

Removal of Mercury, Lead and Copper from Aqueous Solution by Activated Carbon of Palm Oil Empty Fruit Bunch

Rafeah Wahi, Zainab Ngaini and Veronica Usun Jok

Department of Chemistry, Faculty of Resource Science and Technology,
Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia

Abstract: The ability of activated carbon prepared from palm oil empty fruit bunches (EFB) to remove mercury (Hg(II)), lead (Pb(II)) and copper (Cu(II)) from aqueous solutions was investigated. The EFB activated carbon was produced by using chemical and physical activation processes. The adsorption capacity was determined as a function of adsorbate initial concentration and adsorbent dosages. Adsorption isotherms of the studied metals on adsorbent were determined and compared with the Langmuir and Freundlich isotherm models. The EFB activated carbon showed excellent efficiency in removing Pb(II) and Hg(II) with percentage of removal up to 100% even at low adsorbent dosage. In contrast, only 25% removal of Cu(II) by the EFB activated carbon was observed. The study also showed that the adsorption of Hg(II), Pb(II) and Cu(II) by EFB activated carbon is dependent on the dosage of adsorbent and the initial metals concentration. The use of EFB as activated carbon is not only effective for Hg(II) and Pb(II) removal from wastewater but also helps in solving the problem of over-abundance of EFB as agricultural waste product.

Key words: Empty fruit bunch • Activated carbon • Adsorption • Heavy metals • Langmuir isotherm • Freundlich isotherm

INTRODUCTION

The increase in industrial activities has caused many water bodies receiving loads of heavy metals that exceed the maximum permissible limit for wastewater discharge designed to protect the environment, human and animals [1]. Pollution by heavy metal ions, including mercury (Hg(II)), lead (Pb(II)) and Copper (Cu(II)), has become a major issue throughout many countries due to their possible toxic effects [2]. The risks of Hg(II) exposure, for instance, may contribute to adverse effects on central nervous system, pulmonary kidney functions and the chromosomes [3], while Pb(II) can bioaccumulate through the food chain [4]. Prolonged inhalation of Cu(II) spray is claimed to cause an increase in the risk of lung cancer [2]. Based on Malaysian Environmental Quality Act 1974, maximum permissible limits for Hg(II), Pb(II) and Cu(II) in drinking water are 0.005 mg/L, 0.10 mg/L and 0.20 mg/L, respectively.

Hg(II), Pb(II) and Cu(II) are released into the aqueous environment through variety of sources such as metal smelters, effluents from plastics, textiles, microelectronics

and wood preservatives producing industries and usage of fertilizer and pesticides [5]. These metals cannot be degraded or destroyed, but can be removed from water bodies. Conventional methods for the removing of heavy metals include filtration, chemical precipitation and ion exchange, electrochemical deposition and membrane process. However, these methods are either inefficient or expensive especially when the concentration of the heavy metal ion is low, in the range of 1-100 mg/L [5].

Activated carbon is an efficient and versatile adsorbent for purification of water, air and many chemical and natural products [6]. However, the usage of activated carbon is limited by its high preparation cost [3]. Previous studies on the use of various agricultural wastes such as hulls of rice and wheat [3, 4], groundnut shells [6], palm oil shells [7] and physic nut wastes [8] as raw material for activated carbon shows that the preparation cost of activated carbon can be reduced if these waste is used.

Oil palm production is a major agricultural industry in Malaysia. Empty fruit bunches (EFB) are the solid residue left after the fruit bunches are pressed at oil mills and the oil extracted. Due to its high cellulosic fiber content and

also its abundance as a type of agricultural wastes in Malaysia [7,9], EFB was chosen for the preparation of activated carbon materials. In this study, EFB was subjected to carbonization at high temperature followed by chemical activation by using NaOH prior to soaking in HCl. The efficiency of adsorbent prepared from EFB in removing heavy metals such as Hg(II), Pb(II) and Cu(II) in aqueous solution was examined.

MATERIALS AND METHODS

Preparation of Adsorbent: Palm oil EFB were used as precursor for the preparation of the activated carbon and were taken from Mongkos Palm Oil Mill, Serian, Sarawak. EFB was air-dried for 48 h prior to washing by distilled water to remove particulate material from its surface. The EFB was dried at 60°C for 72 h before cooled to room temperature and grinded into sizes range of 0.5-1.0 mm. The dry EFB was carbonized at 400°C for 30 min in a tube and soaked in 20% NaOH at 60°C for 2 h. The treated EFB was dried at 105°C for 24 h followed by second carbonization at 700°C for 1 h. The activated product was treated with 5 M HCl for the removal of impregnating salt followed by successive washing with distilled water until the pH of activated product was 4.5. The EFB activated carbon was finally dried at 105°C overnight before cooled to room temperature.

Proximate and ultimate analysis of the EFB sample and activated carbon was conducted as described in Table 1. The surface morphology of the activated carbon was analyzed by scanning electron microscope (SEM). Perkin Elmer FTIR spectrometer was used to analyze the functional groups presence in EFB, EFB activated carbon and commercial activated carbon. The apparent density of activated carbon was determined by a tapping procedure using a 5 ml graduated glass cylinder [6]. Surface area of the adsorbent was determined by the methods described by Rao *et al.* [10]. The chemical and physical characteristics of the adsorbent were presented in Table 1 and 2.

Preparation of Stock Solution: The Hg(II) stock solution was prepared by dissolving 1 g of Hg(II) metal in 20 ml of 5 M nitric acid prior to dilution with deionised water to 1 L volume. Pb(II) stock solution was prepared by dissolving 1 g of Pb(II) metal in 50 ml of 2 M nitric acid prior to dilution with deionised water to 1 L volume. Cu(II) stock solution was prepared by dissolving 1 g of Cu(II) metal in 50 ml of 5 M nitric acid before diluted to 1 L

volume with deionised water. The heavy metal content in all the three stock solutions were analyzed by using inductively coupled plasma mass-spectroscopy (ICP-MS).

Adsorption Study: Effect of Adsorbent Dosage. Different dosages of adsorbent were added to working standards. The amount of adsorbent used was 0.2, 0.4, 0.6, 0.8 and 1.0 g. All these adsorbents, at pH 4.5, were added to 100 ml heavy metals solution of 10 mg/L concentration in a 250 ml conical at temperature range of 29 to 31°C. These samples were placed on a rotary shaker at 150 rpm. The samples were withdrawn from the shaker after 24 h agitating. The solution was separated by gravity filtration. The concentration of the residual heavy metal solution was determined by using ICP-MS. A control was prepared for every adsorption batch.

Adsorption Study: Effect of Adsorbate Initial Concentration. Metal solutions with concentration of 5, 10, 15 and 20 mg/L were prepared. 1.0 g of adsorbent at pH 4.5 was added to the solutions in a 250 ml conical flask. This was followed by agitating the solution on a rotary shaker with the speed of 150 rpm. After 24 h, the samples were withdrawn and filtered. Concentration of residual heavy metal solution was determined by using ICP-MS.

Adsorption Isotherm Models: In order to estimate the adsorption capacity, Q_m of the EFB activated carbon on the adsorption of Hg(II), Pb(II) and Cu(II), two isotherms have been tested namely the Langmuir and Freundlich isotherm. The relative coefficients of these models were calculated using linear least-squares fitting.

The Langmuir isotherm [3] can be written in linear form as:

$$C_e / q_e = C_e / Q_m + 1 / Q_m b \quad (1)$$

Where, q_e and C_e are the metal equilibrium concentration in adsorbed and liquid phase in mmol/g and mmol/L, respectively. Q_m and b are Langmuir constants representing the sorption capacity (in mg/g) and energy of sorption, respectively. These constants can be calculated from the intercept and slope of the linear plot, C_e / q_e vs C_e .

The Freundlich isotherm [3] equation can be written in the linear form as:

$$\log q_e = \log k_f + 1/n \log C_e \quad (2)$$

Where, k_f and n are indicators of sorption capacity (in mg/g) and intensity respectively. These Freundlich constants can be calculated from the slope and intercept of the linear plot, with $\log q_e$ vs $\log C_e$.

RESULTS AND DISCUSSION

Characteristics of Adsorbent: Based on results in Table 1, the carbon content in the EFB activated carbon was significantly higher compared to the raw material due to high carbonization temperature. On the other hand, the hydrogen and nitrogen contents are lower than the raw material. A slight decrease in the nitrogen content can be explained by lose of amides and amines group which were decomposed at temperature above 400°C [11]. The decrease in hydrogen content was caused by its removal in the form of water during carbonization process.

The volatile matter, moisture and ash content of adsorbent were observed to be less than in the raw material. The decrease in volatile matter was due to its removal during carbonization process. Increase in carbonization temperature promoted the release of volatile matter from breaking of weaker bridges and bonds in organic matrices as well as enhancing the condensation and collapsing reactions of organic matters in the sample to become char with predominantly fixed carbon [11]. Further removal of volatile matter also occurred during chemical activation of EFB by NaOH. The low volatile matter content implied the high porosity of the adsorbent since less volatile matter remained clogging in the pores. The decrease in moisture content was due to repeated heating process which enhanced the removal of moisture.

Surface area is the most important property of activated carbon adsorbents for its adsorption capacity. Generally, the higher the surface area, the larger is its adsorptive capacity [7,12]. In this study, EFB was grinded to the size of 0.5-1.0 mm in order to increase the total surface area and provide more sorption sites for the metal ions [5]. The EFB activated carbon has slightly lower surface area compared to commercially available activated carbon. Nevertheless, the EFB activated carbon is able to give high adsorption capacity up to 52.67 mg/g for adsorption of Hg(II). The apparent density of EFB activated carbon is lower compare to commercial activated carbon. Higher density of commercial activated carbon gives greater volume capacity and this indicated that it has better quality compared with the EFB activated carbon. The different in density however, was mainly due to the difference in nature of starting material used to produce the activated carbon and also because both

Table 1: Chemical properties of the raw material (EFB), EFB activated carbon (EFB a.c.) and commercial activated carbon (commercial a.c.)

Chemical characteristics	EFB	EFB a.c.	Commercial a.c.
^a Moisture content (%)	18.50	6.30	4.10
^b Volatile matter content (%)	23.70	8.10	6.50
^c Ash content (%)	20.20	5.50	1.80
^d Fixed carbon (%)	37.60	80.10	87.60
^e C content (%)	46.84	82.96	68.12
^e H content (%)	2.88	0.25	0.69
^e N content (%)	0.73	0.43	0.38

^asample was dried at 110°C for 24 h; ^bsample was heated to 900°C for 7 min; ^csample was ignited at 800°C for 2 h; ^dcalculated by difference from a, b and c; ^eby CHN Analyzer

Table 2: Physical properties of EFB activated carbon (EFB a.c.) and commercially available activated carbon (commercial a.c.)

Physical characteristics	EFB a.c.	Commercial a.c.
Surface area (m ² /g)	379.37	500.00
Apparent density (g/cm ³)	0.21	0.30

activated carbon undergo different preparation method [10].

The IR absorption spectra of the raw material, commercial activated carbon and the EFB activated carbon are shown in Fig. 1a, 1b and 1c. The IR spectra of the raw material and EFB activated carbon proved that the amides and amines group (at peak 1637 cm⁻¹) contained in the raw material disappear during the production of activated carbon. The IR spectra of the commercial activated carbon and the EFB activated carbon show similar absorption bands with the presence of -OH and C=O functional groups, which responsible for their adsorption characteristics [3]. In commercial and EFB activated carbon, the absorption peaks at 2359 and 2364 could be attributed to C=N stretching. The broad bands appeared at 1300-1000 cm⁻¹ for both adsorbents are due to C-O stretching in alcohols and phenols, indicating that the OH groups in both adsorbents [3]. Although both activated carbons showed a great difference in their surface area, the presence of similar chemical groups on their surfaces could result in almost similar adsorption behaviour [13].

Surface Morphology: The pore structure in both raw material and also activated carbon was observed by using Scanning Electron Microscope (SEM). Fig. 2a and 2b revealed changes in surface morphology of raw material as it underwent both physical and chemical carbonization. The activated carbon showed high porosity compared to

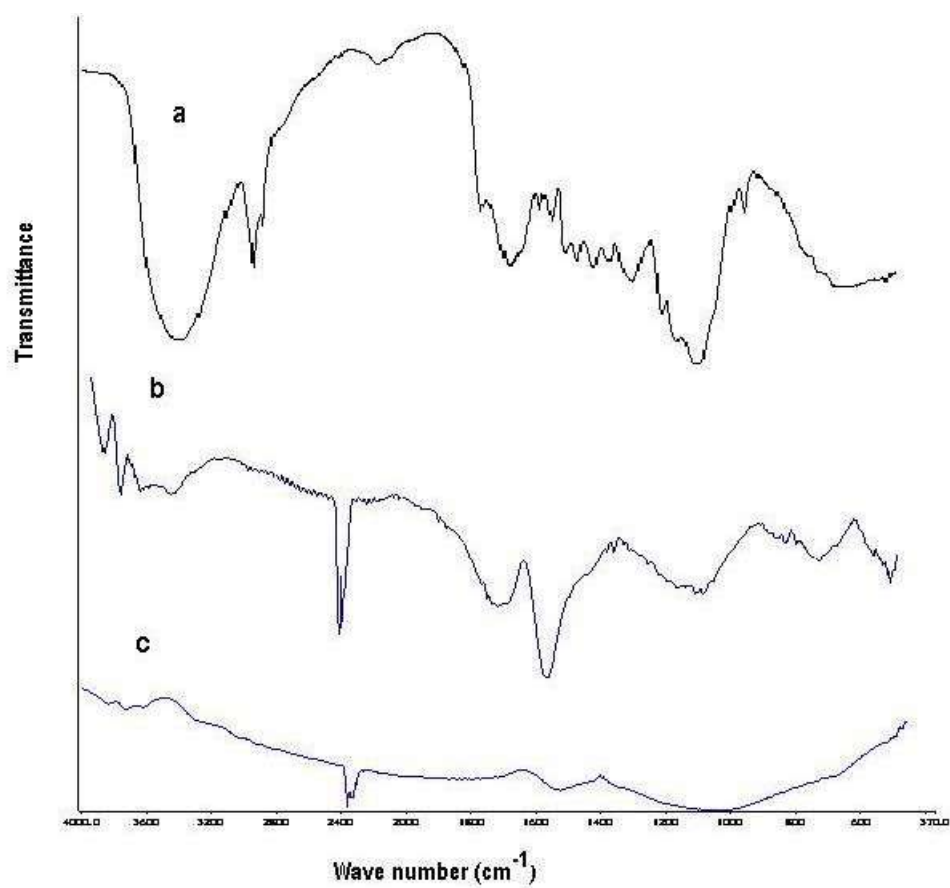


Fig. 1: FT-IR spectrum of the (a) empty fruit bunch (EFB); (b) commercially available activated carbon and (c) EFB activated carbon

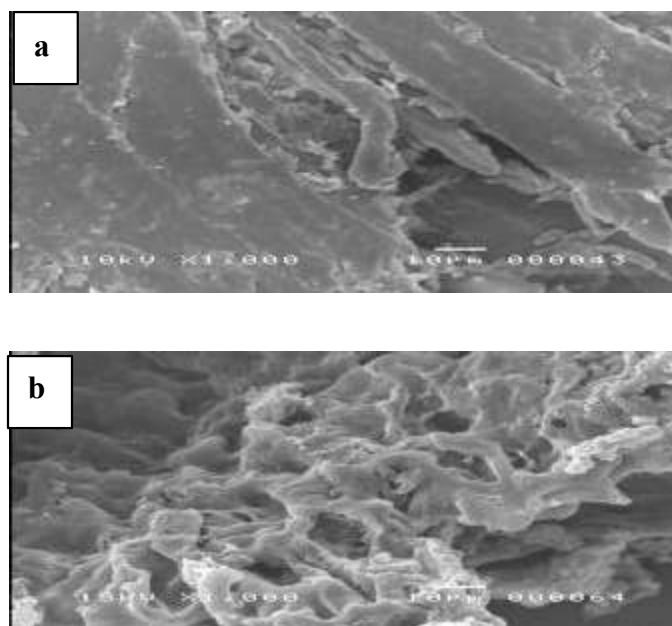


Fig. 2: Pore structures of (a) empty fruit bunch (EFB) and (b) EFB activated carbon

raw material. This was because during carbonization process of raw material at high temperature (700°C), most volatile matter was lost and thus created a system with advanced pore structure. Impregnation with NaOH followed by the second carbonization dehydrated the cellulose material, resulted in weakening of the precursor structure and creation of pores.

During chemical activation process, NaOH was responsible for decomposition of organic material to release volatile matter and development of micro-porous structure which could increase the adsorption capacity [6]. Besides, NaOH was also important in minimizing the formation of tars and other liquid which could clog up the pores and inhibit the development of pores [7]. The porosity created in the carbon structure was also resulted from NaOH removal from carbon structure by intense washing. Pores development in an activated carbon is important since pores act as active sites which played the main role in adsorption. Pores formed on surface of adsorbent are sites for metals to be adsorbed onto the adsorbent.

Effect of Adsorbent Dosage: The dosage of adsorbent was a key parameter to control both availability and accessibility of adsorption sites [14]. The effect of adsorbent dosage on the removal of Cu(II), Pb(II) and Hg(II) was presented in Fig. 3. The removal of metal from both Hg(II) and Pb(II) solutions has reached up to 100% even at lower dosage of adsorbent, which is 0.2 g, respectively. Higher dosage of adsorbent will increase the adsorption due to more surfaces and functional groups are available on adsorbent on which metals could interact with. These chemical groups were important in the formation of Van der Waals bonding as the functional groups played the main role in binding metals to the adsorbent during adsorption process [6]. This provided more possibilities for adsorption to occur since there was less competition between metals for the binding sites. The adsorption of Cu(II), however, shows contradicting result. Percentage of removal for 10 mg/L Cu(II) was observed to increase gradually from 1.7% to 4.7% with the increase of adsorbent dosage from 0.2 g to 1.0 g. Lower Cu(II) removal may be due to the fact that the adsorption of Cu(II) was limited to only monolayer adsorption. This is proved by calculation of correlation coefficient, R^2 value from Langmuir isotherm.

Effect of Adsorbate Initial Concentration: Studies were performed with Hg(II), Pb(II) and Cu(II) initial concentrations ranging from 5 to 20 mg/L. An amount of

Table 3: Constants for Langmuir adsorption isotherms for EFB activated carbon for Hg(II), Pb(II) and Cu(II) removal

	Q_m (mg/g)	b	R^2
Hg	52.67	0.026	0.901
Pb	48.96	0.027	0.843
Cu	0.84	0.904	0.869

1.0 g of adsorbent with pH 4.5 was used for each adsorption experiment. Fig. 4 shows that the removal of Cu(II) was depending on the initial concentration of metal ions which decrease with the increase of initial metal ions concentration. This is due to more adsorption sites are available on the adsorbent at low concentrations of the metal ions [11]. The percentage removal of Cu(II) subsequently remained constant at initial Cu(II) concentrations of 10 to 20 mg/L. This might be due to the fact that the adsorption sites become more saturated as the initial metal ions concentration are increased and the amount of adsorbent concentration remained constant [5]. The result also shows that the removal of Pb(II) and Hg(II) are independent of initial concentration of metal ions. Between 5 to 20 mg/L of metal solutions initial concentration, the removal of these metals has reached 100%.

Adsorption Behaviour of Different Metals: Result from this study shows that Hg(II) and Pb(II) can be highly adsorbed by the EFB activated carbon while the removal percentage of Cu(II) is very low. From the calculation based on Langmuir isotherm, Hg(II) shows the highest adsorption capacity of 52.67 mg/g, followed by Pb(II) and Cu(II) with adsorption capacity of 48.96 and 0.84 mg/g, respectively.

Adsorption Isotherms: The Langmuir and Freundlich isotherms was tested based on the adsorption studies for Hg(II), Pb(II) and Cu(II). The applicability of each isotherm was evaluated by the value of correlation coefficient, R^2 . Fig. 5, Fig. 6 and Table 3 summarizes the value of constants for Langmuir isotherm which were calculated from the best-fit lines. It can be concluded that the adsorption of Hg(II) and Pb(II) were best explained by Freundlich model as the value of correlation regression for both metals were 0.927 and 0.920 respectively. The model implies that the adsorptions of these two metals were based on sorption on heterogeneous surface [1]. This result was proved by higher adsorption of Hg(II) and Pb(II) in both experiments which mainly due to the greater tendency of these metals to be adsorbed onto the adsorbent surface since they undergo heterogeneous adsorption.

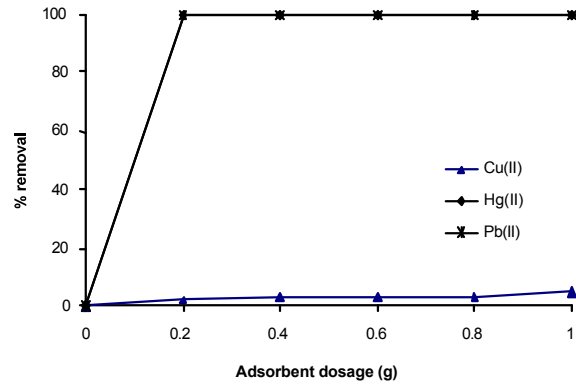


Fig. 3: Effect of adsorbent dosage to adsorption of Hg(II), Pb(II) and Cu(II) by EFB activated carbon

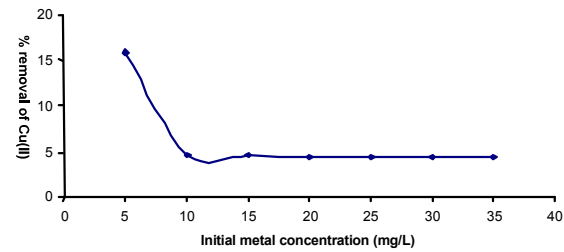


Fig. 4: Effect of initial metal concentration on the removal of Cu(II)

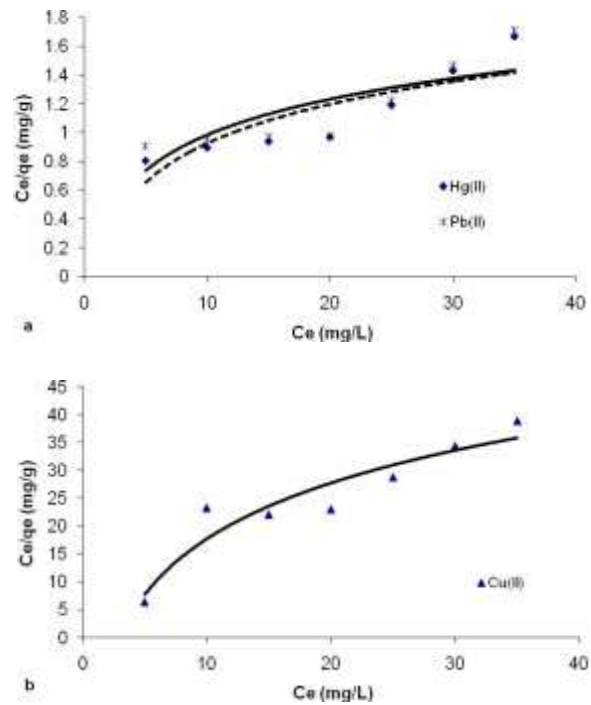


Fig. 5: Langmuir adsorption isotherm of (a) Hg(II) and Pb(II); and (b) Cu(II)

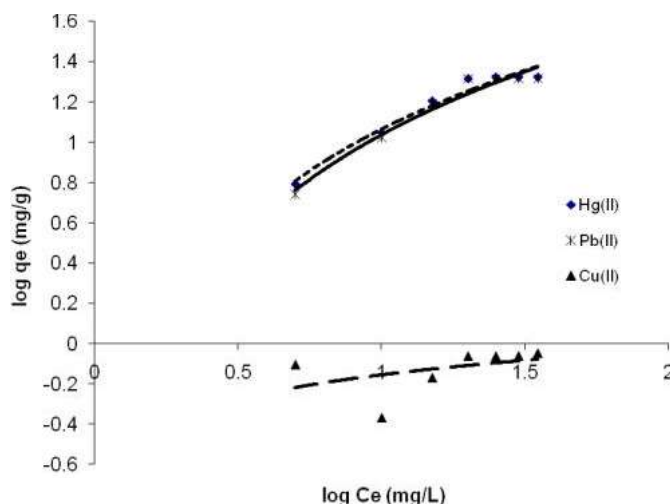


Fig. 6: Freundlich adsorption isotherm of Hg(II), Pb(II) and Cu(II)

Adsorption of Cu(II), can be explained by Langmuir model according to the correlation regression value of 0.868. It was observed that the adsorption of Cu(II) was limited to only monolayer adsorption as Langmuir model is valid for monolayer adsorption onto a surface with a finite number of identical sites [15]. Thus, there are limited available sites on adsorbent surface where Cu(II) can interact in order for adsorption to occur. The adsorbent surface is easily saturated with metal as the adsorption was limited to monolayer. This will further limit the amount of metal that could be adsorbed. This explains why lower adsorption of Cu(II) was given by the EFB activated carbon.

CONCLUSION

The study indicated that the EFB activated carbon produced through chemical activation by using NaOH as the activating agent could be used as an effective adsorbent material for the removal of Hg(II) and Pb(II) from wastewater. However, Cu(II) can only be removed at lower percentage. From the calculation based on Langmuir isotherm, Hg(II) shows the highest adsorption capacity of 52.67 mg/g, followed by Pb(II) and Cu(II) with adsorption capacity of 48.96 mg/g and 0.84 mg/g, respectively. It can also be concluded that the adsorption of Hg(II), Pb(II) and Cu(II) by EFB activated carbon is dependent on the adsorbent dosage and the adsorption of Pb(II) and Hg(II) depends on initial metal concentration. In adsorption isotherm analysis, the Langmuir model provides better correlation to the adsorption data for Cu(II) while Pb(II) and Hg(II) fit to the Freundlich isotherm. This suggests

that the adsorption is limited to monolayer for Cu(II) and heterogeneous for Pb(II) and Hg(II). These results were in agreement with the removal percentage and also the maximum adsorption capacity of each metal. In this study, the EFB used to produce activated carbon was locally and abundantly available agricultural waste product. Hence, the activated carbon prepared from the EFB would be an economically, useful tool as an alternative to the commercially available activated carbon in the treatment of wastewater containing Hg(II) and Pb(II).

ACKNOWLEDGMENT

Thanks were extended to Universiti Malaysia Sarawak for their support to our project (Grant No. SGS/01(S14)/605/2006(38)).

REFERENCES

1. Iqbal, M. and A. Saeed, 2007. Production of an immobilized hybrid biosorbent for the sorption of Ni (II) from aqueous solution. *Process Biochem.*, 42: 148-157.
2. Aydin, H., Y. Bulut and C. Yerlikaya, 2008. Removal of Cu(II) (II) from aqueous solution by adsorption onto low-cost adsorbents. *J. Environ. Manage.*, 87: 37-45.
3. Rao, M.M., D.H.K.K. Reddy, P. Venkateswarlu and K. Seshiah, 2009. Removal of mercury from aqueous solutions using activated carbon prepared from agricultural by-product/waste. *J. Environ. Manage.*, 90(1): 634-643

4. Qiu, Y., H. Cheng, C. Xu and S.D. Sheng, 2008. Surface characteristics of crop-residue-derived black carbon and lead(II) adsorption. *Water Res.*, 42: 567-574.
5. Bhatti, H.N., B. Mumtaz, M.A. Hanif and R. Nadeem, 2007. Removal of zinc ions from aqueous solution using *Moringa oleifera* Lam. (horseradish tree) biomass. *Process Biochem.*, 42: 547-553.
6. Malik, R., D.S. Ramteke and S.R. Wate, 2007. Adsorption of malachite green on groundnut shell waste based powdered activated carbon. *Waste Manage.*, 27: 1129-1138.
7. Wan Nik, W.B., M.M. Rahman, A.M. Yusof, F.N. Ani and C.N. Che Adnan, 2006. Production of activated carbon from palm oil shell waste and its adsorption characteristics. In *Proceedings of the 1st International Conference on Natural Resources Engineering and Technology 2006*, pp: 646-654.
8. Pechyen, C., D. Atong, D. Aht-Ong and S. Viboon, 2007. Investigation of pyrolyzed chars from physic nut waste for the preparation of activated carbon. *J. Solid Mechanics Material Eng.*, 1(4): 498-507.
9. Rahman, S.H.A., J.P. Choudhury and A.L. Ahmad, 2006. Production of xylose from oil palm empty fruit bunch fiber using sulfuric acid. *Biochem. Eng. J.*, 30(1): 97-103.
10. Rao, M.M., G.P.C. Rao, K. Sessaiah, N.V. Choudary and M.C. Wang, 2007. Activated carbon from *Ceiba petandra* hulls, an agricultural waste, as an adsorbent in the removal of Pb(II) and zinc from aqueous solutions. *Waste Manage.*, 28(5): 849-858.
11. Qian, Q., M. Machida and H. Tatsumoto, 2007. Textural and surface chemical characteristics of activated carbons prepared from cattle manure compost. *Waste Manage.*, 98(2): 353-360.
12. Noll, K.E., L.S. Demming and W.S. Hou, 1992. *Adsorption Technology for Air and Water Pollution Control*. Lewis, Michigan, pp: 25.
13. Wu, S. and J.P. Chen, 2001. Modification of a commercial activated carbon for metal adsorption by several approaches. In *Proceedings of the 2001 International Containment and Remediation Technology Conference and Exhibition*. Orlando, Florida, pp: 408-411.
14. Li, F., P. Du and S. Zhang, 2007. Preparation of silica-supported porous sorbent for heavy metal ions removal in wastewater treatment by organic-inorganic hybridization combined with sucrose and polyethylene glycol imprinting. *Analytica Chimica Acta*, 585: 211-218.
15. Safarik, I., F.T.R. Luis, B. Marie, M.S. Ewa, F. Weyda and S. Mirka, 2007. New magnetically responsive yeast-based biosorbent for the efficient removal of water-soluble dyes. *Enzyme Microb. Technol.*, 40: 1551-1556.