ADSORPTION OF MERCURY ONTO 3-UREIDOPROPYLTRIETHOXYSILANE GRAFTED EMPTY FRUIT BUNCHES BIOSORBENTS

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To my beloved mother and father

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ABSTRACT

Mercury is among the heavy metal with high toxicity levels that are commonly released into environment. Heavy metals are persistent, nonbiodegradable and accumulates overtime, reaching health concering concentration. In this study, biosorption studies of mercury and methylmercury onto oil palm empty fruit bunch fibre (OPEFB) were performed to investigate the biosorption performances. In addition, OPEFB was further functionalised by 3-ureidopropyltriethoxysilane via grafting through hydrolisis method. These biosorbents were then characterised by scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FTIR), point of zero charge (pH_{pzc}) and cation exchange capacity (CEC). Batch biosorption experiments were performed to evaluate the effects of several parameters such as ligand concentrations, initial pH, initial concentrations, contact time and temperature. The results indicated that the biosorption performance of Hg (II) and CH_3Hg (I) sorption significantly changed with the changes in the aforementioned parameters. Highest biosorption capacity of 156.99 mg/g was recorded for Hg (II) sorption onto treated sorbent while CH_3Hg (I) sorption did not show any improvement even when tested upon treated sorbent. Biosorption of both metals onto treated and untreated biosorbents was best fitted to Langmuir isotherm model while, pseudo-second order model was chosen to represent all the biosorption data obtained in this study. Mercury metal selectivity study was conducted for each sorbent for Pb, Zn, and CH_3Hg (I) in an individual batch biosorption test. Regeneration ability of treated biosorbent in Hg (II) sorption that was completed for four cycles still performs better than untreated biosorbent despite experiencing gradual reduction in sorption capacity.

ABSTRAK

Merkuri adalah antara logam berat yang mempunyai tahap ketoksidaan tinggi, kerap dicemar ke persekitaran. Logam berat secara umumnya, tidak mengalami proses biodegradasi namun, ia akan mengakumulasi dengan masa sehingga mencapai tahap yang membimbangkan kesihatan. Dalam kajian ini, biojerapan logam merkuri dan metilmerkuri terhadap serat tandan buah kelapa sawit dilakukan bagi mengira kapasiti biojerapan. Di samping itu, serat tersebut difungsikan dengan mengunakan 3-ureidopropiltrietoksilana melalui proses cangkukan. Proses ini dilakukan dengan mengunakan kaedah hidrolisis. Ciri-ciri penjerap ini dikaji mengunakan mikroskop elektron inbasan (SEM), spektroskopi inframerah (FTIR), titik caj sifar (pH_{pzc}) dan kapasiti pertukaran ion (CEC). Eksperimen biojerapan ini dilakukan bagi mengkaji kesan perubahan dalam parameter seperti kepekatan ligan, pH awal larutan, kepekatan awal, masa tindakbalas dan suhu sistem. Keputusan kajian mengesahkan bahawa kapasiti biojerapan akan mengalami perubahan yang ketara apabila parameter-parameter yang disebut tadi diubah. Kapasiti biojerapan yang tertinggi direkod adalah sebanyak 156.99 mg/g untuk penjerapan merkuri (II) terhadap serat yang dirawat. Walaubagaimanapun, ion metilmerkuri tidak menunjukkan peningkatan dalam kapasiti biojerapan walaupun dikaji dengan serat yang dirawat. Model Langmuir dan pseudo-tertib kedua dipilih mewakili data biojerapan dalam kajian ini kerana modelnya adalah yang paling hampir dengan data ujikaji penjerapan. Selektiviti logam ion merkuri dikaji bagi setiap serat untuk penjerapan logam Pb, Zn dan CH_3Hg (I). Keupayaan untuk menjana semula serat terpakai diulang sebanyak empat kali dan didapati keberkesananya tetap lebih baik daripada serat dara meskipun ia mengalami pengurangan secara beransur dalam kapasiti penjerapannya.

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LIST OF SYMBOLS

α	-	Elovich contant related to chemisorptions rate (mg/gmin)
β	-	Elovich contant related to surface coverage (g/mg)
C_e	-	Equilibrium concentration (mg/l)
C_o	-	Initial concentration (mg/l)
k_1	-	Equilibrium rate constant of pseudo-first order kinetic model (l/min)
k_2	-	Equilibrium rate constant of pseudo-second order kinetic model (g/mg.min)
k_d	-	Dissociation constant
K_F	-	Freundlich constant (dm^3/mg)
K_L	-	Langmuir constant(dm^3/mg)
meq	-	miliequivalent
n	-	Intensity of adsorption
P_g	-	Percentage grafting (%)
Q_e	-	Amount adsorbed at equilibrium condition (mg/g)
Q_{max}	-	Maximum adsorption capacity (mg/g)
Q_t	-	Adsorption capacity at time t, (mg/g)
R^2	-	Correlation coefficient
R_L	-	Langmuir parameter

LIST OF ABBREVIATIONS

3-UPTES	-	3-ureidopropyltriethoxysilane
AAS	-	Atomic Absorption Spectrophotometer
AMPEN	-	Advanced Materials and Process Engineering Research Group
Cd	-	Cadmium
CEC	-	Cation Exchange Capacity
CH_3Hg (I)	-	Methylmercury ion
CH_3Hg^+	-	Methylmercury ion
Cu	-	Cuprum
Cr (IV)	-	Chromium (IV)
FTIR	-	Fourier Transform Infrared Spectroscopy
HCl	-	Hydrochloric Acid
H^+	-	Hydrogen ion
Hg (II)	-	Mercury ion
Hg^{2+}	-	Mercury ion
NaOH	-	Natrium Hydroxide
Na^+	-	Natrium ion
Ni	-	Nickel
OPEFB	-	Oil Palm Empty Bunches
Pb	-	Plumbum (lead)
PFO	-	Pseudo-first order (kinetic model)
PSO	-	Pseudo-second order (kinetic model)
pH_{pzc}	-	Point of Zero Charge
ppm	-	part-per-million
SEM	-	Scanning Electron Microscopy
Zn	-	Zinc

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Heavy metals in general, occur in earth crust in a stable form. Centuries of mining and harvesting these heavy metals either for urban development, technological race or for industrial use have somewhat scattered these potentially hazardous heavy metals in the rivers, especially in stagnant lake, ponds and in land soils. Most heavy metal, when reaches its end cycle generally ends up in garbage dump and in landfields. Unfortunately, heavy metals being a persistent pollutant have started to show its adverse effects towards environment, human kind and animals.

Governments and nongovernmental organization worldwide realise this alarming rise in heavy metal pollution and has taken many precautionary steps and solutions to overcome this damaging effects of heavy metal pollution. For example, most organization choose to regulate heavy metal discharge via industrial effluent to be under scrutiny of governmental law with heavier penalties and reducing threshold limits over the pass decades. Besides that, efforts such as campaigns and field research have been made to promote viable ways to dispose these contaminants and also to encourage in industrialist to treat effluents containing heavy metal for example mercury before releasing them into environment. However, the common problem faced by all the parties responsible for pre-treatment of heavy metal contaminants is and has always been the cost factor.

Several conventional treatment process in heavy metal separation still practiced today in many organization are for example; reverse osmosis system using membrane technology, electrodeposition and ion exchange resins appear to be expensive and burden to cope with, thus tempting industrialist to just deal with the waste in an improper manner. Years of irresponsible actions have lead to high rise in heavy metal related disease and disorders as recorded in some countries. In India, a study reveals existent of heavy metals in abnormal amounts in plants like lettuces in some region (Naaz and Pandey, 2009), while discoveries of high metals in sea water fishes (Mukhtar *et al.*, 2010) all are evident that biosphere pollution by heavy metal has accelerated during the last few decades.

An upcoming trend that has caught much attention in the research field in dealing with heavy metal pollution is the science of biosorption. In general, biosorption is a separation process that utilises adsorption via binding molecules or heavy metals in this case by attractive forces, ion exchange and chemical binding. Biosorption utilises solid biomass-based material as means of adsorbent, hence called biosorbent which can be found naturally. Among the main categories of biomasses that can be used for preparing biosorbents are bacteria, fungi, algae, and industrial wastes. Examples of industrial wastes are such as fermented waste, food waste and finally agricultural waste. In the latter stated category, the choice of biomass is vast and it is arguably the preferred and ideal option. Agricultural wastes possess promising adsorption capacity due to its major composition of lignocelluloses. Lignocellulose is a combination lignin, cellulose and hemicelluloses can provide high surface area for metal adsorption. This however can be improved much further by a pre-treatment process using multiple choices of reagents to impose polar functional groups to increase the selectivity towards a particular ion or a group of similar ionic base for that matter.

The favouritism towards biosorption process can be referred mainly to its low cost as compared to conventional technology. The performance of biosorption is arguably parallel to common conventional method using ion exchange resins and activated carbon while cost wise, it can be cheaper with up with to ten times lower. This lower cost factor is due to the fact that biosorbents only requires simple processing and treatment for its preparation and that its source can be found abundantly in nature or as a result of waste generated from industrial by-product. This statement is supported by Bailey *et al*. (1999), on a review of potentially low cost sorbents for heavy metals. Aside from that, biosorption also gives the opportunity to regenerate biosorbents and the given possibility of metal recovery following adsorption in which case conventional methods seldom offer or impractical. Some examples of such agricultural waste are rice straws, soy bean hulls and oil palm empty fruit bunches.

1.2 Problem Statement

The increasing traces of heavy metals contamination recorded each year in food, plants and drinking water have raised concerns among the environmentalist, government and general community. Many actions have been proposed and regulated to impose more stringent law regarding heavy metal pollution. Among the actions taken are reducing the threshold or maximum allowable limit of heavy metal disposal especially from industries and increasing the penalty in non compliance with the law. In consequence, demand for a practical and more feasible method of controlling heavy metal is on the rise to comply with government regulations and environmental safety. Biosorption is a technology with an upcoming trend in heavy metal pollution control. In comparison to common conventional method for example ion exchange resins or activated carbon, biosorbent has the potential of performing the same capacity with a fraction of conventional resin cost. The advantage of having low cost up to ten times cheaper is due to its dependency of raw material which is abundant and practically costless. This will motivate industrialist even further to manage waste in a proper manner before releasing industrial effluent into environment. In addition to that, biosorption utilises similar sorption column used for ion exchange resin which can be fitted immediately barring additional modification. Further possibilities of heavy metal recovery via desorption and reusability of biosorbents increases the economical value of biosorption method. In this study, oil palm empty fruit bunches will be used as biosorbent source due to its immense availability and practically costless. Mercury ion Hg (II) and methylmercury ion CH_3Hg (I) will be focussed due to its high toxicity, high interest in demand and also because they are always detected in industrial waste (Ngah and Hanafiah, 2007). This biosorbent will be further treated using 3-ureidopropyltriethoxysilane (3-UPTES) in an attempt to improve the sorption performance.

1.3 Research Objectives

The objectives of this research are:

1. To synthesize, functionalize and characterize oil palm empty fruit bunches as biosorbents for mercury ion Hg (II) and methylmercury ion CH_3Hg (I),

2. To evaluate the performance of the treated OPEFB as to the untreated OPEFB in terms of biosorption capacity for varying parameters such as solution pH, ligand concentrations, temperatures, contact time and initial concentrations. Appropriate adsorption equilibrium model and kinetic model that best suits the experiment data will be studied. The performance of biosorbents towards mercury metal selectivity and regenerability will be evaluated.

1.4 Research Scopes

OPEFB fibres were obtained from a Sabutek Sdn. Bhd and were grinded to achieve particle size between 100 µm to 70 µm. 3-ureidopropyltriethoxysilane (3-UPTES) was used to graft the organosilane functional groups onto the biosorbents. The characterisation of these adsorbents will be done using scanning electron microscope (SEM), fourier transform infra-red spectrophotometer (FTIR), cation exchange capacity (CEC) and biosorbent point zero charge (pH_{pzc}). British standard ISO 11260: 1994 was used to determine CEC while pH_{pzc} was determined using immersion techniques.

Biosorption experiments were carried out in batch mode with initial metal concentration at 1 milimolar. The adsorbent dosage ratio was fixed at 1:1 i.e., 50 mg adsorbent/50 ml metal solution with agitation speed at a constant 200 rpm for every tests. Atomic adsorption spectrophotometer (AAS) with air-acetylene flame (method 3111B) was used to determine the concentration of metal ions. Langmuir and Freundlich isotherm models were applied to analyse the biosorption isotherm of the biosorbents, while pseudo-first order, pseudo-second order and Elovich kinetic models were applied to investigate the biosorption kinetics. Mercury metal selectivity study was conducted for each sorbent for Pb, Zn, and CH_3Hg (I) in an individual batch biosorption test. Dissociation constant, K_d will be used to evaluate selectivity over metals. Regenerability study was conducted using hydrochloric acid (HCl) at 0.1 M as the desorption agent for a total of four cycles. Range of solution pH studied are from 2-11, while the ligand concentrations tested were at 0.01 M, 0.05 M, 0.10 M, 0.5 M. Batch biosorption experiments were tested in varying temperatures at 30^{o}C, 40^{o}C, 50^{o}C and 60^{o}C. Effect of initial metal concentrations toward biosorption capacity was tested at 25 ppm, 50 ppm, 100 ppm, 200 ppm, 350 ppm and 400 ppm.

1.5 Dissertation Outline

This dissertation outline report comprises of five chapters in total. Chapter 1 provides an introduction to the research background explaining the current scenario in heavy metal pollution, the role of industrialist in overcoming this problem and the advantages of the in-demand biosorption technology as to conventional technology in dealing with heavy metal pollution. These are briefly condensed into a subtopic of problem statement for the interest in this study. Objectives and scopes provide an outline of boundary within this study to be conducted. Chapter 2 illustrates and demonstrates the fundamentals of study behind this research while exposing the past and present literature studies conducted worldwide. It also provides critical review in the current scenario and trends. Chapter 3 discusses about research methodology that was finalised in the sample preparation, functionalisation, characterisation and in biosorption/desorption procedures. These procedures were either adopted or modified from many past successful researches to suit the need of the objectives and scopes in this study. Chapter 4 present the results and discussions about characterisation, modification and biosorption performance of biosorbents when exposed in varying parameter namely, pH, temperatures and others. Appropriate kinetic models and isotherm models that would provide the best fit to the experimental data was also studied in this chapter, besides understanding the mechanisms involved in governing the biosorption taking place. In addition to that, the response of biosorbents toward mercury metal selectivity and regenerability study was investigated and discussed. Summary of research findings and the recommendation for future works are presented in Chapter 5.

1.6 Summary

To sum up, heavy metal pollution that have steadily increase over the past decade has started to take its toll on both the human kind and the wildlife. Persistent as they are toxic in nature, heavy metal do not biodegrade but leaches along into streams and accumulates in soils. Over time, these heavy metals reach its threshold limit whereby it can be hazardous to health. Naked to the eye, these heavy metals could slip into food chain unintentionally via plant intake of nutrients from soils and end up poisoning the food we consume, not to mention the long term ecological treat it possess to the environment. Independent researches elsewhere have shown some level of heavy metal contamination in food chain including mercury metals for examples in seawater fishes and in vegetables. Recent discoveries in biosorption have shown promising result in adsorbing heavy metals. They have potential advantages of lower cost, and sustainability. The performance of biosorbents is generally on par with conventional methods and in some reported cases performs better. On top of that, there is possibility of regeneration and heavy metal recovery that conventional methods seldom offer. This makes biosorption more promising thus more economically viable. Besides that, biosorbent can be readily modified and functionalized with many options of pretreatment to improve sorption capacity. This study will focus on identifying the performance of biosorbent using OPEFB as biomass source in the removal of mercury ions and methylmercury ions as compared to 3-UPTES treated OPEFB biosorbents. Meanwhile, the effects of varying parameters have on biosorption capacity of these biosorbents on mercury and methylmercury metals removal will be investigated to better understand the adsorption mechanism taking place.

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