ADSORPTION OF COPPER IONS FROM AQUEOUS SOLUTION BY DRIED WATER LILY PETIOLES

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ENVIRONMENTAL SCIENCE PROGRAMME
SCHOOL OF SCIENCE AND TECHNOLOGY
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DECLARATION

I declare that this is the result of my own research except as cited in the references. This report has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

19th May 2009

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CERTIFICATION

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ABSTRACT

This work reports the adsorption of Cu (II) from the aqueous solution by dried water lily petioles. It was done to investigate the effects of contact time and initial sorbate concentration on the adsorption of Cu (II) and also to study the maximum adsorption capacity of Cu (II) by dried water lily petioles. The batch studies were performed to evaluate the influences of experimental parameters such as the contact time and initial sorbate concentration. The final Cu (II) concentration was determined by using the flame atomic adsorption spectrophotometer (FAAS). The results shows that the sorption of Cu (II) increased as contact time and initial sorbate concentration increased. In this study, the initial sorbate concentration in the range of 50 to 400 mgL^{-1} were used and results shows that the removal were from 8.295 to 21.250 mgg^{-1}. The Langmuir and Freundlich models were used to describe the sorption equilibrium data. The results show that the Cu (II) adsorption fitted better to Langmuir model than the Freundlich model. The R^2 for the Langmuir model was 0.993 while for the Freundlich model, the R^2 was 0.878. The maximum adsorption capacity, Q_m of Cu (II) by dried water lily petioles was 24.39 mgg^{-1}.

PENJERAPAN ION KUPRUM DARIPADA LARUTAN AKUES OLEH BATANG DAUN KERING TERATAI

ABSTRAK

Hasil kerja ini menunjukkan penjerapan Cu (II) daripada larutan akueus oleh batang daun kering teratai. Tujuannya adalah untuk mengetahui kesan masa sentuhan dan pengaruh kepekatan awal ke atas penjerapan Cu (II) and juga untuk mengkaji kapasiti penjerapan maksimum oleh batang daun kering teratai. Kajian kelompok telah dilakukan untuk menilai pengaruh oleh parameter eksperimen seperti masa sentuhan dan kepekatan awal Cu (II). Kepekatan akhir Cu (II) ditentukan dengan menggunakan mesin FAAS. Serapan oleh Cu (II) didapati meningkat apabila meningkatnya masa sentuhan dan kepekatan awal Cu (II). Dalam kajian ini, kepekatan awal Cu (II) adalah dalam lingkungan 50 sehingga 400 mgL^{-1} dan keputusan menunjukkan penjerapan adalah dari 8.295 sehingga 21.250 mgg^{-1}. Model-model Langmuir dan Freundlich juga digunakan dalam menerangkan data keseimbangan serapan. Keputusan menunjukkan bahawa penjerapan oleh Cu (II) adalah lebih sesuai kepada model Langmuir berbanding model Freundlich. R^2 bagi model Langmuir adalah 0.993 manakala bagi model Freundlich, R^2 adalah 0.878. Kapasiti penjerapan maksimum, Q_m oleh Cu (II) oleh batang daun kering teratai ialah 24.39 mgg^{-1}.

CONTENT

LIST OF ABBREVIATIONS

EIX	Electrochemical ion exchange
FAAS	Flame atomic adsorption spectrophotometer
PP	Polypropylene
RSD	Relative standard deviation
BOD	Biological oxygen demand
COD	Chemical oxygen demand
TOC	Total organic carbon
rpm	Revolution per minute
ppb	Part per billion

LIST OF SYMBOLS

N	Normality
Ø	diameter
C_o	Initial concentration of sorbate
C_e	Concentration of sorbate at equilibrium
Q_e	Adsorption capacity at equilibrium
Q_m	Maximum adsorption capacity
R_L	Separation factor obtained from Langmuir isotherm model.
R^2	Reggresion coefficient
K_L	Langmuir constant related to adsorption affinity
K_F	Freundlich constant related to adsorption capacity
m	Mass of sorbent per unit volume of sorbate
n	Freundlich constant related to adsorption intensity

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CHAPTER 1

INTRODUCTION

1.1 Background

Heavy metals pollution is one of the serious environmental problems and becoming a worldwide concern nowadays. The rapid various industrial activities and technologies have resulted the increasing of heavy metals released into the environment. This situation then causes threats to the environment and public health because of the heavy metals toxicity, bioaccumulation and bioaugmentation in the food chain and persistence in the nature (Younesi *et al.*, 2008).

Heavy metals cause serious threat to the environment, animals and humans for their extreme toxicity. From the many heavy metals, lead (Pb), mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), zinc (Zn) and copper (Cu) are the most concern (Landis and Yu, 1999), even though some of the metals are essential nutrients in animal and human nutrition (Nadella *et al.*, 2008).

When heavy metals are in the ions or compounds forms, they become soluble in water and will be absorbed into the living organisms via food chain (Chang *et al.*, 2008). After the absorption, these heavy metals can bind to vital cellular components such as structural proteins, enzymes and nucleic acids. That process then will interfere with their functioning (Landis and Yu, 1999).

There are many types of technologies such as chemical, physical and also the biological methods (Chergui *et al.,* 2008) that been applied to prevent and treat water pollutions. Among the technologies are chemical precipitation, adsorption, electrolytic method, ion exchange, solvent extraction, chemical oxidation or reduction, filtration, membrane systems and reverse osmosis (Yurtsever and Sengil, 2008). However, these methods show different efficiencies for different methods. Besides, they can be very expensive especially in large volume, low metal concentration and required high standard of cleaning (Hou *et al.*, 2007).

Among these methods, the adsorption with the selection of a suitable adsorbent can be an effective technique for the removal heavy metals from wastewater (Cetin and Pehlivan, 2007). The most common used adsorbent is activated carbon. However, it is an expensive material unless regeneration becomes relatively easy but is unlikely to be cost effective (Malkoc and Nuhoglu, 2007). Therefore, there been a growing studies on various low cost adsorbent as an alternative adsorbents such as tea factory waste (Malkoc and Nuhoglu, 2007), grape bagasse (Arruda *et al.*, 2007), rice husk (Das *et al.*, 2008), shells of hazelnut and almond (Bulut and Tez, 2007).

The degree and rate of adsorption of metals ions not only depend on the physical and surface properties of adsorbent (such as the size and surface area), metal ion properties (for example, concentration) and operating conditions (for example, pH and temperature) (Amarasinghe and Williams, 2007) but also the features of the components as well as the level of metal concentration, residence time and test criteria (Li *et al.*, 2004).

1.2 Aquatic Plants

Aquatic plants are being used in water quality studies to monitor heavy metals and other pollutants of water and also submerged soils (Samecka-Cymerman and Kempers, 2001). It has been known that these aquatic plants, both living and dead, are heavy metal accumulators (Forster *et al.*, 2003) but different aquatic plants have been found to have different metal ions removal rates. Aquatic plants have great potential to accumulate heavy metals inside their plant body which is 100,000 times greater than in associated water (Mishra and Tripathi., 2008). Therefore, the use of aquatic plants for removal of heavy metals from wastewater gained high interest nowadays.

Aquatic plants such as *Eichhornia* and *Lemna* carry out their complete life cycle floating on the surface and they are commonly used for pollutants removal (Boniardi *et al.*, 1998) but somehow become anoxic for fish and macro fauna to survive (Demirezen *et al.*, 2007). *Nymphaea* live on the surface but retain an attachment to the sediments. *Typha* and *Carex* are emergent plants with only roots submerged while a few species (for example *Potamogeton*, *Najas* and *Ruppia*) are live completely submerged (Prasad *et al.*, 2001). Aquatic plants have an important role in the food chain since they are primary producers and regulators of oxygen level. At the same time, they play a significant role in the biogeochemical cycling of the elements (Horvat *et al.* 2007).

In this study, the *Nymphaea* were chosen because they are low cost and high in availability. There is also study done by Lee *et al.*, (2005) which proved *Nymphaea* is a good heavy metals removal in polluted water. The Photo 1.1 below shows the petioles of water lily that been used in the study.

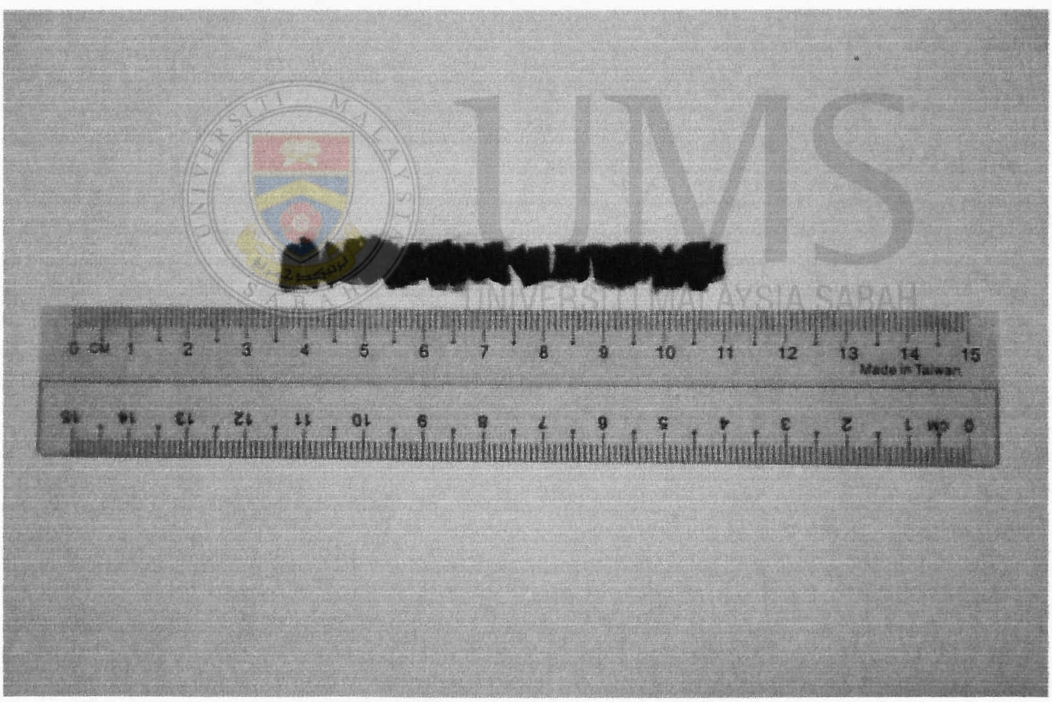

Photo 1.1 The petioles of water lily been used in the study.

1.3 Objectives

The objectives of this study are to investigate the effects of contact time and initial concentration of Cu (II) by dried water lily petioles and also to study the maximum adsorption capacity of Cu (II) by dried water lily petioles.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metals

Heavy metals are defined as those elements (some metalloids) that have atomic density less than 6 gcm^{-3}. These elements include Cd (8.65), cobalt (8.90), Hg (13.50), nickel (Ni) (8.90), Zn (7.10), Pb (11.30) and Cu (11.30) (Naidu *et al.*, 2001). In the periodic table, there are about 70 elements considered to be heavy metals based on their specific gravity which should be less than 4.5 gcm^{-3} (Mukherjee, 2001).

Heavy metals are normally present at low concentration but becoming a common pollutant due to the anthropogenic activities (Horvat *et al.,* 2007) such as electroplating, metal finishing, textile, storage batteries, lead smelting, mining, plating, ceramic and glass industries (Forster *et al.,* 2003). Unlike the organic pollutants, heavy metals cannot be degraded through biological process, so require removal for water decontamination (Cheng *et al.*, 2002).

The heavy metals like Pb, Hg, Cu, Cd, Zn, Cd and Ni are among the most common pollutants found in industrial effluents (Younesi *et al.,* 2008). They are often deposited directly to the environment without any pre treatment (Benhima *et al.,* 2008). This situation will cause serious toxicity to the aquatic ecosystems and human health, and these heavy metals also get accumulated in organisms when exceed the tolerance levels.

2.1.1 Effects

The Table 2.1 shows the specific effects of selected heavy metals in the environment. Among the effects of the heavy metals are such as damage to the human body parts, for example, the kidney, membrane, lungs and liver.

Table 2.1 Effects of heavy metals.

Heavy metal	Effects	References
Pb	Damage liver, kidney, reduction in haemoglobin formation, mental retardation, infertility, blood pressure and abnormalities to pregnant women	Yurtsever and Sengil, 2008 Al-Subu, 2002
Cd	Toxic to aquatic organism.	Hou *et al.,* 2007
Ni	Skin irritation, damage lungs, nervous system and mucous membrane.	Sternberg *et al.,* 2003
Cr	Toxic to animals and humans, can accumulated in flora and fauna which will cause ecological damage.	Razmovski and Šćiban, 2008
Zn	Damage mucous membrane, diarrhea and dizziness.	Abdullah *et al.,* 2008

2.1.2 Sources

The Table 2.2 shows the specific sources of selected heavy metals in the environment. Most of the sources of the heavy metals are from the manufacturing industries such as batteries, laser, metal, electroplating and others.

Table 2.2 Sources of heavy metals.

Heavy metal	Sources	References
Pb	Battery manufacturing, printing, pigment, metal plating, ammunition, photographic materials, soldering material, ceramic and glass industries.	Das *et al.*, 2008 Vilar *et al*, 2005
Cd	Pigments, mining, smelting and electroplating.	Hou *et al.*, 2007
Hg	Smelting, spoil heaps and sewage sludge disposal.	Pushon, 2001
Cr	Metal finishing wastes, wood preservatives, sewage sludge, leather tanning and chromate preparation.	Pushon, 2001 Lodi *et al.*, 2008 Malkoc and Nuhoglu, 2007
Zn	Alloy, galvanized metal, fluorescence components, paint pigments, sunscreen, fast setting dental cements, deodorants, embalming and fireproofing lumber.	Abdullah *et al.*, 2008
As	Manufactured of laser, semi conductors, pharmaceutical products, agricultural and industrial effluents.	Lué-Merú *et al.*, 2008.
Ni	Electroplating, batteries manufacturing, mining, metal finishing and forging.	Malkoc and Nuhoglu, 2006

2.1.3 Copper

Copper is in the group 11 of periodic table, with the atomic number 29 and relative atomic weight of 63.55 $gmol^{-1}$ and the specific gravity 8.96 gcm^{-3}. Copper melts at 1083 °C and boils at 2595 °C. The Pauling electronegativity for Cu is 1.9.

The sources of Cu are mainly from the industrial activities which it is use in the production of electrical accumulators and batteries, in gasoline industries as alkyl additives (Akar and Tunali, 2006), light industry, mechanical manufacturing industry, architecture (Han *et al.,* 2009), paint manufacturing, wood preservatives, Cu polishing and printing operations (Ráhel *et al.,* 2008).

Copper that present in the industrial wastes are primarily in the form of bivalent Cu (II) ions as a hydrolysis product, $CuCO_3$ (aqueous) or organic complexes. In Cu cleaning, Cu plating and metal processing industries, Cu (II) concentrations approach 100 to 120 mgL^{-1}; which is a high value in relation to water quality standards. The value for the Cu (II) concentrations should be reduced to 1.0 to 1.5 mgL^{-1} (Razmovski and Šćiban, 2008).

Copper are micronutrient for plants in low concentration and are structural and catalytic components in many proteins and enzymes (Nyquist and Greger, 2007). Copper actually is not accurately toxic to the humans, but because of the extensive use and also the increasing levels in the environment, Cu can cause serious health problems (Bueno *et al.,* 2008).