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ADSORPTION KINETICS AND EQUILIBRIUM OF
COPPER AND ZINC ON VOLCANIC TUFF

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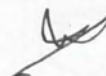
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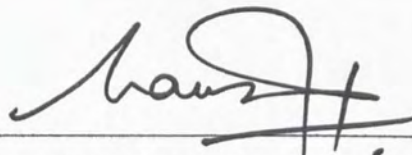
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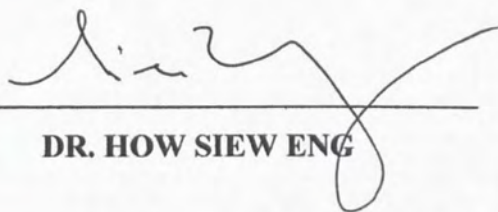
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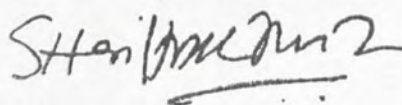
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ABSTRACT

The adsorption kinetics and equilibrium of Cu and Zn on volcanic tuff was investigated according to batch method. For comparison, the same experiments were carried out on natural zeolite. The final Cu and Zn concentration in solution was determined using an atomic absorption spectrophotometer (AAS). The results showed that Cu and Zn adsorption by volcanic tuff was rapid with significant removal of the metal from solution during the first 5 minutes. Equilibrium, however, was only attained after 60 minutes. The adsorption conformed to pseudo – second order kinetic model ($R^2 = 0.999$) as well as to Langmuir ($R^2 = 0.9$) and Freundlich ($R^2 = 0.9$) isotherms. Similar pattern was observed for Cu and Zn adsorption by natural zeolite, except the adsorption conforms better to Langmuir isotherms ($R^2 = 0.98$). The maximum Cu and Zn adsorption capacity is 1000 $\mu\text{g/g}$ and 796.23 $\mu\text{g/g}$, respectively for volcanic tuff; and 1111.11 $\mu\text{g/g}$ and 833.33 $\mu\text{g/g}$, respectively for natural zeolite. Comparatively, Cu and Zn removal by volcanic tuff was less efficient in a mixed metal system compared to single metal system. Overall, the volcanic tuff can potentially be used for the removal of heavy metals, including Cu and Zn, from wastewater.



KINETIK DAN KESEIMBANGAN JERAPAN BAGI KUPRUM DAN ZINK OLEH TUF VOLCANO

ABSTRAK

Kinetik dan keseimbangan jerapan bagi kuprum dan zink oleh tuf volcano telah dikaji berdasarkan kaedah kelompok. Kajian yang sama dilakukan menggunakan zeolit semulajadi sebagai perbandingan. Kepekatan akhir kuprum dan zink ditentukan dengan spektrofotometer serapan atomic (AAS). Hasil kajian menunjukkan jerapan kuprum dan zink oleh tuf volcano adalah pantas pada 5 minit pertama. Keseimbangan jerapan, walau bagaimanapun, dicapai dalam tempoh 60 minit. Jerapan kuprum dan zink mematuhi baik model kinetik tertib pseudo kedua ($R^2 = 0.999$), serta isoterma jerapan Langmuir ($R^2 = 0.9$) dan Freundlich ($R^2 = 0.9$). Corak hasil kajian yang serupa diperolehi untuk jerapan kuprum dan zink oleh zeolit semulajadi, kecuali jerapan adalah lebih mematuhi isoterma Langmuir ($R^2 = 0.98$). Kapasiti jerapan maksimum kuprum dan zink ialah masing – masing 1000 $\mu\text{g/g}$ dan 796.23 $\mu\text{g/g}$ bagi tuf volcano; serta masing – masing 1111.11 $\mu\text{g/g}$ dan 833.33 $\mu\text{g/g}$ bagi zeolit semulajadi. Penyingkiran kuprum dan zink oleh tuf volcano adalah kurang berkesan dalam sistem logam campuran, berbanding dengan sistem logam tunggal. Secara keseluruhannya tuf volcano merupakan penjerap yang berpotensi untuk penyingkiran logam berat, termasuk kuprum dan zink, daripada air sisa.

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SYMBOL, ABBREVIATION AND UNIT LIST

Cu	Copper
Zn	Zinc
Cr	Chromium
Pb	Plumbum
Hg	Mercury
°C	Degree Celsius
%	Percentage
µg/mL	Microgram per milliliter
mg/L	Milligram per liter
CuSO ₄ .5H ₂ O	Copper sulphate pentahydrate
ZnSO ₄ .7H ₂ O	Zinc sulphate heptahydrate
mL	Milliliter
g	Gram
AAS	Atomic absorption spectrometry
min	minute
rpm	rate per minute
nm	nanometer
mm	millimeter
ng/mL	nanogram per millimeter
g/cm ³	Gram per centimeter cube
HDL	High density lipoprotein
LDL	Low density lipoprotein

CHAPTER 1

INTRODUCTION

1.1 Context and Relevance of Study

Many industries, including the electroplating, metal finishing, metallurgical, tannery, chemical manufacturing, mining, and battery manufacturing, produce aqueous effluents containing heavy metal contaminants (Lin *et al.*, 2000). Discharge of such wastewater can cause adverse impacts to the environment. The excessive presence of heavy metals in streams and lakes has been responsible for several health problems with animals, plants and human beings. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders (Barros *et al.*, 2004). Heavy metals such as Cr, Cu, Pb, Hg etc. are known to be toxic to humans (Taty – Costodes *et al.*, 2003).

In order to control heavy metal pollution, industrial effluents need to be treated prior to discharge to the environment. Various techniques have been used to reduce heavy metal concentration from wastewater; the most common ones are chemical precipitation, membrane filtration, ion – exchange, electrolytic methods, chemical



coagulation, and adsorption (Khazali *et al.*, 2007). Many of these methods suffer from some drawbacks such as incomplete metal removal, high capital and operational costs and problem of disposal of residual metal sludge.

Adsorption is one of the preferred methods for metal removal. This method involves the use of adsorbents such as natural zeolite (Khazali *et al.*, 2007), crab shell (Kim, 2003), synthetic zeolite (Hui *et al.*, 2005), activated carbon (Machida *et al.*, 2005), holly oak (Prasad & Freitas, 2000), wheat bran (Bulut & Baysal, 2006), animal bones (Al – Asheh *et al.*, 1999), rice husk (Ajmal *et al.*, 2003), rock (Sarı *et al.*, 2007) and clay (Benhammou *et al.*, 2005). However, some of these are relatively expensive for practical use, thus currently there is an increasing interest on cheap and easily available adsorbents (Aydın *et al.*, 2008).

Volcanic tuff is volcanic ash which settled and forms a rock after explosive volcanism. It comprises a mixture of crystal fragments, bits of lava and pyroclastic rock, and volcanic glass. This material is well known for its high selectivity in removing ammonium from aqueous solution (Marañón *et al.*, 2006). However there are not many studies at present on heavy metals removal by volcanic tuff (Mihaly – Cozmata *et al.*, 2005).



1.2 Research Objectives

The objectives of this study were:

- (a.) To determine the kinetics of copper and zinc adsorption by volcanic tuff.
- (b.) To determine the equilibrium of copper and zinc adsorption by volcanic tuff.
- (c.) To compare copper and zinc removal efficiency by volcanic tuff with that by natural zeolite.

1.3 Scope of Study

The study focused on volcanic tuff samples obtained from Tabin in Lahad Datu, Sabah. Batch adsorption studies were carried out to investigate the effect of contact time and initial metal concentration on heavy metals removal from aqueous solution using the volcanic tuff sample. For comparison, similar studies were carried out using granular activated carbon as the adsorbent. The final zinc and copper concentrations in solutions were determined spectrophotometrically.

CHAPTER 2

LITERATURE REVIEW

2.1 Copper and Zinc

2.1.1 General chemistry of copper and zinc

Copper is a reddish coloured transition metal which occupies the *d* block in the periodic table. It has the symbol Cu and an atomic number of 29. It is malleable, ductile and a good conductor of heat and electricity. It has an atomic weight of 63.546, a melting point of 1083°C, a specific gravity of 8.96 and exhibit both +1 and +2 oxidation state. The average crustal abundance was found to be of 55 – 75 µg/g (Silberberg, 2003).

Zinc is a bluish – white transition metal which occupies the *d* block in the periodic table. It has the symbol Zn and an atomic number of 30, atomic mass of 65.39, density of 7.14 g/cm³, melting point of 419.6 °C, boiling point of 907 °C and only exhibit the +2 oxidation state. It has five stable isotopes namely (⁶⁴Zn, 48.6 %; ⁶⁶Zn, 27.9 %; ⁶⁷Zn, 4.1 %; ⁶⁸Zn, 18.8 %; ⁷⁰Zn, 0.6 %). Zinc is amphoteric, it reacts both with acids and alkalis (Marshall & Fairbridge, 1999).



2.1.2 Sources of copper and zinc

a. Natural sources

Geochemical processes (including weathering of parent materials) and other natural processes (eg. volcanoes, forest fires and sea salt spraying) continuously release copper and zinc into the environment (Cunningham *et al.*, 1998). Table 2.1 shows examples of rocks or mineral ores that mainly contain Cu and Zn.

Table 2.1 Parent materials that can be subjected to weathering and release Cu and Zn.

Copper		Zinc	
<u>Rock</u>	<u>Mineral ore</u>	<u>Rock</u>	<u>Mineral ore</u>
Shale	Chalcocite (Cu ₂ S)	Dolomite	Sphalerite (cubic ZnS)
Sandstone	Chalcopyrite (CuFeS ₂)	Volcanic rock	Wurtzite (hexagonal ZnS)
Gabbro	Malachite (Cu ₂ (OH) ₂ CO ₃)	Limestone	Smithsonite (trigonal ZnCO ₃)
—	Azurite (Cu ₃ (OH) ₂ CO ₃)	—	Hemimorphite (Zn ₄ Si ₂ O ₇ (OH) ₂)

(Sources: Marshall & Fairbridge, 1999; Zaw *et al.*, 2007)

b. Anthropogenic sources

Since copper and zinc are widely used in the industries, there are a number of potential anthropogenic sources of these heavy metals (Table 2.2). The concentration of the respective metal, however, is dependent on the type of source.

Table 2.2 Anthropogenic source of Cu and Zn to the environment.

Heavy metal	Industry
Copper	Mining
	Textile
	Electroplating
	Metal cleaning
	Paper & pulp
	Fertilizer
	Petroleum refining
Zinc	Mining
	Alkaline battery
	Manufacturing (acrylic fiber, rayon, cellophane and special synthetic rubber)
	Automobile
	Agricultural (pesticides / pesticides)
	Pigments
	Metal plating

(Sources: Rao *et al.*, 2006; Sari *et al.*, 2007)

2.1.3 Environmental and health impacts of copper and zinc

The presence of elevated levels of copper, besides causing damage to plants and reducing crops production of farmlands, can result in health effects such as liver and kidney failure or Wilson's disease (NINDS, 2007). Prolonged inhalation of copper-containing sprays is linked with an increase in lung cancer among exposed workers (Yu *et al.*, 2000). Excessive intake of copper results in hemochromatosis and gastrointestinal catarrh diseases because it accumulates in the livers of human and animals (Sari *et al.*, 2007).

At acidic pH values, zinc toxicity to plants is the third most common after aluminium and manganese (Robson, 1993). Excessive intake of zinc by humans can lead to increased LDL and decreased HDL cholesterol, impaired immune system, nausea, vomiting, impaired copper absorption (Williams, 2005).

2.1.4 Wastewater discharge and drinking water quality standards

Industrial effluents or wastewaters can be significant contributors towards increased heavy metals in environment. Environmental regulations enforced worldwide require wastewaters to be treated prior to discharge. In Malaysia, the discharge standard and limits are specified under Environmental Quality Act 1974, especially in Environmental Quality (Sewage and Industrial Effluents) Regulations 1979 (Table 2.3). An identical value of 2 mg/L is set for zinc in both Standard A and Standard B. A higher value of zinc compared to that of copper is due to the fact that zinc is more toxic than copper. A more stringent and lower limit is set in Standard A since this

standard is applicable to water that discharges into catchment areas for human consumption, whereas Standard B only applicable to inland water that are not for human consumption. Meanwhile the maximum permissible concentration of copper in drinking water according to World Health Organization is 2.0 mg/l, while no value was specified for zinc (Table 2.4).

2.2 Wastewater Treatment Methods

In order to control environmental degradation as well to conform to discharge standards, wastewaters need to be treated prior to discharge. Current treatment technologies include adsorption (Amarasinghe & Williams, 2007), ion exchange (Ören & Kaya, 2006; Stylianou *et al.*, 2007), reverse osmosis (Qdais & Moussa, 2004), chemical precipitation (Mauchauffée & Meux, 2007) and electrodialysis (Bruggen & Vandecasteele, 2002).

2.2.1 Adsorption

Adsorption involves the interaction of a solid material with ions or molecules present in solution. The molecule or ion that binds to the surface of the solid is called adsorbate, while the solid is called absorbent (Figure 2.1). The interaction may involves a weak van der waal's forces (i.e. physisorption) or strong chemical bonds (i.e. chemisorption).



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