

**COMPARATIVE STUDY ON THE ADSORPTION OF
HEAVY METAL IONS BY KAOLIN, SAND, ACTIVATED
CARBON AND THEIR ADMIXTURES**



TAN WEI HSIANG

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**FACULTY OF SCIENCE AND NATURAL RESOURCES
UNIVERSITI MALAYSIA SABAH
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**THISIS SUBMITTED IN FULLFILLMENT
OF THE REQUIREMENT FOR DEGREE OF
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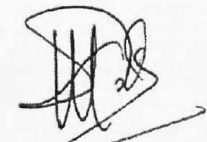
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DECLARATION

I hereby declare that the material in this thesis is my own except for quotations, excerpts, equations, summaries and references, which have been duly acknowledged.

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ABSTRACT

Heavy metals contaminant has been widely spread to the environment. Soils have been noted as a source for heavy metals accumulation or released to the environment. Adsorption was found to be the most important process that responsible for accumulation of heavy metals in soils. This study evaluates the adsorption of selected heavy metals Cu^{2+} , Pb^{2+} and Zn^{2+} onto the adsorbents that are clay, sand, activated carbon, field soil and their mixture composition for the purposes to determine their adsorption isotherms in competitive and non-competitive system. Physiochemical properties of adsorbents were characterized by BET, pycnometer, particles size analyzer, XRD and XRF. Langmuir Isotherm Model based on Pseudo Ideal Monolayer Theory and directly interpreted from excess adsorption isotherm and also Freundlich Model were the adsorption isotherm applied in this present work. The experimental data are well fitted with Langmuir Isotherm Model based on Pseudo Ideal Monolayer Theory and directly interpreted from excess adsorption isotherm with the significant correlation coefficient R^2 (above 0.85). However, the value of Pseudo Ideal Monolayer Theory adsorption capacity ($\times 10^{-7}\text{mg/g}$) is small in comparison with directly interpreted from excess adsorption isotherm ($\times 10^{-3}\text{mg/g}$) due to in Pseudo Ideal Monolayer model, all aqueous speciation was accounted in analysis adsorption isotherm which is totally different from the past research. This study reveals that the mixture of composition contains more clay and activated carbon, respectively increases the adsorption capacity. Eg., clay and sand at ratio 50%:50% to 90%:10%, the adsorption capacity towards Cu^{2+} increase from 0.727mg/g to 2.042mg/g; activated carbon and clay at ratio 10%:90% to 70%:30%, the adsorption capacity towards Cu^{2+} increase from 2.324mg/g to 4.227mg/g. High cation exchange capacity and surface area in activated carbon (90cmol/kg, 621.86m²/g) possesses higher adsorption capacity than clay (13.75cmol/kg, 16.59m²/g) and sand (0.21cmol/kg, 0.57m²/g). The descending adsorption capacities of adsorbents in this study are as the following: activated carbon>clay>sand. The adsorption capacity of field soil toward Cu^{2+} ($5.953 \times 10^{-4}\text{mg/g}$) was more than four times higher than the field soil without organic matter ($1.438 \times 10^{-4}\text{mg/g}$). The adsorption capacities of adsorbents in non-competitive adsorption also found to be higher than the competitive adsorption due to the number of adsorption sites are fixed on the surface of adsorbent whereas heavy metal ions needed to compete in adsorbing onto the adsorption sites. Overall, the adsorption capacity in all types of adsorbents show the same pattern of heavy metals adsorption with $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$. The selectivity of adsorbents toward Pb^{2+} ions is higher than Cu^{2+} and Zn^{2+} as it is influence by the first hydrolysis constant, ionic radius and hydration energy value of heavy metal. The comparison of application on linear and non-linear regression indicates the non-linear regression method providing much more consistent and reliable results (overall correlation coefficients R^2 are above 0.9). In dynamic simulation of adsorption, the presence of clay in the mixed composition of clay and sand proportionally enhances the breakthrough time of Pb^{2+} , Cu^{2+} and Zn^{2+} . The presence of organic matter in soil was also indicates that the adsorption capacity of soil increases by prolonging the breakthrough time of heavy metal. Similarly, in the binary competitive and ternary competitive heavy metal transport, Pb^{2+} shows strong adsorbate characteristics onto clay and sand compared with Cu^{2+} and Zn^{2+} . Therefore, it is suggested this simulation should be extended to type of soil

components which is very close or matching to the real soil texture and composition.



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ABSTRAK

KAJIAN PERBANDINGAN TERHADAP PENYERAPAN ION LOGAM BERAT OLEH KAOLIN, PASIR, KARBON AKTIF DAN CAMPURANNYA

Bahan cemar logam berat telah tersebar meluas ke persekitaran. Tanah telah bertindak sebagai satu sumber penggumpulan logam berat atau dilepaskan ke persekitaran. Penjerapan didapati sebagai penyumbang utama dalam pengumpulan logam berat di tanah. Kajian ini menilai penjerapan logam berat terpilih Cu^{2+} , Pb^{2+} dan Zn^{2+} ke atas penjerap iaitu tanah liat, pasir, karbon aktif, tanah lapangan dan komposisi campurannya untuk tujuan menentukan isoterma penjerapan mereka dalam sistem kompetitif dan tidak kompetitif. Sifat fisiokimia penjerap dicirikan dengan menggunakan BET, fiknometer, penganalisis saiz zarah, XRD dan XRF. Model Langmuir Isoterma berdasarkan Teori Pseudo Ideal Lapisan Tunggal dan taksiran langsung dari isoterma penjerapan berlebihan dan juga Model Freundlich adalah isoterma penjerapan yang diterapkan dalam kerja penyelidikan ini. Data eksperimen adalah berpadanan dengan Teori Pseudo Ideal Lapisan Tunggal dan taksiran secara langsung dari isoterma penjerapan berlebihan dengan pekali korelasi R^2 (melebihi 0.85) yang signifikan. Namun nilai kapasiti penjerapan Teori Pseudo Ideal Lapisan Tunggal ($\times 10^7 \text{mg/g}$) kecil berbanding dengan yang ditafsirkan secara langsung dari isoterma penjerapan berlebihan ($\times 10^3 \text{mg/g}$) kerana dalam Teori Pseudo Ideal Lapisan Tunggal, semua spesies akueus diambilkira dalam analisis isoterma penjerapan yang berbeza sama sekali dengan penyelidikan terdahulu. Kajian ini mendedahkan kapasiti penjerapan meningkat dengan campuran komposisi yang mengandungi lebih banyak tanah liat dan karbon aktif. Contoh, tanah liat dan pasir pada nisbah 50%: 50% hingga 90%: 10%, kapasiti penjerapan ke arah Cu^{2+} meningkat daripada 0.727mg/g kepada 2.042mg/g; karbon teraktif dan tanah liat pada nisbah 10%: 90% hingga 70%: 30%, kapasiti penjerapan ke arah Cu^{2+} meningkat daripada 2.324mg/g kepada 4.227mg/g. Kapasiti pertukaran kation dan luas permukaan karbon teraktif yang lebih tinggi (90cmol/kg, 621.86m²/g) memiliki kapasiti penjerapan yang lebih besar daripada tanah liat (13.75cmol/kg, 16.59m²/g) dan pasir (0.21cmol/kg, 0.57m²/g). Urutan menurun kapasiti penjerapan penyerap dalam kajian ini adalah karbon aktif > tanah liat > pasir. Kapasiti penjerapan tanah lapangan ke arah Cu^{2+} ($5.953 \times 10^4 \text{mg/g}$) adalah lebih daripada empat kali ganda lebih tinggi daripada tanah lapangan tanpa bahan organik ($1.438 \times 10^4 \text{mg/g}$). Kapasiti penjerapan bagi penjerap dalam penjerapan tanpa persaingan juga didapati lebih tinggi daripada penjerapan persaingan kerana jumlah laman penjerapan pada permukaan penjerap ada tetap sedangkan ion logam berat perlu bersaing untuk menjerap ke laman penjerapan. Secara keseluruhan kapasiti penjerapan dalam semua jenis penjerap menunjukkan corak yang sama iaitu $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$. Pemilihan penjerap terhadap Pb^{2+} adalah lebih tinggi daripada Cu^{2+} dan Zn^{2+} kerana dipengaruhi oleh pada pemalar hidrolisis pertama, jejari ion dan nilai tenaga penghidratan logam berat. Perbandingan dalam aplikasi regresi linear dan tidak linear menunjukkan kaedah regresi tidak linear memberikan hasil yang jauh lebih konsisten dan boleh dipercayai (pekali korelasi keseluruhan R^2 berada di atas 0.9). Dalam simulasi penjerapan dinamik, kehadiran tanah liat dalam komposisi campuran tanah liat dan pasir meningkat secara berkadar masa pengekal Cu^{2+} , Pb^{2+} dan Zn^{2+} . Kehadiran

bahan organik di dalam tanah juga menunjukkan bahawa kapasiti penjerapan tanah meningkat dengan menunda masa pengekalan logam berat. Begitu juga, dalam pengangkutan logam berat berdaya saing binari dan terneri, Pb^{2+} menunjukkan ciri penjerap yang kuat dengan tanah liat dan pasir berbanding dengan Cu^{2+} dan Zn^{+} . Oleh itu, adalah disarankan agar simulasi ini dilanjutkan kepada jenis komponen tanah yang sangat dekat atau padan dengan komponen tanah yang sebenarnya.



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LIST OF CONTENTS

| | Page |
|--|------|
| TITLE | i |
| DECLARATION | ii |
| CERTIFICATION | iii |
| ACKNOWLEDGEMENT | vi |
| ABSTRACT | v |
| ABSTRAK | vii |
| LIST OF CONTENTS | ix |
| LIST OF TABLES | xiv |
| LIST OF FIGURES | xvii |
| LIST OF APPENDICES | xix |
| | |
| CHAPTER 1: INTRODUCTION | |
| 1.1 Background of the Study | 1 |
| 1.2 Problem Statement | 5 |
| 1.3 Hypotheses of Study | 7 |
| 1.4 Objectives of Studies | 7 |
| 1.5 Scope of Study | 8 |
| 1.6 Importance of the Study | 9 |
| 1.7 Thesis Outline | 9 |
| | |
| CHAPTER 2: LITERATURE REVIEW | |
| 2.1 Introduction | 11 |
| 2.2 Environmental Impacts of Heavy Metals | 12 |
| 2.3 Treatment of Heavy Metals | 14 |
| 2.3.1 Chemical Precipitation on Removal of Heavy Metals from Water | 14 |
| 2.3.2 Ion Exchange on Removal of Heavy Metals from Water | 15 |

| | | |
|--------|--|----|
| 2.3.3 | Coagulation and Flocculation on Removal of Heavy Metals from Water | 16 |
| 2.3.4 | Filtration on Removal of Heavy Metals from Water | 17 |
| 2.3.5 | Adsorption Process on Removal of Heavy Metals from Water | 18 |
| 2.4 | Types of Adsorbents for Removal of Heavy Metals | 20 |
| 2.4.1 | Activated Carbon | 20 |
| 2.4.2 | Polymers | 21 |
| 2.4.3 | Inorganic Materials | 27 |
| 2.4.4 | Agricultural Waste Materials | 32 |
| 2.4.5 | Soils | 37 |
| 2.4.6 | Selection of Soil as Natural Adsorbent | 47 |
| 2.5 | Adsorption Equilibrium Measurement | 48 |
| 2.5.1 | Soil-column Experiment Method | 48 |
| 2.5.2 | Liquid Phase Batch Experiment Method | 49 |
| 2.6 | Adsorption Isotherm | 49 |
| 2.6.1 | Langmuir Isotherm | 52 |
| 2.6.2 | Freundlich Isotherm | 53 |
| 2.7 | Interpretation of Heavy Metal as Adsorption Isotherm | 53 |
| 2.7.1 | Directly Interpreted from Excess Adsorption Isotherm | 53 |
| 2.7.2 | Justification of Using Pseudo Ideal Monolayer Adsorption Theory | 55 |
| 2.8 | Adsorption Kinetics | 58 |
| 2.8.1 | Intra-particle Diffusion Model | 62 |
| 2.8.2 | Adsorption Kinetic in Column Adsorption Model | 62 |
| 2.9 | Simulation of Dynamic Adsorption | 64 |
| 2.10 | Theory and Mathematical Model Framework of Dynamic Adsorption | 66 |
| 2.10.1 | Theory and Underlying Assumptions | 66 |
| 2.10.2 | Governing Equation of Packed Bed Column Model | 67 |

CHAPTER 3: METHODOLOGY

| | | |
|-------|---|----|
| 3.1 | Introduction | 69 |
| 3.2 | Materials | 71 |
| 3.3 | Characterization of Adsorbents | 73 |
| 3.4 | Measurement of Excess Adsorption Isotherms | 79 |
| 3.4.1 | Contact Time on Adsorption | 79 |
| 3.4.2 | Batch Adsorption | 79 |
| 3.5 | Simulation of Column Adsorption | 83 |
| 3.5.1 | Correlations Used for Estimation of Unknown Model Input | 85 |
| 3.5.2 | Required Data for Model Input from Experiment and Correlations | 85 |
| 3.5.3 | Calculation Procedure Flow Methodology | 86 |
| 3.6 | Analysis and Interpretation of Adsorption Isotherm and Breakthrough Curve of Adsorption | 87 |

CHAPTER 4: CHARACTERIZATION OF SOIL AS ADSORBENT

| | | |
|------|--|-----|
| 4.1 | Introduction | 88 |
| 4.2 | Particle Size Distribution of Adsorbents | 88 |
| 4.3 | Surface Area Analysis of Adsorbents | 89 |
| 4.4 | X-ray Diffraction Analysis of Soil Samples | 94 |
| 4.5 | Elemental Composition of Materials in Soil Samples | 95 |
| 4.6 | Cation Exchange Capacity Analysis of Adsorbents | 97 |
| 4.7 | Soil Particle Density and Soil pH in Clay, Sand, Organic Carbon and field soil | 98 |
| 4.8 | Functional Groups Analysis of Adsorbents | 100 |
| 4.9 | Moisture Content and Organic Matter Content in Field Soil | 102 |
| 4.10 | Summary Characterization of Soil as Adsorbent | 103 |

CHAPTER 5: MEASUREMENT OF EXCESS ADSORPTION ISOTHERM

| | | |
|-----|--|-----|
| 5.1 | Introduction | 105 |
| 5.2 | Equilibrium Time in Adsorption of Cu ²⁺ onto Clay | 105 |

| | | |
|-------|---|-----|
| 5.3 | Excess Adsorption of Heavy Metals onto Soil Samples | 107 |
| 5.3.1 | Excess Adsorption in Non-Competitive of Individual Adsorption of Heavy Metals Cu^{2+} , Pb^{2+} and Zn^{2+} onto Clay and Sand | 108 |
| 5.3.2 | Excess Adsorption in Non-Competitive Adsorption of Heavy Metals onto Different Composition of Clay and Sand, Different Composition of Activated Carbon and Clay, and Field Soil | 110 |
| 5.3.3 | Excess Adsorption in Competitive Adsorption of Heavy Metals Cu^{2+} , Pb^{2+} and Zn^{2+} onto Clay and Sand | 114 |
| 5.4 | Summary of Measurement of Excess Adsorption Isotherm | 119 |

CHAPTER 6: INTERPRETATION OF ADSORPTION ISOTHERM

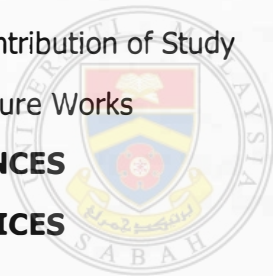
| | | |
|-------|---|-----|
| 6.1 | Introduction | 121 |
| 6.2 | Interpretation of Langmuir Isotherm Model Based on Pseudo Ideal Monolayer Adsorption Theory | 121 |
| 6.2.1 | Adsorption Isotherm of Non-Competitive of Individual Adsorption of Heavy Metals Cu^{2+} , Pb^{2+} and Zn^{2+} onto Clay and Sand | 121 |
| 6.2.2 | Adsorption Isotherm of Non-Competitive Adsorption of Heavy Metals onto Different Composition of Clay and Sand, Different Composition of Activated Carbon and Clay, and Field Soil | 127 |
| 6.2.3 | Adsorption Isotherm of Competitive Adsorption of Heavy Metals Cu^{2+} , Pb^{2+} And Zn^{2+} Onto Clay and Sand | 131 |
| 6.3 | Comparison of Langmuir Isotherm based on Pseudo Ideal Monolayer Adsorption Theory and Directly Interpreted from Excess Adsorption Isotherm | 135 |
| 6.4 | Comparison of Adsorption of Heavy Metals onto Composition Clay, Sand and Activated Carbon | 140 |
| 6.5 | Comparison of Adsorption of Heavy Metals Between Field Soil and Field Soil without Organic Matter | 143 |
| 6.6 | Comparison of Adsorption in Selectivity of Heavy Metals onto Clay and Sand | 144 |
| 6.7 | Linear and Nonlinear Regression Analysis for Competitive and Non-Competitive Adsorption of Heavy Metals onto Clay, Sand and Activated Carbon | 146 |
| 6.8 | Summary of Interpretation of Adsorption Isotherm | 151 |

CHAPTER 7: DYNAMIC ADSORPTION OF HEAVY METALS ONTO SOIL

| | | |
|-------|--|-----|
| 7.1 | Introduction | 153 |
| 7.2 | Non-Competitive System Heavy Metal Transport | 153 |
| 7.3 | Effect of Source Flowrate on Heavy Metals Retention by Soils | 156 |
| 7.4 | Competitive Binary and Ternary System Heavy Metals Transport | 160 |
| 7.4.1 | Cu(II) - Pb(II) Binary System | 160 |
| 7.4.2 | Cu(II) – Zn(II) Binary System | 162 |
| 7.4.3 | Pb(II) – Zn(II) Binary System | 164 |
| 7.4.4 | Pb(II) – Cu(II) – Zn(II) Ternary System | 166 |
| 7.5 | Summary of Dynamic Adsorption of Heavy Metals onto Soil | 168 |

CHAPTER 8: CONCLUSION

| | | |
|-------------------|-----------------------|-----|
| 8.1 | Conclusion | 170 |
| 8.2 | Contribution of Study | 173 |
| 8.3 | Future Works | 174 |
| REFERENCES | | 176 |
| APPENDICES | | 207 |



UMS
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LIST OF TABLES

| | Page |
|---|------|
| Table 2.1 : Types of activated carbon used to adsorb heavy metals | 22 |
| Table 2.2 : Types of polymers used to adsorption various heavy metals | 28 |
| Table 2.3 : Inorganic materials used to adsorb various heavy metals | 33 |
| Table 2.4 : Agricultural byproduct materials used to adsorb various heavy metals | 39 |
| Table 2.5 : Types of soils used to adsorb various heavy metals | 43 |
| Table 2.6 : Material balance of liquid phase adsorption | 56 |
| Table 3.1 : Preparation of heavy metals concentration in competitive and non-competitive adsorption system | 82 |
| Table 3.2 : The required parameters applied in the simulation of adsorption column for producing breakthrough curve | 84 |
| Table 3.3 : Correlations used for the estimation of unknown model parameters | 85 |
| Table 3.4 : Required model input from experiment and correlations for simulation of dynamic transport of heavy metals onto soil using Aspen Adsorption V11 | 86 |
| Table 4.1 : Percentage Particle size distribution of sand, field soil and field soil without organic carbon obtained using sieve shaker | 89 |
| Table 4.2 : Pore volume distribution and surface area of studied adsorbents | 90 |
| Table 4.3 : Percentages of elemental oxides presented in clay and sand | 95 |
| Table 4.4 : Percentages of elemental oxides presented in field soil and field soil without organic matter | 96 |
| Table 4.5 : Cation exchange capacity of studied adsorbents | 97 |
| Table 4.6 : Density, pH and particle size of studied adsorbents | 100 |
| Table 4.7 : Position and assignment of the various absorption bands in the FTIR spectra of the clay, sand, field soil and field soil without organic matter | 101 |
| Table 4.8 : Position and assignment of the various absorption bands in the FTIR spectrum of activated carbon | 101 |
| Table 4.9 : Moisture content and organic matter content in field soil | 102 |

| | | |
|------------|---|-----|
| Table 6.1 | : Equilibrium constant, K and adsorption capacity, N_s of clay and sand toward heavy metal ions Cu^{2+} , Pb^{2+} and Zn^{2+} | 123 |
| Table 6.2 | : Equilibrium constant, K and adsorption capacity, N_s of different composition of clay and sand toward heavy metal ions Cu^{2+} , Pb^{2+} and Zn^{2+} | 128 |
| Table 6.3 | : Equilibrium constant, K and adsorption capacity, N_s of different composition of activated carbon and clay toward Cu^{2+} and field soil toward Cu^{2+} | 129 |
| Table 6.4 | : Equilibrium constant, K and adsorption capacity, N_s of clay toward heavy metal ions (a) Cu^{2+} and Pb^{2+} , (b) Cu^{2+} and Zn^{2+} , (b) Pb^{2+} and Zn^{2+} and (d) Cu^{2+} , Pb^{2+} and Zn^{2+} in competitive adsorption | 132 |
| Table 6.5 | : Equilibrium constant, K and adsorption capacity, N_s of sand toward heavy metal ions (a) Cu^{2+} and Pb^{2+} , (b) Cu^{2+} and Zn^{2+} , (b) Pb^{2+} and Zn^{2+} and (d) Cu^{2+} , Pb^{2+} and Zn^{2+} in competitive adsorption | 133 |
| Table 6.6 | : Comparison of Langmuir Isotherm Model based on Pseudo Ideal Monolayer and directly interpreted from excess isotherm for non-competitive adsorption of heavy metal ions Cu(II) , Pb(II) and Zn(II) (pH: 4.2-4.5; T: 30°C; equilibrium time: 24 h; adsorbent dosage: 0.02g/g) | 137 |
| Table 6.7 | : Comparison of Langmuir Isotherm Model based on Pseudo Ideal Monolayer and directly interpreted from excess isotherm for competitive adsorption of Cu(II) , Pb(II) and Zn(II) (pH:4.2-4.5; T: 30°C; equilibrium time: 24 h; Adsorbent dosage: 0.02g/g) | 138 |
| Table 6.8 | : Comparison of adsorption capacity in different mixed composition | 141 |
| Table 6.9 | : Linear and non-linear regression of Langmuir Isotherm constants for non-competitive adsorption of heavy metal ions Cu(II) , Pb(II) and Zn(II) (pH: 4.2-4.5; T: 30°C; equilibrium time: 24 h; adsorbent dosage: 0.02g/g) | 149 |
| Table 6.10 | : Linear and non-linear regression of Langmuir Isotherm constants for competitive adsorption of heavy metal ions Cu(II) , Pb(II) and Zn(II) (pH: 4.2-4.5; T: 30°C; equilibrium time: 24 h; adsorbent dosage: 0.02g/g) | 150 |
| Table 7.1 | : Breakthrough behaviour of Cu^{2+} , Pb^{2+} and Zn^{2+} ions on different soil materials (F = 10 mL/min, $C_0 = 3.0$ mM, H = 30 cm, D = 1.6 cm) | 155 |

| | | |
|-----------|--|-----|
| Table 7.2 | : Breakthrough behaviour of Cu(II) ions on commercial activated carbon, and mixture of AC and clay ($F = 10$ mL/min, $C_0 = 3.0$ mM, $H = 30$ cm, $D = 1.6$ cm) | 156 |
| Table 7.3 | : The power law relationship between source flowrate and heavy metals retention time onto different soils [$C_0 = 3.0$ mM, $H = 30$ cm, $D = 1.6$ cm] | 158 |
| Table 7.4 | : The breakthrough time of Cu(II), Pb(II) and Zn(II) by different soils during normal and extreme rainfall [$C_0 = 3.0$ mM, $H = 30$ cm, $D = 1.6$ cm] | 159 |



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LIST OF FIGURES

| | Page |
|--|------|
| Figure 2.1 : Soil texture triangle | 38 |
| Figure 2.2 : Types of adsorption Isotherm | 50 |
| Figure 2.3 : Classification of isotherm shapes | 51 |
| Figure 2.4 : Classification of excess adsorption isotherms | 54 |
| Figure 2.5 : Adsorption process of adsorbate from bulk solution diffuse through liquid film and finally adsorbed at the active sites in pores | 59 |
| Figure 2.6 : (a) Types of diffusion in macropore, (b) diffusion processes along the pore that described the adsorption occurred on the active sites | 60 |
| Figure 2.7 : Breakthrough curve for adsorption process in fixed bed C_0 is the inlet solution concentration, C_b is the breakthrough concentration, t_b is the break point time and t_s is the saturation time | 65 |
| Figure 2.8 : Control volume for mass balance around packed bed column, as represented by Equation 2.34 | 67 |
| Figure 3.1 : Representative elementary volume of a small section of subsoil layer using packed bed column. | 83 |
| Figure 3.2 : Simulation setup of fixed-bed column on adsorbing Adsorbates Cu^{2+} , Pb^{2+} and Zn^{2+} onto soil adsorbents | 84 |
| Figure 3.3 : Calculation procedure flow methodology | 87 |
| Figure 4.1 : N_2 adsorption/desorption isotherms and pore size distribution of (a) clay, (b) sand and (c) activated carbon at 77K | 93 |
| Figure 4.2 : N_2 adsorption/desorption isotherms and pore size distribution of (a) field soil (b) field soil without organic matter at 77K | 94 |
| Figure 5.1 : Effect of contact time on adsorption of Cu^{2+} onto clay | 107 |
| Figure 5.2 : Excess adsorption isotherms of heavy metal ions (Cu^{2+} , Pb^{2+} and Zn^{2+}) onto clay at 30°C | 109 |
| Figure 5.3 : Excess adsorption isotherm of heavy metal ions (Cu^{2+} , Pb^{2+} and Zn^{2+}) onto sand at 30°C | 110 |
| Figure 5.4 : Excess adsorption isotherm of heavy metal ions (a) Cu^{2+} , (b) Pb^{2+} and (c) Zn^{2+} onto different composition of clay and sand at 30°C | 111 |

| | | |
|------------|---|-----|
| Figure 5.5 | : Excess adsorption isotherm of Cu^{2+} ion onto different composition of (a) activated carbon and clay at 30°C and (b) field soil and field soil without organic matter at 30°C . | 113 |
| Figure 5.6 | : Competitive excess adsorption isotherm of heavy metal ions (a) Cu^{2+} and Pb^{2+} , (b) Cu^{2+} and Zn^{2+} , (c) Pb^{2+} and Zn^{2+} and (d) Cu^{2+} , Pb^{2+} and Zn^{2+} onto clay at 30°C . | 116 |
| Figure 5.7 | : Competitive excess adsorption isotherm of heavy metal ions (a) Cu^{2+} and Pb^{2+} , (b) Cu^{2+} and Zn^{2+} , (c) Pb^{2+} and Zn^{2+} and (d) Cu^{2+} , Pb^{2+} and Zn^{2+} onto sand at 30°C . | 118 |
| Figure 6.1 | : Pseudo Ideal Monolayer Adsorption Theory of linear regression analysis for non-competitive adsorption of heavy metal ions (Cu^{2+} , Pb^{2+} and Zn^{2+}) onto (a) clay and (b) sand at 30°C . | 122 |
| Figure 6.2 | : Combine graph of individual adsorption isotherms of heavy metal ions (Cu^{2+} , Pb^{2+} and Zn^{2+}) onto (a) clay and (b) sand at 30°C . | 124 |
| Figure 6.3 | : Combine graph of selectivity of heavy metal ions (Cu^{2+} , Pb^{2+} and Zn^{2+}) onto (a) clay and (b) sand at 30°C . | 126 |
| Figure 7.1 | : Breakthrough curves of $\text{Cu}(\text{II})$ - $\text{Pb}(\text{II})$ binary system on (a) clay (b) sand ($F = 10 \text{ mL/min}$, $C_0 = 3.0 \text{ mM}$, $H = 30 \text{ cm}$, $D = 1.6 \text{ cm}$) | 161 |
| Figure 7.2 | : Breakthrough curves of $\text{Cu}(\text{II})$ - $\text{Zn}(\text{II})$ binary system on (a) clay (b) sand ($F = 10 \text{ mL/min}$, $C_0 = 3.0 \text{ mM}$, $H = 30 \text{ cm}$, $D = 1.6 \text{ cm}$) | 163 |
| Figure 7.3 | : Breakthrough curves of $\text{Pb}(\text{II})$ - $\text{Zn}(\text{II})$ binary system on (a) clay (b) sand [$F = 10 \text{ mL/min}$, $C_0 = 3.0 \text{ mM}$, $H = 30 \text{ cm}$, $D = 1.6 \text{ cm}$] | 165 |
| Figure 7.4 | : Breakthrough curves of $\text{Pb}(\text{II})$ - $\text{Cu}(\text{II})$ - $\text{Zn}(\text{II})$ ternary system on (a) clay (b) sand [$F = 10 \text{ mL/min}$, $C_0 = 3.0 \text{ mM}$, $L = 30 \text{ cm}$, $D = 1.6 \text{ cm}$] | 167 |

LIST OF APPENDICES

| | Page |
|--|------|
| Appendix A : Sampling Depth According to Setting Time in Pipette method for clay (cm) | 208 |
| Appendix B : Thermogravimetric analysis (TGA) of field soil | 209 |
| Appendix C : X-ray diffractogram for clay, sand and field soil | 210 |
| Appendix D : XRF spectra of elemental composition in soil samples | 212 |
| Appendix E : FTIR Spectra of Clay, Sand, Field Soil and Activated Carbon | 214 |
| Appendix F : Analysis Data in Non-Competitive of Individual Adsorption of Heavy Metals | 217 |
| Appendix G : Analysis Data in Non-Competitive Adsorption of Heavy Metals onto Different Composition of Adsorbents | 219 |
| Appendix H : Analysis Data in Competitive Adsorption of Heavy Metals onto Clay and Sand | 224 |
| Appendix I : Determination and Calculation for Equilibrium Constant, K and Adsorption Capacity, N_s of Adsorption Cu^{2+} onto Clay | 227 |
| Appendix J : Pseudo Ideal Monolayer Adsorption Theory of linear Regression Analysis for Non-Competitive Adsorption | 229 |
| Appendix K : Individual Adsorption Isotherms of Heavy Metals onto Different Soil Composition | 231 |
| Appendix L : Selectivity of Heavy Metal onto Different Soil Composition | 233 |
| Appendix M : Pseudo Ideal Monolayer Adsorption Theory of Linear Regression Analysis for Competitive Adsorption | 235 |
| Appendix N : Individual Adsorption Isotherms of Heavy Metals onto Clay and Sand in Competitive Adsorption | 237 |
| Appendix O : Selectivity of Heavy Metals onto Clay and Sand in Competitive Adsorption | 239 |
| Appendix P : Langmuir Directly Interpreted from Excess Isotherm Linear Regression Analysis for Non-Competitive Adsorption | 241 |
| Appendix Q : Langmuir Directly Interpreted from Excess Isotherm Linear Regression Analysis for Competitive Adsorption of Heavy Metal Ions on Clay and Sand | 244 |
| Appendix R : Linear and Non-Linear Regression of Freundlich Isotherm Constants for Non-Competitive Adsorption | 246 |

| | | |
|------------|--|-----|
| Appendix S | : Nonlinear Regression of Langmuir and Freundlich Adsorption Isotherm | 248 |
| Appendix T | : Freundlich Linear Regression Analysis for Non-Competitive Adsorption | 263 |
| Appendix U | : Freundlich Linear Regression Analysis for Competitive Adsorption | 266 |
| Appendix V | : Langmuir Isotherm Parameters Conversion Table | 268 |



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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Heavy metal contaminants on soil, air or water are one of commonly known pollution around the globe. It has been seen the pollution caused from heavy metals are widespread in many areas over the world. It is known that heavy metals pollution has been occurs over the past of several decades and many actions, protections, treatments and removals have been taken to remove or reduce the disposal and the spread of heavy metal contaminant to the environment (Zhou *et al.*, 2020a; Yu *et al.*, 2017; Guan *et al.*, 2014; Hu *et al.*, 2013; Bryan, 1980). However, the amount of heavy metals that continuously introduce to the environment is more rapid than the remediation and even in some countries has become increasingly prominent causing the quality of environment getting worse (Hu *et al.*, 2014). This issue has led to heavy metal pollution being a significant problem facing the environment and also global challenges.

In nature, heavy metals are found in several forms of compound and complex such as in oxides, phosphates, sulphates, hydroxides, sulphides, nitrates, silicates and organic (Masindi & Muedi, 2018). These formations of compound and complex are duel with heavy metals possessing various oxidation states that their behaviors are also affected by the oxidation properties. And the hazard of numerous heavy metals in the environment, especially in soil compartments, also depends on their oxidation state. The oxidation state levels are able to influence the determination of heavy metals in natural and artificial geochemical barriers. The oxidation state of some heavy metals such as arsenic, selenium, chromium vanadium and antimony increased under the contaminated soil compartment (Vodyanitskii, 2013). As the oxidation state increases, the heavy metal can become more or less toxic or

hazardous to the environment and other living organisms. For example, chromium(III) is an essential trace element for humans but chromium(VI) is a carcinogen and the most dangerous form of chromium. Whereas arsenic is more toxic at lower oxidation state arsenic(III) than higher state arsenic(V). It is found that the oxidation state of heavy metals also has a close relationship with its mobility specifically in the soil compartment. However, the mobility is different for each heavy metal. The mobilities of arsenic, chromium and vanadium are higher at lower oxidation states but at higher oxidation states of antimony. The mobility indicates the availability of particular heavy metal to form a complex or compound in the same environmental compartment or may be transferred from one compartment to another compartment or ecosystem component such as groundwater or crops.

The sources of heavy metals entering the environment can be from both natural and anthropogenic processes. Natural processes are varied; it can be from rock weathering, volcanic eruption, forest fires and sea-salt sprays. However, all these occurrences of natural processes only change the heavy metals spheres in different environment compartments and would not or seldom affect the stability of heavy metals in nature that will bring to the pollution of the environment. Although anthropogenic processes are found as the main sources that contributed to the increasing of heavy metals to the environment, these anthropogenic activities are kept on continuing to fulfill the demands on human life moreover in rapid social and economic development. Anthropogenic wastes are mainly from industrial discharge, pharmaceutical, mining, smelting operation, domestic disposal and irresponsible disposal of industrial waste or agricultural activities (Yahya *et al.*, 2018; Sankhla *et al.*, 2016; Bagul *et al.*, 2015). These heavy metals may be treated, filtered or direct discharge to the environment through soil and water. Some industries' treatments can be lack of properly equipped plants, inappropriate environmental management especially in many of the developing countries and also operated within or not in the required standards, heavy metals are released in *ad hoc* manner to the environment (Anyanwu *et al.*, 2018). Besides, shortage of environmental technology and lack of regional law enforcement in developing countries also contributed to the increase of rate of heavy metal pollution to the environment (Ding, 2019; Hu *et al.*, 2014). Due to heavy metals are non-biodegradable, non-thermo-degradable, persistence and also cannot be degraded chemically (Taghipour *et al.*, 2013; Oluyemi & Olabanji,