



Heriot-Watt University  
Research Gateway

## Adsorption characteristics of Cu(II) ions in aqueous solutions using *Mangifera indica* (Mango) leaf biosorbents

### Citation for published version:

Sethu, V, Goey, KS, Iffah, FR, Khoo, CM & Andresen, J 2010, 'Adsorption characteristics of Cu(II) ions in aqueous solutions using *Mangifera indica* (Mango) leaf biosorbents', *Journal of Environmental Research And Development*, vol. 5, no. 2, pp. 262-278.  
<<http://www.jerad.org/ppapers/dnload.php?vl=5&is=2&st=262>>

### Link:

[Link to publication record in Heriot-Watt Research Portal](#)

### Document Version:

Publisher's PDF, also known as Version of record

### Published In:

Journal of Environmental Research And Development

### General rights

Copyright for the publications made accessible via Heriot-Watt Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

### Take down policy

Heriot-Watt University has made every reasonable effort to ensure that the content in Heriot-Watt Research Portal complies with UK legislation. If you believe that the public display of this file breaches copyright please contact [open.access@hw.ac.uk](mailto:open.access@hw.ac.uk) providing details, and we will remove access to the work immediately and investigate your claim.

## ADSORPTION CHARACTERISTICS OF Cu (II) IONS IN AQUEOUS SOLUTIONS USING *Mangifera indica* (MANGO) LEAF BIOSORBENTS

V. S. Sethu\*, K. S. Goey, F. R. Iffah, C. M. Khoo and J. M. Andresen

Department of chemical and environmental engineering, Faculty of engineering, University of Nottingham Malaysia Campus, Jalan Broga, Semenyih, Selangor (MALAYSIA)

Received July 06, 2010

Accepted October 15, 2010

### ABSTRACT

Adsorption of Cu(II) ions onto a non-conventional plant biosorbents, mango leaf powder (MLP) developed from mature leaves of mango (*Mangifera indica*), was investigated in batch adsorption experiments. Process parameters which include initial metal ion concentration, adsorbent dosages, initial pH and temperature of solution were varied in order to evaluate their influence on the adsorption process. The results obtained indicate that the adsorption of Cu(II) on MLP is better at higher metal ion concentrations and lower adsorbent dosages. The maximum adsorption capacity was found to be 206.85 mg/g, which was obtained at 100 mg/L Cu(II) ion concentration and 0.4 g/L of MLP dosage. pH 4.5 was chosen as the optimum pH and better adsorption occurred at higher solution temperatures. Besides that, the adsorption of Cu(II) on MLP was found to fit the Freundlich isotherm.

**Key Words** : Biosorption, Mango leaf powder, Cu (II) ions, Heavy metals, Wastewater

### INTRODUCTION

In moving towards the new era of science and technology, the world has seen major transformations in numerous aspects of life. At the heart of this tremendous advancement lies the rapid industrialization occurring at various parts of the globe. Despite being the source of many distinguished benefits for mankind, this revolution has also caused significant degradation to the environment, leading to detrimental effects to human and animal life. One widespread phenomenon

which has drawn much attention is the contamination of toxic metals such as copper, lead, zinc, nickel and chromium in the aquatic environment, which are sourced from chemical industries such as petrochemicals, refineries, fertilizers, pulp and paper<sup>1</sup>. Heavy metal contamination may cause serious health problems such as cancer and brain damage, due to the accumulation in living tissues and organs<sup>2</sup>.

Generally, metals could be divided into four distinguished categories which are toxic metals, strategic metals, precious metals and radionuclides. Among these, toxic metals

---

\* Author for correspondence

are the ones associated for causing serious environmental threats, making its removal from the aquatic environment essential. From the various types of toxic metals present in wastewater, copper was chosen for this biosorption studies with regard to its wide use in industry and potential pollution impact. Copper is listed as one of the pollutants found in wastewater by the United States Environmental Protection Agency (USEPA) in 1978<sup>2</sup>. In industrial waste, copper mainly appears to be in the form of the bivalent Cu(II), which is according to Ullmann's encyclopaedia, more toxic than the metal itself. This is because it is soluble in water in its ionic form and can easily absorb into living organisms. High doses of copper in the aquatic environment generate toxicological concerns as it can deposit into the brain, liver, pancreas and myocardium<sup>3</sup>. Thus, Cu (II) concentrations of wastewater should be reduced to a value of at least 1.0 to 1.5 mg/L.

The increase of metal bearing effluents into the aquatic environment has caused progressive developments in wastewater treatment. A typical wastewater treatment plant is divided into several areas and the removal of metallic pollutants is performed mainly in the tertiary stage. Current developed methods in this stage include filtration, ion exchange, membrane separation, nutrient stripping and adsorption<sup>4</sup>. However, these methods have some limitations due to technical and economical constraints. The ion exchange process needs a high operational cost because it involves the use of excessive amounts of reagent for its resin regeneration. It also requires a high capital cost for the equipment used. Meanwhile, the membrane process application is limited by the condition of the

membrane used. This membrane tends to be unstable in salty or acidic conditions and fouls by organic or inorganic substance present in the wastewater. The major disadvantage for the precipitation process is that it generates a toxic sludge that requires careful disposal as per regulations. For electrolysis, its inefficiency at low concentrations which causes incomplete metal ion recovery is one of its disadvantages<sup>5</sup>. Due to these factors, research has been conducted to study the use of natural adsorbents as an alternative, based on the economical and environmental point of view. The most current technique employed for metal removal from wastewater is biological adsorption or biosorption.

According to Mack *et. al.* (2007), "biosorption" is the term given to the passive sorption and/or complexation of metal ions by biomass<sup>6</sup>. It is a reversible process where concentration of metal ions in solution decrease due to adsorption onto the solid phase until a dynamic equilibrium between the aqueous and solid phase is established. This technology which utilises natural biomass materials is very effective for the detoxification of metal-bearing industrial effluents. The biosorption process involves several mechanisms that differ qualitatively and quantitatively, depending on the origin of the biomass, the species used and its processing<sup>7</sup>. These mechanisms are generally based on physico-chemical interactions between metal ions and functional groups present on the cell surface, which include ion exchange, complexation, electrostatic attraction and microprecipitation<sup>8</sup>.

Various types of biomass have been used as the biosorbent for the removal of toxic metals. Among these, plant leaves are chosen in this study as they are proposed to be natural, simple and cheap biosorbents for the efficient removal of several heavy metal ions. They can be easily found and are a renewable source. Plant leaves are also non-toxic and biodegradable. After the biosorption process, they are expected to precipitate and become sediments which can be disposed safely. A research conducted by Salim and Abu El-Halawa (2002), used mulch plant leaves for the biosorption of cadmium, lead and copper ions. The results proved that the performance of the leaves is close to the efficiency of using activated carbon. The results also showed that oven-dried leaves have better performance compared to the naturally dried ones. The functional group which is commonly found in plant leaves is carboxylate<sup>10</sup>.

Available literature involving the use of mango leaf powder (MLP) for the biosorption of heavy metals is quite limited. Particularly, no study involving MLP for the removal of copper ions was found. One paper was found whose the researcher" used several test plant materials including MLP as the biosorbents for the removal of lead ions<sup>36-41</sup>.

The maximum adsorption capacity for the MLP with lead was found to be 31.54 mg/g. Several researchers have also performed studies using different parts of the mango tree as biosorbents. One such study<sup>12</sup> demonstrated the use of mango tree bark as biosorbents suitable for the removal of Hg<sup>2+</sup> and Cr<sup>3+</sup> from aqueous solutions.<sup>58</sup>

## OBJECTIVES

The main objective of this study is to evaluate the adsorption characteristics of Cu(II) from aqueous media using MLP. The adsorption will be carried out in a batch process, with varying adsorbent dosages, initial metal ion concentrations, initial pH of solution and operating temperature.

## MATERIAL AND METHODS

### Preparation of biosorbent

Mature and fresh mango leaves were collected from local trees and washed thoroughly by using distilled water to clean them from dirt and impurities. After that, the leaves were sun dried for a day on a perforated tray until the leaves turned brownish in colour. The leaves were then dried further in an oven (Memmert, DO6838, Germany) for 24 hours until the leaves became crisp. After drying, the leaves were ground by a mechanical grinder (Retsch-ZM 200), to constant size of 80µm and the resulting MLP was kept in a glass bottle ready for further experiments.

### Preparation of adsorbate

The copper stock solution (1000mg/L) was prepared using analytical grades of Cu<sub>2</sub>SO<sub>4</sub>·5H<sub>2</sub>O, which was purchased from HmbG Chemicals. Necessary dilutions were done to obtain 50mg/L, 75mg/L and 100mg/L of copper solution. Standard concentrations of 10, 20, 30 mg/L of Cu(II) solutions were also prepared for calibration purposes. The initial and final metal concentrations were analyzed via Atomic Absorption Spectrometer (AAAnalyst 400 by Perkin Elmer) using the lamp at specific condition. The pH of the Cu(II) solution was adjusted by adding 0.1 M HCl or 0.1 M

NaOH and the measurement was done by pH meter (Martini instruments, Mi56P).

### Biosorption experiments

The biosorption of Cu (II) from aqueous solution was investigated in batch biosorption experiments. The MLP with different dosages (0.4, 0.6, 0.8, 1.0 and 1.2 g/L) were added each in 5 conical flasks containing 100 mL of 100 mg/L Cu(II) solution. 1 mL of the Cu(II) solution was withdrawn by using a dropper and added in sampling tubes with scale that contained 9 mL of deionised water for the purpose of dilution. After that, the batch shake flask experiments were performed using a gyratory

shaker (Protech, Model 903) with 75 rpm at 30°C for 3 hours. For the first hour, the samples were withdrawn every 15 minutes. For the following hours, the same procedure was repeated at every 30 minutes interval. The samples were tested for their Cu(II) ion concentration with the AAS.

For pH experiments, the pH of the solution was adjusted to 2.5, 4.5, 8.5 and 10.5 by using 0.1 M HCl and 0.1 M NaOH. Five different sets of experiments with variable concentration of Cu(II) solution, pH and temperature were performed. The operating parameters for each set of experiment are summarized in **Table 1**.

**Table 1 : Variation of experimental operating parameters**

Parameter	Values Investigated
Initial Cu(II) concentration (mg/L)	50, 75, 100
Amount of adsorbent (g/L)	0.4, 0.6, 0.8, 1.0, 1.2
Agitation time (hr)	3
Adsorption temperature (°C)	30, 45, 60
pH	2.5, 4.5, 6.5, 8.5, 10.5

The amount of material adsorbed per unit mass of adsorbent (mg/g) is given in equation (1):

$$q = \frac{C_o - C_t}{m} \quad (1)$$

Where,  $C_o$  is the initial concentration of adsorbate (mg/L) and  $C_t$  is the concentration of adsorbate at time  $t$  (mg/L). The

adsorption efficiency can be expressed as percentage adsorption of metal ion per equation (2):

$$\% \text{ adsorption} = \frac{C_o - C_t}{C_o} \times 100\% \quad (2)$$

Where,  $C_o$  and  $C_t$  are the initial adsorbate concentration (mg/L) and the adsorbate concentration at time,  $t$  (min) respectively.

### Equilibrium studies

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems. Classical adsorption models, Langmuir (1918) and Freundlich (1907), were used to describe the equilibrium between Cu(II) ions on the MLP at constant temperature.

The Langmuir equation is valid for a monolayer sorption on a homogenous surface with a finite number of identical sites and when there are no interactions between the sorbed species. The linear form of Langmuir equation is given in equation (3):

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m} \quad (3)$$

where  $C_e$  (mg/L) is the equilibrium concentration of adsorbate,  $q_e$  (mg/g) is the quantity of adsorbed material (mg/g) at equilibrium,  $K_L$  is the Langmuir equilibrium constant related to the energy of sorption ( $L \text{ mg}^{-1}$ ) and  $q_m$  is the maximum amount of metal ions per unit weight of MLP to form a complete monolayer on the surface bound at high  $C_e$ . It also represents a practical limiting adsorption capacity when the surface is fully covered with the metal ions and assists in the comparison of adsorption performance, particularly in cases where the sorbent did not reach its full saturation in experiments<sup>13-15</sup>.

The empirical Freundlich equation applies to multilayer sorption on a heterogeneous surface and can only be employed in the low

intermediate concentration ranges. The Freundlich equation is given in equation (4):

$$\log q_e = \frac{1}{n} \log C_e + \log K_f \quad (4)$$

where the  $K_f$  ( $\text{mg g}^{-1}$ ) and  $n$  (value between 0 and 1) are the Freundlich constant characteristic on the system.  $K_f$  and  $n$  are indicators for adsorption capacity and adsorption intensity, respectively<sup>14,43-50</sup>.

## RESULTS AND DISCUSSION

### Effect of contact time

The effect of contact time was studied at different initial metal ion concentrations and MLP dosages. **Fig. 1** shows the plot of adsorption efficiency against time for a fixed MLP dosage of 1.2 g/L, and varied metal concentration. It can be clearly observed that the percentage of adsorption generally increased until time reached 120 minutes. After this time, there was a drop in the adsorption percentage. Thus, 120 minutes was chosen as the optimum time where the adsorption reached equilibrium. The highest percentage of adsorption was found to be 22.68 %, 44.89 % and 54.99 % for concentration of 50 mg/L, 75 mg/L and 100 mg/L respectively. From the concentration experiments, 100 mg/L of Cu(II) was found to be optimal for the dosage of MLP used.

The relationship of adsorption efficiency with time at varied MLP dosages is depicted in **Fig. 2**. The results reveal a similar trend, where MLP removal is higher at the beginning (for the first 45 minutes) for all the dosages used.

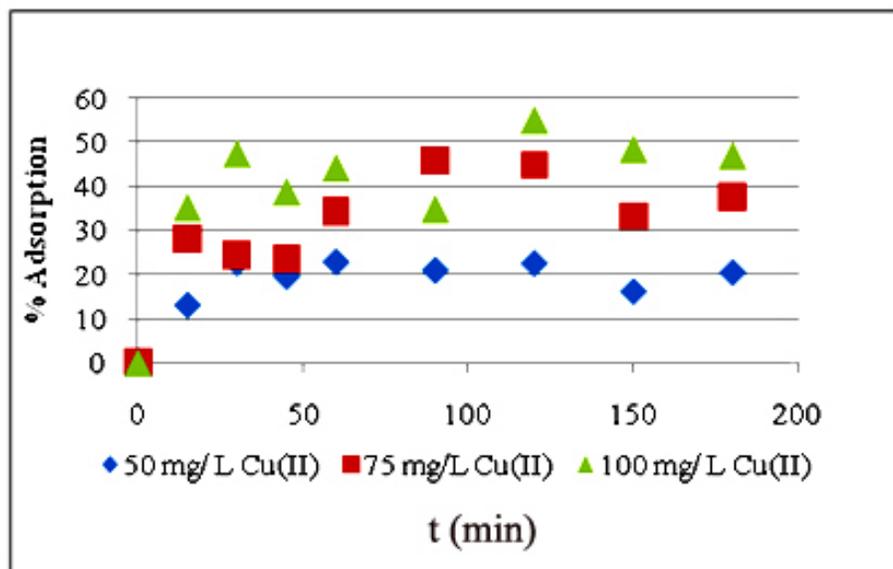


Fig. 1 : Plots of adsorption of Cu (II) (50, 75, 100 mg/L) on MLP (1.2 g/L) at 30°C

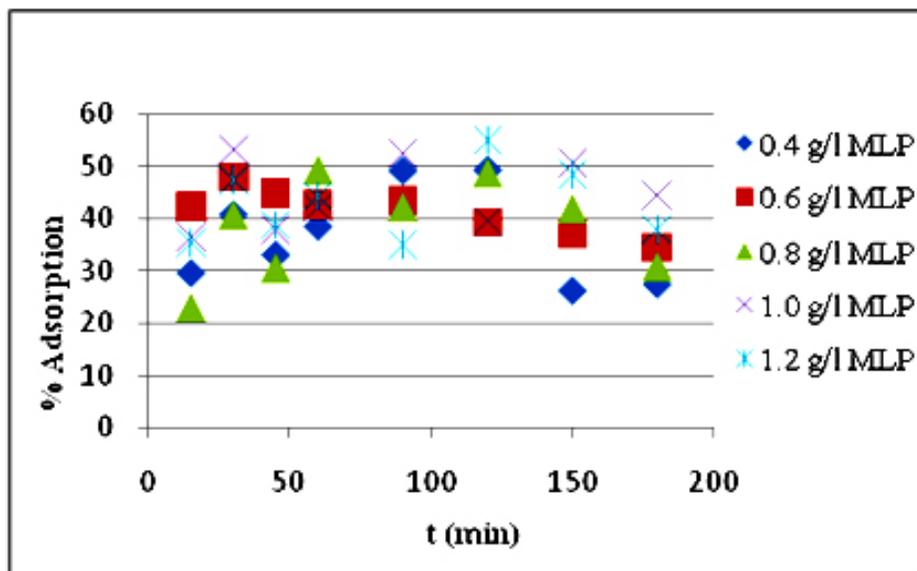


Fig. 2 : Plots of adsorption of Cu (II) (100 mg/L) on MLP (0.4, 0.6, 0.8, 1.0, 1.2 g/L) at 30°C

This is due to the larger surface area of MLP exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the available during the initial contact time. As the surface adsorption sites become

adsorbent particles<sup>15-16</sup> Similar results were reported using wheat shell as the biosorbent<sup>17</sup>.

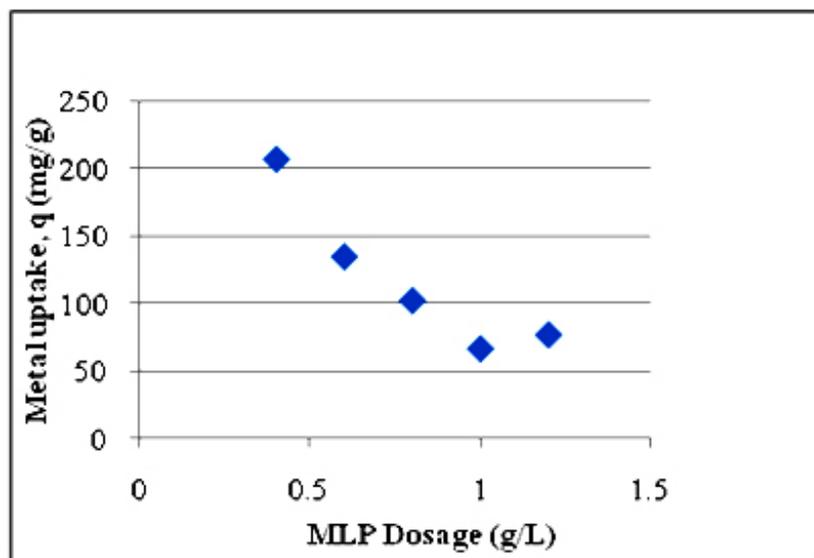
Both figures show that the initial metal ion concentration and MLP dosage did not affect the time for the adsorption to reach its optimum time of 120 minutes.

After the optimum time, both plots also showed a decrease in the removal efficiency. This indicates that desorption process may

have occurred, as adsorption is a reversible process<sup>18, 50-55</sup>.

#### Effect of biosorbent dosage

The influence of the biosorbent dosage on the process was examined by using five different dosages at 0.4, 0.6, 0.8, 1.0 and 1.2 g/L. **Fig. 3** shows the relationship of metal uptake with the biosorbent dosage at Cu(II) concentration of 100 mg/L and time of 120 minutes.



**Fig. 3 :** Plot of metal uptake, q against MLP dosage at 100 mg/L Cu(II) concentration at 30°C

It can be observed that the increase in the biosorbent dosage causes decrease in the metal uptake. Similar results were also observed for Cu(II) concentrations of 50 mg/L and 75 mg/L. Vaghetti *et. al.* (2008)<sup>19</sup> explained that this phenomenon is due to the splitting effect of flux (concentration gradient) between the adsorbate and biosorbent with increasing biomass concentration causing a decrease in amount of metallic ion adsorbed per gram of biomass. Another factor is that at high

sorbent dosages, the available metal ions are insufficient to cover all the exchangeable sites on the biosorbent, usually resulting in a low metal uptake<sup>20</sup>.

Besides, it might be due to the formation of aggregation during biosorption causing a decrease in the effective adsorption area when the biomass concentration increases<sup>18,56</sup>. Thus, it could be concluded that for this studies, the highest metal uptake occurs at the lowest biosorbent dosage (0.4

g/L) if other process conditions are kept constant.

#### Effect of initial metal ion concentration

The initial metal ion concentration plays an important role towards the performance of a batch biosorption. The effect can be studied from the results of experiments at constant dosages of MLP. As shown in Fig. 4, the metal uptake of different dosages of MLP increased as the initial metal ion concentration increased from 50 to 100 mg/L, where the maximum value of metal uptake was observed to be from 14.78 mg/g to 206.85 mg/g respectively. These values were obtained at the optimum contact time of 120 minutes and MLP dosage of 0.4 g/L. The value of 206.85 mg/g is the maximum metal uptake, or the maximum adsorption

capacity that was achieved by the biosorption of Cu(II) on MLP in this study. This observation was also in line with the research performed by two other researcher<sup>21,22</sup>.

According to Dang *et. al.* (2008), this result is expected as the initial metal ion concentration functions as the driving force to overcome mass transfer resistances between the aqueous and solid phases. In addition, the increase in the initial metal ion concentration also increased the number of collisions between the metal ion and the biosorbent, hence increasing the metal uptake<sup>23-57</sup>.

Thus, it could be concluded that the highest metal uptake would occur at the highest metal concentration, which is 100 mg/L, at optimal conditions.

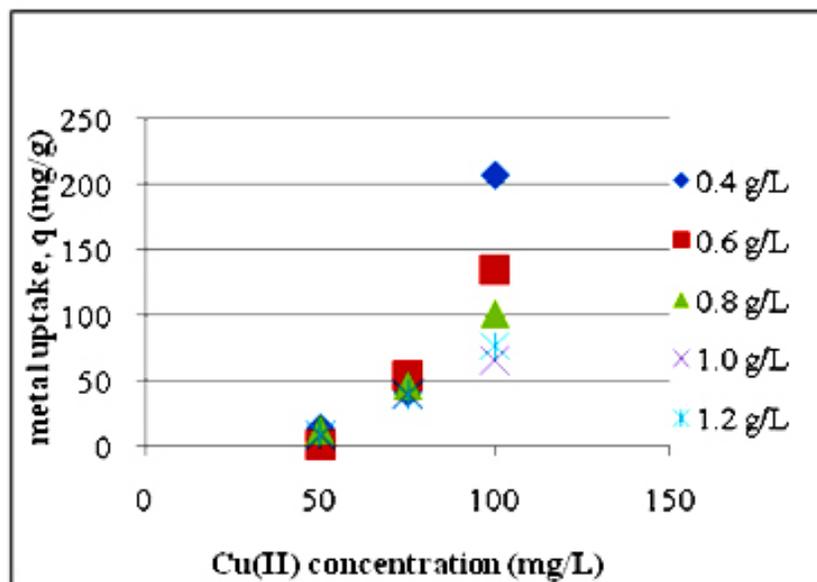


Fig. 4 : Plots of metal uptake,  $q$  against Cu(II) concentration with different MLP dosages at 30°C

#### Effect of initial solution pH

The pH of the adsorbate solution is considered one of the most important factors

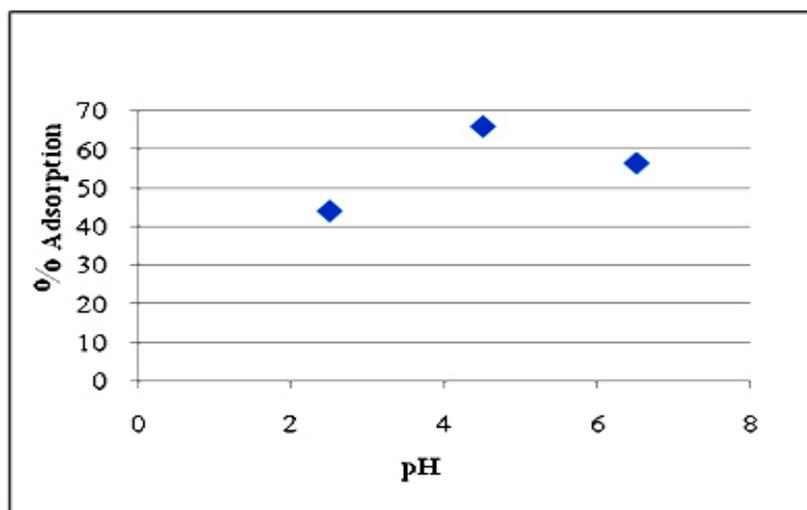
affecting the biosorption process. This factor is capable of influencing not only the binding site dissociation state, but also the solution

chemistry of the target metal in terms of hydrolysis, complexation by organic and/or inorganic ligands and redox potentials (Mack *et al.*, 2007).

The range of pH tested in this experiment was from 2.5 to 6.5. Adsorption could not be carried out beyond pH 7 due to the precipitation of  $\text{Cu}(\text{OH})_2$ . This is supported by several other studies<sup>24-26</sup>. Solutions with pH lower than 2.5 was also not suitable as for these solutions, the surface active sites of the adsorbent would be protonated, resulting in a competition of  $\text{Cu}(\text{II})$  and  $\text{H}^+$  ions for the same surface active sites which would result in a low copper uptake<sup>4</sup>.

In the present study, the pH was adjusted in the range of 2.5-6.5 by using dilute  $\text{H}_2\text{SO}_4$  and 8-11 by using  $\text{NaOH}$ . The experiments were carried out at 100 mg/L of initial metal ion concentration with 0.4 g/L adsorbent dosage for an agitation time of 3 hours at  $30^\circ\text{C}$ . From **Fig. 5**, it can be observed that the adsorption is highest for pH 4.5 followed by pH 6.5 and 2.5.

These results were also presented in many previous studies which involved a maximum adsorption from pH 4.5 to 5.5<sup>27,28</sup>. This trend was expected as at low pH values, most of the binding sites on the root surface would have positive charges making the binding and sorption of the metal ions unattractive to those sites<sup>29</sup>.



**Fig. 5 :** Plot of adsorption efficiency against initial solution pH at 100 mg/L  $\text{Cu}(\text{II})$  concentration, 0.4 g/L MLP at  $30^\circ\text{C}$

The competition of  $\text{Cu}(\text{II})$  with  $\text{H}^+$  ions for appropriate sites on the adsorbent surface lowers the adsorption of  $\text{Cu}(\text{II})$  ions. However, as the pH of the solution increases, this competition weakens, where  $\text{Cu}(\text{II})$  ions replace  $\text{H}^+$  ions bound to the adsorbent since increasing number of protons are dissociated

from functional groups on the cell wall. In addition, at higher pH, there will be a change in the dominant functional groups responsible for binding on the cell wall, with carboxylate groups and diamine groups being the most important ones for  $\text{pH} < 5$  and  $\text{pH} 6$  respectively<sup>30</sup>.

More negative groups were then made available on the adsorbent surface as pH increases.

The negatively charged adsorbent surface increased the electrostatic attraction between positively charged adsorbate and negatively charged adsorbent particles and therefore, leading to an increase in the adsorption of Cu(II) ions. However, further increase in the pH will cause the metals to form precipitates.

### Effect of temperature

In order to examine the effect of temperature on copper biosorption, three different temperatures were selected. Experiments were carried out at 30°C, 45°C and 60°C. Based on Fig. 6, a clear trend can be observed. Temperature variation plays an important role on copper biosorption. The percentage of adsorption increases when the temperature increased.

This is more significant at low copper concentration of 50 mg/L with the highest increase in adsorption efficiency.

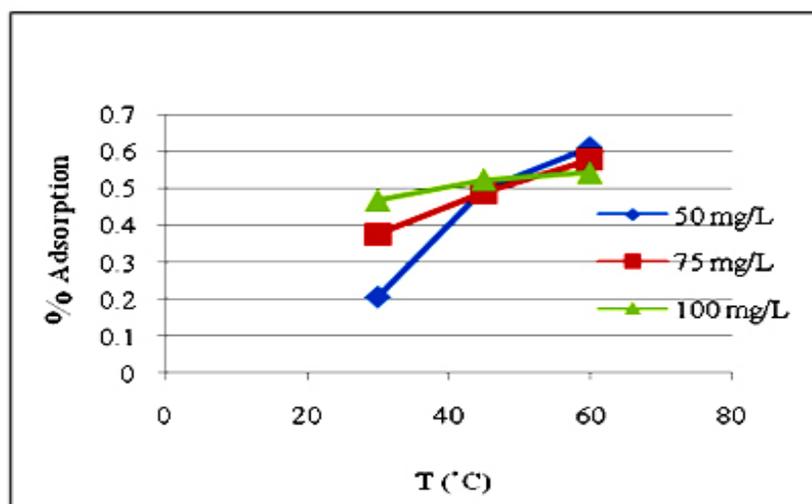


Fig. 6 : Plot of adsorption efficiency against solution temperature with 0.4 g/L MLP

This trend is also reported in studies such as by<sup>31</sup>, where biosorption of Pb (II) was carried out by fungus, *Cephalosporium aphidicola* and biosorption of copper, zinc and cadmium by dried seaweeds, *E. maxima* and *Laminaria pallida*<sup>32</sup>. The increase of percentage of adsorption with temperature signifies the endothermic nature of the adsorption process. By increasing the temperature, the rate of diffusion will also

increase and this leads to the diffusion of adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution.

This enhancement was also reported due to the chemical interaction between adsorbates and adsorbent, creation of some new adsorption sites or the increased rate of

intraparticle diffusion of adsorbate molecules into the pores of the adsorbent at higher temperatures<sup>33</sup>.

**Adsorption isotherms**

Many models have been proposed to explain adsorption equilibria, but the most important factor is to have applicability over the entire range of process conditions. The most widely used isotherms for solid-liquid adsorption are the Langmuir and Freundlich isotherms (Bulut and Tez, 2007). Both of these isotherms relate the adsorption density,  $q_e$  (metal uptake per unit weight of adsorbent) to equilibrium adsorbate concentration in the bulk fluid phase,  $C_e$ <sup>34</sup>.

Langmuir isotherm model is valid for monolayer adsorption onto a surface containing a finite number of identical sites.

This isotherm is derived from the assumption that a maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with constant energy of adsorption, and no transmigration of adsorbate in the plane of the surface<sup>35</sup>. The correlation coefficient that was obtained from the Langmuir plot as shown in Fig. 7 is 0.9984. However, the plot shows a decreasing trend, resulting in a negative gradient with a value of -0.0511. The maximum amount of metal ions per unit weight of MLP,  $q_m$  was found to be -19.5695 while the Langmuir constant,  $K_L$  is -0.00826. This trend is also observed for adsorption at different MLP dosages and initial metal ion concentration. These values prove that the adsorption is not favorable for a Langmuir isotherm, as they are supposed to be positive.

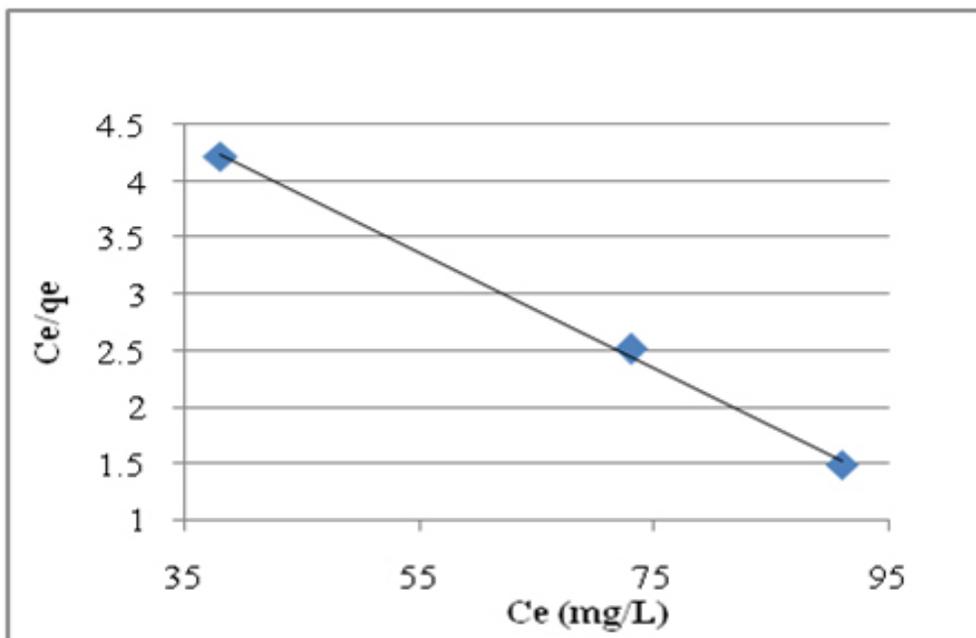
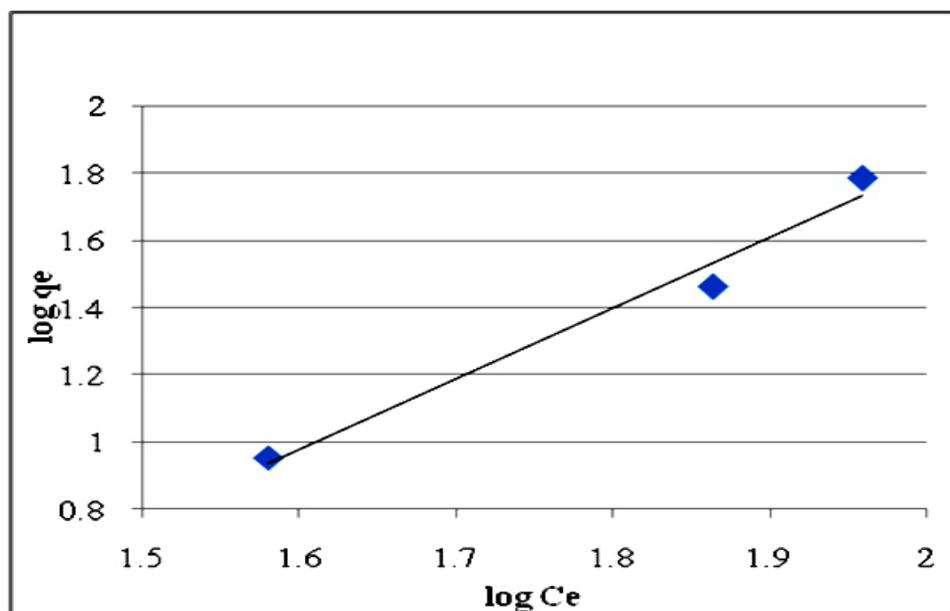


Fig. 7 : Langmuir plot for adsorption of Cu(II) on MLP with dosage of 0.4 g/L and at 30°C

Freundlich isotherm gives the relationship between the equilibrium liquid and solid phase capacity based on multilayer adsorption (heterogeneous surface). The Freundlich isotherm is based on the assumption that the adsorption sites are distributed exponentially with respect to the heat of <sup>35</sup>. Based on **Fig. 8**, the correlation coefficient that was found from the Freundlich plot is 0.9775. This high value

indicates that the adsorption is favorable for a Freundlich isotherm. In addition, the adsorption intensity, *n*, which was found to be 0.4761, further proves this finding. This is as this value is smaller than 1. Meanwhile, the Freundlich constant, *K<sub>F</sub>* was found to be 0.004156.

These results also indicate that the MLP surface is heterogenous in the long range, but may have short range of uniformity<sup>36</sup>.



**Fig. 8 :** Freundlich plot for adsorption of Cu(II) on MLP with dosage 0.4 g/L and at 30°C

**Performance of MLP when compared to other biosorbents**

From the studies carried out, it was found that MLP appears to be a promising

adsorbent for the effective removal of Cu(II) metal ions from wastewater. **Table 2** below gives a comparison of MLP with other types of biosorbents.

Table 2 : Performance of MLP when compared to other biosorbents

Type of biosorbent	pH	Temperature (K)	Maximum adsorption capacity, q	Reference
Crab shell particles	6	298	243.9 mg/g	Vijayaraghavan <i>et. al.</i> , 2006
<b>Mango leaf powder</b>	<b>6</b>	<b>303</b>	<b>206.85 mg/g</b>	<b>Present study</b>
Pretreated powdered waste sludge	N/A	298	156 mg/g	Pamukoglu and Kargi, 2007
Rhizopus Oligosporus	5	298	140 mg/g	Beolchini <i>et. al.</i> , 2003
Crab carapace (Cancer pagurus)	5	N/A	79.4 mg/g	Cochrane <i>et. al.</i> , 2006
Rhizopus oligosporus	4	298	76.2 mg/g	Beolchini <i>et. al.</i> , 2003
Marine algal biomass	5	N/A	72.43 mg/g	Sheng <i>et. al.</i> , 2004
Marine biomass	5	N/A	63 – 75 mg/g	Yu <i>et. al.</i> , 1999
Anaerobic granular biomass	4.5 - 5.5	N/A	55 mg/g	Hawari <i>et. al.</i> , 2006
Wheat bran	5	N/A	51.5 mg/g	Ozer <i>et. al.</i> , 2004
Peat biomass	6	N/A	34.06 mg/g	Qin <i>et. al.</i> , 2006
Carrot residue	5	N/A	32.74 mg/g	Nasernejada <i>et. al.</i> , 2005
Rice husk	5.3	N/A	29 mg/g	Wong <i>et. al.</i> , 2003
Black gram husk	5	N/A	25.5 mg/g	Saeed <i>et. al.</i> , 2005
Sunflower Stalks	4.25	N/A	25.11 mg/g	Sun <i>et. al.</i> , 1998
Marine brown algae Fucus vesiculosus	N/A	298	23.4 mg/g	Dang <i>et. al.</i> , 2008
Sugar beet pulp	5.5	N/A	20.96 mg/g	Reddad <i>et. al.</i> , 2002
Aquatic plant	< 6	N/A	15.59 mg/g	Keskinkan <i>et. al.</i> , 2003
Cladophora glomerata (L.) Kutz (Chlorophyta)	5	298	15 mg/g	Yalcin <i>et. al.</i> , 2008
Pretreated Aspergillus niger biomass	N/A	298	13.4 mg/g	Mukhopadhyay <i>et. al.</i> , 2008
Cotton Ball	5	N/A	11.4 mg/g	Ozsoy <i>et. al.</i> , 2006
Terrestrial moss Pleurozium schreberi	N/A	298	11.1 mg/g	Dang <i>et. al.</i> , 2008
Canola Meal	6	N/A	9.8 mg/g	Al-Asheh <i>et. al.</i> , 1996
Olive shale	6	N/A	9.8 mg/g	Al-Asheh <i>et. al.</i> , 2001
Pine bark	4	N/A	6.4 - 15.6 mg/g	Al-Asheh <i>et al.</i> , 1997

Type of biosorbent	pH	Temperature (K)	Maximum adsorption capacity, q	Reference
Cellulose pulp waste	< 6	N/A	4.98 mg/g	Ulmanu <i>et. al.</i> , 2003
Birch wood <i>Betula sp</i>	N/A	298	4.9 mg/g	Dang <i>et. al.</i> , 2008
Rubber wood sawdust	6	N/A	3.825 mg/g	Kalavathy <i>et. al.</i> , 2005
Bacterial strain isolated from soil	5	298	1.17 mg/g	Tunali <i>et. al.</i> , 2006
Sargassum biomass	5	298	1.11 mg/g	Tsui <i>et. al.</i> , 2006
Wheat straw <i>Triticum aestivum</i>	N/A	298	0.18 mmol/g	Dang <i>et. al.</i> , 2008
Brown alga <i>Fucus vesiculosus</i>	N/A	298	1.66 mmol/g	Mata <i>et. al.</i> , 2008
Ponkan mandarin ( <i>Citrus reticulata</i> ) peel	4.8	298	1.31 mmol/g	Pavan <i>et. al.</i> , 2006
Saltbush ( <i>Atriplex canescens</i> ) leaves	5	297	1.07 mmol/g	Sawalha <i>et. al.</i> , 2007
Orange peel	alkali	353	1.22 mol/kg	Lu <i>et. al.</i> , 2008

## CONCLUSION

The following conclusions can be drawn based on the investigation of Cu(II) adsorption by MLP:

1. The optimum contact time for the maximum adsorption capacity of Cu(II) on MLP was 120 minutes.
2. The metal uptake of Cu(II) on MLP decreased with increasing MLP dosage.
3. The metal uptake and adsorption efficiency of Cu(II) on MLP increased with increasing metal ion concentration.
4. The maximum adsorption capacity of Cu(II) on MLP was 206.85 mg/g which was obtained with 0.4 g/L MLP dosage, 100 mg/L Cu(II) concentration and a pH of 4.5
5. Higher adsorption efficiency of Cu(II) on MLP was observed at higher temperatures.
6. The experimental data for the adsorption of Cu(II) on MLP fits well for the Freundlich isotherm.

## REFERENCES

1. Kaewsarn P. and Yu Q., Cadmium (II) removal from aqueous solutions by pre-treated biomass of marine alga *Padina sp.*, *Environ. Pollut.*, **112**(1), 209–213, (2001).
2. Mukhopadhyay M., Role of surface properties during the biosorption of copper by pretreated *Aspergillus niger* biomass, *Colloids and Surfaces, Physicochemi. Eng. Asp.*, **329**(2), 95-99, (2008).
3. Davis T. A., Volesky B. and Vieira, R.H.S.F., Sargassum seaweed as biosorbent for heavy metals, *Water Res.*, **34**(1), 4270-4278, (2000).
4. Lu D., Cao Q., Li X., Cao X., Luo F. and Shao W., Kinetics and equilibrium of Cu(II) adsorption onto chemically modified orange peel cellulose biosorbents, *Hydro. metallurgy*. doi:10.1016/j. hydromet, (2008).

5. Dang V. B. H., Doan H. D., Dang-Vu T. and Lohi A., Equilibrium and kinetics of biosorption of cadmium (II) and copper (II) ions by wheat straw, *Biores. Tech.*, **100**(2), 211-219, (2008).
6. Mack C., Wilhelmi B., Duncan J. R. and Burgess J. E., 2007., Biosorption of precious metals, *Biotech. Adv.*, **25**(1), 264-271, (2008).
7. Volesky B. and Holan Z. R., Biosorption of heavy metals, *Biotech. Prog.*, **1**(2), 235-250, (1990).
8. Schiewer S. and Volesky B., Modeling the Proton-Metal Ion Exchange in Biosorption, *Environ. Sc. Tech.*, **29**(2), 3049-3058, (1995).
9. Salim R. and Abu El-Halawa R., Efficiency of dry plant leaves (Mulch) for removal of lead, cadmium and copper from aqueous solutions, *Trans IChemE*, **80**(1), 270-277, (2002).
10. Shaban W., Al Rmalli, Abdella A. Dahmani, Mohamed M. Abuein and Amar A. Gleza, Biosorption of mercury from aqueous solutions by powdered leaves of castor tree, *J. Ha. Mate.*, **152**(2), 955-959, (2007).
11. Gupta S., Kumar, D. and Gaur J. P., Kinetics and isotherm modelling of lead (II) sorption onto some waste plant materials, *Chem. Eng. J.*, doi:10.1016/j.cej, (2008).
12. Tiwari D., Mishra S. P., Mishra M. and Dubey R. S., Biosorptive behaviour of mango (*Mangifera indica*) and neem (*Azadirachta indica*) bark for  $Hg^{2+}$ ,  $Cr^{3+}$  and  $Cd^{2+}$  toxic ions from aqueous solutions: a radiotracer study, *App. Radi. Isotop.*, **50**(2), 631-642, (1999).
13. Aksu Z., Determination of the equilibrium, kinetics and thermodynamic parameters of the batch biosorption of nickel(II) ions onto *Chlorella vulgaris*, *Proc. Biochem.*, **38**(1), 89-99, (2002).
14. Ajmal M., Rao R.A.K., Ahmad R. and Ahmad J., Adsorption studies on Citrus reticulata (fruit peel of orange): removal and recovery of Ni(II) from electroplating wastewater, *J. Haz. Mate. B*, **79**, 117-1131, (2000).
15. Bulut Y. and Tez, Z., Adsorption studies on ground shells of hazelnut and almond, *J. Ha. Mate.*, **149**(1), 35-41, (2007)
16. K. L. Dorrls, Yu B., Zhang, Y., Shukla, A. and Shukla, S. S., The removal of heavy metal from aqueous solutions by sawdust adsorption- removal of copper, *J. Ha. Mate., B*, **80**(2), 33-42, (2000).
17. Basci N., Kocadagistan E. and Kocadagistan B., *Biosorption of copper (II) from aqueous solutions by wheat shell Desalination*, **164**, 135-140, (2004).
18. Ekmekyapar F., Ali A., Kemal Y. B. and Avni C., Biosorption of copper (II) by non living lichen biomass of *Cladonia rangiformis* hoffm, *J. Ha. Mate. B*, **137**(1), 293-298, (2006).
19. Vaghetti J.C.P., Lima E.C. and Royer B., Application of Brazilian-pine fruit coat as a biosorbent to removal of Cr(VI) from aqueous solution—Kinetics and equilibrium study, *Biochem. Eng. J.*, **42**(1), 67-76, (2008).
20. Vijayaraghavan K., Palanivelu K. and Velan, M., Biosorption of copper (II) and cobalt(II) from aqueous solutions by crab shell particles, *Biores. Tech.*, **97**(2), 1411-1419, (2006).
21. King P., Anuradha, K., Beena Lahari S., Prasanna Kumar, Y., and Prasad V.S.R.K., Biosorption of zinc from aqueous solution using *Azadirachta indica* bark: Equilibrium and kinetic studies, *J. Ha. Mate.*, **152**(2), 324-329, (2008).
22. Gupta V. K., Srivastava S. K. and Mohan D., Equilibrium uptake, sorption dynamics, process optimization, and column operations for the removal and recovery of Malachite Green from wastewater using activated carbon and activated slag, *Ind. Eng. Chem. Res.*, **36**(1), 2207-2212, (1997).
23. Yalcin E., Cavusoglu K., Maras M. and Mutluhan B., Biosorption of lead (II) and copper (II) metal ions on *Cladophora glomerata* (L.) Kutz. (Chlorophyta) Algae: Effect of Algal surface

- modification, *Acta. Chim. Slov.*, **55**(2), 228-232, (2008).
24. Bhatti H.N., Khalid R. and Hanif, M.A., Dynamic biosorption of Zn(II) and Cu(II) using pretreated *Rosa gruss an teplitz* (red rose) distillation sludge, *Chem. Eng. J.*, **148**(1), 434-443, (2008).
25. Ngeontae W., Aeungmaitrepirom, W., Tuntulani, T. and Imyim, A., Highly selective preconcentration of Cu(II) from seawater and water samples using amidoamidoxime silica, *Talanta*, **43**(2), 1004-1010, (2008).
26. Demirbas E., Dizge N., Sulak M. T. and Kobya M., Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon, *Chem. Eng. J.*, **148**(1), 480-487, (2008).
27. Jiang Y., Pang H., and Liao B., Removal of copper(II) ions from aqueous solution by modified bagasse, *J. Ha. Mate.*, **148**(1), 1-9, (2007).
28. Pavan F. A., Lima I. S., Lima E. C., Airoidi, C. and Gushikem Y., Use of Ponkan mandarin peels as biosorbent for toxic metals uptake from aqueous solutions, *J. Ha. Mate. B.*, **137**(2), 527-533, (2006).
29. Al-Subu M. M., Salim R., Abu-Shqair I. and Swaileh K. M., Removal of dissolved copper from polluted water using plant leaves: Effects of acidity and plant species, *Revi. Interna. de Contam. Ambi.*, **17**(1), 91-96, (2001).
30. Wang G., Biosorption of heavy metal ions from aqueous solutions by nonliving water hyacinth roots, *Ph.D. Dissertation*, University of Nevada, Reno, UMI Company, (1995).
31. Tunali S., Akar T., Ozcan, A.S., Kiran I. and Ozcan A., Equilibrium and kinetics of biosorption of lead(II) from aqueous solutions by *Cephalosporium aphidicola*, *Sep.Purifi. Tech.*, **47**(2), 105-112, (2006).
32. Nigro S. A., Stirk W. A. and Van Staden J., Optimising heavy metal adsorbance by dried seaweeds, *South Afri. J. Botany*, **68**(1), 333-341, (2002).
33. Tan I. A.W., Ahmad A.L., Hameed B.H., Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon, *J. Ha. Mate.*, **164**(2), 473-482, (2008).
34. Kalavathy M. H., Karthikeyan T., Rajgopal S. and Miranda L. R., Kinetic and isotherm studies of Cu(II) adsorption onto H<sub>3</sub>PO<sub>4</sub>-activated rubber wood sawdust, *J. Coll. Interf. Sc.*, **292**(1), 354-362, (2005).
35. Gaballah I. and Killbertus G., Recovery of heavy metal ions through decontamination of synthetic solutions and industrial effluents using modified barks, *J. Geochem. Explor.*, **62**(1), 241-286, (1998).
36. Sarma J., Sarma A. and Bhattacharyya K. G., Biosorption of commercial dyes on *Azadirachta indica* leaf powder: A case study with a basic dye Rhodamine B, *Ind. Eng. Chem. Res.*, **47**(2), 5433-5440, (2008).
37. Pamukoglu Y. M. and Kargi F., Effects of operating parameters on kinetics of copper (II) ion biosorption onto pretreated waste sludge (PWS), *Enzy. Micr.l Tech.*, **42**(2), 76-82, (2007).
38. Cochrane E. L., Lua S., Gibb S. W. and Villaescusa I., A comparison of low-cost biosorbents and commercial sorbents for the removal of copper from aqueous media, *J. Ha. Mate. B.*, **137**(2), 198-206, (2006).
39. Sheng P. X., Ting Y. P., Chen J. P. and Hong L., Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms, *J. Colloid Interf. Sc.*, **275**(3), 131-141, (2004).
40. Yu Q., Matheickal J. T., Yin P. and Kaewsarn P., Heavy metal uptake capacities of common marine macroalgal

- biomass, *Water Res.*, **33** (6), 1534–1537, (1999).
41. Hawari A. H. and Mulligan C. N., Biosorption of lead(II), cadmium(II), copper(II) and nickel(II) by anaerobic granular biomass, *Biores. Tech.*, **97**(1), 692 – 700, (2006).
  42. Ozer A., Ozer D. and Ozer A., The adsorption of copper(II) ions on to dehydrated wheat bran (DWB): determination of the equilibrium and thermodynamic parameters, *Proc. Biochem.*, **39**(2), 2183–2191, (2004).
  43. Qin F., Wen B., Shan X. Q., Xie Y. N., Liu T., Zhang S. Z. and Khan S. U., Mechanisms of competitive adsorption of Pb, Cu (pH = 4), and Cd on peat, *Env. Poll.*, **144**(1), 669–680, (2006).
  44. Nasernejada B., Zadehb T. E., Poura B. B., Bygia M. E. and Zamani A., Comparison for biosorption modeling of Cr, Cu, Zn wastewater by carrot residues, *Proc. Biochem.*, **40**(2), 1319 – 1322, (2005).
  45. Wong K. K., Lee C. K., Low K. S. and Haron M. J., Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions, *Chemos.*, **50** (1), 23–28, (2003).
  46. Saeed A., Iqbal M. and Akhtar M. W., Removal and recovery of lead(II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk), *J. Ha. Mate. B*, **117**(2), 65–73, (2005).
  47. Sun G. and Shi W., Sunflower stalks as adsorbents for the removal of metal ions from wastewater, *Ind. Eng. Chem. Res.*, **37**(2), 1324–1328, (1998).
  48. Reddad Z., Gerente C., Andres Y. and LeCloirec P, Adsorption of several metal ions onto a lowcost adsorbent, kinetic and equilibrium studies, *Environ. Sc. Tech.*, **36**(1), 2067–2073, (2002).
  49. Keskinan O., Goksu M. Z. L., Yuceer A., Basibuyuk M. and Forster, C.F., Heavy metal adsorption characteristics of a submerged aquatic plant *Myriophyllum spicatum*, *Proc. Biochem.*, **39**(2), 179–183, (2003).
  50. Ozsoy H. D. and Kumbur H., Adsorption of Cu(II) ions on cotton ball, *J. Ha. Mate.*, **136**(1), 911–916, (2006).
  51. Al-Asheh S. and Duvnjak Z., Adsorption of copper by canola meal, *J. Ha. Mate.*, **48**, 83-93, (1996).
  52. Al-Asheh S. and Banat F., Adsorption of copper and zinc by oil shale, *Environ. Geo.*, **40** (6), 693-698. (2001).
  53. Al-Asheh S. and Duvnjak Z., Sorption of cadmium and other heavy metals by pine bark, *J. Hazard. Mate.*, **56**(2), 35 – 51, (1997).
  54. Ulmanu M., Marañón E., Fernández Y., Castrillón L., Anger I. and Dumitriu, D., Removal of copper and cadmium ions from diluted aqueous solutions by low cost and waste material adsorbents, *Wat. Air Soil Pollu.*, **142**(2), 357– 373, (2003).
  55. Tsui M. T. K., Cheung K. C., Tam N. F. Y. and Wong M. H., A comparative study on metal sorption by brown seaweed, *Chemosphere*, **65**(2), 51-57, (2006).
  56. Mata Y. N., Blazquez M. L., Ballester A., Gonzalez, F. and Munoz, J. A., Characterization of the biosorption of cadmium, lead and copper with brown algae *Fucus vesiculosus*, *J. Ha. Mate.*, **158**(1), 316-323. (2008).
  57. Sawalha M. F., Peralta-Videa J. R. and Romero-Gonzalez, J., Thermodynamic and isotherm studies of the biosorption of Cu(II), Pb(II), and Zn(II) by leaves of saltbush (*Atriplex canescens*), *J. Chem. Thermody.*, **39**(1), 488-492, (2007).
  58. Singh D., Biosorption of Cu(II) from aqueous solution by NB living *spirogyra sp.* *J. Environ. Res. Develop.*, **1**(3) 227-231, (2006).