ADSORPTION KINETICS AND EQUILIBRIUM OF COPPER AND ZINC ON SPONGE GOURD FIBRE

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DECLARATION

I hereby declare that this dissertation is based on my original work, except for quotations, summaries and references, each of which have been duly acknowledged.

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ABSTRACT

The kinetics and equilibrium of Cu and Zn adsorption by sponge gourd fibre were investigated according to batch method. The final concentration of Cu and Zn in solution was determined using atomic adsorption spectrophotometer. The experimental results showed that the adsorption of both metals was rapid during the first 10 minutes and thereafter slowed down until equilibrium was attained after 60 minutes. The adsorption can be well described (R^2~1.0000) by pseudo-second order kinetic model. The adsorbed amount of Cu and Zn increased while the percentage decreased with increase in initial metal concentration. The adsorption conforms (R^2 >0.96) to both Freundlich and Langmuir isotherms. The maximum adsorption capacity, q_{max}, of sponge gourd fibre for Cu and Zn was 5000.0 $\mu g g^{-1}$ and 2000.0 $\mu g g^{-1}$, respectively. At fixed initial concentration, percentage removal of the metals showed an increasing trend with increase in adsorbent dosage.

KINETIK DAN KESEIMBANGAN JERAPAN KUPRUM DAN ZINK OLEH SERABUT PETOLA

ABSTRAK

Kinetik dan keseimbangan jerapan Cu dan Zn oleh serabut petola telah dikaji. Kepekatan akhir Cu dan Zn dalam larutan diukur dengan spektrofotometer serapan atom. Hasil kajian menujukkan jerapan Cu dan Zn adalah pantas pada 10 minit pertama, kemudian menjadi perlahan sehingga mencapai keseimbangan selepas 60 minit. Jerapan didapati mematuhi (R^2~1.0000) model kinetik pseudo kedua. Amaun Cu dan Zn yang dijerap meningkat manakala peratus menurun apabila kepekatan awal logam dalam larutan meningkat. Jerapan Cu dan Zn mematuhi (R^2>0.96) isoterma Freundlich and isoterma Langmuir. Kapasiti jerapan maksimum serabut petola bagi Cu dan Zn adalah masing-masing 5000.0 $\mu g g^{-1}$ dan 2000.0 $\mu g g^{-1}$. Pada kepekatan awal yang tetap, peratus penyingkiran Cu dan Zn amnya meningkat apabila dos penjerap meningkat.

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LIST OF SYMBOLS

Cu	Copper
Zn	Zinc
Cd	Cadmium
Hg	Mercury
Pb	Lead
Ni	Nickel
Cr	Chromium
Fe	Iron
Mn	Manganese
As	Arsenic
AAS	Atomic Adsorption Spectrophotometer
FAAS	Flame Atomic Adsorption Spectrophotometer
IR	Infrared Spectrophotometer
FTIR	Fourier Transform Infrared Spectrophotometer
q_e	Amount of metal adsorbed at equilibrium
q_t	Amount of metal adsorbed at time, t
k_1	Pseudo-first order rate constant
k_2	Pseudo-second order rate constant
k_p	Intraparticle diffusion rate constant
k_F	Freundlich constant, indicating the adsorption capacity
n	Freundlich constant, indicating the adsorption intensity
b	Langmuir constant
t	Time, minutes
C_0	Initial concentration
C_f	Final concentration
C_e	Equilibrium concentration
°C	Degree Celcius

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Wastewater of various industries, including mining, steel production, electroplating, metal processing and battery manufacturing can contain high levels of heavy metals (Eckenfelder, 2000; Landis & Yu, 1999). Heavy metals such as Cu, Zn, Cd, Pb, As and Hg are known to be toxic to aquatic organism, plant and humans (Keane, 2003; LaGrega *et al.*, 1994). Uncontrolled discharge of metal-rich wastewaters can cause adverse environmental impacts. Such wastewaters, therefore need to be treated to remove the heavy metals prior to discharge. The technologies for this purpose include chemical precipitation, ion-exchange, electrodialysis, reverse osmosis and adsorption (Russell, 2006; Chhatwal, 1996). These methods vary in terms of complexity, efficiency and cost.

Adsorption is one of the preferred treatment methods for metal removal. It involves the use of adsorbents such as activated carbon (Schneider *et al.*, 2007), natural zeolite (Erdem *et al.*, 2004), lignites (Pehlivan & Arslan, 2007), fly ash (Cetin & Pehlivan, 2007) and activated charcoal and wood charcoal (Choksi & Joshi, 2007). However, many of these adsorbents are expensive. Consequently, there is a growing interest on alternative adsorbents such as agricultural wastes or materials including coconut husk (Latif & Jaafar, 1989), oil palm fibre (Latif & Jaafar, 1989), orange peel (Xuan *et al.*, 2006), wheat bran (Özer, 2007), orange waste (Pérez-Marín *et al.*, 2007), grape baggase (Farinella *et al.*, 2007), lemon peel (Schiewer & Patil, 2008), groundnut husks (Dubey & Gopal, 2007) and rice husks (Wan Ngah & Hanafiah, 2008). These agricultural wastes are widely available and environmentally friendly as well as inexpensive (Amuda *et al.*, 2007).

1.2 Sponge Gourd

Sponge gourd (*Luffa cylindrica*) is a widely available fruit vegetable in Malaysia. When mature it produces a tough fibrous biomass (Figure 1.1). The chemical composition of sponge gourd fibre is shown in Table 1.1. Sponge gourd fiber has a lignin-rich outer layer with a cell-like structure joining the inner fibers. The density of sponge gourd fibre is 820 kgm^{-3} (Satyanarayana *et al.*, 2007) while, its specific gravity is 0.92 gcm^{-3} (Annunciado *et al.*, 2005).

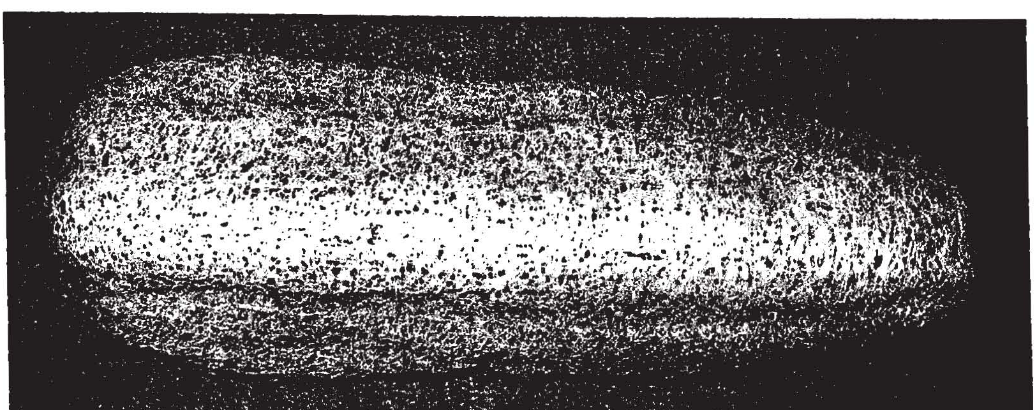

Figure 1.1 Sponge gourd fibre.

Table 1.1 Chemical composition of sponge gourd fibre (Source: Satyanarayana *et al.*, 2007).

Chemical composition	Percentage (%)
α-Cellulose	62
Hemicellulose	20
Lignin	11.2
Ash	0.4
Extratives	3.1

Sponge gourd fibre is commonly used as bathing sponges, scrubber pads, doormats, pillows, mattresses and also for cleaning utensils (Salunkhe & Kadam, 1998). It is also used in the manufacture of palm sole, inner soles for shoes, bolters, leather straps, filters for automobiles and other engines (Satyanarayana *et al.*, 2007).

The sponge's good structural strength, rigidity and porosity are ideal physical attributes of an adsorbent. Although it has been studied as an adsorbent for oil spills (Annuciado *et al.*, 2005), there seemed to be no previous report of sponge gourd as adsorbent for heavy metals. There were, however, reports of the fibre being used as a support matrix for immobilization of algal, fungal, and yeast cells. The immobilized cells were subsequently used for metal removal from solution (Akhtar *et al.*, 2004; Akhtar *et al.*, 2003; Iqbal & Zafar, 1993).

1.3 Objectives of Study

The objectives of study are:

a) To determine and characterize the adsorption kinetics of Cu and Zn on sponge gourd fibre.

b) To determine and characterize the adsorption equilibrium of Cu and Zn on sponge gourd fibre.

1.4 Scope of Study

In this study, the adsorption of Cu and Zn on sponge gourd fibre was determined at different reaction time and initial concentrations of metal according to batch method. The final concentrations of Cu and Zn in solution was analysed using atomic adsorption spectrophotometer (AAS). The kinetics and equilibrium of the adsorption process were subsequently analysed using selected kinetic models and isotherm models, respectively.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metals

2.1.1 Definition

Heavy metal is a general collective term applied to elements with an atomic density greater than 6 gcm^{-3}, specific gravity greater than 4.0 and atomic number greater than 20 (Keane, 2003; Connell, 2005). Examples of heavy metals include Cu, Zn, Cd, Hg, Pb, Ni, Cr, Fe, Mn and As. These metals exist in natural water in the form of free metal ions surrounded by coordinated water molecules, as well as inorganic and organic complexes (Connell, 2005). Trace amounts of certain heavy metals in right concentration are essential to life. These metals are referred to as micronutrients and examples include Co, Cu, Fe, Mn and Zn (Kennish, 1992).

2.1.2 Copper and zinc

Copper (Cu) is a member of Group 1B of the Periodic Table. It has an atomic number 29 and atomic weight 63.546. It occurs either in metallic form, or in compounds of Cu(I) or Cu(II). It has a density of 8.93 g cm^{-3}, a melting point of 1083°C and a boiling point of 2590°C (Ayres & Hellier, 1998). Natural copper consists of an isotopic mixture of 69.1% ^{63}Cu and 30.9% ^{65}Cu (Mevian *et al.*, 2004). Condensed electron configuration of Cu is [Ar] $4s^1$ $3d^{10}$. Cu is used for electrical, plumbing, wire and alloys manufacturing (Mevian *et al.*, 2004).

Zinc (Zn) is a member of Group 2B of the Periodic Table. It has an atomic number 30 and atomic weight 65.409. It has a density of 7.14 g cm^{-3}, a melting point of 419.6°C and a boiling point of 907°C (Ayres & Hellier, 1998). Natural zinc consists of an isotopic mixture of ^{64}Zn (49%), ^{66}Zn (28%), ^{68}Zn (19%), ^{67}Zn (4.1%) and ^{70}Zn (0.62%) (Mevian *et al.*, 2004). Condensed electron configuration of Zn is [Ar] $4s^2$ $3d^{10}$. Thus, its valence in chemical compounds is +2. Zn is used for battery and alloys (brass and bronze) manufacturing, while Zn dust is a widely used catalyst (Mevian *et al.*, 2004).

2.1.3 Anthropogenic sources

Human activities such as mining, steel production, electroplating, metal processing and battery manufacturing, rayon-fibre manufacturing and wood-pulp production are the major anthropogenic sources of metal introduction into the environment (Keane, 2003; Eckenfelder, 2000). The type as well as the concentration of heavy metals discharged, however, are dependent on the type of industries (Table 2.1).

Table 2.1 Anthropogenic sources of heavy metals.

Industries	Metal							
	Cd	Cr	Cu	Pb	Hg	Mn	Ni	Zn
Mining	*	*	*	*	*			*
Paint and dye	*	*	*	*	*			
Pesticide				*	*			*
Electric and electronic			*	*	*			
Plating		*	*					*
Rubber and plastic					*			*
Battery	*			*	*			*
Textile		*	*					
Petroleum				*			*	
Petrochemical	*	*		*			*	
Cement	*							
Leather	*	*						
Pharmaceutical					*			
Paper		*	*	*	*		*	
Fertilizer	*	*		*		*	*	

(Source: Bamhart, 1978; Deans & Dixon, 1992)

2.1.4 Environmental impacts of heavy metals

Excessive concentration of heavy metals in water can cause adverse impacts to aquatic organisms and humans. Accumulation of heavy metals will cause toxic effects to aquatic organism. The level of toxicity depends on metal type and organism type (Connell, 2005). Lethal toxicity values, LC_{50}, which is the concentration of a chemical that is lethal to 50% of the test organism, for some heavy metals are shown in Table 2.2. The smaller the LC_{50} value the more toxic is the metal. Examples of the adverse health effects of heavy metals on humans is shown in Table 2.3.

Heavy metals, in particular Hg, can be bioaccumulated upward the food chain (Figure 2.1). When Hg enters the water, it is transformed into a more toxic form called methylmercury. In aquatic environment, plants and small organisms like planktons take up methylmercury through surface absorption or through food intake. These bacteria and plants are eaten by small fish, which in turn are eaten by larger fish. Over time, humans or animals who consumes aquatic organisms containing methylmercury will acquire high levels of methylmercury, greater than the fish they consume (Chhatwal, 1996; Davis *et al.*, 2003).

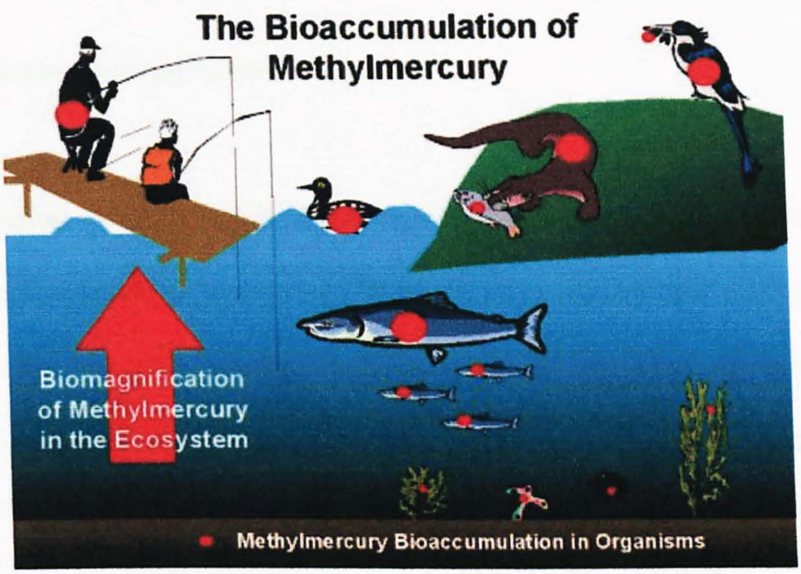

Figure 2.1 Bioaccumulation of methylmercury upward the food chain.

Table 2.2 LC_{50} (mg L^{-1}) of metals to marine organisms.

Classes of organisms	Metals						
	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Fish	22-55	91	2.5, 3.2	0.8, 0.23	350	188	60
Crustaceans	0.015-45	10	0.17-100	0.05-0.5	6, 47	-	0.4-50
Mollusks	2.2-35	14-105	0.14, 2.3	0.058-32	72, 320	-	10-50
Polychaetes	2.5-12.1	2.0 to >5.0	0.16-0.5	0.02-0.09	25, 72	7.7-20	1.8-55

(Source: Connell, 2005)

Table 2.3 Pathological effects of heavy metals on human.

Metal	Pathological effects on human
Cu	Hypertension, uremia, coma, sporadic fever.
Zn	Vomiting, renal damage, cramps.
Hg	Abdominal pain, headache, diarrhea, hemolysis, chest pain.
As	Disturbed peripheral circulation, mental disturbance, liver cirrhosis, hyperkeratosis, lung cancer, ulcers in gastrointestinal tract, kidney damage.
Cd	Diarrhea, growth retardation, bone deformation, kidney damage, testicular atrophy, anaemia, injury of central nervous system and liver, hypertension.
Cr(VI)	Nephritis, gastro-intestinal ulceration, diseases in central nervous system.
Pb	Anaemia, vomiting, loss of appetite, convulsions, damage of liver and kidney.

(Source: Chhatwal, 1996)

2.1.5 Environmental regulations

Industrial effluents or wastewaters can be a significant contributor towards increased level of heavy metals in environment. Therefore, such wastewaters need to be treated prior to discharge. In Malaysia the discharge limits or standards are specified under Environmental Quality Act 1974 (Sewage and Industrial Effluents Regulation 1979) as shown in Table 2.4. The limits for Standard A are more stringent compared to Standard B. In the case of Cu the discharge limit is 0.2 mgL^{-1} and 1.0 mgL^{-1} for Standard A and Standard B, respectively. The values for Zn are 1.0 mgL^{-1} and 1.0 mgL^{-1}.

Table 2.4 Effluent discharge standards according to Sewage and Industrial Effluents Regulation 1979.

Parameter	Unit (mgL^{-1})	Standard	
		A	B
Temperature	°C	40	40
pH	-	6.0-9.0	5.5-9.0
BOD at 20°C	mgL^{-1}	20	50
COD	mgL^{-1}	50	100
Suspended solids	mgL^{-1}	50	100
Mercury (Hg)	mgL^{-1}	0.005	0.05
Cadmium (Cd)	mgL^{-1}	0.01	0.02
Chromium (Cr(VI))	mgL^{-1}	0.05	0.05
Arsenic (As)	mgL^{-1}	0.05	0.10
Cyanide	mgL^{-1}	0.05	0.10
Lead (Pb)	mgL^{-1}	0.10	0.5
Chromium (Cr(III))	mgL^{-1}	0.20	1.0
Copper (Cu)	mgL^{-1}	0.20	1.0
Zinc (Zn)	mgL^{-1}	1.0	1.0
Nickel (Ni)	mgL^{-1}	0.20	1.0
Tin (Sn)	mgL^{-1}	0.20	1.0
Manganese (Mn)	mgL^{-1}	0.20	1.0
Boron (B)	mgL^{-1}	1.0	4.0
Iron (Fe)	mgL^{-1}	1.0	5.0
Phenol	mgL^{-1}	0.001	1.0
Free chloride	mgL^{-1}	1.0	2.0
Sulphide	mgL^{-1}	0.50	0.50
Oil & grease	mgL^{-1}	Not detectable	10.0

2.1.6 Analysis of heavy metals by atomic absorption spectrophotometry

One of the methods for heavy metal analysis is atomic absorption spectrophotometry and the instrument used is known as atomic absorption spectrophotometer (AAS). The principal components of this instrument include light source, atomizer, monochromator and detector (Figure 2.2).

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