>69.195</td>
<td>69.199</td>
<td>69.205</td>
<td>69.210</td>
</tr>
<tr>
<td>(K_L =)</td>
<td>40.324</td>
<td>49.054</td>
<td>66.088</td>
<td>87.814</td>
</tr>
<tr>
<td>(q_m =)</td>
<td>0.583</td>
<td>0.709</td>
<td>0.955</td>
<td>1.269</td>
</tr>
<tr>
<td>(\Delta G =)</td>
<td>-7.063</td>
<td>-7.333</td>
<td>-7.874</td>
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</tr>
<tr>
<td>(\Delta H =)</td>
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<td>0.768</td>
<td>0.768</td>
<td>0.768</td>
</tr>
<tr>
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<td>0.028</td>
<td>0.028</td>
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Table 5.4  The parameters of the Langmuir equation for the sorption of zinc ions onto bone char at different temperatures.

<table>
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<th>$T = 10^\circ C$</th>
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<th>$T = 60^\circ C$</th>
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</thead>
<tbody>
<tr>
<td>$a_L$</td>
<td>62.176</td>
<td>62.176</td>
<td>62.176</td>
<td>62.176</td>
</tr>
<tr>
<td>$K_L$</td>
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<td>$q_m$</td>
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<td>0.505</td>
<td>0.764</td>
<td>0.897</td>
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<tr>
<td>$\Delta G$</td>
<td>-7.063</td>
<td>-7.333</td>
<td>-7.874</td>
<td>-8.418</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>$\Delta S$</td>
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<td>0.028</td>
<td>0.028</td>
<td>0.028</td>
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</table>

Table 5.5  The parameters of the Langmuir-Freundlich equation for the sorption of cadmium ions onto bone char at different temperatures.

<table>
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<tr>
<th></th>
<th>$T = 10^\circ C$</th>
<th>$T = 20^\circ C$</th>
<th>$T = 40^\circ C$</th>
<th>$T = 60^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{LF}$</td>
<td>88.874</td>
<td>88.877</td>
<td>88.883</td>
<td>88.888</td>
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<tr>
<td>$q_{m,LF}$</td>
<td>0.378</td>
<td>0.477</td>
<td>0.736</td>
<td>0.861</td>
</tr>
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<td>$1/n$</td>
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<td>1.295</td>
<td>1.295</td>
<td>1.295</td>
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<td>-2.614</td>
<td>-2.792</td>
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Table 5.6  The parameters of the Langmuir-Freundlich equation for the sorption of copper ions onto bone char at different temperatures.

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<th>$T = 20^\circ C$</th>
<th>$T = 40^\circ C$</th>
<th>$T = 60^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{LF}$</td>
<td>51.336</td>
<td>69.977</td>
<td>122.530</td>
<td>200.595</td>
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<td>$q_{m,LF}$</td>
<td>0.583</td>
<td>0.709</td>
<td>0.955</td>
<td>1.269</td>
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<tr>
<td>$1/n$</td>
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<td>0.843</td>
<td>0.843</td>
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<tr>
<td>$\Delta H$</td>
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<td>5.109</td>
<td>5.109</td>
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<tr>
<td>$\Delta S$</td>
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<td>0.026</td>
<td>0.026</td>
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Table 5.7  The parameters of the Langmuir-Freundlich equation for the sorption of zinc ions onto bone char at different temperatures.

<table>
<thead>
<tr>
<th>T</th>
<th>$a_{LF}$</th>
<th>$q_{m,LF}$</th>
<th>$1/n$</th>
<th>$\Delta G$</th>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10°C</td>
<td>41.188</td>
<td>0.419</td>
<td>1.333</td>
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<td>0.001</td>
<td>0.007</td>
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<td>20°C</td>
<td>41.190</td>
<td>0.505</td>
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<td>-2.166</td>
<td>0.001</td>
<td>0.007</td>
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<tr>
<td>40°C</td>
<td>41.195</td>
<td>0.764</td>
<td>1.333</td>
<td>-2.314</td>
<td>0.001</td>
<td>0.007</td>
</tr>
<tr>
<td>60°C</td>
<td>41.200</td>
<td>0.897</td>
<td>1.333</td>
<td>-2.461</td>
<td>0.001</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Table 5.8  The parameters of the bi-Langmuir equation for the cation exchange capacity of cadmium ions onto bone char at different temperatures.

<table>
<thead>
<tr>
<th>T</th>
<th>$a_{L,1}$</th>
<th>$K_{L,1}$</th>
<th>$q_{m,1}$</th>
<th>$\Delta G_1$</th>
<th>$\Delta H_1$</th>
<th>$\Delta S_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10°C</td>
<td>32.253</td>
<td>3.731</td>
<td>0.116</td>
<td>-1.954</td>
<td>0.001</td>
<td>0.007</td>
</tr>
<tr>
<td>20°C</td>
<td>32.255</td>
<td>5.160</td>
<td>0.160</td>
<td>-2.023</td>
<td>0.001</td>
<td>0.007</td>
</tr>
<tr>
<td>40°C</td>
<td>32.258</td>
<td>11.701</td>
<td>0.363</td>
<td>-2.161</td>
<td>0.001</td>
<td>0.007</td>
</tr>
<tr>
<td>60°C</td>
<td>32.261</td>
<td>14.238</td>
<td>0.441</td>
<td>-2.300</td>
<td>0.001</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Table 5.9  The parameters of the bi-Langmuir equation for the adsorption of cadmium ions onto bone char at different temperatures.

<table>
<thead>
<tr>
<th>T</th>
<th>$a_{L,2}$</th>
<th>$K_{L,2}$</th>
<th>$q_{m,2}$</th>
<th>$\Delta G_2$</th>
<th>$\Delta H_2$</th>
<th>$\Delta S_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10°C</td>
<td>99.982</td>
<td>26.229</td>
<td>0.262</td>
<td>-2.591</td>
<td>0.000</td>
<td>0.009</td>
</tr>
<tr>
<td>20°C</td>
<td>99.983</td>
<td>31.696</td>
<td>0.317</td>
<td>-2.682</td>
<td>0.000</td>
<td>0.009</td>
</tr>
<tr>
<td>40°C</td>
<td>99.984</td>
<td>37.321</td>
<td>0.373</td>
<td>-2.865</td>
<td>0.000</td>
<td>0.009</td>
</tr>
<tr>
<td>60°C</td>
<td>99.985</td>
<td>41.960</td>
<td>0.420</td>
<td>-3.048</td>
<td>0.000</td>
<td>0.009</td>
</tr>
</tbody>
</table>
Table 5.10 The parameters of the bi-Langmuir equation for the cation exchange capacity of copper ions onto bone char at different temperatures.

<table>
<thead>
<tr>
<th></th>
<th>T = 10°C</th>
<th>T = 20°C</th>
<th>T = 40°C</th>
<th>T = 60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{L,1}$</td>
<td>19.426</td>
<td>19.427</td>
<td>19.429</td>
<td>19.431</td>
</tr>
<tr>
<td>$K_{L,1}$</td>
<td>5.671</td>
<td>6.619</td>
<td>12.271</td>
<td>21.570</td>
</tr>
<tr>
<td>$q_{m,1}$</td>
<td>0.292</td>
<td>0.341</td>
<td>0.632</td>
<td>1.110</td>
</tr>
<tr>
<td>$\Delta G_1$</td>
<td>-1.669</td>
<td>-1.728</td>
<td>-1.846</td>
<td>-1.964</td>
</tr>
<tr>
<td>$\Delta H_1$</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>$\Delta S_1$</td>
<td>0.006</td>
<td>0.006</td>
<td>0.006</td>
<td>0.006</td>
</tr>
</tbody>
</table>

Table 5.11 The parameters of the bi-Langmuir equation for the adsorption of copper ions onto bone char at different temperatures.

<table>
<thead>
<tr>
<th></th>
<th>T = 10°C</th>
<th>T = 20°C</th>
<th>T = 40°C</th>
<th>T = 60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{L,2}$</td>
<td>285.293</td>
<td>285.302</td>
<td>285.319</td>
<td>285.334</td>
</tr>
<tr>
<td>$K_{L,2}$</td>
<td>82.972</td>
<td>105.043</td>
<td>92.265</td>
<td>45.301</td>
</tr>
<tr>
<td>$q_{m,2}$</td>
<td>0.291</td>
<td>0.368</td>
<td>0.323</td>
<td>0.159</td>
</tr>
<tr>
<td>$\Delta H_2$</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>$\Delta S_2$</td>
<td>0.011</td>
<td>0.011</td>
<td>0.011</td>
<td>0.011</td>
</tr>
</tbody>
</table>

Table 5.12 The parameters of the bi-Langmuir equation for the cation exchange capacity of zinc ions onto bone char at different temperatures.

<table>
<thead>
<tr>
<th></th>
<th>T = 10°C</th>
<th>T = 20°C</th>
<th>T = 40°C</th>
<th>T = 60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{L,1}$</td>
<td>18.603</td>
<td>18.604</td>
<td>18.606</td>
<td>18.608</td>
</tr>
<tr>
<td>$K_{L,1}$</td>
<td>2.393</td>
<td>4.497</td>
<td>9.509</td>
<td>11.789</td>
</tr>
<tr>
<td>$q_{m,1}$</td>
<td>0.129</td>
<td>0.242</td>
<td>0.511</td>
<td>0.634</td>
</tr>
<tr>
<td>$\Delta G_1$</td>
<td>-1.645</td>
<td>-1.703</td>
<td>-1.819</td>
<td>-1.935</td>
</tr>
<tr>
<td>$\Delta H_1$</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>$\Delta S_1$</td>
<td>0.006</td>
<td>0.006</td>
<td>0.006</td>
<td>0.006</td>
</tr>
</tbody>
</table>
Table 5.13  The parameters of the bi-Langmuir equation for the adsorption of zinc ions onto bone char at different temperatures.

<table>
<thead>
<tr>
<th></th>
<th>T = 10°C</th>
<th>T = 20°C</th>
<th>T = 40°C</th>
<th>T = 60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{L2}$</td>
<td>391.918</td>
<td>391.930</td>
<td>391.952</td>
<td>391.971</td>
</tr>
<tr>
<td>$K_{L2}$</td>
<td>113.971</td>
<td>103.187</td>
<td>98.973</td>
<td>103.174</td>
</tr>
<tr>
<td>$q_{m2}$</td>
<td>0.291</td>
<td>0.263</td>
<td>0.253</td>
<td>0.263</td>
</tr>
<tr>
<td>$\Delta H_2$</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>$\Delta S_2$</td>
<td>0.012</td>
<td>0.012</td>
<td>0.012</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Table 5.14  Selected properties of the metal ions (Lide & Frederikse, 1994; Nightingale, 1959)

<table>
<thead>
<tr>
<th>Metal Ions</th>
<th>Ionic Radius (Å)</th>
<th>Hydrated Ionic Radius (Å)</th>
<th>Pauling’s Electronegativity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>1.00</td>
<td>4.12</td>
<td>1.00</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>0.95</td>
<td>4.26</td>
<td>1.69</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>0.73</td>
<td>4.19</td>
<td>1.90</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>0.74</td>
<td>4.30</td>
<td>1.65</td>
</tr>
</tbody>
</table>

Table 5.15  Amount of total sorption capacity, adsorption capacity and cation exchange capacity.

<table>
<thead>
<tr>
<th></th>
<th>10°C</th>
<th>20°C</th>
<th>40°C</th>
<th>60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd$^{2+}$</td>
<td>Cu$^{2+}$</td>
<td>Zn$^{2+}$</td>
<td>Cd$^{2+}$</td>
</tr>
<tr>
<td>TSC</td>
<td>0.38</td>
<td>0.58</td>
<td>0.42</td>
<td>0.48</td>
</tr>
<tr>
<td>ADS</td>
<td>0.26</td>
<td>0.29</td>
<td>0.29</td>
<td>0.32</td>
</tr>
<tr>
<td>CEC</td>
<td>0.12</td>
<td>0.29</td>
<td>0.13</td>
<td>0.16</td>
</tr>
<tr>
<td>CMS</td>
<td>0.48</td>
<td>1.16</td>
<td>0.52</td>
<td>0.64</td>
</tr>
</tbody>
</table>

[TSC = Total Sorption Capacity (mmole/g), ADS = ADSorption capacity (mmole/g), CEC = Cation Exchange Capacity (mmole/g), CMS = Calcium Metal exchange in Solid (wt%)]
### Table 5.16  Sum of the Square of the Errors (SSEs) of sorption systems

<table>
<thead>
<tr>
<th></th>
<th>Cd(^{2+}) ions</th>
<th>Cu(^{2+}) ions</th>
<th>Zn(^{2+}) ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>8.03 \times 10^{-3}</td>
<td>2.02 \times 10^{-2}</td>
<td>2.19 \times 10^{-2}</td>
</tr>
<tr>
<td>Langmuir-Freundlich</td>
<td>7.90 \times 10^{-3}</td>
<td>1.14 \times 10^{-2}</td>
<td>2.18 \times 10^{-2}</td>
</tr>
<tr>
<td>bi-Langmuir</td>
<td>3.83 \times 10^{-2}</td>
<td>8.82 \times 10^{-2}</td>
<td>5.25 \times 10^{-2}</td>
</tr>
</tbody>
</table>

### Table 5.17  Maximum initial concentration for the sorption of metal ions onto bone char using batch agitation method to meet the HKWPCO.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Cd(^{2+}) (mg/L)</th>
<th>Cu(^{2+}) (mg/L)</th>
<th>Zn(^{2+}) (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>97.8</td>
<td>18.3</td>
<td>12.0</td>
</tr>
<tr>
<td>20</td>
<td>123.3</td>
<td>22.2</td>
<td>14.4</td>
</tr>
<tr>
<td>40</td>
<td>189.7</td>
<td>29.9</td>
<td>21.8</td>
</tr>
<tr>
<td>60</td>
<td>221.9</td>
<td>39.7</td>
<td>25.6</td>
</tr>
</tbody>
</table>

### Table 5.18  External mass transfer coefficients using the Harriott equation.

\[
ShSc = \left( \frac{k_f d_p}{D_m} \right) \left( \frac{V}{D_m} \right)^{-1/3}
\]

\[
Re = \left( \frac{\bar{e} d_p^4}{V^3} \right)^{1/3}
\]

<table>
<thead>
<tr>
<th>Particle size (μm)</th>
<th>250 – 355</th>
<th>355 – 500</th>
<th>500 – 710</th>
<th>710 – 1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ShSc)</td>
<td>0.24</td>
<td>0.32</td>
<td>0.43</td>
<td>0.58</td>
</tr>
<tr>
<td>(Re)</td>
<td>0.95</td>
<td>1.51</td>
<td>2.40</td>
<td>3.81</td>
</tr>
<tr>
<td>(k_f) (cm/sec)</td>
<td>2.79 \times 10^{-3}</td>
<td>2.59 \times 10^{-3}</td>
<td>2.46 \times 10^{-3}</td>
<td>2.38 \times 10^{-3}</td>
</tr>
</tbody>
</table>

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Table 5.19  The external mass transfer coefficients for different particle size ranges using the Harriott equation.

<table>
<thead>
<tr>
<th>Particle size (μm)</th>
<th>Cd(^{2+}) (cm/sec)</th>
<th>Cu(^{2+}) (cm/sec)</th>
<th>Zn(^{2+}) (cm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250-355</td>
<td>2.79 \times 10^{-3}</td>
<td>2.77 \times 10^{-3}</td>
<td>2.74 \times 10^{-3}</td>
</tr>
<tr>
<td>355-500</td>
<td>2.59 \times 10^{-3}</td>
<td>2.57 \times 10^{-3}</td>
<td>2.54 \times 10^{-3}</td>
</tr>
<tr>
<td>500-710</td>
<td>2.46 \times 10^{-3}</td>
<td>2.44 \times 10^{-3}</td>
<td>2.41 \times 10^{-3}</td>
</tr>
<tr>
<td>710-1000</td>
<td>2.38 \times 10^{-3}</td>
<td>2.37 \times 10^{-3}</td>
<td>2.34 \times 10^{-3}</td>
</tr>
</tbody>
</table>

Table 5.20  The parameters of the external mass transfer equations for the sorption of cadmium ions onto bone char at different initial concentrations of solution.

<table>
<thead>
<tr>
<th>(mM)</th>
<th>M&amp;W (cm/sec)</th>
<th>F&amp;S (Linear) (cm/sec)</th>
<th>F&amp;S (Nonlinear) (cm/sec)</th>
<th>Harriott (cm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>6.23E-04</td>
<td>7.30E-04</td>
<td>7.45E-04</td>
<td>2.46E-03</td>
</tr>
<tr>
<td>2.5</td>
<td>5.28E-04</td>
<td>6.14E-04</td>
<td>6.23E-04</td>
<td>2.46E-03</td>
</tr>
<tr>
<td>3.0</td>
<td>4.95E-04</td>
<td>5.84E-04</td>
<td>5.94E-04</td>
<td>2.46E-03</td>
</tr>
<tr>
<td>4.0</td>
<td>4.12E-04</td>
<td>4.94E-04</td>
<td>5.01E-04</td>
<td>2.46E-03</td>
</tr>
<tr>
<td>5.0</td>
<td>3.55E-04</td>
<td>4.36E-04</td>
<td>4.42E-04</td>
<td>2.46E-03</td>
</tr>
</tbody>
</table>

Table 5.21  The parameters of the external mass transfer equations for the sorption of copper ions onto bone char at different initial concentrations of solution.

<table>
<thead>
<tr>
<th>(mM)</th>
<th>M&amp;W (cm/sec)</th>
<th>F&amp;S (Linear) (cm/sec)</th>
<th>F&amp;S (Nonlinear) (cm/sec)</th>
<th>Harriott (cm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>9.14E-04</td>
<td>1.06E-03</td>
<td>1.09E-03</td>
<td>2.44E-03</td>
</tr>
<tr>
<td>2.5</td>
<td>6.84E-04</td>
<td>9.02E-04</td>
<td>9.38E-04</td>
<td>2.44E-03</td>
</tr>
<tr>
<td>3.0</td>
<td>7.02E-04</td>
<td>8.44E-04</td>
<td>8.64E-04</td>
<td>2.44E-03</td>
</tr>
<tr>
<td>4.0</td>
<td>5.60E-04</td>
<td>7.01E-04</td>
<td>7.19E-04</td>
<td>2.44E-03</td>
</tr>
<tr>
<td>5.0</td>
<td>4.80E-04</td>
<td>6.14E-04</td>
<td>6.29E-04</td>
<td>2.44E-03</td>
</tr>
</tbody>
</table>
Table 5.22  The parameters of the external mass transfer equations for the sorption of zinc ions onto bone char at different initial concentrations of solution.

<table>
<thead>
<tr>
<th>(mM)</th>
<th>M&amp;W (cm/sec)</th>
<th>F&amp;S (Linear) (cm/sec)</th>
<th>F&amp;S (Nonlinear) (cm/sec)</th>
<th>Harriott (cm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>5.94E-04</td>
<td>7.39E-04</td>
<td>7.58E-04</td>
<td>2.41E-03</td>
</tr>
<tr>
<td>2.5</td>
<td>5.54E-04</td>
<td>6.34E-04</td>
<td>6.44E-04</td>
<td>2.41E-03</td>
</tr>
<tr>
<td>3.0</td>
<td>4.75E-04</td>
<td>5.95E-04</td>
<td>6.09E-04</td>
<td>2.41E-03</td>
</tr>
<tr>
<td>4.0</td>
<td>4.65E-04</td>
<td>5.53E-04</td>
<td>5.63E-04</td>
<td>2.41E-03</td>
</tr>
<tr>
<td>5.0</td>
<td>3.89E-04</td>
<td>4.75E-04</td>
<td>4.83E-04</td>
<td>2.41E-03</td>
</tr>
</tbody>
</table>

Table 5.23  The parameters of the external mass transfer equations for the sorption of cadmium ions onto bone char at different masses of sorbent.

<table>
<thead>
<tr>
<th>(g)</th>
<th>M&amp;W (cm/sec)</th>
<th>F&amp;S (Linear) (cm/sec)</th>
<th>F&amp;S (Nonlinear) (cm/sec)</th>
<th>Harriott (cm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>4.52E-04</td>
<td>5.47E-04</td>
<td>5.56E-04</td>
<td>2.46E-03</td>
</tr>
<tr>
<td>7.5</td>
<td>4.54E-04</td>
<td>5.61E-04</td>
<td>5.69E-04</td>
<td>2.46E-03</td>
</tr>
<tr>
<td>8.5</td>
<td>4.95E-04</td>
<td>5.84E-04</td>
<td>5.94E-04</td>
<td>2.46E-03</td>
</tr>
<tr>
<td>9.5</td>
<td>5.18E-04</td>
<td>6.28E-04</td>
<td>5.32E-04</td>
<td>2.46E-03</td>
</tr>
<tr>
<td>10.5</td>
<td>5.23E-04</td>
<td>6.23E-04</td>
<td>6.29E-04</td>
<td>2.46E-03</td>
</tr>
</tbody>
</table>

Table 5.24  The parameters of the external mass transfer equations for the sorption of copper ions onto bone char at different masses of sorbent.

<table>
<thead>
<tr>
<th>(g)</th>
<th>M&amp;W (cm/sec)</th>
<th>F&amp;S (Linear) (cm/sec)</th>
<th>F&amp;S (Nonlinear) (cm/sec)</th>
<th>Harriott (cm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>6.32E-04</td>
<td>8.01E-04</td>
<td>8.11E-04</td>
<td>2.44E-03</td>
</tr>
<tr>
<td>7.5</td>
<td>7.24E-04</td>
<td>8.42E-04</td>
<td>8.62E-04</td>
<td>2.44E-03</td>
</tr>
<tr>
<td>8.5</td>
<td>7.02E-04</td>
<td>8.44E-04</td>
<td>8.64E-04</td>
<td>2.44E-03</td>
</tr>
<tr>
<td>9.5</td>
<td>6.70E-04</td>
<td>8.07E-04</td>
<td>8.34E-04</td>
<td>2.44E-03</td>
</tr>
<tr>
<td>10.5</td>
<td>7.74E-04</td>
<td>8.99E-04</td>
<td>9.26E-04</td>
<td>2.44E-03</td>
</tr>
</tbody>
</table>
Table 5.25  The parameters of the external mass transfer equations for the sorption of zinc ions onto bone char at different masses of sorbent.

<table>
<thead>
<tr>
<th>(g)</th>
<th>M&amp;W (cm/sec)</th>
<th>F&amp;S (Linear) (cm/sec)</th>
<th>F&amp;S (Nonlinear) (cm/sec)</th>
<th>Harriott (cm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>4.34E-04</td>
<td>5.34E-04</td>
<td>5.37E-04</td>
<td>2.41E-03</td>
</tr>
<tr>
<td>7.5</td>
<td>5.09E-04</td>
<td>6.20E-04</td>
<td>6.34E-04</td>
<td>2.41E-03</td>
</tr>
<tr>
<td>8.5</td>
<td>4.75E-04</td>
<td>5.95E-04</td>
<td>6.09E-04</td>
<td>2.41E-03</td>
</tr>
<tr>
<td>9.5</td>
<td>4.55E-04</td>
<td>5.71E-04</td>
<td>5.85E-04</td>
<td>2.41E-03</td>
</tr>
<tr>
<td>10.5</td>
<td>5.24E-04</td>
<td>6.40E-04</td>
<td>6.59E-04</td>
<td>2.41E-03</td>
</tr>
</tbody>
</table>

Table 5.26  Effect of film and pore diffusivities on the Biot number.

<table>
<thead>
<tr>
<th>Film Effect</th>
<th>Bi</th>
<th>Pore Diffusion Effect</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_f$</td>
<td>65</td>
<td>$D_p$</td>
<td>65</td>
</tr>
<tr>
<td>0.2 $k_f$</td>
<td>13</td>
<td>0.5 $D_p$</td>
<td>130</td>
</tr>
<tr>
<td>0.1 $k_f$</td>
<td>6.5</td>
<td>0.2 $D_p$</td>
<td>325</td>
</tr>
<tr>
<td>0.05 $k_f$</td>
<td>3.3</td>
<td>0.1 $D_p$</td>
<td>651</td>
</tr>
</tbody>
</table>
Table 5.27  Film mass transfer coefficients and pore diffusivities for the sorption of metal ions onto bone char using the analytical solution.

<table>
<thead>
<tr>
<th></th>
<th>Cd$^{2+}$</th>
<th>Cu$^{2+}$</th>
<th>Zn$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film mass transfer coefficients (cm/s) (Harriott Equation)</td>
<td>2.46 × 10^{-3}</td>
<td>2.44 × 10^{-3}</td>
<td>2.41 × 10^{-3}</td>
</tr>
<tr>
<td>Molecular diffusivities of ion in solutions (cm$^2$/s)</td>
<td>6.52 × 10^{-6}</td>
<td>6.47 × 10^{-6}</td>
<td>6.37 × 10^{-6}</td>
</tr>
<tr>
<td>Calculated film thickness (cm)</td>
<td>$\Delta x = \frac{D_m}{k_f}$</td>
<td>2.65 × 10^{-3}</td>
<td>2.65 × 10^{-3}</td>
</tr>
<tr>
<td>Pore diffusivities (bone char, cm$^2$/s) (Case I: Analytical Method)</td>
<td>1.18 × 10^{-6}</td>
<td>1.63 × 10^{-6}</td>
<td>1.35 × 10^{-6}</td>
</tr>
<tr>
<td>Pore diffusivities (bone char, cm$^2$/s) (Case II: Numerical Method)</td>
<td>1.14 × 10^{-6}</td>
<td>1.59 × 10^{-6}</td>
<td>1.21 × 10^{-6}</td>
</tr>
<tr>
<td>Biot Number, $Bi = \frac{k_f R}{D_p}$</td>
<td>65</td>
<td>46</td>
<td>60</td>
</tr>
<tr>
<td>Hydrated ionic radii (Å) (Nightingale, 1959)</td>
<td>4.26</td>
<td>4.19</td>
<td>4.30</td>
</tr>
<tr>
<td>Tortuosity factor</td>
<td>2.34</td>
<td>1.66</td>
<td>2.17</td>
</tr>
</tbody>
</table>

Table 5.28  SSE, pore diffusivities and surface diffusivities for the film-pore and film-pore-surface diffusion model at 3mM.

<table>
<thead>
<tr>
<th></th>
<th>Cd$^{2+}$</th>
<th>Cu$^{2+}$</th>
<th>Zn$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore diffusivities (cm$^2$/s) (Case II: Film-Pore Model)</td>
<td>1.18 × 10^{-6}</td>
<td>1.63 × 10^{-6}</td>
<td>1.35 × 10^{-6}</td>
</tr>
<tr>
<td>Pore diffusivities (cm$^2$/s) (Case III: Film-Pore-Surface Model)</td>
<td>1.14 × 10^{-6}</td>
<td>1.57 × 10^{-6}</td>
<td>1.20 × 10^{-6}</td>
</tr>
<tr>
<td>Surface diffusivities (cm$^2$/s) (Case III: Numerical Method)</td>
<td>1.79 × 10^{-6}</td>
<td>9.78 × 10^{-7}</td>
<td>1.97 × 10^{-6}</td>
</tr>
<tr>
<td>$D_{so}$ (cm$^2$/sec)</td>
<td>$\downarrow$</td>
<td>$\downarrow$</td>
<td>$\downarrow$</td>
</tr>
<tr>
<td>3.44 × 10^{-6}</td>
<td>2.89 × 10^{-6}</td>
<td>3.97 × 10^{-6}</td>
<td></td>
</tr>
<tr>
<td>$D_{sw}$ (cm$^2$/sec) at ≈3mM</td>
<td>$\downarrow$</td>
<td>$\downarrow$</td>
<td>$\downarrow$</td>
</tr>
<tr>
<td>1.14 × 10^{-6}</td>
<td>1.59 × 10^{-6}</td>
<td>1.21 × 10^{-6}</td>
<td></td>
</tr>
<tr>
<td>$SSE$ (F-P model)</td>
<td>3087</td>
<td>6458</td>
<td>3853</td>
</tr>
<tr>
<td>$SSE$ (F-P-S model)</td>
<td>3013</td>
<td>6257</td>
<td>3697</td>
</tr>
</tbody>
</table>
Table 5.29  The parameters of empirical and Langmuir-type equations for the sorption of cadmium ions onto bone char from single and multicomponent systems.

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th>Cd-Cu</th>
<th>Cd-Zn</th>
<th>Cd-Cu-Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_L$ (dm³/mg)</td>
<td>1.404</td>
<td>0.332</td>
<td>0.204</td>
<td>0.089</td>
</tr>
<tr>
<td>$K_L$ (dm³/g)</td>
<td>75.354</td>
<td>11.155</td>
<td>7.929</td>
<td>2.444</td>
</tr>
<tr>
<td>H (mg/g)</td>
<td>--</td>
<td>0.026</td>
<td>--</td>
<td>0.019</td>
</tr>
</tbody>
</table>

Table 5.30  The parameters of Langmuir-type equation for the sorption of copper ions onto bone char from single and multicomponent systems.

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Cu-Cd</th>
<th>Cu-Zn</th>
<th>Cd-Cu-Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_L$ (dm³/mg)</td>
<td>1.089</td>
<td>0.348</td>
<td>0.187</td>
<td>0.148</td>
</tr>
<tr>
<td>$K_L$ (dm³/g)</td>
<td>49.054</td>
<td>12.606</td>
<td>7.852</td>
<td>4.471</td>
</tr>
<tr>
<td>H (mg/g)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 5.31  The parameters of empirical and Langmuir-type equations for the sorption of zinc ions onto bone char from single and multicomponent systems.

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>Zn-Cd</th>
<th>Zn-Cu</th>
<th>Zn-Cd-Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_L$ (dm³/mg)</td>
<td>0.951</td>
<td>0.190</td>
<td>0.463</td>
<td>0.147</td>
</tr>
<tr>
<td>$K_L$ (dm³/g)</td>
<td>31.399</td>
<td>4.188</td>
<td>9.420</td>
<td>2.016</td>
</tr>
<tr>
<td>H (mg/g)</td>
<td>--</td>
<td>0.020</td>
<td>0.040</td>
<td>0.032</td>
</tr>
</tbody>
</table>

Table 5.32  The pore diffusivities of multicomponent systems using the film-pore diffusion model and empirical method.

<table>
<thead>
<tr>
<th>Metal Ions</th>
<th>Single Component (cm²/sec)</th>
<th>Cd-Cu (cm²/sec)</th>
<th>Cd-Zn (cm²/sec)</th>
<th>Cu-Zn (cm²/sec)</th>
<th>Cd-Cu-Zn (cm²/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>(1.14 \times 10^{-6})</td>
<td>(5.14 \times 10^{-7})</td>
<td>(1.98 \times 10^{-7})</td>
<td>--</td>
<td>(2.01 \times 10^{-7})</td>
</tr>
<tr>
<td>Cu</td>
<td>(1.59 \times 10^{-6})</td>
<td>(1.16 \times 10^{-8})</td>
<td>--</td>
<td>(1.39 \times 10^{-6})</td>
<td>(1.12 \times 10^{-6})</td>
</tr>
<tr>
<td>Zn</td>
<td>(1.21 \times 10^{-8})</td>
<td>--</td>
<td>(5.72 \times 10^{-7})</td>
<td>(2.78 \times 10^{-7})</td>
<td>(2.06 \times 10^{-7})</td>
</tr>
</tbody>
</table>
Table 5.33  The pore diffusivities of multicomponent systems using the film-pore diffusion model and IAST.

<table>
<thead>
<tr>
<th>Metal Ions</th>
<th>Single Component (cm$^2$/sec)</th>
<th>Cd-Cu (cm$^2$/sec)</th>
<th>Cd-Zn (cm$^2$/sec)</th>
<th>Cu-Zn (cm$^2$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>1.14 x 10^{-6}</td>
<td>1.20 x 10^{-6}</td>
<td>2.25 x 10^{-7}</td>
<td>--</td>
</tr>
<tr>
<td>Cu</td>
<td>1.59 x 10^{-6}</td>
<td>1.30 x 10^{-6}</td>
<td>--</td>
<td>1.50 x 10^{-6}</td>
</tr>
<tr>
<td>Zn</td>
<td>1.21 x 10^{-6}</td>
<td>--</td>
<td>1.10 x 10^{-6}</td>
<td>1.00 x 10^{-6}</td>
</tr>
</tbody>
</table>

Table 5.34  The SSEs for multicomponent systems using the empirical method or the IAST incorporating into film-pore diffusion model.

<table>
<thead>
<tr>
<th>Metal Ions</th>
<th>Cd-Cu</th>
<th>Cd-Zn</th>
<th>Cu-Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd (Empirical-FP model)</td>
<td>0.55</td>
<td>1.77</td>
<td>--</td>
</tr>
<tr>
<td>Cd (IAST-FP model)</td>
<td>5.97</td>
<td>2.59</td>
<td>--</td>
</tr>
<tr>
<td>Cu (Empirical-FP model)</td>
<td>0.95</td>
<td>--</td>
<td>1.59</td>
</tr>
<tr>
<td>Cu (IAST-FP model)</td>
<td>8.00</td>
<td>--</td>
<td>8.87</td>
</tr>
<tr>
<td>Zn (Empirical-FP model)</td>
<td>--</td>
<td>0.94</td>
<td>2.10</td>
</tr>
<tr>
<td>Zn (IAST-FP model)</td>
<td>--</td>
<td>1.73</td>
<td>7.11</td>
</tr>
</tbody>
</table>
Figure 3.1  Establishment of contact time for cadmium ions on bone char.

Figure 3.2  Establishment of contact time for copper ions on bone char.

Figure 3.3  Establishment of contact time for zinc ions on bone char.
Figure 5.1 Powder XRD spectrum of bovine bone.

Figure 5.2 Powder XRD spectrum of bone char and the standard spectrum of CaHAP.
Figure 5.3  The cylindrical pore structure on the bone char surface using SEM.

Figure 5.4  The magnification of the bone char surface. The carbon surface (white solid) distributed on the CaHAP surface.
Figure 5.5  Amount of N₂ adsorbed at 77 K versus the reduced pressure.

Figure 5.6  Pore volume distribution of bone char using N₂ condensation and evaporation.
Figure 5.7 XRD pattern for the bone char before and after adsorption of cadmium ions.

Figure 5.8 XRD patterns for the sorption of Cd ions onto bone char at different initial concentrations.
Figure 5.9  XRD patterns for the sorption of Cu ions onto bone char at different initial concentrations.

Figure 5.10  XRD patterns for the sorption of Zn ions onto bone char at different initial concentrations.
Figure 5.11  Effect of pH on sorption of onto bone char.

Figure 5.12  Powder XRD patterns for the sorption of metal ions onto bone char at pH 4.0.
Figure 5.13  Powder XRD patterns for the sorption of metal ions onto bone char at pH 3.0.

Figure 5.14  FT-IR spectrum for the sorption of Cd ions onto bone char with different initial concentrations.
Figure 5.15  FT-IR spectrum for the sorption of Cd ions onto bone char with different initial concentrations.

Figure 5.16  FT-IR spectrum for the sorption of Cu ions onto bone char with different initial concentrations.
Figure 5.17  FT-IR spectrum for the sorption of Cu ions onto bone char with different initial concentrations.

Figure 5.18  FT-IR spectrum for the sorption of Zn ions onto bone char with different initial concentrations.
Figure 5.19  FT-IR spectrum for the sorption of Zn ions onto bone char with different initial concentrations.

Figure 5.20  Sorption of Cd ions onto bone char at different temperatures using the Langmuir isotherm.
Figure 5.21  Sorption of Cu ions onto bone char at different temperatures using the Langmuir isotherm.

Figure 5.22  Sorption of Zn ions onto bone char with different temperatures using the Langmuir isotherm.
Figure 5.23  Sorption of Cd ions onto bone char with different temperatures using the Langmuir-Freundlich isotherm.

Figure 5.24  Sorption of Cu ions onto bone char at different temperatures using the Langmuir-Freundlich isotherm.
Figure 5.25  Sorption of Zn ions onto bone char at different temperatures using the Langmuir-Freundlich isotherm.

Figure 5.26  Sorption of Cd ions onto bone char at different temperatures using the bi-Langmuir isotherm.
Figure 5.27  Calcium exchange capacity for the sorption of Cd ions onto bone char at different temperatures.

Figure 5.28  Sorption of Cu ions onto bone char at different temperatures using the bi-Langmuir isotherm.
Figure 5.29  Calcium exchange capacity for the sorption of Cu ions onto bone char at different temperatures.

Figure 5.30  Sorption of Zn ions onto bone char at different temperatures using the bi-Langmuir isotherm.
Figure 5.31  Calcium exchange capacity for the sorption of Zn ions onto bone char at different temperatures.

Figure 5.32  Experimental data and predictive curves for the sorption of Cd-Cu ions at equal mole ratio.
Figure 5.33  Experimental data and predictive curves for the sorption of Cu-Zn ions at equal mole ratio.

Figure 5.34  Experimental data and predictive curves for the sorption of Cd-Zn ions at equal mole ratio.
Figure 5.35  Experimental data and predictive curves for the sorption of Cd-Cu ions at Cd:Cu = 7:3 mole ratio.

Figure 5.36  Experimental data and predictive curves for the sorption of Cd-Cu ions at Cd:Cu = 6:4 mole ratio.
Figure 5.37  Experimental data and predictive curves for the sorption of Cd-Cu ions at Cd:Cu = 4:6 mole ratio.

Figure 5.38  Experimental data and predictive curves for the sorption of Cd-Cu ions at Cd:Cu = 3:7 mole ratio.
Figure 5.39  Experimental data and predictive curves for the sorption of Cu, Cd, and Zn ions at equal mole ratio using the Langmuir equation.

Figure 5.40  Experimental data and predictive curves for the sorption of Cu, Cd, and Zn ions at equal mole ratio using the Sips equation.
Figure 5.41  Experimental data and predictive curves for the sorption of metal at Cu: Cd: Zn = 46:21:33 mole ratio using the Langmuir equation.

Figure 5.42  Experimental data and predictive curves for the sorption of metal at Cu: Cd: Zn = 46:21:33 mole ratio using the Sips equation.
Figure 5.43  Experimental data and predictive curves for the sorption of metal at

Figure 5.44  Experimental data and predictive curves for the sorption of metal at
Figure 5.45  The sorption of Cd ions onto bone char correlating the Furusawa & Smith equation and film diffusion equation of Mathews & Weber.

Figure 5.46  The sorption of Cu ions onto bone char correlating the Furusawa & Smith equation and film diffusion equation of Mathews & Weber.
Figure 5.47  The sorption of Zn ions onto bone char correlating the Furusawa & Smith equation and film diffusion equation of Mathews & Weber.

Figure 5.48  The Sh/Sc^{0.33} vs Re using the Harriott equation for the sorption of Cd ions onto bone char.
Figure 5.49  The sorption capacity at specified time against the square root of time (Concentration effect for the sorption of Cd ions onto bone char).

Figure 5.50  The sorption capacity at specified time against the square root of time (Particle size effect for the sorption of Cd ions onto bone char).
Figure 5.51  The relationship of adsorption isotherm and the mass transport model. (Effect of initial concentration and sorbent mass for the sorption of Cd ions onto bone char)
Figure 5.52  Initial concentration effect for the sorption of Cd ions onto bone char using the film-pore diffusion equation (analytical method).

Figure 5.53  Mass effect for the sorption of Cd ions onto bone char using the film-pore diffusion equation (analytical method).
Figure 5.54  Initial concentration effect for the sorption of Cu ions onto bone char using the film-pore diffusion equation (analytical method).

Figure 5.55  Mass effect for the sorption of Cu ions onto bone char using the film-pore diffusion equation (analytical method).
Figure 5.56  Initial concentration effect for the sorption of Zn ions onto bone char using the film-pore diffusion equation (analytical method).

Figure 5.57  Mass effect for the sorption of Zn ions onto bone char using the film-pore diffusion equation (analytical method).
Figure 5.58  Initial concentration effect for the sorption of Cd ions onto bone char using the film-pore diffusion equation (numerical method).

Figure 5.59  Mass effect for the sorption of Cd ions onto bone char using the film-pore diffusion equation (numerical method).
Figure 5.60  Initial concentration effect for the sorption of Cu ions onto bone char using the film-pore diffusion equation (numerical method).

Figure 5.61  Mass effect for the sorption of Cu ions onto bone char using the film-pore diffusion equation (numerical method).
Figure 5.62  Initial concentration effect for the sorption of Zn ions onto bone char using the film-pore diffusion equation (numerical method).

Figure 5.63  Mass effect for the sorption of Zn ions onto bone char using the film-pore diffusion equation (numerical method).
Figure 5.64  Initial concentration effect for the sorption of Cd ions onto bone char using the film-pore-surface diffusion equation.

Figure 5.65  Mass effect for the sorption of Cd ions onto bone char using the film-pore-surface diffusion equation.
Figure 5.66  Initial concentration effect for the sorption of Cu ions onto bone char using the film-pore-surface diffusion equation.

Figure 5.67  Mass effect for the sorption of Cu ions onto bone char using the film-pore-surface diffusion equation.
Figure 5.68  Initial concentration effect for the sorption of Zn ions onto bone char using the film-pore-surface diffusion equation.

Figure 5.69  Mass effect for the sorption of Zn ions onto bone char using the film-pore-surface diffusion equation.
Figure 5.70  Connection between bulk and surface concentrations during the adsorption in batch test.

Figure 5.71  The concentration of Cd ions at the bulk solution and at the sorbent surface.
Figure 5.72 Effect of film mass transfer coefficient for the sorption of Cd ions onto bone char.

Figure 5.73 Effect of effective diffusivity to the sorption of Cd ions onto bone char.
Figure 5.74  Temperature effects for the sorption of Cd ions onto bone char (Best-fit and Predictive curves).

Figure 5.75  Predictive effective diffusivities for the sorption of Cd ions onto bone char using the Stokes-Einstein equation.
Figure 5.76  Temperature effects for the sorption of Cu ions onto bone char (Best-fit and Predictive curves).

Figure 5.77  Predictive effective diffusivities for the sorption of Cu ions onto bone char using the Stokes-Einstein equation.
Figure 5.78  Temperature effects for the sorption of Zn ions onto bone char (Best-fit and Predictive curves).

Figure 5.79  Predictive effective diffusivities for the sorption of Zn ions onto bone char using the Stokes-Einstein equation.
Figure 5.80 The rate of ion exchange for the sorption of Ca^{2+} ions and the concentration of Ca^{2+} ions in solution at different temperature.

Figure 5.81 The rate of adsorption for the cadmium ions onto bone char at different temperatures.
Figure 5.82  The rate of ion exchange for the copper ions onto bone char at different temperatures.

Figure 5.83  The rate of adsorption for the copper ions onto bone char at different temperatures.
Figure 5.84  The rate of ion exchange for the zinc ions onto bone char at different temperatures.

Figure 5.85  The rate of adsorption for the zinc ions onto bone char at different temperatures.
Figure 5.86  The cation exchange capacity at time $t$ against square root of time.
(Temperatures effects for the sorption of Cd ions onto bone char).

Figure 5.87  The adsorption rate at time $t$ against square root of time.
(Temperatures effects for the sorption of Cd ions onto bone char).
Figure 5.88  Particle size effect for the sorption of Cd ions onto bone char.

Figure 5.89  Sorption of Cd ions onto bone char from single and multicomponent systems.
Figure 5.90  Sorption of Cu ions onto bone char from single and multicomponent systems.

Figure 5.91  Sorption of Zn ions onto bone char from single and multicomponent systems.
Figure 5.92 Concentration effect for the sorption of Cd ions from Cd-Cu solution onto bone char using the film-pore diffusion equation.

Figure 5.93 Mass effect for the sorption of Cd ions from Cd-Cu solution onto bone char using the film-pore diffusion equation.
Figure 5.94  Concentration effect for the sorption of Cd ions from Cd-Zn solution onto bone char using the film-pore diffusion equation.

Figure 5.95  Mass effect for the sorption of Cd ions from Cd-Zn solution onto bone char using the film-pore diffusion equation.
Figure 5.96  Concentration effect for the sorption of Cd ions from Cd-Cu-Zn solution onto bone char using the film-pore diffusion equation.

Figure 5.97  Mass effect for the sorption of Cd ions from Cd-Cu-Zn solution onto bone char using the film-pore diffusion equation.
Figure 5.98  Concentration effect for the sorption of Cu ions from Cd-Cu solution onto bone char using the film-pore diffusion equation.

Figure 5.99  Mass effect for the sorption of Cu ions from Cd-Cu solution onto bone char using the film-pore diffusion equation.
Figure 5.100  Concentration effect for the sorption of Cu ions from Cu-Zn solution onto bone char using the film-pore diffusion equation.

Figure 5.101  Mass effect for the sorption of Cu ions from Cu-Zn solution onto bone char using the film-pore diffusion equation.
Figure 5.102 Concentration effect for the sorption of Cu ions from Cd-Cu-Zn solution onto bone char using the film-pore diffusion equation.

Figure 5.103 Mass effect for the sorption of Cu ions from Cd-Cu-Zn solution onto bone char using the film-pore diffusion equation.
Figure 5.104  Concentration effect for the sorption of Zn ions from Cd-Zn solution onto bone char using the film-pore diffusion equation.

Figure 5.105  Mass effect for the sorption of Zn ions from Cd-Zn solution onto bone char using the film-pore diffusion equation.
Figure 5.106  Concentration effect for the sorption of Zn ions from Cu-Zn solution onto bone char using the film-pore diffusion equation.

Figure 5.107  Mass effect for the sorption of Zn ions from Cu-Zn solution onto bone char using the film-pore diffusion equation.
Figure 5.108  Concentration effect for the sorption of Zn ions from Cd-Cu-Zn solution onto bone char using the film-pore diffusion equation.

Figure 5.109  Mass effect for the sorption of Zn ions from Cd-Cu-Zn solution onto bone char using the film-pore diffusion equation.
Figure 5.110  Concentration effect for the sorption of Cd ions from Cd-Cu solution onto bone char using the IAST-film-pore diffusion equation.

Figure 5.111  Mass effect for the sorption of Cd ions from Cd-Cu solution onto bone char using the IAST-film-pore diffusion equation.
Figure 5.112 Concentration effect for the sorption of Cu ions from Cd-Cu solution onto bone char using the IAST-film-pore diffusion equation.

Figure 5.113 Mass effect for the sorption of Cu ions from Cd-Cu solution onto bone char using the IAST-film-pore diffusion equation.
Figure 5.114 Concentration effect for the sorption of Cd ions from Cd-Zn solution onto bone char using the IAST-film-pore diffusion equation.

Figure 5.115 Mass effect for the sorption of Cd ions from Cd-Zn solution onto bone char using the IAST-film-pore diffusion equation.
Figure 5.116 Concentration effect for the sorption of Zn ions from Cd-Zn solution onto bone char using the IAST-film-pore diffusion equation.

Figure 5.117 Mass effect for the sorption of Zn ions from Cd-Zn solution onto bone char using the IAST-film-pore diffusion equation.
Figure 5.118 Concentration effect for the sorption of Cu ions from Cu-Zn solution onto bone char using the IAST-film-pore diffusion equation.

Figure 5.119 Mass effect for the sorption of Cu ions from Cu-Zn solution onto bone char using the IAST-film-pore diffusion equation.
Figure 5.120 Concentration effect for the sorption of Zn ions from Cu-Zn solution onto bone char using the IAST-film-pore diffusion equation.

Figure 5.121 Mass effect for the sorption of Zn ions from Cu-Zn solution onto bone char using the IAST-film-pore diffusion equation.