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Removal of Zn and Cu from Wastewater by Sorption on Oil Palm Tree-Derived Biomasses

B. Salamatinia, A.H. Kamaruddin and A.Z. Abdullah
School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus,
14300 Nibong Tebal, Seberang Perai Selatan, Penang, Malaysia

Abstract: In this study Oil Palm Bark (OPB), Oil Palm Frond (OPF) and Empty Fruit Bunch (EFB) were evaluated as low-cost sorbent materials for removal of Cu and Zn from water in a batch mode. All the biomasses were used without any chemical modification to evaluate their initial sorption capacity. The sorption processes were performed in a batch mode with 250 mL Cu and Zn solutions at 100 mg L^{-1} using between 0.5 and 1.0 g of sorbent. The samples were tested every 24 h up to 168 h in normal room temperature. No diffusion limitation was observed in the sorption process. A Zn removal efficiency of 51.5 and 46.0% with 1.0 of OPF and EFB, respectively was observed while OPB showed the lowest removal efficiency. For Cu, the removal achieved was 54% for 1.0 g OPF and 56.5% using 1.0 g of EFB. Cu showed better sorption on the three biomasses. The OPB and EFB introduced excessive amounts of soluble organics into the water. The experimental data obtained with OPF sorbent could fit Freundlich isotherm model better with $R^2 > 0.99$. This result suggested the heterogeneous binding sites in the biomass.

Key words: Oil palm biomass, sorption, heavy metal, wastewater, isotherms

INTRODUCTION

Due to its special physical and chemical properties, water is consumed in many industries, water is used for cleaning, cooling, as a reaction medium, as a solvent for some chemical reactions etc. The effluents from those processes may contain toxic materials, such as heavy metals, dyes, phenols etc., depending on the material involved in the process (Salamatinia et al., 2006; Tewari et al., 2005). Organic materials that are obtained from living or dead creatures are called biomass and they can be used as low-cost sorbents for removing heavy metal. Studies on the use of biosorbents for heavy metal removal have received considerable attention as the sorbents can be readily obtained at low cost and generally shows good sorption capacity (Low et al., 1995).

Various biomasses have been reported to show the ability for sorption of heavy metals. These materials possess different types of functional groups such as carboxylic, sulfates, phosphates and amino-groups that will act as the binding sites for ion exchange and complex reactions (Chubar et al., 2004). Recently, successful Cr (VI) removal has been reported by using sugar beet pulp (Altundogan, 2005). Meanwhile, Cr (III), Cu (II) and Zn (II) have been effectively removed using carrot residues

(Nasernejad et al., 2005), while Sphagnum moss peat was successfully used for the sorption of Cr (VI) by Sharma and Foster (Sharma and Forser, 1995). Nuhoglu et al. (2002) reported the satisfactory removal of Cu (II) by sorption on Ulothrix zonata while Juang et al. (1998) used chitosan for removal of the same heavy metal. Cu (II) has also been sorbed on wheat (Basci et al., 2004) and herbaceous peat (Gündoğan et al., 2004) with high removal efficiency. Rice husk treated with tartaric acid was also developed in order to remove Cu (II) and Pb from wastewater (Wong et al., 2003) while lead was successfully sorbed on peat (Ho and Mckay, 1998). Pb has also been removed from aqueous solution using cone Pinus sylvestris (Ucun et al., 2002), rice husk (Zulkali et al., 2006) and pretreated Spriulina maxima biomass (Gong et al., 2005).

Being a tropical country, Malaysia has enormous supply of biomass resources that are mainly generated by agricultural activities throughout the year. The oil palm industry generates many types of biomass such as the mesocarp fiber, shell, Empty Fruit Bunch (EFB), Oil Palm Frond (OPF) and Oil Palm Bark (OPB) that can be utilized for many applications. It is estimated that more than 50 million tones of biomass is generated from the industry (Yacob et al., 2005). Therefore, the application of those

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Corresponding Author: Dr. Ahmad Zuhairi Abdullah, School of Chemical Engineering, Universiti Sains Malaysia,
Engineering Campus, 14300 Nibong Tebal, Seberang Perai Selatan, Penang, Malaysia
Tel: +604-5996411 Fax: +604-5941013

biomasses for value-added purposes such as in the sorption of heavy metals needs to be explored and investigated. The abundance and cheap supply of the biomasses will justify their use as potential sorbents for heavy metal removal. Until recently, literature reports on the use of oil palm biomasses for this application are hardly found. As an ultimate objective, a highly efficient and low-cost sorbent is expected to be produced from oil palm biomass with proper elucidation of its characteristics and behavior in the sorption of heavy metals. In this study three different parts of oil palm tree i.e., the Oil Palm Frond (OPF), Oil Palm Bark (OPB) and Empty Fruit Bunch (EFB) were chosen to be investigated for heavy metal sorption.

MATERIALS AND METHODS

Stock solutions: The stock solution for Zn and Cu were prepared at a concentration of 100 mg L^{-1} by dissolving the desired quantity of zinc nitrate (Zn $(NO_3)_2$. $6H_2O$) and copper nitrate (Cu $(NO_3)_2$. $3H_2O$) in deionized water. For other concentrations, the stock solutions were diluted with deionized water to obtain the concentration needed. The metal salts were of analytical grade.

Biomass preparation: Three types of biomass from different parts of oil palm tree were used in this study. Oil Palm Frond (OPF) and Oil Palm Bark (OPB) were obtained from oil palm trees in Universiti Sains Malaysia. The Empty Fruit Bunch (EFB) was obtained from United Palm Oil Mill, Nibong Tebal, Penang, Malaysia. In order to remove oil from the surface of the EFB, it was first washed thoroughly with water and detergent and then sun dried. The biomasses were then ground with a blender (Epicson Eb-321) for 1 min and washed thoroughly with distilled water in order to remove any dirt and dust and subsequently oven-dried at 70°C for 12 h to reach constant weight. The dried biomasses were then stored in pre-cleaned airtight containers.

Heavy metal measurement: The Zn concentration in the aqueous solution was measured using a zinc meter (HANNA, model HI93731), while that of Cu was measured using a copper meter (HANNA, model HI93702). The pH of the solution was measured using a pH-meter (WTW, pH330i 2A2O-1012) and the COD test was done using spectrophotometer (CICIL brand CE1010) following Standard Method No. 5220 D (close reflux, colorimetric method).

Sorption experiments: In a typical procedure, two lots of biomass (0.5 and 1.0 g) were contacted with 250 mL of Zn and Cu solution (100 mg L^{-1}) in 250 mL conical flask (Pyrex) at 25°C, unless otherwise specified. The samples

were then agitated in an orbital shaker (Certomat H) at 150 rpm for the desired contact times to reach the maximum uptake of the heavy metals. After that, the mixtures were passed through a Whatman filter paper (110 mm) and the residual concentration of Zn and Cu was measured by the zinc meter and the copper meter, respectively. All the experiments were performed in triplicate and the average values were reported. As a control, a blank sample containing only Zn and Cu solution (100 mg L^{-1}) was subjected to exactly the same procedures except no sorbent was used. The concentration of the solution was measured every 24 h and after a total contact time of 168 h, a COD test was carried out to check for any organic impurity introduced into the water from the biomass.

In the isotherm studies, 0.5 g of untreated OPF was used to sorb Zn and Cu at concentrations of 10, 25, 50, 75 and 100 ppm in a 250 conical flasks that were agitated in an orbital shaker at 150 rpm. The sorption process was carried out for varying contact times of up to 168 h with a sampling interval of 24 h. After the filtration, the liquid samples were analyzed using the zinc meter and copper meter to measure the concentration of Zn and Cu, respectively. The experimental data at equilibrium point were fitted to Langmuir and Freundlich models.

RESULTS AND DISCUSSION

Sorption of Zn: Performance of three different biomasses with a loading amount of 0.5 g in 250 mL sample is shown in Fig. 1. Although a relatively high sorption capacity was observed with EFB (13.2 mg g^{-1}) after 96 h of contact time, the fastest equilibrium was achieved by OPB. However, it showed the lowest uptake in the long run. After 96 h, OPF showed a removal of 13.0 mg g^{-1} and there was no more net sorption because the system already reached its equilibrium. By comparing the three biomasses, OPB showed a relatively lower removal with a maximum removal of 12.5% (a corresponding uptake of 6.3 mg g^{-1}) after 96 h of contact time.
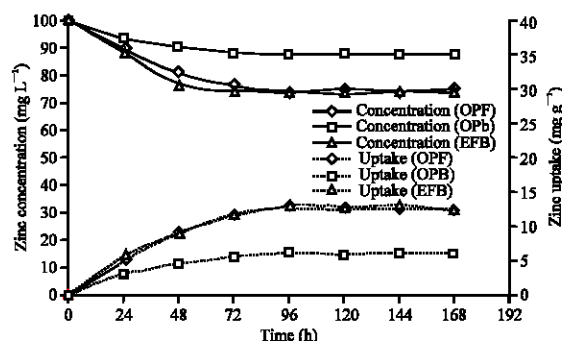

Fig. 1: Zn removal with 0.5 g of biomass loading

For all biomasses, the sorption process generally showed a rapid uptake of metal, followed by a gradual decrease with time until no more net sorption occurred as observed at longer contact time (after 96 h). This trend can be explained based on the availability of active sites that bound heavy metals. Initially, the active sites for binding the heavy metals were fully available for the sorption process so that a sharp metal uptake was observed. After that, equilibrium was gradually reached as the active sites were occupied by the heavy metal ions and no more net sorption could take place. This explained the flat regions of the sorption process for both Zn uptake and concentration at longer time.

Comparison between biomass loadings of 1.0 and 0.5 g will give the correlation between the amount of biomass and the amount of Zn removed. The result indicated that by doubling the amount of biomass, almost double values of metal sorption were achieved (Fig. 2). This was attributed to the doubling of the amount of active sites for the sorption process. Meanwhile, the almost the same sorption capacity was obtained. The highest removal of 51.5% was also obtained with the OPF sorbent, corresponding to an uptake of 12.9 mg g^{-1} of Zn after 96 h of contact time. As with 0.5 g loading, the concentration of heavy metal did not show significant change after 96 h. The EFB showed the highest removal of 49% (12.3 mg g^{-1}) after 96 h of contact time. The maximum uptake for OPB was 6.4 mg g^{-1} for 1.0 g sorbent loading after 96 h. This showed almost similar amount of uptake with 0.5 g of biomass loading (6.3 mg g^{-1}) at the same contact time. The result suggested the absence of diffusion effects in the biomass during the sorption process and the particle sizes of the sorbent materials were sufficiently small so that the metal uptake was the controlling step in the sorption process.

During the sorption process, it was also expected that some soluble organics from the biomass could be introduced into the water to create secondary pollution. This necessitated confirmatory COD test for the liquid samples after the desired contact time. Figure 3 shows that for OPF, there was negligible COD detected in the water to suggest the absence of soluble organics that leached out from the sorbent. As for the OPB and EFB sorbents, considerable amounts of COD were detected to be introduced into the solution. The high amount of COD in the solution in contact with EFB was associated with the fatty acids, sugars and other soluble components of the biomass.

A comparison between the use of 0.5 and 1.0 g of sorbent material led to the conclusion that the amount of COD introduced into the solution was dependent on the amount of biomass loading. By doubling the biomass
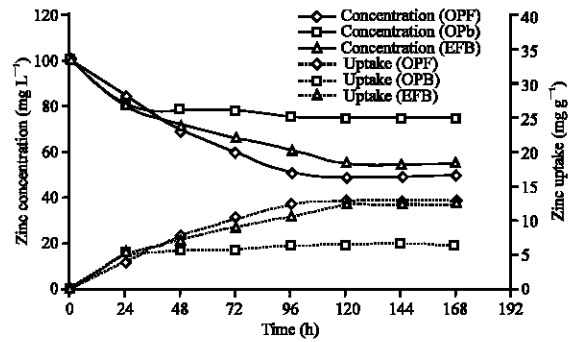

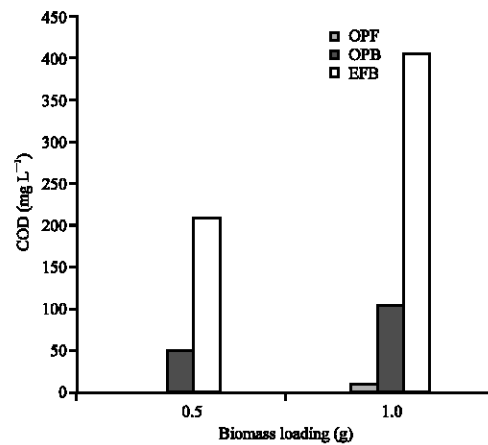Fig. 2: Zn removal with 1.0 g of biomass loading

Fig. 3: COD of the sample after Zn removal

loading, almost double COD values were detected in the solution. The result suggested the completion of the solubilization process of the organics from the sorbent at two different loadings.

Sorption of Cu: Similar behavior was observed when the same three biomasses were used to remove Cu. The conditions used for these experiments were the same with those used in the removal of Zn. As evident in Fig. 4 for 0.5 g biomass loading, relatively rapid sorption in the first 96 h was observed and after that, no significant changes were observed in the Cu concentration for all three sorbents. The highest uptake for OPF, OPB and EFB were 11.8, 8.3 and 14.1 mg g^{-1}, respectively that were achieved after 96 h. The best sorption capacity (an uptake of 14.1 mg g^{-1}) was observed with the use of OPF as the sorbent material. It is also observable in the figure that the removal of Cu was significantly higher than that of Zn.

Figure 5 confirms the similar behavior shown by Zn and Cu sorption processes. A reasonably good uptake was not obtained with OPB and the highest efficiency of this sorbent (34.5%) was obtained at 96 h. The highest
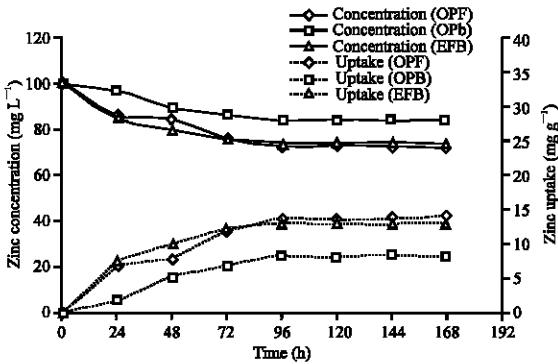
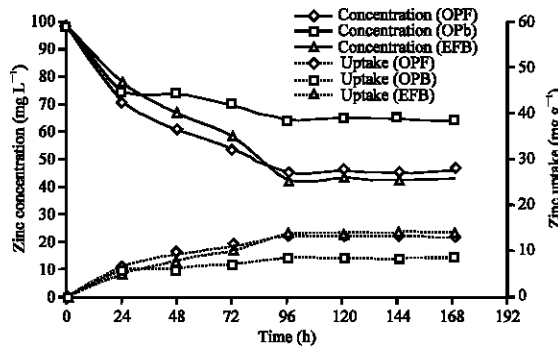Fig. 4: Cu removal with 0.5 g of biomass loading

Fig. 5: Cu removal with 1.0 g of biomass loading

Table 1: Removal percentage, sorption capacity and saturation time for Zn and Cu removal with different biomass

Heavy metal	Biomass	Amount loaded (g)	Removal (%)	Sorption capacity (mg g^{-1})
Zn	OPF	0.5	26.0	13.0
		1.0	51.5	12.9
	OPB	0.5	12.5	6.3
		1.0	25.7	6.4
	EFB	0.5	26.5	13.2
		1.0	49.0	12.3
Cu	OPF	0.5	27.5	13.8
		1.0	54.0	13.5
	OPB	0.5	16.5	8.3
		1.0	34.5	8.6
	EFB	0.5	26.0	13.0
		1.0	56.5	14.1

reduction in Cu concentration in the solution was obtained with EFB, which stood at 56.5%, corresponding to an uptake of 14.1 mg g^{-1}. In the first 24 h, relatively sharp reductions in the metal concentration in the solution were observed for all three kinds of biomass. After 96 h of contact time, the Cu concentration in the solution did not show any significant change. This was attributed to the saturation of the heavy metal binding sites in the biomass.

As shown in Table 1, it is obvious that Cu showed a better sorption on the biomass compared to Zn. In
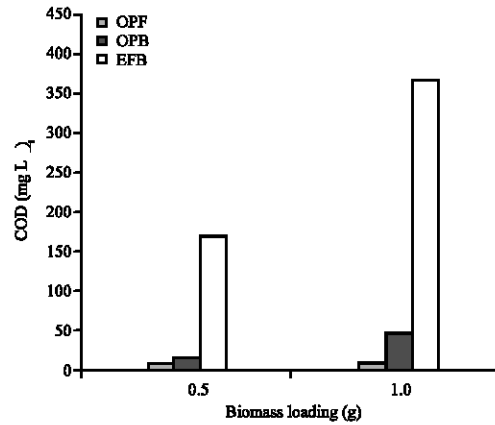

Fig. 6: COD of the sample after Cu removal

addition, the time needed for the saturation of the biomass for Cu sorption was relatively shorter. The sorption capacity for every biomass at 0.5 g of biomass loading compared with that of the higher loading showed nearly the same amount. This result meant that although the amount of biomass was doubled, the amount sorbed was correspondingly doubled so that sorption capacity remained virtually constant for each biomass. As an example, for the removal of Cu with OPF, the highest removals were 27.5 and 54% for 0.5 and 1.0 g of biomass loading while the sorption capacity for both loadings remained almost the same (~13.5 mg g^{-1}). This result suggested the absence of diffusion effects for Cu in the biomass during the sorption process and the uptake of these metals was limited by the kinetics of the sorption process. The maximum sorption capacity for EFB was 14.1 mg g^{-1} i.e., slightly higher compared to that of OPF (13.5 mg g^{-1}). This was because the sorption capacity was also related to the structure and functional groups presented in the biomass.

Figure 6 shows the COD concentration in the solution after the Cu sorption process. The figure suggests considerable amount of COD had been introduced by the EFB into the solution while for OPF, the COD value was negligible. Despite satisfactory Zn and Cu removals by EFB, this sorbent material was not considered a practical sorbent material for further investigation in this application due to the introduction of excessive amount of COD into the solution to create secondary pollution. Instead, OPF was deemed to be a more suitable material on the basis of high removal efficiency and most importantly, it was more stable and did not cause secondary pollution of water.

Adsorption isotherms: Two important operational aspects for the evaluation of the sorption process as a unit

operation are the equilibrium of the sorption and the kinetics. Equilibrium studies for sorbent and sorbate systems are often described by sorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium. Two different isotherms that are mostly studied for the sorption behavior of the biomass are the Langmuir and Freundlich isotherms (Dantas *et al.*, 2001).

Langmuir: The Langmuir equation assumes that: (i) the solid surface presents a finite number of identical sites, which are energetically uniform; (ii) there is no interaction between sorbed species, or in other words, the amount sorbed has no influence on the rate of sorption and (iii) a monolayer is formed when the solid surface reaches saturation. The Langmuir adsorption isotherm is often expressed as:

$$\frac{x}{m} = \frac{abCe}{1 + aCe} \qquad (1)$$

Where:

x = Amount of material adsorbed (mg or g)
m = Weight of adsorbent (mg or g)
C_e = Concentration of material remaining in solution after adsorption is complete
a and b = Constants

Taking the reciprocal of both sides of equation yields:

$$\frac{1}{x/m} = (\frac{1}{b}) + (\frac{1}{abC_e}) \qquad (2)$$

For adsorption that follows the Langmuir isotherm, a linear trace should result when the quantity $\frac{1}{x/m}$ is plotted against $\frac{1}{C_e}$. Values of the constant a and b can be determined from the linear graph:

1/ab = The slope of the graph
1/b = The intercept of the graph

Data for Zn sorption process were used to fit the Langmuir isotherm linear plot as shown in Fig. 7. As the highest sorption capacity for Zn was obtained with OPF, it was further used to test for the Langmuir isotherm fitting. Figure 7 shows that the sorption data unsatisfactorily fitted the Langmuir isotherm with an
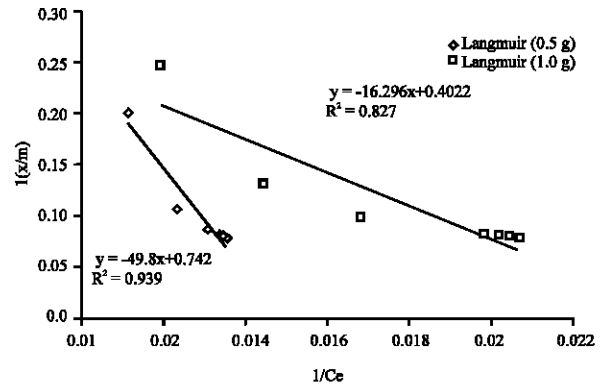
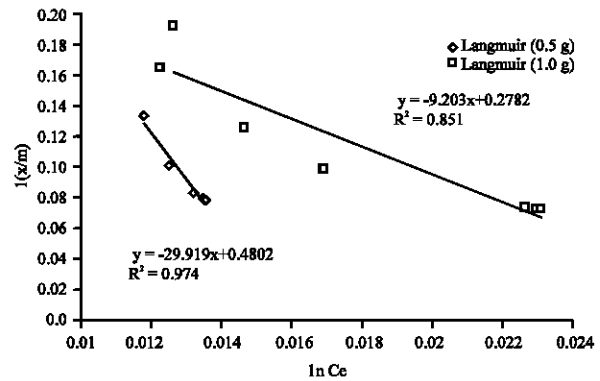

Fig. 7: Langmuir isotherm for Zn removal using OPF

Fig. 8: Langmuir isotherm for Cu removal using EFB

R^2-value of 0.939 for 0.5 g biomass loading and 0.827 for 1.0 g biomass loading. Clear deviation from the linear line was observed, especially in the case of 1.0 g of biomass loading. This deviation was more observable at higher biomass loading. This was partly attributed to the range of the data for lower amount of biomass which was relatively narrow to render smaller deviation.

Figure 8 shows the Langmuir isotherm fitting for Cu removal at 25°C with EFB as for Cu removal, the best result was obtained with this sorbent. An R^2-value of 0.974 for 0.5 g biomass loading and 0.851 for 1.0 g of biomass were obtained when the sorption data were fitted to the isotherm equation. This result was quite similar to that of Zn sorption process, which showed fair fitting at low biomass loading and clear deviation at higher loading.

Freundlich: The Freundlich isotherm model has been shown to be suitable for describing short-term and monocomponent sorption of metal ions (Ho *et al.*, 2002). The Freundlich equation is based on heterogeneous surfaces suggesting that binding sites are not equivalent and/or independent. The Freundlich isotherm is the earliest known relationship describing the sorption equation and is often expressed as:

$$\frac{x}{m} = K_f \cdot C_e^{1/n} \qquad (3)$$

Where:

x   = Amount of material adsorbed (mg or g)

m   = Weight of adsorbent (mg or g)

C_e = Concentration of material remaining in solution after adsorption is complete

K_f and n = Constants that must be evaluated for each solute and temperature

This equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$\ln(x/m) = \ln K_f + (1/n)\ln C_e \qquad (4)$$

A plot of ln (x/m) against ln C_e yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. Values of the constants n and K_f can be determined from the linear graph:

1/n =   The slope of the graph

K_f =   The intercept of the graph

Figure 9 shows the Freundlich isotherm fittings for Zn sorption on OPF at 25°C. Compared to Langmuir isotherm, Freundlich isotherm showed better fit to the experimental data, especially at lower sorbent loading. For Zn removal by OPF, the R^2-values were 0.983 and 0.952 for 0.5 and 1.0 g of biomass loading, respectively.

Similar trend was also observed in the case of Cu sorption process (Fig. 10). Better fitting to the experimental data was observed at lower sorbent loading with an R^2-value of 0.994 for 0.5 g of EFB compared to 0.961 for 1.0 g of the biomass. On overall, Freundlich isotherm showed the accuracy and appropriateness to represent the heavy metal sorption. This behavior was attributed to the structure of the biomass. As the sorbent used was of plant origin, the heterogeneity of the binding sites seemed to be more appropriate while the binding steps appeared to control the sorption process (Dakiky *et al.*, 2002). This result was consistence with the removal of metal ions from aqueous solution by sorption onto rice bran.

The other biomasses could fit both the Langmuir and Freundlich isotherms for both metals but with different degrees of accuracy. The constants of the isotherms were calculated and tabulated in Table 2. The R^2 for all the isotherms were high, but by comparing the Langmuir and Freundlich isotherms, it was evident that
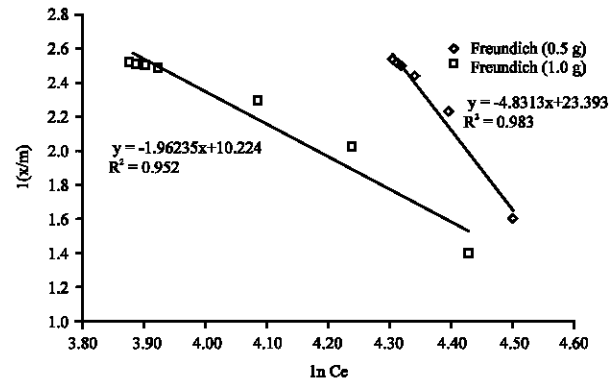

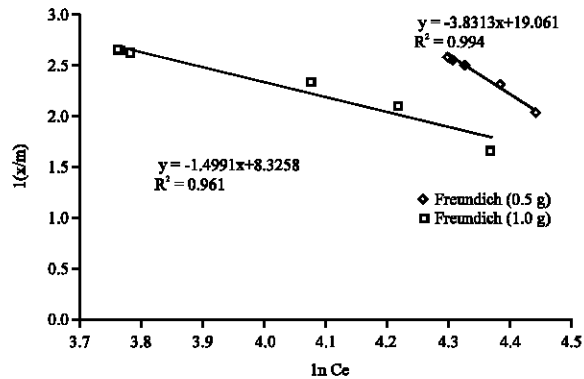Fig. 9: Freundlich isotherm for Zn removal using OPF

Fig. 10: Freundlich isotherm for Cu removal using EFB

the R^2-values for Freundlich isotherms generally showed higher values than those of Langmuir isotherm under the same operating conditions.

Langmuir equation can also be used to calculate the maximum sorption constant Q_o (mg g^{-1}) and the energy parameter of the sorption constant b (L mg^{-1}). The Langmuir isotherm constants (Q_0 and b) varied in a small range and significant differences were not observed. The results achieved by these researches fitted the Langmuir isotherm better than the biomass derived from palm oil tree. The coefficients of determination for this study were above 0.97. This showed the homogeneousity and monolayer sorption of this biomass. Removal of other metals including Cr, Ni, Cd and Mn from wastewater by Brazilian natural scolecite also led to the constants value of the same range. The results show a high fitting ($R^2 = 0.9965$) for Cr while this isotherm could not accurately represent the Cd ($R^2 = 0.9240$) and Mn ($R^2 = 0.9549$) sorptions while showed a very poor fitting ($R^2 = 0.6155$) for Ni sorption.

In the Freundlich equation, K_f (mg g^{-1}) and n are constants that are considered to be relative indicators

Table 2: R^2 and isotherm constants of different biomasses for Langmuir and Freundlich isotherms for Zn and Cu sorption

Biomass loading	Heavy metal	Biomass	Isotherm	R^2	Langmuir constants		Freundlich constants	
					b	Q_0	n	K_f
0.5	Zn	OPF	Langmuir	0.939	0.0149	1.3477	-	-
			Freundlich	0.983	-	-	0.2070	1.44×10^{10}
		OPB	Langmuir	0.970	0.0122	0.4191	-	-
			Freundlich	0.992	-	-	0.1029	4.79×10^{19}
		EFB	Langmuir	0.975	0.0153	1.4870	-	-
			Freundlich	0.995	-	-	0.2193	4.21×10^{9}
	Cu	OPF	Langmuir	0.979	0.0161	1.9948	-	-
			Freundlich	0.995	-	-	0.2573	2.36×10^{8}
		OPB	Langmuir	0.985	0.0134	0.8832	-	-
			Freundlich	0.960	-	-	0.0943	2.08×10^{21}
		EFB	Langmuir	0.974	0.0161	2.0825	-	-
			Freundlich	0.994	-	-	0.2610	1.89×10^{8}
1.0	Zn	OPF	Langmuir	0.827	0.0247	2.4863	-	-
			Freundlich	0.952	-	-	0.5093	2.75×10^{4}
		OPB	Langmuir	0.992	0.0169	1.3196	-	-
			Freundlich	0.998	-	-	0.2993	1.15×10^{7}
		EFB	Langmuir	0.891	0.0229	2.6021	-	-
			Freundlich	0.972	-	-	0.5082	3.03×10^{4}
	Cu	OPF	Langmuir	0.918	0.0308	4.1391	-	-
			Freundlich	0.979	-	-	0.7153	2.90×10^{3}
		OPB	Langmuir	0.988	0.0202	2.1142	-	-
			Freundlich	0.997	-	-	0.4145	2.08×10^{5}
		EFB	Langmuir	0.851	0.0302	3.5945	-	-
			Freundlich	0.961	-	-	0.6670	4.13×10^{3}

of the sorption capacity and sorption intensity, respectively. The K_f constant is related to the sorption capacity with respect to a specific sorbate. In this respect, the values of n were calculated and for different biomasses and different heavy metals, the values were found to vary in the range of 0.0943 to 0.7153. The n values indicate the presence of a heterogeneous surface and binding sites with different energies. This led to a high fitting with an R^2 value approaching 1.0 as shown in Table 2.

The K_f values for Freundlich isotherm were found to be large numbers. The values range of this constant for 0.5 g of biomass loading (1.89×10^8 up to 2.08×10^{21}) was greater than that obtained with 1.0 g of biomass loading (2.90×10^3 to 1.89×10^8). This difference indicated that the amount of biomass loading could significantly affect the sorption process. According to Ahalya *et al.* (2005), n-values between 1 and 10 represent favorable sorption. The magnitude of K_f and n shows degree of difficulty in the separation of heavy metal ions from wastewater and high sorption capacity. Easier heavy metal removal is generally achieved within this range of values for n and lower values for K_f.

CONCLUSIONS

Based on three different biomasses from oil palm tree studied for removal of Zn and Cu from wastewater, the best sorption capacity was demonstrated by OPF for Zn removal and EFB for Cu removal. Although the sorption capacity of these two sorbents was nearly the same, the COD introduction by the EFB into the wastewater limited its practical use. The COD introduced to the water was attributed to some water-soluble organics and fatty acid content of the EFB. The kinetic studies show that better fittings were obtained with the Freundlich isotherm. This indicated the heterogeneous nature of the biomass. A Zn removal efficiency of 51.5 and 46.0% with 1.0 of OPF and EFB, respectively was observed while OPB showed the lowest removal efficiency. For Cu, the removal achieved was 54% for 1.0 g OPF and 56.5% using 1.0 g of EFB. The results also showed that these biomasses had the ability for heavy metal sorption.

REFERENCES

Ahalya, N., R.D. Kanamadi and T.V. Ramachandra, 2005. Biosorption of chromium (VI) from aqueous solutions by the husk of Bengal. Electronic J. Biotechnol. (Online): 8 (3) [Cited 29 June, 2006].

Altundogan, H.S., 2005. Cr (VI) removal from aqueous solution by iron (III) hydroxide-loaded sugar beet pulp. Proc. Biochem., 40: 1443.

Basci, N., E. Kocadagistan and B. Kocadagistan, 2004. Biosorption of copper (II) from aqueous solutions by wheat shell. Desalination, 164: 135.

Chubar, N., J.R. Carvalho and M.J.N. Correia, 2004. Heavy metal biosorption on cork biomass: Effect of the pre-treatment. Colloids Surfaces, 238: 51.

Dakiky, M., M. Khamis, A. Manasra and M. Mer'eb, 2002. Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents. Adv. Environ. Res., 6: 533.

Dantas, T.N.D.C., A.A.D. Neto and M.C.P.D.A. Moura, 2001. Removal of chromium from aqueous solutions by diatomite treated with microemulsion. Water Res., 35: 2219.

Gong, R., Y. Ding, H. Liu, Q. Chen and Z. Liu, 2005. Lead biosorption and desorption by intact and pretreated *Spirulina maxima* biomass. Chemosphere, 58: 125.

Gündoğan, R., B. Acemioğlu and M.H. Alma, 2004. Cu (II) adsorption from aqueous solution by herbaceous peat. J. Colloid Interface Sci., 269: 303.

Ho, Y.S. and G. Mckay, 1999. The sorption of lead (II) ions on peat. Water Res., 33: 578.

Ho, Y.S., C.T. Huang and H.W. Huang, 2002. Equilibrium sorption isotherm for metal ions on fern tree. Proc. Biochem., 37: 1421.

Juang, R., F. Wu and R. Tseng, 1998. Adsorption removal of Cu (II) using chitosan from simulated rinse solutions containing chelating agents. Water Res., 33: 2403.

Low, K.S., C.K. Lee and A.C. Leo, 1995. Removal of metals from electroplating wastes using banana pith. Bioresour. Technol., 51: 227.

Nasernejad, B., T. Esslamzadeh, B. Bonakdarpour, M. Esmaailbygi and A. Zamani, 2005. Comparison for biosorption modeling of heavy metals (Cr (III), Cu (II), Zn (II)) adsorption from wastewater by carrot residues. Proc. Biochem., 40: 1319.

Nuhoglu, Y., E. Malkoc, A. Gürses and N. Canpolat, 2002. The removal of Cu (II) from aqueous solutions by *Ulothrix zonata*. Bioresour. Technol., 85: 331.

Salamatinia, B., A. A. Zinatizadeh, A. H. Kamaruddin and A.Z. Abdullah, 2006. Application of response surface methodology for the optimization of Cu and Zn removals by sorption on pre-treated Oil Palm Frond (OPF). Iran. J. Chem. Eng., 3: 73.

Sharma, D.C. and C.F. Forster, 1995. Column studies into the adsorption of chromium (VI) using sphagnum moss peat. Bioresour. Technol., 52: 261.

Tewari, N., P. Vasudevan and B.K. Guha, 2005. Study on biosorption of Cr (VI) by *Mucor hiemalis*. Biochem. Eng. J., 23: 185.

Ucun, H., Y.K. Bayhan, Y. Kaya, A. Cakici and O. Algur, 2002. Biosorption of lead (II) from aqueous solution by cone biomass of *Pinus sylvestris*. Desalination, 154: 233.

Wong, K.K., C.K. Lee, K.S. Lowand and M.J. Haron, 2003. Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions. Chemosphere, 50: 23.

Yacob, S., M.A. Hassan, Y. Shirai, M. Wakisaka and S. Subash, 2006. Baseline study of methane emission from anaerobic ponds of palm oil mill effluent treatment. Sci. Total Environ., 366: 187.

Zulkali, M.M.D., A.L. Ahmad and N.H. Norulakmal, 2006. *Oryza sativa* L. husk as heavy metal adsorbent: Optimization with lead as model solution. Bioresour. Technol., 97: 21.