Biosorption of copper ions from dilute aqueous solutions on base treated rubber (*Hevea brasiliensis*) leaves powder: kinetics, isotherm, and biosorption mechanisms

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Abstract

The efficiency of sodium hydroxide treated rubber (*Hevea brasiliensis*) leaves powder (NHBL) for removing copper ions from aqueous solutions has been investigated. The effects of physicochemical parameters on biosorption capacities such as stirring speed, pH, biosorbent dose, initial concentrations of copper, and ionic strength were studied. The biosorption capacities of NHBL increased with increase in pH, stirring speed and copper concentration but decreased with increase in biosorbent dose and ionic strength. The isotherm study indicated that NHBL fitted well with Langmuir model compared to Freundlich and Dubinin-Radushkevich models. The maximum biosorption capacity determined from Langmuir isotherm was 14.97 mg/g at 27°C. The kinetic study revealed that pseudo-second order model fitted well the kinetic data, while Boyd kinetic model indicated that film diffusion was the main rate determining step in biosorption process. Based on surface area analysis, NHBL has low surface area and categorized as macroporous. Fourier transform infrared (FT-IR) analyses revealed that hydroxyl, carboxyl, and amino are the main functional groups involved in the binding of copper ions. Complexation was one of the main mechanisms for the removal of copper ions as indicated by FT-IR spectra. Ion exchange was another possible mechanism since the ratio of adsorbed cations (Cu^{2+} and H^+) to the released cations (Na^+, Ca^{2+}, and Mg^{2+}) from NHBL was almost unity. Copper ions bound on NHBL were able to be desorbed at > 99% using 0.05 mol/L HCl, 0.01 mol/L HNO_3, and 0.01 mol/L EDTA solutions.

Key words: copper; treated rubber leaves powder; kinetics; isotherm; ion exchange; desorption

Introduction

Heavy metal ions have been known to be widely discharged into water bodies from industries such as metal plating, pigments, batteries, electrical, tannery, paints, oil refining, and chemical manufacturing. Different methods of treating wastewater containing heavy metal ions have been developed over years which include coagulation, ion-exchange, membrane separation, reverse osmosis, solvent extraction, chemical precipitation, electroflotation etc. (Namasivayam and Ranganathan, 1995). However, the above mentioned methods are effective for treating high concentrations of heavy metal ions. For low concentration of heavy metal ions (< 100 mg/L), adsorption is a much preferable technique and activated carbon has been widely applied for treating industrial wastewater. For the past few decades, attention has been devoted to develop adsorbents from agricultural byproducts, also called biosorbents as alternatives to activated carbon.

Biosorbents are much cheaper since they are highly abundant and have very little or no economic values. The removal of heavy metals by biosorbents has been extensively reviewed by Bailey *et al.* (1999). To enhance the biosorption capacity of biosorbents, numerous types of modifying agents have been applied. Among them are acids (tartaric, hydrochloric, nitric, sulfuric, thioglycollic, and citric acids), bases (sodium hydroxide, sodium carbonate, calcium hydroxide), oxidizing agent (hydrogen peroxide), organic compounds (ethylenediamine, formaldehyde, methanol, epichlorohydrin), dyes, etc. (Wan Ngah and Hanafiah, 2008). Plant wastes have various functional groups such as carboxyl, hydroxyl, sulfate, phosphate, ether and amino groups which act as binding sites for heavy metal ions. Previous studies showed that sodium hydroxide treated sawdust and cork powder had good removal efficiency towards copper ions (Šćiban *et al.*, 2006, Chubar *et al.*, 2004). Base treatment could remove base dissolved materials and could convert the ester groups in biosorbent to carboxylate, a more effective functional group for biosorbing heavy metal ions (Min *et al.*, 2004). Malaysia is one of the main exporters of natural rubber in the world and more than 1.2×10^6 hm² of lands are planted with rubber trees. The large amount of unutilized solid wastes generated from rubber plantations could be used as low cost biosorbents for removal of heavy metal ions. In this work, the usefulness of base treated

rubber leaves powder for the removal of copper ions has been investigated.

The main objectives of this work were: (1) to evaluate the effects of physicochemical parameters on copper removal such as stirring speed, pH, biosorbent dose, initial concentration of copper, and ionic strength; (2) to determine the maximum biosorption capacity of treated rubber leaves powder (NHBL) based on several isotherm models; (3) to discuss the mechanisms of copper biosorption on NHBL; and (4) to determine the desorption percentage of copper ions using various concentrations of desorbing solutions such as HCl, HNO₃, and EDTA.

1 Materials and methods

1.1 Copper solutions

All chemicals used were analytical reagent grade. The stock solution of 1,000 mg/L Cu(II) was prepared by dissolving 1 g of copper metal supplied by BDH Chemicals (England) in 10 ml of concentrated nitric acid in a 100-ml beaker. After the copper metal dissolved, the solution was transferred to a 1-L volumetric flask and diluted to the mark with distilled water. Experimental solutions of the desired copper concentrations were obtained by successive dilutions.

1.2 Preparation of sodium hydroxide treated rubber leaves

Fresh mature rubber leaves were collected during the dry period (February to March, 2007) from a rubber plantation in Jengka, Malaysia. The leaves were washed with running water to remove dust and soluble impurities, dried overnight in an oven at 80°C, ground and sieved to obtain particle size of < 500 μm. A preliminary experiment was conducted to determine the optimum concentration of base and optimum treatment time for achieving maximum copper removal. For determining the optimum concentration of base, a known weight of rubber leaves powder was mixed with 0, 0.10, 0.25, and 0.50 mol/L NaOH at a ratio of 1:15 (*W/V*), stirred at 400 r/min for 30 min. Treatment of rubber leaves with 0.50 mol/L NaOH for 60 and 120 min was also conducted for determining the optimum treatment time. After each base treatment, the leaves powder were filtered, washed extensively with distilled water until the final pH of the washing reached neutral and dried in an oven at 80°C. The treated rubber leaves powder was sieved to obtain the average particle size of 427 μm.

1.3 Batch biosorption studies

Preliminary experiments on the maximum percentage biosorption of copper ions by different base treatment conditions of NHBL was performed by mixing 0.10 g of NHBL with 50 ml of 10 mg/L copper solutions, stirred for 60 min while the initial pH of copper solutions was fixed at 4. Treatment of rubber leaves with 0.50 mol/L NaOH for 30, 60, and 120 min resulted in 87.2%, 87.4%, and 87.7% copper removal, respectively. The treatment of rubber leaves with 0, 0.10, and 0.25 mol/L NaOH for 30 min reduced the copper removal to 71.0%, 76.5%,

and 83.4%, respectively. Based on the above results, concentration of NaOH plays a more important role in the amount of copper removal compared to treatment time. For subsequent biosorption studies, base treated rubber leaves were prepared by treating rubber leaves with 0.50 mol/L NaOH for 30 min.

All biosorption experiments were conducted in duplicates and the results are reported as average. In general, the effects of stirring speed, pH, biosorbent dose, and ionic strength on copper removal were performed at room temperature (27 ± 1°C) in conical flasks by stirring a mass of 0.10 g (unless otherwise stated) of NHBL with 50 ml of 5 mg/L copper solutions. The initial pH of copper solutions was fixed at 4 (unless otherwise stated) by addition of 0.1 mol/L HCl or NaOH solutions. The effect of stirring speed was investigated by varying the stirring speed from 100 to 600 r/min. The effect of pH was investigated over a pH range 2–5. To evaluate the contact time necessary to reach the equilibrium state, kinetic studies were carried out by varying the stirring time (0–90 min) using four different concentrations of copper (3, 5, 7, and 10 mg/L). The effect of biosorbent dose was studied by varying the amounts of NHBL from 0.02 to 1.0 g. For isotherm study, 0.10 g of NHBL was mixed with 50 ml of copper solutions at various concentrations (5–50 mg/L) and the initial pH of the solutions was fixed at 4. The effect of ionic strength was studied using NaCl as the ionic medium. The concentration of this salt was varied within the range 0.10–1.0 mol/L. For desorption study, HCl, HNO₃, and EDTA were chosen as the desorbing solutions. After contacting NHBL with 5 mg/L of copper solution for 60 min, the biosorbent was filtered, dried, and then mixed with 50 ml of different concentrations of desorbing solutions (10^{-4}–10^{-1} mol/L). The mixture was stirred at 400 r/min for 30 min, filtered and analyzed. A blank was also carried out in which deionized water was used for desorbing copper. The amount of Cu(II) ions in the solutions before and after biosorption was analyzed by atomic absorption spectrometer (Analyst 200 AA, PerkinElmer, USA) at a wavelength of 324.7 nm. The amount of copper adsorbed, q_e (mg/g) was computed by using the following expression:

$$q_e = \frac{C_0 - C_e}{m} V \tag{1}$$

where, C_0 (mg/L) and C_e (mg/L) are copper concentrations before and after adsorption, respectively; V (L) is the volume of copper solution, and m (g) is the weight of the adsorbent. The removal percentage (R) of copper is calculated by the following equation:

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \tag{2}$$

The desorption percentage (D_P) of copper ions is defined as:

$$D_P = \frac{C_{e(des)}}{C_{e(ads)}} \times 100\% \tag{3}$$

where, $C_{e(des)}$ (mg/L) and $C_{e(ads)}$ (mg/L) are copper concentrations desorbed from NHBL and adsorbed at equilibrium, respectively.

1.4 Characterization of NHBL

Characterization of a biosorbent is an important analysis for understanding the behaviour or the mechanism of copper removal on the surface of treated biosorbent. Analysis on the functional groups of NHBL was performed using Fourier transform infrared spectrophotometer (FT-IR, System 1600, PerkinElmer, USA) in the range of 400–4000 cm^{-1}. The surface structure of NHBL was observed by scanning electron microscope (Leo Supra 50VP, Carl-Ziess SMT, Germany) with energy dispersive spectroscopy (EDS). The surface area and average pore diameter were determined using a Micromeritics ASAP 2010 gas adsorption surface analyzer (Delta Analytical Instruments Inc., USA). The total content of carbon, hydrogen, nitrogen and oxygen in NHBL was determined by CHNS/O analyzer (Series II CHNS/O Analyzer 2400, PerkinElmer, USA).

1.5 Ion exchange studies

For these experiments, 0.10 g of NHBL was mixed with 50 ml of copper solution (10 mg/L) at pH 4. Two parallel blanks were also carried out; one without any copper ions and the other without any NHBL. All the solutions were stirred at 400 r/min for 1 h. The amounts of cations (Ca^{2+}, Mg^{2+}, Na$^+$) released from NHBL and adsorbed (Cu^{2+} and H$^+$) were measured. The release of cations from the blanks was also measured. The net release of cations due to copper biosorption was calculated by subtracting the amount of cations released from blanks to the amount of cations measured in the effluent after biosorption.

2 Results and discussion

2.1 Characterization of NHBL

The contents of carbon, hydrogen, and nitrogen in NHBL are slightly lower than raw rubber leaves due to the removal of base dissolved materials (Table 1). The surface area of NHBL is also lower than the raw rubber leaves. The low values of surface areas indicate low porosity of NHBL.

Pore sizes are classified in accordance with the classification adopted by the International Union of Pure and Applied Chemistry (USA), that is, micropores (diameter (d) < 20 × 10^{-10} m), mesopores (20 × 10^{-10} m < d < 500 × 10^{-10} m), and macropores (d > 500 × 10^{-10} m). Fig.1 shows that NHBL has a high proportion of pore diameter larger than 500 × 10^{-10} m, therefore NHBL can

Table 1   Characteristics of raw rubber leaves and sodium hydroxide treated rubber leaves powder (NHBL)

Parameter	Raw rubber leaves	NHBL
Carbon (%)	50.23	48.59
Hydrogen (%)	6.63	6.51
Nitrogen (%)	1.09	0.99
Oxygen (%)	42.06	43.91
S_{BET} [a] (m^2/g)	0.478	0.436
S_L [b] (m^2/g)	0.728	0.695
D_p [c] (× 10^{-10} m)	154.6	113.4

[a] BET surface area; [b] Langmuir surface area; [c] average pore diameter (BJH).

be categorized as macroporous biosorbent.

The SEM image of NHBL after copper biosorption is shown in Fig.2. NHBL is a porous biosorbent and has irregular structure, which favours the biosorption of Cu(II) ions on different parts of the biosorbent. The EDS spectra (Fig.3) indicate that the NHBL consist of mainly C and O, and trace amounts of Mg and Ca. Magnesium ions in plant leaves can form complexes with chlorophyll molecules (Fernandes *et al.*, 2007) while Ca(II) ions can bind with phosphates groups (Panda *et al.*, 2007). After biosorption, Ca and Mg peaks diminished and the copper peaks in the spectra are visible, suggesting ion-exchange might be one of the mechanisms involved in copper removal. The presence of Au peaks in both spectra is due to the gold purposely settled to increase electric conduction and to improve the quality of the images.

The FT-IR spectrum of NHBL powder displays a number of absorption peaks (Fig.4), which indicates the presence of different types of functional groups in the biosorbent. The broad and strong band ranging from 3000–3600 cm^{-1} indicates the presence of –OH and –NH groups, which is consistent with the peak at 1060 and 1163 cm^{-1} assigned to alcoholic C–O and C–N stretching vibration. The peaks at 2920 and 2851 cm^{-1} can be assigned to asymmetric and symmetric CH$_2$ groups. The peak located at 1734 cm^{-1} is a characteristic of carbonyl group stretching from carboxylic acid or ester groups. The peak at 1636
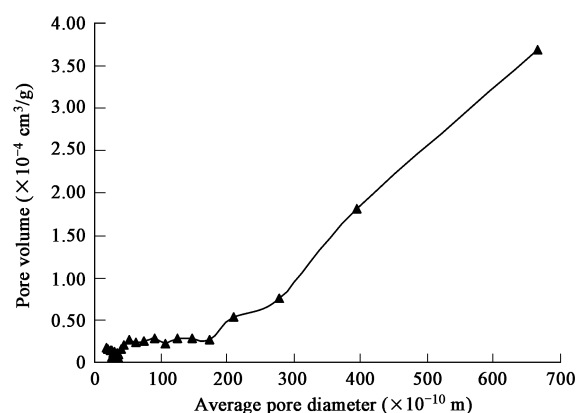

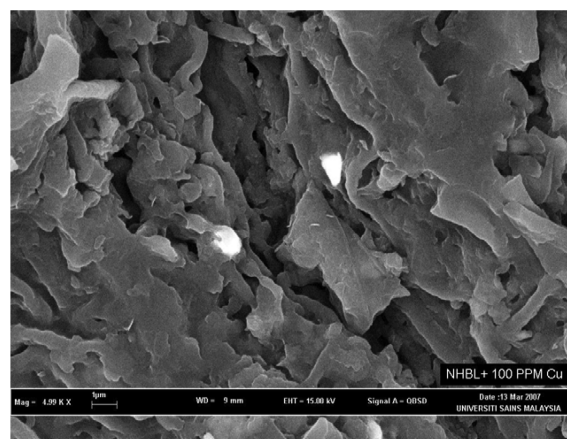**Fig. 1**   Average pore diameter plot of NHBL.

Fig. 2   SEM image of NHBL after copper biosorption at 5000× magnification.
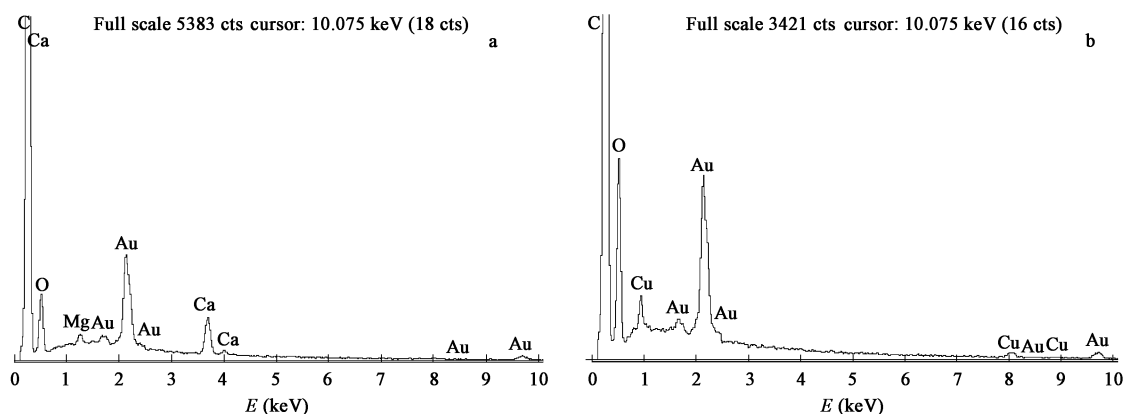
Fig. 3   EDS spectra of NHBL before (a) and after (b) copper biosorption.

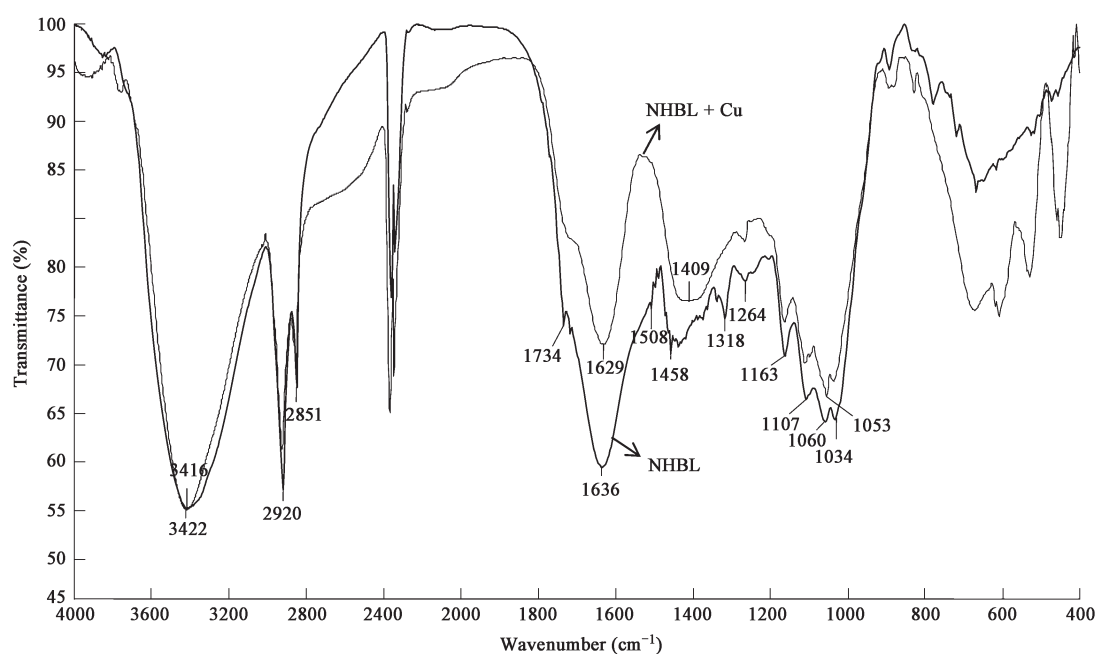**Fig. 4**   FT-IR spectra of NHBL before and after copper biosorption.

cm^{-1} corresponds to the carboxylate (COO^-) or $C=C$ groups. The peak at 1264 cm^{-1} can be attributed to the C–O stretching of phenolic groups. The wavenumbers at 900 to 1034 cm^{-1} are due to the presence of P–O–C and P–O–H link to the organic phosphorous groups. The FT-IR spectrum for copper loaded biosorbent showed wavenumber and intensity of some peaks were shifted or substantially lower than those before biosorption, suggesting the participation of –OH, –COO^-, and –NH_2 in the binding of copper by NHBL. The wavenumbers of NHBL shifted from 3421, 1636, and 1060 cm^{-1} to 3416, 1629, and 1053 cm^{-1}, respectively, after copper uptake. The peak at 1508 cm^{-1} attributed to N–H bending disappeared after copper uptake. In general, hydroxyl, carboxyl, and amino groups are the main functional groups involved in the binding of copper ions. Thus, the mechanism of copper binding on NHBL could also occur by surface complexation.

2.2 Effect of stirring speed

The lowest biosorption capacity (2.05 mg/g) was recorded at the lowest stirring speed (100 r/min), and increased as the stirring speed increased to 400 r/min (Fig.5). The highest biosorption capacity (2.26 mg/g) was recorded at 400 r/min and declined slightly as the speed increased to 600 r/min. The increase in biosorption capacity at a high stirring speed could be explained in terms of boundary layer thickness. By increasing the stirring speed, a good degree of mixing could be achieved, and the boundary layer thickness around the biosorbent particles could be reduced. Hence, the concentration of copper ions near the surface of biosorbent would be increased. However, a more vigorous stirring speed resulted in more copper ions being desorbed from the biosorbent surface, which suggests a possible breaking of newly formed bonds between copper ions and biosorbent surface (Argun *et al.*, 2007). Therefore, stirring speed of 400 r/min was selected for subsequent biosorption
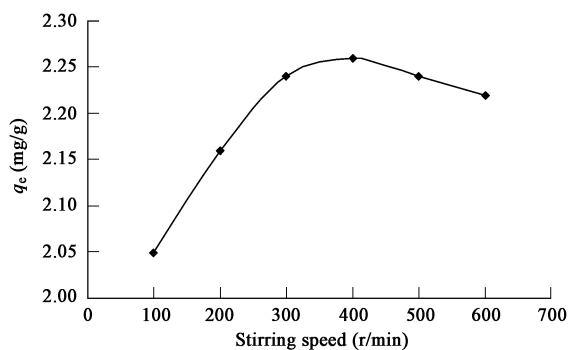
Fig. 5 Effect of stirring speed on copper biosorption.

analyses for NHBL.

2.3 Effect of solution pH

pH of metal solutions has been identified as one of the most important variables in biosorption process (Wan Ngah *et al.*, 2002). Solution pH can affect the chemical speciation of copper ions and surface binding sites of the biosorbent. Based on the speciation diagram of copper (Wang and Qin, 2005), Cu^{2+} is the dominant species at pH < 5. Biosorption experiments were not conducted at pH beyond 5 due to possible precipitation of $Cu(OH)_2$ (Reddy *et al.*, 1997). At pH 2, copper ions could not be adsorbed on NHBL (Fig.6). In this strong acidic medium, the surface of NHBL would be surrounded by H_3O^+ ions which resulted in greater repulsive force between Cu^{2+} and binding sites. With increasing pH, the competing effect of hydronium ions decreases and the positively Cu^{2+} ions could adsorb on the free binding sites of the biosorbent. Furthermore, an increase in solution pH would cause more ligands such as amino, hydroxyl, and carboxyl groups to carry negative charges with subsequent attraction of copper ions (Aksu, 2001). An increase in biosorption capacity occurred at pH range 3–4 and remained constant after pH 4. The biosorption capacities at pH 3, 4, and 5 were 1.73, 2.27, and 2.28 mg/g, respectively. Based on these results, it can be concluded that no significant change in the amount of copper adsorbed was observed after pH 4.

2.4 Effect of biosorbent dose

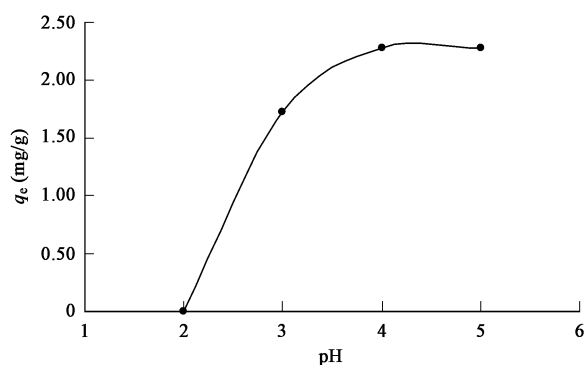The dependence of copper biosorption on the amount of

Fig. 6 Effect of pH on copper biosorption by NHBL. Conditions: biosorbent weight 0.10 g; volume 50 ml; stirring speed 400 r/min.

NHBL was studied at pH 4 by varying the biosorbent dose from 0.02 to 1.0 g, while keeping Cu concentration constant (50 ml of 5 mg/L). It can be seen that the copper removal increased from 66.75% to 93.98% as the dose was increased from 0.02 to 1.0 g (Fig.7). Even at a very low dose (0.02 g), NHBL was able to remove more than 66% of Cu(II). However, an increase in biosorbent dose was linked with the decrease in biosorption capacities (mg/g). According to Han *et al.* (2007), an increase in biosorbent dose resulted in surplus of biosorption sites. These biosorption sites remained unsaturated during biosorption, thus the values of metal biosorbed per unit weight of biosorbent (mg/g) decreased.

2.5 Effects of copper concentration and contact time

As shown in Fig.8, the biosorption capacities of NHBL at equilibrium increased from 1.41 to 4.52 mg/g as the copper concentrations increased from 3 to 10 mg/L. The time taken to reach equilibrium for all copper concentrations was 60 min. The plots showed that the biosorption of copper consisted of two main stages: an initial rapid stage where biosorption was fast and is related to external surface biosorption, and a second slow stage which refers to gradual biosorption stage before copper uptake reached equilibrium. According to Malkoc and Nuhoglu (2005), the initial copper concentration provides an important
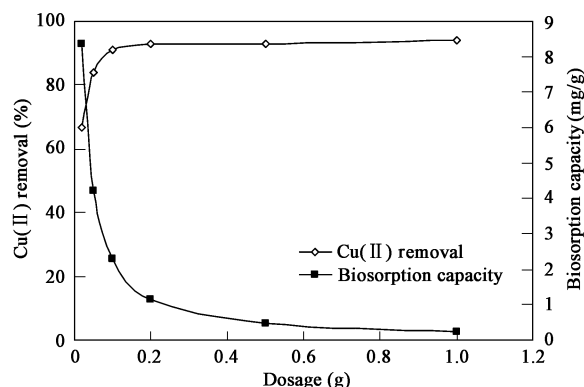

Fig. 7 Amount of Cu(II) ions removed and adsorbed at different biosorbent doses.
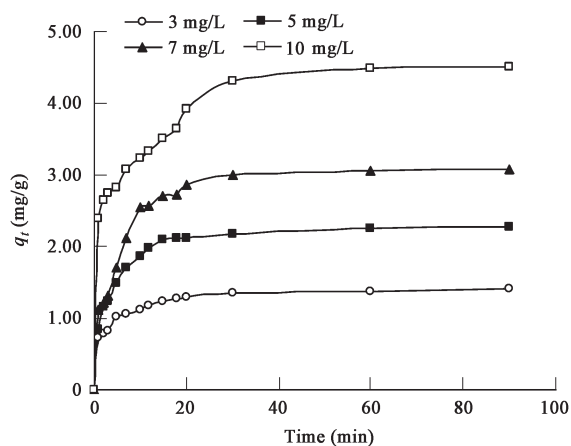

Fig. 8 Effect of initial copper concentration and contact time on copper biosorption by NHBL. Conditions: biosorbent weight 0.10 g; pH 4; volume 50 ml; stirring speed 400 r/min.

driving force to overcome the mass transfer resistance of copper ions between the aqueous and solid phases, therefore the high copper concentration will increase the biosorption capacity.

2.6 Biosorption kinetic models

Biosorption kinetics is important in a biosorption process. Different kinds of kinetic models such as pseudo-first order (Ho and McKay, 1998), pseudo-second order (Ho and McKay, 2000), and Boyd kinetic (Boyd *et al.*, 1947) models were applied for biosorption of copper on NHBL. The pseudo-first order kinetic equation is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{4}$$

where, q_t (mg/g) and q_e (mg/g) is the amount of copper adsorbed at time t (min) and at equilibrium, respectively. k_1 (min^{-1}) is the rate constant of the pseudo-first order biosorption process. Straight-line plots of $\log(q_e - q_t)$ against t were used to determine the rate constants, k_1 and correlation coefficients, R^2 for different copper concentrations (Fig.9a). Although these plots show good linearity, the values of calculated adsorption capacities ($q_{e, cal}$) are different from the experimental ones ($q_{e, exp}$) (Table 2), suggesting that biosorption reaction is not of pseudo-first order.

The pseudo-second order chemisorption rate equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \tag{5}$$

where, $h = k_2 q_e^2$ can be regarded as the initial biosorption rate as $t \to 0$, and k_2 (g/(mg·min)) is the rate constant of

pseudo-second order biosorption. The plot of t/q_t versus t should give a straight line if pseudo-second order kinetic is applicable and q_e, k_2, and h can be determined from the slope and intercept of the plot (Fig.9b). Better linearity was obtained for these plots as shown in Table 2, with correlation coefficient greater than 0.99. The calculated values of biosorption capacities ($q_{e, cal}$) also agree well with the experimental ones ($q_{e, exp}$), suggesting the biosorption of copper follows the pseudo-second order kinetic model.

The prediction on the actual slowest step involved in copper biosorption was analyzed using Boyd kinetic equation as given below:

$$F = 1 - \frac{6}{\pi^2} \sum_{n-1}^{\infty} \frac{e^{-n^2}B_t}{n^2} \tag{6}$$

and

$$F = \frac{q_t}{q_\infty} \tag{7}$$

where, F represents the fraction of copper adsorbed at any time t and is obtained using Eq.(7), q_∞ (mg/g) is the amount of copper adsorbed at infinite time, n is an integer and B_t is a mathematical function of F. The values of effective diffusion coefficients, D_i (cm^2/s) can be calculated using the following equation:

$$B = \frac{\pi^2 D_i}{r^2} \tag{8}$$

where, r (cm) represents the radius of biosorbent by assuming spherical particles. Eq.(6) was proposed based on
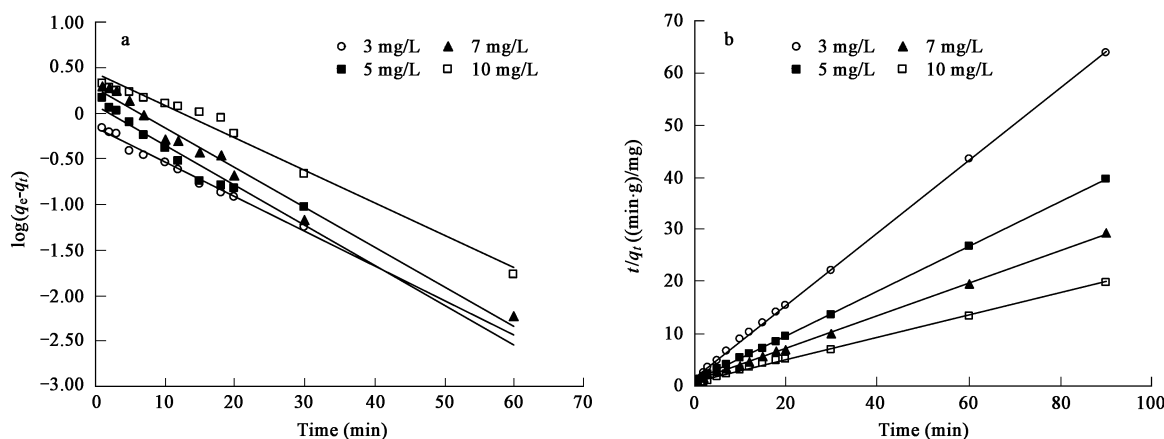

Fig. 9 Pseudo-first order plots (a) and pseudo-second order plots (b) of copper biosorption by NHBL. Conditions: biosorbent weight 0.10 g; pH 4; volume 50 ml; stirring speed 400 r/min.

Table 2 The pseudo-first, pseudo-second order, and effective diffusion constants (D_i) at different concentrations of Cu(II)

| C_{Cu} (mg/L)	Pseudo-first order			Pseudo-second order				Effective diffusion		
	$q_{e, cal}$ (mg/g)	k_1 (min^{-1})	R^2	h (mg/(g·min))	k_2 (mg/(mg·min))	$q_{e, cal}$ (mg/g)	R^2	D_i (cm^2/s)	R^2	$q_{e, exp}$ (mg/g)
3	0.684	0.0868	0.9877	0.6690	0.324	1.436	0.9996	2.45×10^{-6}	0.8854	1.410
5	1.233	0.1013	0.9355	1.0464	0.192	2.334	0.9998	2.96×10^{-6}	0.8828	2.276
7	1.899	0.1006	0.9836	1.0555	0.103	3.202	0.9990	4.54×10^{-6}	0.9882	3.073
10	2.700	0.0818	0.9827	1.4249	0.0653	4.673	0.9974	3.72×10^{-6}	0.9786	4.516
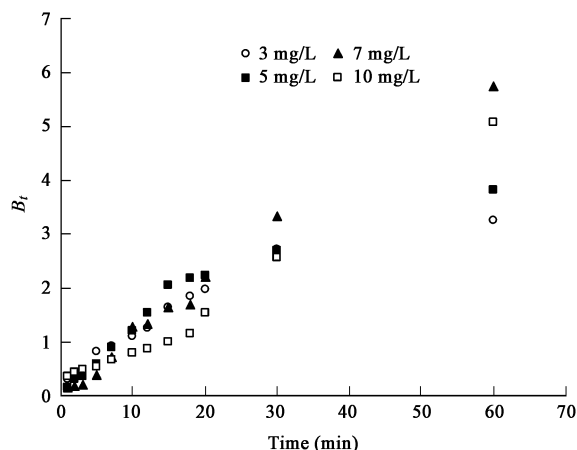
Fig. 10 Boyd kinetic plots of NHBL. Conditions: biosorbent weight 0.10 g; pH 4; volume 50 ml; stirring speed 400 r/min).

particle diffusion as the rate determining step. Substituting Eq.(6) in Eq.(7) simplifies to:

$$B_t = -0.4977 - \ln\left(1 - \frac{q_t}{q_\infty}\right) \tag{9}$$

or

$$B_t = 6.28318 - 3.2899F - 6.28318(1 - 1.047F)^{1/2} \tag{10}$$

Eq.(10) was used for values of F from 0 to 0.85 and Eq.(9) for values from 0.86 to 1 (Reichenberg, 1953). The plots of B_t versus time (t) at different copper concentrations are shown in Fig.10 and the values of B can be obtained from the slopes of the plots. The linearity of the plots can be used to identify whether film diffusion or intraparticle diffusion controls the rate of biosorption. The nonlinear plots indicate that film diffusion mainly governs the copper biosorption process on the modified biosorbents. The values of effective diffusion coefficients (D_i) are shown in Table 2. If film diffusion is to be the rate determining step, the value of D_i should be in the range 10^{-6}–10^{-8} cm^2/s, while if pore diffusion is the rate determining step, the D_i value should be in the range 10^{-11}–10^{-13} cm^2/s (Gasser *et al.*, 2006). The D_i values obtained from this work were in the range 10^{-6}–10^{-8} cm^2/s, confirming that the slowest step in copper biosorption on NHBL was film diffusion.

2.7 Biosorption isotherms

The distribution of metal ions between liquid and solid phases is generally described by using Dubinin-Radushkevich (Dubinin *et al.*, 1947), Freundlich (1906), and Langmuir (1916) biosorption isotherm models. The Dubinin-Radushkevich (D-R) equation can be expressed as:

$$\ln q_e = \ln q_m - K\varepsilon^2 \tag{11}$$

where, ε (Polanyi potential) is equal to $RT\ln(1+1/C_e)$, q_m (mg/g) is the maximum biosorption capacity, K is related to mean biosorption energy E (kJ/mol) as:

$$E = \frac{1}{\sqrt{-2K}} \tag{12}$$

E gives information about chemical and physical biosorption. Table 3 shows that the E value obtained lie between 8–16 kJ/mol, which suggests that biosorption of copper occurred by ion-exchange mechanism (Kilisloğlu and Bilgin, 2003).

The Freundlich isotherm model is derived to model the multilayer biosorption and applicable to highly heterogeneous surface, and is given as:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{13}$$

where, K_F (mg/g) is maximum biosorption capacity and n is related to biosorption intensity. The values of n determined from Freundlich isotherm were greater than 1 (Table 3), indicating that Cu(II) ions are favourably adsorbed by NHBL.

The Langmuir model assumes uniform energies of biosorption onto the biosorbent surface and no transmigration of adsorbate in the plane of the surface. The Langmuir equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}b} + \frac{C_e}{Q_{max}} \tag{14}$$

where, C_e (mg/L) is the equilibrium copper concentration, q_e (mg/g) is the amount of copper adsorbed at equilibrium, Q_{max} (mg/g) is the maximum biosorption capacity, b (L/mg) is a constant related to energy of biosorption which quantitatively reflects the affinity between the biosorbent and adsorbate. The values of Q_{max} can be obtained from the slope of the plot of C_e/q_e versus C_e. Based on Langmuir isotherm model, the Q_{max} of copper by NHBL was 14.97 mg/g as shown in Table 3. Among all the isotherm models, Langmuir model was found to best represent the isotherm data for copper biosorption on NHBL with $R^2 > 0.99$.

2.8 Effect of ionic strength

As shown in Fig.11, the biosorption capacities of copper decreased as NaCl was added to the copper solution. In the absence of NaCl, about 2.26 mg/g of Cu(II) could be adsorbed from the aqueous solutions by NHBL. This value corresponds to 91% Cu(II) removed by NHBL. However, increasing the ionic strength of NaCl to 0.10 mol/L resulted in a decrease in copper removal by about 16%. The addition of 1.0 mol/L NaCl further decreased the copper removal to about one fourth from pure copper solution. The reduction in copper adsorbed in the presence of NaCl was also reported by Villaescusa *et al.* (2004)

Table 3 Dubinin-Radushkevich, Freundlich, and Langmuir isotherm constants and correlation coefficients

Dubinin-Radushkevich			Freundlich			Langmuir		
q_m (mg/g)	E (kJ/mol)	R^2	K_F (mg/g)	n	R^2	q_m (mg/g)	b (L/mg)	R^2
27.43	8.84	0.9716	4.03	2.22	0.9468	14.97	0.412	0.9962

Table 4 Release of Ca^{2+}, Mg^{2+}, Na^+, and H^+ due to biosorption of Cu^{2+}

System	Total Cu^{2+} bound (mmol/L)	$C_{Ca^{2+}}$ (mmol/L)	$C_{Mg^{2+}}$ (mmol/L)	C_{Na^+} (mmol/L)	C_{H^+} (mmol/L)	[a]$R_{b/r}$
Blank	0.000	0.004	0.003	1.070	0.100	0.93
NHBL with Cu^{2+}	0.136	0.049	0.082	1.209	0.004	

Initial copper concentration: 10 mg/L; biosorbent dose: 2 g/L; pH 4.0. [a] Difference between cations released after copper biosorption and that by blanks.
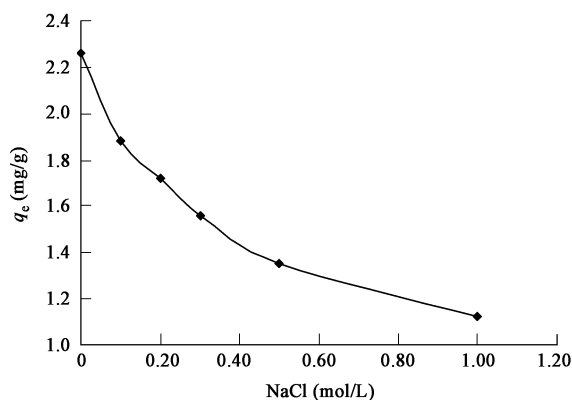
Fig. 11 Effect of NaCl concentration on copper biosorption.

when grape stalk waste was used to treat copper from a wastewater solution. The reduction in copper removal by NaCl could be explained in terms of two aspects: first, the competitive effect of Na^+ on binding sites and secondly, the electrostatic attraction between Cu(II) and the binding sites. At high concentration of NaCl (1.0 mol/L), the Na^+ tend to saturate the binding sites in biosorbents, reducing copper ions access to the biosorbent surface. Hence, more copper ions would remain in the solution. Also, the presence of NaCl causes an increase or expansion of the electrical diffused double layer. Such expansion could inhibit the biosorbent and Cu(II) from approaching each other more closely, resulting in a decrease of electrostatic attraction (Wang *et al.*, 2007). Another possible explanation for the low biosorption of copper is associated with the formation of copper chloro-complexes. An increase in Cl^- concentration may result in a decrease of the free Cu^{2+} species and an increase in the formation of copper chloro-complexes such as $CuCl^+$, $CuCl_2$, and $CuCl_3^-$. This indicates that the biosorbent surface has low affinity for copper complexes.

2.9 Ion exchange mechanism

Ion exchange has been reported as the predominant mechanism involved in many biosorption processes by lignocellulosic wastes (Šćiban *et al.*, 2006; Villaescusa *et al.*, 2004; Fiol *et al.*, 2006). The net release of Ca^{2+}, Mg^{2+}, and Na^+ due to the biosorption process has been calculated by subtracting the amount of cations released from blanks to the amount of cations measured in the effluent after copper biosorption (Table 4).

The ion exchange mechanism is given by the $R_{b/r}$ ratio (Šćiban *et al.*, 2006):

$$R_{b/r} = \frac{C_{Cu^{2+}}}{C_{Ca^{2+}} + C_{Mg^{2+}} + \frac{1}{2}C_{Na^+} + \frac{1}{2}C_{H^+}} \quad (15)$$

Table 5 Desorption of NHBL by HCl, HNO_3, and EDTA as desorbing solutions at various concentrations

Concentration (mol/L)	Desorption (%)		
	HCl	HNO_3	EDTA
1×10^{-4}	1.9	24.7	29.9
1×10^{-3}	20.9	82.8	74.7
1×10^{-2}	93.1	99.8	99.4
2×10^{-2}	97.8	99.8	99.9
5×10^{-2}	99.2	99.9	99.9
1×10^{-1}	99.4	99.9	99.9

where, the concentration of cations is expressed in mmol/L. If the $R_{b/r}$ ratio is equal to 1, the ion exchange is a predominant mechanism (Villaescusa *et al.*, 2004). The results in Table 4 showed the $R_{b/r}$ ratio is close to unity, thus it seems that ion exchange is another mechanism involved in the removal of copper ions on NHBL.

2.10 Desorption studies

Desorption studies are vital as they help to elucidate the behaviour of biosorption, the recovery of copper ions from aqueous solutions, recycling of the biosorbent and practical applications of treatment of industrial effluent. As the concentration of desorbing solutions (HCl, HNO_3, and EDTA) increases, more copper ions were able to be desorbed (Table 5). The maximum desorption of Cu(II) ions (> 99%) was achieved by 0.05 mol/L HCl, 0.01 mol/L HNO_3, and 0.01 mol/L EDTA solutions. This finding also suggests that the ion-exchange was one of the main mechanisms for the desorption process. Washing the metal laden adsorbent with deionized water however exhibited no desorption capability.

3 Conclusions

The results showed that base treated rubber leaves powder could be used as a cheap and effective biosorbent for treating copper containing wastewaters. Biosorption capacities increased with increasing stirring speed, pH, and copper concentration but decreased with increasing dose and ionic strength. The kinetic study revealed that biosorption of copper was rapid and equilibrium was achieved in 60 min. The pseudo-second order equation provided the best correlation for the biosorption data. The slowest step in biosorption process was film diffusion. Based on the isotherm study, biosorption can be expressed better with Langmuir isotherm, while Dubinin-Radushkevich isotherm suggests that ion-exchange could take part in the biosorption process. The binding of copper ions on base treated rubber leaves also took place on various functional groups such as hydroxyl, carboxyl and amino as demonstrated by FT-IR spectra. Ion exchange

and surface complexation have been identified as the main mechanisms involved in the binding of copper ions on NHBL.

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