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Bioremoval and recovery of Cu(II) and Pb(II) from aqueous solution by a novel biosorbent watermelon (*Citrullus lanatus*) seed hulls: Kinetic study, equilibrium isotherm, SEM and FTIR analysis

Gülbahar Akkaya, Fuat Güzel*

Department of Chemistry, Faculty of Education, Dicle University 21280, Diyarbakır, Turkey
Tel. +90 412 2488377; Fax: +90 412 2488257; email: fguzel@dicle.edu.tr

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ABSTRACT

The biosorption of Cu(II) and Pb(II) ions from aqueous solutions using a new sorbent, watermelon seed hulls (WSH), has been studied. The effect of pH (2–6), biosorbent dose (0.1–1.0 g), initial metal ion concentration (10–500 mg L^{-1}), contact time (5–270 min), and temperature (293–333 K) was investigated. Equilibrium adsorption isotherms and kinetics were also investigated based on metals adsorption tests. The experimental data were analyzed by the Langmuir and Freundlich models of adsorption, and the results fitted well to the Langmuir isotherm. The kinetic data have been analyzed using pseudo-first-order, pseudo-second-order, and intraparticle diffusion equations. The experimental data fit very well with the pseudo-first-order kinetic model. The data obtained from adsorption isotherms at different temperatures were used to calculate some thermodynamic quantities, such as free energy (ΔG^o), standard enthalpy (ΔH^o), and standard entropy (ΔS^o), were evaluated. The adsorption of these two metals on the WSH was found to be spontaneous and endothermic process in nature. Desorption experiments were carried out using various acid solutions with a view to regenerate the spent adsorbent and to recover the both adsorbed metal ions. According to the experimental results, WSH seems to be an effective, low-cost and alternative adsorbent precursor for the removal of Cu(II) and Pb(II) ions from aqueous solutions.

Keywords: Bioremoval; Watermelon seed hulls; Copper; Lead; Desorption

1. Introduction

Heavy metal pollution has become a serious problem with the rapid increase in global industrial activities. The pollution of water by toxic heavy metals is considered as a threat due to their immense toxicity and their nonbiodegradability. These heavy metal ions can be accumulated through the food chain even at lower concentration, leading to a threat to aquatic life as well as to animal, plant life, and human health. Toxic heavy metals are derived mainly from lead, mercury, cadmium, chromium, copper, arsenic species constitute a severe health threat [1–3].

Copper is widely used in electrical wiring, plumbing, gear wheel, selenium rectifier and roofing industries, due to its excellent physical and mechanical properties such as electrical and thermal conductivity, good corrosion resistance, ease of fabrication and

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*Corresponding author.

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installation. The potential sources of copper in industrial effluents include metal cleaning and plating baths, pulp, paper board mills, wood pulp production, and the fertilizer industry. [4]. Trace amounts of copper are essential to human and many other living species. However, the intake of excessively large doses of Cu(II) by humans may lead to severe mucosal irritation, a central nervous system irritation, possible necrotic changes in the liver and kidney, etc., and the recommended maximum acceptable concentration of Cu(II) in drinking water by the World Health Organization (WHO) is $1.5\,\mathrm{mg\,L^{-1}}$ [5,6]. Lead is one of the toxic heavy metals and an important contaminant in aquatic environments. Lead is used as an industrial raw material for automobile batteries, printing processes, pigments, fuels, photographic materials, matches and explosives [7]. The presence of low concentrations of lead in drinking water may cause diseases such as anemia, encephalopathy, hepatitis, and nephritic syndrome. Severe exposure to lead has been associated with sterility, abortion, stillbirths and neo-natal deaths [8]. Based on its toxicity, the US Environmental Protection Agency (EPA) has set the maximum permissible limit for lead ions in drinking water as $0.05\,\mathrm{mg\,L^{-1}}$ [9,10].

There is a continuous need for new separation techniques that selectively remove the metal ions from dilute wastewaters and industrial process streams. The main techniques utilized to remove heavy metal ions from aqueous streams include ion-exchange, reverse osmosis, precipitation, and adsorption. However, these technologies are most suitable in situations where the concentrations of the heavy metal ions are relatively high [11]. They are either ineffective or expensive when heavy metals are present in the waste water at low concentrations, or when very low concentrations of heavy metals in the treated water are required. Adsorption is an alternative technology and is highly effective, cheap and easy method among the physicochemical treatment processes. Biosorption is a low-cost technology which utilizes the ability of biological materials to accumulate heavy metals from aqueous solutions by either metabolically mediated or purely physicochemical pathways of uptake [12]. In recent years, there has been considerable interest in the use of biological materials, including algae, bacteria, fungi, agricultural by-products, and residues as adsorbents to remove toxic metals from aqueous solution by adsorption. Among these materials, agricultural by-products and biomass are relatively cheap and exhibit very high adsorption capacities [13]. Some of them are *rice* bran [14], *peanut* hull [15], *oil shale* wastes [16], *water hyacinth* roots [17], *maple wood* sawdust [18], *black carrot* residues [19], *hazelnut* and *almond* shell [20], *pomegranate* peel [21], *tobacco* stems [22].

The objective of the present work is to investigate the biosorption potential of watermelon seed hulls (WSH) for the removal of Cu(II) and Pb(II) ions from aqueous solution. The study is novel since no literature citations are available where WSH has been used for removing heavy metals from aqueous solution. Watermelon cultivation is spread over a wide area in the world. Turkey is the second watermelon producer country in the world with 4 million tons after China. Approximately, 5% of the world production of watermelon is performed in Turkey. Watermelon is a sweet, juicy, healing and refreshing fruit. Seeds are used as snack in Turkey. WSH are thrown as a waste to the environment. In this work, we are investigating the potential of WSH as an alternative low-cost heavy metal biosorbent. Fourier transformer infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) analysis were carried out to understand the surface and functional group of WSH. The batch method was used. Parameters such as pH, biosorbent dosage, contact time, initial Cu(II) and Pb(II) concentration, temperature were studied.

2. Materials and methods

2.1. Equipment

The pH measurements were made using a pH meter (model Hanna pH 211). The concentrations of lead and copper solutions were analyzed using a flame atomic absorption spectrophotometry (model Perkin Elmer AAnalyst 400). The instrument was set at wavelength of 324.7 and 283.3 nm for copper and lead, respectively. Before analysis, the samples were centrifuged (model Hettich centrifuge EBA 20). The surface morphology of WSH was obtained using scanning electron microscope (SEM) (model Leica S360). Analysis on the functional groups of WSH that might be involved in metal adsorption was performed using Fourier transform infrared spectrophotometer (PerkinElmer FT-IR system 100 model) in the range of $400\text{–}4{,}000\,\mathrm{cm^{-1}}$.

2.2. Biosorbent

The raw WSH was collected from Ergani, Diyarbakır, East-South Anatolia region, Turkey and it was used as an adsorbent. This agricultural waste was thoroughly rinsed with water to remove dust and soluble material. Then, it was allowed to dry at room temperature. The above dried waste was grounded and sieved to the $500\,\mu\mathrm{m}$ particle size and stored in glass bottles for further use. No other chemical or physical treatments were used prior to biosorption experiments.

2.3. Metal solutions

Synthetic stock solutions of heavy metals were prepared by dissolving analytical grade Cu(II) sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$ and Pb(II) nitrate, Pb (NO_3) (from Merck company) in distilled water to obtain 1,000 mg L^{-1} of metal solutions. Desired test solutions of heavy metal ions were prepared using appropriate subsequent dilutions from stock solutions.

2.4. Batch biosorption experiments

In this study, batch kinetic and equilibrium studies were carried out to characterize the biosorption ability of WSH in a shaking water bath (J.P. Selecta). All experiments were carried out with the biosorbent material in 50 mL of metal solution to evaluate the optimum values of the experimental parameters. The biosorbent dose was 0.1 g, and the initial metal concentrations were 100 mg L^{-1}. After each biosorption experiment, the samples were centrifuged for biosorbent solution separation and the remaining metal concentration in the supernatant was measured by atomic absorption spectrometer (Perkin Elmer AA Analyst 400).

The effect of pH on the metal biosorption was studied over the pH range from pH 2 to pH 6. The pHs of metal solutions were adjusted by using either 0.1 M HCl or 0.1 M NaOH. The effect of initial metal concentrations was conducted by different concentrations of metals ranging from 10 to 500 mg L^{-1} with 0.1 g WSH at 150 rpm shaking rate and pH 5. The effect of biosorbent dose was carried out with different biosorbent dose mass ranging from 0.1 to 1.0 g with metal solutions (100 mg $L^{-1}$and pH 5) at 150 rpm.

Biosorption kinetic experiments were studied at the optimum conditions of initial solution pH, initial metal concentration and biosorbent dose at different temperatures (293, 313 and 333 K). For the purpose of studying the biosorption isotherm, 0.1 g of biosorbents was kept in contact with 50 mL metal solutions of different initial concentrations until equilibrium was reached at different temperatures. Each experiment was carried out in duplicate, and the average values are given. The amount of biosorption, q (mg g^{-1}), was calculated by:

$$q = \frac{(C_i - C_e)V}{W} \tag{1}$$

where C_i and C_e are the initial and equilibrium concentrations of metal ions (mg L^{-1}), respectively. V is the volume of the solution (L) and W is the amount of biosorbent used (g). The bioremoval efficiency ($R\%$) can be calculated as follows:

$$R(\%) = \frac{C_i - C_e}{C_i} \times 100 \tag{2}$$

Desorption studies were carried out with 0.1 M of different desorbing agents such as HCl, HNO_3, CH_3COOH, and $C_6H_8O_7$. The desorption efficiency was calculated by using the following equation:

$$\text{Deserption } (\%) = \frac{q_d}{q_a} \times 100 \tag{3}$$

where q_d is the amount of metal ion desorbed (mg L^{-1}), q_a is the amount of metal ion adsorbed (mg L^{-1}).

3. Results and discussion

3.1. Biosorbent characterization

3.1.1. SEM analysis

Scanning electron microscopy (SEM) analysis technique was used to observe the surface physical morphology of the biosorbent. The textural structure examination of WSH before and after metal ion biosorption can be observed from the SEM photographs at 500 magnifications (Fig. 1(a–c)). The WSH exhibits an uneven and rough surface with pores and cavities. This indicates that there is a good possibility for metal ions to be adsorbed onto the surface.

3.1.2. FTIR analysis

The type of binding groups present on the WSH was identified by Fourier transform infrared spectroscopy (FTIR). The FTIR spectra of native and metal sorbed WSH are shown in Fig. 2. In the spectra of native WSH, the band observed at 3335 cm^{-1} present bonded –OH group on the surface. This band presents significant wave number changes; 16.54 and 15.79 cm^{-1} variations, after Cu(II) and Pb(II) sorption, respectively. Aliphatic C–H group is represented by the peak at 2924.58 cm^{-1}. After Cu(II) and Pb(II) biosorption, 0.66 and 4.43 cm^{-1} variations are observed, respectively. New bands appeared on the WSH surface at 1986 cm^{-1} and 2124.28 cm^{-1} after metal sorption. These bands can be assigned to aliphatic C-H groups. The peak located at 1,740 cm^{-1} disappeared

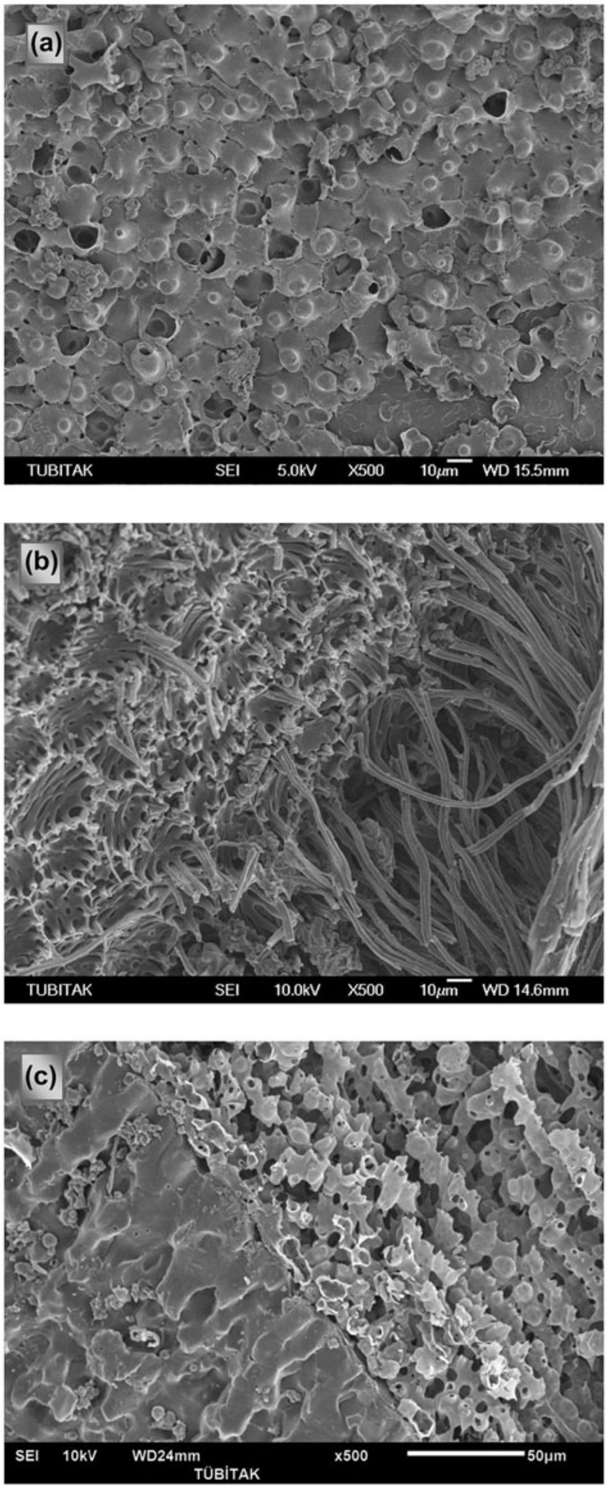

Fig. 1. SEM micrographs of (a) WSH, (b) Cu(II)-loaded WSH, and c) Pb(II)-loaded WSH.

after Cu(II) sorption and shifted to 1737.13 cm^{-1} (2.87 cm^{-1} variation) after Pb(II) sorption. This peak is the indicative of the C=O stretching of aliphatic acids. The peak at 1631.51 cm^{-1} presents fingerprint region of C=O, C–O and O–H groups and this peak shifted to 1646.08 cm^{-1} (14.57 cm^{-1} variation) after Cu(II) sorption and shifted to 1646.37 cm^{-1} (14.86 cm^{-1} variation) after Pb(II) sorption. The peak at 1,509 cm^{-1} is indicative of an amino group. The variations are 3 cm^{-1} and 0.59 cm^{-1} after metal sorption. The peak at 1420.67 cm^{-1} indicates the presence of carboxylic groups. This peak shifted to 1418.46 cm^{-1} (2.21 cm^{-1} variation) after Cu(II) sorption and disappeared after Pb(II) sorption. The peak at 1262.88 cm^{-1} indicates the presence of the C-N from amine. An important variation (31.86 cm^{-1}) was observed in the wavelength of this peak after Pb(II) sorption. The band appeared at 1022.47 cm^{-1} indicated the presence of amino group and shifted to 1023.16 cm^{-1} (0.69 cm^{-1}variation) and 1039.39 cm^{-1} (7.92 cm^{-1} variation) after metal sorption.

3.2. *Effect of physical/chemical parameters*

3.2.1. *pH*

The effect of pH on the biosorption of Cu(II) and Pb(II) ions onto WSH was studied at pH values between 2 and 6. As can be seen from Fig. 3, the solution pH affects the percent removal efficiency (R %) and biosorption capacity, *q*. The results indicate that the maximum uptake of Cu(II) and Pb(II) ions takes place at pH 5. The adsorption was found to increase from 2.52 mg g^{-1} (5.04%) to 15.86 mg g^{-1} (31.72%) for Cu(II) ions and from 7.15 mg g^{-1} (14.2%) to 26.45 mg g^{-1} (52.9%) for Pb(II) ions when pH increased from 2 to 5. The low level of metal ion uptake by the biosorbent at lower pH values could be attributed to the increased concentration of hydrogen (H^+) ions which compete along with Cu(II) and Pb(II) ions for binding sites on the biomass. As the pH is lowered, the overall surface charge on the biosorbent become positive, which will inhibit the approach of positively charged metal cations. Similar trend was observed with the adsorption of Cu(II), Pb(II), and Zn (II) ions by valonia tannin resin [23]. At higher pH values than 5, metal precipitation appeared, therefore, pH 5 was selected to be the optimum pH for further studies.

3.2.2. *Biosorbent dose*

The effect of biosorbent dose ranging from 0.1 to 1.0 g on metal ions biosorption is presented in Fig. 4. The Cu(II) removal percentage increased from 15.52% to 68% and Pb(II) removal percantage increased from 52.4% to 97.82% as the WSH dose was increased from 0.1 to 1.0 g/50 mL and then remained almost constant.

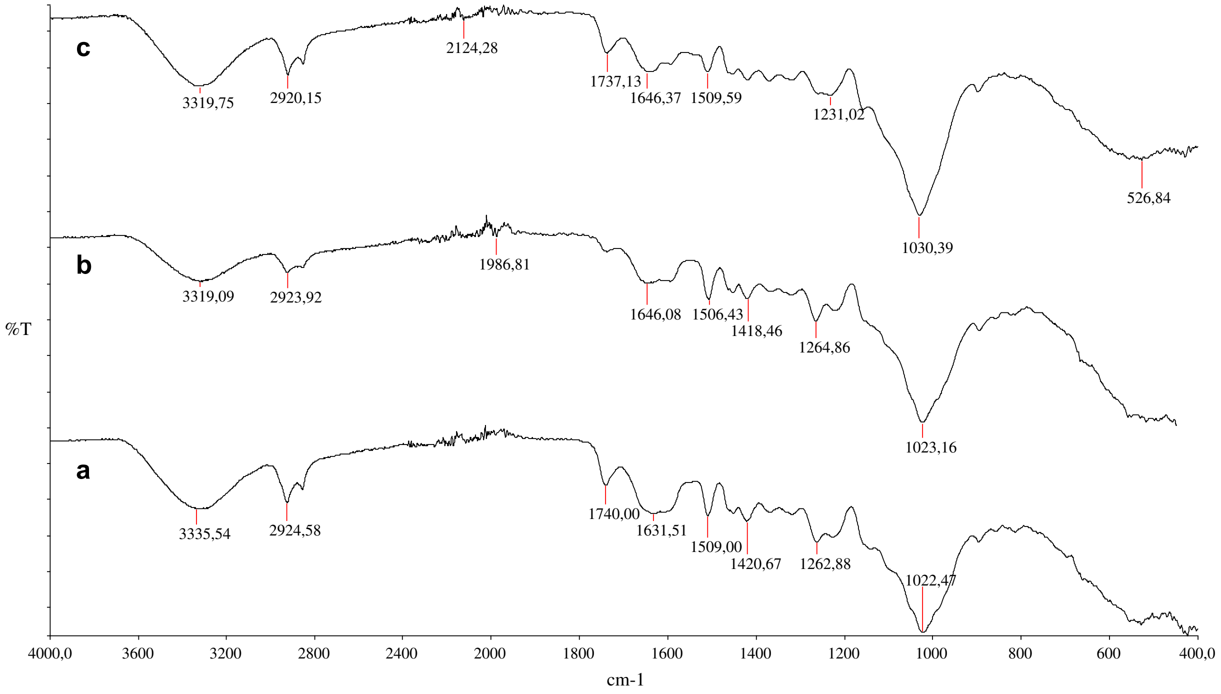

Fig. 2. FTIR spectrum of (a) WSH, (b) Cu(II)-loaded WSH, and (c) Pb(II)-loaded WSH.

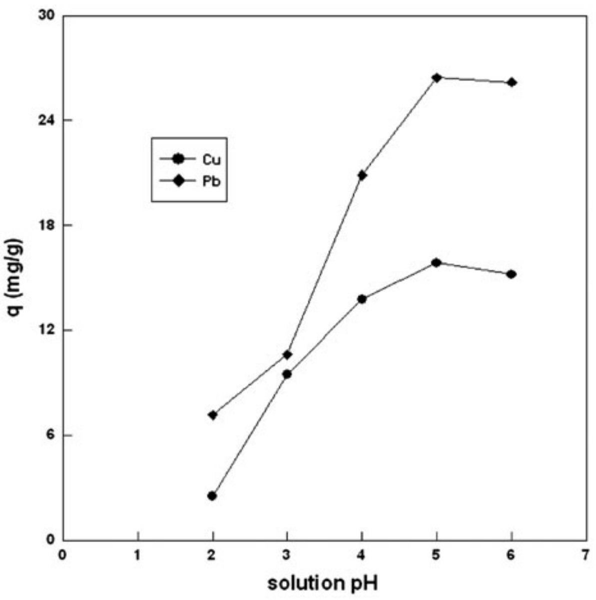

Fig. 3. Effect of (a) pH (biosorbent dose: 0.1 g/50 mL, particle size: 500 μm, shaking rate: 150 rpm, C_0: 100 mg L^{-1}, temperature 293 K).

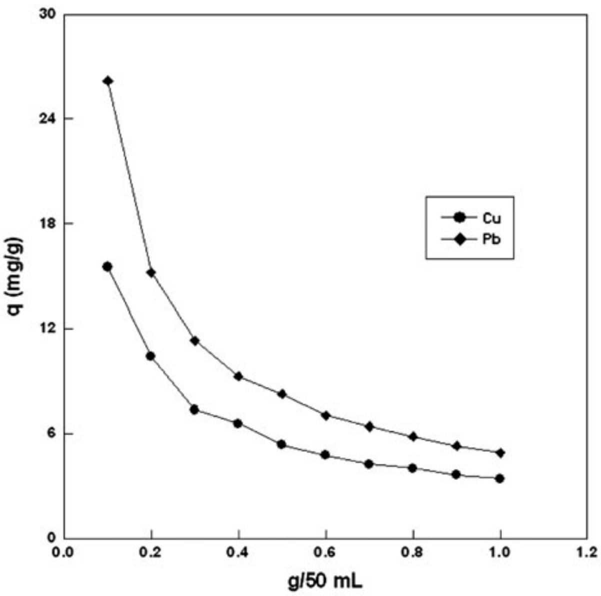

Fig. 4. Effect of (b) initial metal ion concentration (pH: 5, biosorbent dose: 0.1 g /50 mL, particle size: 500 μm, shaking rate: 150 rpm, temperature 293 K).

Increasing the biosorbent dose provided greater surface area and availability of more active sites, thus leading to the enhancement of metal ion uptake. Similar trend was observed with the biosorption of Pb (II) from aqueous solutions by *Moringa oleifera* bark [24]. On the other hand, the amount of adsorbed metal ion per gram (q, mg g^{-1}) decreases from 15.52 to 3.40 mg g^{-1} for Cu(II) ions and decreases from 26.20 to

4.89 mg g^{-1} for Pb(II) with increasing biosorbent dose from 0.1 to 1.0 g. This may be due to the concentration gradient between the sorbent and the sorbate. A similar result was reported for the biosorption of cadmium, lead, and nickel ions from aqueous solutions by chemically modified brown algae [25]. Considering q values, biosorbent dose of 0.1 g was found to be the optimum dosage for all other batch experiments for both metal ion/WSH systems.

3.2.3. Initial metal concentration

The effect of initial metal ion concentration on the Cu(II) and Pb(II) biosorption by WSH was investigated at the ranges of 5–210 mg L^{-1} and the results are shown in Fig. 5. The value of q increased from 1.88 to 14.98 mg g^{-1} for Cu(II) ions and from 4.96 to 26.02 mg g^{-1} for Pb(II) ions with increasing of the initial metal concentration. This may be due to a high driving force for mass transfer. On the other hand, the Cu(II) removal percentage decreased from 75% to 14.68% and the Pb(II) removal percentage decreased from 99.2% to 26.06% with increasing initial concentration of metal ions from 5 to 210 mg L^{-1}. At the lower metal ion concentrations, the removal percentages were higher due to a larger surface area of the sorbent being available for the adsorption of metal ions. When the concentration of the metal ions solution became higher, the removal percentages were lower because the available sites of the adsorption became less. A similar result was reported for the biosorption of Cu(II) ions from aqueous solution by adsorption using cashew nut shell as biosorbent[26]. Initial concentrations higher than 80 mg L^{-1} for Cu(II) and higher than 100 mg L^{-1} for Pb(II) ions, biosorption capacities (q, mg g^{-1}) remained almost constant and reached to surface saturation with the ions, and hence, 80 mg L^{-1} and 100 mg L^{-1} were found to be the optimum initial concentrations for the kinetic experiments of Cu(II) and Pb(II) ions, respectively.

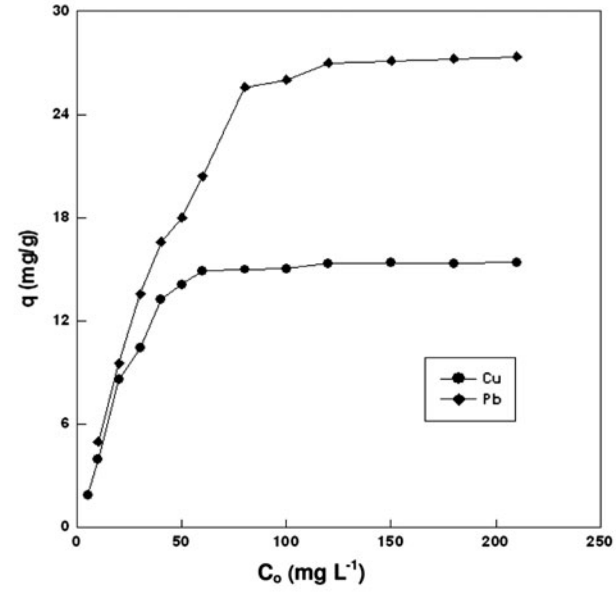

Fig. 5. biosorbent dose (C$_0$: 100 mg L^{-1}, pH: 5, shaking rate: 150 rpm, temperature 293 K, particle size: 500 μm).

3.2.4. Contact time and temperature

Fig. 6(a) and (b) present the biosorption of the metal ions at different temperatures as a function of contact time at optimum initial concentrations, biosorbent dosage, and pH. As seen in the figures, the adsorption capacities of Cu(II) and Pb(II) ions increased as temperature increasing from 293 to 333 K. The amount of Cu(II) sorbed at equilibrium was 23 mg g^{-1} at 293 K and 35 mg g^{-1} at 333 K. The amount of Pb(II) sorbed at equilibrium was 48 mg g^{-1} at 293 K and 70 mg g^{-1} at 333 K. The increase in adsorption in line with temperature may be the result of the increase in the number of active surface sites available for adsorption on the adsorbent surface. In addition, it is observed from the figure that the equilibrium time for maximum Cu(II) uptake is 60 min and for Pb(II) uptake is 80 min. After these equilibrium periods, the amount of metal ions adsorbed does not show time-dependent change and continuous curves are obtained. This may be due to the saturation of the biosorbent surface with metal ions at these levels.

3.3. Biosorption kinetics

Kinetic data were fitted using pseudo-first-order, pseudo-second-order and intraparticle diffusion models.

The linear form of pseudo-first-order equation is given as [27]:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ads,1}}{2.303}t \tag{4}$$

where q_e (mg g^{-1}) is the amount of adsorbate adsorbed at equilibrium, q_t (mg g^{-1}) is the amount of adsorbate adsorbed at time t and $k_{ads,1}$ (min^{-1}) is the rate constant of pseudo-first-order adsorption. If the pseudo-first-order kinetics is applicable, a plot of log (q_e − q_t) vs. t should provide a linear relationship Eq. (4) from which $k_{ads,1}$ and predicted q_e can be determined from the slope and intercept of the plot,

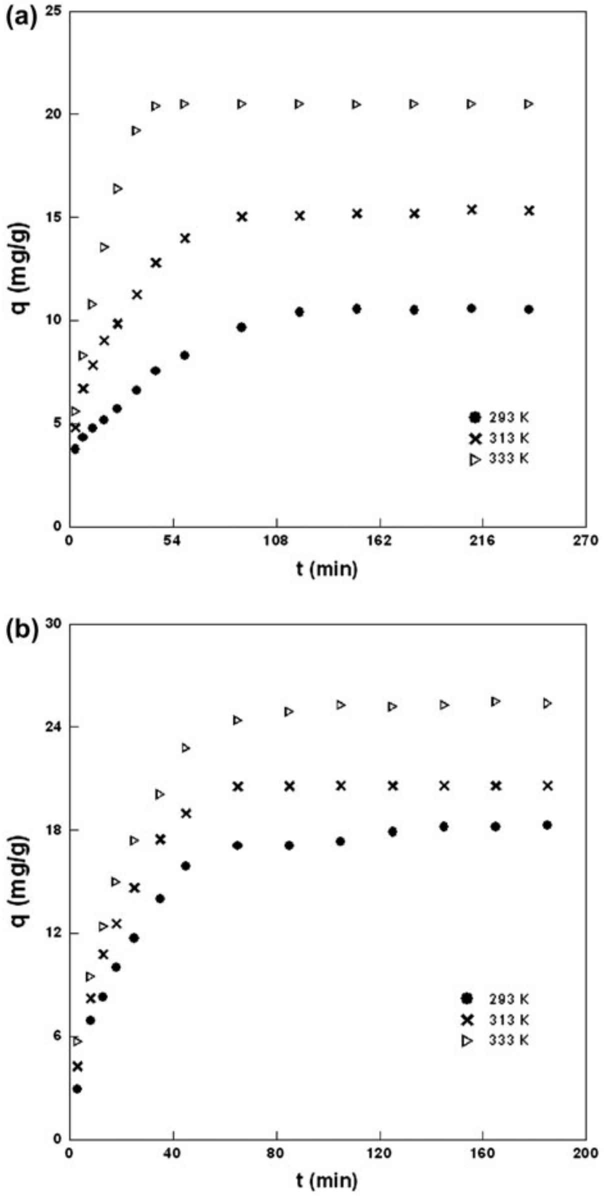

Fig. 6. (a) Effect of temperature and contact time on biosorption of Cu(II) (C_0: 120 mg L^{-1}, biosorbent dose 0.1 g/50 mL, particle size: 500 μm, pH: 5, shaking rate: 150 rpm,) (b) Effect of temperature and contact time on biosorption of Pb(II) (C_0: 200 mg L^{-1}, biosorbent dose 0.1 g/50 mL, particle size: 500 μm, pH: 5, shaking rate: 150 rpm).

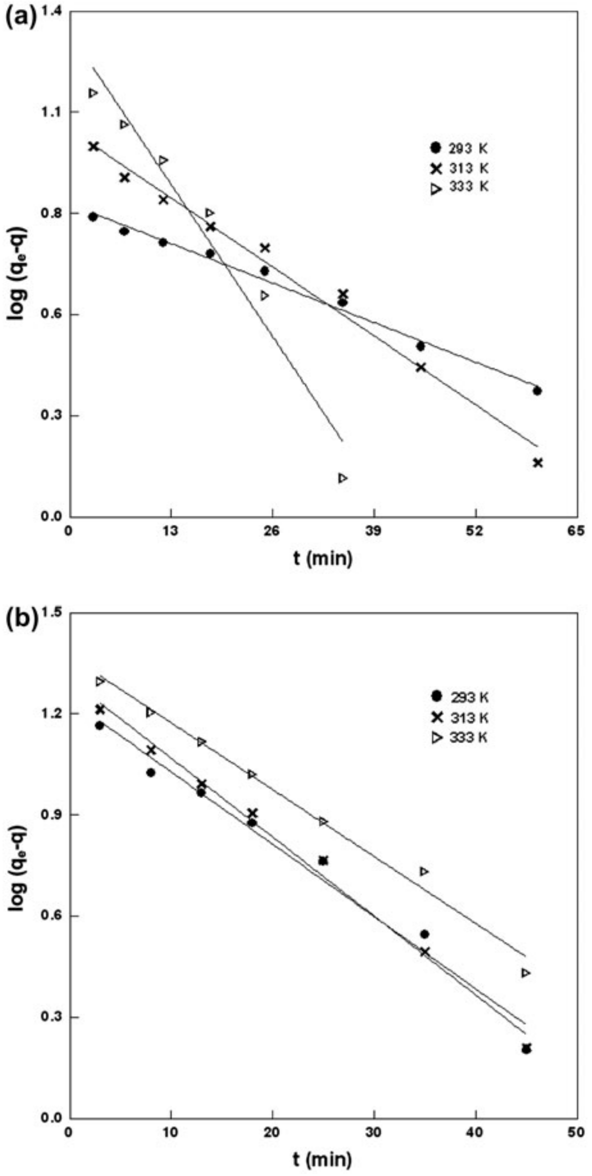

Fig. 7. Pseudo-first-order plots of (a) Cu(II) (b) Pb(II) biosorption onto WSH.

respectively (Fig. 7(a) and (b) and Fig. 8(a) and (b)). The parameters of the pseudo-first-order model are summarized in Table 1.

The pseudo-second-order kinetics is given as [28]:

$$\frac{t}{q_t} = \frac{1}{k_{ads,2} q_e^2} + \frac{t}{q_e} \qquad (5)$$

where $k_{ads,2}$ (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order adsorption. The plots of t/q_t vs. t should give a linear relationship Eq. (5) from which $k_{ads,2}$ and predicted q_e can be determined from the intercept and slope of the plot respectively. The $k_{ads,2}$ and q_e determined from the model are presented in Table 1 with the correlation coefficients. As can be seen from the table, the biosorption of Cu(II) and Pb(II) onto WSH biomass followed pseudo-first-order kinetics.

The intraparticle diffusion model is given as [29]:

$$q_t = k_{id} t^{1/2} + C \qquad (6)$$

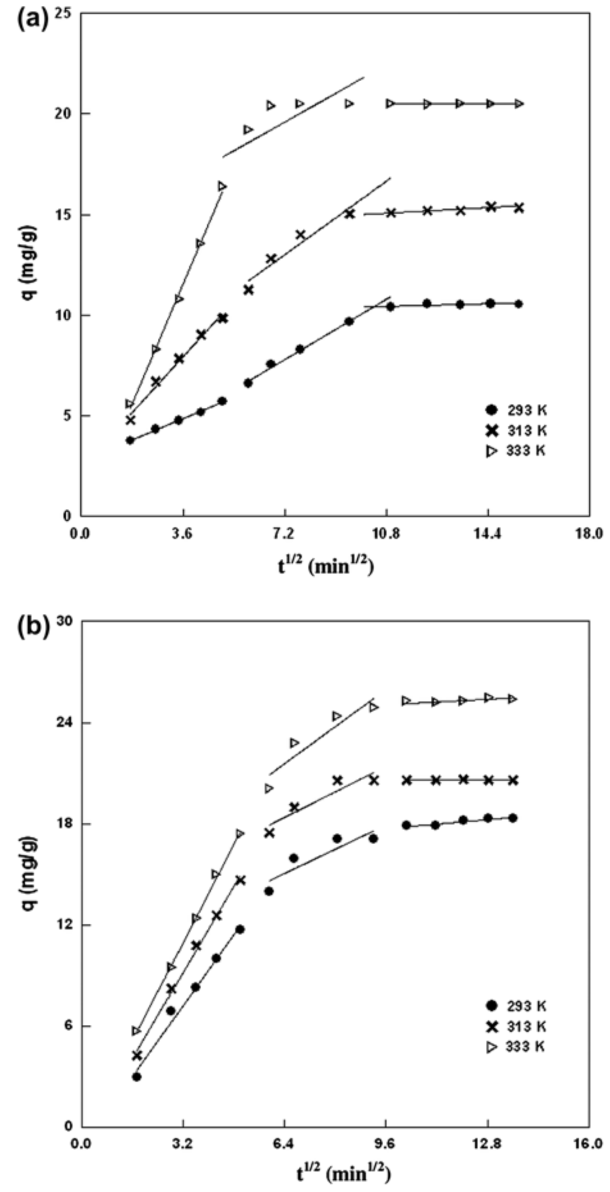

Fig. 8. Intraparticle diffusion model of (a) Cu(II) and (b) Pb(II) biosorption onto WSH.

where C is the intercept, and k_{id} is the intraparticle diffusion rate constant (mg g^{-1} $min^{-0.5}$). For the intraparticle diffusion model, the plots of q_t vs. $t^{1/2}$ Eq. (6) at the different temperatures are presented in Fig. 8(a) and (b). The intraparticle diffusion model plots may present a multilinearity indicating that two or more steps take place. The first sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where intraparticle diffusion is rate-controlled. The third portion is the final equilibrium stage where intraparticle diffusion starts to slow down due to extremely low adsorbate concentrations in the solution. As can be seen from Fig. 8(a) and (b), the biosorption of both metal ions onto WSH take place into three steps and the plots do not pass through the origin, showing that the intraparticle diffusion is not the rate-determining step. The values of k_{id} related to the biosorption of Cu(II) and Pb(II) sorption onto WSH are given in Table 1.

3.4. Biosorption isotherm

The equilibrium data obtained for the biosorption of Cu(II) and Pb(II) ions onto WSH were analyzed by using the Freundlich and Langmuir isotherm models Fig. 9.

The Langmuir model essentially Table 2 describes Table 3 the monolayer type of adsorption. The linear form of the Langmuir equation is given as [30]:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{7}$$

where C_e is the equilibrium concentration of the adsorbate (mg L^{-1}), q_e is the amount of adsorbate adsorbed at equilibrium (mg g^{-1}), q_m is the theoretical maximum adsorption capacity (mg g^{-1}), b is the Langmuir isotherm constant related to the energy of adsorption

Table 1
Kinetic parameters for biosorption of Cu(II) and Pb(II) ions by WSH at different temperatures

Adsorbate	T (K)	$q_{e,exp}$ (mg g^{-1})	First-order kinetic model			Second-order kinetic model			Intraparticle diffusion model	
			$q_{e,cal}$ (mg g^{-1})	$k_{ads,1}$ (1 min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	$k_{ads,2} \times 10^3$ (g(mg min) $^{-1}$)	R^2	k_{id} (mg $g^{-1} min^{-1/2}$)	R^2
Cu(II)	293	10.5	7.33	0.0193	0.9896	9.07	3.02	0.9641	0.5879	0.9970
	313	15.4	15.81	0.0339	0.9914	11.84	5.58	0.9772	1.5380	0.9865
	333	20.5	21.90	0.0744	0.9909	26.11	2.64	0.9628	3.3041	0.9972
Pb(II)	293	17.5	17.45	0.0495	0.9831	22.57	2.11	0.9832	2.6244	0.9980
	313	20.6	20.04	0.0539	0.9925	25.77	2.24	0.9908	3.1821	0.9842
	333	25.5	23.52	0.0456	0.9894	30.03	2.00	0.9790	3.6284	0.9926

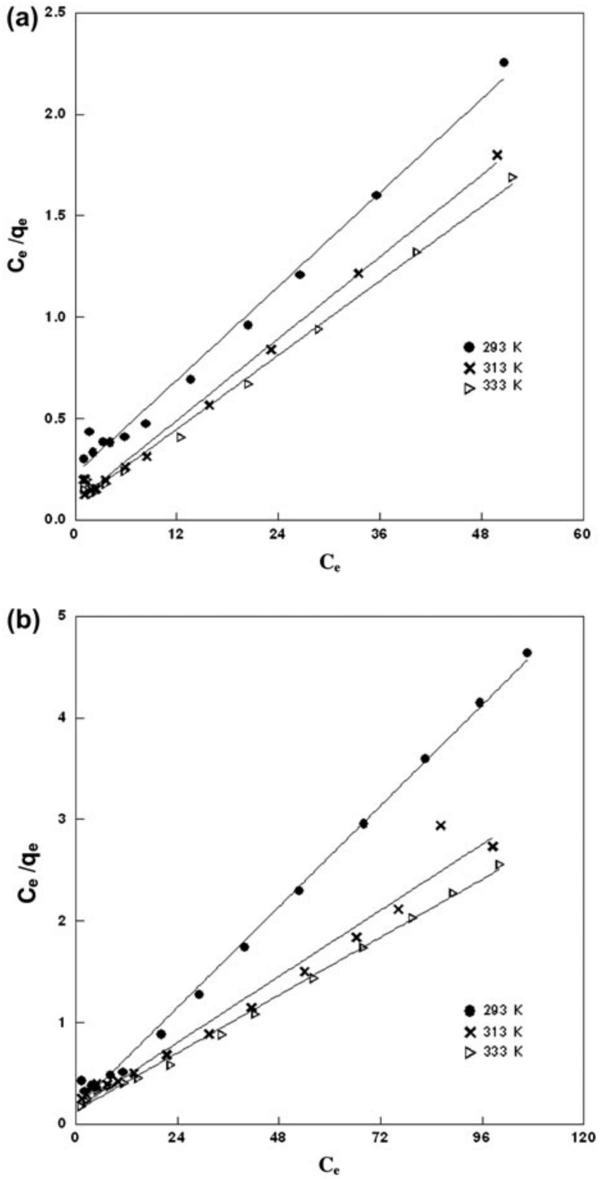

Fig. 9. The linear plots of Langmuir isotherm model for the biosorption of a) Cu(II) and b) Pb(II) ions onto WSH.

(L mg^{-1}). The values of b and q_m can be determined from the slope and intercept of the linear plot of C_e/q_e vs. C_e Eq. (7) (Figs. 9(a) and (b), Table 2).

In order to describe whether the adsorption process is favorable or unfavorable, a dimensionless constant separation factor R_L is defined by the following equation:

$$R_L = \frac{1}{1 + bC_0} \tag{8}$$

where b is the Langmuir isotherm constant (L mg^{-1}) and C_o is the initial concentration (mg L^{-1}). The R_L value reflects the type of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$).

The Freundlich model is also an empirical equation which is used to estimate the adsorption intensity of the sorbent towards the adsorbate and its linear form is given by the equation [31]:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \tag{9}$$

where K_F is the Freundlich adsorption constant related to adsorption capacity of the adsorbent [(mg/g)(L/mg)$^{1/n}$], $1/n$ is the adsorption intensity. The values of K_F and $1/n$ were calculated from the intercept and slope of the plot of log q_e vs. Eq. (9).

Table 2 shows the values of Freundlich and Langmuir parameters. Considering the correlation coefficients, the experimental data for the equilibrium adsorption of Cu(II) and Pb(II) ions on the WSH biosorbent were best described by the Langmuir isotherm model indicating monolayer biosorption process on the homogeneous surfaces. From Table 2, the values of R_L were in the range of 0.0470–0.0850 for Cu(II) ions and in the range of 0.0674–0.0366 for Pb(II) ions, indicating that the biosorptions of the metal ions onto WSH were favorable. The values of q_m increased from

Table 2
Isotherm parameters for biosorption of Cu(II) and Pb(II) ions by WSH at different temperatures

Adsorbate	T (K)	Langmuir				Freundlich		
		q_m (mg g^{-1})	b (L mg^{-1})	R_L	R^2	K_F [(mg/g) (L/mg)$^{1/n}$]	$1/n$	R^2
Cu(II)	293	27.03	0.1346	0.0850	0.9642	3.5059	0.5835	0.8237
	313	31.15	0.2357	0.0504	0.9388	6.5720	0.4826	0.6400
	333	33.90	0.2534	0.0470	0.9721	7.9433	0.4257	0.6582
Pb(II)	293	24.15	0.1383	0.0674	0.9967	5.9965	0.3454	0.7361
	313	39.53	0.1791	0.0529	0.9962	6.7873	0.4203	0.8796
	333	42.19	0.2632	0.0366	0.9966	9.1117	0.3666	0.8729

27.03 to 33.90 mg g^{-1} for Cu(II) ions and from 24.15 to 42.19 mg g^{-1} for Pb(II) ions as the temperature increased from 293 to 333 K confirming the endothermic nature of the process.

Table 3 lists a comparison of maximum adsorption capacities of Cu(II) and Pb(II) ions onto different adsorbents. The q_m values of WSH for Cu(II) and Pb (II) ions are found to be comparable with those of some other adsorbents.

3.5. Biosorption thermodynamics

In order to describe the thermodynamic behavior of the biosorption of Cu(II) and Pb(II) ions onto WSH, thermodynamic parameters including the change in free energy (ΔG°) the enthalpy (ΔH°) and the entropy (ΔS°) were calculated from the following equations:

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

$$\ln K = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \tag{11}$$

where K is obtained from the Langmuir isotherm equation that equals to $q_m b$ (L mg^{-1}), R and T are gas constant (8.314 J mol^{-1} K^{-1}) and absolute temperature (Kelvin), respectively. The values of free energy change of the biosorption process can be calculated using K at all temperatures Eq. (10). The values of ΔH° and ΔS° can be determined from the slope and intercept of the linear plot of *lnK* vs. *1/T* Eq. (11) (Fig. 10). The results are given in Table 4. As seen, the biosorption process of Cu(II) and Pb(II) ions onto WSH gave positive values for ΔH° and ΔS°. The positive ΔH° values indicate that the biosorption process was endothermic for both metal ions. Besides the positive ΔS° values indicated the increased randomness at the solid-solution interface during the biosorption of the metal ions onto WSH. The increasing of randomness may be attributed to the affinities of WSH for Cu(II) and Pb(II) ions. In addition, the positive ΔS° values may be due to some structural changes in the adsorbate and adsorbents during the adsorption process from aqueous solution onto the adsorbents. The negative ΔG° values at different

Table 3
Comparison of adsorption capacities of Cu(II) and Pb(II) ions onto WSH with various low-cost biosorbents

Adsorbent	Adsorption capacities (mg g-1)		References
	Cu (II)	Pb (II)	
Black carrot residues	8.88	–	[19]
Hazelnut shell	–	28.18	[20]
Almond shell	–	8.08	[20]
Pomegranate peel	1.32	13.87	[21]
Newspaper pulp	30.00	–	[32]
Crab shell	–	19.83	[33]
Tree fern	–	40.00	[34]
Fish bones	150.70	–	[35]
Tabacco dust	36.00	–	[36]
Coffee husks	7.50		[37]
Cocoa shells	–	6.23	[38]
Apple residue	–	17.76	[39]
Pleurotus cornucopiae	25.25	–	[40]
Fontinalis antipyretica	–	68.00	[41]
Acacia raddiana	82.63	–	[42]
WSH	33.90	42.19	this study

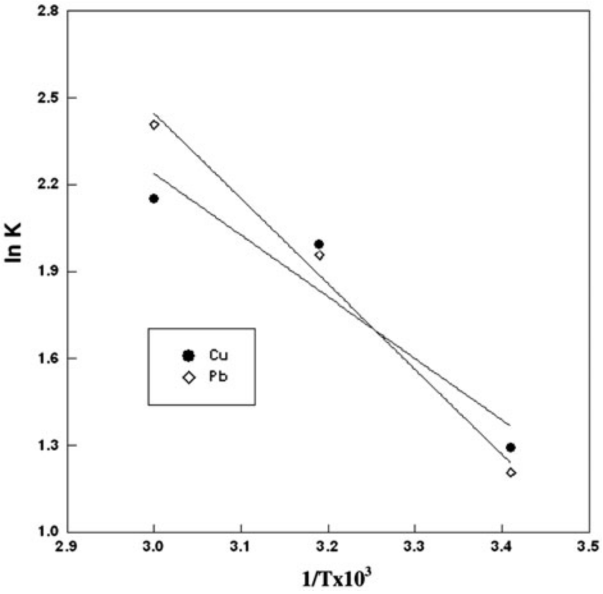

Fig. 10. Thermodynamic parameters for the biosorption of Cu(II) and Pb(II) ions onto WSH.

Table 4
Thermodynamic parameters for biosorption of Cu(II) and Pb(II) ions onto WSH

Adsorbate	T (K)	ΔG^{o} (kJ mol^{-1})	ΔH^{o} (kJ mol^{-1})	ΔS^{o} (J $mol^{-1}K^{-1}$)
Cu(II)	293	−3.1461	17.66	71.57
	313	−5.1879		
	333	−5.9541		
Pb(II)	293	−2.9378	24.47	93.72
	313	−5.0932		
	333	−6.6648		

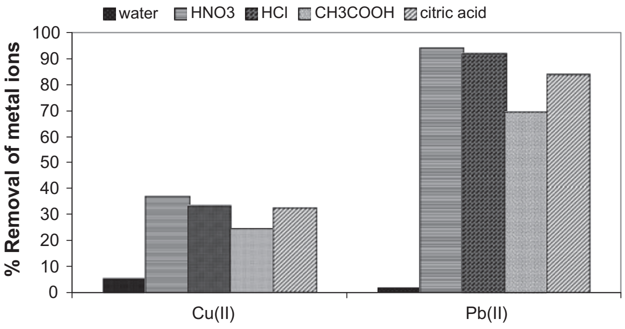

Fig. 11. Effect of various desorbing agents on desorption percentages of Cu(II) and Pb(II) from WSH (Temperature: 293 K, time: 2 h, desorbent concentration: 0.1 mg L^{-1}, biosorbent dose: 0.1 g).

temperatures showed that the biosorption of the metal ions spontaneous and feasible. The values of ΔG° were found to decrease from—3.15 to—5.95 kJ mol^{-1} K for Cu(II) ions and from—2.94 to—6.66 kJ mol^{-1} K^{-1} for Pb(II) ions as the temperature increased from 293 K to 333 K. The decrease in the negative value of ΔG° with an increase in temperature indicates that the biosorption process of the metal ions onto WSH became more favorable at higher temperatures.

3.11. Desorption studies

In order to make the sorption process more economical, it is important recover the metal ions to reuse. The Cu(II) and Pb(II) ions desorption efficiency with 0.1 M solutions of different desorbing agents (HCl, HNO_3, CH_3COOH, and $C_6H_8O_7$) was investigated and the results are shown in Fig. 11. According to the results, the desorption efficiency of Cu(II) was 36.84% with HNO_3, 33.33% with HCl, 32.53% with $C_6H_8O_7$ and 24.39% with CH_3COOH. The desorption efficiency of Pb(II) was 93.88% with HNO_3, 92.12% with HCl, 83.76% with $C_6H_8O_7$ and 69.29% with CH_3COOH. It was observed that the desorption percentages of both metal ions with distilled water were too low. Desorption of metal ions with strong acid solutions (HNO_3, HCl) attributing it to proton exchange agents on desorbing mineral acids that have the capability to dislodge high valence metal ions from the biomass. It can be concluded that adsorption of Cu(II) and Pb(II) ions onto WSH is via ion-exchange process.

4. Conclusions

In this study, batch adsorption experiments for the removal of Cu(II) and Pb(II) ions from aqueous solutions were carried out using WSH as an economic adsorbent.

The biosorption conditions were optimized. The optimum pH was 5, biosorbent dose was 0.1 g/50 mL, and initial Cu(II) concentration was 80 mg L^{-1} and initial Pb(II) concentration was 100 mg L^{-1}. The equilibrium time for the biosorption of Cu(II) ions was 60 min and for Pb(II) ions was 80 min. Kinetic studies were carried out at the optimum removal conditions at different temperatures. The biosorption of metal ions onto the WSH followed pseudo-first-order kinetic model and intraparticle diffusion model indicate the multilinearity of the sorption process; diffusion was not only the rate-limiting step. Equilibrium data indicated favorable adsorption (R_L values were between 0 and 1) and fitted well to the Langmuir model indicating homogeneous adsorption giving maximum adsorption capacities were 33.90 mg g^{-1} for Cu(II) ions and 42.19 mg g^{-1} for Pb(II) ions at 333 K. Thermodynamic parameters indicated that Cu(II) and Pb(II) biosorption onto WSH was spontaneous and endothermic in nature. The positive ΔS^o values showed the affinity of the WSH for Cu(II) and Pb(II) ions. Desorption of metal ions from WSH surface was more effective using the strong acids (HNO_3 and HCl) and this indicates that the biosorption of Cu(II) and Pb(II) ions are by ion exchange.

In conclusion, the results revealed that WSH, an eco-friendly waste material, is a promising and renewable low-cost adsorbent for the removal of heavy metals from aqueous solutions.

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References

[1] A. Murugesan, L. Ravikumar, S.V. Sathya, K.P. Senthil, T. Vidhyadevi, K.S. Dinesh, S.S. Kalaivani, S. Krithiga, S. Sivanesan, Removal of Pb(II), Cu(II) and Cd(II) ions from aqueous solution using polyazomethineamides: Equilibrium and kinetic approach, Desalination 271 (2011) 199–208.

[2] D. Mohan, K.P. Singh, Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from Bagasse — an agricultural waste, Water Res. 36 (9) (2002) 2304–2318.

[3] A.B. Perez-Martin, V.M. Zapata, J.F. Ortuno, M. Aguilar, J.M. Lıorens, Removal of cadmium from aqueous solutions by adsorption onto orange waste, J. Hazard. Mater. 139 (2007) 122–131.

[4] Z. Aksu, I.A. Isoglu, Removal of copper (II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp, Process Biochem. 40(9) (2005) 3031–3044.

[5] A.H.M. Larous, M.B. Lehocine, Experimental study of the removal of copper from aqueous solutions by adsorption using sawdust, Desalinaiton 185(1–3) (2005) 483–490.

[6] M.M. Rao, A. Ramesh, G.P.C. Rao, K. Seshaiah, Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceiba pentandra hulls, J. Hazard. Mater. 129 (2006) 123–129.

[7] V.J.P. Vilar, F. Sebesta, C.M.S. Botelho, R.A.R. Boaventura, Equilibrium and kinetic modeling of Pb^{2+} biosorption by granulated agar extraction algal waste, Process Biochem. 40 (10) (2005) 3276–3284.

[8] D.C.K. Jayaram, M.N.V. Prasad, Removal of Pb(II) from aqueous solution by seed powder of Prosopis juliflora, J. Hazard. Mater. 169 (2009) 991–997.

[9] K.P. Yadava, B.S. Tyagi, V.N. Singh, Effects of temperature on the removal of lead (II) by adsorption on china clay and wollastonite, J. Chem. Technol. Biot. 51(1) (1991) 47–60.

[10] S. Bhattacharjee, S. Chakrabarty, S. Maity, S. Kar, P. Thakur, G. Bhattacharyya, Removal of lead from contaminated water bodies using sea nodule as an adsorbent, Water Res. 37(16) (2003) 3954–3966.

[11] P. Kaewsarn, Biosorption of copper (II) from aqueous solutions by pre-treated biomass of marine algae Padina sp., Chemosphere, 47 (10) (2002) 1081–1085.

[12] A. El-Sikaily, A. El-Nemr, A. Khaled, Copper sorption onto dried red alga *Pterocladia capillacea* and its activated carbon, Chem. Eng. J. 168(2) (2011) 707–714.

[13] N. Feng, X. Guo, S. Liang, Adsorption study of copper (II) by chemically modified orange peel, J. Hazard. Mater. 164(2–3) (2009) 1286–1292.

[14] X.S. Wang, Y. Qin, Z.F. Li, Biosorption of zinc from aqueous solutions by rice bran: Kinetics and equilibrium studies, Separ. Sci. Technol. 41(4) (2006) 747–756.

[15] C.S. Zhu, L.P. Wang, W. Chen, Removal of Cu(II) from aqueous solution by agricultural by-product: Peanut hull, J. Hazard. Mater. 168(2–3) (2009) 739–746.

[16] P.M. Pimentel, M.A.F. Melo, D.M.A. Melo, A.L.C. Assunção, D.M. Henrique, C.N. Silva, G. González, Kinetics and thermodynamics of Cu(II) adsorption on oil shale wastes, Fuel Process. Technol. 89(1) (2008) 62–67.

[17] J.C. Zheng, H.M. Feng, M.H.W. Lam, P.K.S. Lam, Y.W. Ding, H.Q. Yu, Removal of Cu(II) in aqueous media by biosorption using water hyacinth roots as a biosorbent material, J. Hazard. Mater. 171(1–3) (2009) 780–785.

[18] M.S. Rahman, M.R. Islam, Effects of pH on isotherms modeling for Cu(II) ions adsorption using maple wood sawdust, Chem. Eng. J. 149 (2009) 273–280.

[19] F. Güzel, 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(3) (2008) 1275–1287.

[20] E. Pehlivan, T. Altuna, S. Çetin, M.I. Bhangerb, Lead sorption by waste biomass of hazelnut and almond shell, J. Hazard. Mater. 167 (2009) 1203–1208.

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

[22] W. Li, L. Zhang, J. Peng, N. Li, S. Zhang, S. Guo, Tobacco stems as a low cost adsorbent for the removal of Pb(II) from wastewater: Equilibrium and kinetic studies, Ind. Crop. Prod. 28(3) (2008) 294–302.

[23] I.A. Sengil, M. Özacar, Competitive biosorption of Pb^{2+}, Cu^{2+} and Zn^{2+} ions from aqueous solutions onto valonia tannin resin, J. Hazard. Mater. 1661(2–3) (2009) 488–1494.

[24] D.H.K. Reddy, K. Seshaiaha, A.V.R. Reddy, M.M. Rao, M.C. Wang, Biosorption of Pb^{2+} from aqueous solutions by Moringa oleifera bark: Equilibrium and kinetic studies, J. Hazard. Mater. 174(1–3) (2010) 831–838.

[25] M.M. Montazer-Rahmati, P. Rabbani, A. Abdolali, A.R. Keshtkar, Kinetics and equilibrium studies on biosorption of cadmium, lead, and nickel ions from aqueous solutions by intact and chemically modified brown algae, J. Hazard. Mater. 185(1) (2011) 401–407.

[26] P. Senthilkumar, S. Ramalingam, V. Sathyaselvabala, K. S. Dinesh, S. Sivanesan, Removal of copper(II) ions from aqueous solution by adsorption using cashew nut shell, Desalination 266(1–3) (2011) 63–71.

[27] S. Lagergren, About the theory of so called adsorption of soluble substances, Kungliga Svenska Vetenskapsakademiens, Handlingar 24(4) (1898) 1–39.

[28] Y.S. Ho, G. McKay, Pseudo-second-order model for sorption processes, Process Biochem. 34(5) (1999) 451–465.

[29] W.J. Weber, J.C. Morris, Kinetics of Adsorption on Carbon from Solution, J. Sanitary Eng. Div. 89(2) (1963) 31–60.

[30] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. ACS 40(9) (1918) 1361–1403.

[31] H.M.F. Freundlich, About the adsorption in solution, J. ACS 57 (1906) 385–470.

[32] S. Chakravarty, S. Pimple, H.T. Chaturvedi, S. Singh, K.K. Gupta, Removal of copper from aqueous solution using newspaper pulp as an adsorbent, J. Hazard. Mater. 159 (2008) 396–403.

[33] S. Dahiya, R.M. Tripathi, A.G. Hegde, Biosorption of lead and copper from aqueous solutions by pre-treated crab and arca shell biomass, Bioresour. Technol. 99 (2008) 179–187.

[34] Y.S. Ho, W.T. Chiu, C.S. Hsu, C.T. Huang, Sorption of lead ions from aqueous solution using tree fern as a sorbent, Hydrometallurgy 73 (2004) 55–61.

[35] B. Kızılkay, A. A. Tekinay, Y. Dilgin, Adsorption and removal of Cu (II) ions from aqueous solution using pretreated fish bones, Desalination 264 (2010) 37–47.

[36] B.C. Qi, C. Aldrich, Biosorption of heavy metals from aqueous solution with tobacco dust, Bioresour. Technol. 89 (13) (2008) 5595–5601.

[37] W.E. Oliveira, A.S. Franca, L.S. Oliveira, S.D. Rocha, Untreated coffee husks as biosorbents for the removal of heavy metals from aqueous solutions, J. Hazard. Mater. 152 (3) (2008) 1073–1081.

[38] N. Meunier, J. Laroulandie, J.F. Blais, R.D. Tyagi, Cocoa shells for heavy metal removal from acidic solutions, Bioresour. Technol. 90(3) (2003) 255–263.

[39] S.H. Lee, C.H. Jung, H. Chung, M.Y. Lee, J.W. Yang, Removal of heavy metals from aqueous solution by apple residues, Process Biochem. 33(2) (1998) 205–211.

[40] U. Danis, Biosorption of copper(II) from aqueous solutions by Pleurotus cornucopiae, Desal. Water Treat. 22 (2010) 117–126.

[41] R.J.E. Martins, V.J.P. Vilar, R.A.R. Boaventura, Removal of Pb (II) fromwastewaters by Fontinalis antipyretica biomass: Experimental study and modelling, Desal. Water Treat. 20 (2010) 179–188.

[42] M.F. Talhi, A. Cheriti, N. Belboukhari, L. Agha, C. Roussel, Biosorption of copper ions from aqueous solutions using the desert tree *Acacia raddiana*, Desal. Water Treat. 21 (2010) 323–327.