# A performance of hybrid biosorbent 'M-Bios' of Pb(II) and Cu(II) in aqueous solutions.

Mohd Lias Kamal[1,2], Jamil Tajam[1,2], Sharizal Hasan[1], Mohd Halim Shah Ismail[3], Anies Suhaida Mohd Naspu[1], Nur Saliza Awatif Zahala[1]

[1]Faculty of Applied Chemistry, Universiti Teknologi MARA, Perlis, Malaysia
[2]Ocean Research Conservation and Advance (ORCA), Universiti Teknologi MARA, Perlis, Malaysia.
[3]Department of Chemical and Environmental Engineering, Universiti Putra Malaysia, Malaysia.

**Abstract-** 'M-bios' biosorbent is a hybrid of mangrove wasted bark from charcoal industry at Perak, Malaysia and green algae from Sabah to remove heavy metals. This biosorbent is subjected to FTIR and ICP-MS. 'M-Bios' contain N – H (3421.89 cm$^{-1}$, 3465.90 cm$^{-1}$), C = O (1728.72 cm$^{-1}$) and – OH (3531.37 cm$^{-1}$, 3722.01 cm$^{-1}$, 3768.36 cm$^{-1}$) functional groups (weak groups) that that easily replaced by metal ions. The adsorption performances were fitted by pseudo-kinetic, Langmuir and Freundlich study. The plots obey both adsorption isotherm models, Langmuir and Freundlich by R$^2$ values. A good agreement between experimental and theoretical qe for contact time data suggested that adsorption reaction happen in aqueous solution was a rate determination of chemisorption process(pseudo second-order kinetic). In order to prevent precipitation as they forming hydroxide, pH 4 and 5 were used. Surface morphology shows the pore and folded surface which enhance the percent of adsorptions

*Index Terms*- *Mangrove, Biosorbent, Biosorption, Algae, ICP-MS*

## I. INTRODUCTION

W ater is a vital resource used to sustain changes in biodiversity and life on earth. However, some of the surface of water such as rivers is the usual place for the discharging of domestic wastes and also surface runoff of agricultural activities (Kuo Bau, 2010). Hence, the river might contain pollutants such as heavy metals, phosphates, nitrates and phenols and this problem have an adverse effect to human health, nation economy, marine life and environment in Malaysia (Salwa, 2008). Therefore, the study on biosorption was gaining intention due to the high potential and an innovative technology on the removal of heavy metal from water system.

Biosorption can be defined as the passive uptake of toxicants by inexpensive dead/inactive biological materials and the mechanisms of the pollutant uptake were differ according to the biomass type (Gupta et al., 2000; Farooq et al., 2010). In this study, an innovative idea of biosorbent namely 'M-bios' was produced, in the line with the 'go-green' concept to overcome the problem on water pollution especially heavy metals. 'M-bios' was produced from combination of mangrove and algae was then cross linked with chitosan.

The objectives of the present study are to study on the initial concentration, pH and contact time. Therefore, 'M-Bios' was exposed in laboratory scale in order to investigate the performance effects based on isotherms and kinetics studies.

## II. MATERIALS AND METHODS

### 1.1. Mangrove and brown algae.

Mangroves bark used in this study were collected from the charcoal factory as the waste product at Kuala Sepetang, Perak, Malaysia. Meanwhile, *P. Gymnaspora* was ordered from Sabah. These samples were washed with distilled water for several times before undergoes NaOH and NaCl treatment. These samples were incubated with NaOH at room temperature for 4 hours. After that, the treatment was proceeding with NaCl treatment for another 4hours before washed several times until the remaining colour gone. The samples were left to dry overnight.

### 1.2. Preparation of cross linked hybrid of mangrove-brown algae with chitosan biosorbent.

The ratio used for hybrid is 7 to 1 of mangrove bark to brown algae. 0.7 grams of mangrove bark and 0.3 grams of algae were weighed and both were mix together. The used of 7:1 ratio mangrove bark to brown algae based on our preliminary study which is the maximum uptake of metal ions. 1% v/v of acetic acid was prepared to prepare 1% w/v chitosan viscous solution. The solution was heated for about half an hour (Laus et al., 2010). 8ml of viscous chitosan was mixed together with the hybrid samples. The mixture was then stirred for 20 minutes. After that, the mixture was placed in oven at 60°C for overnight to dry.

### 1.3. Heavy metals quantifications.

Pb and Cu elements were chosen as they are usually found in industrial waste. The biosorption of these elements were conducted in batch equilibrium studies with control variable of mass of 'M-Bios', 1 gram and volume used was 10 ml. For study on initial concentration, standard solutions of 1, 5, 10, 30, 50 and 100 ppb were prepared. Immersed 'M-Bios' was incubated for one hour in each of standards solution prepared. For contact time study, time was varied to 15 minutes, 30 minutes, 45 minutes, 60 minutes, 2 hours, and 3 hours. Study of pH was done by varied the pH of 2, 3, 4, 5 and 6. These studies were agitated by using orbital shaker with speed of 150 rpm. The equilibrium adsorption, qe (µg/g) for these studies was calculated by using formula below:

$$q_e = \frac{c_i - c_f}{m} \times V$$
(i)

Where $c_i$ and $c_f$ are representing initial and final concentration of aqueous solution (μg/L), respectively, V is the volume of solution used (ml) and m is mass of biosorbent used (g) (Tirtom et al., 2012; Boddu et al., 2008).

### 1.4. Quality control.

All studies were carried out by triplicate as control. Control flask also prepared by immersed biosorbent into Mili Q-plus and was incubated on the same condition mentioned before. Fresh standard solutions were prepared for each time before using ICP-MS.

### 1.5. Fourier transform-infrared spectroscopy (FTIR)

FTIR spectrum of hybrid mangrove-algae and cross-linked hybrid were recorded with PerkinElmer 2000 FTIR Spectrometer. Samples were run by using Ge plate; therefore, samples must be in powder form. The scanning wavenumber of infrared was at 4000cm$^{-1}$ – 400cm$^{-1}$ range.

### III.  RESULT AND DISCUSSION

### 1.6. FTIR analysis

Figure 1 shows the IR spectra hybrid mangrove-algae and cross linked chitosan-hybrid. Hybrid mangrove-algae showed the broad band at 3421.89 cm-1 and 3465.90 cm-1 which correspond to the N – H stretch vibration. N – H bending vibration also showed at 1555.40 cm-1. These peaks indicate the presence of amine group in the compound. Peak at 1728.72 cm-1 assigned by the presence of C = O stretch vibration. These N – H and C = O bonds providing site for heavy metals to attached on the biosorbent in order to remove them from aqueous solution.

Besides that, – OH groups seemed at region 2500-3500 cm-1 indicates – OH stretch and O- H bending vibration also show peaks at 3531.37 cm-1, 3722.01 cm-1 and 3768.36 cm-1 in the spectrum. These functional groups influent the adsorption of metals on biosorbent as they are weak groups which easy to be replaced by stronger group such as metal ions. Other than the presence of O – H, N – H, and C = O bonds, there are a few more vibration stretch such as C = N, C – O and C – Cl which increased the adsorption ability. C =N, C – O and C – Cl stretch vibration are located at 2271.60 cm-1, 1728.72 cm-1 and 688.43 cm-1, respectively. Cross linked chitosan hybrid was encouraged more – OH and – NH groups on the surface of biosorbent. Therefore, the adsorption of metal ions increased as increase the number of active sites. Table 1 shows the frequencies and attribution of hybrid and cross linked biosorbent.
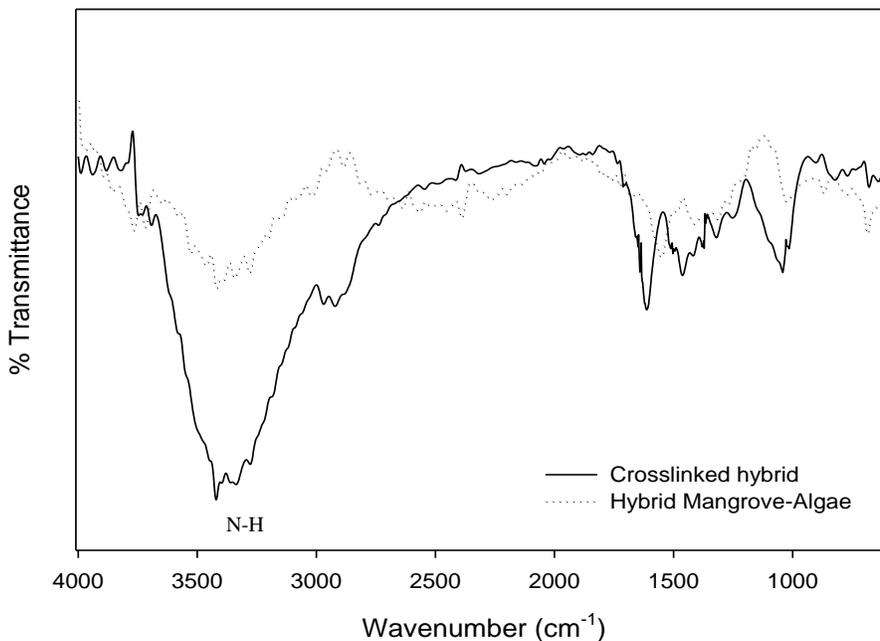


**Figure 1 Spectrum of hybrid mangrove-algae and cross linked chitosan-hybrid**

**Table 1 Frequencies and attribution of hybrid and cross linked biosorbent.**

| Frequencies (cm$^{-1}$) | Attribution |
|---|---|
| 3421.89 and 3465.90 | - NH stretch |
| 1555.40 | N-H bending |
| 1728.72 | C=O stretch |
| 3531.37, 3722.01 and 3768.36 | O- H bending |
| 2271.60 | C=N stretch |

| 1728.72 | C-O stretch |
|---------|-------------|
| 688.43  | C-Cl stretch |

### 1.7. The Effect of Initial Concentration

Figure 2 shows the effect of initial concentration of Pb(II) and Cu(II) biosorption onto 'M-Bios'. The effects show the increases of equilibrium adsorption for both Pb(II) and Cu(II) as the concentration was increased. The same result of adsorption increased was shown in previous study (Zhang et al., 2007; Vinod et al., 2009; Hameed et al., 2008). The increases of equilibrium adsorption for Pb(II) and Cu(II) from 1 ppb to 100 ppb as the initial concentration increase was due to the occurrence of driving force (Hameed et al., 2008). Driving force

is defined by the difference concentration between the biosorbent and the sorbet in the aqueous solution. This driving force was higher in 100 ppb aqueous solution compared to 1 ppb thus; this condition would lower the mass resistance between biosorbent and sorbet and help the adsorption process (Vijayaraghavan & Yun, 2008; Vilar et al., 2006).

Therefore, as the initial concentration is increases, the equilibrium adsorption is increases as well, as the driving force higher and lower the mass transferred between biosorbent and sorbet in the aqueous solution.
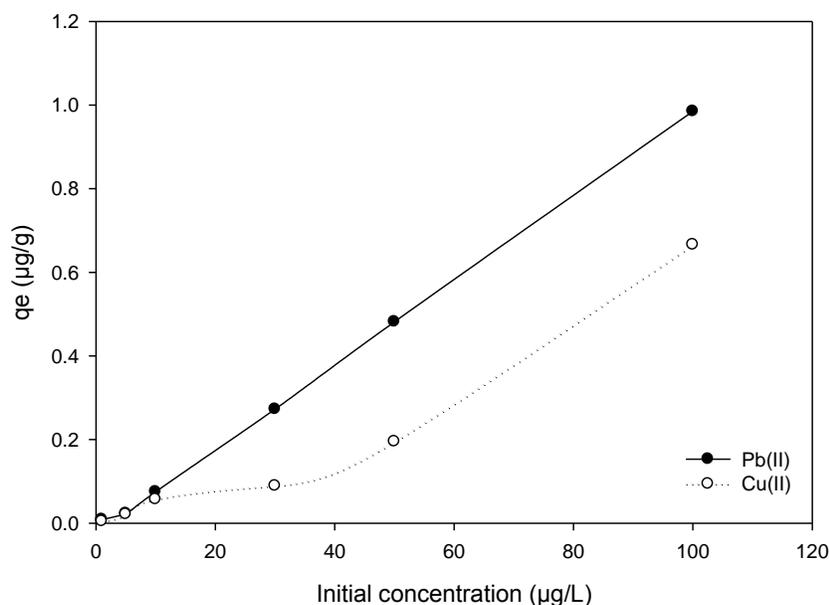


**Figure 2 Effect of initial concentration of Pb(II) and Cu(II) biosorption onto 'M-Bios'**

### 1.8. Effect of Contact Time

The effect of contact time of Pb(II) and Cu(II) biosorption onto 'M-Bios' was shown in Figure 3. The contact time was varied from 15 to 240 minutes and the equilibrium adsorptions were observed. The equilibrium adsorption was increases and the increases of contact time for both metal ions. The rapid adsorption start at the first 15 minutes and gradually reached equilibrium at 45 and 60 minutes for Pb(II) and Cu(II), respectively. The same results were shown by previous studies

(Jaikumar, 2009; W. Ngah & Hanafiah, 2008). This happen because between the biosorbent and sorbet in aqueous solution, there are strong attractive forces which make the diffusion faster in the surface of the biosorbent to obtained the equilibrium (Jaikumar, 2009). Thus, the adsorptions of Pb(II) and Cu(II) were depend on the time contact varied. As the contact increases, the adsorption might as well increases.
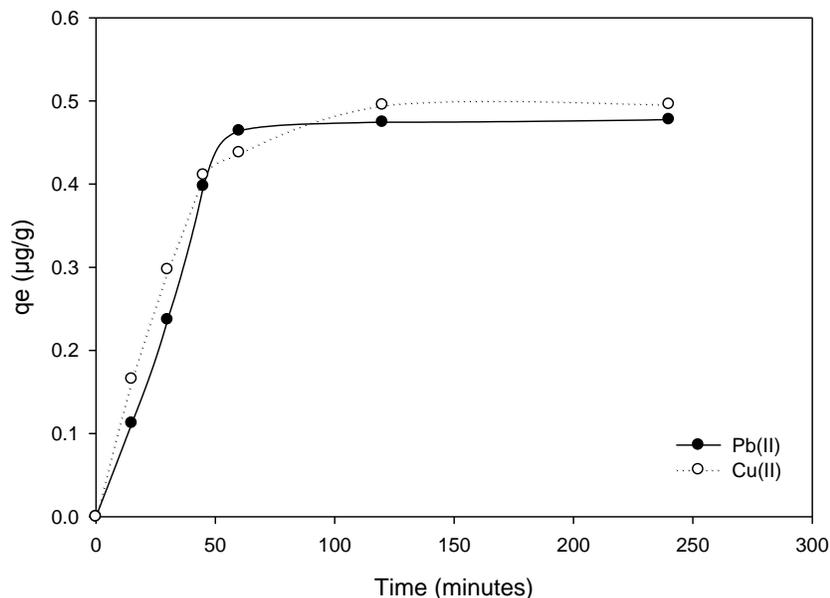
**Figure 3 Effect of contact time of Pb(II) and Cu(II) biosorption onto 'M-Bios'**

### 1.9. Effect of pH

pH is one of the most important parameter in biosorption study as it is charge the sites of biosorbent functional group and might as well influence the speciation of metal ions (Farooq et al., 2010 ). The effect of pH of Pb(II) and Cu(II) biosorption onto 'M-Bios' show in Figure 4. Optimum pH values obtained for Pb(II) and Cu(II) ions adsorption are at pH 4 and 5, respectively. This is due to the decreases of hydrogen ions in low pH, so less competitive with Cu(II) and Pb(II) ions to be adsorbed onto 'M-Bios'. Therefore, the negatively charged surface of biosorbent would attract more cations as electrostatic interaction occurs (Ooa et al., 2009).

However, as the pH values increase, the adsorption on 'M-Bios' decreased. This is happen because the increases of pH causing the coagulation between the metals ions and the aqueous solution, therefore, fewer ions would be attached onto the surface of biosorbent. Other than that, it is because the occurrence of electrical repulsion between biosorption and metal ions as they have the same charge (Jaikumar, 2009). The effect of pH of Pb(II) and Cu(II) biosorption onto 'M-Bios' is shows in Figure 4. Therefore, in order to have the optimum adsorption of metal ions, pH 4 and 5 were used to prevent precipitation as they forming hydroxide (Ooa et al., 2009).
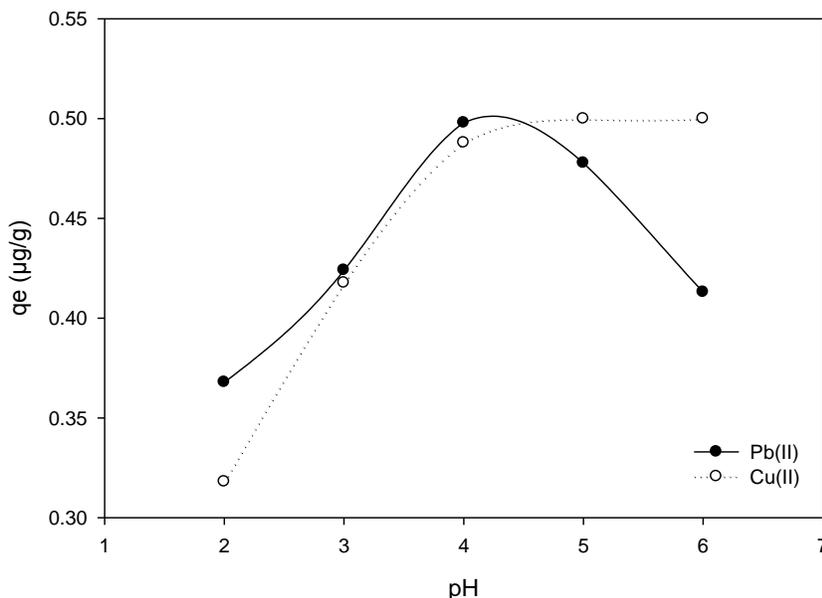


**Figure 4 Effect of pH of Pb(II) and Cu(II) biosorption onto 'M-Bios'**

### 1.10. Two parameter adsorption isotherms

These batch equilibrium data obtained for adsorption of Pb(II) and Cu(II) on 'M-Bios' with different initial concentrations were used to explain the adsorption phenomenon. There are two types of isotherm studies that we concern in this research; Langmuir and Freundlich isotherm.

Langmuir is defined by (Ooa et al., 2009), as adsorption by monolayer and he assumes that the adsorption sites are energetically equivalent and the adsorption happen on a homogeneous adsorbent, which mean no interaction between sorbed species. Langmuir isotherm is written on mathematical form as in equation (ii) below:

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q} \quad \text{(ii)}$$

Straight line graphs with a slope of 1/Q were obtained by plotting graph of $C_e/q_e$ against $C_e$ (µg/L). $C_e$ is an equilibrium concentration of metal (µg/L) and qe is the amount of metal adsorbed per gram of biosorbent.

Freundlich isotherm describing the reversible adsorption and not only for single layer adsorption but it is describing the heterogeneous system (Tirtom, 2012). Freundlich assumes the surface supporting sites will be varied by the affinities of the metals itself. Freundlich isotherm is written on mathematical form as in equation (iii) below (Ooa et al., 2009):

$$\log q_e = \log K_F + (1/n) \log C_e \quad \text{(iii)}$$

1/n is the slope of the straight line by plotting log $q_e$ against log $C_e$ and log $K_F$ is the y-intercept. Langmuir and Freundlich plots for elements Pb(II) and Cu(II) are shown in Figure 5.

Based on the data obtained Figure 5, Langmuir and Freundlich plots for Pb(II) and Ni(II) adsorption onto 'M-Bios', Langmuir and Freundlich models in this research were found to be successfully described in term of linearity of coefficient, $R^2$ (Hamideh et al., 2011) which $R^2$ result for all plots are equally to value 1. From the linearized Langmuir and Freundlich isotherm adsorption plots, table 2 shows the Langmuir and Freundlich isotherm correlation coefficient for element of Pb(II) and Cu(II). Langmuir isotherm model predict the formation of single layer on the surface of biosorbent, which mean Langmuir is obeyed by the character of strong sorption onto specific active site (Iqbal & Saeed, 2007).

According to the Freundlich data obtained, $R^2$ for Pb(II) and Cu(II) represent a better experimental adjustment to the heterogeneous material biosorbent active sites and adsorption mechanism (Copelloa et al., 2013).
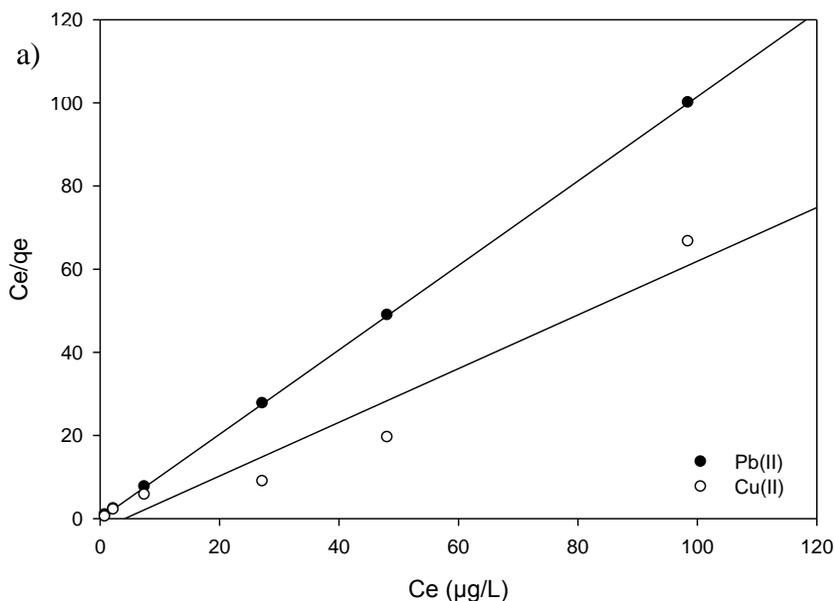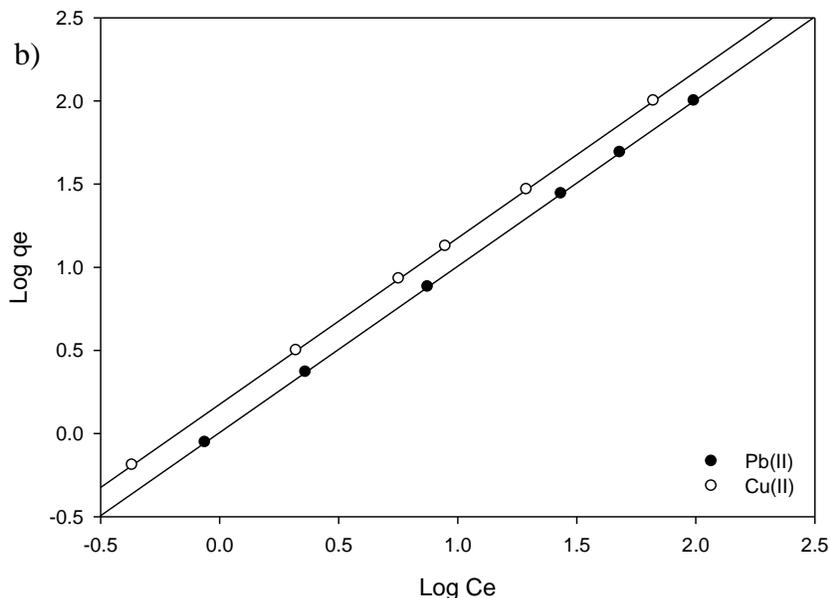
**Figure 5 (a) Langmuir and (b) Freundlich isotherm of Pb(II) and Cu(II)**

**Table 2 Langmuir and Freundlich isotherm correlation coefficient for biosorption of Pb(II) and Ni(II).**

| Elements | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| | $1/Q$ | $b$ | $R^2$ | $1/n$ | $Log\ K_F$ | $R^2$ |
| Pb(II) | 1.0152 | 0 | 1 | 1 | 0.0066 | 1 |
| Cu(II) | 1.5015 | 0 | 1 | 1 | 0.1765 | 1 |

### 1.11. Adsorption Kinetics

Data from contact time studies then was used to analyse the adsorption kinetic models, pseudo first-order and pseudo second-order. The mechanism of the process can be obtained by kinetic constants by calculating using linearized plot of both models. These two models were analysed in linear form after been rearranged from the equations (Ooa et al., 2009). Pseudo first-order is used for reversible reaction with an equilibrium established between biosorbent and sorbet in aqueous solution (Ooa et al., 2009). Pseudo first-order equation is given as (iv);

$$\frac{d_q}{d_t} = K_1(q_e - q_t) \tag{iv}$$

Equation (iv) is integrated for boundary condition: t=0-t and q=0-qe to have (v);

$$\log(q_e - q_t) = log q_e - \frac{K_1 t}{2.303} \tag{v}$$

Where $q_t$ is the concentration metal ions absorbed at time, t ($\mu g/g$) and $K_1$ is the first-order constant (1/min).

Pseudo second-order is based on assumption that the rate limiting factor maybe chemisorption (Ooa et al., 2009; Hamideh et al., 2011). In chemical adsorption (chemisorption), by forming the covalent bond, metal ions stick to the biosorbent surface and have tendency to bind with the sites that minimizes their coordination number with the surface (Hamideh et al., 2011). Pseudo second-order equation is given as below (vi);

$$\frac{d_q}{d_t} = K_2(q_e - q)^2 \tag{vi}$$

Equation (vi) is integrated and rearranged for the same boundary condition to have (vii);

$$q_t = \frac{1}{q_e} t + \frac{1}{K_2 q_e^2} \tag{vii}$$

Where $q_t$ is the concentration of metal ions absorbed at equilibrium and time is t, while $K_2$ is the second-order kinetic constant, ($g/\mu g.min$).

In the adsorption of Pb(II) and Cu(II) on 'M-Bios', pseudo second-order kinetic model gave the higher correlation coefficient values of 0.9557 and 0.9898 for Pb(II) and Cu(II), respectively than pseudo first-order. This data also obtained by previous study (Ooa et al., 2009). A good adjustment to pseudo second-order for both metals ions indicate that chemisorption is the rate limiting step in adsorption process. This fact can be supported by comparing the experimental $q_e$ with theoretical $q_e$ of second-order model. Theoretical $q_e$ of second-order model should be accordance with experimental $q_e$. From the data obtained, theoretical $q_e$ had good agreement in the experimental

$q_e$, which suggested that adsorption reaction happen between biosorbent and sorbet in aqueous solution was a rate determination of chemisorption process. Table 3 show the pseudo first and second-order kinetic model correlation coefficient for biosorption of Pb(II) and Ni(II) (Ooa et al., 2009; Copelloa et al., 2013).

**Table 3 Pseudo first and second-order kinetic model correlation coefficient for biosorption of Pb(II) and Ni(II).**

| Kinetic models | | | Pb(II) | CuII |
|---|---|---|---|---|
| | $q_e$ (exp.) | | 0.4775 | 0.4959 |
| Pseudo-first order | $K_1$ | | 0.0461 | 0.0461 |
| | $q_e$ (theo.) | | 0.7847 | 0.9160 |
| | $R^2$ | | 0.9315 | 0.9677 |
| Pseudo-second order | $K_1$ | | 0.0530 | 0.0794 |
| | $q_e$ (theo.) | | 0.5647 | 0.5549 |
| | $R^2$ | | 0.9557 | 0.9898 |

## IV. CONCLUSION

In conclusion, amine, hydroxyl and carboxyl help in adsorption of Pb(II) and Cu(II) from aqueous solutions and driving force that lowers the mass transferred between biosorbent and sorbet in the aqueous solution. In initial concentration study, the linearized plots obey both adsorption isotherm models, Langmuir and Freundlich by $R^2$ values were 1. The adsorptions depend on the time contact varied, as the contact increases, the adsorption increase. A good agreement between experimental and theoretical $q_e$ suggested that adsorption reaction happen was a rate determination of chemisorption process (obey pseudo second-order kinetic model). In order to prevent precipitation pH 4 and 5 were used. Surface morphology of 'M-bios' shows the pore and folded surface which enhance the percent of adsorptions. 'M-Bios' is an interesting commercial product as its low cost of preparation and largely abundance in Malaysia.

## REFERENCES

[1] Boddu, V.M., Abburi, K., Talbott, J.L., Smith, E.D., Haasch, R., 2008. Removal of arsenic(III) and arsenic(v) from aqueous medium using chitosan-coated biosorbent. Water Research. 42. 633–642

[2] Copelloa, G.J., Pesentia, M.P., Relinea, M., Meberta, A.M., Pietile, L.L., Rubil de Celis, E., Diaza, C.E. 2013. Polyphenol-SiO2 hybrid biosorbent for heavy metal removal. Yerba mate waste (Ilex paraguariensis) as polyphenol source: Kinetics and isotherm studies. Colloids and Surfaces B: Biointerfaces. 102. 218-226

[3] Farooq, U., Kozinski J.A., Khan, M.A., Athar, M., 2010. Biosorption of heavy metal ions using wheat based biosorbents - A review of the recent literature. Bioresource Technology. 101. 5043–5053

[4] Gupta, R., Ahuja, P., Khan, S., Saxena, R.K., Mohapatra, H., 2000. Microbial biosorbents: Meeting Challenges of heavy metal pollution in aqueous solutions. . Current science. 78. 967-973.

[5] Hameed, B.H., D.K. Mahmoud, and A.L. Ahmad, 2008. Equilibrium modelling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (Cocos nucifera) bunch waste. Journal of Hazardous Materials. 158. 65–72.

[6] Hamideh, R., A.G. Ali, and Y. Habibollah, 2011. Isotherm and Kinetic of Fe(II) adsorption onto chitosan in batch process. Iranica Journal of Energy & Enviroment. 2. 250-257

[7] Iqbal, M. and A. Saeed, 2007. Production of an immobilized hybrid biosorbent for the sorption of Ni(II) from aqueous solution. Process Biochmistry. 42. 148–157.

[8] Jaikumar, V., 2009. Effect of Biosorption Parameters Kinetics Isotherm and Thermodynamics for Acid Green Dye Biosorption from Aqueous Solution by Brewery Waste. International Journal of Chemistry. 1. 1-12

[9] Kuo Bau, J.L., 2010. Water quality study and its relationship with high tide and low tide at Kuantan river. Faculty of Civil Engineering and Earth Resources. Universiti Malaysia Pahang.

[10] Laus, R., Costa, T.G., Szpoganics, B., Favere, V.T., 2010. Adsorption and desorption of Cu(II), Cd(II) and Pb(II) ions using chitosan crosslinked with epichlorohydrin-triphosphate as the adsorbent. Journal of Hazardous Materials. 183. 233–241

[11] Ooa, C.W., M.J. Kassima, and A. Pizzi, 2009. Characterization and performance of Rhizophora apiculata mangrove polyflavonoid tannins in the adsorption of copper (II) and lead (II). Industrial Crops and Products. 30. 152–161

[12] Salwa, I., 2008. Water quality data observation and management for Sungai Johor. Faculty of Civil Engineering. University of Technology Malaysia.

[13] Tirtom, V.N., Dincer, A., Becerik, S., Aydemir, T., Ali, C., 2012. Comparative adsorption of Ni(II) and Cd(II) ions on epichlorohydrin crosslinked chitosan-clay composite beads in aqueous solution. Chemical Engineering Journal. 197. 379–386

[14] Vijayaraghavan, K. and Y.-S. Yun, 2008. Polysulfone-immobilized Corynebacterium glutamicum: A biosorbent for Reactive black 5 from aqueous solution in an up-flow packed column. Chemical Engineering Journal. 145. 44-49.

[15] Vilar, V.ɪ.J.P., C.a.M.S. Botelho, and R.A.R. Boaventura, 2008. Methylene blue adsorption by algal biomass based materials: Biosorbents characterization and process behaviour. Journal Hazard Materials. 147. 120-132

[16] Vinod, V.T.P., Sashidhar, R.B., Sredhar, B., Rama Rao, B., Nageswara Rao, T., Abraham, J.T., 2009. Interaction of Pb2+ and Cd2+ with gum kondagogu (Cochlospermum gossypium): A natural carbohydrate polymer with biosorbent properties. Carbohydrate Polymers. 78. 894–901

[17] Wan Ngah, W.S. and M.A.K.M. Hanafiah, 2008. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. Bioresource Technology. 99. 3935–3948

[18] Zhang, Y.-j., J.-r. Chena, and X.-y. Yan, 2007. Equilibrium and kinetics studies on adsorption of Zn(II) from aqueous solutions onto a graft copolymer of cross-linked starch/acrylonitrile (CLSAGCP). Colloids and Surfaces A: Physicochem. Engineering. 316. 190–193

## AUTHORS

**First Author** – Mohd Lias Kamal, Ocean Research Conservation and Advance (ORCA), Universiti Teknologi MARA, Perlis, Malaysia., Email: mohdlias@perlis.uitm.edu.my

**Second Author** – Jamil Tajam, Ocean Research Conservation and Advance (ORCA), Universiti Teknologi MARA, Perlis, Malaysia.

**Third Author** – Sharizal Hasan, Faculty of Applied Chemistry, Universiti Teknologi MARA, Perlis, Malaysia

**Fourth Author** – Mohd Halim Shah Ismail, Department of Chemical and Environmental Engineering, Universiti Putra Malaysia, Malaysia.

**Fifth Author** – Anies Suhaida Mohd Naspu, Faculty of Applied
Chemistry, Universiti Teknologi MARA, Perlis, Malaysia
**Sixth Author** – Nur Saliza Awatif Zahala, Faculty of Applied
Chemistry, Universiti Teknologi MARA, Perlis, Malaysia