ADSORPTION KINETICS AND EQUILIBRIUM OF
COPPER AND ZINC ON VOLCANIC TUFF

FREDERICK BONG HSIAO PAU

DISSERTATION SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
BACHELOR OF SCIENCE WITH HONOURS

INDUSTRIAL CHEMISTRY PROGRAMME
SCHOOL OF SCIENCE AND TECHNOLOGY
UNIVERSITI MALAYSIA SABAH

MAY 2008

PUMS99:1

UNIVERSITI MALAYSIA SABAH

BORANG PENGESAHAN STATUS TESIS@

JUDUL: Adsorption Kinetics and Equilibrium of Copper and Zinc on Volcanic Tuff.

IJAZAH: Sarjana Muda Sains (Kepujian)

SAYA FREDERICK BONG HSIAO PAU (HURUF BESAR) SESI PENGAJIAN: 2005 - 2008

mengaku membenarkan tesis (LPSM/Sarjana/Doktor Falsafah) ini disimpan di Perpustakaan Universiti Malaysia Sabah dengan syarat-syarat kegunaan seperti berikut:-

1. Tesis adalah hakmilik Universiti Malaysia Sabah.
2. Perpustakaan Universiti Malaysia Sabah dibenarkan membuat salinan untuk tujuan pengajian sahaja.
3. Perpustakaan dibenarkan membuat salinan tesis ini sebagai bahan pertukaran antara institutsi pengajian tinggi.
4. Sila tandakan (/)

- [ ] SULIT (Mengandungi maklumat yang berdarjah keselamatan atau Kepentingan Malaysia seperti yang termaktub di dalam AKTA RAHSIA RASMI 1972)
- [x] TERHAD (Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan)
- [ ] TIDAK TERHAD

Disahkan Oleh

(TANDATANGAN PENULIS)

(TANDATANGAN PUSTAKAWAN)

Alamat Tetap: Lot 979, Piasau Utara 6, 98000 Miri. Sarawak.

Nama Penyelia

Tarikh: 15/5/2008

Tarikh:

CATATAN:- *Potong yang tidak berkenaan.

**Jika tesis ini SULIT atau TERHAD, sila lampirkan surat daripada pihak berkuasa /organisasi berkenaan dengan menyatakan sekali sebab dan tempoh tesis ini perlu dikelaskan sebagai SULIT dan TERHAD.

@Tesis dimaksudkan sebagai tesis bagi Ijazah Doktor Falsafah dan Sarjana secara penyelidikan atau disertai bagi pengajian secara kerja kursus dan Laporan Projek Sarjana Muda (LPSM).

DECLARATION

I hereby declare that this dissertation is based on my original work, except for the quotations of which have been fully acknowledged.

MAY, 2008

FREDERICK BONG HSIAO PAU
HS 2005 – 4441

VERIFICATION

Name: Frederick Bong Hsiao Pau

Title: Adsorption Kinetics and Equilibrium of Cu and Zn on Volcanic Tuff

ASSOC. PROF. DR. MARCUS JOPONY

DR. HOW SIEW ENG

DR. MD. LUTFOR RAHMAN

ASSOC. PROF. DR. SHARIFF A. K. S. OMANG

MAY, 2008

ACKNOWLEDGEMENTS

I wish to thank my supervisor, Assoc. Prof. Dr. Marcus Jopony for providing me so many helpful comments during the entire period on completing this final year project. Besides, I also wish to thank all the lab assistants for assisting me in the lab work. Lastly, I would like to thank my family members for giving me mental and financial supports throughout the whole project.

ABSTRACT

The adsorption kinetics and equilibrium of Cu and Zn on volcanic tuff was investigated according to batch method. For comparison, the same experiments were carried out on natural zeolite. The final Cu and Zn concentration in solution was determined using an atomic absorption spectrophotometer (AAS). The results showed that Cu and Zn adsorption by volcanic tuff was rapid with significant removal of the metal from solution during the first 5 minutes. Equilibrium, however, was only attained after 60 minutes. The adsorption conformed to pseudo – second order kinetic model (R^2 = 0.999) as well as to Langmuir (R^2 = 0.9) and Freundlich (R^2 = 0.9) isotherms. Similar pattern was observed for Cu and Zn adsorption by natural zeolite, except the adsorption conforms better to Langmuir isotherms (R^2 = 0.98). The maximum Cu and Zn adsorption capacity is 1000 μg/g and 796.23 μg/g, respectively for volcanic tuff; and 1111.11 μg/g and 833.33 μg/g, respectively for natural zeolite. Comparatively, Cu and Zn removal by volcanic tuff was less efficient in a mixed metal system compared to single metal system. Overall, the volcanic tuff can potentially be used for the removal of heavy metals, including Cu and Zn, from wastewater.

KINETIK DAN KESEIMBANGAN JERAPAN BAGI KUPRUM DAN ZINK OLEH TUF VOLCANO

ABSTRAK

Kinetik dan keseimbangan jerapan bagi kuprum dan zink oleh tuf volcano telah dikaji berdasarkan kaedah kelompok. Kajian yang sama dilakukan menggunakan zeolit semulajadi sebagai perbandingan. Kepekatan akhir kuprum dan zink ditentukan dengan spektrofotometer serapan atomic (AAS). Hasil kajian menunjukkan jerapan kuprum dan zink oleh tuf volkano adalah pantas pada 5 minit pertama. Keseimbangan jerapan, walau bagaimanapun, dicapai dalam tempoh 60 minit. Jerapan kuprum dan zink mematuhi baik model kinetik tertib pseudo kedua (R^2 = 0.999), serta isoterma jerapan Langmuir (R^2 = 0.9) dan Freundlich (R^2 = 0.9). Corak hasil kajian yang serupa diperolehi untuk jerapan kuprum dan zink oleh zeolit semulajadi, kecuali jerapan adalah lebih mematuhi isoterma Langmuir (R^2 = 0.98). Kapasiti jerapan maksimum kuprum dan zink ialah masing – masing 1000 µg/g dan 796.23 µg/g bagi tuf volcano; serta masing – masing 1111.11 µg/g dan 833.33 µg/g bagi zeolit semulajadi. Penyingkiran kuprum dan zink oleh tuf volkano adalah kurang berkesan dalam sistem logam campuran, berbanding dengan sistem logam tunggal. Secara keseluruhannya tuf volkano merupakan penjerap yang berpotensi untuk penyingkiran logam berat, termasuk kuprum dan zink, daripada air sisa.

CONTENTS

		Page
DECLARATION		ii
VERIFICATION		iii
ACKNOWLEDGEMENTS		iv
ABSTRACT		v
ABSTRAK		vi
CONTENTS		vii
TABLE LIST		x
FIGURE LIST		xii
SYMBOL, ABBREVIATION AND UNIT LIST		xv
CHAPTER 1 INTRODUCTION		
1.1	Context and Relevance of Study	1
1.2	Research Objectives	3
1.3	Scope of Study	3
CHAPTER 2 LITERATURE REVIEW		4
2.1	Copper and Zinc	4
	2.1.1 General chemistry of copper and zinc	4
	2.1.2 Sources of copper and zinc	5
	a. Natural sources	5
	b. Anthropogenic sources	6
	2.1.3 Environmental and health impacts of copper and zinc	7
	2.1.4 Wastewater discharge and drinking water quality standards	7
2.2	Wastewater Treatment Methods	8
	2.2.1 Adsorption	8
	2.2.2 Ion exchange	11
	2.2.3 Reverse osmosis	12
	2.2.4 Chemical precipitation	12
	2.2.5 Electrodialysis	13

2.3	Copper and Zinc Adsorption		14
	2.3.1	Adsorbents for copper and zinc removal	14
	2.3.2	Kinetics of copper and zinc adsorption	14
		a. Pseudo – first order kinetic model	16
		b. Pseudo – second order kinetic model	17
		c. Intraparticle diffusion kinetic model	18
	2.3.3	Equilibrium of copper and zinc adsorption	20
		a. Langmuir isotherm	21
		b. Freundlich isotherm	22
	2.3.4	Effect of adsorbent dosage	24
	2.3.5	Effect of grain size	25
	2.3.6	pH	26
2.4	Volcanic Tuff		27
	2.4.1	General characteristic	27
	2.4.2	Volcanic tuff as adsorbent	29

CHAPTER 3 MATERIALS AND METHODOLOGY 32

3.1	Adsorbents		32
3.2	Adsorbates		33
	3.2.1	Preparation of 1000 µg/mL zinc stock solution	33
	3.2.2	Preparation of 1000 µg/mL copper stock solution	33
	3.2.3	Preparation of 100 µg/mL stock solutions	33
	3.2.4	Preparation of binary metal working solutions	34
	3.2.5	Preparation of working solutions	34
	3.2.6	Preparation of standard solutions	35
3.3	Batch Adsorption Experiments		36
	3.3.1	Effect of contact time	36
	3.3.2	Effect of initial metal concentration	36
3.4	Analysis of Copper and Zinc		38
	3.4.1	Instrumentation	38
	3.4.2	Preparation of calibration graph	39
	3.4.3	Determination of heavy metal ions	39

CHAPTER 4 RESULTS AND DISCUSSIONS 40

4.1 Effect of Contact Time on Cu and Zn adsorption 40

4.2 Kinetics of Cu and Zn Adsorption on Volcanic Tuff and Natural Zeolite 43

4.3 Effect of Initial Metal Concentration on Cu and Zn adsorption 53

4.4 Adsorption Isotherm 53

4.5 Adsorption Mechanism 61

4.6 Cu and Zn Adsorption in Mixed Metal System 62

CHAPTER 5 CONCLUSION 64

REFERENCES 65

APPENDIXES 71

TABLE LIST

Page

Table 2.1 Parent materials that can be subjected to weathering and releasing Cu and Zn 5

Table 2.2 Anthropogenic source of Cu and Zn to the environment 6

Table 2.3 Parameter limits for effluents of Standard A and Standard B 9

Table 2.4 Guideline values for chemicals that are of health significance in drinking water 10

Table 2.5 Solid materials that have been studied as Zn and Cu adsorbents 15

Table 2.6 Kinetic models that describe Cu and Zn adsorption 19

Table 2.7 Effect of initial concentration on adsorption of Cu (II) by low cost adsorbents 21

Table 2.8 Adsorption isotherms that describe Cu and Zn adsorption 23

Table 2.9 Comparison of maximum adsorption capacity on different adsorbents 23

Table 2.10 Influence of zeolite particle size on Cu^{2+} removal 26

Table 2.11 Effect of grain size fractions on Zn^{2+} uptake 26

Table 2.12 Natural zeolite as adsorbent to remove Cu^{2+} and Zn^{2+} in previous studies 30

Table 2.13 The effect of contact time and temperature on Cu^{2+} adsorption by volcanic tuff 30

Table 3.1 Calculation for the preparation of 100 mL of binary metal working solutions 34

Table 3.2 Calculation for the preparation of 100 mL copper and zinc working solutions 35

Table 3.3 Calculation for the preparation of 100 mL copper and zinc standard solutions 35

Table 3.4 Experimental design for effect of contact time on adsorption by volcanic tuff and activated carbon 37

Table 3.5	Experimental design for effect of initial metal concentration on adsorption by volcanic tuff and activated carbon	38
Table 3.6	Parameters for AAS instrument	38
Table 4.1	Pseudo – first order, pseudo – second order and intraparticle diffusion parameters for Cu ion and Zn ion adsorption by volcanic tuff and natural zeolite	50
Table 4.2	Langmuir and Freundlich isotherm constants for Cu and Zn adsorption by volcanic tuff and natural zeolite	60
Table 4.3	Comparison of maximum adsorption capacity on various adsorbents	60

FIGURE LIST

		Page
Figure 2.1	Interaction between an adsorbent and an adsorbate	11
Figure 2.2	The influences of pH value on Cu (II) removal	13
Figure 2.3	Equilibrium time for the adsorption of Zn (II) on Ermenek fly ash	15
Figure 2.4	Various steps involved in adsorption process	16
Figure 2.5	Effect of initial concentration on adsorption of Cu (II) onto teawaste	20
Figure 2.6	Effect of adsorbent dosage on the adsorption of Cu (II) onto expended perlite	24
Figure 2.7	Effect of fly ash dosage on the adsorption of Zn (II) metal ion	25
Figure 2.8	Effect of pH on the adsorption of Cu (II) onto spent activated carbon	28
Figure 2.9	Effect of pH on the adsorption of Zn (II) by Ermenek fly ash	28
Figure 2.10	Crystal structure of clinoptilolite	29
Figure 2.11	The influence of pH upon the ammonium adsorption onto volcanic tuff	31
Figure 2.12	The influence of initial ammonium concentration upon removal efficiency in single, three and multicomponent solutions	31
Figure 3.1	Volcanic tuff	32
Figure 3.2	A mock calibration curve of metal solution	39
Figure 4.1	Effect of contact time on the Cu adsorption by volcanic tuff	41
Figure 4.2	Effect of contact time on the Zn adsorption by volcanic tuff	41
Figure 4.3	Effect of contact time on the Cu adsorption by natural zeolite	42
Figure 4.4	Effect of contact time on the Zn adsorption by natural zeolite	42
Figure 4.5	Pseudo – first order kinetic plot for Cu adsorption by volcanic tuff	44
Figure 4.6	Pseudo – second order kinetic plot for Cu adsorption by volcanic tuff	44

Figure 4.7	Pseudo – first order kinetic plot for Zn adsorption by volcanic tuff	45
Figure 4.8	Pseudo – second order kinetic plot for Zn adsorption by volcanic tuff	45
Figure 4.9	Pseudo – first order kinetic plot for Cu adsorption by natural zeolite	46
Figure 4.10	Pseudo – second order kinetic plot for Cu adsorption by natural zeolite	46
Figure 4.11	Pseudo – first order kinetic plot for Zn adsorption by natural zeolite	47
Figure 4.12	Pseudo – second order kinetic plot for Zn adsorption by natural zeolite	47
Figure 4.13	Intraparticle diffusion kinetic plot for Cu adsorption by volcanic tuff	48
Figure 4.14	Intraparticle diffusion kinetic plot for Zn adsorption by volcanic tuff	48
Figure 4.15	Intraparticle diffusion kinetic plot for Cu adsorption by natural zeolite	49
Figure 4.16	Intraparticle diffusion kinetic plot for Zn adsorption by natural zeolite	49
Figure 4.17	Intraparticle diffusion kinetic plot for Cu adsorption by volcanic tuff	51
Figure 4.18	Intraparticle diffusion kinetic plot for Zn adsorption by volcanic tuff	51
Figure 4.19	Intraparticle diffusion kinetic plot for Cu adsorption by natural zeolite	52
Figure 4.20	Intraparticle diffusion kinetic plot for Zn adsorption by natural zeolite	52
Figure 4.21	Cu and Zn removal by volcanic tuff at different initial metal concentrations	54
Figure 4.22	Amount of Cu and Zn adsorbed on volcanic tuff at different initial metal concentrations	54
Figure 4.23	Cu and Zn removal by natural zeolite at different initial metal	

concentrations 55
Figure 4.24 Amount of Cu and Zn adsorbed on natural zeolite at different initial metal concentrations 55
Figure 4.25 Cu adsorption isotherm for volcanic tuff and natural zeolite 56
Figure 4.26 Zn adsorption isotherm for volcanic tuff and natural zeolite 56
Figure 4.27 Langmuir isotherm plot for Cu and Zn adsorption by volcanic tuff 58
Figure 4.28 Freundlich isotherm plot for Cu and Zn adsorption by volcanic tuff 58
Figure 4.29 Langmuir isotherm plot for Cu and Zn adsorption by natural zeolite 59
Figure 4.30 Freundlich isotherm plot for Cu and Zn adsorption by natural zeolite 59
Figure 4.31 Cation exchange between Cu or Zn and cation zeolite 61
Figure 4.32 Cu and Zn removal by volcanic tuff at different initial binary metal concentrations 63
Figure 4.33 Cu and Zn removal by natural zeolite at different initial binary metal concentrations 63

SYMBOL, ABBREVIATION AND UNIT LIST

Cu	Copper
Zn	Zinc
Cr	Chromium
Pb	Plumbum
Hg	Mercury
^{o}C	Degree Celsius
%	Percentage
μg/mL	Microgram per milliliter
mg/L	Milligram per liter
$CuSO_4.5H_2O$	Copper sulphate pentahydrate
$ZnSO_4.7H_2O$	Zinc sulphate heptahydrate
mL	Milliliter
g	Gram
AAS	Atomic absorption spectrometry
min	minute
rpm	rate per minute
nm	nanometer
mm	millimeter
ng/mL	nanogram per millimeter
g/cm^3	Gram per centimeter cube
HDL	High density lipoprotein
LDL	Low density lipoprotein

CHAPTER 1

INTRODUCTION

1.1 Context and Relevance of Study

Many industries, including the electroplating, metal finishing, metallurgical, tannery, chemical manufacturing, mining, and battery manufacturing, produce aqueous effluents containing heavy metal contaminants (Lin *et al.*, 2000). Discharge of such wastewater can cause adverse impacts to the environment. The excessive presence of heavy metals in streams and lakes has been responsible for several health problems with animals, plants and human beings. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders (Barros *et al.*, 2004). Heavy metals such as Cr, Cu, Pb, Hg etc. are known to be toxic to humans (Taty – Costodes *et al.*, 2003).

In order to control heavy metal pollution, industrial effluents need to be treated prior to discharge to the environment. Various techniques have been used to reduce heavy metal concentration from wastewater; the most common ones are chemical precipitation, membrane filtration, ion – exchange, electrolytic methods, chemical coagulation, and adsorption (Khazali *et al*., 2007). Many of these methods suffer from some drawbacks such as incomplete metal removal, high capital and operational costs and problem of disposal of residual metal sludge.

Adsorption is one of the preferred methods for metal removal. This method involves the use of adsorbents such as natural zeolite (Khazali *et al*., 2007), crab shell (Kim, 2003), synthetic zeolite (Hui *et al*., 2005), activated carbon (Machida *et al*., 2005), holly oak (Prasad & Freitas, 2000), wheat bran (Bulut & Baysal, 2006), animal bones (Al – Asheh *et al*., 1999), rice husk (Ajmal *et al*., 2003), rock (Sarı *et al*., 2007) and clay (Benhammou *et al*., 2005). However, some of these are relatively expensive for practical use, thus currently there is an increasing interest on cheap and easily available adsorbents (Aydın *et al*., 2008).

Volcanic tuff is volcanic ash which settled and forms a rock after explosive volcanism. It comprises a mixture of crystal fragments, bits of lava and pyroclastic rock, and volcanic glass. This material is well known for its high selectivity in removing ammonium from aqueous solution (Marañón *et al*., 2006). However there are not many studies at present on heavy metals removal by volcanic tuff (Mihaly – Cozmuta *et al*., 2005).

1.2 Research Objectives

The objectives of this study were:

(a.) To determine the kinetics of copper and zinc adsorption by volcanic tuff.

(b.) To determine the equilibrium of copper and zinc adsorption by volcanic tuff.

(c.) To compare copper and zinc removal efficiency by volcanic tuff with that by natural zeolite.

1.3 Scope of Study

The study focused on volcanic tuff samples obtained from Tabin in Lahad Datu, Sabah. Batch adsorption studies were carried out to investigate the effect of contact time and initial metal concentration on heavy metals removal from aqueous solution using the volcanic tuff sample. For comparison, similar studies were carried out using granular activated carbon as the adsorbent. The final zinc and copper concentrations in solutions were determined spectrophotometrically.

CHAPTER 2

LITERATURE REVIEW

2.1 Copper and Zinc

2.1.1 General chemistry of copper and zinc

Copper is a reddish coloured transition metal which occupies the *d* block in the periodic table. It has the symbol Cu and an atomic number of 29. It is malleable, ductile and a good conductor of heat and electricity. It has an atomic weight of 63.546, a melting point of 1083°C, a specific gravity of 8.96 and exhibit both +1 and +2 oxidation state. The average crustal abundance was found to be of 55 – 75 μg/g (Silberberg, 2003).

Zinc is a bluish – white transition metal which occupies the *d* block in the periodic table. It has the symbol Zn and an atomic number of 30, atomic mass of 65.39, density of 7.14 g/cm^3, melting point of 419.6 °C, boiling point of 907 °C and only exhibit the +2 oxidation state. It has five stable isotopes namely (^{64}Zn, 48.6 %; ^{66} Zn, 27.9 %; ^{67} Zn, 4.1 %; ^{68} Zn, 18.8 %; ^{70} and Zn, 0.6 %). Zinc is amphoteric, it reacts both with acids and alkalis (Marshall & Fairbridge, 1999).

2.1.2 Sources of copper and zinc

a. Natural sources

Geochemical processes (including weathering of parent materials) and other natural processes (eg. volcanoes, forest fires and sea salt spraying) continuously release copper and zinc into the environment (Cunningham *et al.*, 1998). Table 2.1 shows examples of rocks or mineral ores that mainly contain Cu and Zn.

Table 2.1 Parent materials that can be subjected to weathering and release Cu and Zn.

Copper		**Zinc**	
Rock	Mineral ore	Rock	Mineral ore
Shale	Chalcocite (Cu_2S)	Dolomite	Sphalerite (cubic ZnS)
Sandstone	Chalcopyrite ($CuFeS_2$)	Volcanic rock	Wurtzite (hexagonal ZnS)
Gabbro	Malachite ($Cu_2(OH)_2CO_3$)	Limestone	Smithsonite (trigonal $ZnCO_3$)
–	Azurite ($Cu_3(OH)_2CO_3$)	–	Hemimorphite ($Zn_4Si_2O_7(OH)_2$)

(Sources: Marshall & Fairbridge, 1999; Zaw *et al.*, 2007) *b. Anthropogenic sources*

Since copper and zinc are widely used in the industries, there are a number of potential anthropogenic sources of these heavy metals (Table 2.2). The concentration of the respective metal, however, is dependent on the type of source.

Table 2.2 Anthropogenic source of Cu and Zn to the environment.

Heavy metal	Industry
Copper	Mining
	Textile
	Electroplating
	Metal cleaning
	Paper & pulp
	Fertilizer
	Petroleum refining
Zinc	Mining
	Alkaline battery
	Manufacturing (acrylic fiber, rayon, cellophane and special synthetic rubber)
	Automobile
	Agricultural (pesticides / pesticides)
	Pigments
	Metal plating

(Sources: Rao *et al*., 2006; Sarı *et al*., 2007)

2.1.3 Environmental and health impacts of copper and zinc

The presence of elevated levels of copper, besides causing damage to plants and reducing crops production of farmlands, can result in health effects such as liver and kidney failure or Wilson's disease (NINDS, 2007). Prolonged inhalation of copper-containing sprays is linked with an increase in lung cancer among exposed workers (Yu *et al.*, 2000). Excessive intake of copper results in hemochromatosis and gastrointestinal catarrh diseases because it accumulates in the livers of human and animals (Sarı *et al.*, 2007).

At acidic pH values, zinc toxicity to plants is the third most common after aluminium and manganese (Robson, 1993). Excessive intake of zinc by humans can lead to increased LDL and decreased HDL cholesterol, impaired immune system, nausea, vomiting, impaired copper absorption (Williams, 2005).

2.1.4 Wastewater discharge and drinking water quality standards

Industrial effluents or wastewaters can be significant contributors towards increased heavy metals in environment. Environmental regulations enforced worldwide require wastewaters to be treated prior to discharge. In Malaysia, the discharge standard and limits are specified under Enviromental Quality Act 1974, especially in Environmental Quality (Sewage and Industrial Effluents) Regulations 1979 (Table 2.3). An identical value of 2 mg/L is set for zinc in both Standard A and Standard B. A higher value of zinc compared to that of copper is due to the fact that zinc is more toxic than copper. A more stringent and lower limit is set in Standard A since this standard is applicable to water that discharges into catchment areas for human consumption, whereas Standard B only applicable to inland water that are not for human consumption. Meanwhile the maximum permissible concentration of copper in drinking water according to World Health Organization is 2.0 mg/l, while no value was specified for zinc (Table 2.4).

2.2 Wastewater Treatment Methods

In order to control environmental degradation as well to conform to discharge standards, wastewaters need to be treated prior to discharge. Current treatment technologies include adsorption (Amarasinghe & Williams, 2007), ion exchange (Ören & Kaya, 2006; Stylianou *et al.*, 2007), reverse osmosis (Qdais & Moussa, 2004), chemical precipitation (Mauchauffée & Meux, 2007) and electrodialysis (Bruggen & Vandecasteele, 2002).

2.2.1 Adsorption

Adsorption involves the interaction of a solid material with ions or molecules present in solution. The molecule or ion that binds to the surface of the solid is called adsorbate, while the solid is called absorbent (Figure 2.1). The interaction may involves a weak van der waal's forces (i.e. physisorption) or strong chemical bonds (i.e. chemisorption).

REFERENCES

Ahmed, S., Chughtai, S. & Keane, M. A. 1998. The removal of cadmium and lead from aqueous solution by ion exchange with Na – Y zeolite. *Separation and Purification Technology* **13**, 57 – 64.

Ajmal, M., Rao, R. A. K., Anwar, S., Ahmad, J. & Ahmad, R. 2003. Adsorption studies on rice husk: removal and recovery of Cd (II) from wasterwater. *Bioresource Technoloy* **86**, 147 – 149.

Al – Asheh, S., Banat, F. & Mohai, F.1999. Sorption of copper and nickel by spent animal bones. *Chemosphere* **39**, 2087 – 2096

Amarasinghe, B. M. W. P. K. & Williams, R. A. 2007. Tea waste as low cost adsorbent for the removal of Cu and Pb from wastewater. *Chemical Engineering Journal* **132**, 299 – 309.

Anghel, I., Turin, H. J. & Reimus, P. W. 2002. Lithium sorption to Yucca Mountain tuffs. *Applied Geochemistry* **17**, 819 – 824.

Argun, M. E., Dursun, S., Ozdemir, C. & Karatas, M. 2007. Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. *Journal of Hazardous Materials* **141**, 77 – 85.

Aydın, H., Bulut, Y. & Yerlikaya, Ç. 2008. Removal of copper (II) from aqueous solution by adsorption onto low – cost adsorbents. *Journal of Environment Management* **87**, 37 – 45.

Álvarez – Ayuso, E., García – Sánchez, A. & Querol, X. 2003. Purification of metal electroplating waste waters using zeolites. *Water Research* **37**, 4855 – 4862.

Barros, M. A. S. D., Silva, E. A., Arroyo, P. A., Tavares, C. R. G., Schneider, R. M., Suszek, M. & Sousa – Aguiar, E. F. 2004.Removal of Cr (III) in the fixed bed column and batch reactors using as adsorbent zeolite NaX. *Chemical Engineering Science* **59**, 5959 – 5966.

Bedelean, H., Stanca, M., Măicăneanu, A. & Burcă, S. 2006. Zeolitic volcanic tuffs from Măcicaş (Cluj County), natural raw materials used for NH^{4+} removal from wastewaters. *Geologia* **51**, 43 – 49.

Benhammou, A., Yaacoubi, A., Nibou, L. & Tanouti, B. 2005. Adsorption of metal ions onto Moroccan stevensite: kinetic and isotherm studies. *Journal of Colloid and Interface Science* **282**, 320 – 326.

Bosso, S. T. & Enzweiler, J. 2002. Evaluation of heavy metal removal from aqueous solution onto scolecite. *Water Research* **36**, 4795 – 4800.

Bruggen, B. & Vandecasteele C. 2002. Distillation vs. membrane filtration : overview of process evolutions in seawater desalination. *Desalination* **143**, 207 – 218.

Bulut, Y. & Baysal, Z. 2006. Removal of Pb(II) from wasterwater using wheat bran. *Journal of Environmental Management* **78**, 107 – 113.

Cesur, H. & Nilgün, B. 2007. Zinc removal from aqueous solution using an industrial by – product phosphogypsum. *Chemical Engineering Journal* **131**, 203 – 208.

Cetin, P. & Pehlivan, E. 2007. The use of fly ash as a low cost, environmentally friendly alternative to activated carbon for the removal of heavy metals from aqueous solutions. *Colloid and Surfaces* **298**, 83 – 87.

Chakravarty, S., Bhattacharjee, S. Gupta, K. K., Singh, M., Chaturvedi, H. T. & Maity, S. 2007. Adsorption of zinc from aqueous solution using chemically treated newspaper pulp. *Bioresource Technology* **98**, 3136 – 3141.

Corami, A., Mignardi, S. & Ferrini, V. 2007. Copper and zinc decontamination from single- and binary-metal solutions using hydroxyapatite. *Journal of Hazardous Materials* **146**, 164 – 170.

Cunningham, W. P., Cooper, T. H., Gorham, E. & Hepworth, M. T. (eds). 1998. *Environmental Encyclopedia.* 2nd ed. Gale Research, Detroit.

Deliyanni, E. A. & Peleka, E. N. & Matis, K. A. 2007. Removal of zinc ion from water by sorption onto iron – based nanoadsorbent. *Journal of Hazardous Materials* **141**, 176 – 184.

Du, Q., Liu, S., Cao, Z. & Wang, Y. 2005. Ammoia removal from aqueous solution using natural Chinese clinoptilolite. *Separation and Purification Technology* **44**, 229 – 234.

El – Kamash, Zaki, A. A. & El – Geleel, M. A. 2005. Modeling batch kinetics and thermodynamics of zinc and cadmium ions removal from waste solutions using synthetic zeolite A. *Journal of Hazardous Materials* **B 127**, 211 – 220.

Gilluly, J., Waters, A. C. & Woodford, A. O. 1975. *Principles of Geology*. 4th ed. W. H. Freeman & Company, San Francisco.

Hui, K. S., Chao, C. Y. H. & Kot, S. C. 2005. Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash. *Journal of Hazardous Materials* **B 127**, 89 – 101.

Inglezakis, V. J., Loizidou, M. D. & Grigoropoulou, H. P. 2002. Equilibrium and kinetic ion exchange studies of Pb^{2+}, Cr^{3+}, Fe^{3+} and Cu^{2+} on natural clinoptilolite. *Water Research* **36**, 2784 – 2792.

Khazali O., Abu – El – Halawa R. & Al – Sou'od K. 2007. Removal of copper (II) from aqueous solution by Jordanian pottery materials. *Journal of Hazardous Materials* **B 139**, 67 – 71.

Kim, D. S. 2003.The removal by crab shell of mixed heavy metal ions in aqueous solution. *Bioresource Technology* **87**, 355 – 357.

Kocaoba, S., Orhan, Y. & Akyüz, T. 2007. Kinetics and equilibrium studies of heavy metal ions removal by use of natural zeolite. *Desalination* **214**, 1 – 10.

Kurniawan, T. A., Chan, G. Y. S., Lo, W. H. & Babel, S. 2006. Physico-chemical treatment techniques for wastewater laden with heavy metals. *Chemical Engineering Journal* **118**, 83 – 98.

Li, Y., Zeng, X., Liu, Y., Yan, S., Hu, Z. & Ni, Y. 2003. Study on the treatment of copper – electroplating wastewater by chemical trapping and flocculation. *Separation and Purification Technology* **31**, 91 – 95.

Lin, S. H., Lai, S. L. & Leu, H. G. 2000. Removal of heavy metals from aqueous solution by chelating resin in a multistage adsorption process. *Journal of Hazardous Materials* **B76**, 139 – 153.

Lind, B., Ban, Z. & Bydén, S. 2000. Nutrient recovery from human urine by struvite crystallization with ammonia adsorption on zeolite and wollastonite. *Bioresource Technology* **73**, 169 – 171.

Liu, C. & Bai, R. 2006. Adsorptive removal of copper ions with highly porous chitosan/cellulose acetate blend hollow fiber membranes. *Journal of Membrane Science* **284**, 313 – 322.

Machida, M., Aikawa, M & Tatsumoto, H. 2005. Prediction of simultaneous adsorption of Cu(II) and Pb(II) onto activated carbon by conventional Langmuir type equations. *Journal of Hazardous Materials* **B120**, 271 – 275.

Malaysia. 2006. *Environmental Quality Act 1974 (Revised 2006) (Act 127)*. MDC Sdn.Bhd, Kuala Lumpur.

Marañón, E., Ulmanu, M., Fernández, Y., Anger, I. & Castrillón, L. 2006. Removal of ammonium from aqueous solutions with volcanic tuff. *Journal of Hazardous Material* **B 137**, 1402 – 1409.

Marshall, C. P. & Fairbridge, R. W. (eds). 1999. *Encyclopedia of Geochemistry*. Kluwer Academic Publishers, Dordrecht.

Mauchauffée, S. & Meux, E. 2007. Use of sodium decanoate for selective precipitation of metals contained in industrial wastewater. *Chemosphere* **69**, 763 – 768.

Meunier, N., Drogui, P., Montané, C., Hausler, R., Mercier, G. & Blais, J. 2006. Comparison between electrocoaggulation and chemical precipitation for metals removal from acidic soil leachate. *Journal of Hazardous Materials* **B 137**, 581 – 590.

Mihaly – Cozmuta, L., Visan, T., Mihaly – Cozmuta, A., Varga, C., Viman, V. & Vatca, G. 2005. Energetic aspects related to heavy metals adsorption on the surface of volcanic tuff: I. The influence of activation parameters in Cu^{2+} adsorption. *American Journal of Environmental Science* **1(2)**, 159 – 163.

National Institute of Neurological Disorders and Stroke. 2007. *NINDS Wilson's Disease Information Page.* Retrieved 10 October 2007 from http://www.ninds.nih.gov/disorders/wilsons/wilsons.htm.

Ok, Y. S., Yang, J. E., Zhang, Y. S., Kim, S. J. & Chung, D. Y. 2007. Heavy metal adsorption by a formulated zeolite – Portland cement mixture. *Journal of Hazardous Materials* **147**, 91 – 96.

Ören, A. H. & Kaya, A. 2006. Factors affecting adsorption characteristics of Zn^{2+} on two natural zeolites. *Journal of Hazardous Materials* **B 131**, 59 – 65.

Panayotova , M. I. 2001. Kinetics and thermodynamics of copper ions removal from wastewater by use of zeolite. *Waste Management* **21**, 671 – 676.

Perić, J., Trgo, M. & Medvidović, N. V. 2004. Removal of zinc, copper and lead by natural zeolite – a comparison of adsorption isotherms. *Water Research* **38**, 1893 – 1899.

Pitcher, S. K., Slade, R. C. T. & Ward, N. I. 2004. Heavy metal removal from motorway stormwater using zeolites. *Science of the Total Environment* **334 – 335**, 161 – 166.

Prasad, M. N. V. & Freitas, H. 2000. Removal of toxic metals from solution by leaf, stem and root phytomass of *Quercus ilex* L. (holly oak). *Environmental Pollution* **110**, 277 – 283.

Qdais, H. A. & Moussa, H. 2004. Removal of heavy metals from wastewater by membrane processes: a comparative study. *Desalination* **164,** 105 – 110.

Rao, C. G. P., Satyaveni, S., Ramesh, A., Seshaiah, K., Murthy, K. S. N. & Choudary, N. V. 2006. Sorption of cadmium and zinc from aqueous solutions by zeolite 4A, zeolite 13X and bentonite. *Journal of Environmental Management* **81**, 265 – 272.

Robson, A. D. (eds). 1993. *Zinc in Soils and Plants*. Kluwer Academic Publishers, Dordrecht.

Sarı, A., Tuzen, M., Cıtak, D. & Soylak, M. 2007.Adsorption characteristics of Cu(II) and Pb(II) onto expanded perlite from aqueous solution. *Journal of Hazardous Material* **148**, 387 – 394.

Sheta, A. S., Falatah, A. M., Al – Sewailem, M. S., Khaled, E. M. & Sallam, A. S. H. 2003. Sorption characteristics of zinc and iron by natural zeolite and bentonite. *Microporous and Mesoporous Materials* **61**, 127 – 136.

Silberberg, M. S. 2003.*Chemistry: The Molecular Nature of Matter and Change*. 3rd ed. McGraw – Hill, New York.

Stylianou, M. A., Hadjiconstantinou, M.P., Inglezakis, V. J., Moustakas, K. G. & Loizidou, M. D. 2007. Use of natural clinoptilolite for the removal of lead, copper and zinc in fixed bed column. *Journal of Hazardous Materials* **143**, 575 – 581.

Šćiban, M., Radetić, B., Kevrešan, Ž. & Klašnja, M. 2007. Adsorption of heavy metals from electroplating wastewater by wood sawdust. *Bioresource Technology* **98**, 402 – 409.

Taty – Costodes, V. C., Fauduet, H., Porte, C. & Delacroix, A. 2003. Removal of Cd (II) and Pb (II) ions, from aqueous solutios, by adsorption onto sawdust of *Pinus sylvestris*. *Journal of Hazardous Materials* **B105**, 121 – 142.

Üçer, A. Uyanik, A. & Aygün, Ş, F. 2006. Adsorption of Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III) ions by tannic acid immobilized activated carbon. *Separation and Purification Technology* **47**, 113 – 118.

Veli, S. & Alyüz, B. 2007. Adsorption of copper and zinc from aqueous solutions by using natural clay. *Journal of Hazardous Materials* **149**, 226 – 233.

Wang, Y., Liu, S., Xu, Z., Han, T., Chuan, S. & Zhu, T. 2006. Ammonia removal from leachate solution using natural Chinese clinoptilolite. *Journal of Hazardous Materials* **B 136**, 735 – 740.

Weng, C. H., Tsai, C. Z., Chu, S. H. & Sharma, Y. C. 2007. Adsorption characteristics of copper (II) onto spent activated clay. *Separation and Purification Technology* **54**, 187 – 197.

Williams, M. H. 2005. *Nutrition for Health, Fitness, & Sport*. 7^{th} ed. McGraw – Hill, New York.

World Health Organization. 2006. *Guidelines for Drinking – water Quality: incorporating first addendum*. Vol 1. 3rd ed. World Health Organization, Geneva.

Yu, B., Zhang, Y., Shukla, A., Shukla, S. S. & Dorris, K. L. 2000. The removal of heavy metal from aqueous solutions by sawdust adsorption – removal of copper. Journal of *Hazardous Materials* **B80**, 33 – 42.

Zaw, K., Peters, S. G., Cromie, P. Burrett, C. & Hou, Z. 2007. Nature, diversity of deposit types and metallogenic relations of South China. *Ore Geology Reviews* **31**, 3 – 47.