Removal of copper(II) ions by a biosorbent—*Cinnamomum camphora* leaves powder

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ABSTRACT

In the present study, *Cinnamomum camphora* leaves powder (CLP) was investigated as a biosorbent for the removal of copper ions from aqueous solutions. The biosorbents before and after adsorption were measured by EDS and FT-IR. Kinetic data and sorption equilibrium isotherms were carried out in batch process. The adsorption kinetic experiments revealed that there are three stages in the whole adsorption process. It was found that Cu(II) adsorption onto CLP for different initial Cu(II) concentrations all followed pseudo-second order kinetics and were mainly controlled by the film diffusion mechanism. Batch equilibrium results at different temperatures suggest that Cu(II) adsorption onto CLP can be described perfectly with Langmuir isotherm model compared to Freundlich and D–R isotherm models, and the characteristic parameters for each adsorption isotherm were also determined. Thermodynamic parameters calculated show that the adsorption process has been found to be endothermic in nature. The analysis for the values of the mean free energies of adsorption (E_a), the Gibbs free energy (ΔG^0) and the effect of ionic strength all demonstrate that the whole adsorption process is mainly dominated by ion-exchange mechanism, accompanied by a certain amount of surface complexation which has been verified by variations in EDS and FT-IR spectra and pH value before and after adsorption. Regeneration studies show CLP possesses an excellent reusability.

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1. Introduction

Today, heavy metal pollution has become one of the most important environmental problems. Copper(II) is known to be one of the heavy metals and a widely used in many industries including metal cleaning and plating, paper board, printed circuit board, wood pulp, fertilizer, paints and pigments, etc. [1,2]. The effluents in these industries usually contain a considerable amount of copper, which spreads into the environment through soils and water streams and accumulates along the food chain, resulting in a high risk to human health, as high concentrations of copper will cause stomach upset and ulcer, mental retardance, liver and brain damage, and so on [3]. As copper(II) does not degrade biologically, the control of Cu(II) pollution has special importance for both organisms that live in waters and those that benefit from waters.

Different methods of treating wastewaters containing heavy metal ions have been developed over years which include coagulation, ion-exchange, membrane separation, reverse osmosis, solvent extraction, chemical precipitation, electroflotation, etc. [4]. However, most of these techniques have some disadvantages such as complicated treatment process, high cost, and energy use. Among

these methods, adsorption is a much preferable technique for the removal of heavy metals from polluted waters compared to others due to ease of operation and cost-effective process [5]. Even though the most promising adsorbent for adsorption is activated carbon, which has a high surface area and a high adsorption capacity, it is very expensive, has high operation costs and there is a need for regeneration after each adsorption cycle [6,7]. Hence, it is imperative to find alternate low-cost sorbent material to replace high cost activated carbon for water and wastewater treatment. Over the past two decades, numerous low-cost materials have been tested for their heavy metal sorption potential [8–14]. Of these materials, plants waste materials, such as peat, rice husk, sugar beet pulp, banana pith, saw dust, plant leaves, bark, coir, etc., are causing scientist's interest in wastewater treatment due to broad availability and relative cheapness. These wastes as heavy metal adsorbents have been extensively reviewed by Demirbas [12], Wan Ngah and Hanafiah [13] and Sud et al. [14].

Camphor tree (*Cinnamomum camphora*) is an everygreen tree native to China, distributed in the provinces south of the Yangtze River and Japan, India, Malaysia area. Its wood, bark and leaves can be used to extract camphor oil, which has an important antifungal activity [15,16]. In southwestern China, many cities have planted *C. camphora* tree in main roads, parks and schools. The *C. camphora* tree regularly sheds its leaves during spring, which become waste. To date, some types of tree leaves were used as

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Nomenclature

CLP	*Cinnamomum camphora* leaves powder
C_0	the initial concentration of the adsorbate in solution ($mg\,L^{-1}$)
C_e	the equilibrium concentration of the adsorbate in solution ($mg\,L^{-1}$)
C_t	the concentration of the adsorbate in solution at any time t ($mg\,L^{-1}$)
V	the volume of the solution added (L)
m	the mass of the biosorbent used (g)
pH_i	The initial pH value of solution
pH_f	The final pH value of solution
q_d	desorption capacity of the biosorbent ($mg\,g^{-1}$)
E_d	desorption efficiency of the biosorbent
Q_d	amount of metal desorbed in one cycle (mg)
Q_e	amount of metal loaded in one cycle (mg)
t	adsorption time (min)
k_1	pseudo-first order rate constant of adsorption (min^{-1})
k_2	pseudo-second order rate constant of adsorption ($g\,mg^{-1}\,min^{-1}$)
k_i	intra-particle diffusion rate constant ($mg\,g^{-1}\,min^{-1/2}$)
q_e	adsorption capacity of the biosorbent at equilibrium ($mg\,g^{-1}$)
q_t	adsorption capacity at any time t ($mg\,g^{-1}$)
q_{max}	the monolayer capacity of the biosorbent ($mg\,g^{-1}$)
b	the Langmuir constant ($L\,mg^{-1}$)
K_f	the Freundlich constant ($mg^{1-1/n}\,L^{1/n}\,g^{-1}$)
n	experimental constant indicative of the adsorption intensity of the biosorbent
β	a constant related to the mean free energy of adsorption ($mol^2\,kJ^{-2}$)
q_m	the theoretical saturation capacity ($mg\,g^{-1}$)
ε	the Polanyi potential, which is equal to $RT\ln(1+(1/C_e))$
T	the absolute temperature (K)
ΔG^0	change in the Gibbs free energy ($kJ\,mol^{-1}$)
ΔH^0	change in the enthalpy ($kJ\,mol^{-1}$)
ΔS^0	change in the entropy ($kJ\,mol^{-1}\,K^{-1}$)

copper ions biosorbents [17–19]. Kumar et al. [17] have studied the adsorption of copper(II) ion from aqueous solution by *Tectona grandis* L.f. (teak leaves powder). Sawalha et al. [18] have investigated the thermodynamic and isotherm of Cu(II) onto leaves of saltbush (*Atriplex canescens*) and compared biosorption characteristics of Cu(II) with those of Pb(II) and Zn(II). Wan Ngah and Hanafiah [19] have studied kinetics, isotherm, and biosorption mechanisms of copper ions from dilute aqueous solutions on base treated rubber (*Hevea brasiliensis*) leaves powder. However, to our best knowledge, there is still no reported about the use of *C. camphora* leaves as heavy metals biosorbent.

In the present study, finely ground powder prepared from *C. camphora* leaves (CLP), a bio-based waste material, was used as biosorbent for the removal of Cu(II) from an aqueous solution. The adsorption kinetics, isotherm and thermodynamics under various experimental conditions (i.e., pH, ionic strength of the solution, contact time, concentration and temperature) were investigated. Pseudo-first order, pseudo-second order, and intra-particle diffusion models [20–22] were used to analyze the adsorption kinetics. The Langmuir, Freundlich and Dubinin–Radushkevich isotherms models [23–25] were used to fit the adsorption equilibrium data. The thermodynamic parameters were determined using Van't Hoff

equation. The equations corresponding to these models are given in Appendix A. The performance of the repeated use of the biosorbent was also studied. The adsorption mechanism is discussed comprehensively based on the results.

2. Experimental

2.1. Materials and chemicals

The *C. camphora* tree's leaves used in the present investigation were collected in spring 2009 from campus of Taizhou University, China. A stock solution of Cu(II) was prepared by dissolving $CuSO_4\cdot5H_2O$ in double distilled water. Other agents used, such as HCl, NaOH, were all of analytical grade and all solutions were prepared with double distilled water.

2.2. Preparation of the biosorbent

The collected leaves were washed repeatedly with distilled water for several times to remove dirt particles and soluble impurities and were allowed to dry in an air oven at 353 K for a period of 24 h when the leaves became crisp. These were crushed into a fine powder in a mechanical grinder to obtain the leaves powder. The powder was sieved to obtain particle size of >200 mesh. The obtained material was washed repeatedly with distilled water till the washings were free of colour and turbidity. Finally, the obtained material was then completely dried in an air circulating oven at 353 K for 2 days and preserved in glass bottles for use as a biosorbent.

2.3. Adsorption studies

Adsorption experiments were evaluated in batch equilibrium mode. All experiments were conducted by mixing 25 mL of aqueous Cu(II) solutions with 0.05 g of the biosorbent. The pH values of solutions were adjusted with dilute HCl or NaOH solution by using a Mettler Toledo 320 pH meter. The mixtures of the biosorbent and Cu(II) solution were shaken in a thermostatic shaker bath (THZ-98A mechanical shaker) at 120 rpm at desired temperature and contact time, and then the suspensions were centrifuged at 5000 rpm for 10 min.

To examine the effect of pH, adsorption experiments were conducted at different pH ranging from 2 to 5 at $150\,mg\,L^{-1}$ of Cu(II) solution. Concentrations of Cu(II) solutions before and after adsorption were measured with an atomic absorption spectrophotometer (PerkinElmer SIMAA 6000). The adsorption capacity of the biosorbent at equilibrium was calculated using the equation:

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

For kinetic studies a series of different initial concentrations (25, 50, $100\,mg\,L^{-1}$) of Cu(II) solution with adjusting pH of 4.0 were chosen as the initial concentration of Cu(II) solution. The adsorption capacity of the biosorbent at any time was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{2}$$

Adsorption experiments were also carried out to obtain isotherms at different temperatures. This was done at 303.2, 313.2, 323.2 and 333.2 K, respectively. The mixture of the biosorbent and Cu(II) solution was shaken for 1 h to reach equilibrium at different temperatures. In this group of experiments Cu(II) solutions with different initial concentration, in the range of $12.5–150\,mg\,L^{-1}$, were selected.

The effect of ionic strength was studied using NaCl as the ionic medium. The concentration of this salt was varied within the range
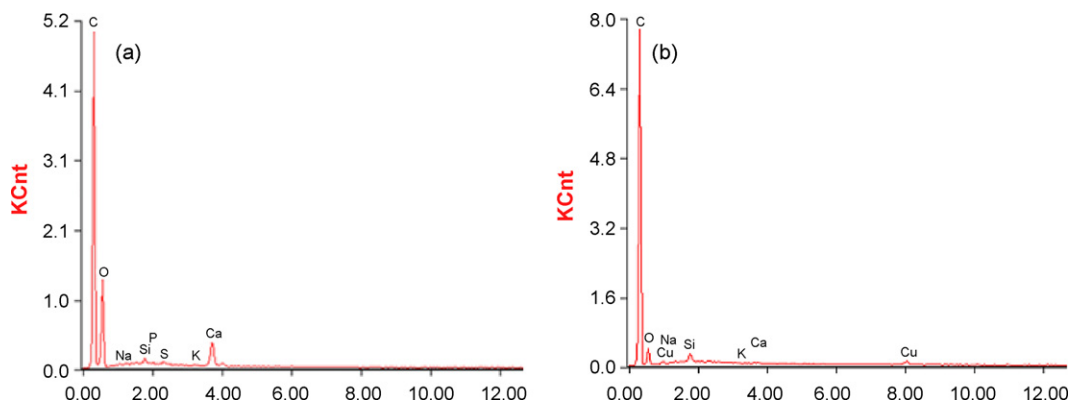
Fig. 1. EDS spectra of CLP before (a) and after (b) copper adsorption.

0.001–0.5 mol L^{-1}. The final pH values of solutions at equilibrium were measured in order to more in-depth understanding of adsorption mechanism.

Normally, pH 4.0; ionic strength of almost 0 and 303.2 K were selected as adsorption conditions unless otherwise stated in the whole study. Each experiment was triplicated under identical conditions and only mean values were presented. To evaluate the validity of kinetic and isotherm models to represent the experimental data, statistical analyses for the standard errors (S.E.) and *F* values of *F*-test were performed at a 95% confidence interval (CI) using statistical software (SPSS 13.0 for Windows; SPSS Inc., Chicago, IL, USA).

2.4. Desorption and regeneration studies

The biosorbent utilized for the adsorption of an initial metal concentration of 150 mg L^{-1} was separated from the Cu(II) solution by centrifugation. The Cu(II)-loaded biosorbent was gently washed with 25 mL double distilled water to remove any un-adsorbed Cu(II) and then carried out by shaking with 25 mL of 0.1 mol L^{-1} HCl solution at 303.2 K for 4 h. After this, the biosorbent was washed three times with double distilled water, and then dried and reused for adsorption studies. The adsorption–desorption process was performed in five times. Desorption capacity and desorption efficiency were defined in Eqs. (3) and (4), respectively.

$$q_d = \frac{Q_d}{m} \tag{3}$$

$$E_d = \frac{Q_d}{Q_e} \times 100\% \tag{4}$$

2.5. Characterization of samples

Energy dispersive spectroscopy (EDS) analyses of CLP before and after copper adsorption were done in a Jeol JSM-5600LV with samples fixed in an aluminum stub. In order to avoid the interference of Au element, is carried out on samples without gold spray.

In order to investigate the effect of pH on spectral changes of the functional groups, control sample, CLP$_{blank}$ (not including metal bearing solution but the biosorbent and distilled water, whose pH was adjusted to 4.0) were also tested simultaneously in metal uptake experiments. FT-IR spectra measurements of CLP, CLP$_{blank}$ and Cu(II)-loaded CLP were done on a Thermo Nicolet NEXUS TM spectrophotometer using the KBr pellets. The spectrum was collected 32 times in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} and corrected for the background noise. CLP$_{blank}$ and Cu(II)-loaded CLP used for FT-IR study were obtained by extracting the biosorbent from the liquid phase after centrifugation and drying in an oven at 60 °C for 2 h.

The pH at point zero charge (pH$_{PZC}$) of the biosorbent was determined by the solid addition method [26].

3. Results and discussion

3.1. Characterization of the biosorbent

In this study, EDS is used to probe the change in element compositions of CLP and Cu(II)-loaded CLP (Fig. 1). It is clearly observed in Fig. 1 that the CLP consist of mainly C and O, and small amounts of Si, Ca, Na, K, P and S. After adsorption, Ca, Na, K, P and S peaks almost diminished and the copper peaks in the spectra are visible, suggesting ion-exchange might be one of the mechanisms involved in copper removal [19].

Fourier transform infrared spectral analysis is important to identify some characteristic functional groups, which are responsible for adsorbing metal ions [19,27–29]. Taking into account wavenumber of peaks may change before Cu(II) adsorption by the influence of solution pH, a blank sample was added in FT-IR analysis. The FT-IR spectra of CLP, CLP$_{blank}$ and Cu(II)-loaded CLP and corresponding changes in peaks are presented in Fig. 2 and summarized in Table 1. The resolution of the apparatus used was 4 cm^{-1}, which means any shift of equal to or less than 4 cm^{-1} may be caused by the instrument itself. So the shifts of more than 4 cm^{-1} were mainly focused in this study. In general, the relevant functional groups on the CLP could be determined based on the FT-IR adsorption band. Based on the attribution of peaks in the table, it can be known that CLP contains a number of functional groups such as –OH, –NH$_2$, –COOH, –POH, etc. The comparison of the spectral changes of CLP and CLP$_{blank}$ showed that there are very similar infrared spectra, indicating solution pH did not cause an evident
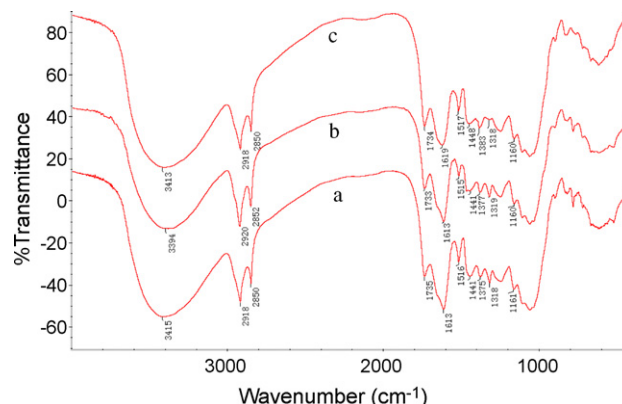

Fig. 2. FT-IR spectra of CLP, CLP$_{blank}$ and Cu(II)-loaded CLP.

Table 1
Band position in the FT-IR spectra of CLP, CLP_{blank} and Cu(II)-loaded CLP.

Frequency (cm^{-1})			Assignment	Reference
CLP	CLP_{blank}	Cu(II)-loaded CLP		
3415	**3394**	**3413**	–OH stretching	[30]
2918	2920	2918	C–H	
2850	2852	2850	C–H	
1735	1733	1734	C=O stretching	
1613	**1613**	**1619**	N–H stretching	[31]
1516	1515	1517	C=C stretching	[32]
1441	**1441**	**1448**	C–H and in-plane –OH bending	[33]
1375	**1377**	**1383**	CH_3 deformation and –OH bending	
1318	**1319**	**1318**	N–H	[31]
1246	1247	1247	C–O stretching	[33]
1161	1160	1160	C–N stretching	[33]
1105	1106	1107	C=O bending	
1059	1059	1059	C–OH in-plan bending	[29,30]
1030	1030	1030	and stretching	

The bold figures represent significant changes.

structural change on biomass surface. However, the wavenumber ascribing to –OH blueshifted from 3415 to 3394 cm^{-1}, which might be caused by acidic solution. H$^+$ ions in solution as donors can bind to the sites on the surface of CLP and form neutral functional groups (–OH, –NH$_2$ and –COOH, etc.), which result in the stretching vibrations of a lower frequency in FT-IR spectra [34,35].

After Cu(II) binding, the most of characteristic peaks corresponding to these groups changed. The wavenumber of –OH group redshifted from 3394 to 3413 cm^{-1} compared with that of CLP_{blank}, indicating complexation occurred considering the formation of surface complexes can affect the peak position of –OH. The peaks at 1441 and 1375 cm^{-1} show a remarkable increase in wavenumbers, and the peak intensity decreased to some extent after adsorption, indicating that hydroxyl involved in adsorption to a large extent. In addition, significant changes have also taken place for the characteristic peaks corresponding to amino after adsorption. Specifically, the peak at 1613 cm^{-1} redshifted of 6 cm^{-1} and the peak at 1318 cm^{-1}, was not changed, but intensity of the peak dramatically weakened. This indicates that amino has an important contribution to the adsorption. Compared to the hydroxyl and amino, the amount of carboxyl groups involved in adsorption was significantly smaller than those of the two groups, which can be easily seen from the extent in changes of its characteristic peaks. Overall, the above mentioned groups all participated adsorption process for Cu(II), with the main contribution of hydroxyl and amino. Based on the analysis, the mechanism of copper adsorption on CLP could also occur by surface complexation [19,28].

3.2. Effect of pH

The pH of the aqueous solution is an important variable in the adsorption of metals on the biosorbents. So the influence of the initial pH of solution on the adsorption of Cu(II) onto CLP was examined in the pH range of 2–5 (Fig. 3). As can be seen, the adsorption capacity of Cu(II) tended to increase with increasing pH value. The q_e increases rapidly with increasing pH from 2 to 3, and then increases slowly with further increase in pH. Similar variations of q_e versus pH have been earlier recorded in study on heavy metals adsorption onto some leaf biosorbents [19,29,31].

The influence of the solution pH on the metal ions uptake can be explained on the basis of the pH at point zero charge (pH_{PZC}) of the biosorbent [36]. This is a convenient index when the surface of biosorbent becomes either positively or negatively charged as a function of pH. When pH of mixture of the biosorbent and solution is lower than pH_{PZC}, which means that the biosorbent surface presents positively charged as a whole. Otherwise it would show negatively charged. The pH_{PZC} of CLP determined by the solid

addition method was about 5.9 (Fig. 3). For the blank experiment without adding copper ions or the adsorption experiments, pH values after solid-liquid interactions are both significantly lower than the pH at point zero charge (pH_{PZC}) of the biosorbent (see details in second paragraph of Section 3.6). So, it is clear that the surface of the biosorbent is positively charged as a whole in this study. Accordingly, electrostatic attraction mechanism can be easily excluded. In fact, the variation in q_e versus pH can be interpreted by following facts. In a highly acidic solution (pH of 2), a high concentration of H$^+$ ions compete with Cu(II) for exchangeable cations on the surface of biosorbent, resulting in the suppression of Cu(II) adsorption on CLP surface and a low q_e was observed. As pH value is higher, more exchangeable cations contained in the biosorbent can be exchanged with Cu(II) due to weak competitive adsorption of H$^+$ ions. Furthermore, an increase in solution pH would cause protonation of more ligands such as amino, hydroxyl, and carboxyl groups, which could benefit for the removal of copper ions. So, a rapid increase in adsorption capacity occurred at pH range of 2–3. The slow increase in q_e after pH 3 might be related to the fact that adsorption mechanisms above mentioned is affected indistinctively by a change of pH here. In order to increase the adsorption capacity as possible and keep Cu(II) as a simple form, i.e. Cu^{2+} in the solutions, pH of 4.0 was selected for the rest of the batch experiments.

3.3. Adsorption kinetics

Fig. 4 shows the effect of contact time on the adsorption capacity of CLP for Cu(II) at different initial concentrations. As can be
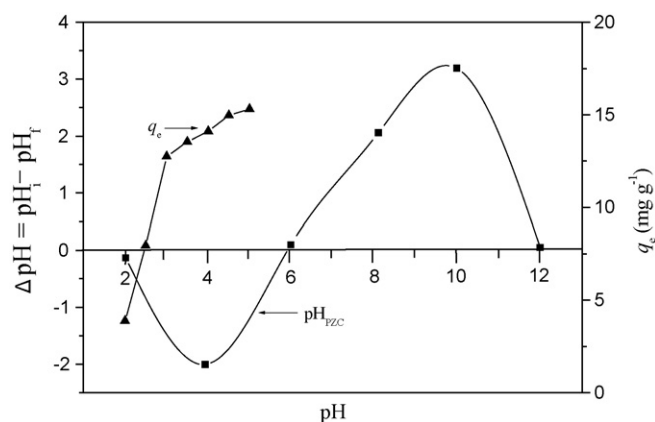

Fig. 3. Point of zero charge of CLP and effect of pH on the adsorption capacity for Cu(II) ($C_0 = 150$ mg L^{-1}, contact time 1 h, $T = 303.2$ K).

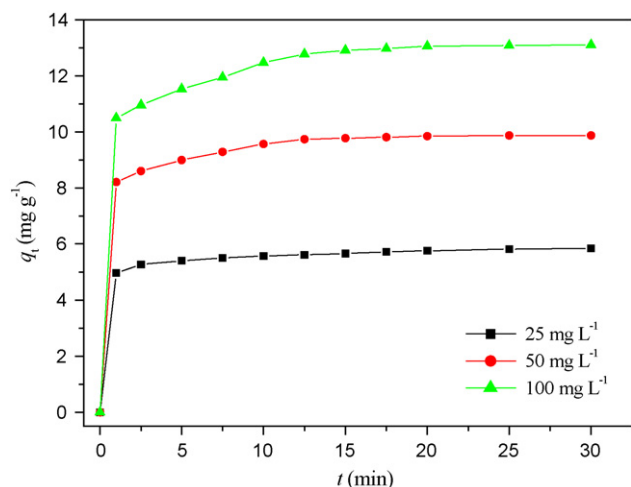**Fig. 4.** Effect of contact time on the adsorption of Cu(II) onto CLP at different copper concentrations (initial pH 4.0, $T = 303.2$ K).

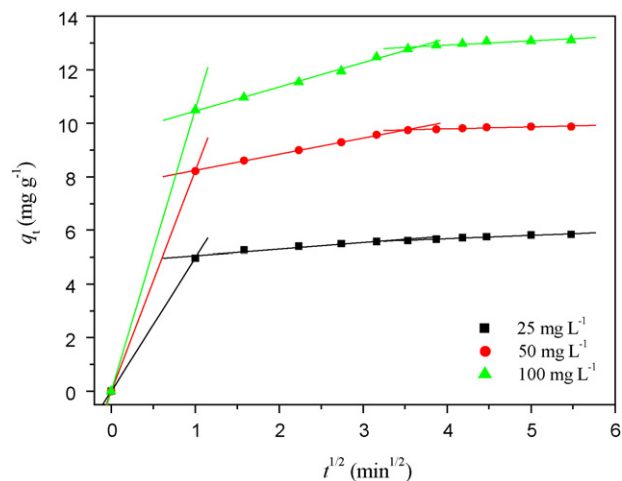**Fig. 5.** Intra-particle diffusion kinetic plots for the adsorption of Cu(II) onto CLP at different copper concentrations.

seen in Fig. 4, the adsorption of Cu(II) is rapid from the beginning of the experiment and thereafter it proceeds at a slower rate and finally reaches to equilibrium. With the increase in concentration, the trend becomes more obvious. It is also observed from the graphs that Cu(II) adsorption on CLP was a very fast process, where >90% of the adsorption took place within the first 10 min and equilibrium was attained within 30 min. Similar findings for Cu(II) adsorption onto bio-waste materials have been reported by other investigators [19,27].

In order to investigate the adsorption kinetics of Cu(II) on CLP, three different kinetic models, pseudo-first order, pseudo-second order, and intra-particle diffusion, have been used to fit experimental data obtained from batch Cu(II) removal experiments. Table 2 lists the results of the rate constant studies for different initial copper concentrations by the three kinetic models. At all studied initial copper concentrations, the extremely high correlation coefficients (>0.999) were obtained by calculating with pseudo-second order kinetic equation. In addition, the calculated q_e values also agree with the experimental data in the case of pseudo-second order kinetics. These suggest that the adsorption data are well represented by pseudo-second order kinetics in comparison to the

other two kinetics, which can be further validated by F values. It is also observed from Table 2 that the value of the rate constant k_2 decreases with increasing initial copper concentration for CLP. The reason for this behaviour can be attributed to the lower competition for the sorption surface sites at lower concentration. At higher concentrations, the competition for the surface active sites will be high and consequently lower sorption rates are obtained. Similar phenomena have been observed in the adsorption of Cu(II) on other natural adsorbent materials [3,17,19,27].

It was found from Table 2 that the correlation coefficients for the intra-particle diffusion model are all lower evidently than those of the pseudo-first order and the pseudo-second order models. This indicates that the adsorption of Cu(II) onto CLP do not follow the intra-particle diffusion kinetics. However, the plots of q_t versus $t^{1/2}$ can be divided into a multi-linearity correlation (Fig. 5), which indicates that three steps occur during adsorption process. For the first sharper portion i.e. from 0 to 1 min, it is postulated that Cu(II) was transported to the external surface of the biosorbent through film diffusion and its rate, the values of k_{i1} were between 4.97 and 10.50 mg g^{-1} min$^{-1/2}$, which shows this adsorption process is very fast. The second portion is the gradual adsorption stage where the intra-particle diffusion with k_{i2} (0.24283, 0.60277 and 0.90756 mg g^{-1} min$^{-1/2}$ for 25, 50 and 100 mg L^{-1}, respectively) can be rate controlling. The third portion (after 12.5 min) is the final equilibrium stage where the intra-particle diffusion starts to slow down due to the extremely low solute concentration in solution [37]. Moreover, it can be observed that the larger slope is represented for higher initial concentration whether the first or the second portions. From the above analysis, it can be concluded that both film diffusion and intra-particle diffusion were simultaneously operating during the process of the adsorption of Cu(II) on CLP and were both enhanced with the increase of initial concentration.

3.4. Adsorption isotherms

The equilibrium adsorption isotherms are one of the most important data to understand the mechanism of the adsorption systems. Hence, the adsorption of Cu(II) onto CLP at different temperatures are determined as a function of equilibrium (residual) Cu(II) concentration (C_e) and the corresponding adsorption isotherms are plotted in Fig. 6. The parameters and correlation coefficients obtained from the plots of Langmuir, Freundlich and D-R (figures not shown) are listed in Table 3. The values of r^2 and F all suggest that the Langmuir model gave closer fittings than those of Freundlich and D–R models. In addition, the adsorption capacity
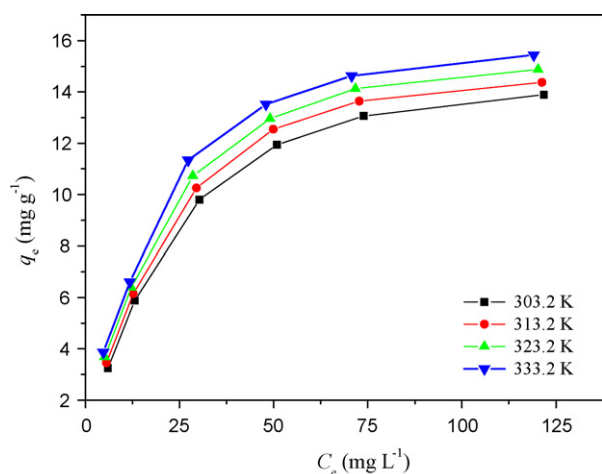
Table 2
A comparison of pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models rate constants calculated from experimental data.

Model	C_0 (mg L^{-1})		
	25	50	100
Pseudo-first order			
q_e (exp) (mg g^{-1})	5.854	9.882	13.11
k_1 (min^{-1})	0.15124	0.23661	0.22662
q_e (cal) (mg g^{-1})	1.4874	3.4507	5.6604
r^2	0.91946	0.97862	0.98198
S.E.	0.24369	1.38731	0.1643
F	49.213	204.714	242.986
Pseudo-second order			
k_2 (g mg^{-1} min^{-1})	0.3798	0.2344	0.1228
q_e (cal) (mg g^{-1})	5.8983	10.031	13.389
r^2	0.99986	0.99994	0.99984
S.E.	0.0277308	0.0109519	0.0130339
F	32264.15	71518.05	28343.94
Intra-particle diffusion			
k_i (mg g^{-1} min$^{-1/2}$)	0.68718	1.21421	1.67213
C (mg g^{-1})	2.9630	4.8641	6.0873
r^2	0.70223	0.72668	0.75811
S.E.	1.2132	2.0018	2.5021
F	9.729	11.189	13.513

Fig. 6. Adsorption isotherms of Cu(II) on CLP at different temperatures (initial pH 4.0, contact time 1 h).

Table 3
Isotherm constants and correlation coefficients for the adsorption of Cu(II) on CLP at different temperatures.

Model	T (K)			
	303.2	313.2	323.2	333.2
Langmuir isotherm				
q_{max} (mg g^{-1})	16.756	17.085	17.434	17.870
b (L mg^{-1})	0.04373	0.04859	0.05334	0.05834
R_L	0.13228	0.12066	0.11110	0.10255
r^2	0.9988	0.99874	0.99906	0.99901
S.E.	0.1416	0.14248	0.119663	0.1195
F	1669.59	1580.117	2132	2014.454
Freundlich isotherm				
K_f (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	1.5605	1.7497	1.9648	2.1672
n	2.0313	2.0981	2.1779	2.2359
r^2	0.97097	0.97118	0.9728	0.97136
S.E.	0.066088	0.064977	0.062136	0.063422
F	65.92	66.502	70.562	66.817
Dubinin–Radushkevich isotherm				
q_m (mg g^{-1})	56.241	55.818	54.680	54.899
ε (mol^2 kJ^{-2})	0.00503	0.00454	0.00409	0.00373
r^2	0.98274	0.98301	0.98427	0.98304
E_a (kJ mol^{-1})	9.9701	10.494	11.057	11.578
S.E.	0.11768	0.115	0.1091	0.112654
F	112.926	114.694	124.162	115.012

(q_{max} and K_f) increases with an increase in temperature while the opposite behavior is presented for q_m. Seen overall, the information thus obtained specifies an endothermic nature of the existing process. The maximum monolayer adsorption capacity of CLP for Cu(II) ions was also noted to be higher than the other previously reported adsorbents (Table 4). Differences of metal uptake are due to the properties of each adsorbent material such as structure, functional groups and surface area.

Through the discussion for isotherm constants, it can predict whether an adsorption system is favorable or unfavorable. The essential characteristics of the Langmuir isotherm can be expressed by means of 'R_L', a dimensionless constant referred to as separation factor or equilibrium parameter, which is defined by [47]

$$R_L = \frac{1}{(1 + bC_0)} \tag{5}$$

where C_0 is the highest initial metal concentration. The parameter indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). As seen from Table 3, at all temperatures the R_L values were between 0 and 1.0, indicating that adsorption of Cu(II) onto CLP are all favorable.

The n values of Freundlich equation can give an indication on the favorability of sorption. It is generally stated that values of n in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor sorption characteristics [48]. The result shows that the values of n are all greater than 2 indicating that the copper ions are favorably adsorbed by CLP. This is in great agreement with the findings regarding to R_L value.

Based on D–R isotherm equation, E_a can be calculated using the equation, $E_a = (2\beta)^{-1/2}$ [49]. The isotherm constants, E_a and correlation coefficients are calculated and presented in Table 3. As seen in the table, the values of E_a at different temperatures are found to lie between 9.97 and 11.58 kJ mol^{-1} in the whole range of investigated copper concentrations. The mean energy of adsorption is the free energy change when one mole of the ion is transferred to the surface of the solid from infinity in the solution. The value of this parameter can give information about adsorption mechanism. When one mole of ions is transferred, its value in the range of 1–8 kJ mol^{-1} indicates physical adsorption [50], the value of E_a is between 8 and 16 kJ mol^{-1}, which indicates the adsorption process follows by ion-exchange [51], while its value in the range of 20–40 kJ mol^{-1} is indicative of chemisorption [52]. Combination of the preceding analysis for EDS and FT-IR, it is likely that the whole adsorption process were predominated by ion-exchange
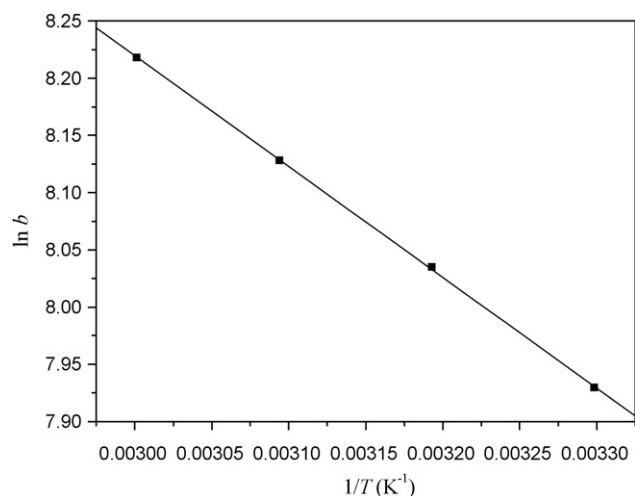
Table 4
A comparison of maximum adsorption capacities of Cu(II) onto different low-cost adsorbents.

Adsorbent	pH	Temperature (°C)	q_m (mg g^{-1})	References
Sugar beet pulp	4	25	28.5	[1]
Dehydrated wheat bran	5	60	51.5	[2]
Peanut hull	5.5	30	21.25	[3]
T. grandis L.f. leaves powder	5	NA	15.43	[17]
Leaves of saltbush	5.0	24	68.0	[18]
Base treated rubber leaves	4	27	14.97	[19]
Pine cone powder	5	18–74	6.80–9.22	[27]
Tea waste	5–6	22	48.00	[38]
Spent grain	4.2	NA	10.47	[39]
Tree fern	NA	20	10.6	[40]
Groundnut shells	5.24	35	7.60	[41]
Kaolinite	NA	40	11.04	[42]
Litter of poplar forests	4.5	25	19.53	[43]
Pretreated *Aspergillus niger*	5.5 ± 0.5	NA	2.61	[44]
Lentil shell	6	20–60	8.98–9.59	[45]
Wheat shell	6	20–60	7.39–17.42	[45]
Rice shell	6	20–60	1.85–2.95	[45]
Herbaceous peat	5.5	21	4.84	[46]
CLP	4	30–60	16.76–17.87	This study

NA represents not available.

Fig. 7. Van't Hoff plot for the adsorption of Cu(II) by CLP.

Fig. 8. Effect of ionic strength on the adsorption of Cu(II) onto CLP ($C_0 = 150\,mg\,L^{-1}$, initial pH 4.0, contact time 1 h, $T = 303.2\,K$).

mechanism, accompanied by a certain degree of surface complexation.

3.5. Thermodynamic parameters

According to values of thermodynamic parameters, what process will occur spontaneously can be determined. ΔG^0 can be calculated using the relation:

$$\Delta G^0 = -RT\ \ln b \qquad (6)$$

ΔH^0 and ΔS^0 were calculated from the slope and intercept of the linear plot of $\ln b$ versus $1/T$ (Fig. 7) according to the Van't Hoff equation. Obtained thermodynamic parameters are given in Table 5. As shown in the table, ΔH^0 was positive value, suggesting endothermic reaction. The positive value of ΔS^0 suggests the increased randomness at the solid/solution interface during the adsorption of Cu(II) onto CLP. The negative values of ΔG^0 imply the spontaneous nature of the adsorption process. Further, the decrease in the values of ΔG^0 with the increasing temperature indicates the adsorption was more spontaneous at higher temperatures [53]. Generally, the change in free energy for physisorption is between −20 and 0 kJ mol^{-1}, but chemisorption is a range of −80 to −400 kJ mol^{-1} [54]. The values of ΔG^0 obtained in this study are within the ranges of neither the physisorption nor chemisorption, indicating that the other adsorption such as ion-exchange and/or surface complexation is likely the main mechanism.

3.6. Effect of ionic strength

Heavy metal wastewaters from many industries contain various types of suspended solids and salts. The presence of ions leads to high ionic strength, which may significantly affect the performance of the adsorption process. Fig. 8 presents the effect of ionic strength on the removal of Cu(II). It was observed that the adsorption capacity fluctuates insignificantly in the range of ionic strength from 0 to 0.1 mol L^{-1}, and then slightly decreases with a larger concentration of NaCl. Compared with data related to lower ionic strength, the
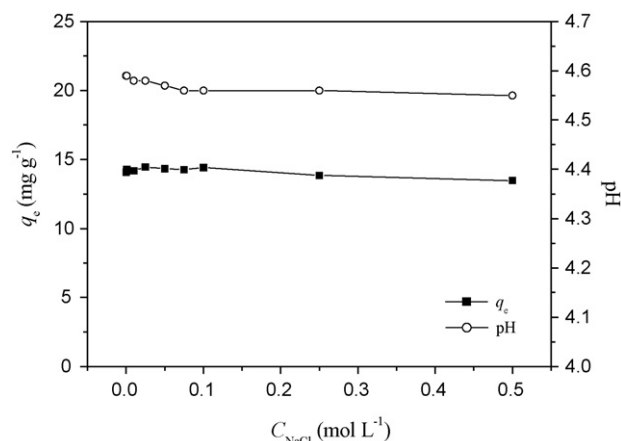
adsorption capacity is only a drop of 7% even if the ionic strength has reached 0.5 mol L^{-1}. The result indicates that the presence of external electrolyte, such as sodium chloride, has a limited effect on the adsorption capacity between CLP and copper ions.

The pH value of final Cu(II) solution is indicative of the property of liquid system because it is the result of interaction between biosorbent and Cu(II) solution. Hence, the variation of the pH of the Cu(II) solution before and after adsorption in the conditions of different ionic strengths were investigated. As seen in Fig. 8, pH of final solution decreases slightly from 4.60 to 4.55 with the increase of NaCl concentration. In the blank experiment without adding copper ions, pH value after adsorption is 4.35, which is lower than the above values of 4.55–4.60. Based on the previous kinetic and isothermal studies, it is considered that the ion-exchange and surface complexation occurred simultaneously during the adsorption process. Ion-exchange would induce the increase in pH value of solution due to the lower hydrolyse constant of Cu(II) compared to cations such as Na$^+$, K$^+$, Ca^{2+}, etc. on CLP. In contrast to the former, surface complexation on the CLP can bring a decrease in final pH because hydrogen ions will go into the solution after adsorption.
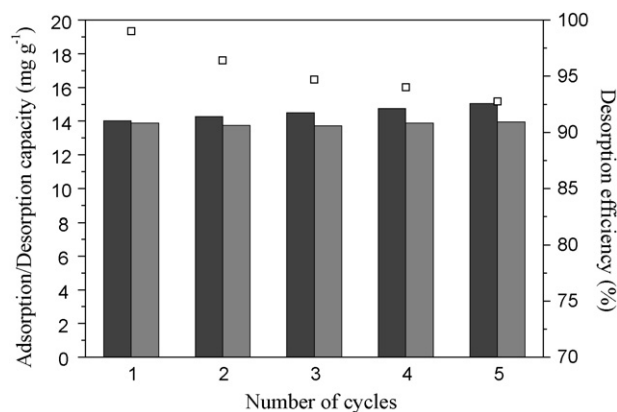

Fig. 9. Repeated adsorption–desorption studies for Cu(II) adsorption onto CLP.

Table 5
Thermodynamic parameters for the adsorption of Cu(II) onto the CLP.

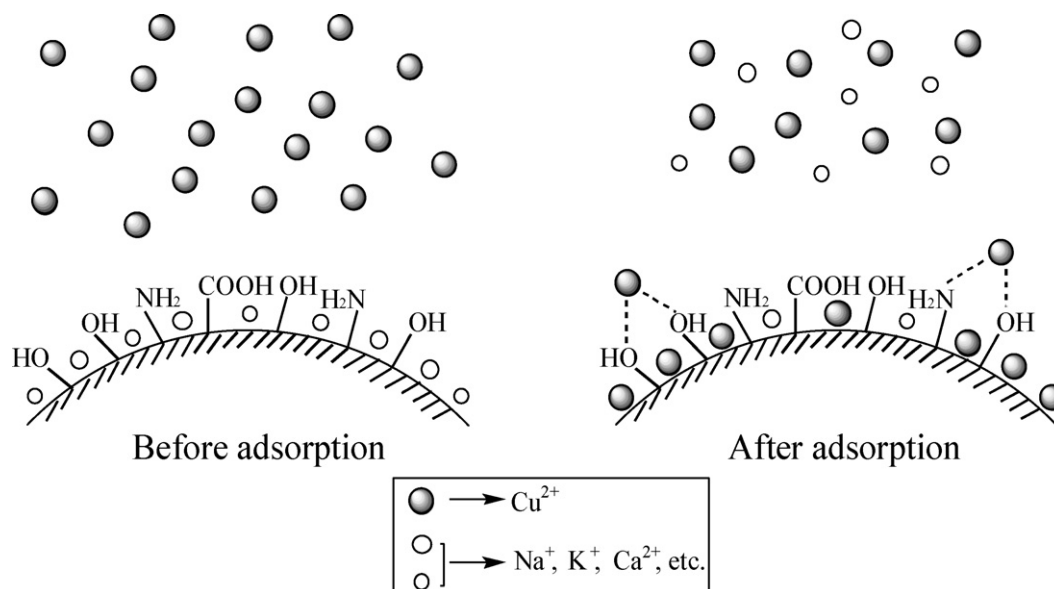| T (K)	b (L mol^{-1})	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (kJ mol^{-1} K^{-1})
303.2	2778.6	−19.989	8.0509	0.09249
313.2	3087.1	−20.255		
323.2	3389.1	−20.490		
333.2	3706.9	−20.716		

Fig. 10. Schematic illustration of proposed mechanisms for Cu(II) adsorption onto CLP.

According to the results of pH values above, it can be concluded that the whole adsorption process is mainly dominated by ion-exchange mechanism, accompanied by a certain degree of surface complexation. The result well corroborates the previous speculation in Section 3.4.

3.7. Regeneration studies

Recovery of copper from the loaded biosorbent is necessary for disposal as well as for reuse of the adsorbate [55]. In this study, $0.1\,mol\,L^{-1}$ of HCl was used in the adsorption–desorption experiments. The result is shown in Fig. 9. It is observed from Fig. 9 that the adsorption capacity increases gradually with the increase of cycle time, which seems unreasonable. Copper ions adsorbed onto CLP could not be removed thoroughly from the leaf by desorption (Fig. 9). So, when the number of cycle related to the reutilization of the leaves increases, the amount of the newly adsorbed Cu^{2+} should decrease under the condition of an unchanged total amount of available adsorption sites. Usually strong acid treatment at high concentration and quite high temperature can increase the adsorption capacity of the biosorbent due to the increase of the porosity or surface area [13]. In this study, an increase in adsorption capacity observed after desorption with dilute HCl, which cause protonation of biosorbent surface, may be attributed to the exchange of bound hydrogen ions with heavy metal ions. Accordingly, it is believed that hydrochloric acid selected in this study played a dual role of desorption and protonation. For each adsorption–desorption cycle, the number of newly active sites generated by dilute HCl treatment was higher than those of undesorbed sites, resulting in an increase adsorption capacity with the increase in cycle number. Fig. 9 also shows that desorption capacity did not change evidently in the whole regeneration studies. It can be easily known that desorption efficiency decreases slowly with the increasing cycle number due to the increase of adsorption capacity. Even after 5 cycles, the desorption efficiency is still as high as 92.7%. In general, Cu(II)-loaded CLP can be easily desorbed by selecting HCl as a regenerant and reuse efficiency of the biosorbent is satisfying.

4. Conclusions

The aim of this work was to find the possible use of *C. camphora* leaves powder as a sorbent for the removal of Cu^{2+} from aque-

ous solutions. In kinetic study, the pseudo-second order kinetic model was found to be well suited for the entire adsorption process of Cu(II) on CLP. Adsorption kinetic studies also reveal that there are three stages in the whole adsorption process and film diffusion mechanism should be a main rate control mechanism. All equilibrium data obtained at different temperatures fit perfectly with Langmuir isotherm model compared to Freundlich and D–R isotherm models, and the maximum adsorption capacities of Cu(II) adsorbed onto CLP are 16.756, 17.085, 17.434 and $17.870\,mg\,g^{-1}$ at 303.2, 313.2, 323.2 and 333.2 K, respectively. The Langmuir and Freundlich models coefficients both implied that the adsorption of Cu(II) onto CLP is favorable. According to variations in EDS and FT-IR spectra before and after adsorption, it is considered that ion-exchange was the major removal mechanism and a certain amount of surface complexation mechanism coexisted. A schematic presentation of the adsorption process is given in Fig. 10 Regeneration studies show Cu(II)-loaded CLP can be easily desorbed by $0.1\,mol\,L^{-1}$ HCl as a regenerant and high adsorption and desorption efficiencies were obtained in five cycles of adsorption–desorption. The overall results indicated that the *C. camphora* leaves is an effective and low-cost biosorbent for the removal of Cu(II) from aqueous solutions.

Appendix A.

Model	Equation
Pseudo-first order kinetics	$\log(q_e - q_t) = \log\ q_e - \frac{k_1 t}{2.303}$
Pseudo-second order kinetics	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$
Intra-particle diffusion kinetics	$q_t = k_i t^{1/2} + C$
Langmuir isotherm	$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}}$
Freundlich isotherm	$\log\ q_e = \log K_f + \frac{1}{n}\log C_e$
Dubinin–Radushkevich isotherm	$\ln\ q_e = \ln q_m - \beta\varepsilon^2$
Van't Hoff	$\ln\ b = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$

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