Removal of Zn(II) and Pb(II) Ions by Calabrian Pine Bark Wastes

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Summary: In this study, the removal of Zn(II) and Pb(II) ions from aqueous solution by Calabrian pine (*Pinus brutia* Ten) bark wastes was investigated at different temperatures and concentrations at fixed pH. The amounts of Zn(II) and Pb(II) ions adsorbed onto the bark increased with increasing concentration. As temperature increased, the amount of Zn(II) ions adsorbed increased partially, and the amount of Pb(II) ions decreased slightly. The time required for the adsorption equilibrium of Zn(II) ions was found to be greater than that of Pb(II) ones. When reached adsorption equilibrium, approximate percentages of the metal ions removed by the bark were 64-74 for Zn(II) ions and 58-87 for Pb(II) ions at the concentrations studied, respectively. For both metal ions, kinetics studies showed that adsorption process followed the pseudo-second order kinetic model. While adsorption isotherm of Zn(II) ions obeyed both Langmiur and Freundlich models, that of Pb(II) ions did not follow the both models. Furthermore, the obtained thermodynamic parameters demonstrated that adsorption process was endothermic for Zn(II) ions and exothermic for Pb(II) ions.

Introduction

Industrial waste water streams containing tremendous amounts of heavy metal, such as Zn, Pb, Co, Cd, Ni, Cr, etc., which are of atomic density and related with toxicity, will seriously endanger public health and the environment if they were discharged without suitable treatment [1-4]. The heavy metals results from several anthropogenic sources such as metal extraction, metal fabrication, surface finishing, paints, pigments and the production of batteries, gasoline, toys, brass alloys, etc. [1]. The certain amounts of heavy metals are allowed to be used in irrigation and other kinds of water by legislation. For example, as required by EPA, maximum concentrations of zinc and lead metals in sewage sludge applied to agricultural land are 7500 and 420 mg/l, respectively [5].

The most common methods for the removal of the heavy metals are chemical precipitation, chemical oxidation, or reduction, electrochemical treatment, evaporative recovery, filtration, ion exchange and membrane technologies, adsorption on activated carbon, etc. [3, 4, 6]. However, these methods may not be satisfactory and economic and result in metal-bearing sludge [7]. Recently, researchers have extensively studied on the removal of the heavy metals by using biomass such as crab shell [7], cellulose [8] lignin [9-11], waste tea leaves [12], peanut shell [13], peat [14], bark [15, 16], banana and orange peels [17] etc. as biosorbents. This type of biosorption process may include chelation, complexation, adsorption and micro-precipitation as well [6].

To add value to tree bark, attention has been focused on the utilization of the bark as waste biosorbent [7, 15, 16]. The bark of tree, which are of low density, great volume forestry and agricultural waste and a complex chemical mixture of various organic compounds (e.g., cellulose, hemicellulose, lignin and, particularly, tannin-type extractives) [18], has been used as power fuel, erosion controller and slope stabilizer, odor scavenger in sulfate pulp mills and oil pollutant, mulch, and soil conditioner, phenol source in resol adhesives and polymer industries, etc. [18-20]. In addition, the substantial components (i.e., lignin and tannins, about more than 50%-based on oven-dry weight of the bark) of the pine bark contain

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aromatic phenolic rings bearing a large number of hydroxyl and methoxyl groups [18]. These groups are well known to act as excellent binding sites as well as cation exchange sites for heavy metals [9, 21, 22].

In this work, the bark of Calabrian pine was used as adsorbent for removal of Zn(II) and Pb(II) ions from aqueous solution. The effects of concentration and temperature on the removal of Zn(II) and Pb(II) ions by the bark and the kinetics of the adsorption were undertaken.

Results and Discussion

Figures 1 and 2 show the adsorption of Zn(II) and Pb(II) ions onto the bark wastes of Calabrian pine for different initial concentrations (varying from $2x10^{-4}$ to $4x10^{-4}$ M) of $ZnSO_4.7H_2O$ and $Pb(CH_3COO)_2.3H_2O$ at 30°C and pH 5 as a function of contact time, respectively. As one can see from Fig. 1, the absolute amount of Zn(II) ions adsorbed onto the bark increases with increasing contact time from 2 to about 40 min and then levels off with further increase in the time for all the concentrations undertaken. As shown in Figure 2, the absolute amount of Pb(II) adsorbed rises when changing contact time from 1 to 20 min for the initial concentrations of $2x10^{-4}$ and $3x10^{-4}$ M and thereafter becomes constant. Yet, the equilibrium time of the adsorption process is 15 min for the initial concentration of $4x10^{-4}$ M.

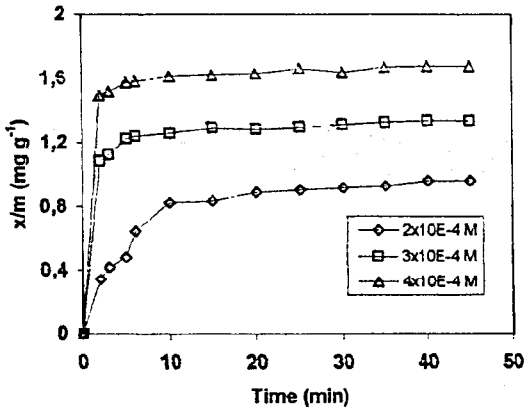

Fig. 1. Effect of initial adsorbate concentration on the adsorption of Zn(II) ions onto bark at 30°C.

It can be seen that the equilibrium time of Pb(II) ions is shorter than that of Zn(II) ions. This fact can be ascribed to the much more electronegativity of Pb(II) ions (1.9) compared with Zn(II) ones (1.6) to the bark. This is in the agreement with some studies performed on the removal of a variety of heavy metals by biomass wastes [25].

As depicted in Fig. 1, with changing the initial concentration of the aqueous solution of $ZnSO_4.7H_2O$ from $2x10^{-4}$ to $4x10^{-4}$ M, the absolute amount of Zn(II) ions adsorbed per unit of the bark increases from 0.96 (73.6%) to 1.68 mg/g (64.23%) at the temperature studied. As the initial concentration increases, the absolute amount of Zn(II) removed by the bark increases, and the percentage of the removal of Zn(II) ions decreases.

As also presented in Fig. 2, when increasing the initial concentration of the aqueous solution of $Pb(CH_3COO)_2.3H_2O$ from $2x10^{-4}$ and $4x10^{-4}$ M, the absolute amount of Pb(II) ions adsorbed per unit of the adsorbent goes up from 2.40 (58.01%) to 7.18 mg/g (86.72%). On contrast to Zn(II), the percentage of Pb(II) ions removed shows an increase in the initial concentration. The amount of Pb(II) ions removed by the bark was higher than that of Zn(II) ions. The same tendency was reported for the removal of Zn(II) and Pb(II) ions by modified peanut shells and various resins [13].

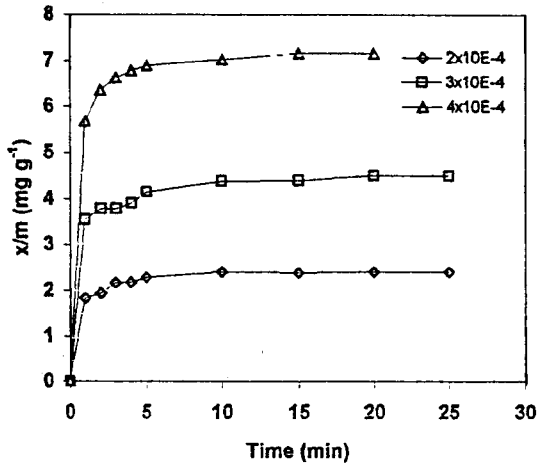

Fig. 2. Effect of initial adsorbate concentration on the adsorption of Pb(II) ions onto bark at 30°C.

Figs. 3 and 4 show the effect of temperature on the adsorption of both metal ions for initial concentration of $4x10^{-4}$ M as a function of contact

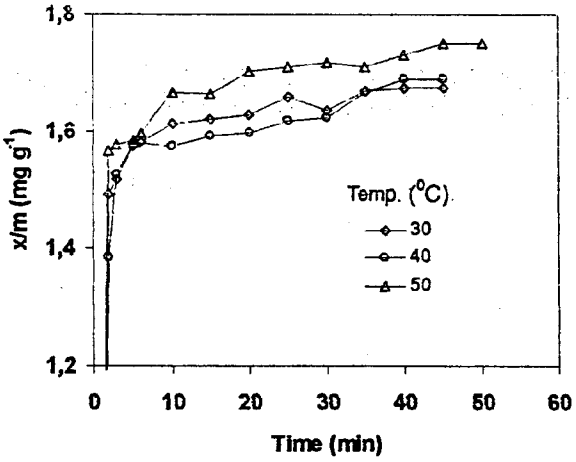

Fig. 3. Effect of temperature on the adsorption of Zn(II) ions onto bark for $4x10^{-4}$ M initial concentration.

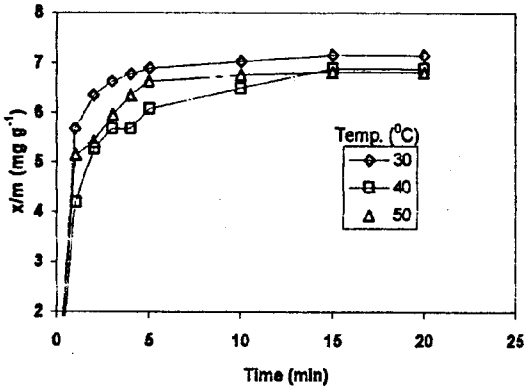

Fig. 4. Effect of temperature on the adsorption of Pb(II) ions onto bark for $4x10^{-4}$ M initial concentration.

time. It is obvious from the figures that the absolute amount of Zn(II) ions removed increases slightly when increasing temperature from 30 to 50°C at the conditions studied. However, the absolute amount of Pb(II) ions removed by the bark decreases with an increase in temperature, which may be explained by the escaping behavior of the Pb(II) ions at higher temperatures. The amount of Zn(II) ions adsorbed on the bark ranges between about 1.68 (64.23%) and 1.76 mg/g (67.38%) when changing temperature from 30 to 50°C (Fig. 3). In the case of Pb(II) ions, the adsorbed amount is found to be between about 7.18 (86.72%) and 6.86 mg/g (82%) at the same temperatures (Fig. 4).

The equilibrium time of Pb(II) adsorption on the bark is 15 min and independent from the temperature. And, the equilibrium time of adsorption of Zn(II) ions is 40 min at 30 and 40 °C, and 45 min at 50°C. Thermodynamic parameters estimated as a function of temperature will be presented in proceeding section. It is well-known fact that the reaction sites or functional groups of the bark are primary and secondary hydroxyls, carbonyls, carboxyls (esters), carbon-carbon, ether and acetal linkages [25].

Thus, the adsorption of heavy metals on the bark is due, most probably, to the displacement of H^+ of free hydroxyl groups on carbohydrate (cellulose and hemicellulose), lignin and tannins (particularly catechin) (Fig. 5a) and due to ionic bonds between ester groups on hemicellulose compound and metals as illustrated in Fig. 5b. Thus, the surface complex is said to be formed in the adsorption of the metals on the bark. As described in the kinetic section, the fact that the adsorption kinetics of both metal ions follows the pseudo-second order model indicates that a surface reaction or complex can be taken place between functional groups of the bark with metal ions.

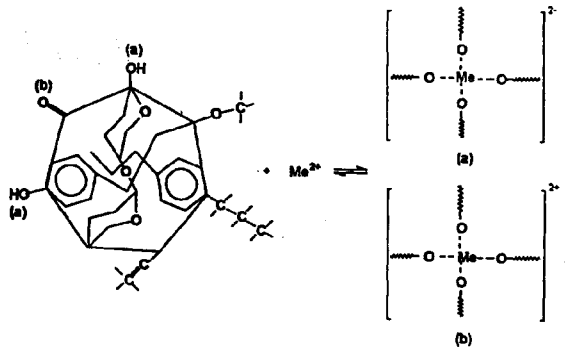

Fig. 5. Adsorption mechanism of metal ions onto functional groups of pine bark.

Specifically, Calabrian pine bark contains about 10% of low molecular weight flavanoids such as catechin in particular. For example, catechin will enable to complex with metal ions resulting in a chelated structure through its catechol rings of phenolic monomers [27] (Fig. 6).

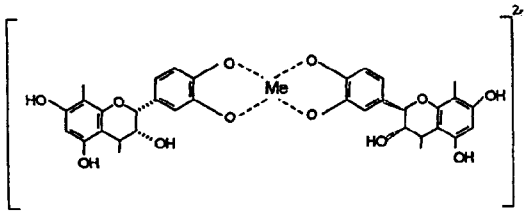

Fig. 6. The adsorption mechanism of metal ions on catechin.

The adsorption data obtained for Zn(II) and Pb(II) ions was investigated in terms of pseudo-first and-second order kinetic models given elsewhere [28, 29]. For both Zn(II) and Pb(II), the adsorption process is determined to follow a pseudo-second order kinetic model.

Pseudo-first order kinetic equations can be given as follows [28-30]:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad (1)$$

where, q_e is the amount of solute adsorbed at equilibrium per the unit weight of adsorbent (mg /g), q_t is the amount of solute adsorbed on the surface of the adsorbent at any time t (mg/g) and k_1 is the rate constant of pseudo-first adsorption (1/min).

As is known, the intercept of the straight line plots of log ($q_e - q_t$) *vs t* should be equal to. log (q_e). And, if the intercept value does not equal or is reasonably close to log (q_e), the reaction is not likely to obey a first order kinetic model, even at high correlation coefficient with experimental data [28]. For both metal cations, the values of k_1 were calculated from the slopes of plots of log ($q_e - q_t$) *vs t* (the relevant figures are not shown due to low correlation) at various initial concentrations of the metal ions and solution temperatures. The correlation coefficients (r_1^2) obtained are slow. Furthermore, the experimental q_e values are not found to have a good agreement with those calculated from the intercept of the linear plots (see Table 1). This indicates that the adsorption of metal ions onto the bark is not a pseudo-first order reaction.

On the other hand, the pseudo-second order kinetic model can be expressed as follows [28, 29]:

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

where, k_2 is rate constant for pseudo-second order reaction (g/mg min), q_e and q_t are the same as in the (Eq. 1). If adsorption obeys the pseudo-second order reaction, the plot of t/q_t *vs t* should be linear. Herein, such a linear line has been observed with a high correlation coefficient for the pseudo-second order model, and the plots obtained at different initial concentrations for both metal cations are shown in Figs. 7 and 8. However, the plots for different

Table 1. Kinetic Data Estimated from Pseudo-First and -Second Order Models for Zn(II) and Pb(II) at Different Initial Concentrations and Solution Temperatures

Parameters	Pseudo First-order kinetic model				Pseudo Second-order kinetic model			
	q_e (exp) (mg g^{-1})	k_1 (min^{-1})	q_e (cal.) (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (cal.) (mg g^{-1})	R^2	Metal Cation
$C_{init.}$ [a](M)								
$2x10^{-4}$	0.963	0.0875	0.568	0.93	0.2370	1.026	0.9976	Zn(II)
$3x10^{-4}$	1.334	0.0262	0.865	0.79	1.1506	1.347	0.9998	Zn(II)
$4x10^{-4}$	1.680	0.0156	1.195	0.79	1.1845	1.685	0.9998	Zn(II)
Temp[b]. (°C)								
30	1.680	0.0156	1.195	0.79	1.1845	1.685	0.9997	Zn(II)
40	1.692	0.0502	0.232	0.81	1.1905	1.696	0.9994	Zn(II)
50	1.758	0.0541	0.210	0.93	1.1968	1.766	0.9998	Zn(II)
$C_{init.}$ [a](M)								
$2x10^{-4}$	2.40	0.224	0.616	0.93	1.061	2.44	0.9999	Pb(II)
$3x10^{-4}$	4.49	0.169	1.027	0.91	0.422	4.58	0.9997	Pb(II)
$4x10^{-4}$	7.18	0.254	1.283	0.89	0.162	7.24	1	Pb(II)
Temp[b]. (°C)								
30	7.18	0.254	1.283	0.89	0.162	7.24	1	Pb(II)
40	6.92	0.196	2.548	0.94	0.169	7.17	0.9996	Pb(II)
50	6.86	0.381	2.362	0.94	0.332	6.95	0.9999	Pb(II)

[a]Values obtained at 30°C, [b]Values obtained for initial concentration of $4x10^{-4}$ M.

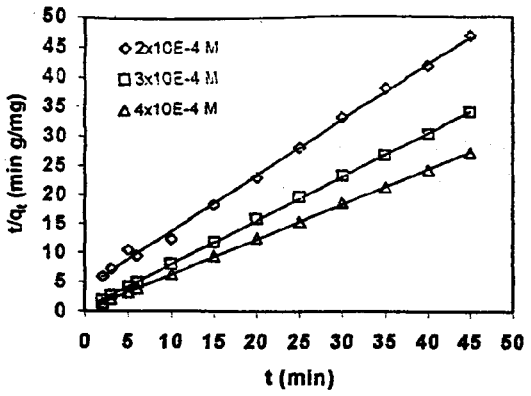

Fig. 7. Pseudo-second order kinetics fit of Zn(II) adsorption data onto bark for different initial concentrations at 30°C.

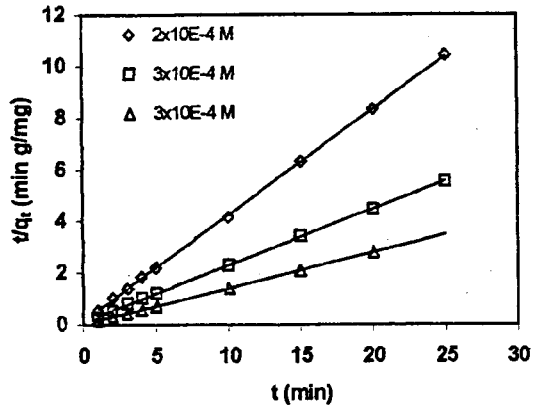

Fig. 8. Pseudo-second order kinetics fit of Pb(II) adsorption data onto bark for different initial concentrations at 30°C.

solution temperatures have not been illustrated here because of overlapping the data.

The pseudo-second order rate constants (k_2) and q_e values were calculated from the intercept and the slopes of the plots of t/q_t *vs* t, respectively. The linear plots of t/q_t against t show a good agreement with experimental data under conditions studied.

As shown from Table 1, the correlation coefficients from the pseudo-second order model are greater than those of the pseudo-first order model, and they range between 0.997-1. Moreover, the calculated q_e values agree with the experimental data very well. These indicate that adsorption follows the pseudo-second order kinetic model. Similar kinetic results were also reported for the adsorption of Cu(II) and Pb(II) onto bottom ash [31] and the adsorption of Cd(II) onto reed leaves [32].

Since the determination of adsorption isotherm is important in designing the nature of adsorption system, several isotherm equations have been applied in this study. In this study, the Langmiur and Freundlich isotherms have been evaluated. In this section, isotherm studies were performed at 5 different concentrations, namely, $2x10^{-4}$, $2.5x10^{-4}$, $3x10^{-4}$, $3.5x10^{-4}$ and $4x10^{-4}$ M. The experimental data are fitted to Langmiur and Freundlich equations. On the basis of these isotherm equations, the adsorption of Zn(II) ions from aqueous solution onto the bark has a good agreement with both the Langmiur and Freundlich isotherms, while the adsorption of Pb(II) ions follows neither Langmiur nor Freundlich isotherm.

The rearranged Langmiur isotherm is given in the following equation [2, 8, 33]

$$C_e/x/m = 1/Q_0b + C_e/Q_0 \quad (3)$$

where, x/m is the amount of metal ions adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of metal ions (mg/l), Q_0 and b are Langmiur constants, which are the adsorption capacity (mg/g) and energy of adsorption (l/mg), respectively.

The Langmiur isotherm thus obtained at different temperatures is shown in Fig. 9. As one can see from this figure, the adsorption of Zn(II) ions on

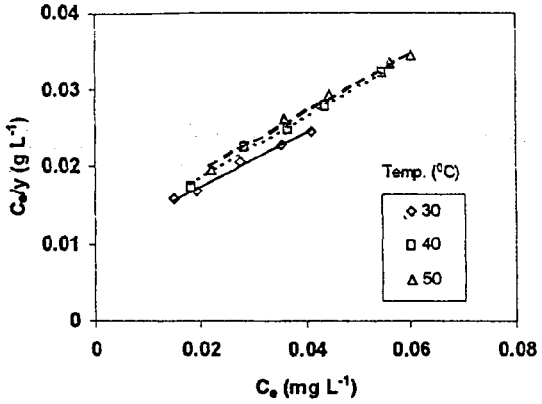

Fig. 9. Langmiur isotherm of Zn(II) adsorption at different temperatures.

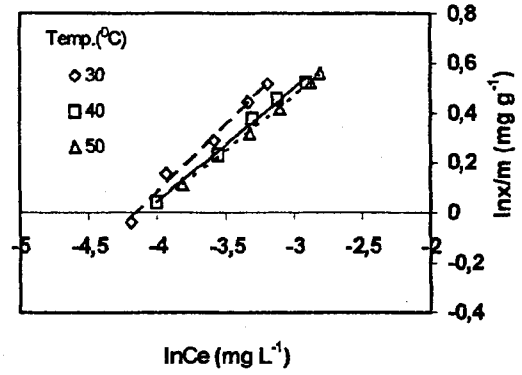

Fig.10. Freundlich isotherm of Zn(II) adsorption at different temperatures.

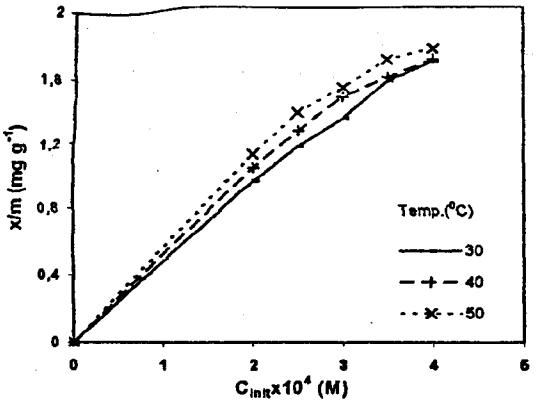

Fig. 11.Adsorption isotherm of Zn(II) at different temperatures.

the bark follows Langmiur isotherm evidently, having a 99%-correlation coefficient for all temperatures. The values of Q_0 and b were determined from the slope and intercept of the plots of $C_e/x/m$ against C_e, respectively. The constant values obtained for Langmiur isotherm are presented in Table 2. Moreover, the adsorption isotherm of Zn(II) is illustrated in Fig. 11.

On the other hand, Freundlich isotherm is expressed by the following equation [8, 34]

$$\ln x/m = \ln k + 1/n \ln C_e \quad (4)$$

where, k (mg/g) and n (g/l) are Freundlich constants.

The Freundlich isotherm at various temperatures is demonstrated in Fig. 10. It is obvious from this figure that with a 99%-correlation coefficient for all temperatures, the adsorption of Zn(II) on the bark complies with the Freundlich isotherm. The values of n and k were calculated from the slopes and intercepts of the plots of ln x/m *vs* ln C_e, respectively. The constant values determined for Freundlich isotherm are presented in Table 2. As listed in this table, the fact that the adsorption of Zn(II) onto the bark obeys Langmiur and Freundlich isotherms shows the monolayer coverage of Zn(II) ions on the outer surface of the adsorbent.

Table 2. Langmiur and Freundlich Constants of Zn(II) Ions at Different Solution Temperatures

T (°C)	Q_0 (mg g^{-1})	b (L mg^{-1})	k (mg g^{-1})	n (g L^{-1})
30	2.47	32.50	9.392	1.86
40	2.51	32.75	6.428	2.20
50	2.60	32.87	5.981	2.27

In the case of Pb(II) adsorption, the monolayer coverage cannot be mentioned because the adsorption does not follow both isotherms. However, as can easily be seen from the adsorption isotherm of Pb(II) in Fig.12, the adsorption is in the multi-layer form.

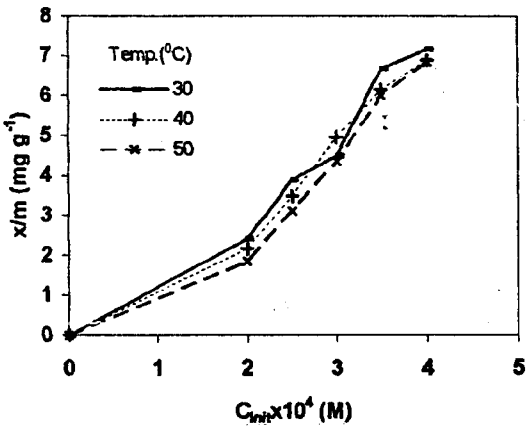

Fig. 12.Adsorption isotherm of Pb(II) at different temperatures.

In order to understand the effects of temperature on the adsorption well, the various thermodynamic parameters, i.e., standard free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°), related with adsorption of Zn(II) and Pb(II) ions onto the bark were determined by using the following equations [2, 8, 23, 33]:

$$\Delta G^\circ = -RT\ln K_c \quad (5)$$

$$\Delta H^\circ = R(T_1.T_2/T_2-T_1)\ln(K_{c2}/K_{c1}) \quad (6)$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T \quad (7)$$

where, R is the gas constant, K_c is the equilibrium constant and k_{c1} and k_{c2} are equilibrium constants at T_1 and T_2 temperatures, respectively.

The equilibrium constant K_c at various temperatures was determined from the following equation [8, 33]:

$$K_c = \frac{C_{Ae}}{C_{Se}} \quad (8)$$

where, C_{Ae} and C_{Se} are the equilibrium concentrations of metal ions on the adsorbent (mg/l) and in solution (mg/l), respectively.

Table 3 indicates the values of thermodynamic parameters stated above for both metal ions. For the adsorption of Zn(II) and Pb(II) ions on the bark, the negative values of ΔG° obtained at various temperatures show the spontaneous nature of the adsorption process. Also, it is evident from the same table that while the positive values of ΔH° estimated for the Zn(II) adsorption on the bark reveal the adsorption to have endothermic nature, the negative values of ΔH° determined for Pb(II) adsorption suggest the adsorption to be exothermic. The values of K_c obtained for both metal ions confirm the adsorption nature (see Table 3). As shown in Table 3, the K_c values estimated for Zn(II) is lower than those of Pb(II).

Table 3. The Thermodynamic Parameters for the Adsorption of Zn(II) and Pb(II) Ions onto Calabrian Pine Bark at Different Temperatures

Metal ions	*Temp. (°C)*	K_c	ΔG° *(J mol^{-1})*	ΔH° *(J mol^{-1})*	ΔS° *(J mol^{-1} K^{-1})*
Zn(II)	30	1.77	-1438	2196	12.00
Zn(II)	40	1.82	-1558	9178	33.30
Zn(II)	50	2.03	-1901	—	—
Pb(II)	30	6.38	-4668	-19851	-50.10
Pb(II)	40	4.96	-4167	-4884	-2.290
Pb(II)	50	4.68	-4144	—	—

Furthermore, the positive values of ΔS° obtained for the adsorption of Zn(II) ions show that some structural exchanges may occur among the active sites of the adsorbent and the metal ions (Table 3). Also, the negative values of ΔS° calculated for Pb(II) adsorption indicate the quicker interaction of active surface of adsorbent with the Pb(II) ions.

Experimental

The bark wastes of Calabrian pine (*Pinus brutia* Ten) species used as adsorbent were provided from sawmill (Veziroglu Co.) established in the province of Kahramanmaras, Turkey. And then, bark purified from dust was grounded by using Waley-Mil. The bark powders passed (Moisture content: 12%) through 100-mesh sieve were utilized for adsorption experiments. Zn(II) stock solutions were prepared from an analytical-grade sulfate salt, i.e., zinc sulfate heptahydrate ($ZnSO_4.7H_2O$) and Pb(II) stock solutions were prepared from an analytical-grade acetate salt, i.e., lead acetate trihydrate ($Pb(CH_3COO)_2.3H_2O$). In the preparation of the aqueous solution of the cations, distilled water was used. As described in elsewhere [13, 23, 24], pH values of aqueous solutions of $ZnSO_4.7H_2O$ and $Pb(CH_3COO)_2.3H_2O$ were adjusted to 5 by dropping of sulfuric and acetic acids using a pH meter (WTW pH Meter 320, Germany), respectively.

Batch adsorption experiments were performed using 0.50 g of the pine bark with 50 ml of $ZnSO_4.7H_2O$ and $Pb(CH_3COO)_2.3H_2O$ aqueous solutions in 250-mL erlenmeyer flasks, of which concentrations, pH and temperature have already been known. The samples were shaken at 125 rpm in a temperature-controlled shaking water bath. After reaching contact time, suspensions were filtered by filter paper (Selecta filter, 589^2 Weißband, Germany). The filtrate was analyzed for Zn(II) and Pb(II) ions by using an atomic absorption spectrometer (Perkin Elmer spectrometer 3110). Blank solutions containing no cations were used for each series of experiments. The amounts of Zn(II) and Pb(II) adsorbed were calculated from by subtracting both concentration of Zn(II) and Pb(II) ions adsorbed onto the filter paper used herein and final solution concentration from the initial concentrations of aqueous solutions. For each adsorption process, the average of two replications was reported.

Acknowledgement

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