Desalination and Water Treatment
www.deswater.com

51 (2013) 2411–2422
February

1944-3994/1944-3986 © 2013 Balaban Desalination Publications. All rights reserved
doi: 10.1080/19443994.2012.747472

Evaluation of biosorption of copper ions onto pinion shell

M. Calero, G. Blázquez, E. Dionisio-Ruiz, A. Ronda, M.A. Martín-Lara*

Department of Chemical Engineering, University of Granada, Granada 18071, Spain
Tel. +34 958 243311; Fax: +34 958 248992; email: marianml@ugr.es

Received 13 October 2011; Accepted 19 June 2012

ABSTRACT

Biosorption of Cu(II) by pinion shell (PS) was investigated in batch and packed-bed systems. The biosorbent was characterized by elemental analysis, potentiometric titrations, surface area and pore size distribution, and Fourier transform infrared (FTIR) analyses. Potentiometric titrations and FTIR spectroscopy indicated the presence of functional groups in the PS, some of which were involved in the sorption process. Batch adsorption experiments were carried out as a function of solution pH, particle size, biosorbent dosage, contact time, and initial metal ion concentration. The rate of the biosorption process followed pseudo-second-order kinetics, while the sorption equilibrium data well fitted to the Langmuir and Freundlich isotherm models. The maximum monolayer Cu(II) biosorption capacity was 4.29 mg/g at 25°C. Finally, the dynamic biosorption studies were carried out using a packed-bed column and the main column parameters were determined. The present study suggests that the PS can be used as a potential, alternative, low-cost biosorbent for the removal of Cu(II) ions from aqueous media.

Keywords: Biosorption; Pinion shell; Copper; Equilibrium; Kinetics; Agricultural waste

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, and ease of fabrication and installation. Ultra-trace amount of copper is essential for human, animals, and micro-organisms. However, excessive copper can be detrimental for the environment. For instance, for human it will cause stomach upset and ulcer, mental retardance, and liver and brain damage. 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, fertilizer industry, etc. [1]. Therefore, the 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 [2].

The conventional technologies for the removal of heavy metals from wastewater include, mainly, chemical precipitation, ion exchange, adsorption, and membrane processes and evaporation that require high capital investment and running costs [3,4]. Therefore, there is an urgent need for the development of innovative but low-cost processes, where metal ions can be removed economically. The search for new treatment technologies has focused on biosorption [5].

Biosorption is a term that describes the removal of heavy metals by the passive binding to nonliving micro-organisms (bacteria, fungi, and algae) and other

---

*Corresponding author.

The Third International Congress Smallwat11—Wastewater in Small Communities 25–28 April 2011, Seville, Spain

biomass (such as olive stone, rice hull, fruit peel, leave, and bark of tree) from an aqueous solution. Biosorption has many advantages including low capital and operating costs, the selective removal of metals, biosorbent regeneration and metal recovery potentiality, rapid kinetics of adsorption and desorption, and no sludge generation.

In particular, pinion shell (PS) may constitute promising low-cost adsorbent among biomaterials, since this waste is produced in great quantities in the Mediterranean area, and is of no market value.

The objective of this study was to examine the copper(II) removal from aqueous solution using a PS in batch and in a packed-bed column. The characterization of PS was carried out using potentiometric titration and Fourier transform infrared (FTIR) spectroscopy. The effect of different parameters (solution pH, particle size, biosorbent dosage, contact time, and initial copper concentration) on copper biosorption by PS was analyzed in batch system, and finally, the main column parameters of copper biosorption by PS in a packed-bed column were determined.

2. Materials and methods

2.1. Biosorbent preparation

PS was provided by Carsan Biocombustibles S.L. factory from Granada (Spain). The solid was milled with an analytical mill (IKA MF-10) and the <1.000 mm fraction was chosen for the characterization and biosorption tests without any pretreatment.

2.2. Preparation of Cu(II) solutions

The aqueous solutions of Cu^{2+} were prepared using $CuSO_4{\cdot}5H_2O$. A stock solution (500 mg/L) of Cu^{2+} was prepared by dissolving the required quantity of $CuSO_4{\cdot}5H_2O$ in distilled water. It was further diluted to obtain standard solutions. For all biosorption experiments, Cu^{2+} solutions containing 10–300 mg/L were prepared and used. The pH of the solution was adjusted using HCl and NaOH solutions.

2.3. Measurement of Cu(II) concentrations

The copper concentration in the solutions was determined by atomic absorption spectroscopy (AAS) using a Perkin–Elmer (model AAnalyst 200) equipment. Standard solutions with several copper concentrations were prepared to obtain the calibration curve along the linear calibration range of the equipment. The standard solutions were prepared using a reference copper solution (Panreac PA) for AAS calibrations.

The percentage of removal of Cu(II) was calculated using the following equation:

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

The amount of metal uptake was obtained by the following equation:

$$q_e = \frac{(C_0 - C_e)}{m} \times V \tag{2}$$

where q_e (mg/g) is the amount biosorbed at equilibrium, C_0 (mg/L) and C_e (mg/L) are the initial and the equilibrium concentrations, respectively, while m (g) is the mass of biosorbent and V (L) is the volume of solution.

2.4. Characterization tests for biosorbent

2.4.1. Potentiometric titrations

Potentiometric titration measurements were carried out using an automated titrator (Metrohm 794 Basic Titrino). Biosorbent suspensions (2 g in 50 mL of deionized water) were fluxed by N_2 to remove CO_2 and were titrated by standard solutions of NaOH 0.1 N (basic branch) and HCl 0.1 N (acid branch). After each addition of titrant (NaOH or HCl), the pH of suspension was allowed to reach equilibrium under magnetic stirring and then measured by a pH meter.

2.4.1.1. Titration modeling. Titration data were reported as total negative charge concentration in the solid phase (Q, mol/g) vs. solution pH:

$$Q = \frac{C_b \times V_b - C_a \times V_a + ([\mathrm{H}^+] - [\mathrm{OH}^-]) \times V_T}{m} \tag{3}$$

where C_a (M) and C_b (M) are the acid and base concentrations for each titrant addition, respectively, and V_T (L) is the total suspension volume after each titrant addition ($V_T = V_0 + V_t$), where V_0 and V_t are the initial volume and the titrant volume, respectively.

Biosorbent charge can be both negative and positive, negative when active sites in the dissociated form are negatively charged (reaction A) and positive when the active sites in the dissociated form are neutral and after proton binding become positive (reaction B):

$$A_j\mathrm{H(s)} \Leftrightarrow A_j^-\mathrm{(s)} + \mathrm{H^+(aq)}$$

$$B_j(\mathrm{s}) + \mathrm{H}^+(\mathrm{aq}) \Leftrightarrow B_j\mathrm{H}^+(\mathrm{s})$$

Heterogeneity of acid–base groups in natural matrices can be represented by a continuous approach [6], introducing a probability density function for the logarithm of the reaction equilibrium constant $K_{i,j}$ of the active sites, such as the quasi-Gaussian distribution of Sips [7]:

$$f(\log K_{i,j}) = \frac{\ln(10)\sin(m\pi)}{\pi\left[\left(\frac{K_{i,j}}{\tilde{K}_{i,j}}\right)^{-m_{i,j}} + 2 \times \cos(m\pi) + \left(\frac{K_{i,j}}{\tilde{K}_{i,j}}\right)^{m_{i,j}}\right]} \tag{4}$$

where $K_{i,j}$ is the median value of the distribution and $m_{i,j}$ $(0 < m < 1)$ is a parameter related to the shape of the distribution.

Dependence of charge concentration in the solid phase on solution pH can be then represented by the following model in which n-types of distributed acidic sites and m-types of basic sites were hypothesized [8,9]:

$$Q = \sum_{j=1}^{n} \frac{[A_j]_T}{1 + \left(\frac{[\mathrm{H}^+]}{K_{A,j}}\right)^{m_{A,j}}} - \sum_{j=1}^{m} \frac{[B_j]_T}{1 + \left(\frac{1}{K_{B,j} \times [\mathrm{H}^+]}\right)^{m_{B,j}}} \tag{5}$$

where $[A_j]_T$ (mol/g) is the maximum charge on solid for the jth acidic site type characterized by a median value of reaction constant $K_{A,j}$ and a shape parameter $m_{A,j}$ and $[B_j]_T$ (mol/g) is the maximum charge on solid for the jth basic site type characterized by a median value of protonation constant $K_{B,j}$ and a shape parameter $m_{B,j.}$

2.4.2. FTIR analysis

The native biosorbent and biosorbent after its use in column biosorption experiments (Section 2.6) were dried, ground, and were analyzed with a FTIR Spectrometer (Perkin–Elmer, Spectrum 65) in the range of 4,000–400 cm^{-1} to identify the chemical groups present in it and to complete the study of the functional groups. No additional preparation of the samples was necessary for this equipment in order to obtain a good quality spectrum.

2.5. Batch biosorption experiments

2.5.1. Effect of pH solution

The effect of pH on the adsorption capacity of PS was investigated using solutions of 10 mg/L of metal ion concentration at pH range of 3–10 at 25°C. The 0.5 g of biosorbent was added to 50 mL of Cu(II) solutions. Flasks were agitated on a shaker for 100 min to ensure that equilibrium was reached. Then the mixture was centrifuged and filtrated and finally, the Cu^{2+} in the remaining solution was analyzed in an Atomic Absorption Spectrometer (Perkin–Elmer, model AAnalyst 200).

Also blank tests were performed using the same conditions, but without biosorbent.

2.5.2. Effect of particle size

To assess the effect of particle size on copper biosorption, particles in a range of <0.250–1 mm were used at an initial pH of 5, temperature of 25°C, and initial copper concentration of 10 mg/L.

2.5.3. Effect of biosorbent dosage

To study the effect of biosorbent dosage on copper biosorption, the mixture of copper solution and biomass was prepared as described in Section 2.5.1, with varying biomass concentrations, i.e. 1, 5, 10, 20, and 40 g/L. The samples were then subjected to the procedure described in Section 2.5.1.

2.5.4. Effect of contact time. Kinetic studies

In order to assess the required time to reach an equilibrium state, the batch dynamics of Cu(II) removal was studied for PS. The Cu(II) removal was monitored around 0–100 min. In this experiment, the PS dosage used was 10 g/L and the solution with an initial metal ion concentration of 10 mg/L was adjusted to pH 5.

2.5.5. Effect of initial copper concentration. Equilibrium studies

The biosorption isotherm study was conducted at pH 5 during 100 min by varying the initial copper concentrations (from 10 to 300 mg/L), while the PS dosage (10 g/L) and temperature (25°C) were kept constant.

2.6. Column biosorption experiments

The column study was conducted using a jacket glass column having an internal diameter of 15 mm and a length of 230 mm. To enable a uniform inlet flow of the solution into the column, glass beads of 5 mm diameter were placed to attain a height of

44 mm and 134 mm (5 g and 15 g of PS, respectively). The glass beads layer at the bottom of the column helped in even distribution of the copper solution through the top of the column and also prevented washing away of the sorbent at the bottom. The copper solution of 100 mg/L was pumped through the bottom of the column at a constant flow rate of 6 mL/min by means of a peristaltic pump. The pH of the copper solution was maintained at 5. Column effluent samples were collected at frequent time interval and analyzed for effluent copper concentration until the column achieved breakthrough (i.e. effluent to influent concentration of 0.90 or higher).

3. Results and discussion

3.1. Characterization of the biosorbent

Table 1 shows a typical physio-chemical analysis of PS. Elemental analysis results showed that PS has an elemental composition composed mainly of carbon and oxygen. The specific surface area was found to be 0.579 m^2/g and pores of PS have an average pore width of 55.4 Å and total pore volumes of 0.973 cm^3/g. The moisture content was 6.36%. This low moisture content facilitates the preparation of this solid as biosorbent, since they require no drying before use.

3.1.1. Potentiometric titrations

Biosorbent of this work is characterized by a certain degree of surface chemical heterogeneity, which is related to the presence of different functional groups, such as carboxyl and phenolic groups. The content of these groups varies depending on the nature of the biosorbent. These functional groups are important in determining the acidity/basicity of biosorbent surfaces in aqueous dispersion.

In this work, acid–base properties of the active sites of PS were determined by potentiometric titrations and represented by a continuous model accounting for two main kinds of active sites [8,9].

Fig. 1 shows an acid–base titration of a 40 g/L suspension of the PS. The data for the PS samples illustrate that the surface exhibited a slightly acidic character. On the other hand, the presence of biosorbent imparts a significant buffering capacity to the water. This buffering is due to the presence of active functional groups on the sorbent surface, which consume added acid or base by taking or losing their protons. However, the PS suspension shows relatively weak inflection points. This behavior has been attributed to the existence of several functional groups with an overlapping range of pH over which they protonate or deprotonate. In order to determine how many such sites were present on the biosorbent surface, data from each of several titrations were fitted successively with two sites (one acid and one basic). Reactions for these sites were included in the equilibrium model (see Section 2.4.1.1).

A nonlinear regression of the experimental data was performed to determine the adjustable parameters that are characteristic of each site: site concentration ($[A]_T$ or $[B]_T$, position (K_H), and shape of the affinity distribution (m_A or m_B) (Table 2).

There was a major concentration of acid sites than basic ones on PS. The values of the parameters suggest that PS can be characterized by a concentration of carboxylic groups. This hypothesis seems to be reasonable considering the literature data of the acidic constants of carboxylic acids ($pK_H \approx 3$–5). Furthermore, this observation is consistent with results obtained from previous studies on agricultural wastes [8–12]. However, it is not possible to identify the other active site (group B) in the function of the pK_B value (−11.05) and the reaction supposed. Consequently, for explaining positive values of Q, reactions in acidic medium of hemicellulose and cellulose (basic components of PS) can be supposed, based on the hydrolysis of the β-glucosidic linkages between the glucose base units. But the positive charge on the biosorbent surface can also be correlated well with other reactions as the acid–base reactions of amine or amide group. In conclusion, the reactions that provided posi-

Table 1
Characteristics of PS

% Moisture content	Elemental analysis				
	% C	% H	% N	% S	% O
6.36	46.30	6.92	0.45	<0.1	46.28
BET surface area, m^2/g	Pore volume, cm^3/g		Pore diameter, Å		
0.579	0.973		55.4		

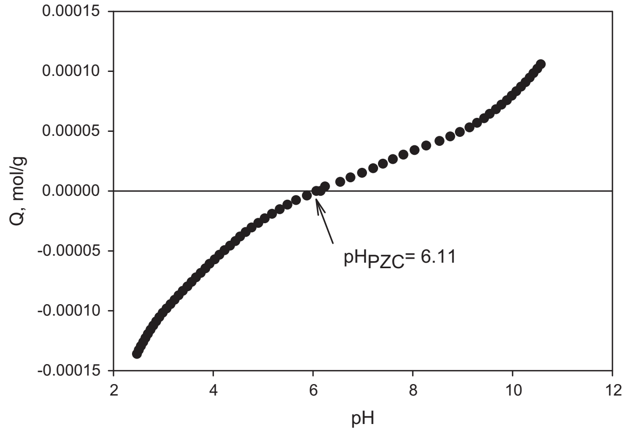


Fig. 1. Potentiometric titration data for PS plotted as surface negative charge vs. pH.

tive charge to the biosorbent cannot indicate with absolute certainty.

3.1.2. Infrared spectroscopy (IR)

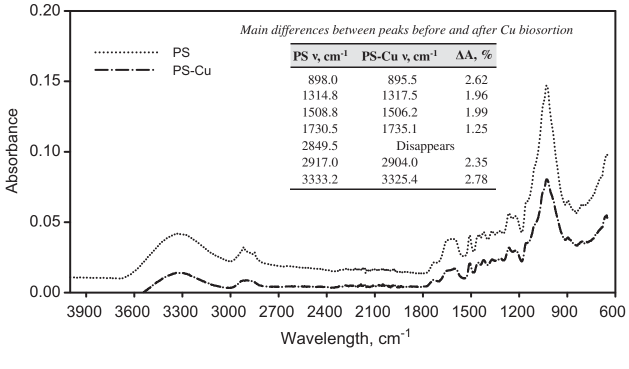
The IR has played an important part in the investigation of biosorbent surface chemistry. Direct information on the presence of surface functional groups can be obtained from IR studies. FTIR spectra before and after copper biosorption are presented in Fig. 2.

The broad form and high intensity of the peak at 3,333 cm^{-1} is typical, and corresponded to OH bonds, with possible overlap of low-NH groups [13]. The peaks located at 2,917 cm^{-1} and 2,849 cm^{-1} are characteristics of aliphatic C–H bonds [14,15]. The peak at 1,730 cm^{-1} is assigned to a carbonyl group or carboxyl ester due to the appearance of a strong peak at 1,260 cm^{-1} corresponding to stretching vibration of C–O–R compounds [15,16]. The peak at 1,605 cm^{-1} has usually been assigned in bibliography to C=O bonds of carboxyl groups [17,18]. The absorption peak at 1,508 cm^{-1} could be due to the presence of aromatics rings or rings with C=C bonds [19]. The weak peaks at 1,460–1,420 cm^{-1} are also assigned to symmetrical vibrations of carbonyl groups in different conformations as –COO– and C=O of different organic compounds [16]. The peaks located at 1,370–1,310 cm^{-1} are difficult to assign and could correspond to COO–, C–H_3, or O–H groups and also to C–N of amides II or even at deformation of C–H bonds [15,20]. The frequency of 1,028 cm^{-1} can be caused by alcoholic C–O bonds and C–N links [13,19]. The peaks of 898 and 654 cm^{-1} can be assigned to aliphatics or aromatics C–H_n bonds [19].

On the other hand, changes in the FTIR spectra were observed after copper biosorption. The intensity clearly decreased after Cu^{2+} biosorption. It suggests that there may be an ion exchange process, and metal, more voluminous, somehow prevents the vibration of the bonds. Also in Fig. 2, a table with bands and peaks that presented higher changes after copper biosorption has been provided. Hydroxyl and carboxyl may be some of the main groups involved in the biosorption process. These results confirm the findings of potentiometric titrations.

Table 2
Average pK values and proton binding site concentrations for titrations of PS performed at 25℃

$[A]_T$	$\Delta[A]_T$	$[B]_T$	$\Delta[B]_T$	pK_A	ΔpK_A	pK_B	ΔpK_B	m_A	Δm_A	m_B	Δm_B	SSR, mol^2/g^2	r^2
2.40×10^{-4}	6.17×10^{-5}	1.88×10^{-4}	4.23×10^{-5}	3.93	0.40	−11.05	0.37	0.26	0.07	0.42	0.14	2.65×10^{-9}	0.993



Main differences between peaks before and after Cu biosortion

PS ν, cm^{-1}	PS-Cu ν, cm^{-1}	ΔA, %
898.0	895.5	2.62
1314.8	1317.5	1.96
1508.8	1506.2	1.99
1730.5	1735.1	1.25
2849.5	Disappears	
2917.0	2904.0	2.35
3333.2	3325.4	2.78

Fig. 2. The FTIR spectra of native PS and PS after copper biosorption.

3.2. Batch biosorption

3.2.1. Effect of pH

The pH has been recognized as one of the most important environmental factors influencing not only the active site dissociation, but also the solution chemistry of the metal. Therefore, preliminary experiments have been performed to find out the optimum pH for maximizing the copper removal.

For discerning between biosorption and metal precipitation, blank tests (without biosorbent) were carried out. The results (Fig. 3(a)) showed that Cu^{2+} is the main specie present at pH values lower than approximately 6. However, when the pH exceeds 6, concentration of Cu^{2+} in solution, C_f, decreases and precipitation was observed. In order to confirm these results, a chemical equilibrium program (HYDRA MEDUSA) was used to calculate the speciation of copper in the aqueous solution as a function of solution pH and for total salt concentration of 10 mg/L (Fig. 3(b)). When pH is lower than 5.5, species present in the solution are Cu^{2+} and $CuSO_4$, being the Cu^{2+} the predominant. However, when pH increases, the fraction of soluble species decreases while the fraction of solid formed (CuO) increases. Finally, when pH is higher than 6 the Cu precipitated as CuO is the main specie in the solution. The effect of pH in the solutions on the removal efficiency of Cu(II) was studied at different pHs ranging from 3 to 6 and the results are shown in Fig. 4. The removal efficiency of Cu(II) tended to increase with increasing the pH value. In the pH range of 3–5, the removal (%) increases sharply from 9.7 to 70.5% with the pH increasing. The competition of protons for the same binding sites on the PSs reduces the amount of copper biosorbed at low pH. Also, the pH dependence of copper uptake could be related to the ionic states of the functional groups of the biomass. The net negative charge of the biosorbent increased when the pH elevated. In the pH range from 5 to 6, a decrease on removal (%) is obtained. It is apparently due to the occurrence of copper precipitation and the presence of others species in solution. In this paper, maximum biosorption is observed at pH 5. Hence, the optimum pH for Cu (II) uptake by PS used in this research is 5 and all the subsequent studies were conducted at this value of pH.

3.2.2. Effect of the sorbent particle size

The particle size range of the biosorbent was determined by passing 100 g of PS through different sieves and shaken for 10 min with a bottom pan in place to collect samples finer than the meshes. Table 3 shows the particle size distribution against the biomass particle size of PS. Percents of copper removal are also given in Table 3. Experimental results showed that PS has good copper removal efficiency from aqueous solution, particularly with particle sizes below

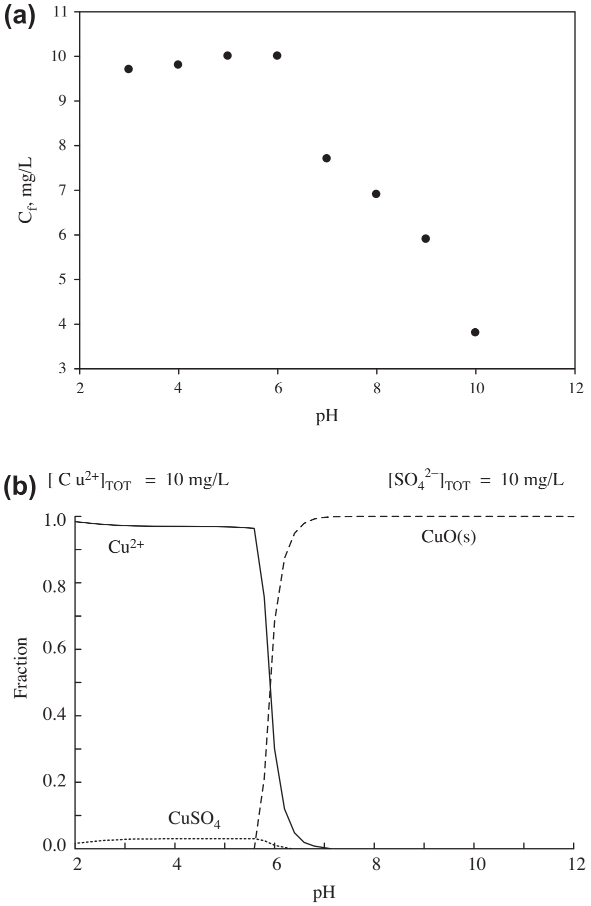


Fig. 3. Effect of pH on the speciation of copper in solution (metal ion solubility). (a) Experimental tests and (b) Medusa software.

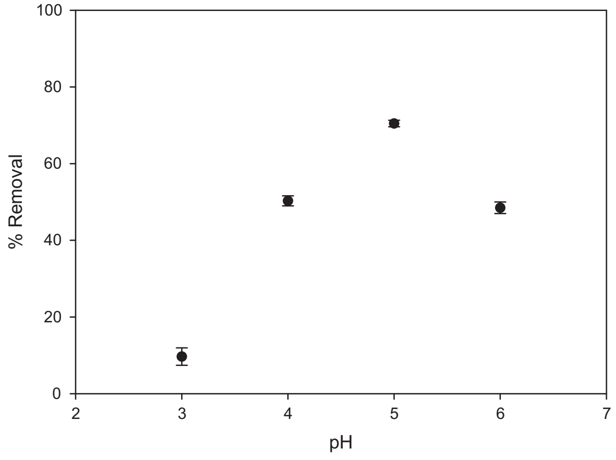


Fig. 4. Effect of pH on the biosorption of Cu(II) onto PS (initial metal concentration 10 mg/L; biosorbent concentration 10 g/L; and temperature 25°C).

0.710 mm. Moreover, percentage of adsorption decreased also with the increase in sample sizes. Acheampong et al. [21] reported similar behavior in copper biosorption using agricultural materials from tropical regions (coconut shell, coconut husk, *Moringa oleifera* seeds, and sawdust). The removal percentage decreased from smaller (0.25–0.5 mm) to larger particle (1.4–1.6 mm) size range due to decreased surface area. Malkoc and Nuhoglu [22] found a similar behavior in nickel biosorption using waste of tea factory for sizes ranging between 0.15–0.25 and 1.0–3.0 mm.

3.2.3. *Effect of biosorbent dosage*

Fig. 5 shows the effect of different biomass dosages on Cu(II) uptake at pH 5. The Cu(II) uptake by PS was found to increase with increasing biomass dosage. The increasing metal uptake at higher biosorbent dosage can be explained by considering an increase in the number of the active sites. But, because the values of 10; 20; and 40 g/L are close to each other, the biosorbent dosage was selected as 10 g/L in all the experiments. These results are in good accordance to those obtained by other researchers studying the copper biosorption on different biomaterials [23–26].

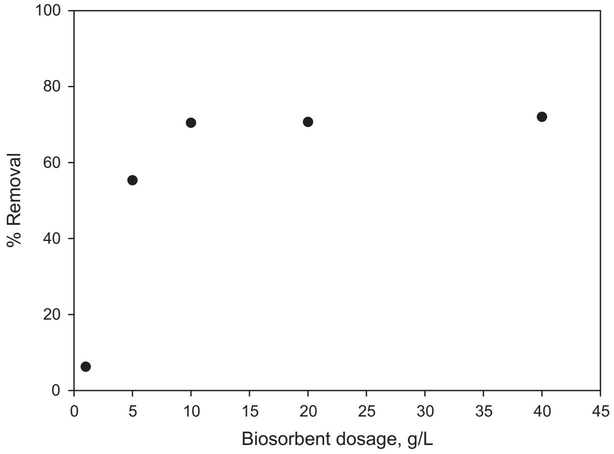


Fig. 5. Effect of biosorbent dosage on the biosorption of Cu (II) onto PS (initial metal concentration 10 mg/L; temperature 25°C; and pH 5).

3.2.4. *Effect of contact time. Kinetics studies*

Depending on the system used, the contact time of the sorbate with the sorbent is of great importance [27]. Fig. 6 shows the amount of copper biosorbed as a function of time. The Cu(II) biosorption rate is high at the beginning and the saturation levels are completely reached at about 40 min.

The results are similar to those obtained by other researchers. Altun and Pehlivan [24] found an equilibrium time between 20 and 60 min for copper biosorption by walnut, hazelnut, and almond shell; Ho [23] indicated that the equilibrium time for biosorption of copper from tree fern is less than 60 min; Chowdhury and Saha [28] on studying the biosorption kinetics of sorption of Cu(II) onto *Tamarindus indica* seed powder reported that at a contact time of 100 min equilibrium was reached, or Ofomaja et al. [29] indicated that the time needed to reach equilibrium in copper biosorption by pine cone powder is less than 15 min.

Table 3
Particle size distribution of PS and effect of particle size on biosorption of copper at pH 5 and 25°C

Size, mm	% Mass	% Copper removal
>1.000	26.54	55.64
1.000–0.710	41.94	61.29
0.710–0.500	11.79	76.73
0.500–0.355	4.03	78.24
0.355–0.250	2.63	76.83
<0.250	11.67	79.25

3.2.4.1. *Biosorption kinetics.*

Pseudo-second-order model has been used for testing kinetic experimental data. The pseudo-second-order model proposed by Ho and McKay [30] was based on the assumption that the adsorption follows second-order chemisorption. The pseudo-second-order equation can be expressed as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{6}$$

where q_e (mg/g) and q_t (mg/g) are the biosorbed amount of Cu(II) at equilibrium and time t (min), respectively, and k_2 is the rate constant in the pseudo-second-order biosorption process (g/mg min).

Integrating this equation between the boundary conditions, $t = 0$, $q_t = 0$ and $t = t$, $q_t = q_t$, and rearranging, the following was obtained:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \tag{7}$$

where $h = k_2 \cdot q_e^2$ is the initial biosorption rate (mg/(g min)) for the pseudo-second-order adsorption. The

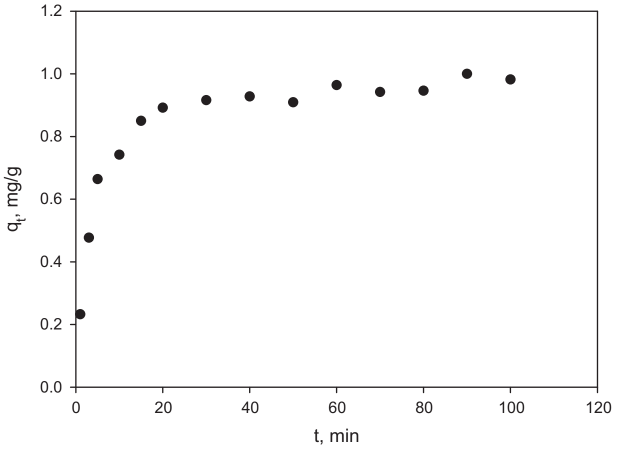


Fig. 6. Effect of contact time on the biosorption of Cu(II) onto PS (initial metal concentration 10 mg/L; biosorbent concentration 10 g/L; temperature 25˚C; and pH 5).

values of k_2, h, and q_e were calculated from the plot of t/q_t vs. t and they are listed in Table 4.

From Table 4, q_e has a value of 1.003 mg/g and initial biosorption rate, h, has a value of 0.303 mg/(g min). The rate constant of pseudo-second-order, k_2, has a value of 0.302 g/(mg min). By observing the fitting result by pseudo-second-order kinetic model, this model seems to give a very good representation (correlative coefficient >0.99). Moreover, the calculated q_e values from pseudo-second-order model agree quite well with experimental data.

3.2.5. Effect of initial copper concentration. Equilibrium studies

The biosorption of Cu^{2+} ions was carried out at different initial Cu^{2+} ion concentrations ranging from 10 to 300 mg/L at pH 5 and 100 min of contact time. The results are presented in Fig. 7, and the study showed that as higher was the initial metal ion concentration, more metal ion was adsorbed per unit weight at equilibrium. A higher initial concentration provides an important initial force to overcome pollutant mass transfer resistances between the aqueous and the solid phases.

Table 4
Pseudo-second-order rate parameters for biosorption of copper on PS

Experimental	Pseudo-second-order			
$q_{e,\exp}$, mg/g	$q_{e,\mathrm{calc}}$, mg/g	h, mg/g min	k_2, g/mg min	r^2
1.000	1.003	0.303	0.302	0.997

3.2.5.1. Biosorption equilibrium.

In the evaluation of a biosorbent, the quantification of its biosorptive features is required and the drawing of profiles based on sorption isotherm is helpful for this purpose. The drawing of sorption isotherm requires the determination of the specific metal uptake as a function of the equilibrium concentration. The evaluation of the specific uptake, q_e, is performed according to Eq. (2) as mentioned in Section 2.3. The equilibrium data on Cu (II) adsorption are further analyzed using two well-known two-parameter isotherms: Langmuir [31] and Freundlich [32] to facilitate a comparison of adsorption performance and to describe the deposition of Cu (II) as either a mono- or multilayer on the PS. A simple statistical discrimination of these two models was carried out using the correlation coefficient (R^2) estimation.

Langmuir isotherm: The Langmuir adsorption isotherm is derived from consideration based upon an assumption of maximum monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies of adsorption with no transmigration of adsorbate in the plane of the surface. The Langmuir adsorption isotherm equation is represented in Eq. (8):

$$q_e = \frac{b\, q_m\, C_e}{1 + b\, C_e} \tag{8}$$

where q_m (mg/g) is the maximum copper uptake under the given conditions and b (L/mg) is a coefficient related to the affinity between the sorbent and the sorbate which is related to the energy of adsorption through the Arrhenius equation.

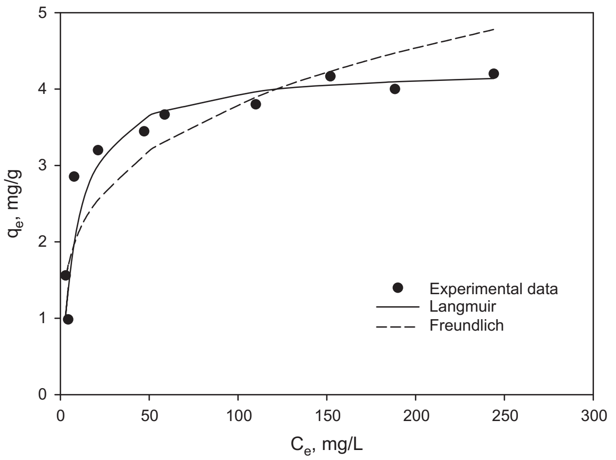


Fig. 7. Langmuir and Freundlich plots for Cu(II) ion biosorption by PS (biosorbent concentration 10 g/L; temperature 25˚C; and pH 5).

Table 5
The comparison of the Langmuir and Freundlich constants obtained from biosorption isotherms of Cu(II) ions by PS

Langmuir		
q_m, mg/g	b, L/mg	r^2
4.293 ± 0.181	0.110 ± 0.035	0.997
Freundlich		
K_F, (mg/g)·(L/mg)$^{1/n}$	n	r^2
1.159 ± 0.164	3.88 ± 0.78	0.742

The Langmuir isotherm is based on these assumptions: (a) metal ions are chemically adsorbed at a fixed number of well-defined sites; (b) each site can only hold one ion; (c) all sites are energetically equivalent; and (d) there is no interaction between the ions.

Kratochvil and Volesky [33] reported that qualities of a good biosorbent include a high q_m value and a high value for the constant b. High values of b can be seen in an isotherm with a steep initial slope, indicating a high affinity of the sorbate for the sorbent.

As seen from Fig. 7, the biosorbent fit quite well into the Langmuir model. The correlation coefficient was high as shown in Table 5. The maximum biosorption capacity of PS is found to be 4.29 mg/g and the value of b is 0.110 L/mg.

Table 6 summarizes the comparison of Cu(II) adsorption capacities (q_m) by various agricultural by-products. The PS presents a good biosorption capacity, reflecting a promising future for its utilization in copper ion removal from aqueous solutions.

Hence, in order to understand whether the adsorption of Cu(II) ions by PS is favorable or not, Hall et al. [41] introduced a dimensionless equilibrium term R_L, also known as the separation factor to express the Langmuir constant b. The significance of the R_L term is based upon an initial assumption of the applicability of the given data to Langmuir isotherm model, beyond which the value of R_L provides important information about the nature of the adsorption isotherm. This equilibrium parameter R_L is defined by,

$$R_L = \frac{1}{1 + b\, C_0} \tag{9}$$

where b is the Langmuir isotherm constant and C_0 is the initial Cu(II) ion concentration. The value of the parameter indicates the nature of the isotherm accordingly as follows: while $R_L > 1$ indicates unfavorable biosorption and $R_L = 1$ shows a linear isotherm; $0 < R_L < 1$ indicates a highly favorable biosorption and $R_L = 0$ shows an irreversible nature of biosorption.

The values of R_L are given in Fig. 8. The separation factor R_L for the Langmuir model equations at pH 5 was greater than zero and less than one indicating that the Langmuir isotherm was favorable for describing the biosorption of copper by PS. Fig. 8 also indicates that the biosorption is more favorable for the higher initial Cu(II) ion concentrations than for the lower ones. It is thus apparent that the biosorption of Cu(II) ions on PS is favorable within the experimental conditions studied.

Freundlich isotherm: The Freundlich isotherm model describes a multilayer adsorption with the assumption of heterogeneous surface in which the energy varies as a function of the surface coverage. The model can be presented as [32] follows:

Table 6
A number of agricultural by-products available for biosorption of copper ions

Biosorbent	q_m, mg/g	Temperature, ℃/pH	Reference
Almond shell	3.62	25/6.0	Altun and Pehlivan [24]
Walnut shell	6.74		
Hazelnut shell	6.65		
Cashew nut shell	20.00	30/5.0	SenthilKumar et al. [34]
Carrot residues	8.74	20/5.3	Guzel et al. [35]
	9.08	40/5.3	
	12.39	60/5.3	
Cinnamomum camphora leaves	16.76	30/4.0	Chen et al. [36]
Sawdust	4.90	22/5.5	Grimm et al. [37]
Pomegranate peel	1.32	26/5.8	El-Ashtoukhy et al. [38]
Sour orange residue	21.7	30/5.0	Khormaei et al. [39]
Raw Ipomoea carnea	7.65	20/6.0	Miranda et al. [40]
Pinion shell	4.29	25/5.0	In this work

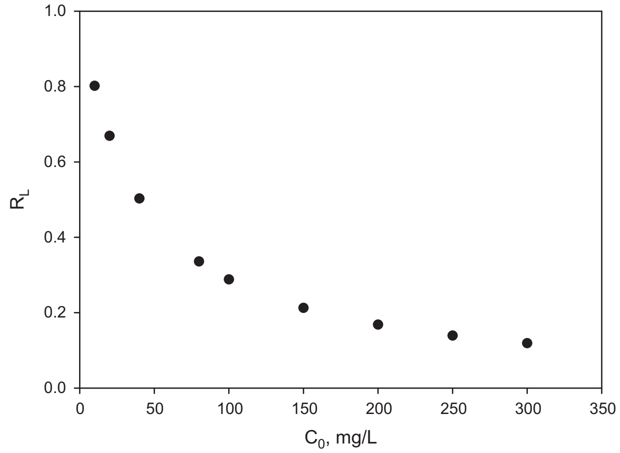


Fig. 8. Equilibrium parameter, R_L for the biosorption of Cu (II) ion onto PS.

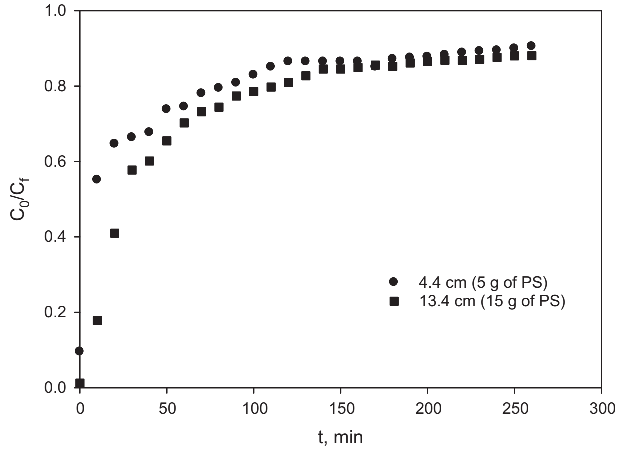


Fig. 9. Plot of effluent to influent copper concentration ratio vs. time (flow rate 6 mL/min; influent pH 5; and influent metal concentration 100 mg/L).

$$q_e = K_F C_e^{\frac{1}{n}} \tag{10}$$

where K_F is the equilibrium constant indicative of adsorption capacity (mg/g) and $1/n$ is an empirical parameter related to the adsorption intensity.

The characteristic parameters for the Freundlich adsorption model have been determined and they are reported in Table 5. The correlation coefficient indicated that Freundlich isotherm model described the experimental data worse than the Langmuir isotherm model. Nevertheless, n parameter can provide information about the biosorption process of copper onto PS. As n parameter of Freundlich isotherm was greater than unity, the copper biosorption process is favorable [42].

3.3. Dynamic biosorption

A column study was conducted for 220 min using a copper solution with an influent concentration of 100 mg/L, an influent pH of 5, a flow rate of 6 mL/min, and two-bed depth of 4.4 and 13.4 cm (5 and 15 g of biosorbent mass, respectively). The plots of the ratio of effluent to influent copper ion concentration (C_0/C_f) vs. time (breakthrough curves) for PS are shown in Fig. 9. The main parameters of the column were calculated and reported in Table 7.

The volume of the effluent, V_{ef} (mL), can be calculated through the following equation:

$$V_{ef} = Q\, t_{\text{total}} \tag{11}$$

where t_{total} is the total time in min and Q is the flow rate which circulates through the column in mL/min.

The area under the breakthrough curve represents the total mass of metal biosorbed, q_{total}, in mg, for a given feed concentration and flow rate and it can be determined by integration,

$$q_{\text{total}} = \frac{Q}{1,000} \int_{t=0}^{t=t_{\text{total}}} C_R \, \mathrm{d}t \tag{12}$$

where C_R is the concentration of metal removal in mg/L.

The total amount of metal ions sent to the column, in mg, can be calculated from the following expression:

Table 7
Column data and parameters obtained at a flow rate of 6 mL/min, at an inlet Cu(II) concentration of 100 mg/L, and at pH of 5

Bed depth, cm	V_{ef}, mL	t_b, min	q_{total}, mg	m_{total}, mg	q_e, mg/g	C_e, mg/L	R, %
4.4	1,560	–	35.69	179.77	7.14	92.36	19.85
13.4	1,560	1	48.97	159.87	3.26	71.09	30.63

$$m_{\text{total}} = \frac{C_0\ Q\ t_{\text{total}}}{1,000} \tag{13}$$

and the total metal removal (%) can be calculated from the ratio of metal mass biosorbed (q_{total}) to the total amount of metal ions sent to the column (m_{total}) as follows,

$$\%\,R = \frac{q_{\text{total}}}{m_{\text{total}}} 100 \tag{14}$$

The amount of metal biosorbed at equilibrium or biosorption capacity, q_e (mg of sorbated metal/g of sorbent), and the equilibrium metal concentration, C_e (mg/L), can be determined using the following equations:

$$q_e = \frac{q_{\text{total}}}{m} \tag{15}$$

$$C_e = \frac{m_{\text{total}} - q_{\text{total}}}{V_{ef}} 1,000 \tag{16}$$

where m is the mass of sorbent in g.

The total mass of metal biosorbed, q_{total}, increases by increasing the bed depth. However, the biosorption capacity at equilibrium, q_e, decreases from 7.14 mg/g for a bed depth of 4.4 cm to 3.26 mg/g for a bed depth of 13.4 cm. It could be because the amount of biosorbent used to treat the same volume of effluent increases. Also, the breakthrough time (t_b is the time at which outlet Cu(II) concentration reached a value near to 2 mg/L) was only reached when the bed depth is 13.4 cm and it practically coincides with the start of column operation.

4. Conclusions

The results showed that PS can be used as sorbent for the effective removal of Cu(II) from aqueous solutions. A surface complexation model was proposed for the development of charge on the surface of PS. This model describes satisfactorily the potentiometric titration data. The batch study parameters, such as pH of solution, particle size, biosorbent dosage, contact time, and initial copper concentrations, were found to be important parameters on the biosorption processes. The kinetic studies indicated that equilibrium in the biosorption of Cu(II) ions on PS was reached in 10 min of contact time. The kinetic biosorption data fit well to the second-order kinetic model. The adsorption isotherms followed the Langmuir model ($r^2 > 0.99$). The maximum biosorption capacity of Cu(II) was 4.29 mg/g at an optimum pH 5 and at 25° C. After the evaluation of the batch and column operation, the packed column effectively exploited the biosorbent copper biosorption capacity rather than the batch mode.

Acknowledgments

The authors are grateful to the Spanish Ministry of Science and Innovation for financial support received (Project CTM2009-10294).

References

[1] Z. Aksu, Ì.A. Ìsoglu, Removal of copper(II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp, Process Biochem. 40 (2005) 3031–3044.

[2] Z. Chun-Shui, W. Li-Ping, C. Wen-bin, Removal of Cu(II) from aqueous solution by agricultural by-product: Peanut hull, J. Hazard. Mater. 168 (2009) 739–746.

[3] Z. Aksu, Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel(II) ions onto *Chlorella vulgaris*, Process Biochem. 38 (2002) 89–99.

[4] V.K. Gupta, A.K. Shrivastava, N. Jain, Biosorption of chromium(VI) from aqueous solutions by green algae *Spirogyra* species, Water Res. 35 (2001) 4079–4085.

[5] F. Kargi, S. Cikla, Determination of model parameters for zinc(II) ion biosorption onto powdered waste sludge (PWS) in a fed-batch system, J. Environ. Manage. 85 (2007) 883–890.

[6] L.K. Koopal, W.H. van Riemsdijk, D.G. Kinniburgh, Humic matter and contaminants. General aspects and modeling metal ion binding, Pure Appl. Chem. 73 (2001) 2005–2016.

[7] R. Sips, Structure of a catalyst surface, J. Chem. Phys. 16 (1948) 490–495.

[8] M.A. Martín-Lara, F. Pagnanelli, S. Mainelli, M. Calero, L. Toro, Chemical treatment of olive pomace: Effect on acid–basic properties and metal biosorption capacity, J. Hazard. Mater. 156 (2008) 448–457.

[9] M.A. Martín-Lara, F. Hernáinz, M. Calero, G. Blázquez, G. Tenorio, Surface chemistry evaluation of some solid wastes from olive-oil industry used for lead removal from aqueous solutions, Biochem. Eng. J. 44 (2009) 151–159.

[10] F. Pagnanelli, S. Mainelli, F. Veglio, L. Toro, Heavy metal removal by olive pomace: Biosorbent characterisation and equilibrium modelling, Chem. Eng. Sci. 58 (2003) 4709–4717.

[11] F. Pagnanelli, S. Mainelli, L. Toro, New biosorbent materials for heavy metal removal: Product development guided by active site characterization, Water Res. 42 (2008) 2953–2962.

[12] M.A. Martín-Lara, I.L. Rodríguez, I.C. Alomá, G. Blázquez, M. Calero, Modification of the sorptive characteristics of sugarcane bagasse for removing lead from aqueous solutions, Desalination 256 (2010) 58–63.

[13] P. Lodeiro, J.L. Barriada, R. Herrero, M.E. Sastre de Vicente, The marine macroalga *Cystoseira baccata* as biosorbent for cadmium(II) and lead(II) removal: Kinetic and equilibrium studies, Environ. Pollut. 142 (2006) 264–273.

[14] A.N. Kosasih, J. Febrianto, J. Sunarso, Y.H. Ju, N. Indraswati, S. Ismadji, Sequestering of Cu(II) from aqueous solution using cassava peel (*Manihot esculenta*), J. Hazard. Mater. 180 (2010) 366–374.

[15] Q.Q. Peng, Y.G. Liu, G.M. Zeng, W. Xua, C. Yang, J. Zhang, Biosorption of copper(II) by immobilizing *Saccharomyces cerevisiae* on the surface of chitosan-coated magnetic nanoparticles from aqueous solution, J. Hazard. Mater. 177 (2010) 676–682.

[16] S. Liang, X.Y. Guo, N.C. Feng, Q. Tian, Isotherms, kinetics and thermodynamic studies of adsorption of Cu^{2+} from aqueous solutions by Mg^{2+}/K^{+} type orange peel adsorbents, J. Hazard. Mater. 174 (2010) 756–762.

[17] V.S. Munagapati, V. Yarramuthi, S.K. Nadavala, S.R. Alla, K. Abburi, Biosorption of Cu(II), Cd(II) and Pb(II) by *Acacia leucocephala* bark powder: Kinetics, equilibrium and thermodynamics, Chem. Eng. J. 157 (2010) 357–365.

[18] R. Zein, R. Suhaili, F. Earnestly, E. Indrawati, E. Munafy, Removal of Pb(II), Cd(II) and Co(II) from aqueous solution using *Garcinia mangostana* L. fruit shell, J. Hazard. Mater. 181 (2010) 52–56.

[19] D. Suteu, T. Malutan, D. Bilba, Removal of reactive dye Brilliant Red HE-3B from aqueous solutions by industrial lignin: Equilibrium and kinetics modeling, Desalination 255 (2010) 84–90.

[20] A. Celekli, M. Yavuzatmaca, H. Bozkurt, An eco-friendly process: Predictive modelling of copper adsorption from aqueous solution on *Spirulina platensis*, J. Hazard. Mater. 173 (2010) 123–129.

[21] M.A. Acheampong, J.P.C. Pereira, R.J.W. Meulepas, P.N.L. Lens, Biosorption of Cu(II) onto agricultural materials from tropical regions, J. Chem. Technol. Biotechnol. 86 (2011) 1184–1194.

[22] E. Malkoc, Y. Nuhoglu, Removal of Ni(II) ions from aqueous solutions using waste of tea factory: Adsorption on a fixed-bed column, J. Hazard. Mater. 135 (2006) 328–336.

[23] Y. Ho, Removal of copper ions from aqueous solutions by tree fern, Water Res. 37 (2003) 2323–2330.

[24] T. Altun, E. Pehlivan, Removal of copper(II) ions from aqueous solutions by walnut-, hazelnut- and almond-shells, Clean 35 (2007) 601–606.

[25] A.E. Ofomaja, E.B. Naidoo, S.J. Modise, Removal of copper(II) from aqueous solution by pine and base modified pine cone powder as biosorbent, J. Hazard. Mater. 168 (2009) 909–917.

[26] S. Rathnakumar, R.Y. Sheeja, T. Murugesan, Removal of copper(II) from aqueous solutions using teak (*Tectona grandis* L. f.) leaves, World Acad. Sci., Eng. Technol. 56 (2009) 880–884.

[27] Z. Baysal, E. Cinar, Y. Bulut, H. Alkan, M. Dogru, Equilibrium and thermodynamic studies on biosorption of Pb(II) onto *Candida albicans* biomass, J. Hazard. Mater. 161 (2009) 62–67.

[28] S. Chowdhury, P.D. Saha, Biosorption kinetics, thermodynamics and isosteric heat of sorption of Cu(II) onto *Tamarindus indica* seed powder, Colloids Surf. B 88 (2011) 697–705.

[29] A.E. Ofomaja, E.B. Naidoo, S.J. Modise, Dynamic studies and pseudo-second order modelling of copper(II) biosorption onto pine cone powder, J. Hazard. Mater. 251 (2010) 112–122.

[30] Y.S. Ho, G. Mc Kay, Pseudo-second order model for sorption process, Process. Biochem. 34 (1999) 451–459.

[31] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[32] H.M.F. Freundlich, Über die adsorption in lösungen [Over the adsorption in solution], Z. Phys. Chem. 57 (1906) 385–470.

[33] D. Kratochvil, B. Volesky, Advances in the biosorption of heavy metals, Trends Biotechnol. 16 (1998) 291–300.

[34] P. SenthilKumar, S. Ramalingam, V. Sathyaselvabala, S. Dinesh Kirupha, S. Sivanesan, Removal of copper(II) ions from aqueous solution by adsorption using cashew nut shell, Desalination 266 (2011) 63–71.

[35] F. Guzel, H. Yakut, G. Topal, Determination of kinetic and equilibrium parameters of the batch adsorption of Mn(II), Co (II), Ni(II) and Cu(II) from aqueous solution by black carrot (*Daucus carota* L.) residues, J. Hazard. Mater. 153 (2008) 1275–1287.

[36] H. Chen, G.L. Day, J. Zhao, A. Zhong, J. Wu, H. Yan, Removal of copper(II) ions by a biosorbent-*Cinnamomum camphora* leaves powder, J. Hazard. Mater. 177 (2010) 236–238.

[37] A. Grimm, R. Zanzi, E. Bjornbom, A.L. Cukierman, Comparison of different types of biomasses for copper biosorption, Bioresour. Technol. 99 (2008) 2559–2565.

[38] E.-S.Z. El-Ashtoukhy, N.K. Amin, O. Abdelwahab, Removal of lead(II) and copper(II) from aqueous solution using pomegranate peel as new adsorbent, Desalination 223 (2008) 162–173.

[39] M. Khormaei, B. Nasernejad, M. Edrisi, T. Eslamzadeh, Copper biosorption from aqueour solutions by sour orange residue, J. Hazard. Mater. 149 (2007) 269–274.

[40] M.A. Miranda, P. Dhandapani, M.H. Kalavathy, L.R. Miranda, Chemically activated *Ipomoea carnea* as an adsorbent for the copper sorption from synthetic solutions, Adsorption 16 (2010) 74–84.

[41] K.R. Hall, L.C. Egleton, A. Acrivos, T. Vemeulen, Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions, Ind. Eng. Chem. Fund. 5 (1966) 212–223.

[42] M.A.H. Hanif, R. Nadeem, H.N. Bhatti, N.R. Ahmad, T.M. Ansari, Ni(II) biosorption by *Cassia fistula* (golden shower) biomass, J. Hazard. Mater. B139 (2007) 345–355.