



## Equilibrium, kinetic and thermodynamic studies on the biosorption of Cu(II) onto chestnut shell

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### ABSTRACT

The biosorption of Cu(II) onto chestnut shell, a residue of the food processing industry, in a batch adsorber has been studied. Equilibrium isotherms, kinetic data, and thermodynamic parameters have been evaluated. Equilibrium data agreed well with Langmuir isotherm and Redlich–Peterson isotherm models. The adsorption capacity of chestnut shell for Cu(II) was determined with the Langmuir model and was found to be  $12.56 \text{ mg g}^{-1}$  at 293 K. The kinetic data were found to follow the pseudo-second-order model. Intra-particle diffusion is not the sole rate-controlling factor. Gibbs free energy was spontaneous for all interactions, and the adsorption process exhibited exothermic enthalpy values. Chestnut shell was shown to be a promising biosorbent for Cu(II) removal from aqueous solutions.

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### 1. Introduction

Rapid industrialization has led to tremendous increase in the use of heavy metals over the past few decades and inevitably resulted in an increased flux of metallic substances in the aquatic environment. The heavy metals reach tissues through the food chain and accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders. Therefore, it is necessary to treat metal-contaminated wastewater prior to its discharge to the environment. Copper is one of the most widely used heavy metals. Its waste sources include mining wastes, drainage discharge, plating baths, fertilizer industry, paints and pigments, etc. [1]. Intake of excessively large doses of copper by man leads to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage, central nervous system irritation followed by depression, gastrointestinal irritation, and possible necrotic changes in the liver and kidney [1,2]. Conventional heavy metal clean-up technologies cover precipitation, ion exchange, chemical oxidation/reduction, reverse osmosis, electrodialysis, ultrafiltration, solvent extraction, etc. [3–9]. However some disadvantages of the technologies, such as high cost, sensitive operating conditions and production of secondary sludge [9,10], choke their popularization in industries.

Although the adsorption of heavy metals by activated carbon is another powerful technology, its high cost has prevented its application at least in developing countries. Alternatively, some low cost biomass, such as rice husk, coconut shell, hazelnut shell, walnut shell, cotton seed hull, bagasse pitch, tea factory waste, etc. [9,11–14], are being paid more attention to recently. Those biomass seem to be viable option for heavy metal removal because of their economic and eco-friendly traits due to natural chemical composition, availability in abundance, low cost, high efficiency of heavy metals removal from diluted solutions, regeneration of the bio-adsorbent, and the possibility of metal recovery [12,15].

In China, the yearly production of chestnut is *ca.*  $9.25 \times 10^5$  metric tons (in 2007) which is 75.61% of total world production [16]. Chestnut shell is generated as a residue of the food processing industry, and has no significant industrial and commercial uses, but becomes an issue and contributes to serious environmental problems. Some research reports reveal chestnut shell adsorption function. Ke and coworkers [17] utilized chestnut shell as an adsorbent to recover heavy metals from soil flushing solutions. However, few reports have been focused on the equilibrium and kinetics of any heavy metal adsorption on this biomass. In this paper, Cu(II) was chosen as a model pollutant in aqueous solution to carry out an investigation on chestnut shell adsorption action. In order to understand the nature of the adsorption, equilibrium isotherms, kinetic data, and thermodynamic parameters have been evaluated.

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**Table 1**  
Physico-chemical characterization of the chestnut shell.

Parameter	Value
Particle size (mm)	0.197
Bulk density (g mL <sup>-1</sup> )	0.490
Porosity (%)	62.931
BET surface area (m <sup>2</sup> g <sup>-1</sup> )	1.087
Moisture content (%)	6.593
Ash content (%)	1.562
pH <sub>zpc</sub>	4.9
Carboxylic group (mmol g <sup>-1</sup> )	0.70
Phenolic group (mmol g <sup>-1</sup> )	7.92
Total acidity (mmol g <sup>-1</sup> )	8.62
Lignin (%) <sup>a</sup>	28.48
Cellulose (%) <sup>a</sup>	47.96
Pentosan (%) <sup>a</sup>	12.54
Benzene–alcohol extract (%) <sup>a</sup>	8.07

<sup>a</sup> On a dry basis; data source: Ref. [21].

## 2. Materials and methods

### 2.1. Preparation and characterization of biosorbent

Commercial chestnut fruits (*Castanea mollissima* Blume) were purchased from a local market and peeled manually. The shell was washed thoroughly with distilled water to remove the dirt, and dried in an air oven at 65 °C for 24 h, finally crushed and sieved through with 40 mesh size (British Standard Sieve) and used as such. Particle size of the adsorbent was determined by Sieve Analysis. Bulk density and porosity were measured according to Ref. [18]. The specific surface area was measured by the Brunauer–Emmett–Teller (BET) method with a Quadrasorb SI (QuadraWin 3.0) apparatus (Quantachrome Corporation, USA). The point of zero charge (pH<sub>pzc</sub>) was determined by immersion technique described by Nomanbhay and Palanisamy [19]. Total acidity was determined with Ba(OH)<sub>2</sub> and the carboxylic groups were quantified by using Ca(CH<sub>3</sub>COO)<sub>2</sub> [20]. The amount of phenolic hydroxyl groups was determined by the difference between the total acidity and the carboxyl content. The results are summarized in Table 1.

### 2.2. Preparation of adsorbate solutions

Stock solution of Cu(II) was prepared (1000 mg L<sup>-1</sup>) by dissolving the desired quantity of CuCl<sub>2</sub>·2H<sub>2</sub>O (AR grade) in distilled water. The test solutions were prepared by diluting the stock solution to the desired Cu(II) concentrations.

### 2.3. Adsorption experiments

In batch pH studies, 0.5 g chestnut shell and 50 mL Cu(II) solutions (50 mg L<sup>-1</sup>) with a range of pH values from 2.0 to 6.0 were transferred in a conical flask, and shaken on a temperature controlled shaker incubator at 120 rpm for 4 days (the time required for equilibrium to be reached). The pH of the solutions was adjusted with HCl or NaOH solution by using a pH meter. Removal efficiency of copper (*P*) was defined as:

$$P (\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where *C*<sub>0</sub> (mg L<sup>-1</sup>) and *C*<sub>*e*</sub> (mg L<sup>-1</sup>) are the liquid-phase concentrations of Cu(II) at initial and equilibrium, respectively.

In the determination of equilibrium adsorption isotherm, 0.5 g chestnut shell and 50 mL of different concentrations (25–200 mg L<sup>-1</sup>) of copper solutions were shaken for 4 days at the initial pH 5 and different temperatures (293–313 K). The amount of

Cu(II) adsorption at equilibrium, *q*<sub>*e*</sub> (mg g<sup>-1</sup>), was calculated by:

$$q_e = \frac{C_0 - C_e}{M} V \quad (2)$$

where *V* (L) is the volume of the solution, *M* (g) the mass of dry adsorbent used.

In the adsorption kinetic experiments, batch adsorptions were conducted by shaking each 0.5 g chestnut shell with 50 mL different concentrations of Cu(II) solution at the initial pH 5 and the temperature 303 K for different contact times (2–180 min). The amount of adsorption at time *t* (min), *q*<sub>*t*</sub> (mg g<sup>-1</sup>), was calculated by:

$$q_t = \frac{C_0 - C_t}{M} V \quad (3)$$

where *C*<sub>*t*</sub> (mg L<sup>-1</sup>) is the liquid-phase concentrations of Cu(II) at time *t*.

All the mixtures after adsorption operation were filtered using filter paper, and the Cu(II) concentration were determined by an atomic adsorption spectrophotometer (GBC932, Australia). To ensure the accuracy, reliability, and reproducibility of the collected data, all the batch experiments were carried out in triplicate and the mean values of three data sets are presented. The equilibrium data fitted to the isotherm models used in this study were solved by using the nonlinear regression of SPSS program. Linear regressions were employed to obtain the optimum adsorption kinetic parameters by using Microsoft Excel software.

### 2.4. Fourier transform infrared spectroscopy (FT-IR) analysis

Infrared spectra of the native and Cu(II) laden chestnut shell were obtained after drying the biomass at 70 °C for 24 h. The finely powdered samples were encapsulated with potassium bromide to prepare translucent sample disks, and the spectra were recorded using a Fourier transform infrared spectroscope (Bruke EQUINOX 55, Germany).

## 3. Result and discussion

### 3.1. FT-IR test

The FT-IR spectra of chestnut shell before and after adsorption of copper were used to determine the frequency changes in the functional groups in the adsorbent. The spectra were measured within the range of 500–4000 cm<sup>-1</sup> and given in Fig. 1. It can be identified that hardly change of characteristic peaks ranging from 3407.6 to 1444.4 cm<sup>-1</sup> is observed except for 1735.6 cm<sup>-1</sup> before and after adsorption, however, some visible shifts of peak locations are presented after 1380.8 cm<sup>-1</sup>. The peaks around 1735.6 cm<sup>-1</sup> show the carbonyl (C=O) stretching vibration of the carboxyl groups [22] while the peaks at 1380.8 cm<sup>-1</sup> are initiated by carboxylate group (–COO<sup>-</sup>) stretching [23]. The peaks ranging from 1300 to 1000 cm<sup>-1</sup> are ascribed generally to the C–O stretching vibration in carboxylic acids and alcohols [24]. When chestnut shell was loaded with copper ions, the bond energy of C=O, –COO<sup>-</sup> and C–O was impacted by chemical action generated in adsorption process, consequently, resulting in the shifts on the characteristic peak locations from 1735.6, 1380.8 and 1052.9 cm<sup>-1</sup> to 1733.7, 1371.1 and 1054.9 cm<sup>-1</sup>, respectively. So, C=O, –COO<sup>-</sup> and C–O seem to participate in the copper binding. Cu(II) can be bound at the surface of biomass due to the –COOH groups and –OH groups present in the biosorbents [25]. The peak at 3407.6 cm<sup>-1</sup> is attributed to the –OH stretching vibration [26] and there was no distinct shift of this peak after copper loading. The –COOH comprises the functional groups C=O, –COO<sup>-</sup> and C–O. These support that –COOH is expected to be responsible for the copper biosorption onto the chestnut shell.

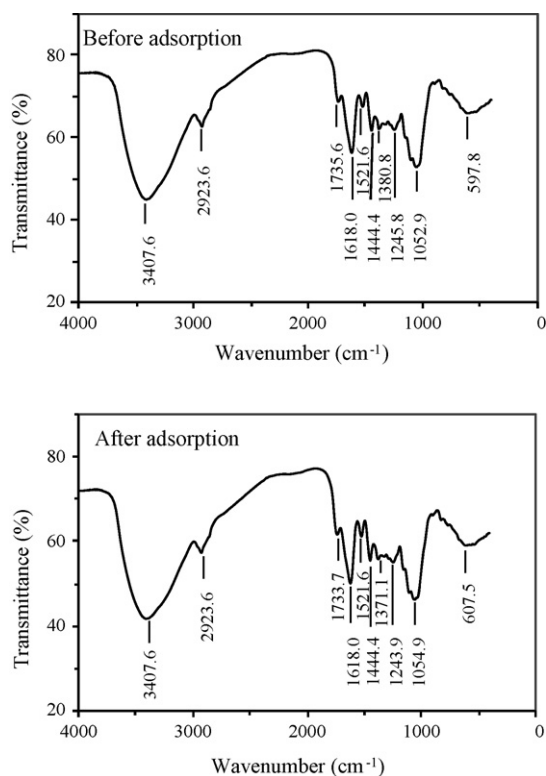


Fig. 1. FT-IR spectra of chestnut shell before and after Cu(II) adsorption.

### 3.2. Effect of pH

The pH plays an important role in the adsorption process by affecting the surface charge of adsorbent, the degree of ionization and speciation of the adsorbate. Thus the effect of pH in the solutions on the removal efficiency of Cu(II) was studied at different pH ranging from 2.0 to 6.0. Results are shown in Fig. 2. It was observed that a sharp increase in the copper removal from 20.4% to 92.4% occurred when the pH values of the solutions changed from 2.0 to 5.0 and after 5.0 a plateau is obtained. Precipitation was observed at pH 6, so pH 5.0 was selected as optimum pH for Cu(II) adsorption. The low removal efficiency at low pH is apparently due to the presence of higher concentration of  $H^+$  in the solution which compete with the Cu(II) ions for the adsorption sites of the chestnut shell. With the pH increasing, the  $H^+$  concentration decreases leading to increased Cu(II) uptake.

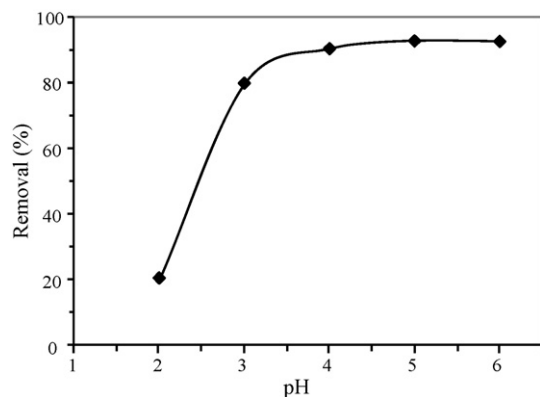
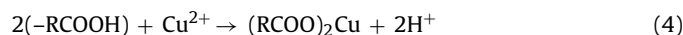


Fig. 2. Effect of the solution pH on the adsorption of Cu(II) onto chestnut shell ( $C_0 = 50 \text{ mg L}^{-1}$ ,  $V = 50 \text{ mL}$ ,  $M = 0.5 \text{ g}$ ,  $T = 303 \text{ K}$ ).

On considering the  $pH_{pzc}$  of chestnut shell and the speciation of Cu(II) in the solution another plausible explanation for Cu(II) adsorption can be provided. At a pH below 4.9 ( $pH_{pzc}$ ), the surface of the chestnut shell is positively charged due to protonation. This protonation effect is more pronounced at low pH values due to the presence of high concentration of  $H^+$  ions in the solution and results in more unfavorable for Cu(II) adsorption at a lower pH value owing to the electrostatic repulsion between both positively charged adsorbent surface and the metal ions. At optimum pH value (pH 5.0), the surface of the chestnut shell is negatively charged plausibly due to the dissociation of the  $-COOH$  groups ( $pK_a = 3.8\text{--}5.0$  [27]) and favorable to the adsorption of  $Cu^{2+}$  and  $Cu(OH)^+$  which are dominating species of the Cu(II) in the solution at pH 5.0 according to Elliott and Huang [28]. Copper may most likely be bound on the surface of the chestnut shell via ion exchange mechanism as following equations:



(where  $-R$  represents the matrix of the chestnut shell).

In addition, the HCl was used to adjust the solution pH value. The  $Cl^-$  added may result in a decrease of the free  $Cu^{2+}$  species and an increase in the formation of complex  $CuCl^+$ . This chloro-complex has larger molecular size than the free  $Cu^{2+}$  and is adverse to the biosorption, leading to a decrease in copper uptake. However, the effect was very limited because less than 1.65% of Cu(II) was complexed as  $CuCl^+$  under our experimental conditions (calculated using the software Visual Minteq v2.61).

### 3.3. Adsorption isotherms

The adsorption isotherm indicates how the adsorbate molecules distribute between the liquid phase and the solid phase at equilibrium. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose. In this research, adsorption isotherm study was carried out on three well known isotherms, i.e., Langmuir, Freundlich and Redlich–Peterson.

The Langmuir model is obtained under the ideal assumption of a totally homogenous adsorption surface [29] and represented as follows [30]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

where  $q_m$  ( $\text{mg g}^{-1}$ ) is the monolayer adsorption saturation capacity, and  $K_L$  ( $\text{L mg}^{-1}$ ) Langmuir constant relating to adsorption energy. Fig. 3 shows the Langmuir plots at different temperatures and the constants  $q_m$  and  $K_L$  are tabulated in Table 2. High  $R^2$  values ( $>0.98$ , Table 2) indicate that the biosorption of Cu(II) onto chestnut shell follows the Langmuir model. The constants  $q_m$  and  $K_L$  decreased with increasing temperature, which indicates that, at lower temperatures, the adsorption density was higher and the adsorption energy was lower. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor ( $R_L$ ), which is defined as [31]:

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

The value of  $R_L$  indicates the type of isotherm to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ) [31]. The calculated  $R_L$  values at different initial Cu(II) concentrations and temperatures are shown in Fig. 4. It can be seen that  $R_L$  value drops into the range 0–1 in all experimental systems, which confirms the favorable uptake of the copper process. Lower  $R_L$  values at higher initial Cu(II) concentrations and lower

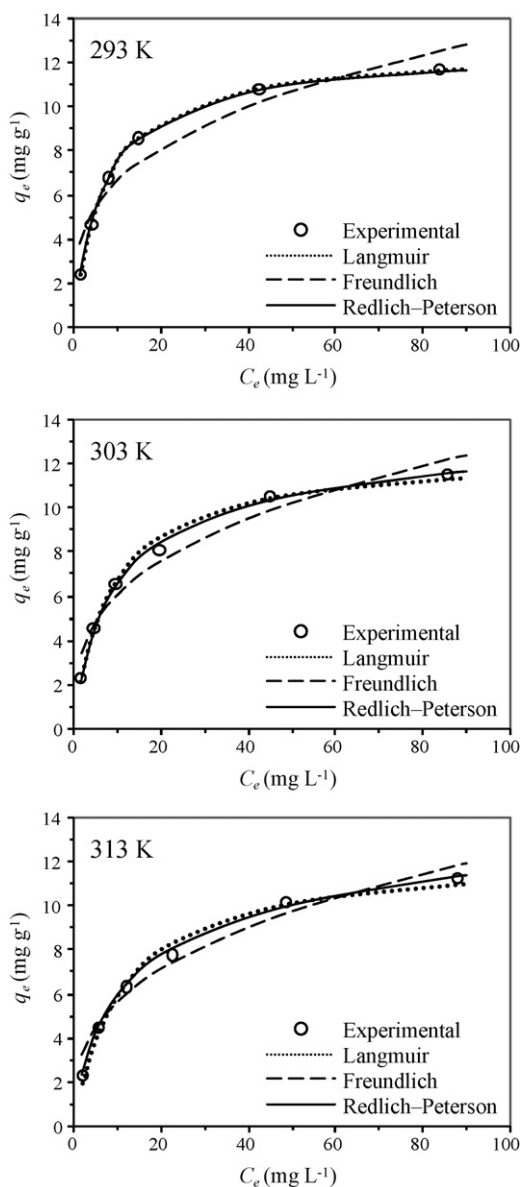


Fig. 3. Comparison of different isotherm models for Cu(II) adsorption onto chestnut shell ( $V = 50$  mL,  $M = 0.5$  g,  $\text{pH} = 5.0$ ).

temperature showed that adsorption was more favorable at higher concentration and lower temperature.

Table 3 summarizes the comparison of Cu(II) adsorption capacities ( $q_m$ ) by various agricultural by-products. Chestnut shell presents higher adsorption capacity than 12 from 16 different adsorbents, reflecting a promising future for chestnut shell utilization in copper ion removal from aqueous solutions.

The Freundlich isotherm is suitable for a highly heterogeneous surface [29] and expressed by the following [44]:

$$q_e = K_F C_e^{1/n} \quad (8)$$

Table 2  
Isotherm parameters for Cu(II) adsorption onto chestnut shell at different temperatures.

Temperature (K)	Langmuir			Freundlich			Redlich–Peterson			
	$q_m$ ( $\text{mg g}^{-1}$ )	$K_L$ ( $\text{L mg}^{-1}$ )	$R^2$	$K_F$ ( $\text{mg}^{1-1/n} \text{g}^{-1} \text{L}^{1/n}$ )	$1/n$	$R^2$	$K_R$ ( $\text{L g}^{-1}$ )	$a_R$ ( $\text{L}^g \text{mg}^{-g}$ )	$g$	$R^2$
293	12.558	0.141	0.998	3.247	0.304	0.924	1.785	0.144	0.997	1.000
303	12.420	0.114	0.993	2.851	0.326	0.955	1.702	0.192	0.923	0.997
313	12.324	0.091	0.989	2.493	0.347	0.969	1.588	0.233	0.869	0.998

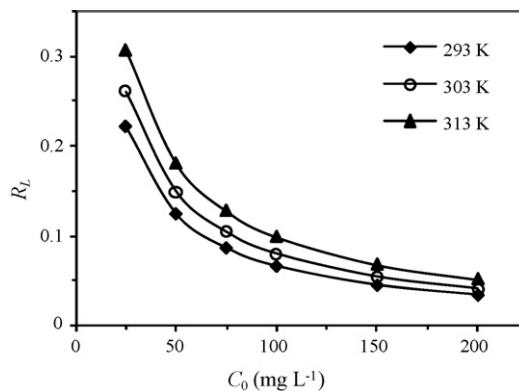


Fig. 4. Plot of separation factor versus initial Cu(II) concentration ( $V = 50$  mL,  $M = 0.5$  g,  $\text{pH} = 5.0$ ).

Table 3

A number of agricultural by-products available for adsorption of copper ions.

Adsorbent	$q_m$ ( $\text{mg g}^{-1}$ )	Reference
Rice bran	33.58	[32]
Carrot residue	32.74	[33]
Sugar beet pulp	31.4	[34]
Sour orange residue	21.70	[35]
Chestnut shell	12.56	This study
Tree fern	11.7	[36]
Cotton boll	11.4	[37]
Apple wastes	10.8	[38]
Grape stalks wastes	10.12	[39]
Tea-industry waste	8.64	[11]
Sawdust	8.45	[40]
Peanut hulls	8.37	[41]
Wheat shell	8.34	[42]
Walnut shell	6.74	[12]
Hazelnut shell	6.65	[12]
Almond shell	3.62	[12]
Pomegranate peel	1.32	[43]

where  $K_F$  ( $\text{mg}^{1-1/n} \text{g}^{-1} \text{L}^{1/n}$ ) and  $1/n$  (–) are the Freundlich constants, denoting the adsorption capacity and intensity, respectively. Fig. 3 shows the Freundlich plots at different temperatures and the constants  $K_F$  and  $1/n$  are tabulated in Table 2. The values of  $1/n$  less than 1 represent a favorable adsorption [45]. Compared with the Langmuir isotherm and the Redlich–Peterson isotherm, the theoretical values calculated from the Freundlich isotherm were further deviated from experimental data as shown in Fig. 3. These facts imply that the Freundlich isotherm is poorly appropriate to characterize the Cu(II) adsorption onto chestnut shell.

The Redlich–Peterson isotherm model [46] combines both Langmuir isotherm and Freundlich isotherm equation and the mechanism of adsorption is a hybrid and does not follow ideal monolayer adsorption. The equation is:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \quad (9)$$

where  $K_R$  ( $\text{L g}^{-1}$ ) and  $a_R$  ( $\text{L}^g \text{mg}^{-g}$ ) are Redlich–Peterson isotherm constants and  $g$  (–) the exponent which lies between 1 and 0. For  $g = 1$ , the equation converts to the Langmuir isotherm; for  $g = 0$ , it

**Table 4**  
Kinetic parameters for Cu (II) adsorption onto chestnut shell at different initial concentrations.

$C_0$ (mg L <sup>-1</sup> )	$q_{e,exp}$ (mg g <sup>-1</sup> )	Pseudo-first-order			Pseudo-second-order			Intra-particle diffusion			
		$q_{e,cal}$ (mg g <sup>-1</sup> )	$k_1$ (min <sup>-1</sup> )	$R^2$	$q_{e,cal}$ (mg g <sup>-1</sup> )	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$h_0$ (mg g <sup>-1</sup> min <sup>-1</sup> )	$R^2$	$K_d$ (mg g <sup>-1</sup> min <sup>-1/2</sup> )	$I$ (mg g <sup>-1</sup> )	$R^2$
25	2.326	0.461	0.013	0.748	2.278	0.217	1.126	0.999	0.063	1.599	0.665
50	4.531	1.176	0.014	0.771	4.435	0.075	1.475	0.997	0.161	2.688	0.668
100	8.040	2.419	0.016	0.874	7.962	0.033	2.105	0.998	0.304	4.585	0.729
200	11.450	3.752	0.018	0.851	11.429	0.020	2.623	0.997	0.508	5.834	0.721

simplifies to Henry's law equation; and for  $1 \ll a_R C_e^g$ , it is identical with the Freundlich isotherm. Table 2 lists these parameters together with the  $R^2$  values. A comparison between the theoretic and experimental results on the Cu(II) adsorption onto chestnut shell was made and exhibited in Fig. 3. The Redlich–Peterson equation provides a best fit over the entire range of concentration for the experimental data. As can be seen from Table 2, the  $R^2$  values are closest to 1 for Redlich–Peterson isotherm, confirming its best fit for Cu(II) adsorption onto chestnut shell in three studied models. The values of  $g$  in Table 2 are closer to 1 than 0, which means that the isotherm is approaching the Langmuir but not the Freundlich isotherm. Hence, the good fit of equilibrium data in both Langmuir and Redlich–Peterson isotherm expressions confirms the monolayer coverage process of copper onto chestnut shell.

### 3.4. Adsorption kinetics

In order to further expose the adsorption mechanism of Cu(II) onto chestnut shell and rate-controlling steps, a kinetic investigation was conducted. Pseudo-first, pseudo-second-order and intra-particle diffusion kinetic models have been used for testing experimental data.

The pseudo-first-order reaction equation of Lagergren [47] was widely used for the adsorption of liquid/solid system on the basis of solid capacity. Its linear form is generally expressed as the following:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (10)$$

where  $q_e$  (mg g<sup>-1</sup>) and  $q_t$  (mg g<sup>-1</sup>) are the adsorption amount at equilibrium and time  $t$  (min), respectively.  $k_1$  (min<sup>-1</sup>) is the rate constant in the pseudo-first-order adsorption process. The constants were determined experimentally by plotting of  $\log(q_e - q_t)$  versus  $t$  and list in Table 4. The lines were drawn in Fig. 5a. The theoretic values ( $q_{e,cal}$ ) are far lower than those experimental data,  $q_{e,exp}$  (Table 4), implying that the adsorption process does not follow fully the pseudo-first-order adsorption rate expression.

The pseudo-second-order model proposed by Ho and McKay [48] is based on the assumption that the adsorption follows second-order chemisorption. The linear form can be written as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (11)$$

where  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) is the rate constant of adsorption. By plotting a curve of  $t/q_t$  against  $t$ ,  $q_e$  and  $k_2$  can be evaluated. The initial adsorption rate,  $h_0$  (mg g<sup>-1</sup> min<sup>-1</sup>) is defined as [36]:

$$h_0 = k_2 q_e^2 \quad (12)$$

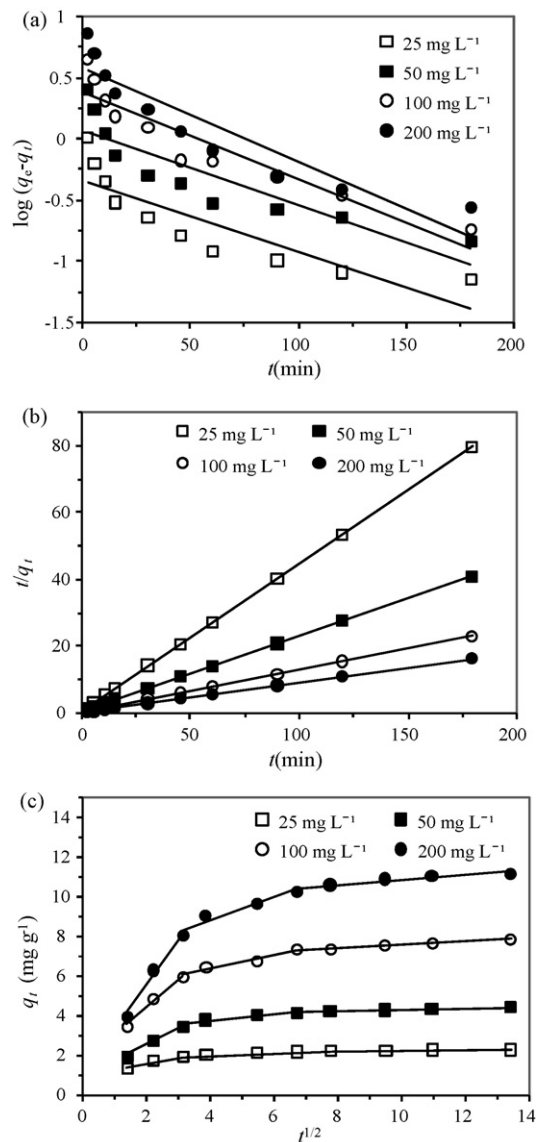
The values of  $q_e$ ,  $k_2$ ,  $h_0$  and  $R^2$  are list in Table 4. The dependence of  $t/q_t$  versus  $t$  gives an excellent straight line relation for all the experimental concentrations (Fig. 5b), and all the  $R^2$  values are close to 1 (Table 4), confirming the applicability of the pseudo-second-order equation. In addition, there is only a little difference between the  $q_{e,exp}$  and  $q_{e,cal}$  (Table 4), reinforcing the applicability of this model. It can also be seen in Table 4 that, with an increase in initial metal concentration, the initial adsorption rate ( $h_0$ ) increases while

the rate constant of adsorption ( $k_2$ ) decreases. A similar observation was also reported by the earlier researchers [49] who studied the adsorption characteristics of Cu(II) on the pellets made from fired coal fly ash.

The kinetic data were analyzed by an intra-particle diffusion model to elucidate the diffusion mechanism [50]:

$$q_t = k_d t^{1/2} + I \quad (13)$$

where  $k_d$  (mg g<sup>-1</sup> min<sup>-1/2</sup>) is the intra-particle diffusion rate constant, and  $I$  (mg g<sup>-1</sup>) a constant that gives idea about the thickness of the boundary layer. According to this model, if the plot of  $q_t$  versus



**Fig. 5.** Adsorption kinetics of Cu(II) onto chestnut shell at different initial concentrations ( $V = 50$  mL,  $M = 0.5$  g,  $T = 303$  K,  $pH = 5.0$ ).

**Table 5**  
Thermodynamic parameters for the adsorption of Cu(II) onto chestnut shell.

T (K)	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	R <sup>2</sup>
293	-1.392	-17.423	-54.667	0.999
303	-0.876			
313	-0.298			

$t^{1/2}$  gives a straight line, then the adsorption process is controlled by intra-particle diffusion, while, if the data exhibit multi-linear plots, then two or more steps influence the adsorption process [29]. In the present study, the plots presents multi-linearity (Fig. 5c), indicating three steps take place. At the first, sharper portion may be considered as an external surface adsorption or faster adsorption stage. The second portion describes the gradual adsorption stage, where the intra-particle diffusion is rate-controlled. The third portion is attributed to the final equilibrium stage, where intra-particle diffusion starts to slow down due to the extremely low adsorbate concentrations in the solution [51]. In the intermediate stage where the adsorption is gradual, the process may be controlled by intra-particle diffusion. This indicates that intra-particle diffusion involved in the Cu(II) adsorption onto chestnut shell, but it was not the sole rate-controlling-step.

### 3.5. Adsorption thermodynamics

The Gibbs free energy change of the adsorption process is related to the equilibrium constant by the classic Van't Hoff equation:

$$\Delta G^\circ = -RT \ln K \quad (14)$$

where  $\Delta G^\circ$  is the standard free energy change (J mol<sup>-1</sup>),  $T$  the absolute temperature (K) and  $R$  gas constant (J mol<sup>-1</sup> K<sup>-1</sup>),  $K$  (L g<sup>-1</sup>) an equilibrium constant obtained by multiplying the Langmuir constants  $q_m$  and  $K_L$  [34].

According to thermodynamics, the Gibbs free energy change is also related to the entropy change and heat of adsorption at constant temperature by the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (15)$$

where  $\Delta H^\circ$  is enthalpy change (J mol<sup>-1</sup>),  $\Delta S^\circ$  entropy change (J mol<sup>-1</sup> K<sup>-1</sup>).  $\Delta H^\circ$  and  $\Delta S^\circ$  can be calculated from the plot of  $\Delta G^\circ$  versus  $T$  (not shown).

The calculated thermodynamic parameters for the adsorption of copper by chestnut shell are given in Table 5. The negative value of  $\Delta G^\circ$  indicates the feasibility of the process and indicates the spontaneous nature of the adsorption.  $\Delta G^\circ$  value is more negative with decreasing temperature, which suggests that lower temperature makes the adsorption easier. The negative value of  $\Delta H^\circ$  implies that the adsorption phenomenon is exothermic. The negative value of  $\Delta S^\circ$  suggests the process is enthalpy driven.

## 4. Conclusions

The ability of chestnut shell biosorbent to remove Cu(II) from aqueous solution was investigated in equilibrium, kinetics and thermodynamics. Equilibrium data agreed well with Langmuir isotherm and Redlich–Peterson isotherm models. The kinetic data were found to follow the pseudo-second-order model. Intra-particle diffusion is not the sole rate-controlling factor. The negative values of  $\Delta H^\circ$  and  $\Delta G^\circ$  revealed the exothermic nature and the feasibility of adsorption. The investigation shows that chestnut shell is a promising biosorbent for the removal of Cu(II) from aqueous solutions.

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