

**REMOVAL OF MANGANESE (Mn) FROM  
AQUEOUS SOLUTION USING MIXTURE OF  
FERROMANGANESE ORE AND HUMUS**

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MIXTURE OF FERROMANGANESE ORE AND HUMUS**

**by**

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## TABLE OF CONTENTS

	<b>Page</b>
<b>ACKNOWLEDGEMENT</b>	ii
<b>TABLE OF CONTENTS</b>	iii
<b>LIST OF TABLES</b>	viii
<b>LIST OF FIGURES</b>	x
<b>LIST OF PLATES</b>	xiii
<b>LIST OF ABBREVIATIONS</b>	xiv
<b>ABSTRAK</b>	xvi
<b>ABSTRACT</b>	xvii
<b>CHAPTER ONE : INTRODUCTION</b>	
1.1 Background of the Study	1
1.2 Problem Statement	3
1.3 Objectives of Research	5
1.4 Scope of Study	5
1.5 Organization of Thesis	6
<b>CHAPTER TWO : LITERATURE REVIEW</b>	
2.1 Production of Metallic Minerals in Malaysia	7
2.2 Overview of Mining Operation	8
2.3 Introduction to Mine Effluent Management	9
2.3.1 Mine Effluent Characteristics	10
2.3.2 Mine Effluent Treatment	10
2.3.3 Mineral Development (Effluent) Regulations 2016	12
2.4 Manganese	14
2.4.1 Speciation of Manganese	14
2.4.2 Application of Manganese	14

2.4.3	Environmental Concerns and Health Hazard	15
2.5	Treatment of Mn	16
2.5.1	Precipitation	17
2.5.2	Oxidation-filtration	18
2.5.3	Ion-exchange	21
2.5.4	Membrane Process	22
2.5.5	Electrochemical Treatment	22
2.5.6	Adsorption	23
2.6	Oxide-based Adsorbent	24
2.7	Organic-based Adsorbent	29
2.8	Mechanism of Mn Adsorption	32
2.8.1	Principle of Adsorption	32
2.8.2	Mechanism of Mn Adsorption by Oxide-based Adsorbent	32
2.8.3	Mechanism of Mn Adsorption by Organic-based Adsorbent	35
2.8.4	Adsorption Isotherm	37
2.8.5	Re-adsorption	38
2.9	Factors Affecting Mn Adsorption by Oxide and Organic Adsorbent	39
2.9.1	Effect of pH	39
2.9.2	Effect of Adsorbent Dosage	39
2.9.3	Effect of Contact Time	40
2.9.4	Effect of Particle Size	40
2.9.5	Effect of Shaking Speed	40
2.10	Column Study of Mn Adsorption by Oxide and Organic Adsorbent	41
2.11	Design of Experiment	43
2.12	Summary of Literature Review	44

## **CHAPTER THREE : METHODOLOGY**

3.1	Introduction	46
3.2	Research Flowchart	47
3.3	Equipment and Chemical Reagents	48
3.4	Preparation of Aqueous Solution of Manganese	50
3.5	Sampling of Ferromanganese Ore (FMO) and Humus	52
3.6	Characterization Analysis of Adsorbent Media	53
3.6.1	Particle Size Distribution Analysis	54
3.6.2	pH Analysis	56
3.6.3	X-Ray Fluorescence (XRF) Analysis	56
3.6.4	X-Ray Diffraction (XRD) Analysis	57
3.6.5	Carbon, Hydrogen, Nitrogen & Sulphur (CHNS) Analysis	58
3.6.6	Surface Area, Pore Size and Pore Volume Analysis	59
3.6.7	Fourier Transform Infrared (FT-IR) Analysis	59
3.6.8	Field Emission Scanning Electron Microscopy (FESEM) Imaging	60
3.6.9	Cation Exchange Capacity (CEC) Analysis	60
3.7	Batch Study of Adsorption Experiment	62
3.7.1	Effect of Particle Size of FMO	63
3.7.2	Effect of Dosage	64
3.7.3	Effect of Mix Ratio	64
3.7.4	Effect of pH	65
3.7.5	Effect of Shaking Speed	65
3.7.6	Effect of Contact Time	65
3.7.7	Experimental Control	66
3.7.8	Adsorption Isotherm Model Study	66

3.8	Optimization Study by Central Composite Design (CCD)	69
3.9	Re-adsorption Study	71
3.10	Column Study	72
3.11	Summary	73
<b>CHAPTER FOUR : RESULTS AND DISCUSSION</b>		
4.1	Characterization Analysis of Adsorbent Media	74
4.1.1	Particle Size Analysis Distribution	74
4.1.2	pH analysis	76
4.1.3	X-Ray Fluorescence (XRF) Analysis	76
4.1.4	X-Ray Diffraction (XRD) Analysis	79
4.1.5	Carbon, Hydrogen, Nitrogen & Sulphur (CHNS) Analysis	80
4.1.6	Surface Area, Pore Size and Pore Volume Analysis	80
4.1.7	Fourier Transform Infrared (FT-IR) Analysis	81
4.1.8	Field Emission Scanning Electron Microscopy (FESEM) Imaging	87
4.1.9	Cation Exchange Capacity (CEC) Analysis	89
4.2	Batch Study of Adsorption Experiment	89
4.2.1	Optimum Particle Size of FMO	90
4.2.2	Optimum Dosage	92
4.2.3	Optimum Mix Ratio	95
4.2.4	Optimum pH	96
4.2.5	Optimum Shaking Speed	100
4.2.6	Optimum Contact Time	102
4.2.7	Result Summary of Batch Study	104
4.2.8	Experimental Control	105
4.2.9	Adsorption Isotherm Model Study	109

4.3	Optimization Study	113
4.3.1	Statistical Analysis	113
4.3.2	Effects of Operating Variables	116
4.3.3	Optimization and Validation	118
4.3.4	Characteristics of FMO-Humus Mixture after Optimization Study	119
4.4	Re-adsorption Study	124
4.5	Column Study	124
4.5.1	Breakthrough Curve	124
4.5.2	Characteristics of FMO-Humus Mixture after Column Study	126
<b>CHAPTER FIVE : CONCLUSION AND RECOMMENDATIONS</b>		
5.1	Conclusion	131
5.2	Recommendations	133
<b>REFERENCES</b>		135
<b>APPENDICES</b>		
<b>LIST OF PUBLICATIONS</b>		

## LIST OF TABLES

	<b>Page</b>
Table 2.1. Malaysia's metallic mineral production in 2015 (JMG 2015)	7
Table 2.2. Parameter and limit of mine effluent discharge (NRE 2016)	13
Table 2.3. Advantages and disadvantages of Mn treatment (Patil et al. 2016)	16
Table 2.4. Summary on experimentation of Mn treatment by oxide-based adsorbents	29
Table 2.5. Summary on experimentation of Mn treatment using organic-based adsorbents	32
Table 2.6. Equations of adsorption isotherm models (Itodo et al. 2010; Chaudhry et al. 2016)	39
Table 3.1. List of equipment that have been used in this research study	48
Table 3.2. List of chemical reagents that have been used in this research study	50
Table 3.3. Average metals concentrations of mine effluent in accordance to pH (Azmi et al. 2016)	52
Table 3.4. Characterization analysis of the adsorbent media	54
Table 3.5. Central composite design for three factors with their levels	70
Table 3.6. Design parameters of column study of FMO-humus mixture	72
Table 4.1. Components of FMO in oxide form	77
Table 4.2. Components of humus in oxide form	78
Table 4.3. Carbon, hydrogen, nitrogen and sulphur contents in humus	80
Table 4.4. Surface area, pore size and pore volume of FMO	81
Table 4.5. Surface area, pore size and pore volume of humus	81
Table 4.6. Summary table of FT-IR wavenumbers for FMO	82
Table 4.7. Summary table of FT-IR wavenumbers for humus	83
Table 4.8. Summary table of FT-IR wavenumbers for FMO-humus mixture	86
Table 4.9. Optimum operating variables of adsorption experiments	105

Table 4.10.	Concentration of metals (mg/L) for effect of particle size of FMO	106
Table 4.11.	Concentration of metals (mg/L) for effect of dosage	106
Table 4.12.	Concentration of metals (mg/L) for effect of pH	107
Table 4.13.	Concentration of metals (mg/L) for effect of shaking speed	107
Table 4.14.	Concentration of metals (mg/L) for effect of contact time	108
Table 4.15.	Langmuir isotherm parameters for Mn adsorption on the adsorbent	111
Table 4.16.	Freundlich isotherm parameters for Mn adsorption on the adsorbent	112
Table 4.17.	Experimental design data with the corresponding actual response	113
Table 4.18.	Results of analysis of variance (ANOVA)	115
Table 4.19.	Changes in surface area, pore size and pore volume of FMO-humus mixture after optimization study	120
Table 4.20.	Summary table of FT-IR wavenumbers for optimization study	121
Table 4.21.	Changes in surface area, pore size and pore volume of FMO-humus mixture after column study	127
Table 4.22.	Summary table of FT-IR wavenumbers for column study	127

## LIST OF FIGURES

	<b>Page</b>
Figure 2.1. Common stages in mine operation (Environment Canada 2009)	8
Figure 2.2. Graphical representation of typical adsorption process (Lyubchik et al. 2011)	33
Figure 2.3. Graphical representation of van de Waals attraction	33
Figure 2.4. Graphical representation of electrostatic interaction	33
Figure 2.5. Graphical representation of ion-exchange mechanism (Esfandiar et al. 2014)	37
Figure 3.1. Flowchart of research study	47
Figure 4.1. Particle distribution plot of FMO	75
Figure 4.2. Particle size distribution of humus	76
Figure 4.3. X-Ray diffraction pattern of FMO shows goethite (G), hematite (H), pyrolusite (P), quartz (Q) and kaolinite (K) peaks	80
Figure 4.4. FT-IR spectrum of FMO	83
Figure 4.5. FT-IR spectrum of humus	85
Figure 4.6. FT-IR spectrum of FMO-humus mixture	87
Figure 4.7. FESEM images of FMO under 5000 X magnifications shows a rough surface with accumulation of fine particles	89
Figure 4.8. FESEM images of humus under (a) 600 X and (b) 2500 X magnifications shows abundance of open pores on the surface	90
Figure 4.9. Effect of particle size of FMO on Mn removal using FMO	90
Figure 4.10. Effect of particle size of FMO on Mn removal using FMO-humus mixture	93
Figure 4.11. Effect of dosage on Mn removal using FMO	93
Figure 4.12. Effect of dosage on Mn removal using humus	94
Figure 4.13. Effect of dosage on Mn removal using FMO-humus mixture	95
Figure 4.14. Effect of mix ratio (w/w) on Mn removal using FMO-humus mixture	96

Figure 4.15.	Concentration of Mn according to pH	97
Figure 4.16.	Effect of pH on Mn removal using FMO	98
Figure 4.17.	Effect of pH on Mn removal using humus	99
Figure 4.18.	Effect of pH on Mn removal using FMO-humus mixture	100
Figure 4.19.	Effect of contact time on Mn removal using FMO	102
Figure 4.20.	Effect of contact time on Mn removal using humus	103
Figure 4.21.	Effect of contact time on Mn removal using FMO-humus mixture	104
Figure 4.22.	Langmuir isotherm plots for (a) FMO, (b) humus and (c) FMO-humus mixture	111
Figure 4.23.	Freundlich isotherm plots for (a) FMO, (b) humus and (c) FMO-humus mixture	113
Figure 4.24.	Predicted vs. actual values plot for Mn removal (%)	116
Figure 4.25.	3D surface plot showing the effect of (a) dosage and pH at constant time = 180 min, (b) dosage and time at constant pH = 5.25,(c) contact time and pH at constant dosage = 3 g on Mn removal (%)	119
Figure 4.26.	FT-IR spectrum of FMO-humus mixture before and after optimization study	121
Figure 4.27.	FESEM images of FMO-humus mixture under 150 X magnification shows FMO in grain form and humus in flake-shaped	122
Figure 4.28.	FESEM images of FMO (a) before and (b) after optimization study under 5000 X magnification display changes on the ore surface with more deposits of fine particles were observed after the study	123
Figure 4.29.	FESEM images of humus (a) before and (b) after optimization study under 500 X magnification show changes in pores sizes and some pores were filled with build-up of particles after the study	124
Figure 4.30.	Mn adsorption (%) by FMO-humus mixture for several cycles	124
Figure 4.31.	Breakthrough curve for Mn removal by FMO-humus mixture	125

Figure 4.32.	FT-IR spectrum of FMO-humus mixture before and after column study	128
Figure 4.33.	FESEM images of FMO (a) before and after column study under (b) 5000 X and (c) 10000 X magnifications display changes on the ore surface with formation of porous spherical flakes were spotted after the study	130
Figure 4.34.	FESEM images of humus (a) before and (b) after column study under 500 X magnification show changes in pores sizes with plenty of pores were covered with build-up of particles	131

## LIST OF PLATES

	<b>Page</b>
Plate 2.1. Mine effluent in tailing ponds (Azmi et al. 2016)	9
Plate 3.1. Sample of FMO	52
Plate 3.2. Sample of humus	53
Plate 3.3. Batch study of adsorption experiment	62
Plate 3.4. Column study of the FMO-humus mixture	73
Plate 4.1. After treatment solution with shaking speed of 150 rpm and settling time of 1.5 hrs (from left: FMO, humus and FMO-humus mixture)	102
Plate 4.2. After treatment solution with shaking speed of 300 rpm and settling time of 1.5 hrs (from left: FMO, humus and FMO-humus mixture)	102

## LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
ANOVA	Analysis of variance
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
CCD	Central Composite Design
CHNS	Carbon, Hydrogen, Nitrogen and Sulphur
CV	Coefficient of variance
FMO	Ferromanganese ore
FESEM	Field Emission Scanning Electron Microscopy
ca.	Approximately
CEC	Cation exchange capacity
FT-IR	Fourier Transform-Infrared Spectroscopy
e.g.	for example
HRT	Hydraulic retention time
ICP-OES	Inductively-Coupled Plasma - Optimal Emission Spectroscopy
i.e.	that is
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
LOF	Lack-of-fit
LOI	Loss on ignition
meq	miliequivalent
MnO <sub>x</sub>	Oxide of manganese
OVAT	One-Variable-At-a-Time

rpm	Rotation per minute
RSM	Response Surface Methodology
w/w	weight-to-weight ratio
wt	Weight
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

# **PENYISIHAN MANGAN (Mn) DARI LARUTAN AKUEUS MENGUNAKAN CAMPURAN BIJIH FERROMANGAN DAN HUMUS**

## **ABSTRAK**

Kajian ini dijalankan untuk mengkaji keberkesanan campuran bijih ferromangan (FMO) dan humus dalam menyisihkan mangan (Mn) dari larutan akueus. Interaksi antara permukaan FMO dan bahan humik daripada humus menghasilkan kompleks melalui pertukaran ligan, ikatan hidrogen, interaksi hidrofobik dan sebagainya. Kompleks ini berperanan sebagai tapak penjerapan tambahan dalam menyediakan lebih banyak permukaan yang aktif untuk penjerapan Mn. Kaedah kajian dimulakan dengan pencirian FMO dan humus. Seterusnya, eksperimen penjerapan dilakukan secara kajian kelompok untuk mengkaji keberkesanan campuran FMO-humus dalam menyisihkan Mn. Keberkesananya dibandingkan dengan penggunaan FMO dan humus secara individu. Kemudian, data yang diperoleh daripada kajian kelompok disuai padankan pada model isoterma penjerapan Langmuir dan Freundlich bagi menentukan model isoterma yang terbaik. Seterusnya, kajian pengoptimuman bagi campuran FMO-humus telah dijalankan dengan menggunakan Central Composite Design. Kajian penjerapan semula juga dilakukan untuk mengkaji kebolegunaan semula media tersebut. Analisis terakhir adalah eksperimen kolum menggunakan campuran FMO-humus untuk penentuan lengkung bulus. Keputusan keseluruhan kajian kelompok menunjukkan campuran FMO-humus mempunyai keberkesanan yang lebih baik sedikit berbanding humus. Selain itu, isoterma Freundlich adalah model yang paling sesuai untuk kesemua media penjerap dengan nilai  $r^2 > 0.9$ . Keputusan kajian pengoptimuman bagi campuran FMO-humus menunjukkan 93.82% Mn dapat disingkirkan secara optimum. Untuk kajian penjerapan semula, campuran FMO-humus dapat diguna semula sehingga 5 kitaran dengan rekod penyisihan Mn sebanyak 92.25 hingga 95.22% tanpa perlu kepada pengolahan penyahjerapan. Akhir sekali, titik “breakthrough” dan titik “exhaustion” bagi campuran FMO-humus dalam kajian kolum telah direkodkan pada hari ke-16 dan hari ke-29.

# REMOVAL OF MANGANESE (Mn) FROM AQUEOUS SOLUTION USING MIXTURE OF FERROMANGANESE ORE AND HUMUS

## ABSTRACT

This study examined effectiveness of mixture of ferromanganese ore (FMO) and humus to remove Mn from aqueous solution. Interactions between the FMO surface and humic substances from humus form complexation through ligand exchange, hydrogen bonding, hydrophobic interaction, etc. The complexation acts as additional binding sites thus provide more active surfaces for Mn adsorption. The methodology of this study had commenced with characterization of FMO and humus. Then, batch adsorption experiments were performed to evaluate effectiveness of FMO-humus mixture to remove Mn. Its performance was compared to the individual performance of the FMO and the humus. Furthermore, the batch experimental data was fitted to Langmuir and Freundlich isotherms to determine the best-fit model. Next, optimization study of the FMO-humus mixture was conducted by using Central Composite Design. Re-adsorption study was also performed to examine reusability of the media. Last analysis was a column study of FMO-humus mixture for determination of a breakthrough curve. Results from the adsorption experiments had shown FMO-humus mixture had slightly better performance compared to humus. Apart from that, Freundlich isotherm was the best-fit model towards all media with  $r^2 > 0.9$ . Result from the optimization study of FMO-mixture had yielded 93.82% optimum removal of Mn. As for the re-adsorption study, FMO-humus mixture can be reused until 5 cycles with Mn removal of 92.25 to 95.22% without desorption treatment. Lastly, the breakthrough point and the exhaustion point for FMO-humus mixture of the column study were recorded on the 16<sup>th</sup> day and the 29<sup>th</sup> day respectively.

## CHAPTER ONE

### INTRODUCTION

#### 1.1 Background of the Study

According to statistics in Malaysian Mineral Yearbook 2015, there are 176 metallic mineral mines with majority of them are iron ore mines producing RM 2.21 billion worth of minerals (Minerals and Geoscience Department Malaysia [JMG] 2015). Apart from the well-off economy activity generated by this industry, environmental drawbacks associated with mining industry become an alarming topic. Although mining land accounts for only a small percentage of the total land area of the country, environmental impacts from mining activities are very noticeable especially towards water pollution of receiving waterways.

Mine effluent contamination from the mining industry is one of the environmental concerns encountered by mining operators. High level of heavy metals include iron (Fe), manganese (Mn), aluminium (Al), copper (Cu), zinc (Zn), etc are often presence in the mine effluent. These hazardous metals are usually originated from ore minerals associated with the mined minerals. They are soluble metal ions which easily dissolved in the mine effluent thereby becoming mobilised and bio-available (Masindi 2017). The untreated mine effluent possesses detrimental impacts on the environment if it left unattended. This problem may cause surface and ground water contamination, disturbs wetland ecosystem, damages aquatic life, bioaccumulation of heavy metal in living organisms and causing various diseases and illnesses (Shabalala et al. 2017).

In general, treatment of mine effluent can be categorized into active and passive treatment systems. Active treatment system using common neutralization agents such as lime, magnesite, hydrated lime, limestone, periclase, brucite, soda ash and caustic soda in treating the effluent. This treatment produce fast result but involves ongoing maintenance and high running cost (Masindi 2017). On the other hand, passive treatment system incurs minimal maintenance and low cost but takes longer time to response. Examples of the passive treatment system are anoxic limestone drain (ALD), reducing and alkalinity producing system (RAPS), sulphate-reducing bioreactor (SRB) and constructed wetland (Macías et al. 2012). Often, passive treatment system is favoured due to its low cost benefit (Macías et al. 2012; Al-Abed et al. 2017; Rakotonimaro et al. 2017).

Neutralization method often incorporated into active and passive treatment systems (Taylor et al. 2005; Tolonen et al. 2014). Mine effluent is often acidic thus requires neutralization process to raise pH. In fact, most heavy metals associated with mine effluent are amphoteric. Their solubility are high in acidic condition and low in alkaline region (Taylor et al. 2005). Most of them can be removed significantly by raising pH to 7 (neutral level) except for Mn. It only begins to precipitate in alkaline region at pH 8.5 because it requires high activation energy to be converted into hydroxides precipitates (Seo et al. 2017). The most common treatment of Mn involves usage of caustic chemical or neutralization agent to raise pH > 9. Some active treatment system utilize both caustic chemicals and oxidants, e.g. ozone. This removal process produces precipitation of manganese (II) hydroxide,  $Mn(OH)_2$  or oxide of manganese ( $MnO_x$ ) as by-products (Luan et al. 2012).

## 1.2 Problem Statement

A preliminary study on heavy metals level in mine effluent across metallic mineral mines in West Malaysia conducted by Mineral Research Centre, Minerals and Geoscience Department Malaysia had shown that mines in certain areas had generated effluent with high level of heavy metals including Mn (Azmi et al. 2016). This finding is an alarming situation whereby it possesses threats to human and to the environment. High level of Mn may cause toxicity in human body which can affect brain tissues, damage liver and kidney functions, harm central nervous system and cause neurological disorders, for e.g. idiopathic Parkinson's disease (Silva et al. 2010; Jia et al. 2015). Other illnesses caused by Mn toxicity are dementia, ataxia, anxiety and manganism (Patil et al. 2016). Moreover, excess level of Mn creates problem to water industry such that it may generate accumulation of Mn oxides, thus cause blockages within water supply distribution pipes (Bamforth et al. 2006).

Treatment of Mn include oxidation, precipitation, adsorption, ion-exchange, membrane technology and electrochemical treatment (Taylor et al. 2005; Ince 2013; Goher et al. 2015; Patil et al. 2016; Du et al. 2017). Among these processes, adsorption is an attractive option because it has been proven effective and inexpensive. Iron and manganese oxides are commonly used as adsorbents in heavy metal removal due to their large surface area, high density of reactive sites and favourable functional groups for chelate complexation (Kan et al. 2013). In natural soils, iron and manganese oxides exist in organo-mineral complexes which their compositions combined with other metals and usually coated with organic matter in the form of humic substances. Similar to pure oxides, these organo-mineral complexes are good adsorbents for various types of contaminants including cations (Farina et al. 2017).

Previous studies had found metal ions adsorption to the organo-mineral complexes were enhanced due to the presence of organics in low to mid pH region (Fan et al. 2017; Farina et al. 2017). Organics in the form of humic substances were adsorbed to the metal oxide surfaces or mineral complexes by ligand group exchange, hydrogen bonding, electrostatic interaction, hydrophobic interaction, etc. to form metal oxide–organo complexes or organo-mineral complexes. It can be attached to the mineral surfaces and also interact with the organic matters originally coated on the mineral complexes (Ding et al. 2010; Fan et al. 2017). These additional binding sites related to the organic fractions provides more active surfaces for metal ions adsorption (Farina et al. 2017).

Mixture of oxide-based adsorbent and organic-based adsorbent is expected to promote enhancement of Mn ions adsorption. This is due to the availability of new binding sites which resulted from interaction between humic substances and oxides surfaces. Ferromanganese ore (FMO) as a representative organo-mineral complexes is an oxide-based adsorbent, mainly composed of Fe and Mn minerals. Previous study had successfully adopted FMO to remove Mn from mine water (Hallberg and Johnson 2005). On the other hand, humic substances can be found largely in humus, a composition of decayed natural organic matters. It has plenty of negatively charged sites on its surface (Chaturvedi et al. 2007), high cation-exchange capacity and favourable functional groups (Andretta et al. 2016) which can be exploited for adsorption of Mn ions. In particular, several studies demonstrated that humus was a good organic-based adsorbent for Mn (Chaturvedi et al. 2007; Zhu et al. 2011; Fu et al. 2017). To date, there is no reported literature exists regarding mixture of FMO and

humus to treat Mn. Thus, this research study aims to examine effectiveness of the mixture of FMO and humus for removal of Mn from an aqueous solution.

### **1.3 Objectives of Research**

The objectives of this research study are like the following:

- i. To characterize FMO and humus as adsorbent media for the removal of Mn from aqueous solution.
- ii. To analyze the effect of particle size, dosage, mix ratio, pH, shaking speed and contact time towards FeMn, humus and FeMn-humus mixture on removal of Mn from aqueous solution and to evaluate the best fitting adsorption isotherm model.
- iii. To obtain optimized values for dosage, pH and reaction time of FeMn-humus mixture in removing Mn from aqueous solution and to examine its re-adsorption efficiency for reusability.
- iv. To determine breakthrough points and exhaustive points of FMO-humus mixture for Mn treatment in aqueous solution by means of a column study.

### **1.4 Scope of Study**

The aim of the study is to examine performance of FMO-humus mixture as adsorbent for the removal of Mn from aqueous solution. This study was conducted by laboratory work in accomplishing the research objectives. Concentration of Mn aqueous solution was selected to be 2 to 3 mg/L, based on a publication report in 2016

acquired from Mineral Research Centre, Minerals and Geoscience Department Malaysia. Mn concentration. The FMO-humus mixture was evaluated against FMO and humus alone for its effectiveness to remove Mn from aqueous solution. Optimum operating variables which are particle size, dosage, mix ratio (w/w), pH, shaking speed and contact time were determined in series of batch experiments for all adsorbent media. Besides, evaluations of isotherm models were analyzed by applying data from the batch experiments (effect of dosage). Moreover, optimization of dosage, pH and contact time for the FMO-humus mixture by Response Surface Methodology were performed based on the optimum operating variables of the batch experiments. Then, re-adsorption efficiency of the FMO-humus mixture was analyzed by applying optimum operating variables obtained from the batch and the optimization studies. Finally, breakthrough points and exhaustive points of the FMO-humus mixture were determined via continuous-flow mode of column study.

## **1.5 Organization of Thesis**

This thesis consists of five chapters. Chapter 1 presents introduction of the thesis. It covers background of study, problem statement, objectives of research and scope of study. Next, Chapter 2 elaborates on literature review which covers the essence on previous related research work. Also, this chapter serves as a guide for gap of knowledge identification in establishing a new research. Chapter 3 focuses on details of methodology involved in completing the study. Furthermore, Chapter 4 presents results and discussion which is an essential chapter because it provides detailed explanation on effectiveness of FMO-humus mixture for Mn removal from aqueous solution. Lastly, Chapter 5 is the conclusion chapter which summarizes overall findings and future recommendations for the research study.