Equilibrium, kinetics and thermodynamics of Cu(II) biosorption on Chinese chestnut shell pretreated with steam explosion

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ABSTRACT

The shells of Chinese chestnuts (*Castanea mollissima*) are an agricultural residue. This work aimed to evaluate this feasibility of using steam explosion to modify this residue for Cu(II) biosorption from aqueous solutions. Equilibrium, kinetic and thermodynamic parameters were evaluated. The steam-explosion pretreatment increased the surface area of the chestnut shell and exposed more hydroxyl and carboxyl groups, which are binding sites for Cu(II). It changed the sorption from a spontaneous process driven by enthalpy to a nonspontaneous one driven by entropy. It increased the Cu(II) sorption capacity at higher temperatures while it decreased the capacity at lower ones. Compared with untreated chestnut shell, the steam-exploded shell is preferable for Cu(II) sorption at higher temperatures.

Key words | biosorption, Chinese chestnut shell, heavy metal, steam explosion

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INTRODUCTION

Heavy metals have been widely used in large quantities in many industries over the past few decades, which has inevitably brought about an increase in the discharge of metallic substances into adjacent water bodies. These substances can get into the human body and accumulate in the organs, causing serious health problems if ingested beyond the recommended concentrations. Therefore, metal-contaminated wastewater needs to be treated prior to its discharge into the environment.

Copper, an important heavy metal widely used in industry, agriculture and household products, is emitted into the environment from sources such as drainage discharge, mining, plating, paints, pigments, and the fertilizer industry (Malik *et al.* 2017). Intake of acute dosage of copper by humans can cause serious mucosal corrosion, nervous irritation, capillary damage, and hepatic and renal failure (Malik *et al.* 2017). Copper-loaded wastewater can be treated by ion exchange, precipitation, chemical oxidation, chemical reduction, solvent extraction, reverse osmosis, ultrafiltration, electrodialysis, and sorption (Yao *et al.* 2010). Biosorption, a subcategory of sorption, is based on the ability of biomolecules or biomass to adsorb and

concentrate some ions or other molecules from aqueous solutions (Cataldo *et al.* 2018). It is considered a promising technology for heavy-metal removal from wastewater.

Some low-cost agricultural biomass, such as the shells from chestnuts, walnuts, hazelnuts, and almonds (Yao *et al.* 2010; Cataldo *et al.* 2018), have been given more attention recently thanks to their eco-friendly and economic characteristics. However, these agricultural wastes are generally poor in their sorption capacities for heavy metals and incapable of meeting the requirements of industrial applications. Therefore, they need to be modified or treated to overcome this disadvantage. Many chemicals have been employed for the modifications, including organic and mineral acids/bases, oxidants, and organic compounds (Vijayaraghavan & Balasubramanian 2015). Physical methods are generally very simple and inexpensive. Autoclaving, steaming, thermal drying, lyophilization, cutting and grinding have been used for biosorbent modification. Steam explosion, which originally was used in the pulping process, has been recognized as a cost-effective technology for pretreating lignocellulosic biomass. Chi & Chen (2009) showed that steam explosion affects the specific surface

area of corn stalk and its structure, making it better for etha-
nol production. Steam explosion has also been used for
chestnut shell pretreatment to produce fermentable sugars,
and its effect on enzymatic saccharification was reported
by Maurelli *et al.* (2013). However, there have been no
reports of applying steam explosion to modifying biomass
for biosorption.

In China, the yearly production of Chinese chestnuts
(*Castanea mollissima*) is about 1.88 million tons (FAO
2017), and the shells are the waste remaining after pro-
duction. Our previous work (Yao *et al.* 2010) revealed the
potential use of Chinese chestnut shell for the sorptive
removal of copper ions from aqueous solutions. Here, our
goal is to examine the applicability of steam explosion to
improving the sorption performance of Chinese chestnut
shell for copper removal from water. The biosorption by
the steam-exploded chestnut shell was characterized by
equilibrium isotherms, kinetics, thermodynamics, and Four-
ier transform infrared spectroscopy (FT-IR). To evaluate the
effects of steam explosion on sorption, the results were
compared with previously determined results of Cu(II)
biosorption by raw chestnut shell (Yao *et al.* 2010).

MATERIALS AND METHODS

Preparation of the biosorbent

Chinese chestnuts were purchased from a market in
Shenyang, China, and peeled by hand. The shells were
steam exploded at 1.3 MPa (about 192 °C) for 5 min with a
QBS-200B-type steam blasting machine (Bio Energy Co.,
Ltd, Hebi, China), washed thoroughly with distilled water,
air-dried in an oven for 24 hours at 65 °C, crushed, and
sieved through a sieve with a 0.38 mm mesh.

Preparation of sorbate solutions

Stock copper solution (10,000 mg/L) was made by dissol-
ving the desired quantity of $Cu(NO_3)_2 \cdot 3H_2O$ (AR grade) in
pure water. The test solutions were made by diluting the
stock solution to the required Cu(II) concentrations with
pure water.

Biomass characterization

The specific surface area was determined by the Brunauer-
Emmett-Teller (BET) method with an ASAP2020 sorption
apparatus (Micromeritics, USA). The point of zero charge

(pH_{pzc}) was measured by the immersion technique
reported by Nomanbhay & Palanisamy (2005). The scan-
ning electron microscopy (SEM) analysis was conducted
with a Hitachi S-3000N SEM. FT-IR spectra were
recorded with a Bruker Tensor 27 FT-IR spectrometer,
using the KBr disc technique. The samples were dried
over P_2O_5 in a desiccator for 7 days prior to the FT-IR
measurement.

Sorption experiments

Batch pH studies were carried out according to our previous
work (Yao *et al.* 2010). In brief, pretreated chestnut shell
(0.5 g) and 50 mL Cu(II) solution (50 mg/L) with pH
values ranging from 2.0 to 6.0 (with HNO_3 or NaOH sol-
utions to adjust the pH) were transferred to flasks and
shaken on an orbital shaker at 120 rpm for 24 hours at
298 K. Copper removal efficiency was obtained as:

$$\text{Removal}\,(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (1)$$

where C_0 (mg/L) and C_e (mg/L) are the Cu(II) concen-
trations in the solution before and after sorption,
respectively.

Kinetic experiments were carried out by vibrating each
0.5 g of chestnut shell with 50 mL Cu(II) solutions of pH 5
with different concentrations at 303 K for different contact
times. The amount of adsorbed copper, q_t (mg/g), was
given as:

$$q_t = \frac{(C_0 - C_t)v}{m} \qquad (2)$$

where C_t (mg/L) is the Cu(II) concentration in the solutions
at time t (min), v (L) is the solution volume, and m (g) is the
sorbent mass.

To determine the sorption isotherms, the sorbent (0.5 g)
and the copper solutions (50 mL) of various concentrations
(25–200 mg/L) with a pH of 5 were shaken at different temp-
eratures (303–333 K) for 24 hours. The amount of adsorbed
copper at equilibrium, q_e (mg/g), was calculated as:

$$q_e = \frac{(C_0 - C_e)v}{m} \qquad (3)$$

After the sorption process, the mixtures were filtered
through a microporous membrane with 1.2-μm pores and
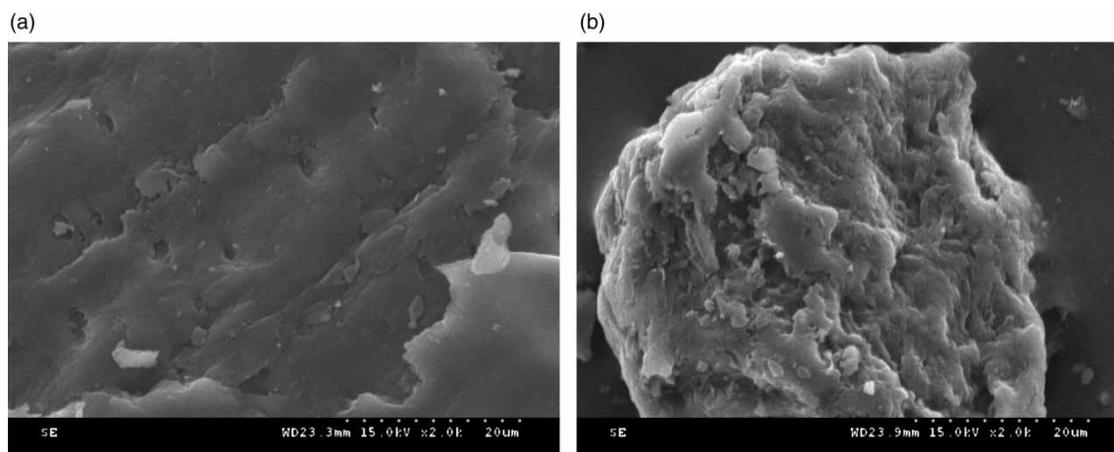the copper concentrations were measured with a flame

(a)   (b)

Figure 1 │ SEM images of the untreated (a) and steam-exploded (b) chestnut shell.

atomic sorption spectrophotometer (AA-100, Perkin-Elmer Inc., Foster City, USA).

All the sorption experiments were conducted three times, and the mean values are presented. The equilibrium and kinetic data fitted to the models were solved by linear regression using Microsoft® Excel.

RESULTS AND DISCUSSION

Biomass characterization

The pretreated and untreated chestnut shell were characterized to illustrate the effect of steam-explosion pretreatment on the properties of the biosorbent. Steam explosion can decrease the pH_{pzc} from 4.9 for the untreated biomass (Yao *et al.* 2010) to 3.8 for the modified biomass. This may be due to the increased acidity of the biosorbent (Jacquet *et al.* 2015), which was confirmed by FT-IR spectra. The surface morphology of the biomass with and without pretreatment was characterized using SEM and indicated that the untreated particle surface is smooth with some pores while the particle surface of the steam-exploded chestnut-shell particle is rough (Figure 1). The roughness of the particle is caused by breakage and destruction of the biomass during the rapid escape of steam from the internal pores. Generally, an enlarged surface area endows sorbents with higher sorption capacity. Steam-explosion treatment has been shown to expand the specific surface area of some lignocellulosic materials (Chi & Chen 2009); it increased the surface area of the chestnut shell from 14.44 m²/g to 29.27 m²/g.

The FT-IR spectra of the untreated chestnut shell (Figure 2(a)) and the steam-exploded chestnut shell before (Figure 2(b)) and after (Figure 2(c)) Cu(II) sorption exhibit similar absorption bands, indicating that steam explosion did not produce new functional group species on the chestnut shell. However, significant changes were found in the absorption bands around 3,440, 1,740 and 1,521 cm⁻¹ for stretches in OH, COOH and C = C of aromatic rings. The steam explosion made the bands at 3,440 and 1,521 cm⁻¹ stronger and changed the band at 1,740 cm⁻¹ from a shoulder to a small peak, suggesting more hydroxyls, carboxyls, and aromatic rings were exposed by the pretreatment. After the sorption of copper onto the steam-exploded chestnut shell, the band at 3,440 cm⁻¹ was weakened and the peak at 1,740 cm⁻¹ for the carboxyl shifted to a band at 1,695 cm⁻¹ for copper carboxylate, indicating hydroxyls and carboxyls played important roles in binding copper onto the biomass. These functional groups have also been found to take part in the sorption of copper onto the untreated chestnut shell (Yao *et al.* 2010).

Effect of pH

The pH usually plays a crucial role in biosorption. It affects both the surface charge of biosorbents, and the degree of ionization and speciation of sorbates. The effect of the pH of the solution on Cu(II) removal was that the copper removal surged with increasing pH from 2.0 to 3.0, then gradually rose to the maximum of 98.2% at pH 5.0, and finally slightly decreased with the further increase of the pH value to 6.0 (Figure 3(a)). Therefore, pH 5.0 was selected as the optimum pH for the sorption process of Cu(II) onto the steam-exploded chestnut shell. At low pH values, more
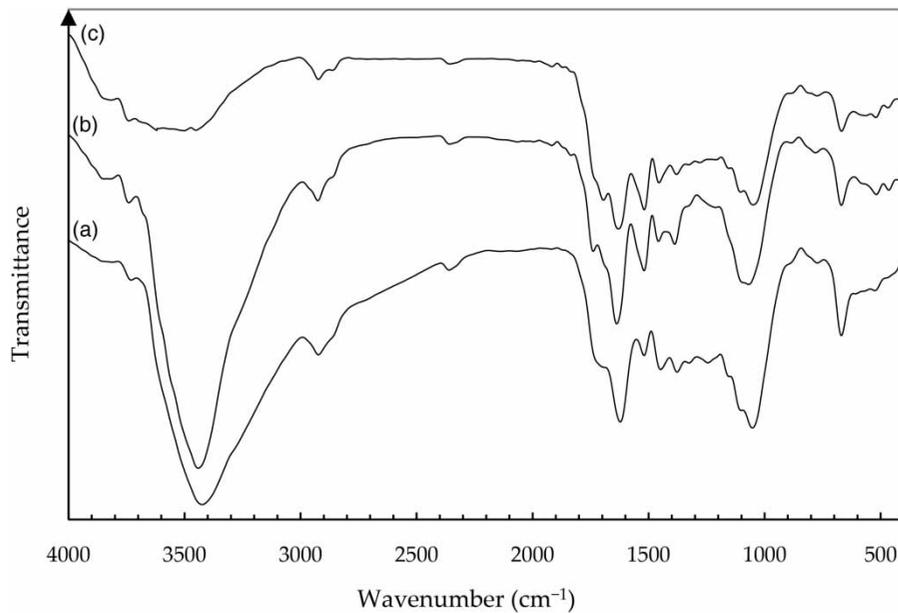
Figure 2 | FT-IR spectra of the untreated chestnut shell (a) and the steam-exploded chestnut shell before (b) and after (c) Cu(II) sorption.
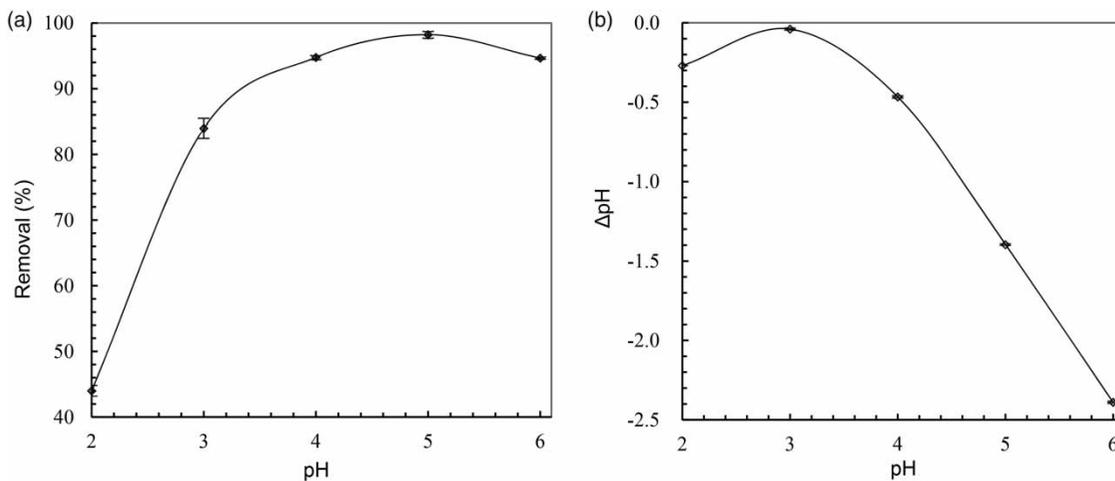

Figure 3 | Effect of the solution pH on the Cu(II) sorption onto chestnut shell pretreated by steam explosion (a) and pH change of the solution after the sorption (b) (copper concentration: 50 mg/L, adsorbent dosage: 0.5 g, temperature: 298 K, contact time: 24 hours).

H^+ is present in the solution, which competes with the Cu(II) ion for the sorption sites on the biosorbent. This may explain why the removal efficiency goes up with the pH increasing from 2.0 to 5.0. The effect of the solution pH on the Cu(II) sorption can also be explained based on the biosorbent's pH_{pzc} and the copper speciation. The pH_{pzc} of the steam-exploded chestnut shell was found to be 3.8. Consequently, the charges on the biosorbent surface are positive at a pH below 3.8 and negative at a pH over 3.8. At pH values ranging from 2.0 to 6.0 in the Cu(II) solution of 50 mg/L, Cu^{2+} and $Cu(OH)^+$ are the dominant Cu(II) species, according to simulation results performed with the Visual Minteq v2.61 software. The biosorbent surface is protonated more pronouncedly at a low pH owing to the presence of concentrated protons in the solution. This condition is more unfavorable to copper capture because the positively charged biosorbent surface electrostatically repulses the metal cations. At the optimum pH value (pH 5.0), the surface is negatively charged and favorable to the sorption of the dominant species, Cu^{2+} and $Cu(OH)^+$. To further explain the removal mechanism, all the final pHs after the sorption were measured, and the

ΔpH (pH$_{final}$ – pH$_{initial}$) values are shown in Figure 3(b). All the solution pHs went down after sorption (negative ΔpH), indicating that H$^+$ was replaced from the phenolic hydroxyls and carboxyls on the biosorbent to the solution by Cu^{2+} and/or Cu(OH)$^+$. Ion exchange was also involved in the sorption process of Cu(II) onto the untreated chestnut shell (Yao et al. 2010). This sorption mechanism was retained after steam-explosion pretreatment.

Sorption kinetics

Sorption kinetics is a physicochemical way of evaluating the performance of a process. The pseudo-first-order, pseudo-second-order, and intra-particle diffusion equations were fitted to the kinetic data. In this study, equilibrium was attained within 300 min and the equilibrium times were the same for all tested concentrations. Therefore, sorption data for 2.5–300 min were fitted to the kinetic models.

The pseudo-first-order equation, which is extensively used in liquid-solid sorption systems, is linearly expressed in Equation (4) (Lagergren 1898):

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

where q_e (mg/g) and q_t (mg/g) are the amounts sorbed at equilibrium and at any time t (min), respectively, and k_1 (min^{-1}) is the rate constant in the pseudo-first-order sorption model. The constants (Table 1) were evaluated by plotting $\log (q_e - q_t)$ against t (Figure 4(a)). Although this model had high R^2 values, the theoretical values ($q_{e,cal}$) were lower than those directly obtained from the experiments ($q_{e,exp}$). These results showed that the experimental data did not fit the pseudo-first-order kinetic model.

The pseudo-second-order model is written in the linear form as follows (Ho 2003):

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \tag{5}$$

where k_2 (g/mg/min) is the rate constant of sorption. The values of q_e and k_2 were determined by plotting a curve of

Table 1 | Kinetic parameters of the pseudo-first-order and pseudo-second-order models for Cu(II) sorption onto steam-exploded chestnut shell

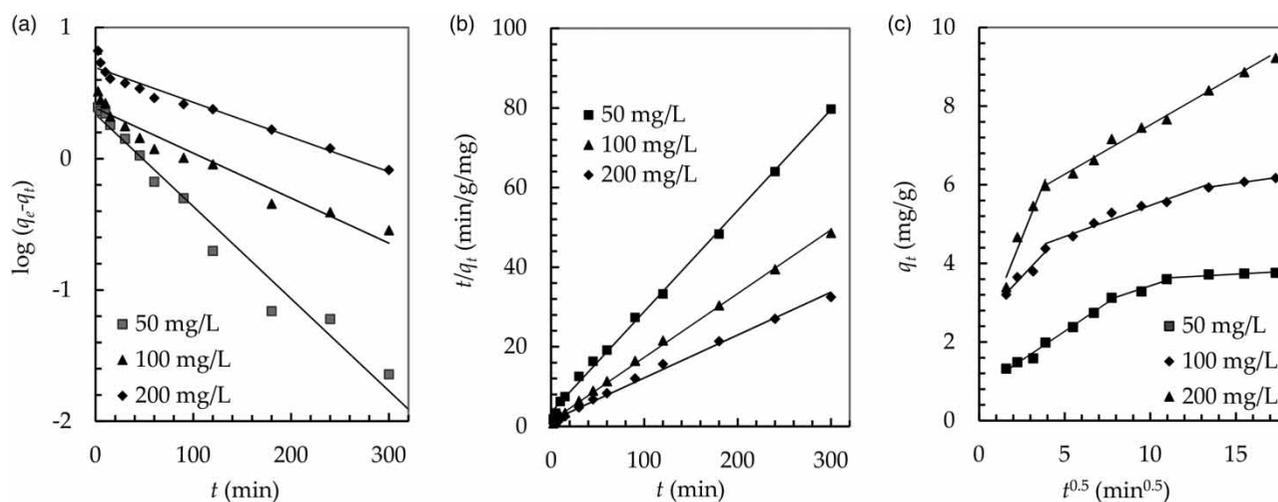| C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-first-order			Pseudo-second-order			
		$q_{e,cal}$ (mg/g)	k_1 (10^{-3} min^{-1})	R^2	$q_{e,cal}$ (mg/g)	k_2 (g/mg/min)	h_0 (mg/g/min)	R^2
50	3.81	2.18	16.12	0.973	3.94	0.0185	0.287	0.998
100	6.48	2.43	7.83	0.944	6.25	0.0195	0.760	0.998
200	10.08	4.94	5.99	0.958	9.28	0.0084	0.724	0.994

Figure 4 | (a) The pseudo-first-order, (b) the pseudo-second-order, and (c) the intra-particle diffusion kinetic plots for Cu(II) sorption onto steam-exploded chestnut shell (copper concentration: 50 mg/L, adsorbent dosage: 0.5 g, temperature: 298 K, pH: 5).

t/q_t against t. The initial sorption rate, h_0 (mg g^{-1} min^{-1}) is defined as (Ho 2003):

$$h_0 = k_2 q_e^2 \qquad (6)$$

The values of q_e, k_2, h_0, and R^2 are shown in Table 1. The plot of t/q_t versus t gives good straight lines for all the copper concentrations (Figure 4(b)), and all of the R^2 values are over 0.99 (Table 1). The theoretical values ($q_{e,cal}$) obtained from this equation are close to the experimental ones ($q_{e,exp}$). These signify that the sorption systems are a good fit for the pseudo-second-order kinetic model, on the basis of the assumption that the rate-limiting step might be chemisorption, involving electron sharing or exchange of sorbent with sorbate (Ho 2003). We found the Cu(II) sorption onto the untreated chestnut shell also obeyed the pseudo-second-order kinetic model (Yao *et al.* 2010). By comparison with the Cu(II) sorption onto the untreated chestnut shell (Yao *et al.* 2010), the steam-explosion pretreatment led to reductions of the sorption rate constant and the initial sorption rate (h_0), which is disadvantageous to a sorption process. Currently, there is no evidence to explain the decrease in sorption on steam-exploded biomass. As a thermo-mechanicochemical process, steam explosion opens lignocellulosic structures, modifies the chemical properties of the lignin and cellulose, and forms organic acids, etc. (Jacquet *et al.* 2015). Steam explosion made the chestnut shell more favorable to working as a biosorbent in both physical (rough surface and bigger surface area) and chemical (more binding functional groups) aspects. The contradiction between the sorption performance and the physicochemical properties is very interesting and worth further investigation.

To elucidate the diffusion mechanism, the kinetic data were further fitted to the intra-particle diffusion model (Weber & Morris 1963):

$$q_t = k_d t^{0.5} + I \qquad (7)$$

where k_d (mg/g/min$^{0.5}$) is the intra-particle diffusion rate constant, and I (mg/g) is a constant that gives an idea of the boundary layer thickness. If the plot of q_t against $t^{0.5}$ is a straight line, sorption is controlled by intra-particle diffusion. In this study, the plot exhibits a two- or three-line behavior (Figure 4(c)), suggesting more than one step affects the sorption process. The first stage is sharper, which is assigned to the sorbate diffusing from the solution through the boundary film to the external surface of the

sorbent. The second portion is a gradual sorption stage, which may be considered to be intra-particle diffusion. The third portion describes a final equilibrium stage, during which the intra-particle diffusion slowed down due to extremely low sorbate concentrations in the solution (Lorenc-Grabowska & Gryglewicz 2005). As is shown in Figure 4(a), the plots of the linearized intra-particle diffusion model at all concentrations studied are not linear over the whole time range but show multi-linearity. This implies that intra-particle diffusion was involved in the Cu(II) sorption onto the steam-exploded chestnut shell but it was not the exclusive rate-controlling step. A similar observation was also made for Cu(II) sorption onto untreated chestnut shell (Yao *et al.* 2010). The parameters (k_d and I) together with the determination coefficients for both the whole time range and the second linear portion from Figure 4(c) are listed in Table 2.

Sorption isotherms

The sorption isotherm shows the distribution behavior of sorbate between the liquid and the solid phases at equilibrium. The right isotherm model can be used to design the sorption process. Therefore, fitting the equilibrium data to different isotherms is a meaningful step in obtaining an applicable isotherm for design purposes. In this study, a sorption isotherm study was conducted using two famous isotherms, i.e., the Langmuir and Freundlich models.

The Langmuir model is derived under the ideal assumption of a totally homogenous sorption surface, and its linear form is represented as (Langmuir 1918):

$$\frac{1}{q_e} = \frac{1}{(q_m K_L)} \times \frac{1}{C_e} + \frac{1}{q_m} \qquad (8)$$

where q_m (mg/g) is the monolayer sorption saturation capacity, and K_L (L/mg) is the Langmuir constant related to sorption energy.

Table 2 | Parameters of the intra-particle diffusion model for Cu(II) sorption onto steam-exploded chestnut shell

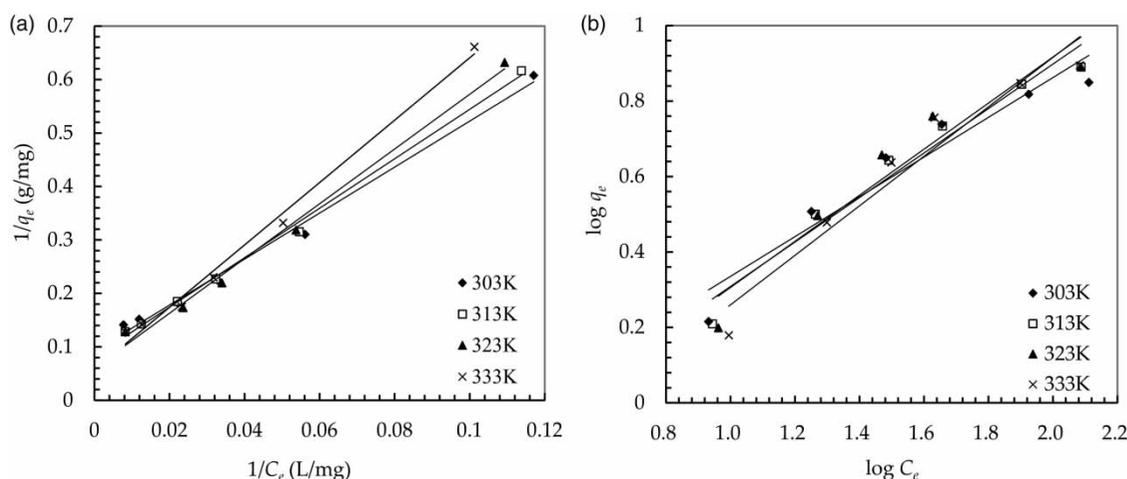| C_0 (mg/L)	Whole time range			Second linear portion		
	k_d (mg/g/min$^{0.5}$)	I (mg/g)	R^2	k_d (mg/g/min$^{0.5}$)	I (mg/g)	R^2
50	0.150	1.42	0.843	0.146	1.97	0.946
100	0.163	3.58	0.887	0.159	3.89	0.958
200	0.291	4.36	0.908	0.251	5.01	0.960

Figure 5 | Linear forms of (a) the Langmuir and Freundlich isotherms for Cu(II) sorption onto steam-exploded chestnut shell (copper concentration: 50 mg/L, adsorbent dosage: 0.5 g, contact time: 24 hours, pH: 5).

The constants K_L and q_m at different temperatures were calculated from the plots of $1/q_e$ against $1/C_e$, as shown in Figure 5, and their values, as well as the coefficient of determination (R^2), are shown in Table 3. High R^2 values (>0.99, Table 3) indicate that the Langmuir model is a good fit for the biosorption of Cu(II) onto the chestnut shell pretreated by steam explosion.

The K_L values for sorption both onto the steam-exploded (Table 3) and onto the untreated (Yao et al. 2010) chestnut shell decreased with the increasing sorption temperature. At the same temperatures, the K_L values for sorption onto the steam-exploded shell are lower than for untreated shell. With increasing sorption temperature, q_m increases for copper sorption onto the steam-exploded biosorbent (Table 3) while it decreases for the untreated biosorbent (Yao et al. 2010). Below 313 K, the pretreatment impaired the Cu(II) sorption capacity. Under the experimental conditions, the maximum q_m value is 17.54 mg/g (Table 3) for the sorption onto the steam-exploded chestnut shell at 333 K and 12.56 mg/g (Yao et al. 2010) for sorption

onto the untreated chestnut shell at 293 K. Therefore, the steam-exploded shell is preferable for the sorption of copper ions at higher temperatures, while the untreated shell is more effective at lower temperatures. The steam-exploded chestnut shell shows higher copper-sorption capacity than many biosorbents from various agricultural by-products, such as date stones, palm-tree waste (Belala et al. 2014), peanut husk (Li et al. 2007), wheat bran (Renu & Singh 2018), wheat straw (Muhamad et al. 2010), hazelnut shell, apricot stone (Šoštarić et al. 2015) and corn cob (Petrović et al. 2015) . Therefore, steam-exploded chestnut shell is promising for Cu(II) removal from wastewater.

The Freundlich isotherm is fit for a highly heterogeneous surface, and its linear expression can be written as Equation (9) (Freundlich 1906):

$$\log q_e = \log K_F + 1/n \log C_e \tag{9}$$

where K_F ($mg^{1-1/n}/g/L^{1/n}$) is a Freundlich constant associated with sorption capacity, and $1/n$ is another Freundlich constant denoting sorption intensity. The linearized Freundlich plots are shown in Figure 5, and the constants, which were calculated using the intercept and the slope, are listed in Table 3. The value of $1/n$ indicates whether the biosorption is irreversible ($1/n = 0$), favorable ($0 < 1/n < 1$), or unfavorable ($1/n > 1$) (Alley 2007). The $1/n$ values obtained from this research are less than 1 (Table 3), further confirming favorable sorption.

Both the Langmuir and the Freundlich isotherms had R^2 values over 0.9 and the values derived from the former are closer to unity (Table 3), implying that the Langmuir model is more appropriate for characterizing Cu(II) sorption

Table 3 | Isotherm parameters for Cu(II) sorption on to steam-exploded chestnut shell at different temperatures

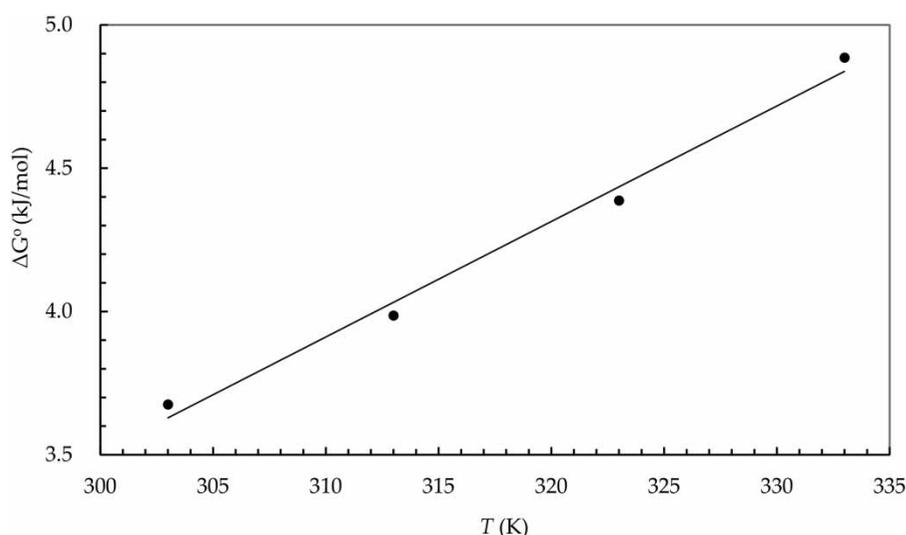| Temperature (K)	Langmuir			Freundlich		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F ($mg^{1-1/n}/g/L^{1/n}$)	$1/n$	R^2
303	10.86	0.0214	0.993	0.643	0.527	0.927
313	12.24	0.0177	0.997	0.523	0.590	0.960
323	16.58	0.0118	0.991	0.496	0.610	0.918
333	17.54	0.0098	0.992	0.402	0.656	0.941

Figure 6 | Thermodynamic plot for Cu(II) biosorption by steam-exploded chestnut shell (copper concentration: 50 mg/L, adsorbent dosage: 0.5 g, contact time: 24 hours, pH: 5).

onto the steam-exploded chestnut shell than the Freundlich model. This confirms the monolayer coverage process of copper onto the steam-exploded chestnut shell according to the Langmuir model.

Sorption thermodynamics

In engineering practice, the effects of temperature on sorption are usually considered. The temperature dependence of the sorption process is related to several thermodynamic parameters, including the Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°). The ΔG° (J/mol) of the sorption process is associated with the equilibrium constant by the classic van 't Hoff equation:

$$\Delta G^\circ = -RT \ln K_c^\circ \tag{10}$$

where R is the gas constant (8.314 J/mol/K), T the absolute temperature (K), and K_c° (L/g) an equilibrium constant obtained by multiplying the Langmuir constants q_m and K_L (Aksu & İşoğlu 2005). According to thermodynamics, the relationship between ΔG° and ΔH° (J/mol) as well as ΔS° (J/ mol/K) can be described by Equation (11).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{11}$$

The values of ΔH° and ΔS° were obtained from the plot of ΔG° against T, as shown in Figure 6. The calculated thermodynamic parameters are given in Table 4. The positive value of ΔG° indicates that steam-exploded chestnut shell

Table 4 | Thermodynamic parameters for Cu(II) sorption on to steam-exploded chestnut shell

T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol/ K)	R^2
303	3.68	− 8.59	− 40.3	0.989
313	3.99			
323	4.39			
333	4.89			

is unable to capture Cu(II) spontaneously. The negative value of ΔH° indicates that the sorption is exothermic, thereby demonstrating that the product is energetically stable (Khan & Singh 1987). The negative value of ΔS° suggests that the process is entropy driven and indicates that the Cu(II) sorption does not significantly alter the internal structure of the biosorbent. The Cu(II) sorption onto the untreated chestnut shell is an exothermic process driven by enthalpy, and it has negative ΔG° values which show it is a feasible and spontaneous process (Yao *et al.* 2010).

CONCLUSIONS

The steam-explosion pretreatment reduced the sorption rate constant and the initial sorption rate of the pseudo-second-order kinetic model. The Cu(II) sorption capacity was enhanced at higher temperatures. Additionally, the sorption process was changed from a spontaneous process driven by enthalpy to a nonspontaneous one driven by entropy. It

increased the surface area of the chestnut shell and exposed more hydroxyl and carboxyl groups, which are binding sites for copper ions. Compared with untreated chestnut shell, steam-exploded shell is preferable for sorbing copper ions from higher-concentration solutions at higher temperatures. Steam explosion is a simple and inexpensive physical process. The pretreatment improved some aspects of the biosorbent while impairing others. Unfortunately, this is a pilot study without a systematic investigation into the sorption response to the pretreatment parameters such as temperature, pressure and time. The negative aspects might be ameliorated by optimizing the steam-explosion conditions, which should be further explored.

ACKNOWLEDGEMENTS

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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