



## Removal of Cu(II) from aqueous solution by agricultural by-product: Peanut hull

Chun-Shui Zhu<sup>a,b,\*</sup>, Li-Ping Wang<sup>a</sup>, Wen-bin Chen<sup>a,b</sup>

<sup>a</sup> School of Environment Science and Spatial Informatics, China university of Mining and technology, Xuzhou, Jiangsu 221008, China

<sup>b</sup> School of Chemical Engineering, Huai-hai institute of Technology, Lian Yungang, Jiangsu 222005, China

### ARTICLE INFO

#### Article history:

Received 18 August 2008  
Received in revised form 17 January 2009  
Accepted 17 February 2009  
Available online 25 February 2009

#### Keywords:

Peanut hull  
Biosorption  
Cu(II)  
Kinetic  
Thermodynamic parameters

### ABSTRACT

Peanut hull, an agricultural by-product abundant in China, was used as adsorbent for the removal of Cu(II) from aqueous solutions. The extent of adsorption was investigated as a function of pH, contact time, adsorbate concentration and reaction temperature. The Cu(II) removal was pH-dependent, reaching a maximum at pH 5.5. The biosorption process followed pseudo-second-order kinetics and equilibrium was attained at 2 h. The rate constant increased with the increase of temperature indicates endothermic nature of biosorption. The activation energy ( $E_a$ ) of Cu(II) biosorption was determined at 17.02 kJ/mol according to Arrhenius equation which shows that biosorption may be an activated chemical biosorption. Other activation parameters such as  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$ , and  $\Delta G^\ddagger$  were also determined from Eyring equation. The equilibrium data were analyzed using the Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models depending on temperature. The equilibrium biosorption capacity of Cu(II) determined from the Langmuir equation was 21.25 mg/g at 30 °C. The mean free energy  $E$  (kJ/mol) got from the D-R isotherm also indicated a chemical ion-exchange mechanism. The thermodynamic parameters such as changes in Gibbs free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) were used to predict the nature of biosorption process. The negative  $\Delta G^0$  values at various temperatures confirm the biosorption processes are spontaneous.

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

Copper is a widely used metal in industry as electrical wiring, plumbing, gear wheel, selenium rectifier, air conditioning tubing and roofing owing to its excellent physical and mechanical properties such as electrical and thermal conductivity, good corrosion resistance, ease of fabrication and installation. Ultra-trace amount of copper is essential for human, animals, and microorganisms. However, excessive copper can be detrimental for the environment. For instance, for human it will cause stomach upset and ulcer, mental retardance, liver and brain damage, and so on. The potential sources of copper in industrial effluents include metal cleaning and plating baths, pulp, paper board mills, printed circuit board production, wood pulp production, and the fertilizer industry, etc. [1]. Therefore, removal of copper from effluents is essential not only to protect the water resources but also to slow down the fast depletion of copper sources.

Various methods to remediate heavy metal contaminated soils and wastes exist, including thermal, biological and physical/chemical treatments. However, Chemical methods, such as precipitation, adsorption, ion-exchange and solvent extraction

require high capital and operation costs and many produce large volumes of solid wastes [2–4]. Hence, there is a crucial need for the development of a method that is highly selective, more efficient, easy to operate and hence cost effective. Biosorption could be a good alternative technology.

In recent years, there has been an increase in the use of biological materials including agricultural and industrial solid wastes as adsorbents for the removal of heavy metals [5]. The advantage of using solid wastes is that it saves disposal costs while alleviating potential environmental problems. Agricultural by-products, such as peat, wood, pine park, banana pith, rice bran, wheat bran, peanut hull, wool, sunflower, grape stalks wastes, sugar beet pulp, olive mill solid residue, sawdust, leaves, walnut expeller meals, orange peel, have been demonstrated to remove heavy metal ions from wastewater [6–29]. The output of peanut in China accounts for one third of the gross production of the world. During the processing of peanut produces 500 thousand tons of by-products, peanut hull.

This paper presents the study of biosorption characteristics of powdered peanut hull biomass for removing Cu(II) from aqueous solutions in batch system. The binding capacity of powdered peanut hull for Cu(II) was shown as a function of initial pH, contact time, temperature and initial copper(II) concentration in this study. The biosorption equilibrium was expressed by the Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherms. The experimental data were analyzed using three different adsorption kinetic models and kinetic constants were calculated depending

\* Corresponding author.

E-mail address: [silk588@126.com](mailto:silk588@126.com) (C.-S. Zhu).

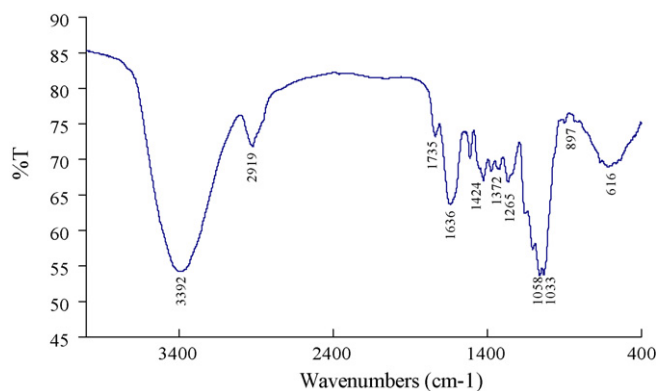


Fig. 1. FT-IR spectrum of peanut hull.

on temperature. The activation energy of biosorption process, which is an indicator of adsorption type, was also evaluated. Since the evaluation of the heat change of the biosorption process is very important for reactor design, the thermodynamics of the biosorption process was also investigated.

## 2. Materials and methods

### 2.1. Adsorbent and adsorbent characterization

The peanut hull was obtained from a market in Wuhan, China. The material was washed with tap water, rinsed with ultra-pure water, oven-dried at 60 °C for 2 days, and ground to pass a 100-mesh (0.133 mm) sieve.

As a biomass, the peanut hull is a complex material consisted of polyphenol such as catechol, pyrogallol acid and *m*-trihydroxybenzene, mineral, lipid, and cellulose, etc. [30]. Chemical sorption can occur by the polar functional groups of these constituents, which include carboxyl groups and phenolic hydroxyl as chemical bonding agents.

Fourier transform infrared (FT-IR) spectrum of the peanut hull was recorded on a Thermo Nicolet Nexus spectrometer in the range of 4000–400  $\text{cm}^{-1}$  using a KBr disc containing 1% of finely ground sample with the aid of a bench press. From Fig. 1, it could be seen, the band at 3392  $\text{cm}^{-1}$  was ascribed to the mixed stretching vibration absorption band of amino and hydroxyl groups. The small band obtained at 1735  $\text{cm}^{-1}$  was assigned to the carboxyl group stretching vibration. The peak at 1424  $\text{cm}^{-1}$  was caused by the  $\text{CH}_2$  bending and 1372  $\text{cm}^{-1}$  by the O–H bending. The peak at 1265  $\text{cm}^{-1}$  is indicative of the OH in-plane bending cellulose. A small sharp band at 897  $\text{cm}^{-1}$  represents the glycosidic  $\text{C}_1$ –H deformation with ring vibration contribution and OH bending, which is characteristic of  $\beta$ -glycosidic linkages between glucose and cellulose.

Crystallinity of the material was determined by X-ray diffraction using a diffractometer (Rigaku, D/Max-III A) operated at 40 kV and 50 mA. The scanning scope and scanning speed were 5°–70° and 15°/min, respectively, using Cu  $\text{K}\alpha$  radiation. The XRD pattern (Fig. 2) of peanut hull showed typical spectrum of cellulosic material, having main and secondary peaks at  $2\theta$  of 22° and 16°, respectively. The main peak is taken as indicative of the presence of highly organized crystalline cellulose, while the secondary rather weak peak is a measure of a less organized polysaccharide structure. The conclusion is accordant with that of the FT-IR analysis.

### 2.2. Chemicals

Stock solutions of Cu(II) were prepared by dissolving accurately weighed amount of metal copper (purity >99.999%) in nitric acid and diluting with ultra-pure water. The test solutions were pre-

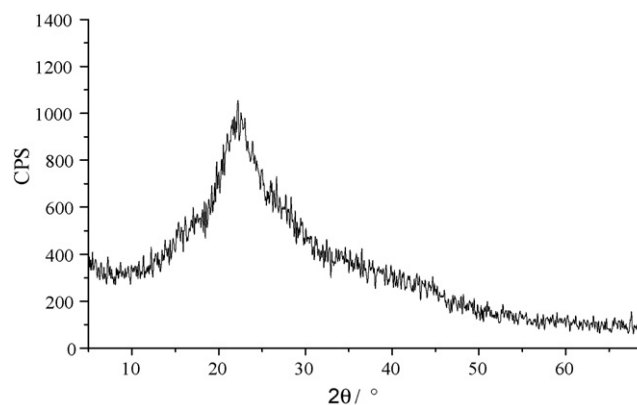


Fig. 2. XRD diagram of peanut hull.

pared by diluting 1 g/L of stock solution of Cu(II) to the desired concentrations. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value with  $\text{HNO}_3$  and NaOH solutions. The pH measurements were achieved with Orion 290A+ model pH meter during all of the experiments.

### 2.3. Biosorption studies

Batch biosorption experiments were performed using 0.20 g of powdered and dried peanut hull with 100 mL of Cu(II) aqueous solutions in 250 mL stoppered flasks, whose concentrations, temperatures, and pHs have previously been known. The mixtures of the peanut hull and the solutions were shaken in a thermostatic air bath (HZQ-QX, HDL instrument Co. Ltd.) at 120 rpm. After the target contact time was reached suspensions were filtered by filter paper. The first 30 mL filtrates were abandoned owing to the consideration of adsorption of filter paper. Then the posterior filtrate was analyzed for Cu(II) ions using an atomic absorption spectrometer (TAS-990AFG, PGeneral instrument Co. Ltd., China). Blank solutions (containing no Cu(II) ions) were used for each experiment. Some samples were diluted to fit with the calibration range. The calibration coefficient ( $R$ ) obtained for all analyses was 0.99 or better. The wavelength used for the analyses were 324.8 nm. The amount of Cu(II) captured by the adsorbent was calculated from the difference between the initial and final concentrations of the metal ions in solution. Experiments were triplicated and the results averaged.

## 3. Theoretical basis

### 3.1. Kinetic of biosorption

The kinetic of biosorption process was studied by carrying out a set of biosorption experiments at four constant temperatures and monitoring the amount captured with time. Assuming pseudo first order kinetics, the rate of the adsorptive interaction can be evaluated by using the simple Lagergren equation [31,32]:

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (1)$$

where  $q$  and  $q_e$  are the solid phase copper ion concentrations at any time ( $t$ ) and at the equilibrium (mg/g), respectively and  $k_1$  is the pseudo-first-order adsorption rate constant. The values of  $k_1$  can be obtained from the slope of the linear plot of  $\ln(q_e - q)$  vs.  $t$ .

The pseudo-second-order kinetic model can be presented by the linear equation:

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

where  $k_2$  is the second order rate constant and  $k_2q_e^2$  known as the initial adsorption rate, could be tested. The linear plots of  $t/q$  vs.  $t$  allow computation of  $q_e$ ,  $k_2$  and the initial rate.

As it is known, two intra-particle diffusion mechanisms are involved in the adsorption rate: (1) diffusion within the pore volume, known as pore diffusion or intra-particle diffusion, and (2) diffusion along the surface of the pores, known as surface diffusion. Pore diffusion and surface diffusion occur in parallel within the adsorbent particle. The intra-particle diffusion equation is given as follows [32]:

$$q = k_p t^{0.5} \quad (3)$$

When intra-particle diffusion plays a significant role in controlling the kinetics of the adsorption process, the plots of  $q$  vs.  $t^{0.5}$  yield straight lines passing through the origin and the slope gives the rate constant,  $k_p$ .

However, when the transport of the solute molecules from the liquid phase up to the solid phase boundary plays the most significant role in adsorption, the liquid film diffusion model may be applied [32]:

$$\ln(1 - F) = -k_{fd}t \quad (4)$$

where  $F$  is the fractional attainment of equilibrium ( $F = q/q_e$ ),  $k_{fd}$  is the adsorption rate constant. The plots of  $\ln(1 - F)$  vs.  $t$  with zero intercept would suggest that the kinetics of the adsorption process is controlled by diffusion through the liquid film surrounding the solid adsorbents.

### 3.2. Biosorption isotherm

The most often used isotherm equations are Langmuir and Freundlich models which are used to find out the relation between the equilibrium concentrations of the adsorbate in the liquid phase and in the solid phase.

#### (1) Langmuir isotherm

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (5)$$

where  $q_m$  is the maximum amount of the Cu(II) per unit weight of dried peanut hull to form a complete monolayer on the surface bound at high  $C_e$  (mg/g), and  $b$  is a constant related to the affinity of the binding sites (L/mg).  $q_e$  is the biosorption capacity at equilibrium (mg/g). The dimensionless biosorption intensity ( $R_L$ ) is calculated using the following equation:

$$R_L = \frac{1}{1 + b C_0} \quad (6)$$

where  $C_0$  is the initial concentration in the solution (mg/L). For favorable adsorption,  $0 < R_L < 1$ ; while  $R_L > 1$ ,  $R_L = 1$  and  $R_L = 0$  describe unfavorable, linear and irreversible adsorption, respectively [32].

#### (2) Freundlich isotherm

$$q_e = K_f C_e^{1/n} \quad (7)$$

where  $K_f$  is Freundlich capacity constant (mg/g);  $n$  the affinity constant.

#### (3) Dubinin-Radushkevich isotherm

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (8)$$

Where  $\beta$  is a constant related to the mean free energy of biosorption per mole of the biosorbate ( $\text{mol}^2/\text{kJ}^2$ ),  $q_m$  theoretical saturation capacity, and  $\varepsilon$  is Polanyi potential, which is equal to  $RT \ln(1 + 1/C_e)$ , where  $R$  (J/mol K) is the gas constant, and  $T$  (K) is the absolute temperature [33].

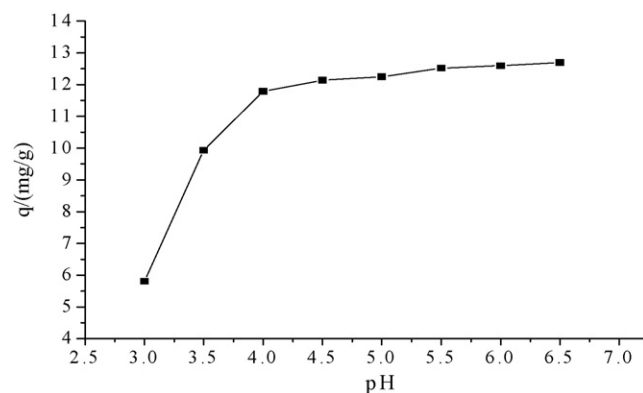


Fig. 3. Effect of pH on biosorption of Cu(II) on peanut hull.

### 3.3. Thermodynamic study

(1) Activation energy The activation energy for the Cu (II) biosorption was calculated by the Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (9)$$

Where  $k$  is the rate constant value for the Cu(II) biosorption,  $E_a$  the activation energy in kJ/mol,  $T$  the temperature in Kelvin, and  $R$  the gas constant.  $E_a$  value can be calculated from the slope of a plot of  $\ln k$  vs.  $1/T$ . The activation entropy ( $\Delta S^\ddagger$ ), activation enthalpy ( $\Delta H^\ddagger$ ) in the biosorption process were calculated by the Eyring equation [34]:

$$\ln \left( \frac{k}{T} \right) = \ln \left( \frac{k_B}{h} \right) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (10)$$

Where  $k$  is the rate constant value for the Cu(II) biosorption,  $k_B$ ,  $h$  and  $R$  are Boltzmann constant, Plank constant and gas constant,  $T$  is the temperature in Kelvin.  $\Delta S$  and  $\Delta H$  can be calculated from the slope and intercept of a plot of  $\ln(k/T)$  vs.  $1/T$ .

(2) Thermodynamic parameters The thermodynamic parameters for the biosorption process,  $\Delta H^0$ ,  $\Delta S^0$  and  $\Delta G^0$ , were evaluated using the following equation:

$$\ln b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (11)$$

where  $b$  is Langmuir constant. The plot of  $\ln b$  vs.  $1/T$  is linear with the slope and the intercept giving values of  $\Delta H$  and  $\Delta S$ . These values could be used to compute  $\Delta G$  from the Gibbs relation,  $\Delta G^0 = \Delta H^0 - T\Delta S^0$  at constant temperature. All these relations are valid when the enthalpy change remains constant in the temperature range.

## 4. Results and discussion

### 4.1. Biosorption of Cu(II)

#### 4.1.1. Effect of pH

The pH of the aqueous solution is an important variable in the biosorption of metals on the sorbents. In the present work, biosorption of Cu(II) on the sorbent was studied over the pH range of 3–6.8 for a constant peanut hull amount of 2 g/L and Cu(II) concentration of 30 mg/L at 20 °C. The pH values were adjusted prior to the experiments and the values were limited to less 6.8 because of precipitation at higher pH.

Fig. 3 shows the effect of pH on the removal of Cu(II). As can be seen, the removal efficiency of Cu(II) tended to increase with increasing pH value. Similar observations have been earlier recorded [11]. In the pH range of 3–4, the  $q_e$  increases sharply with

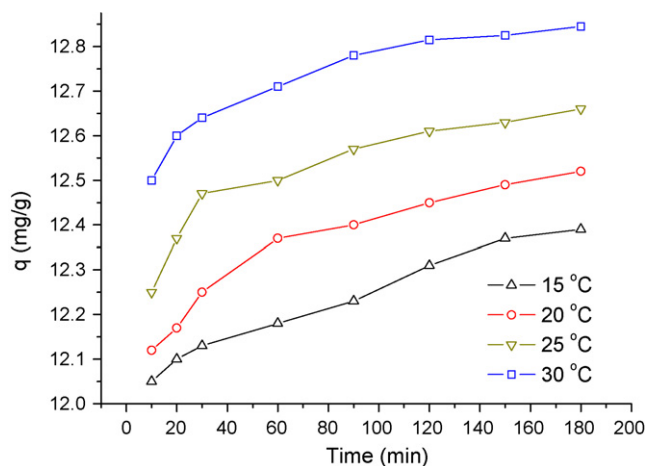


Fig. 4. Influence of temperature on kinetic curve of Cu(II) biosorption on peanut hull.

the pH increasing, while that increases slightly after pH higher than 4.5. This is because the point of zero charge ( $pH_{ZPC}$ ) for peanut hull was about 3.5. The net negative charge of the adsorbent increased when pH elevated, which induced the initial sharp increment of the  $q_e$ . When pH reach 4.5, the  $q_e$  value approaches the maximum capacity of Cu(II) on the adsorbent, hence the increment of  $q_e$  not obvious with pH increasing.

Chemical species are also possible mechanism affecting the adsorption of metal ions. In this paper, maximum biosorption is observed at pH 5.5, which might be due to a partial hydrolysis of  $Cu^{2+}$ , leading to the formation of  $CuOH^+$ .

#### 4.1.2. Determination of equilibrium time and kinetics of biosorption

The kinetics of biosorption of Cu(II) onto peanut hull were investigated with initial Cu(II) and peanut hull concentrations of 30 mg/L and 2 g/L, respectively at four temperatures (15, 20, 25, 30 °C). Fig. 4 depicts variation of aqueous and solid phase copper concentrations with time. The biosorption rapidly increased in the first 30 min after which biosorption slowly approached towards equilibrium. In general, about 98% of the total Cu(II) biosorption was achieved within 120 min. Therefore 2 h was deemed sufficient to establish equilibrium in subsequent equilibrium experiments.

In order to investigate the mechanism of biosorption and rate controlling steps, the kinetic data were modeled using Lagergren first order, second order, and diffusion model [32].

The rates of biosorption were first analyzed with the pseudo-first-order equation proposed by Lagergren by plotting  $\ln(q_e - q)$  vs. time (Fig. 5). This equation is for the adsorption in liquid/solid system based on solid capacity and assumed that the rate of change in sorbate uptake with time is directly proportional to the difference in the saturation concentration and the amount of solid uptake with time. These plots have good linearity. But in order to find a more reliable description of the kinetics, second order kinetic equation was applied to the adsorption data by plotting  $t/q$  vs.  $t$  (Fig. 6). A pseudo-second-order equation based on adsorption equilibrium

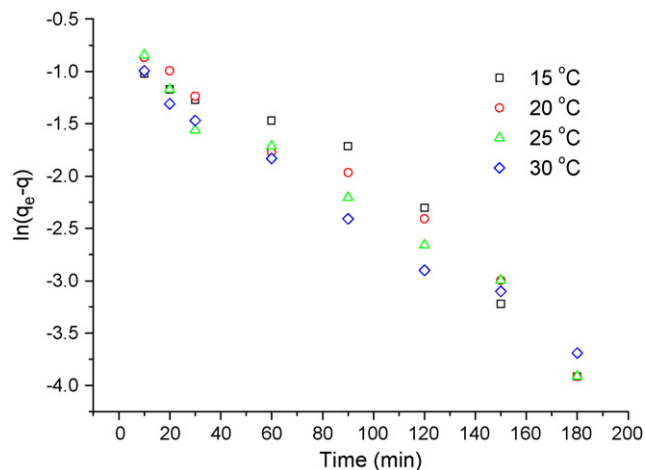


Fig. 5. A plot of  $\ln(q_e - q)$  vs. time according to pseudo-first-order biosorption kinetics.

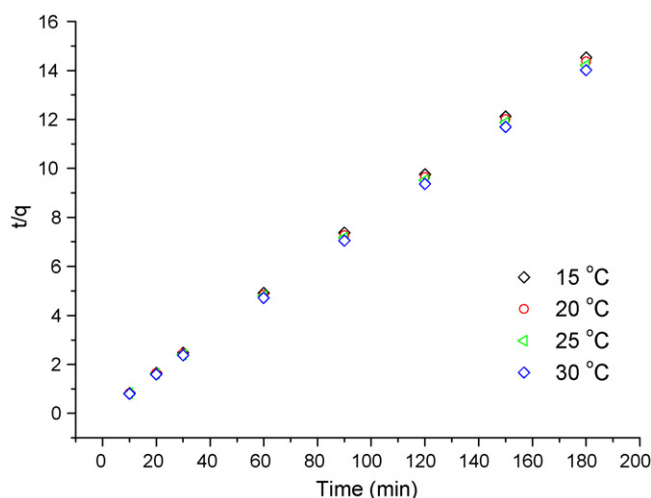


Fig. 6. A plot of  $t/q$  vs. time according to pseudo-second-order biosorption kinetics.

capacity assumes that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites.

The comparison of experimental biosorption capacities and the theoretical values estimated from the pseudo-first and second-order rate equations are presented in Table 1. The theoretical  $q_e$  values estimated from the pseudo-first-order kinetic model gave significantly different values than that of the experimental values, and the correlation coefficients were also found to be lower. These results indicate that the pseudo-first-order kinetics model does not describe biosorption of Cu(II) on peanut hull. The correlation coefficients for the linear plots of  $t/q$  against  $t$  for the second-order equation are close to 1 or equal to 1. The theoretical  $q_e$  values were very close to the experimental  $q_e$  values in the case of second-order kinetic model and the maximum deviation was 0.16% at different temperatures. The results suggest that pseudo-second-order

Table 1  
First order rate constant and second order rate constant for biosorption of Cu(II) at different temperatures.

Temperature (°C)	Experimental	Pseudo-first-order			Pseudo-second-order		
	$q$ (mg/g)	$q_e$ (mg/g)	$k_1$ (1/min)	$r$	$q_e$ (mg/g)	$k_2$ (g/(mg min))	$r$
15	12.39	0.506	0.016 1	0.967 4	12.41	0.109 2	0.999 9
20	12.52	0.514	0.016 4	0.986 5	12.54	0.115 9	0.999 9
25	12.66	0.441	0.015 9	0.986 5	12.68	0.135 7	0.999 9
30	12.85	0.382	0.015 2	0.995 4	12.87	0.153 3	1.000 0

**Table 2**

Intra-particle diffusion rate constant and liquid film diffusion model rate constants for sorption of Cu(II) on peanut hull.

Temperature (°C)	Intra-particle diffusion			Liquid film diffusion		
	$r$	Intercepts	$k_p$ (mg/(g min <sup>0.5</sup> ))	$r$	Intercepts	$k_{fd}$ (min <sup>-1</sup> )
15	0.9923	11.94	0.033	0.9674	-3.19	-0.0161
20	0.9858	12.02	0.039	0.9865	-3.19	-0.0164
25	0.9586	12.21	0.036	0.9865	-3.36	-0.0159
30	0.9752	12.44	0.032	0.9954	-3.52	-0.0152

**Table 3**

Isotherm parameters for the biosorption of Cu(II) onto peanut hull at different temperatures.

T (K)	Langmuir isotherm			Freundlich isotherm			D-R isotherm		
	$b$ (L/mg)	$q_m$ (mg/g)	$R$	$1/n$	$K_f$ (mg/g)	$R$	$q_m$ (mmol/g)	$E$ (kJ/mol)	$R$
288	0.1431	16.92	0.9991	0.2097	5.6786	0.8250	0.44	14.11	0.8646
293	0.1478	17.99	0.9992	0.2034	6.2287	0.8477	0.45	14.74	0.8855
298	0.1516	19.70	0.9978	0.1851	7.4227	0.8836	0.46	14.98	0.9179
303	0.1557	21.25	0.9974	0.1670	8.7384	0.9386	0.45	15.87	0.9697

kinetic model, in contrast to the pseudo-first-order model, provided a good correlation for the biosorption of Cu(II) on peanut hull.

From the plots of second-order kinetic model,  $k_2q_e^2$  known as the initial biosorption rate were also obtained, 16.82, 18.23, 21.82, 25.39 mg/(g min) at different temperatures, respectively. The value of  $k_2q_e^2$  and  $q_e$  indicates higher temperature favors the biosorption process by increasing biosorption rate and capacity.

Many studies published in literature also report pseudo-second-order kinetics for biosorption reactions such as the biosorption of Cu(II) by cedar sawdust and crushed brick [35], adsorption of arsenite by a nano-crystalline hybrid surfactant-akaganeite sorbent [36], biosorption of Pb(II) by palm kernel fiber [37]. The pseudo-second-order kinetic model is based on the assumption that the rate-controlling step may be chemisorption involving valency forces through sharing or exchange of electrons between biosorbent and sorbate [38].

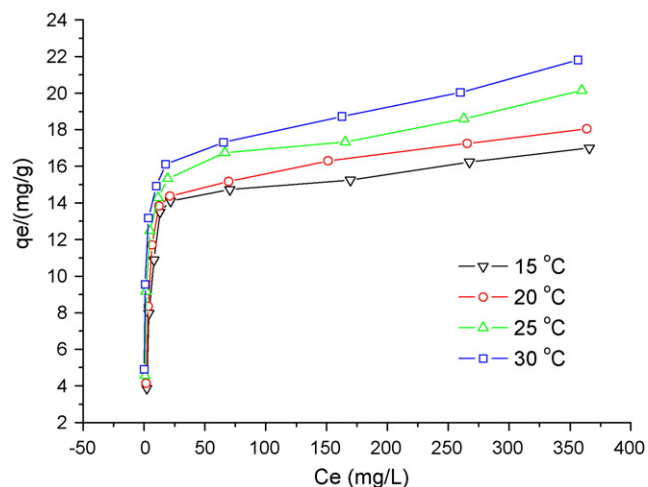
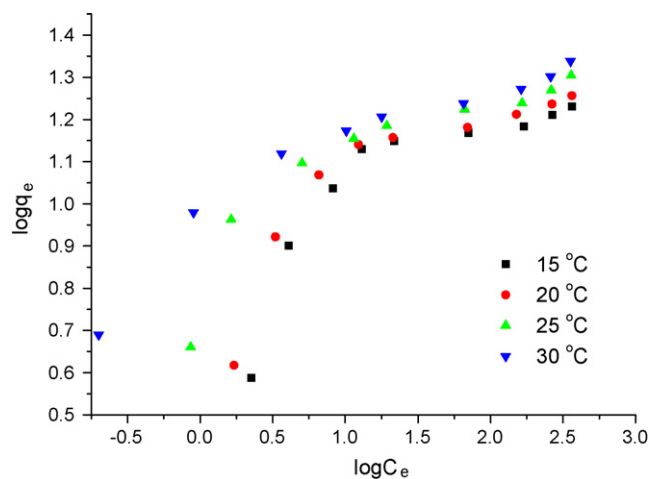
Diffusion from the solid-liquid interface to the interior of the solid particles plays a very important role in adsorption of metal ions. The plots of  $q_t$  vs.  $t^{0.5}$  were linear with regression coefficient of 0.96–0.99. The intra-particle diffusion rate constant,  $k_p$ , has values from 0.032 to 0.039 mg/(g min<sup>0.5</sup>) (Table 2) which is a bit small revealing that few Cu(II) ions diffuse into the pores before being adsorbed. It is obvious that the plots did not have a zero intercept as proposed by Eq. (3). The intercepts was all about 12 indicating that intra-particle diffusion may not be the controlling factor in determining the kinetics of the process because there is a boundary layer resistance.

Diffusion from the bulk liquid phase to the surface of an adsorbent might also play an important role in determining the rate processes. The plots of  $-\ln(1-F)$  vs.  $t$  in accordance with the Eq. (4) yield linear plots ( $r$ : 0.967–0.995) with intercepts of -3.52 to -3.19. The rate constant,  $k_{fd}$ , is in the range of -0.0164 to -0.0152 (Table 2). The none-zero intercepts again show that despite giving linear plots, the predictions of the model will have only limited applicability in biosorption of Cu(II) on peanut hull.

#### 4.1.3. Biosorption isotherm

The equilibrium concentration dependence data of Fig. 7 was tested using different biosorption isotherm models in order to develop an equation which accurately represented the result and could be used for design purposes. Several isothermal equations are available for analysis. In this study, two isothermal equations, i.e., Langmuir and Freundlich isothermal equations were employed to study the biosorption process. These two isotherms are used most commonly to describe the biosorption characteristics of adsorbent used in water and wastewater treatment.

The equilibrium data for Cu(II) ions over the range from 10 to 400 mg/L at four temperatures have been correlated with the Freundlich isotherm (Fig. 8) and the constants were shown in Table 3. Above this concentration level, the graphs deviates from linearity and curvatures were observed. Other investigator [39] also obtained data that exhibit such behavior. This behavior may be due to the fact that two different modes of adsorption process,

**Fig. 7.** Biosorption isotherms of Cu<sup>2+</sup> on peanut hull at different temperatures.**Fig. 8.** Freundlich isotherm of Cu(II) on peanut hull.

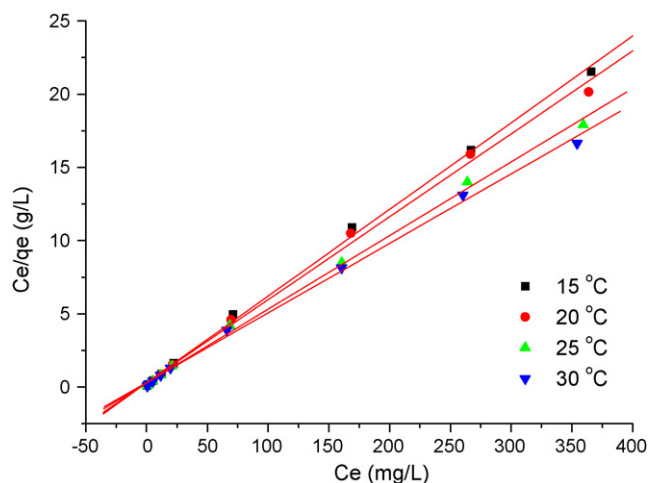


Fig. 9. Langmuir isotherm of Cu(II) on peanut hull.

i.e., surface diffusion and intraparticle diffusion is taking place. However, from the variation trend of constants  $k_f$  and  $1/n$  in Table 3, conclusion can also be get that the increase of temperature favors Cu(II) ion removal by peanut hull.

Langmuir equation was also fitted to the isotherm data as shown in Fig. 9. Linear plots are obtained when  $C_e/q_e$  is plotted against  $C_e$  over the entire concentration range of metal ions investigated. The Langmuir model parameters and the statistical fits of the biosorption data to this equation are given in Table 3. The Langmuir model effectively described the biosorption data with all  $r > 0.99$ . The biosorption isotherms of Cu(II) exhibit Langmuir behavior, which indicate a monolayer biosorption. The increase of maximum monomolecular capacity ( $q_m$ ) and Langmuir constant ( $b$ ) with increase of temperature reveals that the biosorption is favorable in high temperature and the process is endothermic in nature. The Table 4 present the comparison of biosorption capacity (mg/g) of peanut hull biomass from the Langmuir isotherm for Cu(II) with that of various biomass reported in literature [1,6,11,13,40–44]. Direct comparison of adsorbent capacity is difficult due to the varying experimental conditions employed in those studies, however, the biosorption capacity of peanut hull is comparable to many biomass. If the biomass was chemically modified it would exhibit more potential for the retention of heavy metals.

**Table 4**  
A comparison of copper adsorption capacities for various adsorbents.

Adsorbent	pH	Metal uptake (mg/g)	Experimental temperature (°C)	Refs.
Sugar beet pulp	4	31.4	25	[1]
Herbaceous	5.5	4.84	21	[6]
Dehydrated wheat bran*	5	51.5	60	[11]
Wheat Shell	5	8.34	25	[13]
Wheat Straw	4	4.48	23 ± 2	[40]
Soybean Straw	4	5.44	23 ± 2	[40]
Corn	4	3.78	23 ± 2	[40]
Corn Cob	4	2.18	23 ± 2	[40]
Walnut hull	5	4.04	30	[41]
Rice Bran	5	27.81	40	[41]
Wheat bran	5	8.62	40	[41]
<i>Focus vesiculosus</i> *	5.5	23.4	22	[42]
<i>Pleurozium schreberi</i> *	5.5	11.1	22	[42]
<i>Betula sp.</i> sawdust	5.5	4.9	22	[42]
<i>Arca shell</i> *	4.5	26.88	Room temperature	[43]
<i>Crab shell</i> *	4.5	44.94	Room temperature	[43]
Peanut hull	5.5	21.25	30	Present study

\* The labeled adsorbents were pretreated with certain method.

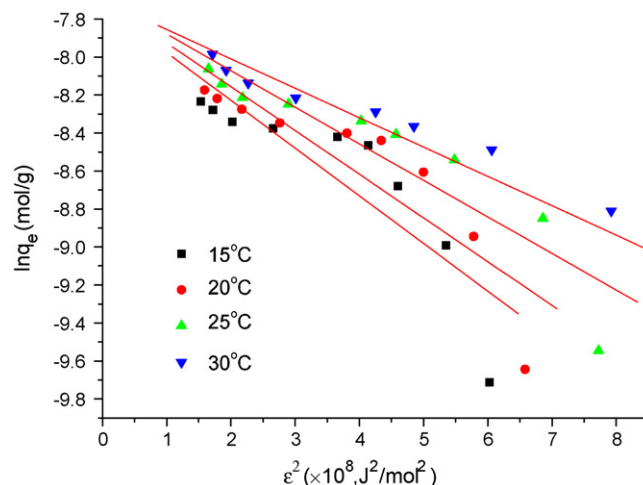


Fig. 10. D-R isotherm of Cu(II) on peanut hull.

The essential feature of Langmuir model can be expressed in terms of a dimensionless constant separation factor ( $R_L$ ) given by following equation:

$$R_L = \frac{1}{1 + bC_0} \quad (12)$$

where  $b$  is the Langmuir constant (L/mg) and  $C_0$  is the initial copper concentration (mg/L). It has been established that for favorable adsorption,  $0 < R_L < 1$ ; unfavorable adsorption,  $R_L > 1$ ; linear adsorption,  $R_L = 1$ ; and adsorption process is irreversible if  $R_L = 0$ . All the values of  $R_L$  lie between 0.10 and 0.45 for the initial copper concentration range from 10 to 400 mg/L indicating favorable biosorption of copper onto peanut hull.

The Dubinin-Radushkevich isotherm is more general than Langmuir isotherm since it does not assume a homogeneous surface or constant biosorption potential. It was applied to distinguish between the physical and chemical biosorption of Cu(II). By plotting  $\ln q_e$  vs.  $\varepsilon^2$  it is possible to generate the value of  $q_m$  (mol/g) from the intercept, and the value of  $\beta$  from the slope. Fig. 10 shows the D-R isotherm for Cu(II) biosorption onto peanut hull.

The constant  $\beta$  gives an idea about the mean free energy  $E$  (kJ/mol) of biosorption per mole of the biosorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship [33]:

$$E = \frac{1}{\sqrt{2\beta}} \quad (13)$$

The parameter gives information about the type of biosorption mechanism as chemical ion-exchange or physical biosorption. According to the literature, the magnitude of  $E$  between 8 and 16 kJ/mol corresponds to a chemical ion-exchange process while the value of  $E < 8$  kJ/mol represents a physical nature process. The results were found to be higher than 14 kJ/mol for all studied temperatures which indicated that the biosorption process may be a chemical ion-exchange mechanism.

#### 4.1.4. Thermodynamics of biosorption

(1) Activation parameters From the pseudo-second-order rate constant  $k_2$  (Table 1), the activation energy  $E_a$  for the biosorption of Cu(II) on peanut hull was determined using the Arrhenius equation (Eq. (9)). By plotting  $\lg k_2$  vs.  $1/T$  (see Fig. 11) and from the slope and the intercept, values of  $E_a$  and  $A$  can be obtained. The value of  $E_a$  for the biosorption of Cu(II) on peanut hull was 17.02 kJ/mol. The magnitude of activation energy may give an idea about the type of adsorption. According to literature

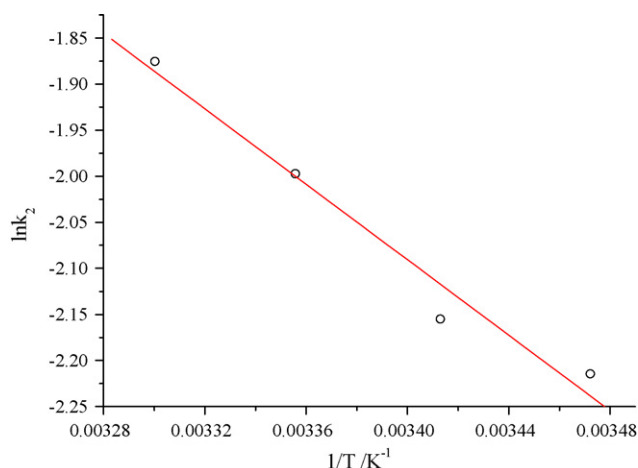


Fig. 11. Plot of  $\ln k_2$  vs.  $1/T$ .

Table 5

Thermodynamic parameters for the biosorption of Cu(II) on peanut hull.

T (K)	b	$\Delta G^0$ (kJ/mol)	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (kJ/(mol K))
288	0.1431	-21.85	4.04	89.9
293	0.1487	-22.30		
298	0.1516	-22.75		
303	0.1557	-23.20		

[44], the process may be an activated chemical biosorption. The Eyring equation was used to calculate the standard enthalpy of activation ( $\Delta H^\ddagger$ ), entropy of activation ( $\Delta S^\ddagger$ ), and free energy of activation ( $\Delta G^\ddagger$ ). The values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were calculated from the slope and intercept of a plot of  $\ln(k/T)$  vs.  $1/T$  (figure not shown). The free energy of activation ( $\Delta G^\ddagger$ ) was obtained from:  $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ . The values of  $\Delta G^\ddagger$  were found to be (61.24, 62.31, 63.37 and 64.43) kJ/mol at  $T=(288, 293, 298, 303)$  K, respectively. The larger positive  $\Delta G^\ddagger$  values suggest that biosorption reactions require energy to convert reactants into products. The  $\Delta G^\ddagger$  value determines the rate of the reaction, rate increases as  $\Delta G^\ddagger$  decreases, and hence the energy requirement is fulfilled, the reaction proceeds. The positive value of  $\Delta H^\ddagger$  (14.57 kJ/mol) confirms the endothermic process, meaning the reaction consumes energy. The negative value of  $\Delta S^\ddagger$  ( $-212.6$  J/(K mol)) indicates that the biosorption leads to order by combining with peanut hull and was supportive of an interaction between the Cu(II) ion and the peanut hull.

(2) Thermodynamic parameters The thermodynamic parameters include the changes in enthalpy ( $\Delta H^0$ ), entropy ( $\Delta S^0$ ), and Gibbs free energy ( $\Delta G^0$ ). The values of  $\Delta H^0$  and  $\Delta S^0$  were determined from the slopes and intercepts of the plots of  $\ln b$  versus  $1/T$  (figure not shown) and listed in Table 5. The negative values of  $\Delta G^0$  confirm the feasibility of the process and the spontaneous nature of biosorption with a high preference of Cu(II) on peanut hull. The increase of the absolute value of  $\Delta G^0$  as temperature rises indicates that the affinity of Cu(II) on peanut hull was higher at high temperature. The value of  $\Delta H^0$  is positive, indicating that the biosorption reaction is endothermic. The positive value of  $\Delta S^0$  also shows the increasing randomness at the solid/liquid interface during the biosorption of Cu(II) on peanut hull.

## 5. Conclusions

The study indicated that peanut hull could be used as an effective adsorbent material for the treatment of Cu-bearing aque-

ous waste stream. Adsorption data indicate the applicability of pseudo-second-order kinetics. An increasing equilibrium biosorption capacity with the rise in temperature indicated that the nature of adsorption is a spontaneous process which is also supported by the thermodynamic parameters calculated from the Langmuir isotherm at various temperatures. The activation energy ( $E_a$ ) and mean free energy ( $E$ ) calculated from Arrhenius equation and D-R isotherm respectively commonly confirm the chemical biosorption mechanism. Compared to various other sorbents reported in the literature, the peanut hull in present study shows good promise for practical applicability due to its easy availability of the material and easy recovery of metal entrapped by combustion method.

## References

- [1] Z. Zümriye Aksu, İ.A. İsoğlu, Removal of copper(II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp, *Process Biochem.* 40 (2005) 3031–3044.
- [2] B. Volesky, *Biosorption of heavy metals*, CRC press, Boca Raton, Florida, 1990.
- [3] D. Kratochvil, B. Volesky, *Advances in the biosorption of heavy metals*, *Tibtech* 16 (1998) 291–299.
- [4] Z. Aksu, Application of biosorption for the removal of organic pollutants: a review, *Process Biochem* 40 (2005) 997–1026.
- [5] K. Periasamy, C. Namasivayam, Removal of copper (II) by adsorption onto peanut hull carbon from water and copper plating industry wastewater, *Chemosphere* 32 (1996) 769–789.
- [6] R. Gündoğan, B. Acemioğlu, M.H. Alma, Copper (II) adsorption from aqueous solution by herbaceous peat, *J. Colloid Interface Sci.* 269 (2004) 303–309.
- [7] E.W. Shin, K.G. Karthikeyan, M.A. Tshabalala, Adsorption mechanism of cadmium on juniper bark and wood, *Bioresour. Technol.* 98 (2007) 588–594.
- [8] K. Seki, N. Saito, M. Aoyama, Removal of heavy metal ions from solutions by coniferous barks, *Wood Sci. Technol.* 31 (1997) 441–447.
- [9] C. Namasivayam, D. Prabha, M. Kumutha, Removal of direct red and acid brilliant blue by adsorption on banana pith, *Bioresour. Technol.* 64 (1998) 77–79.
- [10] X.S. Wang, Y. Qin, Z.F. Li, Biosorption of zinc from aqueous solutions by rice bran: kinetic and equilibrium studies, *Sep. Sci. Technol.* 41 (2006) 747–756.
- [11] A. Özer, D. Özer, A. Özer, The adsorption of copper(II) ions on to dehydrated wheat bran (DWB): determination of the equilibrium and thermodynamic parameters, *Process Biochem.* 39 (2004) 2183–2191.
- [12] M.A. Farajzadeh, A.B. Monji, Adsorption characteristics of wheat bran towards heavy metal cations, *Sep. Purif. Technol.* 38 (2004) 197–207.
- [13] N. Basci, E. Kocadagistan, B. Kocadagistan, Biosorption of copper(II) from aqueous solutions by wheat shell, *Desalination* 164 (2004) 135–140.
- [14] P.D. Johnson, M.A. Watson, J. Brown, I.A. Jefcoat, Peanut hull pellets as a single use sorbent for the capture of Cu(II) from wastewater, *Waste Manage.* 22 (2002) 471–480.
- [15] P. Brown, I.A. Jefcoat, D. Parrish, S. Gill, E. Graham, Evaluation of the adsorptive capacity of peanut hull pellets for heavy metals in solution, *Adv. Environ. Res.* 4 (2000) 19–29.
- [16] P. Taddei, P. Monti, G. Freddi, T. Arai, M. Tsukada, Binding of Co(II) and Cu(II) cations to chemically modified wool fibres: an IR investigation, *J. Mol. Struct.* 650 (2003) 105–113.
- [17] G. Sun, W. Shi, Sunflower stalks as adsorbents for the removal of metal ions from wastewater, *Ind. Eng. Chem. Res.* 37 (1998) 1324–1328.
- [18] N. Fiol, C. Escudero, J. Poch, I. Villaescusa, Preliminary studies on Cr(VI) removal from aqueous solution using grape stalk wastes encapsulated in calcium alginate beads in a packed bed up-flow column, *React. Funct. Polym.* 66 (2006) 795–807.
- [19] V.M. Dronnet, C.M.G.C. Renard, M.A.V. Axelos, J.-F. Thibault, Binding of divalent metal cations by sugar-beet pulp, *Carbohydr. Polym.* 34 (1997) 73–82.
- [20] H.S. Altundogan, Cr(VI) removal from aqueous solution by iron (III) hydroxide-loaded sugar beet pulp, *Process Biochem.* 40 (2005) 1443–1452.
- [21] F. Pagnanelli, L. Toro, F. Vegliò, Olive mill solid residues as heavy metal sorbent material: a preliminary study, *Waste Manage.* 22 (2002) 901–907.
- [22] S.H. Gharabeh, W.Y. Abu-el-sha'r, M.M. Al-Kofahi, Removal of selected heavy metals from aqueous solutions using processed solid residue of olive mill products, *Water Res.* 32 (1998) 498–502.
- [23] M.E. Argun, S. Dursun, C. Ozdemir, M. Karatas, Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics, *J. Hazard. Mater.* 141 (2007) 77–85.
- [24] Q. Li, Z. Zhai, W. Zhang, M. Wang, J. Zhou, Kinetic studies of adsorption of Pb(II), Cr(III) and Cu(II) from aqueous solution by sawdust and modified peanut husk, *J. Hazard. Mater.* 141 (2007) 163–167.
- [25] Y. Prasanna Kumar, P. King, V.S.R.K. Prasad, Zinc biosorption on *Tectona grandis* L.f. leaves biomass: equilibrium and kinetic studies, *Chem. Eng. J.* 124 (2006) 63–70.
- [26] K.G. Bhattacharyya, A. Sharma, Adsorption of Pb(II) from aqueous solution by *Azadirachta indica* (Neem) leaf powder, *J. Hazard. Mater.* 113 (2004) 97–109.
- [27] J.-W. Kim, M.-H. Sohn, S.-S. Kim, S.-M. Sohn, Y.-S. Kwon, Production of granular activated carbon from waste walnut shell and its adsorption characteristics for  $\text{Cu}^{2+}$  ion, *J. Hazard. Mater.* 85 (2001) 301–315.

- [28] Z. Xuan, Y. Tang, X. Li, Y. Liu, F. Luo, Study on the equilibrium, kinetics and isotherm of biosorption of lead ions onto pretreated chemically modified orange peel, *Biochem. Eng. J.* 31 (2006) 160–164.
- [29] X. Li, Y. Tang, Z. Xuan, Y. Liu, F. Luo, Study on the preparation of orange peel cellulose adsorbents and biosorption of  $\text{Cd}^{2+}$  from aqueous solution, *Sep. Purif. Technol.* 55 (2007) 69–75.
- [30] C. Liao, Z. Liao, Application of peanut hull: I. preparation of heavy metal ion adsorbent, *Journal of Guangxi Teachers Education University (Natural Science Edition)* 21 (2004) 68–70 [In Chinese].
- [31] F. Kargi, S. Cikla, Biosorption of Zinc(II) ions onto powered waste sludge (PWS): kinetic and isotherms, *Enzyme Microb. Technol.* 38 (2006) 705–710.
- [32] S.G. Susmita, G. Krishna, Bhattacharya, Adsorption of Ni(II) on clays, *J. Colloid Interface Sci.* 295 (2006) 21–32.
- [33] Q. Li, L. Chai, Z. Yang, Q. Wang, Kinetics and thermodynamics of Pb(II) adsorption onto modified spent grain from aqueous solutions, *Appl. Surf. Sci.* 255 (2009) 4298–4303.
- [34] Q. Li, Q. Yue, B. Gao, et al., Kinetics of Adsorption of Disperse Dyes at Cationic Bentonites, *Chem. J. Chin. Universities* 6 (2006) 1113–1117.
- [35] R. Djeribi, O. Hamdaoui, Sorption of copper(II) from aqueous solutions by cedar sawdust and crushed brick, *Desalination* 225 (2008) 85–112.
- [36] E.A. Deliyanni, L. Nalbandian, K.A. Matis, Adsorptive removal of arsenites by a nanocrystalline hybrid surfactant-akaganeite sorbent, *J. Colloid Interface Sci.* 302 (2006) 458–466.
- [37] Y.-s. Ho, E. Augustine, A.E. Ofomaja, Kinetics and thermodynamics of lead ion sorption on palm kernel fibre from aqueous solution, *Process Biochem.* 40 (2005) 3455–3461.
- [38] M. Iqbal, A. Saeed, Production of an immobilized hybrid biosorbent for the sorption of Ni(II) from aqueous solution, *Process Biochem.* 42 (2007) 148–157.
- [39] R. Qadeer, Adsorption behavior of ruthenium ions on activated charcoal from nitric acid medium, *Colloid Surfaces A: Physicochem. Eng. Aspects* 293 (2007) 217–223.
- [40] M. Šciban, M. Klačnja, B. Škrbic, Adsorption of copper ions from water by modified agricultural by-products, *Desalination* 229 (2008) 170–180.
- [41] X. Wang, Z.z. Li, C. Sun, A comparative study of removal of Cu(II) from aqueous solutions by locally low-cost materials: marine macroalgae and agricultural by product, *Desalination* 235 (2009) 146–159.
- [42] A. Grimm, R. Zanzi, E. Björnbo, A.L. Cukierman, Comparison of different types of biomasses for copper biosorption, *Bioresour. Technol.* 99 (2008) 2559–2565.
- [43] S. Dahiya, R.M. Tripathi, A.G. Hegde, Biosorption of lead and copper from aqueous solutions by pretreated crab and arca shell biomass, *Bioresour. Technol.* 99 (2008) 179–187.
- [44] W. Zou, R. Han, Z. Chen, et al., Kinetic study of adsorption of Cu(II) and Pb(II) from aqueous solutions using manganese oxide coated zeolite in batch mode, *Colloids Surfaces A: Physicochem. Eng. Aspects* 279 (2006) 238–246.