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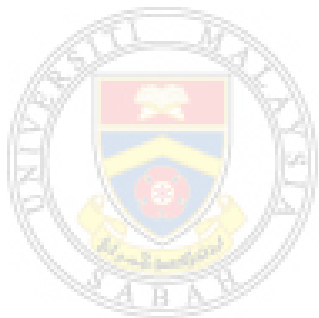
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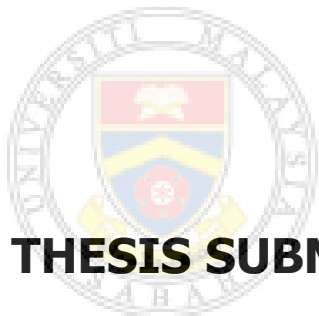
SCHOOL OF SCIENCE AND TECHNOLOGY

UNIVERSITI MALAYSIA SABAH

2012

ADSORPTION OF COPPER(II) AND LEAD(II) IONS FROM AQUEOUS SOLUTIONS BY UNMODIFIED OIL PALM SHELL

CHIA PUI SAN

THESIS SUBMITTED IN FULFILLMENT FOR THE DEGREE OF MASTER OF PHILOSOPHY

SCHOOL OF SCIENCE AND TECHNOLOGY

UNIVERSITI MALAYSIA SABAH

2012

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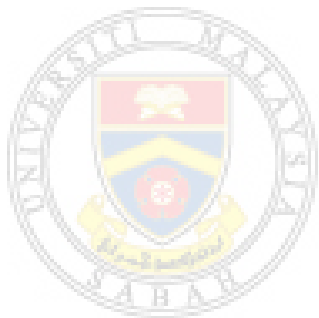
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TITLE : **ADSORPTION OF COPPER(II) AND LEAD(II) IONS FROM AQUEOUS SOLUTIONS BY UNMODIFIED OIL PALM SHELL**

DEGREE : **MASTER OF PHILOSOPHY (ENVIRONMENTAL SCIENCE)**

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ABSTRACT

ADSORPTION OF COPPER(II) AND LEAD(II) IONS FROM AQUEOUS SOLUTIONS BY UNMODIFIED OIL PALM SHELL

Heavy metals can cause poisoning in living organisms. One of the treatment methods that is economical and environmentally friendly is by adsorption. In this study, the characteristics of adsorbent prepared from spent oil palm shell was analysed and the adsorbent was used for adsorption of Cu(II) and Pb(II) ions. Experiments were conducted through batch adsorption experiments technique to assess the effect of particle size, contact time, agitation rate, dosage, initial adsorbate concentration and initial pH. The residual Cu(II) and Pb(II) ions were detected using atomic absorption spectrometer. The oil palm shell were sieved into various sizes with 27.47% of particles were size $8 < \chi \leq 10$ mm, 23.26% of particles with size $10 < \chi \leq 13$ mm and 21.96% with size $6.5 < \chi \leq 8$ mm. The distribution of oil palm shell particles has uniformity coefficient of less than three indicating potential as filter bed material from hydraulic point of view. Adsorption of Cu(II) and Pb(II) ions could occur in absence of agitation, fulfilling the criteria as filter bed material for slow water feeding system. The pH_{pzc} was found to be at pH 4.1 with maximum adsorption occurred between pH 4.1 to pH 6. Adsorption equilibrium was achieved in 480 min in 150 rpm agitation. Adsorption capacity was enhanced with smaller particle size, lower dosage and higher initial adsorbate concentration. Adsorption isotherms were modeled using Langmuir and Freundlich models and Freundlich model fitted the adsorption data well. This suggested multilayer adsorption manner. The maximum adsorption capacity was found to be 1.76 and 3.39 mg/g for Cu(II) and Pb(II) ions, respectively. Four kinetic models employed in this study were intraparticle diffusion model, expression of Boyd, pseudo-first-order model and pseudo-second-order models. The adsorption data fitted into pseudo-second-order model suggesting occurrence of chemisorption. The results showed that oil palm shell is a potential adsorbent for Cu(II) and Pb(II) ions.

ABSTRAK

Logam berat boleh menyebabkan keracunan pada organisma hidup. Salah satu kaedah rawatan yang ekonomik dan mesra alam adalah melalui penjerapan. Dalam kajian ini, ciri-ciri penjerap yang disediakan daripada sisa tempurung kelapa sawit dianalisa dan penjerap tersebut digunakan untuk menjerap ion Cu(II) dan Pb(II). Eksperimen dijalankan melalui teknik ekperimen kelompok untuk menilai kesan saiz zarah, masa sentuhan, kadar goncang, dos, kepekatan awal larutan jerapan dan pH awal. Sisa ion Cu(II) dan Pb(II) dikesan menggunakan spektrometer penyerap atom. Tempurung kelapa sawit ditapis kepada pelbagai saiz dengan 27.47% zarah bersaiz $8 < \chi \leq 10$ mm, 23.26% zarah dengan saiz $10 < \chi \leq 13$ mm dan 21.96% dengan saiz $6.5 < \chi \leq 8$ mm. Taburan saiz zarah tempurung kelapa sawit sawit mempunyai pekali keseragaman kurang daripada tiga menunjukkan potensi sebagai bahan penuras dari segi hidraulik. Penjerapan ion Cu(II) dan Pb(II) boleh berlaku tanpa kehadiran goncangan, menepati kriteria sebagai bahan penuras untuk sistem saliran perlahan. Nilai pH_{pzc} didapati berada pada pH 4.1 dengan penjerapan maximum berlaku antara pH 4.1 dan pH 6. Keseimbangan penjerapan tercapai dalam 480 min dengan kadar goncangan 150 rpm. Kapasiti penjerapan meningkat dengan saiz zarah yang lebih kecil, dos yang lebih rendah dan kepekatan awal larutan jerapan yang lebih tinggi. Isoterma penjerapan telah dimodelkan dengan model Langmuir dan Freundlich dan model Freundlich lebih bersesuaian dengan data penjerapan. Ini mencadangkan penjerapan secara multi lapisan. Kapasiti penjerapan maksimum masing-masing adalah sebanyak 1.76 dan 3.39 mg/g untuk ion Cu(II) dan Pb(II). Empat model kinetik yang digunakan dalam kajian ini adalah model difusi intrapartikal, ungkapan Boyd, model tertib pertama pseudo and model tertib kedua pseudo. Data penjerapan sesuai dengan model tertib kedua pseudo mencadangkan kehadiran proses kimia jerapan. Keputusan menunjukkan bahawa tempurung kelapa sawit merupakan potensi penjerap untuk ion Cu(II) dan Pb(II).

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LIST OF SYMBOLS

A_p	Surface area of particle
A_s	Surface area of sphere
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_o	Initial adsorbate concentration (mg/L)
C_t	Adsorbate concentration at time t (mg/L)
C_u	Uniformity coefficient
d_{10}	Diameter of the particle that 10% (w/w) passes the sieve (mm)
d_{60}	Diameter of the particle that 60% (w/w) passes the sieve (mm)
F	Fraction of solute adsorbed at different time t
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_{id}	Intraparticle diffusion rate constant (mg/g min$^{1/2}$)
K_L	Energy adsorption constant (L/mg)
n	Freundlich intensity constant
$\emptyset$	Diameter (mm)
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_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)
u	Initial adsorption rate (mg/g min)

V	Volume of adsorbate (L)
W	Mass of adsorbent (g)
χ	Geometrical mean particle size (mm)
ψ	Shape factor
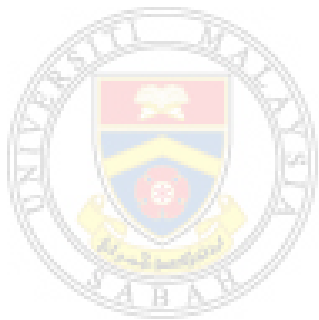
LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrometer
BDH	4-bromoaniline-azo-1,8-dihydronaphthalene-3,6-disodiumsulphate
BET	Brunauer-Emmett-Teller
FT-IR	Fourier transform infrared spectroscopy
IUPAC	International Union of Pure and Applied Chemistry
MB	Methylene blue
MG	Malachite green
MPOB	Malaysian Palm Oil Board
OPS	Cleaned dried oil palm shell
PEI	Polyethyleneimine
POME	Palm oil mill effluent
SEM	Scanning electron microscope
TGA	Thermogravimetry analysis
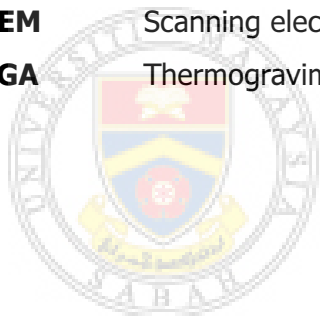
CHAPTER 1

INTRODUCTION

1.1 Heavy Metals

Several elements that are grouped under heavy metal include arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), gold (Au), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), platinum (Pt), silver (Ag) and zinc (Zn) (Ngah and Hanafiah, 2008). Some of these elements are categorised as precious metals such as Au, Pt and Ag. They have economical value especially in jewellery industry. Therefore, they are recovered even from the effluent rather than being discharged to the environment.

Heavy metals in the environment are caused by discharge from mining and smelting activities, battery industry and runoff from agricultural practice (Dong *et al.*, 2010). Heavy metal pollution occur when the level of heavy metal presents exceed the allowable limit. Heavy metal is persistent in nature, whereby it is non-biodegradable (Al-Qodah, 2006). It also possesses tendency to be bioaccumulated in living organisms especially in vital organs such as kidney, bones and liver (Singh *et al.*, 2010).

The presence of some heavy metals in trace amount in diet is essential for human health (Asci *et al.*, 2010). For example, Fe is essential as a component in haemoglobin. Deficiency in Fe can result in anaemia. Other listed essential heavy metals are Cu, Mn and Zn which function together to participate in enzymatic reactions (Yoshihara *et al.*, 2010).

However, excessive exposure to heavy metals can result in toxicity (Xiong *et al.*, 2006). Globally known heavy metal toxicity incidents include Itai-itai disease due to Cd poisoning (Nomiyama *et al.*, 1973; Nogawa *et al.*, 1975; Kawano *et al.*, 1986; Whelton *et al.*, 1997; Inaba *et al.*, 2005) and Minamata disease caused by Hg poisoning (Igata, 1993; Harada *et al.*, 1999; Ekino *et al.*, 2007; Yorifuji *et al.*, 2009). Due to the severity of heavy metal poisoning, it is vital to develop methods to address heavy metal pollution.

1.2   Heavy Metal Pollution Scenario in Malaysia

Three categories of water in Malaysia are river water, groundwater and marine water. In general, heavy metal content in river water complied well with Class III of National Water Quality Standards of Malaysia with the exception to Fe, which only 94% compliance was reported (DOE, 2010). Class III water is suitable for common fishery with tolerant species and livestock drinking. However, extensive treatment is required if it is to be used as water supply. Table 1.1 is a summary of the limits on various heavy metals in National Water Quality Standards of Malaysia.

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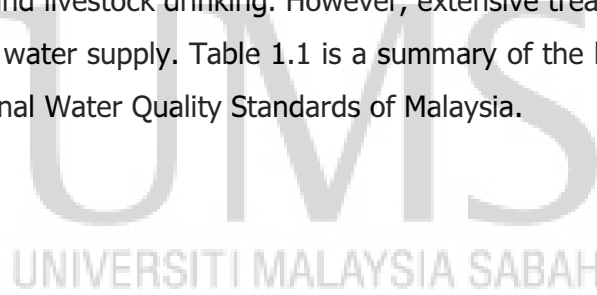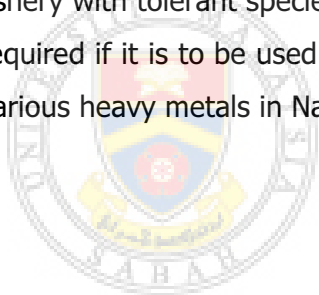
Table 1.1: Heavy Metal Limit in National Water Quality Standards for Malaysia

Metal	Class				
	I (mg/L)	IIA/IIB (mg/L)	III (mg/L)	IV (mg/L)	V (mg/L)
As		0.05	0.4	0.1	
Cd		0.01	0.01	0.01	
Cr(IV)	Natural level or absent	0.05	1.4	0.1	Level above IV
Cr(III)		-	2.5	-	
Cu		0.02	-	0.2	
Fe		1	1	1	
Pb		0.05	0.02	5	
Mn		0.1	0.1	0.2	
Hg		0.001	0.004	0.002	
Ni		0.05	0.9	0.2	
Se		0.01	0.25	0.02	
Ag		0.05	0.0002	-	
Zn		5	0.4	2	

Class	Uses
I	Conservation of natural environment. Water Supply I – Practically no treatment necessary. Fishery I – Very sensitive aquatic species.
IIA	Water Supply II – Conventional treatment required. Fishery II – Sensitive aquatic species.
IIB	Recreational use with body contact.
III	Water Supply III – Extensive treatment required. Fishery III – Common, of economic value and tolerant species; livestock drinking.
IV	Irrigation
V	None of the above.

Source: DOE (2006)

Groundwater on the other hand showed non-compliance to National Guidelines for Raw Drinking Water Quality for heavy metal from 2006 to 2010 with the exception of Cu which showed 100% compliance. At least 60% of non-compliance occurred for Fe within the five years period while for Mn and As, 40% and 30% respectively. Other heavy metals including Hg, Cd, Cr, Pb, Zn and selenium (Se) had shown less than 15% non-compliance (DOE, 2006; DOE, 2007; DOE, 2008; DOE, 2009; DOE, 2010). Table 1.2 summarised the benchmark allowed for heavy metal content in drinking water.

Table 1.2: Heavy metal limits in National Guidelines for Raw Drinking Water from Groundwater (Revised December 2000)

Metal	Benchmark (mg/L)
As	0.01
Cd	0.003
Cr	0.05
Cu	1.0
Fe	0.3
Pb	0.01
Mn	0.1
Hg	0.001
Se	0.01
Zn	3

Source: DOE (2006)

Heavy metal pollution in marine water showed varying degree of non-compliance with Interim Marine Water Quality Standards (Table 1.3) which was enforced throughout the period from 2004 to 2008 and replaced by Marine Water Quality Criteria and Standards (Table 1.4) from year 2009 onwards.

Table 1.3: Heavy metal limit in Interim Marine Water Quality Standards

Metal	Standards (mg/L)
As	0.1
Cd	0.1
Cr	0.5
Cu	0.1
Pb	0.1
Hg	0.001

Source: DOE (2006)

Table 1.4: Heavy metal limit in Malaysia Marine Water Quality Criteria and Standards

Metal	Class 1 (µg/L)	Class 2 (µg/L)	Class 3 (µg/L)	Class E (µg/L)
As	3	20 (3)	50	20 (3)
Cd	0.5	2 (3)	10	2
Cr(VI)	5	10	48	10
Cu	1.3	2.9	10	2.9
Pb	4.4	8.5	50	8.5
Hg	0.04	0.16 (0.04)	50	0.5
Zn	15	50	100	50

Class	Uses
1	Preservation, marine protected areas, marine parks
2	Marine life, fisheries, coral reefs, recreational and mariculture
3	Ports, oil and gas fields
E	Mangroves estuarine and river-mouth water

* Values in bracket applied for coastal and marine water areas where seafood for human consumption.

Source: DOE (2010)

The non-compliance of Cu, Pb and Cd was reduced from year 2004 to 2008. The percentage of non-compliance was reduced from 15.9% to 6.7% for Cu while for Pb from 29.2% to 15.3% and Cd from 9.1% to 2.8%. The non-compliance level of Hg, As and Cr throughout the same period fluctuated from 7.6% to 18.2%, 0.9% to 1.1% and 0.1% to 2.2%, respectively (DOE, 2006; DOE, 2008).

However, the non-compliance level from year 2009 to 2010 for Cu, Pb, Cd and Cr increased while Hg and As reduced. The highest level of non-compliance was recorded on Cu which was 64.1% of incompliance in coastal water and 62.7% incompliance in estuary water. This was followed by Pb which was 44.4% and 46.6% of incompliance in coastal water and estuary water, respectively (DOE, 2010). Action has to be taken to control and reduce the pollution by Cu and Pb.

As in Sabah, copper mine at Mamut produced Cu, some Au and Ag. This mine operated from year 1975 but ceased in 1999. During its operation, there was massive generation of tailings which were disposed at Lohan Tailing Dam (Mohd. Azizli *et al.*, 1995). This tailings release heavy metals and toxic substances that pose threat to human health (Baba *et al.*, 2010). The mining also resulted in acid mine drainage that was found to consist of Fe (0.1 − 5.4 mg/L), Mn (2.7 − 79.8 mg/L), Cu (2.0 − 47.0 mg/L) and Zn (0.4 − 25.4 mg/L) (Jopony and Tongkul, 2009).

1.3   Methods of Heavy Metal Removal

Due to adverse effects that heavy metal can bring and also to comply with the guideline standard, various methods have been employed to remove heavy metals from polluted water. These methods include chemical precipitation, ion exchange, coagulation, solvent extraction, adsorption and constructed wetland (Dobson and Burgess, 2007; Abdul *et al.*, 2009; Mahmood *et al.*, 2011; Lizama *et al.*, 2011).

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1.3.1 Chemical Precipitation

Addition of chemical to separate pollutant from solution through the formation of insoluble solid phase is termed chemical precipitation (Chen *et al.*, 2009). The precipitate is further removed through sedimentation or filtration (Cohen, 2006). Formation of precipitate can occur through charge neutralisation between ions. It can be applied to remove metals, organic and inorganic compounds, suspended solids, fats, oils and greases (Benatti *et al.*, 2009).

Heavy metals can be precipitated through the formation of metal hydroxides, sulfides, phosphates or carbonates. Metal hydroxides formed by the addition of alkaline reagents or hydroxide salts such as calcium oxide (CaO), calcium hydroxide ($Ca(OH)_2$), magnesium hydroxide ($Mg(OH)_2$), sodium hydroxide (NaOH) and ammonium hydroxide (NH_4OH). Precipitating agents such as disodium phosphate (Na_2HPO_4), sodium sulphide (Na_2S), sodium hydrosulphide (NaHS), iron sulphide (FeS), sodium bicarbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3) on the other side are used to form insoluble metal phosphates, metal sulphides and metal carbonates (Djedidi *et al.*, 2009). Due to lower solubility of metal phosphates, metal sulphides and metal carbonates in acidic environment, these precipitates of metallic sludge have better thickening and dewatering properties (Hille *et al.*, 2005).

Precipitation can be formed through various steps. An example of three possible precipitation reactions in removing Fe using sulphide is shown in Equation 1.1 to 1.3. Reaction in Equation 1.1 dominates in acidic environment while in Equation 1.2 dominates in neutral to alkaline environment. After the formation of $Fe(HS)_2$ in Equation 1.2, the precipitate of $Fe(HS)_2$ condenses to form FeS precipitate by releasing hydrogen sulphide (H_2S) into the solution (Lewis, 2010).

$$Fe^{2+} + H_2S \rightarrow FeS\ (s) + 2H^+ \tag{1.1}$$
$$Fe^{2+} + 2HS^- \rightarrow Fe(HS)_2\ (s) \tag{1.2}$$
$$Fe(HS)_2\ (s) \rightarrow FeS\ (s) + H_2S \tag{1.3}$$