



## Biosorption of Pb(II) ions from aqueous solution by pine bark (*Pinus brutia* Ten.)

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### ABSTRACT

The biosorption potential of pine (*Pinus brutia* Ten.) bark in a batch system for the removal of Pb(II) ions from aqueous solutions was investigated. The biosorption characteristics of Pb(II) ions on the pine bark was investigated with respect to well-established effective parameters including the effects of solution pH, initial Pb(II) concentration, mass of bark, temperature, and interfering ions present, reusability, and desorption. Initial solution pH and contact time were optimized to 4.0 and 4 h, respectively. The Langmuir and Freundlich equilibrium adsorption models were studied and observed to fit well. The maximum adsorption capacity of the bark for Pb(II) was found to be 76.8 mg g<sup>-1</sup> by Langmuir isotherms (mass of bark: 1.0 g L<sup>-1</sup>). The kinetic data fitted the pseudo-second-order model with correlation coefficient greater than 0.99. The thermodynamic parameters Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ) changes were also calculated, and the values indicated that the biosorption process was spontaneous. Reutilization of the biosorbent was feasible with a 90.7% desorption efficiency using 0.5 M HCl. It was concluded that pine bark can be used as an effective, low cost, and environmentally friendly biosorbent for the removal of Pb(II) ions from aqueous solution.

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### 1. Introduction

Heavy metals can enter a water supply from either industrial activities such as microelectronics, electroplating, battery manufacture, metallurgical, and fertilizer industries or acid rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater. Heavy metals are taken into the body via inhalation, ingestion, and skin adsorption. Most are extremely harmful to humans, animals and plants mainly because of their accumulation in the body [1–4].

Lead is a particularly hazardous heavy metal because once it gets into human body, it disperses throughout the body immediately and causes harmful effects wherever it lands. For example, it can damage the red blood cells and limit their ability to carry oxygen to the organs and tissues. It can also affect the nervous system, kidneys and hearing [5]. In particular unborn babies and young children are at risk of health problems from lead poisoning because their smaller bodies make them more susceptible to absorbing lead ions. Lead compounds are known as metabolic poisons and enzyme inhibitor [6]. Many industrial activities such as battery manufacturing, metal plating and oil refining are the major sources of lead pollution. Lead also spreads into environmental waters through melting of sulfide ore and utilization of fossil fuels.

Lead is taken into the body via inhalation, ingestion, and skin adsorption. In drinking water, maximum allowable limit of total Pb of 50 µg L<sup>-1</sup> is considered safe by the World Health Organization (WHO), whereas less than 15 µg L<sup>-1</sup> is adopted by the United States Environmental Protection Agency (USEPA) [7]. It is, thus, important to remove lead and other toxic heavy metal ions from waters and wastewaters before they are released to the environment.

The conventional removal methods for lead and other heavy metals from water and wastewaters include reverse osmosis, chemical precipitation, solvent extraction, filtration, ion exchange, phytoremediation, electrodialysis, electroflotation, chemical oxidation or reduction, and coagulation. However, the applicability of all these methods is often limited because of several disadvantages including incomplete metal removal, high capital and operational costs, low selectivity, high reagent and energy requirements, and generation of toxic sludge or other waste products that are difficult to be removed [8–10]. Among the traditional techniques, ion exchange method is particularly reliable for the removal of heavy metals from water, but its high cost and partial removal of certain ions limit its use. The phytoremediation is the use of certain plants to clean up soils, sediments, and waters contaminated with various pollutants such as heavy metals. However, the process requires a long time for the removal of metals because the growth rates are very low [11].

Among the various wastewater treatment techniques, biosorption of heavy metals is a promising alternative method due to its

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high selectivity, easy handling, lower operating costs, high efficiency in removing very low levels of heavy metals from dilute solutions, reduced quantity of chemical or biological sludge, and regenerability of biosorbents [6]. Biosorption is the binding and concentration of heavy metals or other pollutants from aqueous solutions by certain types of living or dead biomass. Although biosorption is an effective and versatile technique, its mechanism is not well understood. Biosorption of heavy metal ions can take place via several mechanisms including ion exchange, complexation, coordination, chelating, physical adsorption, microprecipitation, oxidation, and reduction [8]. The degree and rate of biosorption of heavy metals onto biosorbent depend on the properties of metal ion, operating conditions, physical and surface properties of biosorbent [12]. New, economical, easily available, and effective biosorbents possessing high loading capacity are needed for the treatment of heavy metal contaminated waters and wastewaters. The biosorbents can be divided into two categories: the living or non-living microorganisms such as algae, fungi and bacteria, and agricultural or forestry by-products such as peanut shells, soybean hulls, and tree bark. The advantages of the agricultural and forestry by-products as biosorbents in comparison to the microorganisms are the facts that they do not have to be specially produced for this purpose, they are by-products or wastes from agricultural or forestry processes, and they are already available in large quantities [13]. In recent years, a number of agricultural and forestry by-products such as rice husk [14], pine bark [15], saw dust [16], technical lignin [17], and cork biomass [18] have been used for heavy metal removal from waters and wastewaters. The biosorption of heavy metals by these materials might be attributed to their proteins, carbohydrates and phenol compounds, having carboxyl, hydroxyl, phosphate, sulfate, and amino groups, which can bind metal ions [18].

In this study we used pine (*Pinus brutia* Ten.) bark as a biosorbent due to its low cost, high efficiency, and ready availability. Pine is one of the important forest trees that are naturally distributed in the Mediterranean and Aegean region of Turkey. It is an economically important forest tree in the country, providing both timber resources and amenity, used widely in afforestation and reforestation programs. *P. brutia* has a wide range in Turkey [19,20]. *P. brutia* bark has a high tannin content, so it is expected to be an effective biosorbent for the removal of Pb(II) ions from aqueous solutions. The polyhydroxy and polyphenol groups are the active species of tannin [21].

The aim of the present work was to investigate the possible use of *P. brutia* bark as an alternative biosorbent material for removal of Pb(II) ions from aqueous solutions. The study includes an evaluation of the effects of various process parameters such as initial pH of the solution, contact time, initial Pb(II) concentration and initial mass of bark, reutilization of the bark, and desorption from the metal-loaded bark. The effects of hard ions were also evaluated on the uptake of Pb(II) by bark biomass. The Langmuir and Freundlich adsorption models were used to fit the equilibrium isotherms. Kinetic and thermodynamic parameters were also calculated to describe the adsorption mechanism.

## 2. Materials and methods

### 2.1. Preparation of biosorbent

Pine barks were obtained from the Faculty of Forestry of Karadeniz Technical University, Trabzon, Turkey. Before use, they were washed with deionized water several times to remove surface impurities and then dried in an oven (Nüve FN 400) at 40 °C for 4 days. The dried bark samples were ground in a blender, sieved according to the particle size required, and stored in glass containers until use for biosorption experiments.

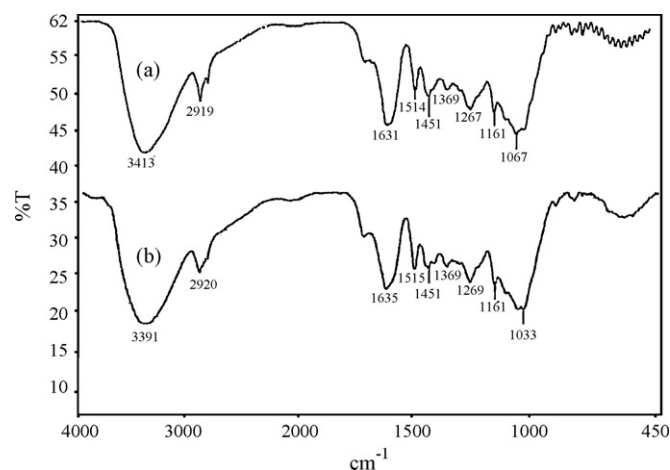


Fig. 1. IR spectra of the bark (a) before and (b) after biosorption of Pb(II) ions.

### 2.2. IR spectra of original bark and Pb(II)-loaded bark

In order to determine the main functional groups of pine bark for assessment of the lead(II) sorption mechanism, a Fourier transform infrared (FTIR) analysis in solid phase with an IR PerkinElmer 1600 Series FTIR Spectrometer was performed on the biomass prepared in a KBr disk. IR spectra of the bark biomass free and after lead(II) ions loaded are depicted in Fig. 1.

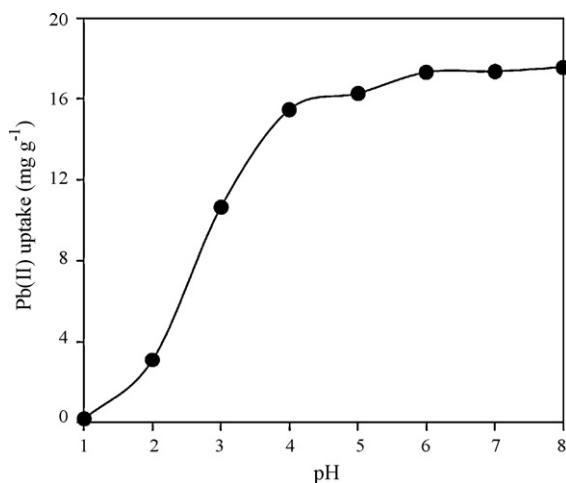
The broad and strong band ranging from 3000 to 3600  $\text{cm}^{-1}$  indicates the presence of –OH and –NH groups, which is consistent with the peak at 1033 and 1161  $\text{cm}^{-1}$  assigned to alcoholic C–O and C–N stretching vibration. The peaks observed at near 2920  $\text{cm}^{-1}$  can be assigned to the C–H group. Bands around 1631 and 1635  $\text{cm}^{-1}$  are indicative of carboxyl groups (C=O). The IR spectra indicate that the carbons possess different surface structures, e.g., aliphatic, aromatic, cyclic as one can observe the bands at 1451  $\text{cm}^{-1}$  and over the 1369–1267  $\text{cm}^{-1}$  range.

### 2.3. Biosorption experiments

All chemicals were of analytical reagent grade and purchased from Merck (Darmstadt, Germany). All glassware and sample bottles were cleaned by soaking overnight in 10% (w/v)  $\text{HNO}_3$  and rinsed with deionized water several times. A stock solution containing 5000  $\text{mg L}^{-1}$  Pb(II) ions was prepared from  $\text{Pb}(\text{NO}_3)_2$  in deionized water. The working solutions were prepared by appropriate dilutions of the stock solution immediately prior to their use. The biosorption of Pb(II) ions on the bark was studied by batch technique. The general method for this study is as follows: 50 mg of bark was equilibrated with 10 mL of Pb(II) solution (in the concentration range of 50–1000  $\text{mg L}^{-1}$ ) in a polyethylene centrifuge tube. The initial pH of the solution was adjusted to 4.0 with diluted HCl or NaOH solutions. The content of the tube was agitated on a shaker (Edmund Bühler, GmbH) at 400 rpm for 4 h. After reaching the equilibrium, the biosorbent was removed by vacuum filtration through 0.45  $\mu\text{m}$  nitrocellulose membrane (Sartorius Stedim Biotech., GmbH), then the equilibrium concentration of Pb(II) ions in the filtrate was determined by a flame atomic absorption spectrophotometer, FAAS (Unicam AA-929). The amount of Pb(II) adsorbed was calculated from the difference between the initial concentration and the equilibrium concentration. All the biosorption experiments were repeated in triplicate.

### 2.4. Desorption tests

Desorption of adsorbed Pb(II) ions from pine bark was also studied in a batch system. Desorption experiments were carried out by



**Fig. 2.** Effect of solution pH on Pb(II) uptake by bark (initial Pb(II) concentration: 100 mg L<sup>-1</sup>; mass of bark: 5.0 g L<sup>-1</sup>).

using 0.1 M HCl solution. Pb(II) ions were adsorbed according to the process described above (Section 2.3). The bark loaded with Pb(II) ions was collected by filtration and washed with deionized water for three times, then dried in air for one day. The bark loaded with Pb(II) ions was treated with 10 mL of HCl solutions in the concentration range of 0.01–0.5 M, and shaking the content of tubes at 400 rpm for 4 h. The solution was separated by vacuum filtration through 0.45 μm nitrocellulose membrane and the filtrate was analyzed to determine the concentration of Pb(II) ions desorbed.

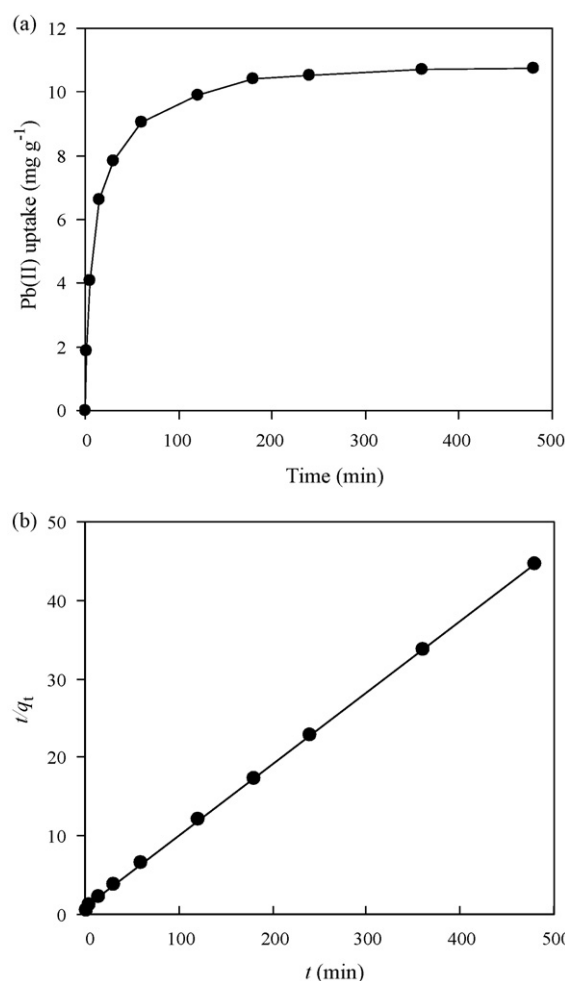
### 3. Results and discussion

#### 3.1. The effect of initial pH on the biosorption of Pb(II) ions

It is well known that pH of the medium affects the form and quantity of heavy metal ions, biosorbent surface sites in water, and the interaction between heavy metals and the functional groups on the biosorbent surface, so pH is an important parameter on the biosorption of heavy metal ions from aqueous solutions. The effect of the pH on the biosorption of Pb(II) ions on the bark was evaluated by using initial Pb(II) concentration of 100 mg L<sup>-1</sup> and 5.0 g L<sup>-1</sup> mass of bark (bark particle size: 150–355 μm) at the pH range of 1–8, and the results were illustrated in Fig. 2. Under highly acidic conditions (pH 1.0–2.0) the amount of Pb(II) uptake was very small, while the sorption was enhanced over pH 3.0. At lower pH values the surface charge of the bark is positive and, thus, Pb(II) biosorption on the bark is not favorable. In addition, hydronium ions compete with Pb(II) ions for the active sites on the surface of the bark, so biosorption capacity is small. When pH was increased, electrostatic repulsion between Pb(II) ions and bark surface sites and competing effect of hydronium ions decreased, so Pb(II) uptake was increased [22]. Experiments were not conducted beyond pH 8.0 to avoid precipitation of Pb(II) ions as Pb(OH)<sub>2</sub>. The optimum pH was established as 4.0.

#### 3.2. The effect of contact time and kinetics of biosorption

The effect of the contact time on biosorption of Pb(II) onto the bark was studied in the time range of 1–480 min by using 100 mg L<sup>-1</sup> of Pb(II) solutions at pH 4.0 with 5.0 g L<sup>-1</sup> of bark. The mixtures were agitated at 400 rpm. The samples were taken at various periods of time, filtered immediately through nitrocellulose membrane, and then analyzed for their Pb(II) concentrations. The biosorption of Pb(II) content was increased within 1 h, and then it continued to increase at a lower rate until equilibrium was reached



**Fig. 3.** (a) Effect of contact time on Pb(II) uptake by bark, (b) the pseudo-second-order kinetic model for adsorption of Pb(II) ions on the bark (initial Pb(II) concentration: 100 mg L<sup>-1</sup>; mass of bark: 5.0 g L<sup>-1</sup>; initial pH: 4.0).

(Fig. 3(a)). Based on these results, a contact time of 4 h was assumed to be suitable for subsequent biosorption experiments.

The kinetics of the bark–Pb(II) interactions was tested with different kinetic models including pseudo-first-order, pseudo-second-order, and intraparticle diffusion models.

The pseudo-first-order equation is among the most widely used to predict metal adsorption experiments. The model has the following form [23];

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (1)$$

where  $q_t$  (mg g<sup>-1</sup>) is the amount of metal ions adsorbed at time  $t$ ,  $q_e$  is the amount of metal ions adsorbed at equilibrium (mg g<sup>-1</sup>), and  $k_1$  is the rate constant of the adsorption (min<sup>-1</sup>).

After definite integration by applying the conditions  $q_t = 0$  at  $t = 0$  and  $q_t = q_t$  at  $t = t$ , it turns into the following equation,

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

Straight line in the graph of  $\ln(q_e - q_t)$  versus  $t$  suggests the applicability of this kinetic model, and  $q_e$  and  $k_1$  can be determined from the intercept and slope of the plot, respectively.

The pseudo-first-order data do not fall on straight lines indicating that this model is not appropriate. The pseudo-first-order rate constant  $k_1$  and the value of  $q_e$  were calculated from the model and are presented in Table 1. The correlation coefficient is less than 0.96, which is indicative of a poor correlation and also  $q_{e,cal}$  determined

from the model is not in a good agreement with the experimental values of  $q_{e,exp}$ . Therefore, the pseudo-first-order model is not suitable for modeling the biosorption of Pb(II) on the bark.

The pseudo-second-order kinetic model is in the following form [24];

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

where  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the rate constant of the second order equation;  $q_t$  ( $\text{mg g}^{-1}$ ) the amount of adsorption at time  $t$  (min), and  $q_e$  ( $\text{mg g}^{-1}$ ) is the amount of adsorption at equilibrium.

After definite integration by applying the conditions  $q_t = 0$  at  $t = 0$  and  $q_t = q_e$  at  $t = t$  the equation above turns into the following,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

The plot of  $t/q_t$  versus  $t$  should give a straight line if second order kinetics is applicable, and  $q_e$  and  $k_2$  can be determined from slope and intercept of the plot, respectively.

The linear plot of  $t/q_t$  versus  $t$  for the pseudo-second-order kinetic model is shown in Fig. 3(b). The pseudo-second-order rate constant  $k_2$  and the value of  $q_e$  were determined from the model and are presented in Table 1. The value of correlation coefficient is very high (0.999), and the theoretical  $q_{e,cal}$  value is closer to the experimental  $q_{e,exp}$  value.

The intraparticle diffusion equation is expressed as [25];

$$q_t = k_{id}t^{1/2} + c \quad (5)$$

where  $q_t$  ( $\text{mg g}^{-1}$ ) is the amount of adsorption at time  $t$  (min) and  $k_{id}$  ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ) is the rate constant of intraparticle diffusion.

A straight line in the graph of  $q_t$  versus  $t^{1/2}$  suggests the applicability of the intraparticle diffusion model.  $k_{id}$  and  $c$  can be determined from the slope and intercept of the plot, respectively.

The intraparticle rate constant  $k_{id}$  and  $c$  parameters were obtained from the plot of  $q_t$  versus  $t^{1/2}$  and the results are given in Table 1. The correlation coefficient obtained from the model is not satisfactory, and also the value of  $c$  is not zero, indicating that the intraparticle diffusion model may not be the controlling factor in determining the kinetics of the process.

As a result, compared to pseudo-first-order and intraparticle diffusion kinetic models, a good correlation coefficient was obtained for pseudo-second-order kinetic model, which indicates that the Pb(II) biosorption on the bark follows pseudo-second-order rate expression.

### 3.3. The effect of bark and initial Pb(II) concentrations

The equilibrium adsorption isotherms provide very useful data to understand the mechanism of adsorption. Several isotherm models are used to describe the behavior of adsorbent–adsorbate couples. Langmuir and Freundlich isotherm models were preferred in order to evaluate the data in this study. These isotherm models are widely used to establish the relationship between the amount of Pb(II) ions adsorbed on an adsorbent and its equilibrium concentration in aqueous solution.

The Langmuir isotherm model is acceptable for monolayer adsorption onto a surface containing a finite number of identical

sites. The model has the general equation [26];

$$q_e = \frac{bq_{max}C_e}{1 + bC_e} \quad (6)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) is the amount of metal ions adsorbed per unit mass of adsorbent,  $C_e$  the equilibrium metal concentration in the solution ( $\text{mg L}^{-1}$ ),  $q_{max}$  the Langmuir constant related to the maximum monolayer adsorption capacity ( $\text{mg g}^{-1}$ ) and  $b$  is the constant related to the free energy or net enthalpy of adsorption ( $\text{L mg}^{-1}$ ). The equation providing a linear line graph in Langmuir model is obtained as;

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \quad (7)$$

The shape of isotherm can be used to predict whether a sorption system is favorable or unfavorable. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor, or equilibrium parameter  $R_L$ , which is defined by the following equation [27,28];

$$R_L = \frac{1}{1 + bC_0} \quad (8)$$

where  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial amount of adsorbate and  $b$  ( $\text{L mg}^{-1}$ ) is the Langmuir constant described above.

There are four probabilities for the  $R_L$  value: (i) for favorable adsorption  $0 < R_L < 1$ , (ii) for unfavorable adsorption  $R_L > 1$ , (iii) for linear adsorption  $R_L = 1$ , and (iv) for irreversible adsorption  $R_L = 0$ .

The Freundlich isotherm model assumes that the removal of metal ions occurs on a heterogeneous adsorbent surface, and the model can be applied for multilayer sorptions. The Freundlich model has the form [29];

$$q_e = K_f C_e^{1/n} \quad (9)$$

where  $K_f$  is a constant related to the adsorption capacity ( $\text{mg g}^{-1}$ ) and  $1/n$  is an empirical parameter related to the adsorption intensity. The Freundlich model in linear form is as follows;

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (10)$$

The influence of the bark and Pb(II) concentrations on the present biosorption process was investigated by employing Pb(II) solutions (pH 4.0) with initial concentrations in the range of 50–1000  $\text{mg L}^{-1}$  and mass of bark in the range of 1–20  $\text{g L}^{-1}$  (bark particle size of  $<150 \mu\text{m}$ ). After reaching equilibrium, Pb(II) concentrations in each system were measured. The Langmuir and Freundlich isotherms were applied for the biosorption of Pb(II) ions on the bark, and plotted as a function of mass of bark as shown in Fig. 4(a) and (b), respectively. The results showed that, as the amount of adsorbent increased, the number of adsorbent sites increased, and, hence, more Pb(II) ions can bind to the surface of bark. Moreover, level of Pb(II) removal was decreased when the Pb(II) concentration increased in the solution, which is an expected result. In addition, the bark at the lowest concentration (1  $\text{g L}^{-1}$ ) showed the highest adsorption capacity for Pb(II) ions among the tested values. This can be explained by the higher amount of interactions between biomass and metal ions as the amount of sorbent decreases at fixed initial metal ion concentration.

The plots of  $C_e/q_e$  versus  $C_e$  were found to be linear indicating the applicability of the Langmuir isotherm model (Fig. 4(a)). The

**Table 1**

Parameters of pseudo-first-order, pseudo-second-order, and intraparticle diffusion models at 25 °C.

Exp. $q_e$ ( $\text{mg g}^{-1}$ )	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
	$k_1$ ( $\text{min}^{-1}$ )	$q_e$ ( $\text{mg g}^{-1}$ )	$R^2$	$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$q_e$ ( $\text{mg g}^{-1}$ )	$R^2$	$k_{id}$ ( $\text{mg g}^{-1} \text{min}^{-1/2}$ )	$C$ ( $\text{mg g}^{-1}$ )	$R^2$
10.76	$-1.37 \times 10^{-2}$	5.99	0.954	$9.18 \times 10^{-3}$	10.98	0.999	0.370	4.44	0.742



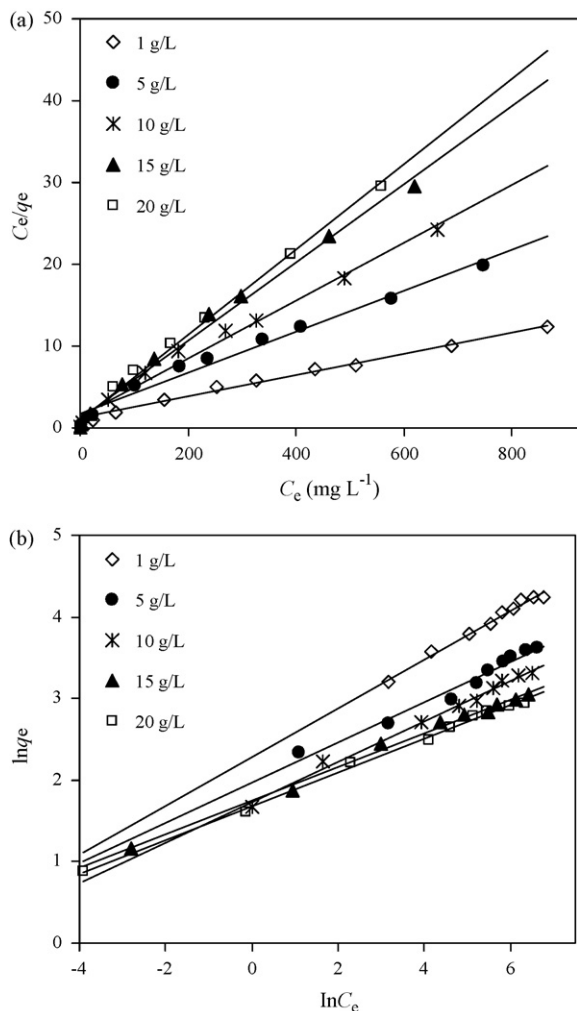


Fig. 4. Relationship between equilibrium Pb(II) concentration and its uptake at various masses of bark using (a) Langmuir, (b) Freundlich isotherm models (initial pH: 4.0; selected masses of bark: 1, 5, 10, 15, and 20  $\text{g L}^{-1}$ ).

Langmuir constants  $q_{\text{max}}$  and  $b$  were obtained from the slope and intercept of the linear plots of  $C_e/q_e$  versus  $C_e$ , respectively, as listed in Table 2. The values of correlation coefficient were extremely high. These results imply that the data on the biosorption of Pb(II) on the bark may be concluded to perfectly fit the Langmuir isotherm model. Fig. 4(b) shows the Freundlich isotherms obtained by plotting  $\ln q_e$  versus  $\ln C_e$ . The values of Freundlich constants,  $K_f$  and  $1/n$  were determined from the intercept and slope of the linear plots, respectively, and are presented in Table 2. The correlation coefficients were found in the range of 0.97–0.99 for the biosorption of Pb(II) ions indicating that the equilibrium data fitted well with the Freundlich model. The values of  $1/n$  were smaller than 1

Table 2  
Langmuir and Freundlich isotherm constants and correlation coefficients for the biosorption of Pb(II) on bark at various masses of bark at pH 4.0 (bark particle size:  $<150 \mu\text{m}$ ).

Mass of bark ( $\text{g L}^{-1}$ )	Langmuir constants			Freundlich constants		
	$q_{\text{max}}$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{L mg}^{-1}$ )	$R^2$	$K_f$ ( $\text{mg g}^{-1}$ )	$n$	$R^2$
1	76.8	0.011	0.991	2.29	3.34	0.989
5	39.9	0.014	0.980	1.98	4.06	0.974
10	28.3	0.024	0.986	1.73	4.04	0.993
15	20.9	0.044	0.993	1.75	4.85	0.994
20	19.1	0.055	0.995	1.68	4.81	0.997

Table 3

Comparison of maximum adsorption capacity of Pb(II) on different adsorbents in the literature.

Biosorbent	Mass of biosorbent ( $\text{g L}^{-1}$ )	pH	Capacity ( $\text{mg g}^{-1}$ )	Ref.
Barley straws	6.25	6.0	23.20	[30]
Snowberry	4.0	5.5	62.16	[31]
Rice husk	3.0	6.0	58.1	[32]
Hazelnut shell	10.0	6.0	28.18	[33]
Pecan nutshell	4.0	5.5	211.7	[34]
Macrofungus	4.0	5.0	38.4	[35]
<i>Strychnos potatorum</i> seed	1.0	5.0	16.42	[36]
Sawdust	7.5	5.0	88.49	[37]
<i>Pinus silvestris</i> sawdust	1.0	5.0	22.22	[38]
Pine bark	1.0	4.0	76.8	This work

indicating that the biosorption process was favorable under studied conditions. Also the  $R_L$  values calculated for Pb(II) with initial concentration range of 50–1000  $\text{mg L}^{-1}$  were in the range of 0.067 and 0.588 at constant mass of bark ( $5.0 \text{ g L}^{-1}$ ). This result also supports the fact that the biosorption of Pb(II) on the pine bark was a favorable process.

The two isotherm models used fit very well according to the correlation coefficients values given in Table 2. This may be due to both homogeneous and heterogeneous distribution of active sites on the surface of the bark.

Table 3 shows the biosorption capacity values of various biosorbents for lead(II). The comparison between our results and those of the literature shows that the pine barks without any pre-treatment exhibit very good sorption efficiency. It can be seen that our capacity result, 76.8  $\text{mg lead/g bark}$  at pH 4.0, is relatively better than most of results shown in the works cited in Table 3 [30–38].

#### 3.4. The effect of temperature and thermodynamic parameters on biosorption

In order to investigate the effect of temperature on the uptake of Pb(II), the process was carried out at different temperatures ranging from 0 to 40 °C with 100  $\text{mg L}^{-1}$  of initial Pb(II) concentrations at pH 4.0. The temperature affected the equilibrium uptake as shown in Fig. 5(a). The equilibrium Pb(II) ion biosorption capacity of the pine bark was better at higher temperatures as the adsorbed amount of Pb(II) ions increased with the rise in temperature. Higher uptake at high temperature is due to the increase in molecular diffusion or may be attributed to the availability of more active sites on the surface of the bark by expansion of the pores.

Temperature dependence of the biosorption process is related with several thermodynamic parameters including free energy change ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ), which are used to decide whether the biosorption is a spontaneous process or not. Thermodynamic parameters can be calculated from the following equation;

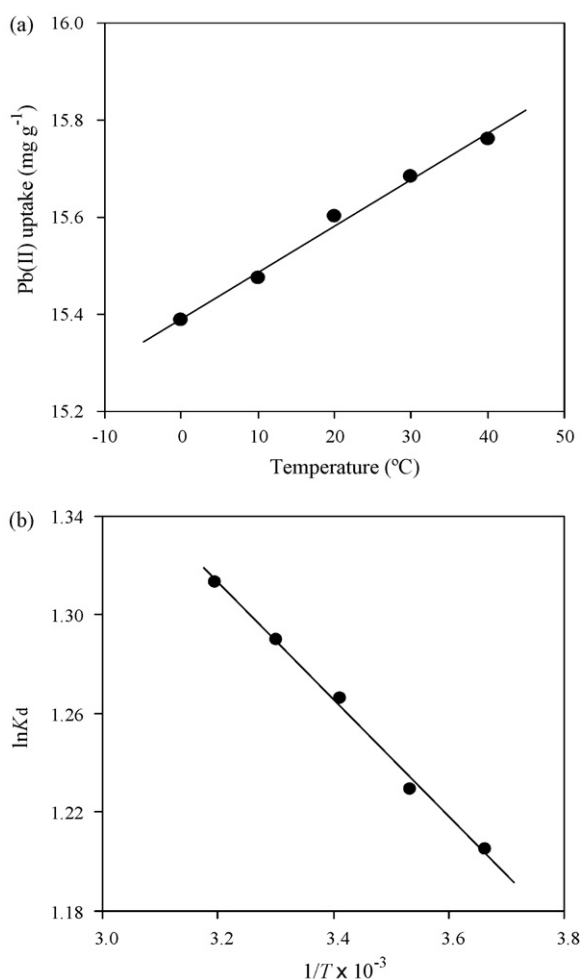
$$\Delta G^\circ = -RT \ln K_d \quad (11)$$

where  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  the temperature ( $K$ ), and  $K_d$  is the distribution coefficient. If the value of  $\Delta G^\circ$  is negative, the chemical reaction can occur spontaneously at a given temperature. The  $K_d$  value was calculated using the following equation [9];

$$K_d = \frac{q_e}{C_e} \quad (12)$$

where  $q_e$  and  $C_e$  are the equilibrium concentrations of metal ions ( $\text{mg L}^{-1}$ ) on the adsorbent and in the solution, respectively. The enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) of biosorption can be calculated from the following equation;

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (13)$$



**Fig. 5.** (a) Effect of temperature on Pb(II) uptake, (b) plot of  $\ln K_d$  versus  $1/T$  for estimation of thermodynamic parameters for the biosorption of Pb(II) on the bark (initial Pb(II) concentration:  $100 \text{ mg L}^{-1}$ ; mass of bark:  $5.0 \text{ g L}^{-1}$ ; initial pH: 4.0).

This equation can be written as;

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (14)$$

The thermodynamic parameters of  $\Delta H^\circ$  and  $\Delta S^\circ$  were obtained from the slope and intercept of the plot between  $\ln K_d$  versus  $1/T$ , respectively (Fig. 5(b)). The Gibbs free energy changes ( $\Delta G^\circ$ ) were calculated from Eq. (11), and the values of  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  for the biosorption of Pb(II) on the bark are given in Table 4. The negative values of  $\Delta G^\circ$  indicated the spontaneous nature of the biosorption process. The magnitude of  $\Delta G^\circ$  also increased with increasing temperature indicating that the biosorption was more favorable at higher temperatures. The value of  $\Delta H^\circ$  was positive, indicating the endothermic nature of the biosorption of Pb(II) on the bark in the

**Table 4**  
Thermodynamic parameters of the Pb(II) biosorption on the bark at different temperatures.

T (°C)	Thermodynamic equilibrium constant ( $K_d$ )	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> ) <sup>a</sup>	$\Delta H^\circ$ (kJ mol <sup>-1</sup> ) <sup>a</sup>
0	3.34	-2.74		
10	3.42	-2.89		
20	3.55	-3.08	17.21	1.97
30	3.63	-3.25		
40	3.72	-3.42		

<sup>a</sup> Measured between 0 and 40 °C.

temperature range of 0–40 °C. The magnitude of  $\Delta H^\circ$  gives an idea about the type of sorption. There are two main types of adsorption: physical and chemical. The enthalpy for physical adsorption is usually no more than  $1 \text{ kcal mol}^{-1}$  ( $4.2 \text{ kJ mol}^{-1}$ ) and the enthalpy for chemical adsorption is more than  $5 \text{ kcal mol}^{-1}$  ( $21 \text{ kJ mol}^{-1}$ ) [39]. Therefore, the biosorption of Pb(II) ions on the bark is a physical process because the obtained  $\Delta H^\circ$  value is  $1.97 \text{ kJ mol}^{-1}$ . Hence, the biosorption equilibria were rapidly attained and there were weak interactions between the Pb(II) ions and the functional groups on the surface of the bark. In addition, the positive value of  $\Delta S^\circ$  suggested an increase in randomness at the solid/liquid interface during the biosorption of Pb(II) ions on the bark.

### 3.5. Applicability of the bark without regeneration

In order to investigate the applicability of the bark without regeneration, the biosorption experiment was performed using an initial Pb(II) concentration of  $102 \text{ mg L}^{-1}$  in  $5.0 \text{ g L}^{-1}$  of bark suspension for 4 h contact time. Then the bark was filtered, dried in air for one day, and then transferred into another Pb(II) solution of the same concentration. This process was repeated five times, and after each repeat, the bark was capable of adsorbing some Pb(II) ions. The largest amount of Pb(II) adsorbed was in the first application ( $10.6 \text{ mg g}^{-1}$ ). After each cycle, the amount of adsorbed Pb(II) ions decreased ( $6.0 \text{ mg g}^{-1}$  for cycle 2,  $4.7 \text{ mg g}^{-1}$  for cycle 3). After cycles 4 and 5, the newly adsorbed Pb(II) were  $2.9$  and  $2.3 \text{ mg g}^{-1}$ , respectively. This indicates that the quantity of Pb(II) removed significantly decreased compared to the first 3 cycles. The results suggest that the already used bark can be applied to fresh metal solutions and used at least five times without regeneration.

### 3.6. Desorption of Pb(II) ions

Desorption is of utmost importance when the biomass preparation/generation is costly, as it is possible to decrease the biosorption process cost and also dependency of the process on a continuous supply of biosorbent. After desorption, the biosorbent should be close to its original form, and should not lose its adsorption ability. A successful desorption process requires the proper selection of the eluents, which strongly depends on the type of biosorbent and the mechanism of biosorption [40]. The selected eluent must be effective, harmless for the biosorbent, non-polluting, and cheap. For that purpose, dilute solutions of mineral acids such as hydrochloric acid, sulfuric acid, acetic acid, and nitric acid can be used. In this study, HCl solution was selected as an eluent to desorb Pb(II) ions from the metal-loaded pine bark. In acidic conditions, heavy metal cations are displaced by protons from the binding sites. Desorption experiments were carried out as described in Section 2.3. The effect of HCl concentration on the desorption of Pb(II) is investigated. The regeneration efficiency reached from 64.6 to 90.7% when the concentration of HCl increased from 0.01 to 0.5 M, indicating that higher concentration of HCl was more efficient in releasing Pb(II) ions. However a complete desorption of Pb(II) ions could not be obtained even with 0.5 M HCl, which might be due to Pb(II) ions becoming trapped in the intrapores and, therefore, difficult to release [41].

### 3.7. Reutilization of the bark after regeneration

In order to evaluate the reutilization of the bark, the biosorption–desorption cycles were repeated five times by using same preparations. In these tests, desorption of Pb(II) ions from the bark, which was treated with  $100 \text{ mg L}^{-1}$  of initial Pb(II) concentration, was performed with 10 mL of 0.1 M HCl solution. The bark was separated by filtration, washed several times with deionized water

until the pH of the wash solution was 4.0, because the use of 0.1 M HCl solution as an eluent deposits  $H_3O^+$  ions on the biomass surface. Excessive amounts of  $H_3O^+$  ions can reduce the metal biosorption capacity of the biosorbent, and washing the biomass with deionized water is, thus, necessary to remove  $H_3O^+$  ions [42]. The results are illustrated in Fig. 6. After the first cycle, the biosorption capacity decreased 20%, and for all consecutive cycles, as the number of cycle increased, the amount of newly adsorbed Pb(II) decreased; however, the total amount of Pb(II), the sum of the amount of the newly adsorbed and that which could not be removed from the bark by desorption, increased. The reasons of this situation can be explained as: (i) although HCl has a high capacity to desorb metals, several studies show that it decreases metal sorption ability of biosorbent in successive cycles because it damages metal binding sites and hydrolyzes polysaccharides on the surface of the biomass [43,44], (ii) after each sorption process, the number of already occupied sites increases leaving little space for further sorption [45,46], and (iii) some of biomass may be lost during the biosorption–desorption process. It can be concluded that the bark biomass can be used at least 5 times effectively with repeated regeneration.

### 3.8. The effect of alkali metal ions over the biosorption yield of Pb(II) ions

In wastewaters and natural waters, Pb(II) ions are usually found with a number of other metal ions such as  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ , and  $Ca^{2+}$ , which may interfere with the removal of Pb(II) ions by a biomass. Hence, the effect of these ions on the biosorption of Pb(II) ions onto the bark was studied. The biosorption studies were performed by adding  $100\text{ mg L}^{-1}$  of  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ , and the mixture of these ions, individually, in  $100\text{ mg L}^{-1}$  of Pb(II) solution containing  $5.0\text{ g L}^{-1}$  of bark. The biosorption procedure was carried out as described in Section 2.2. None of these ions have significant interference effects on the biosorption of Pb(II) on the bark (Fig. 7(a)).

In order to evaluate the effect of increasing alkali ions concentration on the biosorption of Pb(II) ions on the bark, the biosorption experiments were carried out by adding hard ions in the concentration range of  $100\text{--}500\text{ mg L}^{-1}$ , individually into  $100\text{ mg L}^{-1}$  of Pb(II) solution containing  $5.0\text{ g L}^{-1}$  of bark. As the concentration of these alkali ions increased from  $100$  to  $500\text{ mg L}^{-1}$ , the uptake of Pb(II) ions by bark biomass decreased (Fig. 7(b)).

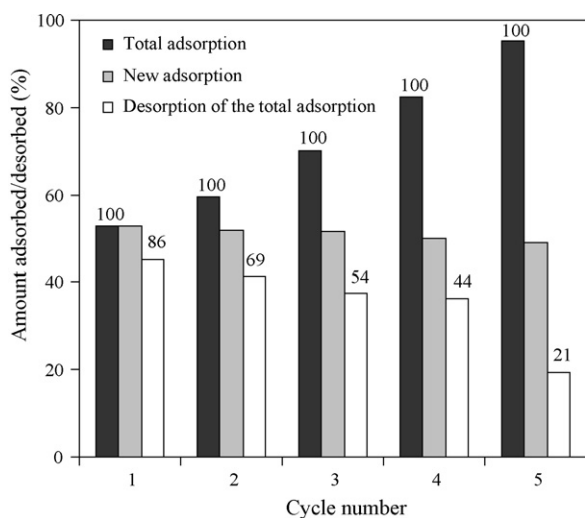


Fig. 6. Reuse of the bark for biosorption/desorption of Pb(II) ions (initial Pb(II) concentration:  $100\text{ mg L}^{-1}$ ; mass of bark:  $5.0\text{ g L}^{-1}$ ; initial pH: 4.0; desorption solution:  $10\text{ mL}$  of  $0.1\text{ M HCl}$ ).

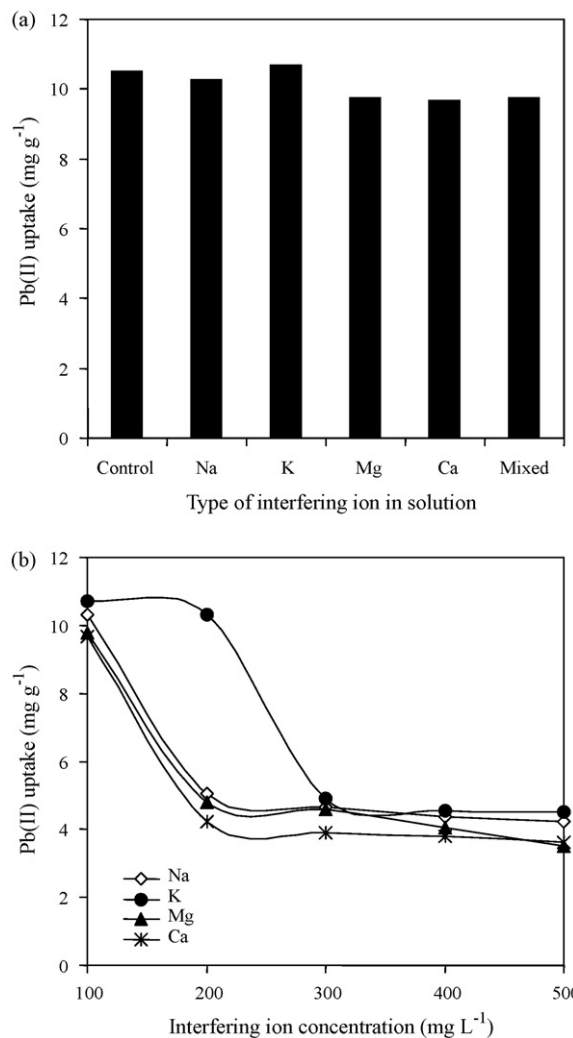


Fig. 7. (a) Effect of hard ions on Pb(II) uptake by bark (initial Pb(II) and hard ions concentrations:  $100\text{ mg L}^{-1}$  of each), (b) effect of increasing hard ions concentrations on Pb(II) uptake by bark (initial Pb(II) concentration:  $100\text{ mg L}^{-1}$ ).

### 3.9. Biosorption ability of bark for other heavy metals

Wastewaters such as industrial effluents may contain large amounts of various heavy metal ions. In addition to biosorption efficiency of Pb(II) ions on the biomass, biosorption capacity of pine bark was also tested for removal of the heavy metal ions Cu(II), Cd(II), and Ni(II) from aqueous solution. The metal solutions with  $100\text{ mg L}^{-1}$  initial concentrations containing  $5.0\text{ g L}^{-1}$  of bark were treated separately at pH 4.0. For single metal uptake, the results showed that pine bark was more sensitive to Pb(II) ions than the others. The following order of metal uptake per unit weight of bark was observed:  $Pb^{2+}$  ( $10.46\text{ mg g}^{-1}$ ) >  $Cu^{2+}$  ( $6.73\text{ mg g}^{-1}$ ) >  $Cd^{2+}$  ( $6.35\text{ mg g}^{-1}$ ) >  $Ni^{2+}$  ( $2.39\text{ mg g}^{-1}$ ).

## 4. Conclusions

Pine bark was found to be one of the most promising biosorbents for the removal of Pb(II) ions from aqueous solutions due to its low cost, easy availability, high metal uptake capacity, and reusability in repeated cycles. The biosorption process with bark was pH dependent. The kinetics of Pb(II) ion adsorption followed pseudo-second-order equation with  $R^2 > 0.99$ . The equilibrium data followed the linear Langmuir and Freundlich isotherm models well. The adsorbed amount of Pb(II) ions increased with increasing tem-

perature. The negative  $\Delta G^\circ$  values indicated that the biosorption of Pb(II) ions on the bark was feasible and spontaneous. The positive value of  $\Delta H^\circ$  confirmed the endothermic nature of biosorption. The bark biomass can be used at least five times for further biosorption processes with regeneration, and also without regeneration. In order to desorb the Pb(II) ions from metal-loaded bark, 0.1 M HCl solution was used as an eluent. The higher concentration of some interfering ions including  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  are efficient in suppressing Pb(II) uptake by bark biomass.

The results indicated that pine (*P. brutia* Ten.) bark without any pre-treatment can be used effectively for the removal of Pb(II) ions from aqueous solutions using present biosorption process.

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