

SORPTION OF Cu(II) BY POLY(HYDROXAMIC ACID) CHELATING EXCHANGER PREPARED FROM POL(YMETHYL ACRYLATE) GRAFTED OIL PALM EMPTY FRUIT BUNCH (OPEFB)

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This paper describes the preparation of chemically modified oil palm empty fruit bunch (OPEFB) with hydroxamic acid functional group and its use for the sorption of Cu(II) from aqueous solution. OPEFB was grafted with poly(methylacrylate) (PMA), using $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ as initiator. The PMA grafted OPEFB (PMA-OPEFB) was treated with hydroxylammonium chloride in alkaline medium to produce hydroxamic acid grafted fiber (PHA-OPEFB). The FTIR spectrum of OPEFB grafted with PMA showed an intense absorption band at 1734 cm^{-1} which is attributed to C=O vibration in the grafted ester. After hydroxylamine treatment, the intensity of absorption band at 1734 cm^{-1} decreased and new bands appeared at the 1640 cm^{-1} related to C=O vibration in hydroxamic acid and at the 1568 cm^{-1} related to the N-H amide. Sorption of Cu(II) by PHA-OPEFB was effective over a pH range of 4 to 6. The sorption followed the Langmuir model with maximum capacities of 74.1 mg g^{-1} at $25\text{ }^\circ\text{C}$. The sorption process was exothermic, as shown by the negative value of enthalpy change, ΔH° . The free energy change (ΔG°) for the sorption was negative, showing that the sorption process was spontaneous. A kinetic study showed that the Cu(II) sorption followed a second order kinetic model.

Keywords: Methyl acrylate; Grafted; OPEFB; Hydroxamic acid; Cu(II); Sorption

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INTRODUCTION

Removal and recovery of heavy metal ions from wastewater has become an important research area in terms of environmental issues in recent years. Ion exchange is one of the important techniques that have been developed for this purpose. Synthetic resins having functionalities to form chelate structures with metal ions have been used by many researchers for the removal and recovery of heavy metal ions in wastewater (Dinu and Dragan 2008). However, in many cases the petroleum-based synthetic copolymers such as styrene-divinyl benzene and xylene-aldehyde have been utilized (Lin and Juang 2005; Haron et al. 1994; Trivadi et al. 2002). Most petroleum-based synthetic polymers resin are in beads form and neither renewable nor biodegradable. Biomass is more biodegradable, and it could thus be an alternative and economical material for heavy metal removal from wastewater. Oil palm is one of the important economic plants of Malaysia, and the plantation area has been increased every year. Oil palm empty fruit bunch (OPEFB) is one of the biomass wastes of the oil palm industry (Law et al. 2007).

Therefore, the application of OPEFB for added-value purposes such as in sorption of heavy metals is worth exploring. However native OPEFB that contains about 70% cellulose and lignin generally have quite low carboxyl and other functional groups compared to what would be most suitable for metal chelating capability (Salamatinia et al. 2007). Hence, the fiber has to be functionalized by appropriate chelating functional groups before it can be used effectively to adsorb and hold onto heavy metals (Nada et al. 2007; Saito and Isogai 2005). In this research, the OPEFB was functionalized with the hydroxamic acid chelating group, which is capable to form a complex with Cu(II) (Kurzak et al. 1992). The functionalized OPEFB was characterized by FTIR spectroscopy and its sorption behavior towards Cu(II) from aqueous solution was studied. Parameters investigated included pH, initial metal concentration, temperature, and various kinetic parameters.

EXPERIMENTAL

Materials

OPEFB fiber was obtained from Sabutek Sdn. Bhd., Malaysia. The OPEFB obtained was ground to 100 to 200 μm and washed with hot water and then with acetone to remove oily matter from the fiber. It was then dried in an oven at 60 $^{\circ}\text{C}$ to constant weight. Methyl acrylate (MA) monomer, purity more than 99% was purchased from Fluka Chemie, Switzerland and purified by passing through a glass column packed with 20 cm height activated alumina (BDH). Hydroxylamine hydrochloride and copper sulphate pentahydrate were purchased from Fluka.

Methods

Graft copolymerization of methyl acrylate onto OPEFB

About 30 g of OPEFB and 500 ml distilled water were placed in a four-neck flask, which was equipped with a mechanical stirrer, nitrogen gas inlet, and condenser. To maintain an inert atmosphere, a flow of nitrogen gas was bubbled through the mixture for about 20 minutes and throughout the grafting procedure. Radical sites on the fiber were created with addition of 20 ml of hydrogen peroxide and stirred continuously for 10 minutes. About 1.6 g of ferrous ammonium sulfate was then added into the flask. After continuous stirring for another 10 minutes, 50 ml of methyl acrylate monomer was added. After stirring for 2 h, the polymerization product was filtered, washed several times with distilled water, and dried in an oven at 60 $^{\circ}\text{C}$ to a constant weight. The dried grafted product was extracted with acetone using a Soxhlet extractor for 24 hours to remove the ungrafted poly(methyl acrylate). The grafted fiber (PMA-g-OPEFB) was dried in an oven at 60 $^{\circ}\text{C}$ to a constant weight.

Preparation of PHA grafted OPEFB

Hydroxylamine solution was prepared by dissolving 10.0 g of hydroxylamine hydrochloride in 150 ml methanolic solution (methanol: water; 5:1). The pH of the mixture was adjusted to pH 13 by addition of 1M sodium hydroxide solution. About 10.0 g of PMA-g-OPEFB was placed in a two-neck round bottom flask, which was equipped

with a mechanical stirrer and condenser. Then, 150 ml hydroxylamine solution (prepared earlier) was added into the flask. The reaction was carried out at 75 °C for 2 hr. The product was washed several times with methanolic solution (methanol: water; 4:1). It was then treated with 100 ml of methanolic solution of 0.2 M HCl for 5 minutes. Finally, the fiber product was filtered and washed several times with methanolic solution and dried at 60 °C to constant weight.

Characterization of sorbent

About 0.1 g of PHA-OPEFB was reacted with vanadium (V) ion in dilute hydrochloric acid solution. A dark purple colored complex on the PHA-OPEFB will be formed if the sorbent contained hydroxamic acid group. The infrared spectra of OPEFB, PMA-g-OPEFB, and PHA-OPEFB samples were obtained by FT-IR spectrometer (Perkin-Elmer 1725) using KBr pellets.

Sorption capacity of Cu(II) by PHA-OPEFB.

Exactly 1.00 ml of 5000 ppm Cu(II) solution was pipetted into a series of 25 ml volumetric flasks. Then, 0.1 M sodium acetate buffer of various pH (pH 1, pH 2, pH 4, and pH 6) were added to the mark. The mixture was well-shaken. 20 ml of the solution was transferred into a 30 mL Nelgene polycarbonated centrifuge tubes that contained about 0.1 g PHA-OPEFB fiber. The remaining 5 ml of the solution was used for determination of Cu(II) initial concentration. The mixture of Cu(II) solution and PHA-OPEFB in the polycarbonated tube was shaken on a Hotech rotary shaker for about 16 hours. After equilibration, the fiber was filtered, and the filtrate was analysed for Cu(II) concentration. The initial and the equilibrium metal ion concentrations were determined by Inductive Couples Plasma Atomic Emission Spectrometer (ICP-AES) model Perkin Elmer 1000. The experiments were repeated for unmodified OPEFB. All sorption experiments were done in three replicates, and only the results of concentrations with relative standard deviation of below 10% were recorded. Sorption capacity was calculated as mg of metal ion sorbed per gram sorbent as below:

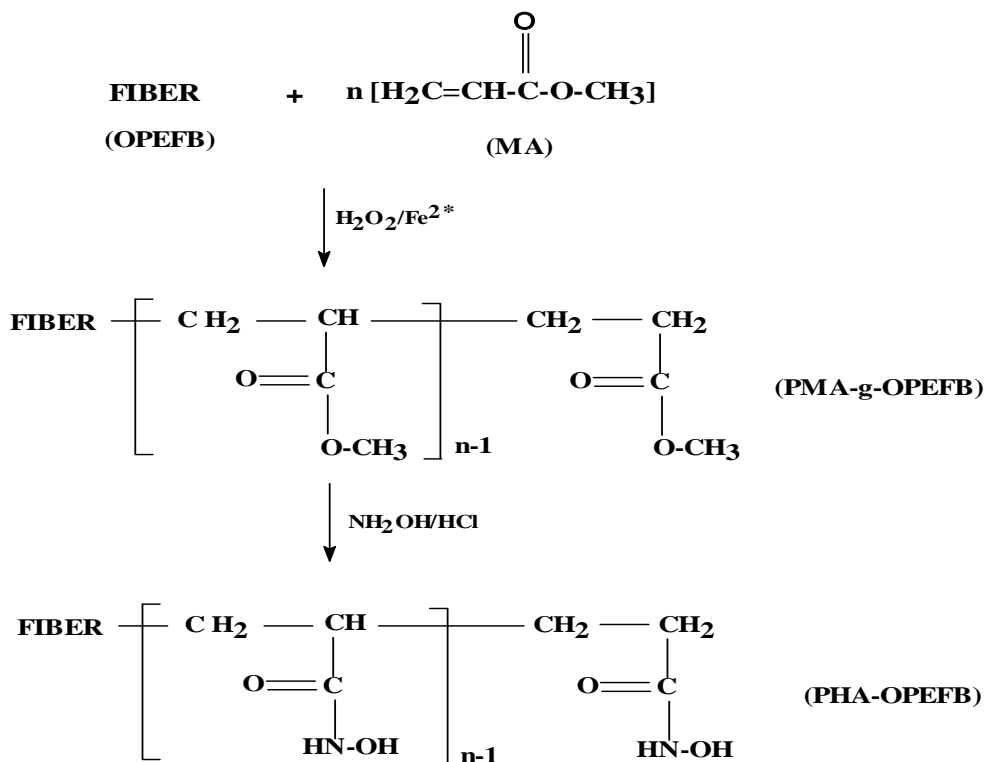
$$\text{Sorption capacity, } q = \frac{(C_o - C_e) \times V}{M} \quad (1)$$

where q (mg g⁻¹) is the amount of metal ion sorbed; C_o and C_e are initial and equilibrium concentrations of the metal ion in solution (mg L⁻¹), respectively; V (L) is the solution volume and M (g) is the weight of the sorbent. The sorption isotherm was obtained by shaking about 0.1000 g of PHA-OPEFB fiber in 20 mL of Cu(II) solutions of different concentrations (100, 200, 300, 400, 600, 800, 1000, 1500 mg L⁻¹) for 16 h at pH 4 and at 25 °C. The initial and the equilibrium Cu(II) concentration were measured and sorption capacity was calculated as above. The kinetic study was carried out by shaking about 0.1000 g of the PHA-OPEFB sorbent in 20 mL of 200 mg L⁻¹ of Cu(II) at various time periods (5, 10, 20, 30, 60, and 120 min) at 25 °C. The effect of temperature on the Cu(II) sorption was studied by equilibrating 0.1000 g of PHA-OPEFB fiber in 20 mL of 100 ppm Cu(II) solutions at 25, 50, and 70 °C.

RESULTS AND DISCUSSION

Characterization of PHA-OPEFB Fiber

The proposed reactions for the grafting of OPEFB fiber with PMA and its conversion to hydroxamic acid are outlined in Scheme 1 (Raju et al. 2007; Lutfor et al. 2001). FTIR spectra for raw OPEFB, PMA-g-OPEFB, and PHA-OPEFB are shown in Fig. 1. Generally as shown in the figure, broad absorption bands around 3600-3200 cm^{-1} could be seen in all spectra. This is attributed to O-H stretching vibration of cellulose, hemicelluloses, lignin, and the absorbed water constituents of OPEFB (Raju et al. 2007). The FTIR spectrum of PMA-g-OPEFB showed an intense absorption band at 1744 cm^{-1} , which is due to C=O vibrations in the grafted ester. The bands of lower frequencies (1456 and 1390 cm^{-1}), usually used to characterize a methyl group, were also present in the PMA-g-OPEFB spectrum. When PMA-g-OPEFB was functionalised with hydroxamic acid, the C=O band of 1744 cm^{-1} shifted to 1738 cm^{-1} , and new bands appeared at 1640 cm^{-1} , which can be related to C=O vibration in hydroxamic acid, and at the 1568 cm^{-1} , which was related to the N-H amide (Lutfor et al. 2001). The existence of a peak at around 2900 cm^{-1} in both grafted and ungrafted fiber could be due to C-H stretching. The presence of hydroxamic acid group was also evident by the vanadium (V) test, in which the brownish yellow color of the PHA-OPEFB fiber turns into a dark purple when reacted with acidic solution of vanadium (V) (Haron et al. 1994).



Scheme 1. The proposed reactions for the grafting of OPEFB fiber with PMA and its conversion to hydroxamic acid

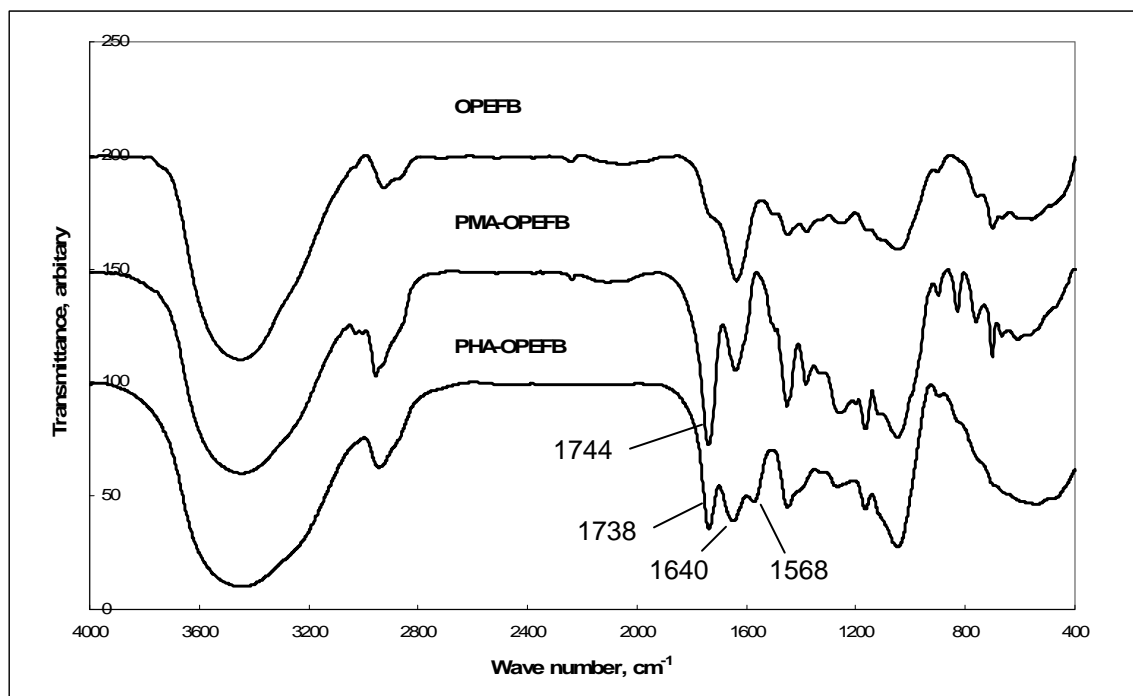


Fig. 1. FTIR spectra of OPEFB, PMA-OPEFB, and PHA-OPEFB

Effect of pH on Cu(II) Sorption

The pH of the aqueous solution is an important controlling parameter in many sorption processes (Ajmal et al. 1998). Sorption of Cu(II) onto PHA-OPEFB as a function of pH is shown in Fig. 2. It can be seen that the sorption capacity of the metal ion by PHA-OPEFB was clearly affected by the pH. The sorption capacity was low at pH 1.0 and increased as the pH increased to a maximum at about pH 4.0. However, the sorption decreased when pH was increased further. A similar trend of sorption was reported by Shah and Devi (1990) and Haron et al (1994) using synthetic polymer base poly(hydroxamic acid).

Figure 2 also shows that the sorption capacity of Cu(II) by unmodified OPEFB was much lower compared to PHA-OPEFB. The results confirmed that the sorption capacity of metal ion by OPEFB was very much improved after functionalized with a chelating group such as hydroxamic acid. The low sorption of Cu(II) by PHA-OPEFB at pH 1.0 could be due to the fact that there are more protons at lower pH available to protonate the active groups of the OPEFB surface, and compete with metal ions in the solution. At higher pH values, a greater number of deprotonated hydroxamic functional groups resulted in greater metal ion sorption. The pH in subsequent kinetic study and isotherm experiments were controlled at 4.0.

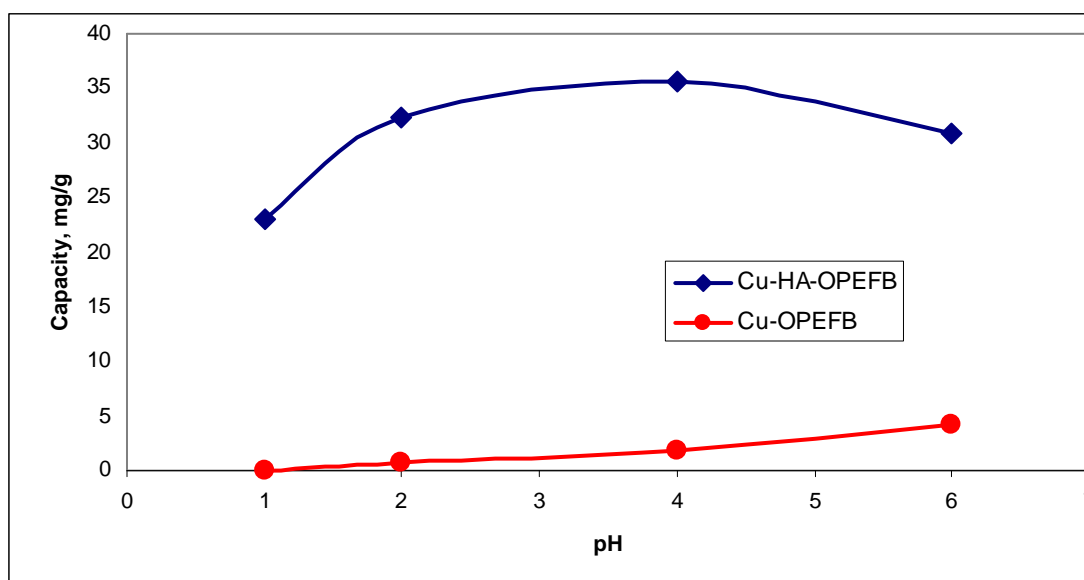


Fig. 2. The effect of initial pH on the sorption of Cu(II) by PMA-OPEFB and PHA-OPEFB. Conditions: C_0 : 200 mg/L; Contact time: 16 h; Temperature: 25 °C; Sorbent dosage concentration: 0.10 g/20 mL

Sorption Kinetics

Figure 3 shows the effect of contact time on sorption of 200 mg L⁻¹ Cu(II) at 25 °C. The amount of Cu(II) sorption sharply increased with increasing contact time in the initial stage (0–20 min), and then gradually increased to reach an equilibrium value in approximately 60 min. Accordingly, the contact time was fixed at 2 h for the rest of the experiments in order to ensure the equilibrium was reached. In order to investigate the mechanism of sorption of Cu(II) by PHA-OPEFB and the potential rate-controlling steps, such as mass transport and chemical reactions, Lagergren's pseudo first-order and pseudo second-order kinetic models (Ho and McKay 1998) were applied to evaluate the experimental data. The pseudo first-order Lagergren's model is expressed as,

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

where q_t (mg g⁻¹) and q_e (mg g⁻¹) are the amounts of sorbate on the sorbent at time t (min) and equilibrium, respectively, and k_1 (min⁻¹) is the first-order kinetic rate constant. The parameters k_1 and q_e were determined from the slope and intercept of the straight line plot of $\log(q_e - q_t)$ versus t (not shown), respectively, and are given in Table 1. Although the correlation coefficient value (R^2) of the plot is reasonably high (0.959), the experimental q_e values do not agree with the calculated value obtained from the linear plots (Table 1). The equation for pseudo-second-order model can be written as:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{q_e^2 k_2} \quad (3)$$

where k_2 ($\text{g} (\text{mg min})^{-1}$) is the second-order rate constant, and q_t (mg g^{-1}) and q_e (mg g^{-1}) are as defined above. A plot of t/q_t versus t gave a straight line (not shown) and the values of q_e and k_2 were determined from the slope and intercept of the plot, respectively. The corresponding parameters and regression coefficients for the model are given in Table 1. As can be seen in Table 1, the good fit ($R^2 = 0.999$) was obtained and the theoretical

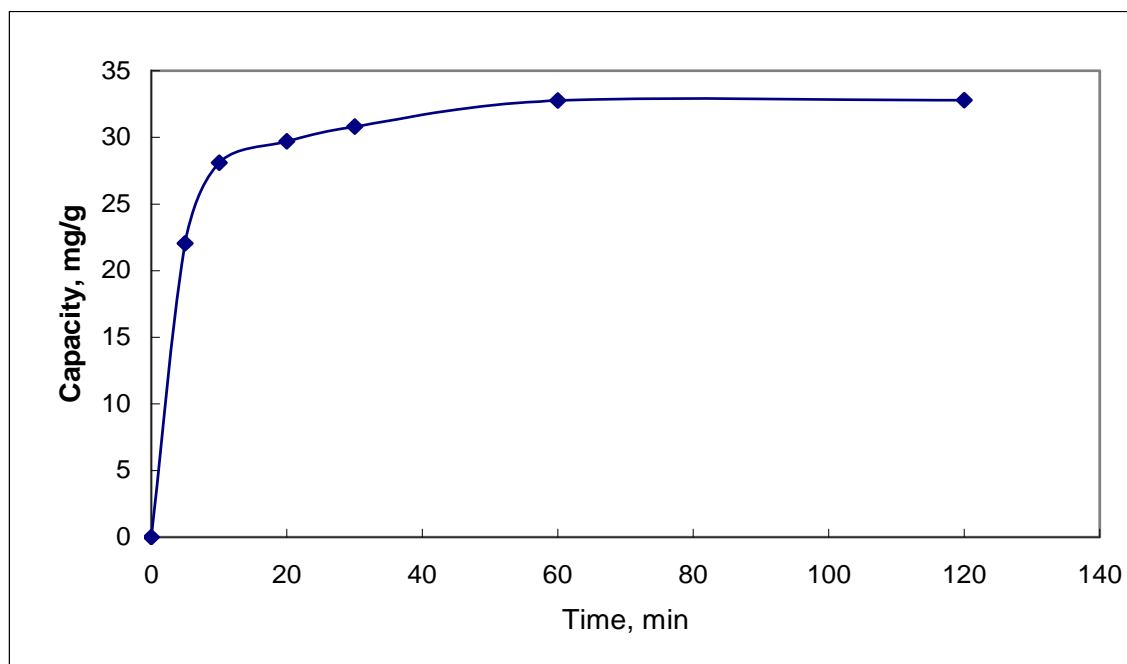


Fig. 3. Effect of contact time on the sorption of Cu(II). Conditions: pH: 4.0; Temperature: 25 °C; sorbent dosage : 0.10 g/20 mL

Table 1. Kinetic Parameters of the Pseudo-first and Pseudo-second Order Model for Cu(II) Sorption by PHA-OPEFB

	Experimental	Pseudo-first order	Pseudo-second order
	q_e	k_1 (min^{-1})	k_2 ($\text{g mg}^{-1}\text{min}^{-1}$)
Rate constant	-	0.113	0.013
q_e (mg g^{-1})	32.8	25.8	33.5
R^2	-	0.959	0.999

values of q_e also agree well with the experimental values, indicating that the sorption conformed to the pseudo-second-order reaction mechanism and the adsorption rate was controlled by chemical sorption (Dogan et al. 2004).

Effect of Initial Cu(II) Concentration and Adsorption Isotherms

Figure 4 presents the experimental adsorption isotherms of Cu(II) on PHA-OPEFB. It can be seen that q_e increases initially with an increase of C_e until equilibrium is reached, thereafter q_e remains constant with further increase of C_e . Langmuir, BET and Freundlich models were used to describe the equilibrium sorption isotherms (Araujo et al. 2007). The Langmuir isotherm assumes monolayer coverage of sorbate over a

homogeneous sorbent surface, and the sorption of each ion on the surface has equal adsorption activation energy. The BET model extends the Langmuir isotherm for multilayer sorption. On the other hand, the Freundlich isotherm supposes a heterogeneous surface with a nonuniform distribution of energy of sorption over the surface, and a multilayer sorption can be assumed. The amount of Cu(II) sorbed q_e (mg g^{-1}) at an equilibrium metal concentration of C_e (mg L^{-1}) can be related by the Langmuir equation as

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \quad (4)$$

where q_{\max} is the theoretical monolayer saturation capacity (mg g^{-1}), and K_L is the adsorption constant (L mg^{-1}) that relates to the affinity of the binding sites. The plot of C_e/q_e versus C_e gave a straight line (Fig. 5) with slope of $1/q_{\max}$ and intercept of $1/q_{\max}b$. The BET equation can be written as

$$\frac{C_e}{(C_s - C_e)q_e} = \frac{1}{K_B q_{\max}} + \left(\frac{K_B - 1}{K_B q_{\max}} \right) \left(\frac{C_e}{C_s} \right) \quad (5)$$

where C_s is the saturation concentration of solute (mg/L) and K_B is the BET constant expressive of energy of interaction between the solute and the surface of the adsorbent.

K_B and q_{\max} can be calculated from the slope and the intercept of plot of $\frac{C_e}{(C_s - C_e)q_e}$ versus C_e/C_s as shown in Fig. 6. On the other hand the Freundlich equation can be expressed as

$$\text{Log } q_e = \text{Log } K_F + \frac{1}{n} \text{Log } C_e \quad (6)$$

where K_F and $1/n$ are Freundlich isotherm constants related to sorption capacity and intensity of sorption, respectively. A plot of $\log q_e$ versus $\log C_e$ gave a straight line (Fig. 7) with the slope of $1/n$ and intercept of K_F . The Langmuir, BET, and Freundlich constants evaluated from the isotherms with the correlation coefficients are listed in Table 2. The results show that the equilibrium data agreed well to the Langmuir model, with a high coefficient of determination, R^2 . The maximum monolayer capacity q_{\max} was found to be 74.1 mg/g . The value of the Freundlich constant, $1/n$ obtained indicates favorable sorption, since it lies between 0 and 1. A comparison of the maximum sorption capacity of PHA-OPFB with other natural fiber reported in literatures is given in Table 3. The data show that the sorption capacity of PHA-OPEFB was much higher compared to untreated OPEFB, as reported by Salamatina et al. (2007), and to some other untreated and treated fibers.

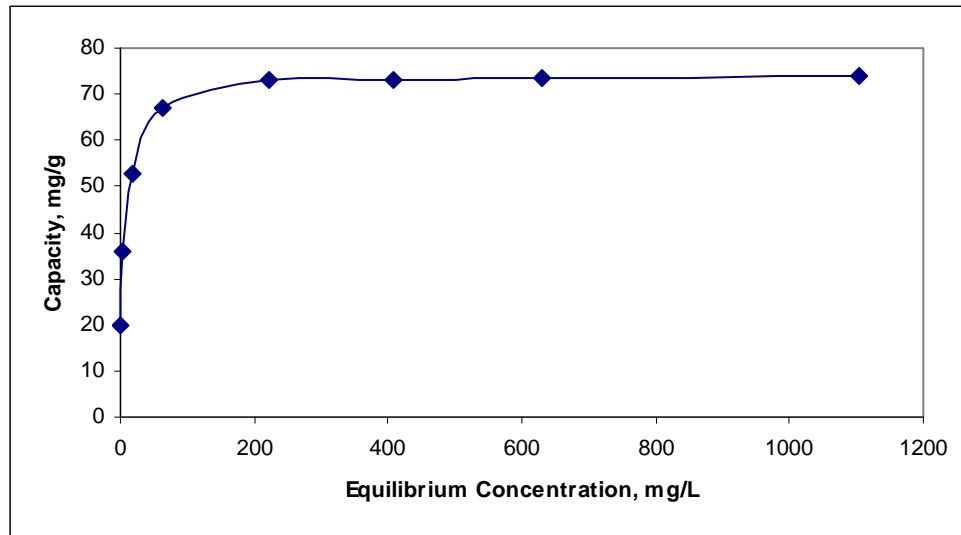


Fig. 4. Effect of initial Cu(II) concentration on sorption capacity. Conditions: pH: 4.0; Temperature: 25 °C; sorbent dosage : 0.10 g/20 mL.

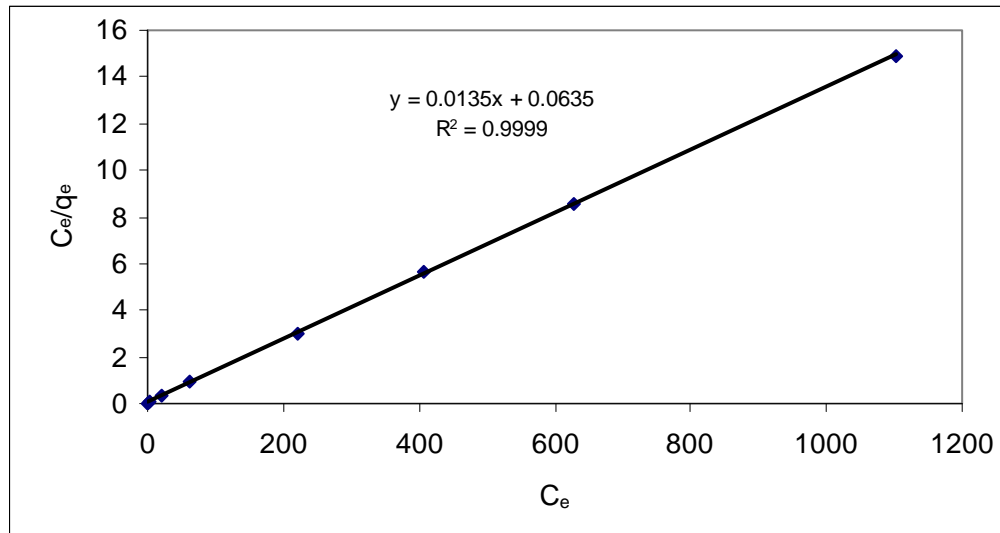


Fig. 5. Langmuir isotherm for Cu(II) sorption by PHA-OPEFB

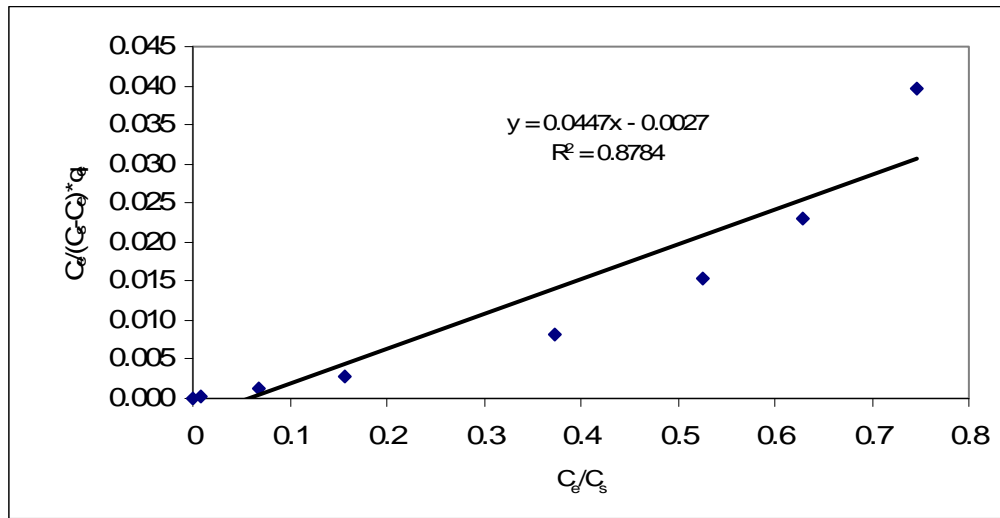


Fig. 6. BET isotherm for Cu(II) sorption by PHA-OPEFB

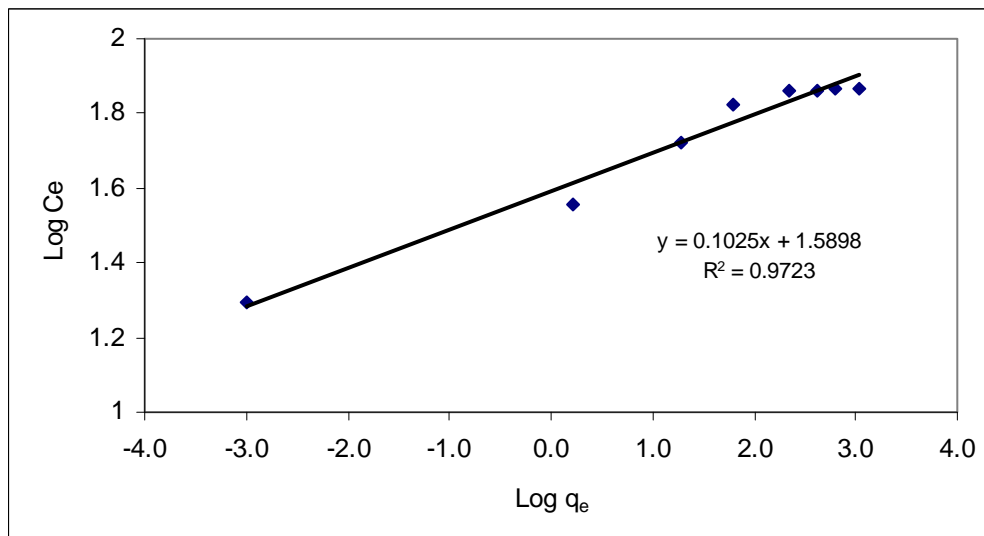


Fig. 7. Freundlich isotherm for Cu(II) sorption by PHA-OPEFB.

Table 2. Langmuir, BET and Freundlich Constants for Sorption of Cu(II) by PHA-OPEFB Fiber

Isotherm	q_{\max} mg/g	K_L L/mg	K_B	K_F L/g	$1/n$	R^2
Langmuir	74.1	0.2125	-	-	-	0.999
BET	21.1	-	17.5	-	-	0.878
Freundlich	-	-	-	38.8	0.102	0.972

Table 3. Cu(II) Sorption Capacities for Various Treated and Untreated Natural Fiber

Adsorbents	Adsorption Capacity, mg/g	pH	Adsorption isotherm/ constant mg/g	Reference
Dye treated oil palm fiber	15.87	4.0	Langmuir	Low et al. 1993
TEMPO oxidized cotton fiber	5.5	3.1	NA	Saito and Isogai 2005
Dye loaded jute	8.40	6.5	Langmuir	Shukla and Pai 2005
HCl treated palm kernel fiber	13.08	NA	Second order	Ho and Ofamaja 2006
Pine bark	24.1	5.1	Langmuir	Oh and Tshabalala 2007
OPEFB	3.6	-	-	Salamatina et al. 2007
Base treated rubber leaves	14.97	4.0	Langmuir	Wan Ngah and Hanafiah 2008
Newspaper pulp	27.77	5.8	Langmuir	Chakravarty et al. 2008
Carboxymethylated-bacterial cellulose	20.35	4.5	Langmuir	Chen et al. 2009
Cone of Pinus Sylvestris	28.83	4.0	Langmuir	Ucun et al. 2009
Barly Straw	67.08	6.0	Langmuir	Pehlivan et al. 2009
PHA-OPEFB	74.1	4	Langmuir	This study

Thermodynamics of the Sorption

The values of distribution coefficients, K_D (mL g^{-1}), from Cu(II) sorption at an initial concentration of 100 mg L^{-1} decreased as temperature increased from 25 to 70 °C, indicating that the sorption is an endothermic process. The relationship between K_D and T is given by the Van't Hoff equation,

$$\ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (7)$$

where ΔS^0 = standard entropy, ΔH^0 = standard enthalpy, T = absolute temperature (K), and R = gas constant. The values of ΔH^0 and ΔS^0 were calculated from the slopes and intercepts of linear regression of the plots of $\ln K_D$ versus $1/T$ (not shown). The standard Gibbs free energy, ΔG^0 , value was calculated from the equation:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (8)$$

The values of ΔH° and ΔS° were $-61.29 \text{ kJ mol}^{-1}$ and $-123.27 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The negative value of ΔH° confirmed that the sorption reaction of Cu(II) on PHA-OPEFB was exothermic. The decrease in ΔS° is expected, since the Cu(II) sorption on the fiber reduced the randomness of the system (Zhang et al. 2007). The free energy, ΔG° values were -24.55 , -21.47 , and $-19.00 \text{ kJ mol}^{-1}$ at 25, 50, and 70 °C, respectively, showing that the sorption was spontaneous at all temperatures studied. The decrease in the value of ΔG° with increasing temperature shows that the reaction was favorable at lower temperature. The change of standard free energy for the sorption at 25 and 50 °C was in the range between -20 and -80 kJ/mol , indicating that the sorption process was physical sorption together with chemisorption (Yu et al. 2001).

CONCLUSIONS

1. OPEFB was successfully functionalised with hydroxamic groups via grafting with PMA and reaction with hydroxylamine, and used for sorption of Cu(II) from aqueous solution.
2. Sorption of Cu(II) by PHA-OPEFB is effective over a pH range of 4 to 6. The sorption capacity was much higher compared to original OPEFB.
3. Sorption of Cu(II) follows the second order kinetic and the Langmuir isotherm models with maximum capacities of 74.1 mg g^{-1} at 25 °C.
4. The sorption process is exothermic, as shown by the negative value of enthalpy change, ΔH° . The free energy change (ΔG°) for the sorption was negative, showing that the sorption process is spontaneous.
5. The PHA-OPEFB has a potential to be used as sorbent for removal of Cu(II) from aqueous systems.

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