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

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by

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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_x	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 MENGGUNAKAN 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 pengoptimaan bagi campuran FMO-humus telah dijalankan dengan menggunakan Central Composite Design. Kajian penjerapan semula juga dilakukan untuk mengkaji kebolehgunaan 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 16th day and the 29th 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 (Andreetta 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.