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ORIGINAL PAPER

Otostegia persica biomass as a new biosorbent for the removal of lead from aqueous solutions

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Abstract Biosorption characteristics of Pb(II) ions from aqueous solution were studied using some residues of solvent-extracted *Otostegia persica* known as *goldar* residue biomass. The effects of contact time (0–120 min), the initial pH 3–8, biomass dosage (0.53–2.6 g/L) and the initial lead concentration (5–25 mg/L) on biosorption were investigated. The maximum adsorption capacity of 17.3 mg/g at pH 5.5, the initial lead concentration of 25 mg/L and goldar residue biomass dosage of 1.06 g/L were obtained. The results of equilibrium adsorption were studied through different isotherm models of Langmuir, Freundlich, Temkin, Halsey, Scachard and Dubinin–Radushkevich. Different kinetic models including pseudo-first-order, pseudo-second-order and intraparticle diffusion were applied. The pseudo-second order described the adsorption kinetics data properly. Thermodynamic investigation at temperatures ranging from 25 to 45 °C showed a reduction in both the possibility of adsorption and randomness at the solid–solution interface of *goldar* residue. Fourier transforms infrared analysis confirmed the presence of several functional groups on the surface of the *goldar* residue biomass during lead adsorption. *O. persica* residue biomass showed good properties to use as a new biosorbent for removal of low concentrations of lead ions from water.

Keywords Biosorption · *Otostegia persica* · Lead ions · Adsorption kinetics · Adsorption isotherm

Introduction

Nowadays, heavy metals such as lead, cadmium, nickel, mercury, zinc and copper are quite risky to the aquatic ecosystem as well as the human health. Rapid growth in industrial process and chemical manufacturing has given rise to the generation of large amounts of aqueous effluents containing significant quantities of various heavy metals (Chojnacka 2010; Bable and Kumiawan 2003). Pb is the most common metal contaminant in wastewater which is discharged by industrial processing methods such as electroplating, smelting, alloying, pigmenting, plastic manufacturing, mining, metallurgy and refining (Farooq et al. 2010). However, standards of lead in drinking water and foods have been declined during the last years by European Commission (EU) and US Food and Drug Administration (FDA).

Physicochemical methods such as precipitation, chemical oxidation or reduction, reverse osmosis, cementation and ion exchange processes have been employed for heavy metal elimination from industrial wastewater stream (Patrón-Prado et al. 2010; Ahn et al. 2009; Ali and Gupta 2006; Ali et al. 2012). These techniques are expensive from an economic viewpoint and have drawbacks such as incomplete metal removal, high energy requirements, generation of toxic sludge and other disposable waste products (Aksu 2001; Ali 2010, 2012). Recently, considerable attention has been given to the use of environmentally friendly materials for the elimination of heavy metals from diluted large volume streams. The use of biomass for removing heavy metals has been extensively practiced over the last decade, representing itself as an alternative to the present technologies.

Different types of biomass have been investigated for the biosorption of Pb(II) ions from aqueous solution. A

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variety of microorganisms have been found to have an innate capability to take off heavy metals. Recent biosorption experiments have been carried out using by-products or the waste materials from large-scale industrial operations such as the waste from cork production (Mesas et al. 2011), grape fruit (Bayo 2012), crop milling waste (Saeed et al. 2005), peat, the waste of tea leaves, sugar beet pulp, rice straw (Hlihor and Gavrilescu 2009; Bakir et al. 2010), sawdust (Costodes et al. 2003) and the waste from olive oil (Blazquez et al. 2010). These techniques have shown to be promising when compared to conventional treatment methods due to its low cost, high efficiency, easy regeneration of biosorbents and the possibility of metal recovery (Devaprasath et al. 2007).

Otostegia persica, known as *goldar*, is an endemic plant that can be found in its natural habitat in Kerman Province, Iran. Recent investigations on the aqueous extract of the plant have shown that it is antispasmodic, antihistaminic and antiarthritis (Ebrahimpoor et al. 2009). The residues of plant, after extractions, are not usable and therefore are discarded as waste. In this article, the residue of *O. persica* was used as a low-cost biosorbent. The aim of this study was to examine the ability of *goldar* residue to remove lead ions from a low initial concentration aqueous solution. This was followed by investigating the suitable isotherm along with the kinetic models. All the researches throughout this study were carried out from September 2012 to September 2013 in the Laboratory of Biotechnology, Isfahan University of Technology, Iran.

Materials and methods

Biosorbent preparation

The *O. persica,* provided from Kerman Desert, was finely powdered and extracted with methanol. After the removal of the solvent under the reduced pressure, the residue was re-extracted using hexane and chloroform (Yassa et al. 2005). The residue of extraction was collected and washed with distilled water to remove the residual and the extractor. It was finally dried at 60 °C. Then the residue was milled and sieved to assume a size within 600–850 μm.

Lead solutions preparation

The standard stock solution of Pb^{2+} was prepared by dissolving an appropriate amount of $Pb(NO_3)_2$ in distilled water. The pH of the metal solution was adjusted to a desired value with 0.1 M NaOH and 0.1 M HCl using pH meter (Metrohm, 620, Switzerland). All the chemicals ($Pb(NO_3)_2$, NaOH and HCl) were purchased from Merck Company.

Batch biosorption experiments

Batch experiments included the analysis of the effect of the initial lead concentration, temperature, pH, and biosorbent dosage on lead biosorption by *goldar* residue. These experiments were performed in 75 mL of Pb^{2+} solution for 120 min at room temperature (25 °C) on a rotary shaker (Labcon, FSIM-SPO16) at 140 rpm. The duration was long enough to reach the equilibrium state between the aqueous lead and the biosorbent. The optimum conditions of the adsorption were determined by experiments and maintained within various reaction time durations (0–120 min), biomass dosages (0.53–2.6 g/L), initial lead concentrations (5–25 mg/L) and initial pHs (3–8). Each experiment was conducted at least twice. At the end of the experiments, a sample of 10 ml was taken and centrifuged at 6,000 rpm for 15 min. The metal uptake was calculated as:

$$Q = \frac{V(C_0 - C_{\mathrm{eq}})}{M} \qquad (1)$$

where Q is the lead uptake (mg/g), C_0 and C_{eq} are the initial and final lead concentrations in solution (mg/L), V is the volume (L) and M is the amount of biosorbent based on dry weight (g).

Biosorption isotherms

The isotherm of adsorption was investigated by batch tests. Experiments were carried out in 100-mL conical flasks containing 75 mL of the lead solution with the initial concentration range of 5–25 mg/L and the initial pH of 5.5. A known amount of adsorbents (0.08 g) was added to each flask. The mixture was shaken in a rotary shaker at 140 rpm, keeping temperature constant (25 ± 2 °C). After 40 min, the samples were centrifuged and analyzed quantitatively. Then, the most commonly adsorption isotherms were applied and investigated via the Langmuir, Freundlich, Scatchard, Halsey, Temkin and Doubinin–Radushkevich (D–R) models (Malkoc and Nuhoglu 2007; Asia and Oladoja 2008).

Kinetics of adsorption

Batch tests were performed to determine the kinetic adsorption properties of *goldar* residue for Pb ions. Experiments of adsorption kinetics were carried out in 100-mL conical flasks containing 75 mL of the lead solutions by using 1.06 g/L of biosorbents at the initial pH of 5.5. The flasks were agitated on a rotary shaker at 140 rpm under a constant temperature (25 ± 2 °C). Two bottles were removed at each predetermined time interval, and the samples were taken, centrifuged and analyzed. The results were studied and investigated using pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models (Mata et al. 2008).

Thermodynamic study

The experiments related to thermodynamic parameters were performed by varying temperature from 25 to 45 °C using 1.06 g/L of biosorbents added to 75 mL of lead solutions in 100-mL conical flasks. After 40-min agitation, the samples were centrifuged and analyzed. Various thermodynamic parameters such as Gibbs free energy changes ($\Delta G°$), enthalpy changes ($\Delta H°$) and entropy changes ($\Delta S°$) were determined to study the adsorption process.

Fourier transforms infrared spectra study

Fourier transforms infrared (FTIR) spectra within the range of 600–4,000 cm^{-1} were recorded on a Bruker spectrometer. Biosorption experiment was performed with the initial lead concentration of 20 mg/L, the initial pH of 5.5 and 1.06 g/L of *goldar* residue. After 40 min, the sample was centrifuged and washed with distilled water to remove the loosely bound ions or impurities. The adsorbent, before and after lead sorption, was dried at room temperature for 24 h and used for analysis. The samples were pulverized and pressed for the preparation of pellets. The background spectrum was automatically subtracted from that of sample.

Results and discussion

The effect of contact time on adsorption capacity

The effect of contact time on the biosorption of Pb(II) onto *goldar* residue biomass is shown in Fig. 1. The experimental data showed a rapid increase in the initial lead adsorption up to 40 min. After this, the biosorption rate became slower, and finally, no further significant biosorption was noted beyond 2 h. This could be attributed to a large number of vacant binding sites available for biosorption during the initial stage, which carried out via physical adsorption or ion exchange on the surface of *goldar* residues. After prolonging the contact time, the occupation of the remaining vacant sites was difficult as a result of the repulsive forces between Pb^{2+} ions in solid and liquid phases (Ozcan et al. 2009). The slower adsorption mentioned above may involve other mechanisms such as complexation, micro-precipitation and binding site saturation (Mohan et al. 2002). The very fast biosorption of *goldar* residue biomass makes this material appropriate for continuous water treatment systems. Baysal et al. used *Candida albicans* for removing Pb ions from aqueous solution, where adsorption was achieved almost within 30 min (Baysal et al. 2009). Modified *Symphoricarpus albus* biomass was used for the treatment of lead solution, and the biosorption equilibrium was reached after 20 min (Tunali Akar et al. 2012).

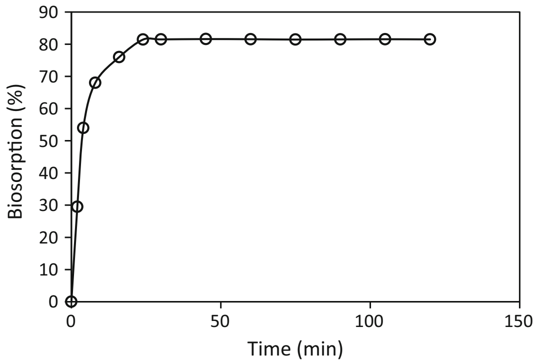

Fig. 1 Influence of interaction time on Pb(II) ions biosorption by *goldar* residue (pH 5.5, $T = 25 \pm 2$ °C, the initial Pb concentration = 20 mg/L, biomass dosage = 1.066 g/L)

The effect of the initial pH

The effect of pH on metal biosorption has been studied by many researchers. The results have indicated that the pH values of solution can significantly influence biosorption. Different metal ions may have different pH optima, possibly due to the different solution chemistry of the species. The effect of the initial pH on the equilibrium uptake of lead ions has been investigated for pH values from 3 to 8 (Fig. 2). The sorption capacity of lead can be significant, reaching 15.27 mg/g at pH 5.5, and then decreased upon increasing the pH of solution. The low metal biosorption at pH below 3 could be expounded by the protonating active sites, resulting in a competition between H^+ and Pb^{2+} to take up the binding sites. On raising pH, carboxyl groups were dissociated, leading to the attraction between negative charges and the metal ions, which, in turn, increased the adsorption onto the surface (Aksu 2001). Generally, metal biosorption involves complex mechanisms of ion exchange, chelating, adsorption by physical forces, microprecipitation, heavy metal hydroxide condensation and ion entrapment in the cell structural network of the biosorbent. It is well accepted that a combination of several mechanisms, each functioning independently, contributes to the overall metal uptake. The ATR–FTIR spectroscopic analysis showed that the moss biomass had a variety of functional groups, such as carboxyl, carbonyl (ketone), hydroxyl and amine. These groups were involved in almost all potential binding mechanisms. Moreover, depending on the pH value of the aqueous solution, these functional groups participate in metal ion bindings.

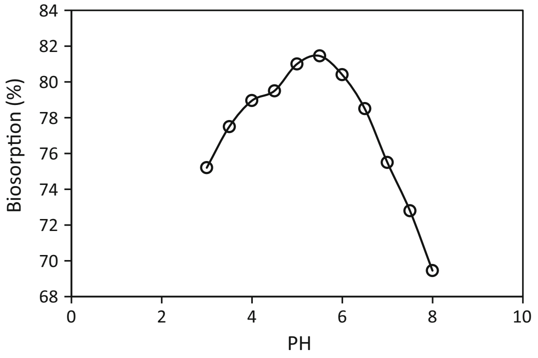

Fig. 2 Effect of the initial pH of the solution on the biosorption of Pb(II) by *goldar* residue ($T = 25 \pm 2$ °C, the initial Pb concentration = 20 mg/L, biomass dosage = 1.066 g/L)

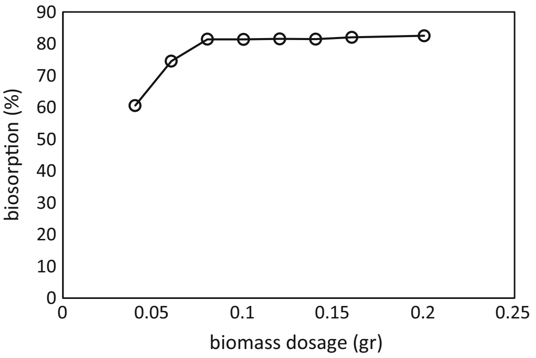

Fig. 3 Effect of *goldar* residue dosage on Pb(II) biosorption (pH 5.5, $T = 25 \pm 2$ °C, the initial Pb concentration = 20 mg/L)

The effect of biomass dosage

The results from biosorption of lead studies using different biomass dosages in the range of 0.53–2.66 g/L are illustrated in Fig. 3. The increase in adsorption upon increasing the adsorbent dosage can be attributed to the availability of a larger surface area and a higher number of sorption sites. At the low biomass dosage, it is known that the biosorbent surface becomes saturated with the metal ions, while the residual metal ion concentration in the solution is high (Romero-Gozalez et al. 2005). With an increase in biomass dosage, the lead ion removal is intensified. For the biomass dosage of 1.06 g/L, the incremental lead ion removal became very low as the surface metal ion concentration and the aqueous metal ion concentration reached the equilibrium state. For the higher adsorbent dosage, the removal efficiency of lead ions onto *goldar* residue was leveled off. Therefore, the optimum biomass dosage was chosen to be 1.06 g/L for further experiments. Schiewer and Balaria investigated the biosorption of lead onto *citrus peels* biomass for the sorbent dosages of 0.1 up to 1.0 g/L; the results of this study showed the maximum sorption at 1.0 g/L of biomass dosage (Schiewer and Balaria 2009). In another study by Qaiser et al., the *Ficus religiosa* leaves were used for the biosorption of lead ions and 10 g/L biomass dosage (in the range of 1.0–50 g/L) was obtained for the maximum removal of lead (Qaiser et al. 2007). Elsewhere, waste biosorbent from *Cucumis melo* biomass was exploited for biosorption within the dosage of 0.6–4.0 g/L, where the biosorbent dosage of 1.8 g/L yielded the optimum biosorption (Tunali Akar et al. 2012).

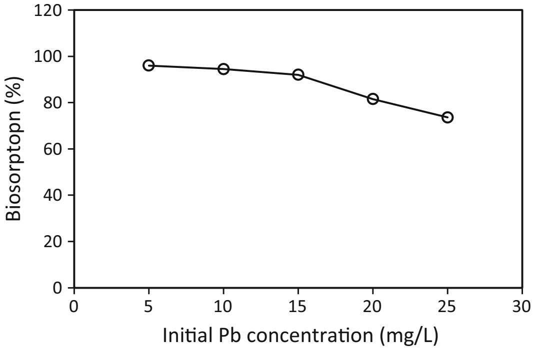

Fig. 4 Effect of the initial Pb(II) ions concentration on its biosorption by *goldar* residue (pH 5.5, $T = 25 \pm 2$ °C, biomass dosage = 1.066 g/L)

The effect of the initial lead concentration

The effect of lead concentration in the range of 5–25 mg/L on the sorption by *goldar* residue is shown in Fig. 4 at pH of 5.5 for 40 min equilibrium time. The biosorption was decreased from 96 to 73.6 % upon increasing the initial lead concentration, while q_e was increased from 4.5 to 17.25 mg/g. This behavior could be attributed to the fact that all binding sites on the biomass surface are vacant, resulting in the high initial metal biosorption. The initial Pb(II) concentration in the solution, which provided an important driving force to overcome the mass transfer resistance of the metal ions between the aqueous and solid phases, together with the high contact and collision between Pb ions and the biosorbent caused an increase in the biosorption of Pb ions (Donmez and Aksu 2002). When the adsorbent to metal ratio was low, Pb(II) ions in the solution were not only adsorbed onto the surface of the adsorbent, but also they penetrated into the intracellular part as a result of the concentration gradient of Pb ions (Ozcan et al. 2009).

The effect of temperature

The influence of temperature was explored within 25–45 °C under the optimum pH value of 5.5 and the biomass dosage of 1.06 g/L. The biosorption percentage was decreased from 81.5 to 76.5 % as temperature was increased from 25 to 45 °C. This indicated the exothermic nature of lead biosorption using *goldar* residue biomass. A decrease in the biosorption of Pb(II) ions by raising the temperature could be due to deactivation of the biosorbent surface or destruction of some active sites on the biosorbent surface due to bond ruptures (Meena et al. 2005). In addition, the decrease in biosorption efficiency could be attributed to an increase in the tendency to desorb the metal ions from the interface to the solution (Ozer and Ozer 2003). In another study on the biosorption of Pb(II) ions using marine green algae (*U. lactuca sp.*), it was found that with increasing the temperature form 10 to 40 °C, the rate of metal uptake was decreased from 55.9 to 43.5 mg/L (Bulgariu and Bulgariu 2012).

Modeling of adsorption isotherms

Isotherm studies provide information on the capacity of sorbent as the most important parameter for an adsorption process. The experiments were carried out with different initial concentrations of lead solution in the range of 5–25 mg/L. Characterization of a sorption system is often done using several isotherm models encompassing Langmuir, Freundlich, Temkin, Halsey, Scatchard and Dubinin–Radushkevich (D–R) isotherm equations (Asia and Oladoja 2008; Dawodu et al. 2012). All of these isotherm models were applied. The respective data are presented in Table 1. The Langmuir model assumes the monolayer adsorption of metal ions on a homogenous surface without any interaction between the adsorbed ions. The Langmuir isotherm can be described according to the following formula:

$$q_e = \frac{q_m b C_e}{1 + bC_e} \tag{2}$$

where q_e is the equilibrium metal ion concentration on the sorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L), q_m is the monolayer biosorption capacity of the sorbent (mg/g), and b is the Langmuir biosorption constant (L/mg), which is related to the free energy of biosorption. Langmuir isotherm for the adsorption of Pb ions on *goldar* residue is shown in Fig. 5a, where the maximum sorption capacity (q_m) equals 18.86 mg/g. The Freundlich model assumes a heterogeneous adsorption surface and active sites with different energy levels. The Freundlich model is expressed as:

$$q_e = K_f C_e^{1/n} \tag{3}$$

where K_f is a constant related to the biosorption capacity and 1/n is an empirical parameter connected with the biosorption magnitude, which varies with the heterogeneity of the material. Freundlich isotherm for the adsorption of Pb ions on *goldar* residue is shown in Fig. 5a. From nonlinear Freundlich isotherm plots, K_f and n values were found to be 9.76 mg/g and 2.739, respectively. The Dubinin–Radushkevich isotherm model was used to predict the characteristics of adsorption processes in terms of physical or chemical aspects. The linearized D–R isotherm equation can be written as follows:

Table 1 Isotherm constants of lead adsorption by *goldar* residue biomass

Isotherm model	Constants		R^2
Langmuir	$q_m = 18.86$	$b = 1.6$	0.998
Freundlich	$K_f = 9.76$	$n = 2.739$	0.905
D–R model	$q_m = 15.54$	$\beta \times 10^8 = 6.525$	0.971
Scatchard	$q_m = 18.76$	$K_b = 1.606$	0.984
Halsey	$K = 38.46$	$n = 1.92$	0.695
Temkin	$A_T = 21.067$	$b_T = 691.47$	0.975

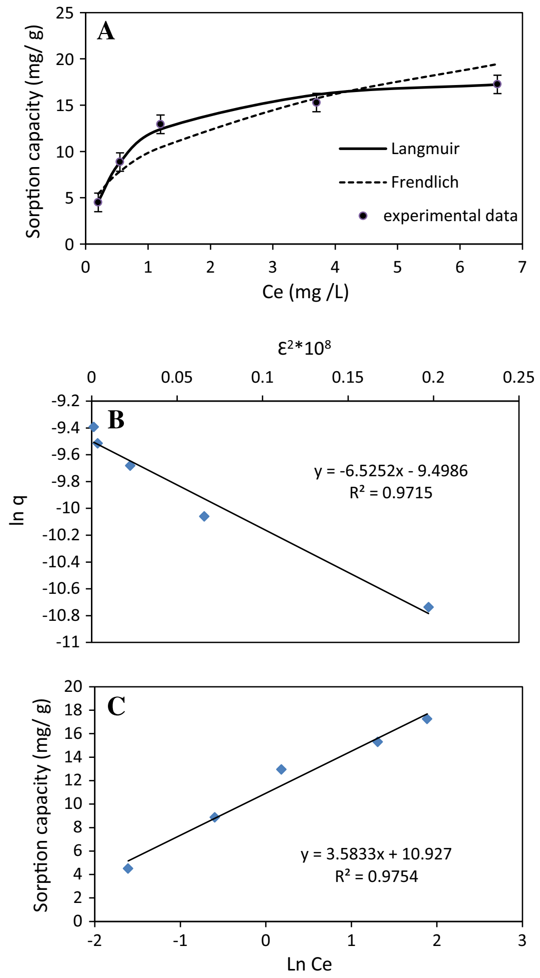

Fig. 5 Experimental and calculated adsorption isotherms of Pb(II) on *goldar* residue **a** Langmuir and Freundlich, **b** Temkin isotherm and **c** D–R biosorption isotherm (pH 5.5, $T = 25 \pm 2$ °C, biomass dosage = 1.066 g/L)

$$q_e = q_m \exp(-\beta\varepsilon^2) \tag{4}$$

where q_m is the maximum sorption capacity (mg/g), β is the activity coefficient related to mean sorption energy (mol^2/j^2), and ε is the Polanyi potential according to:

$$\varepsilon = RT\ln(1 + 1/C_e) \tag{5}$$

The D–R isotherm model fitted well the equilibrium data, where R^2 value was around 0.971 (Fig. 5b). The q_m value was found from intercept to be 15.54 mg/g. The sorption energy can also be calculated using the following equation:

$$E = \frac{1}{\sqrt{2\beta}} \tag{6}$$

If E value lies between 8 and 16 kJ/mol, the biosorption process takes place chemically and when $E < 8$ kJ/mol, the biosorption process proceeds physically (Lodeiro et al. 2006). The value of $E = 2.768$ kJ/mol shows that the physical adsorption is predominant in the biosorption process.

The Scatchard plot analysis, also called independent site-oriented model, was applied to study the affinity of binding sites and analyze the result of the adsorption isotherm. The Scatchard plot equation is given as:

$$q_e/c_e = q_m K_b - q_e K_b \tag{7}$$

where q_m (mg/g) and K_b (L/mg) are the Scatchard adsorption isotherm constants. If the plot of q_e/C_e versus q_e gives a straight line, then the adsorbent consists of only one type of binding site (homogenous surface) (Anirudhan and Suchithra 2012).

The Halsey adsorption isotherm is suitable for multilayer adsorption, and by fitting the experimental data to this equation, it confirms the heteroporous nature of the adsorbent. The Scatchard plot is linear with a negative slope related to the interaction between the Pb ions and the binding sites that obeys the Langmuir model. The isotherm equation is (Basar 2006):

$$\ln q_e = \frac{1}{n}\ln k - \frac{1}{n}\ln c_e \tag{8}$$

where k and n are isotherm parameters. The Halsey isotherm model fitted the equilibrium data, and the R^2 value was 0.695. These results showed that this model was not suitable for experimental data.

The Temkin isotherm, whose formula follows, takes into account the interactions between *goldar* residue and Pb ions. It is based on the assumption that the free energy of sorption is a function of the surface coverage (Deng and Ting 2005):

$$q_e = \frac{RT}{b_T}\ln(A_T C_e) \tag{9}$$

where A_T is equilibrium binding constant corresponding to the maximum binding energy (L/mg), b_T is the Temkin isotherm constant, T is the temperature (K), and R is the ideal gas constant (8.314 J/mol/K). Temkin isotherm for the adsorption of Pb ions is shown in Fig. 5c. The value of R^2 for this model was estimated to be 0.975. The whole calculated isotherm parameters are presented in Table 1.

Kinetic modeling of lead adsorption

The prediction of adsorption rate is useful for properly designing the batch adsorption systems. The experimental data were fitted with pseudo-first-order, pseudo-second-order and intraparticle models to study the adsorption kinetics of lead onto *goldar* residue. Adsorption rate of Pb(II) ions was rapid at the first adsorption process. It was, however, slowed down after 40 min. The adsorption rate in pseudo-first-order model depends on the concentration of only one reactant. The rate constant k_1 for the adsorption of Pb(II) has been studied by Lagergren rate equation (Yu et al. 2003) with the initial Pb(II) concentration of 20 mg/L:

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

where q_e and q_t (mg/g) are the amounts of Pb(II) ions adsorbed at equilibrium and instant t (min), respectively; k_1 represents the rate constant of the equation (min^{-1}). The adsorption rate constant k_1 is presented in Table 2. The plots of log (q_e–q_t) versus t for the pseudo-first-order model are almost linear, indicating the validity of Lagergren rate equation of the first-order kinetics.

The pseudo-second-order equation, based on adsorption equilibrium capacity, assumes that the rate at which the adsorption sites are filled is proportional to the square of the number of unoccupied sites. It is expressed as (Parab et al. 2005):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{11}$$

where K_2 is the rate constant of sorption (g/mg min). The rate constant k_2 and R^2 values are presented in Table 2. The experimental value of q_e was not matched well with the calculated value for the pseudo-first-order kinetics. Therefore, the pseudo-second-order model is more useful for describing the biosorption kinetic process precisely. This means that the physical adsorption is fast, while the chemical adsorption is slow. So, chemisorption mechanism, like valence forces and ion exchange on the surface, could be the rate controlling step, not the intraparticle diffusion.

In order to evaluate the contribution of the diffusion of lead ions within the *goldar* residue in the whole biosorption

Table 2 Kinetic parameters of lead adsorption by *goldar* residue biomass

Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
$k_1 \times 10^1$ (1/min)	q_1 (mg/g)	R^2	$k_2 \times 10^2$ (g/mg min)	q_2 (mg/g)	R^2	k_{id} (mg/g min$^{0.5}$)	C	R^2
1.32	10.196	0.983	1.74	17.24	0.99	2.378	4.289	0.934

process, the intraparticle diffusion model was applied to the experimental data. They are mathematically written as (Ma et al. 2007):

$$q_t = k_{id} t^{0.5} + c \tag{12}$$

where k_{id} is the intraparticle diffusion rate constant and C is the adsorption constant. The rate constant k_{id} and the R^2 values are given in Table 2 and Fig. 6. The mechanism of this model is delineated based on the following steps: bulk diffusion into the solid–liquid interface, intraparticle diffusion including the penetration of metal ions into the interior solid surface from available pores of the adsorbent and finally, metal adsorption at the active sites of the adsorbent (Chen et al. 2010).

Thermodynamic study of lead adsorption

In order to investigate the thermodynamics of lead sorption by *goldar* residue, the experiments were performed at different temperatures with an initial lead concentration of 20 mg/L. The thermodynamic parameters, including standard enthalpy changes ($\Delta H°$), standard entropy changes ($\Delta S°$) and standard Gibbs free energy changes ($\Delta G°$), were estimated from the following equations (Ho 2007):

$$\Delta G^0 = -RT \ln K_D \tag{13}$$

$$\ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{14}$$

where R is the universal gas constant (8.314 J/mol K), T is temperature (K), and K_D (q_e/C_e) is the distribution coefficient. Gibbs free energy change ($\Delta G°$) was found to be −1.956, −1.516, −1.247, −0.986 and −0.664 kJ/mol at 298, 303, 308, 313 and 318 K, respectively. Biosorption is usually a spontaneous process, and negative values of $\Delta G°$ at all temperatures result from this characteristic. The feasibility of biosorption is decreased upon raising the temperature. The calculated value for $\Delta H°$ was −20.508 kJ/mol. At the temperature range of 20–45 °C, $\Delta H°$ was negative, indicating the exothermic nature of the biosorption processes. Furthermore, the negative value of $\Delta S°$ (−62.447 J/mol K) was suggestive of a decrease in the randomness at the solid–solution interface during biosorption (Table 3).

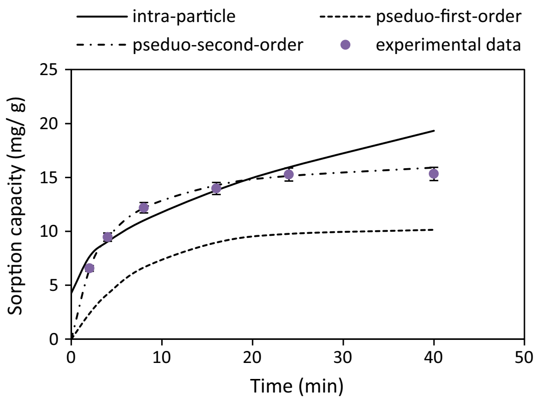

Fig. 6 Kinetic model plots for the adsorption of Pb(II) ions by *goldar* residue (pH 5.5, $T = 25 \pm 2$ °C, the initial Pb concentration = 20 mg/L, biomass dosage = 1.066 g/L)

ATR–FTIR analysis of lead ions–goldar residue interaction

ATR–FTIR spectroscopy was used to detect vibrational frequency changes in the adsorbent. The results are illustrated in Fig. 7. They show the FTIR spectra of *goldar* residue biomass before and after lead adsorption. These results give information regarding the available functional groups on the surface of *goldar* residue biomass which can be used for possible interactions between these functional groups and Pb(II) ions (Javanbakht et al. 2014). There are some changes in *goldar* residue samples before and after Pb adsorption. The strong and broad band at 3,393 cm^{-1} might be related to the overlap between amine (N–H) and hydroxyl (O–H) stretching vibrations. The bands peaks at 2,920 and 2,851 cm^{-1} could be due to the bounded (–CH) group. However, the strong peaks at 1,700, 1,606 and 1,512 cm^{-1} could be related to asymmetric and symmetric stretching vibration of C = O groups, and the peaks at 1,512 and 1,419 cm^{-1} might be assigned to the stretching of N–H group on the biomass surface (Gao et al. 2011). The bands observed at 1,371 and 1,318 cm^{-1} were due to –N = O stretching vibrations for *goldar* residue. The bands at 1,251 and 1,079 cm^{-1} were ascribed to the stretching of C–O groups on the biomass surface, and some peaks in the fingerprint region could be related to the phosphate groups. It could be

Table 3 Thermodynamic constants of lead adsorption by *goldar* residue biomass

ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)	ΔG^0 (kJ/mol)					R^2
		298 K	303 K	308 K	313 K	318 K	
−20.508	−62.447	−1.956	−1.516	−1.247	−0.986	−0.664	0.99

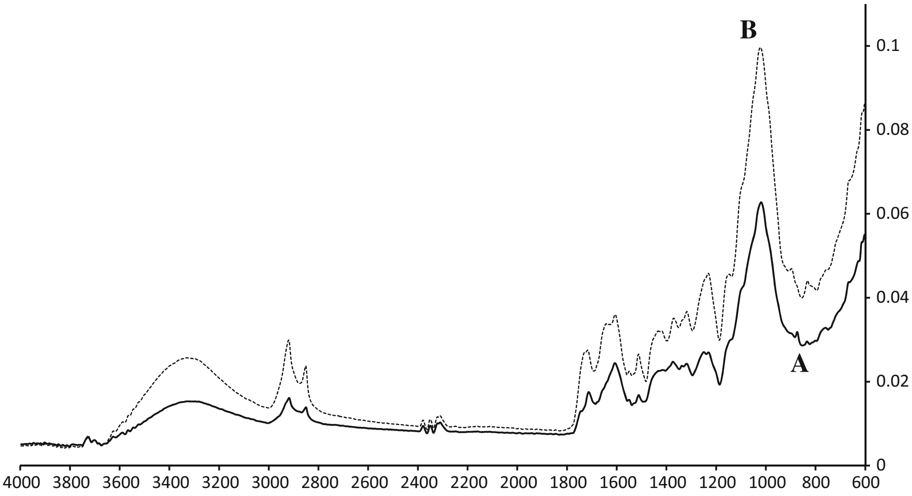

Fig. 7 ATR–FTIR spectra of *goldar* residue before (*a*) and after (*b*) the biosorption process (pH 5.5, $T = 25 \pm 2$ °C, the initial Pb concentration = 20 mg/L, biomass dosage = 1.066 g/L)

Table 4 Comparison of adsorption capacities of different adsorbents for removal of lead ions

Biosorbent	Concentration range of Pb (mg/L)	Contact time (min)	Sorbent dosage (g/L)	Removal capacity (mg/g)	References
Algal biomass *Sargassum glaucescens*	0–100	120	2	45.8	Montazer-Rahmati et al. (2011)
Algal biomass *Nizimuddinia zanardini*	0–100	120	2	50.4	Montezer-Rahmati et al. (2011)
Raw agave bagasse	0–100	–	1–2	35.6	Velazquez-Jimenez et al. (2013)
Treated agave bagasse	0–100	–	1–2	54.3	Velazquez-Jimenez et al. (2013)
Raw corncob	–	–	–	16.2	Tan et al. (2010)
Modified corncob	–	–	–	43.4	Tan et al. (2010)
Coconut tree sawdust	10–200	90	4	25.0	Putra et al. (2014)
Egg shell	10–200	90	4	90.9	Putra et al. (2014)
Sugarcane bagasse	10–200	90	4	21.3	Putra et al. (2014)
Otostegia persica waste biomass	2–25	40	1.1	17.3	This study
Pseudomonas aeruginosa in beads	73.4	15	200	0.7	Lin and Lai (2006)
Ethanol-treated baker's yeast	5–25	15–60	1	17.5	Goksungur et al. (2005)
Live *Aspergillus niger*	10	300	1.3	2.3	Kapoor et al. (1999)
NaOH-pretreated *A. niger*	10	**300**	**1.3**	7.2	Kapoor et al. (1999)

observed that the bands at 3,324, 1,713, 1,249 and 874 cm^{-1} were shifted to 3,330, 1,717, 1,232 and 833 cm^{-1}, respectively, after loading Pb(II). The changes in the wave number of these bands after the loading of Pb(II) indicated the involvement of the functional groups (C–O and C = O, amido, hydroxyl) in the biosorption of Pb(II) on the surface of *goldar* residue biomass (Murphy et al. 2007; Lodeiro et al. 2006).

A comparison of adsorption capacities of different biosorbents, which have been used by researchers for removal of lead ions from aqueous solutions, is presented in Table 4. Together with biosorbent capacity, availability of the biosorbent and its preparation cost are factors affecting the practical use of biosorbents (Kapoor et al. 1999). Contact time to reach equal conditions and biomass dosage are also other parameters which have been very different. Initial concentration of Pb(II) ions is an important parameters, in which, it can affect the residual concentration of metal ions in the aqueous solution. As it is seen in Table 4, different researchers have applied different initial concentration, while the aim of this work was adsorption of low concentrations of lead ions.

Conclusion

The residue of solvent-extracted *O. persica* or *goldar* residue biomass was used for the first time in the adsorption of lead from water. A maximum adsorption capacity of 17.3 mg/g was obtained at the pH of 5.5, the initial lead concentration of 25 mg/L and goldar residue biomass dosage of 1.06 g/L. Kinetics of adsorption was properly described by the pseudo-second-order model. FTIR analysis confirmed the presence and responsibility of several functional groups on the surface of *goldar* residue biomass during lead adsorption. These results showed that *goldar* residue biomass could be the high potential biosorbent of heavy metals.

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