PHYSICOCHEMICAL CHARACTERISATION OF UNMODIFIED OIL PALM MILL FLY ASH AND ITS ADSORPTION OF COPPER(II) AND LEAD(II) IONS FROM AQUEOUS SOLUTIONS

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DECLARATION

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

29th August 2016.

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ABSTRACT

This study was conducted to test the capability of locally abundant oil palm mill fly ash (OPMFA) in its ability to adsorb copper(II) and lead(II) ions from aqueous solutions. The OPMFA sample was collected from a local palm oil mill. Sample characterisation was carried out in order to understand its physicochemical properties. Different experiments related to characterisation including, particle size distribution analysis, leaching test, surface area and pore distribution, elemental analysis, Fourier transform infrared analysis, surface morphology, point of zero charge, adsorbent pH in distilled water and thermogravimetric analysis were conducted to understand its behaviour as an adsorbent. The OPMFA was observed to be fine in nature from grey to black in colour with highly porous irregular structure with BET specific surface area of 24.04 m^2/g and average pore diameter of 2.37 nm. The OPMFA was found to be safe for use, as an adsorbent, as no heavy metal leach out was detected upon Atomic Absorption Spectrometry analysis. The point of zero charge of OPMFA found in this study was 8.9, which favours the adsorption of copper(II) and lead(II) ions, and specific functional groups responsible for adsorption were found upon FT-IR analysis. Batch adsorption experiments were conducted to test the ability of OPMFA to adsorb copper(II) and lead(II) ions from aqueous solutions. The effects of particle size, contact time, agitation rate, adsorbent dosage, initial concentration, pH and accompanying anions were experimented. The particle size fraction of $0.150 < x \leq 0.200$ mm with 60 min of contact time at agitation speed of 150 rpm were the optimum conditions observed in this study. Additionally the adsorbent dosage of 0.1 g per 100 mL with the initial concentration of metal ions of 10 mg/L at the natural pH 5.5 are the suitable conditions for effective adsorption. Nitrate ions were selected in this study as the counter ion effect was the lowest compared to sulphate, acetate and chloride ions. The isotherm studies revealed that the adsorption of copper(II) and lead(II) ions followed the monolayer adsorption pattern with maximum adsorption capacity of 153.85 and 181.82 mg/g, respectively. The kinetic studies illustrated that the pseudo-second order model better fitted the kinetic data compared to other kinetic models suggesting that chemisorption is the rate limiting step.

Keywords: Physicochemical characterisation, OPMFA, adsorption, isotherm, kinetic

ABSTRAK

PENCIRIAN FIZIKOKIMIA DAN PENJERAPAN ION KUPRUM(II) DAN ION PLUMBUM(II) DARIPADA LARUTAN-LARUTAN AKUEUS MENGGUNAKAN ABU TERBANGAN KILANG MINYAK KELAPA SAWIT
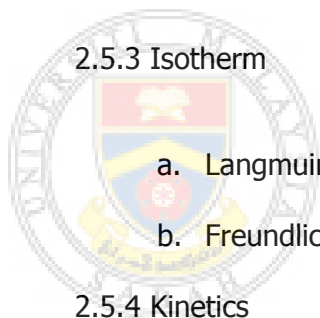
Kajian ini dijalankan untuk menguji keupayaan abu terbangan kilang kelapa sawit (OPMFA) secara lokal yang banyak untuk menjerap ion kuprum (II) dan plumbum (II) dari larutan akueus. Sampel OPMFA dikumpul dari Kilang Kelapa Sawit Pitas, Sabah. Pencirian sampel telah dijalankan untuk memahami komposisi, tekstur dan keliangan sampel tersebut. Eksperimen yang berbeza yang berkaitan dengan pencirian termasuk, analisis taburan saiz zarah, ujian larut lesap, luas permukaan dan pengedaran liang, analisis unsur, Fourier mengubah inframerah (FT-IR) analisis, morfologi permukaan, titik caj sifar, adsorben pH dalam air suling dan analisis termogravimetri telah dijalankan untuk memerhati tingkah laku sampel sebagai adsorben. Kajian ini telah mendapati bahawa OPMFA adalah baik dalam keadaan semulajadi yang berwarna dari kelabu ke hitam dengan struktur yang tidak teratur dan sangat berliang dengan kawasan permukaan BET daripada 24.04 m2/g dan purata diameter liang 2.37 nm. OPMFA telah didapati selamat untuk digunakan sebagai adsorben, kerana tiada logam berat meluluh keluar dikesan apabila Penyerapan Spektrometer Atom (AAS) analisis dijalankan. Titik caj sifar OPMFAyang ditemui dalam kajian ini adalah ialah 8.9, yang telah membantu penjerapan kation kuprum (II) dan plumbum (II), dan kumpulan berfungsi khusus yang bertanggungjawab untuk penjerapan telah dikenalpasti dalam analisis FT-IR. Eksperimen penjerapan Batch telah dijalankan untuk menguji keupayaan OPMFA untuk menjerap kuprum(II) dan plumbum(II) ion membentuk larutan akueus.Kepentingan parameter berbeza yang diambilkira termasuklah kesan saiz zarah, masa sentuhan, kadar pergolakan, dos bahan penjerap, kepekatan awal, pH dan ion kaunter untuk menguji kesan ke atas proses penjerapan. Pecahan saiz zarah kecil daripada pada 0.150 <x ≤ 0.200 mm dengan 1 jam masa sentuhan pada kelajuan penggoncang 150 rpm adalah keadaan optimum dalam kajian ini. Selain itu dosej adsorben sebanyak 0.1 g per 100 mL dengan kepekatan awal 10 mg/L pada pH semula jadi 5.5 adalah keadaan yang sesuai untuk penjerapan yang berkesan. Ion nitrat dipilih dalam kajian ini kerana kesan kaunter ion adalah paling rendah berbanding dengan ion sulfat, asetat dan klorida. Kajian ini isoterma mendedahkan bahawa penjerapan kuprum(II) dan plumbum(II) ion mengikuti corak monolayer penjerapan dengan kapasiti penjerapan maksimum 153.85 dan 181.82 mg/g, masing-masing.Kajian kinetik digambarkan bahawa urutan model bagi pseudo-kedua lebih baik dilengkapi data kinetik berbanding model kinetik lain di mana kajian ini mencadangkan bahawachemisorption yang mengehadkan langkah kadar.

Kata kunci: Pencirian fizikokimia, OPMFA, penjerapan, isoterma, kinetik

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B	Boyd constant (1/min)
C	Adsorption constant (mg/g)
C_e	Adsorbate concentration at equilibrium (mg/L)
C_o	Initial adsorbate concentration (mg/L)
C_t	Adsorbate concentration at time t (mg/L)
C_u	Uniformity coefficient
d_{10}	Diameter of the sieve where 10% (w/w) passes
d_{60}	Diameter of the sieve where 60% (w/w) passes
F	Fraction of solute adsorbed at different time t
h	Initial adsorption rate (mg/g min)
k_1	Pseudo-first-order rate constant (1/min)
k_2	Pseudo-second-order rate constant (g/mg min)
K_F	Freundlich adsorption capacity constant
k_{int}	Intraparticle diffusion rate constant (mg/g min$^{1/2}$)
K_L	Energy adsorption constant (L/mg)
n	Freundlich intensity constant
pH_f	Final pH
pH_i	Initial pH
pH_{pzc}	pH point of zero charge
Q_e	Amount of adsorbate adsorbed at equilibrium (mg/g)
$Q_{e\ cal}$	Calculated amount of adsorbate adsorbed at equilibrium (mg/g)
$Q_{e\ exp}$	Experimental amount of adsorbate adsorbed at equilibrium (mg/g)
Q_m	Maximum amount of adsorbate adsorbed (mg/g)
Q_t	Amount of adsorbate adsorbed at time t (mg/g)
R_L	Hall separation factor
t	Time (min)
x	Particle diameter (mm)

CHAPTER 1

INTRODUCTION

1.1 Introduction and Relevance of Study

Rapid industrialisation and urbanisation have increased the ecological problems in all over the world (Benaïssa and Elouchdi, 2007) and water contamination by heavy metals has become a major environmental concern (Fu and Wang, 2011). Wastewater effluents from industries such as mining, electronic industries, paint and pigment manufacturing, electroplating, metal finishing, battery manufacturing, steel industry, tanneries, fertilisers, pesticides, refinery and petrochemicals, ceramic and glass industries are sources of heavy metals into the aquatic system (Williams *et al.*, 1998). However, other sources of heavy metals are weathering of rocks and volcanic eruptions, domestic and urban runoff, thereby producing large quantities of contaminated water (Park *et al.*, 2010). The heavy metals released into water can be carried in surface waters either in the form of metallic compounds or as free metal ions.

The heavy metal pollution occur when the concentration of heavy metal in discharged water exceed the allowed limit. The heavy metals are persistent and can exist in the environment for prolonged time (Miretzky *et al.*, 2004). Contrary to organic pollutants, heavy metals cannot be biodegraded, enter into food chain and possesses tendency to be bio-accumulated in living organisms especially in liver, kidney and bones (Lane and Morel, 2000; Singh *et al.*, 2010).

The treatment of heavy metal is inevitable because of its persistency and adverse health effects. In recent years, various methods of heavy metal removal from

wastewater were extensively employed. These include chemical precipitation, ion exchange, coagulation and flocculation, flotation, membrane filtration, and adsorption (Fu and Wang, 2011; Mahmood *et al.*, 2011; Lizama *et al.*, 2011).

Adsorption is one of the recognised efficient processes of heavy metals removal from aqueous solutions. In spite of the usefulness and effectiveness of alumina, silica, iron oxide, zeolite and activated carbon as absorbents of heavy metals, their high costs have limited their widespread use. Therefore, some studies have been carried out with the intention of applying cost effective materials including agricultural and industrial wastes as adsorbents for the removal of heavy metals from wastewaters. These materials should have high affinity, selectivity and capacity towards metals.

Oil palm mill fly ash (OPMFA) was one of the materials that was studied and approved as a competitive absorbent. Its selection results in helping overcome two problems at a time, which are the disposal of produced ash and its usage as a low cost adsorbent for the treatment of wastewater and soils (Foo and Hameed, 2009).

1.2   Problem Statement

Currently Malaysia is the world's second largest palm oil producer after Indonesia (MPOB, 2015), and industry related waste. The waste such as oil palm fibre, nut shell, palm kernel and empty fruit bunch are the solid waste obtained from palm oil processing for oil extraction. Additionally, these wastes are usually burned in boilers and from this process two types of palm ashes are produced which are boiler ash and OPMFA. The total production of oil palm ash was 4 million tonnes (Mohamed *et al.*, 2005) and the estimated production of OPMFA has increased to 5.64 million tonnes and is being discarded without further use and Malaysia as a whole is facing heavy metal pollution. Presently, there are low-end strategies for the utilisation of this abundant waste material. The OPMFA presents a huge environmental conern as the

unused ash is disposed in landfills. It has been shown in the literature that OPMFA can be effectively used as adsorbent for different contaminants from aqueous media (Foo and Hameed, 2009). Hence, it is proposed to use the un-attended waste material to utilise it for heavy metal removal from aqueous solution. The application of OPMFA for the treatment of heavy metal containing water offers a solution for both major problems, which are the heavy metal pollution and the effective management of OPMFA.

The review of literature enables us to identify the existing data gap of research. The existing data gap is in the physicochemical characterisation of unmodified oil palm mill fly ash from North-East Borneo, and its adsorption of Cu(II) and Pb(II) ions from aqueous solutions.

1.3   Research Objectives

The OPMFA has not been used yet to assess its potential on heavy metal removal from aqueous solutions, thus, indicating data gap. Hence, the objectives of this work are given below;

(i)   To investigate the physico-chemical properties of OPMFA.

(ii)   To study the effect of various conditions (particle size, contact time, agitation rate, dosage, initial concentration, initial pH and accompanying anions) on the adsorption performance of OPMFA as heavy metal adsorbent utilising Cu(II) and Pb(II) ions as model heavy metals.

(iii)   To investigate the adsorption isotherm and kinetic involved.

1.4   Scope of Study

Present work has been designed to conduct the laboratory based experiments. The results from previous studies show that OPMFA can replace conventional adsorbents

(Aziz *et al.*, 2014). This study is aimed at finding out how a manipulation of the following parameters; particle size, contact time, agitation rate, adsorbent dosage, initial concentration, pH and accompanying anions affect the adsorption potentials of OPMFA on Cu(II) and Pb(II) ions. Langmuir and Freudlich adsorption isotherm constants will be empirically determined for the systems in the study. Additionally, different kinetic models will be applied to understand and explain the adsorption kinetics involved in the process. Moreover, the characterisation of OPMFA will help us better understand the character and behaviour of adsorbent.

1.5   Significance and Limitations

In recent years, researchers had introduced new cost effective adsorbents for heavy metal removal from aqueous solutions. The application of OPMFA as adsorbent can be cost effective and easy compared to conventional expensive activated carbon. It may allow many researchers and industrialist to utilise this harmful industrial waste efficiently as the present practice is dumping the OPMFA in land-fills. The above mentioned strategy of recycling waste material will help save money to contribute in national economy.

There are some limitations in this study as the present work is completely a laboratory scale approach. In general, contaminated wastewaters contain more than one heavy metal with other organic pollutants. Present study has been designed for single metal synthetic solution which is a limitation because from the point of view of environmental protection, adsorption studies from multi-metal systems with organic contaminants, to which much work has been dedicated, is imperative.

CHAPTER 2

LITERATURE REVIEW

2.1 Copper

Copper (Cu) is one of the element of 4th period in the Periodic Table and a member of 11th group also known as d-block element. It is found in group 1B alongwith other elements like silver (Ag) and gold (Au). Copper has atomic mass of 63.546 g/mol or 63.546 amu and has atomic number of 29. Copper has as many as six isotopes (Chang, 2007; Moore, 1972). The melting and boiling points of copper are 1083.0°C and 2567.0°C respectively. It has an electronegativity value of 1.9 (Pauling scale) and a density of 8.9 g/cm^{-3} at 20°C. It shows different oxidations state (1^+, 2^+, 3^+ and 4^+) by which it forms a variety of compounds (Holleman and Wiberg, 2001).

Pure copper is soft, malleable, ductile and very high thermal and electrical conductivity. It is a reddish-orange metal with a bright metal lustre and face centred cubic crystalline structure (Engel and Reid, 2005; Chang, 2007). Being in group 11 of the Periodic Table it shares certain attributes having one s-orbital electron with a filled d-electron shell on top and are termed as highly ductile and electrical conductive. In contrast to other metals it has metallic bonds lacking a covalent character and are relatively weak, which explains the low hardness and high ductility of single copper crystal (Trigg and Immergut, 1992).

Copper does not react with water but it reacts with atmospheric oxygen forming a greenish layer which helps protect it from further corrosion (Monk, 2004; Chang, 2007). Its compounds are commonly known as copper salts, which give green or blue colour to minerals.

Copper is present in earth's crest and most of copper is mined or extracted as copper sulphides also known as chalcopyrite (John, 2003). Copper is also found in other minerals such as azurite, malachite, bornite and cuprite. Usually it is obtained through the process of smelting, leaching and electrolysis (Monk, 2004).

Copper is abundant in the environment with a concentration of 50 ppm in the Earth's crust and 0.25 ppb in Ocean water (Chester, 1990) to over 100 ppm in sediments. Copper is introduced in to the aquatic environment through a number of natural methods. The sources of copper in the aquatic environment are (i) minerals in soil and weathered rock that form the sediments and suspended particles in the water, (ii) extraction of copper from rock into a dissolved state, (iii) biological particles, including both living and dead organic material, (iv) hydrothermal systems in which heated or chemically altered water are found and it includes volcanic action and thermal vents, (v) input from sediments, (vi) deposition from the atmosphere and (vii) anthropogenic inputs - either directly into the water or leached after deposition on land (Lewis, 1995). Additional sources of copper are industrial, agricultural activities and runoffs from land, roads and roofs (Nirel and Pasquini, 2010). These include electroplating, metal finishing, paper board mills, wood pulp production, fertilisers, paints and pigments, urban and storm water run-off (Benaïssa and Elouchdi, 2007). Copper may exist in water in either the monovalent copper(I) or divalent copper(II) valence states. The copper(III) and copper(IV) valence states are known to exist only at high temperature and usually in the presence of high oxygen concentrations (Cotton and Wilkinson, 1988). However, copper metal may undergo following electrochemical transformations given in Equations 2.1 and 2.2 in potable water:

$$Cu_{(s)} \qquad Cu^+ + e^- \qquad\qquad (2.1)$$

$$Cu^+ \qquad Cu^{2+} + e^- \qquad\qquad (2.2)$$

The above shown transformation from Cu^+ to Cu^{2+} is essentially the rate limiting factor with Cu^+ existing essentially in reversible equilibrium with the Cu metal at the pipe surface (Mattsson, 1980).

2.2   Lead

Lead (Pb) is one of the element of 6th period in the Periodic Table and a memeber of 14th group which is known as poor metals. The other elements included in this group (14th) are germanium (Ge) and stannum (Sn) also known as tin. Lead has an atomic mass of 207.2 g/mol or 207.2 amu and has atomic number of 82. It has four stable isotopes which are ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. The melting and boiling points of lead are 327.5 °C and 1749.0 °C respectively. It has an electronegativity value of 1.87 (Pauling scale) and a density of 11.34 g/cm^{-3} at 20°C. It shows different oxidations state (1^+, 2^+, 3^+ and 4^+) by which it forms a variety of compounds.

Lead is a soft and malleable metal, which is categorised as a heavy metal. Metallic lead has a bluish-white colour after being freshly cut and soon tarnishes to a dull greyish colour upon exposed to air. Usually lead has a shiny chrome-silver lustre when it is melted into a liquid. It has characteristic properties including high density, softness, poor electrical conductance, anti-corrosive, ductile and ability to react with other organic chemicals. It does not react with water but it reacts with oxygen, sulphur, halogens, carbonate and nitrate to form lead oxide, sulphide, halide, carbonate and nitrate, respectively. Lead reacts with sodium metal that reacts with alkyl halides to form organometallic compounds of lead such as tetraethyllead (Windholz, 1976).

Lead is found in the solar atmosphere, and much more abundant in the atmospheres of some hot sub dwarfs (Naslim *et al.*, 2013). It is hard to find free lead in nature, and is usually obtained from the ores such as galena (PbS), anglesite

(PbSO$_4$), cerussite (PbCO$_3$) and minum (Pb$_3$O$_4$) (Holleman *et al.*, 1985). Although lead makes up only about 0.0013% of the earth's crust, it is not considered to be a rare element since it is easily mined and refined. Most lead is obtained by roasting galena in hot air, and nearly one third of it is obtained through recycling efforts.

The commercial importance of lead is based on the following aspects, which are ease of casting, relative abundance, low melting point (327°C), high density, low strength, acid resistant, ease of fabrication, chemical stability and electrochemical reaction with sulphuric acid. There are three primary sources of lead exposure worldwide including lead-based paint found in older homes, in urban soil and dust and in drinking water. Lead based paint was extensively used in pigments and drying agents for oil based paints all over the world. Emission of lead compounds from automobiles during the last century was the single largest anthropogenic source of lead in history. Petrol containing tetraethyl lead to boost octane number was placed worldwide in early 1920s despite the opposition by leading scientists and public health officials (Lin, 1992). Large quantities of lead were redistributed into soil and dust, particularly in urban environments, which have elevated levels resulting in contamination of the food chain and drinking water.

2.3   Water Contamination

Water pollution has become a growing concern over the last century as more and more waste is being disposed of in our oceans, rivers, streams and lakes. The increase in pollution is spoiling our food supplies, drinking water and environment. Additionally, it is responsible in creating issues in the oceans ecosystem and hurting the animals and plant life that rely on the ocean and rivers for their survival. Water pollution is caused by the intentional or unintentional release of toxic chemicals/materials, contaminants and harmful compounds into various bodies of water such as rivers, lakes and the ocean. Without proper disposal or filtration of

these pollutants they can spread throughout the water bodies and effect all living things that requires water for survival.

In addition to harming animals, water pollution can also affect plants, trees, the soil and other natural materials and resources of the earth. Water pollution is generally caused by human actives but may also be caused by natural resources. Once water becomes polluted it becomes unsafe for consumption due to the dangerous or toxic materials that are contained within the water.

2.3.1 Water pollution in Malaysia

In general, water can be categorised to groundwater, river water and marine water. According to a report by Department of Environment (DOE) the heavy metal content in river water was in agreement with Class III of National Water Quality Standards of Malaysia (NWQSM) with only 94 %, exception to iron (DOE, 2010). Table 2.1 summarises the permissible limit of different heavy metals in NWQSM. Class III water can be utilised for common domestic use, fishery and livestock drinking, but treatment is required if it is to be used as water supply. However, the Class IIA water can be used for sensitive aquatic species and water supply after conventional treatment and IIB can be used for bathing and other recreational uses. The Class IV is advised to use for irrigational purpose.