Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions

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Abstract

In this study, the adsorption conditions of Cu(II), Pb(II) and Cd(II) metal ions onto sporopollenin have been studied. The different variables effecting the sorption capacity such as pH of the solution, adsorption time, initial metal ion concentration and temperature have been investigated. Adsorption isotherms correlated well with the Freundlich type adsorption isotherm and adsorption capacities were found to be 0.0195, 0.0411 and 0.0146 mmol g^{-1} for Cu(II), Pb(II) and Cd(II) metal ions, respectively. Experimental data were also evaluated to find out kinetic characteristics of the adsorption process. Adsorption processes for three target heavy metal ions were found to follow pseudo-second order type adsorption kinetics. Intraparticle diffusion was found to take part in adsorption processes but it could not be accepted as the primary rate-determining step. The mean free energies of adsorption (E) were found to be between 8 and 16 kJ mol^{-1} for the metal ions studied and therefore adsorption mechanism for the adsorbent was explained as an ion-exchange process. But it was observed that chelating effect is also playing an important role in the adsorption of metal ions onto sporopollenin.

Thermodynamic parameters, ΔH°, ΔS° and ΔG° were also calculated from graphical interpretation of the experimental data. Standard heats of adsorption (ΔH°) were found to be endothermic and ΔS° values were calculated to be positive for the adsorption of Cu(II), Pb(II) and Cd(II) ions onto the adsorbent. Negative ΔG° values indicated that adsorption process for these three metal ions onto sporopollenin is spontaneous.
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1. Introduction

Environmental pollution arisen from industrial waste streams as a consequence of the industrialization process is one of the major problems that has to be solved or controlled. Many industrial facilities such as metal plating, mining operations, fertilizer industry, tanneries, textile industries discharge heavy metals via their waste effluents [1,2]. The disposal of these effluents into natural water resources causes damage to the aquatic environment and in humans some of these metals, even in small amounts can cause severe physiological and health effects [3,4]. Therefore, heavy metals are permitted to be discharged only a very low concentrations in waste waters to prevent public streams and water resources from becoming contaminated.

Conventional methods for the removal of heavy metal ions from waste streams include chemical precipitation, membrane filtration, ion exchange, carbon adsorption and coprecipitation/adsorption. But these methods have some disadvantages. Conventional precipitation method does not always provide a satisfactory removal rate to meet the pollution control limits and synthetic ion-exchange resins are often subjected to be expensive [1,5]. Therefore the need for cost effective alternative technologies or sorbents for treatment of metals from the waste streams resulted in search for unconventional methods and materials. Alternative cost effective adsorbents are also important for preconcentration and determination of the metal ions in analytical applications. Natural materials that are available in large quantities, or certain waste products from industrial waste or agricultural operations, may have potential as inexpensive sorbents [1]. Bailey et al. has reviewed those low cost adsorbents including bark/tannin-rich materials, lignin, chitin/chitosan, dead biomass, etc. [1].

Sporopollenin is a natural biopolymer which occurs in the outer membranes of moss and fern spores and most pollen grains [6]. It has been shown that spore and pollen membranes have two layers, an inner one known as intine, and an outer one containing

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a material which the name sporopollenin was given, the exine [7]. Sporopollenin is highly resistant to chemicals, is stable has a constant chemical structure and exhibits very good stability after even prolonged exposure to mineral acids and alkalis [8]. The mechanism of its synthesis and its consolidation are not yet understood [9]. Infra-red and ^{13}C NMR spectroscopic studies on sporopollenin derived from pteridophyta and spermatophyta have shown that sporopollenin has aliphatic, aromatic, hydroxyl, carbonyl/carboxyl and ether functions in various portions in its polymeric structure [10].

In past two decades modified forms of sporopollenin have been utilized as anion, and ligand exchangers [11–13], and as cation exchangers for removal of heavy metal ions from aqueous solutions [14,15]. Only a few studies have been done on sporopollenin itself for removal of heavy metal ions. Yiğitoğlu and Arslan [16] studied Cu(II) ion adsorption onto sporopollenin from *Lycopodium clavatum* spores and the highest adsorption capacity was reported as 3.4×10^{-2} mM Cu(II)/g sporopollenin. They also studied the effect of temperature on adsorption and copper ion adsorption is reported to decrease with increasing temperature. Arslan et al. [17] reported the removal of Cd(II) from aqueous solutions using sporopollenin from *L. clavatum* spores. They found the adsorption capacity as 82.3 μmol g^{-1} and adsorption process was reported as an endothermic process in that case. There is still need to clarify dynamics and thermodynamics of the adsorption of heavy metal ions onto sporopollenin itself.

In this study, the feasibility of removal of heavy metal ions from aqueous solutions by sporopollenin was investigated. Sporopollenin with its polymeric structure would be a candidate sorbent as a low cost adsorbent for removal of heavy metals from aquatic media or analytical preconcentration determination purposes. In the present study the adsorption conditions of heavy metal ions (Pb(II), Cu(II) and Cd(II)) onto sporopollenin has been investigated and also the nature of the adsorption process with respect to its kinetic and thermodynamic aspects were evaluated. Sporopollenin of *L. clavatum* spores is used for these purposes.

2. Materials and methods

2.1. Materials

The resin used was *L. clavatum* spores (sporopollenin) with 20 μm particle size mesh obtained from Fluka Chemicals. *L. clavatum* spores were used as the resin material in the adsorption studies without any chemical treatment. All the other reagents used were of analytical reagent grade (Merck). Metal salts of $CuCl_2 \cdot 2H_2O$, $Pb(NO_3)_2$, $CdCl_2 \cdot H_2O$ were used to prepare metal ion solutions. The solutions (1000 mg/L) were prepared by dissolving appropriate amounts of metal salts in doubly distilled water. The working solutions were prepared by diluting the stock solutions to appropriate volumes. Heavy metals are often present in industrial waste waters together with complex forming organic compounds. Under these conditions various metal ligand complexes are formed and consequently the removal and the recovery of heavy metal cations from aqueous solutions and

their separation from complexing compounds is very complicated because of the high stability constants of these complexes [18]. Therefore adsorption studies are conducted in an acetic acid–acetate medium as the representative of complexing agent. In all experimental conditions 0.1 M of acetic acid–sodium acetate medium was also used to maintain an approximate equal ionic strength for the working solutions.

2.2. Sorption experiments

All the adsorption equilibrium experiments were conducted batchwise; the sorption equilibrium was attained by shaking 0.5 g of sporopollenin in 30 mL of aqueous solutions containing metal ions which were shaken at 100 rpm for a predetermined time period. Adsorption experiments were carried out in an incubator at controlled temperature. After the predetermined adsorption time, solution was filtered and the metal ion concentrations were measured. Initial and equilibrium metal ion concentrations in the aqueous solutions were determined by using a UNICAM 930 model flame atomic absorption spectrometer equipped with deuterium lamp background correction, Hallow Cathode Lamp and air acetylene burner. Initial pH of the solutions was adjusted to desired pH by adding hydrochloric acid or sodium hydroxide solutions to the medium to maintain a constant pH. A JENWAY 3010 model pH meter was used to adjust a desired pH value. The pH of the solution was buffered only between the pH values of 4 and 5.5. Temperature experiments were carried out between 20 and 65 °C at optimum pH values for each metal ions. Experiments were repeated three times in each case. The amount of sorbed metal ion was calculated from the change in the metal concentration in the aqueous solution before and after equilibrium and the weight of the dry sporopollenin. The amount of metal ion adsorbed by sporopollenin was calculated as

$$q = \frac{(C_0 - C)V}{W}$$

where q is the amount of metal ions adsorbed onto unit amount of the resin (mmol g^{-1}), C_0 and C the concentrations of metal ions in the initial and equilibrium concentrations of the metal ions in aqueous phase (mmol L^{-1}), V the volume of the aqueous phase (L), and W is the dry weight of the resin (g).

3. Results and discussion

3.1. Effect of pH

The pH of a solution is an important parameter in adsorption process because of the pH dependencies of the complexation reactions or electrostatic interactions in physisorption processes at the adsorption surface. Since sporopollenin with its polymeric structure has aliphatic, aromatic, hydroxyl, carbonyl/carboxyl and ether functional groups in various portions, pH dependencies of the metal ions have to be determined. Thus, the effect of pH on adsorption capacities of heavy metal ions were examined by varying the initial pHs of the solutions with different pH intervals depending on the metal ions studied. The initial concentrations of metal ions were taken as 10, 20, 30 mg/L for
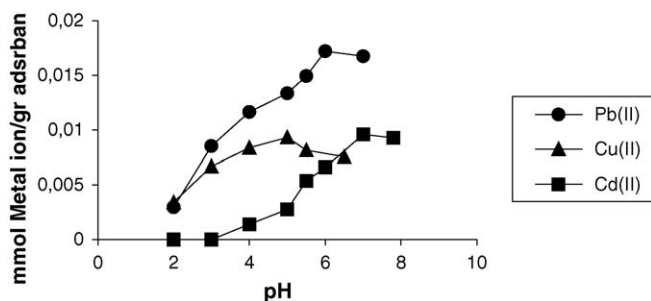
Fig. 1. The effect of pH on the sorption of Cu(II), Pb(II) and Cd(II) metal ions. [●, Pb(II)] $C_0 = 20$ mg L^{-1}; [▲, Cu(II)] $C_0 = 10$ mg L^{-1}; [■, Cd(II)] $C_0 = 30$ mg L^{-1}; t: 120 min; m(sporopollenin): 0.5 g; medium: 0.1 M acetic acid–acetate; temperature: 20 °C.

Cu(II), Pb(II) and Cd(II), respectively. Variation of the metal uptake with pH has shown in Fig. 1. The adsorption capacities were found to be low at lower pH values and increased with increase in pH. This can be explained with competitive adsorption of HO$_3^+$ ions and metal ions for the same active adsorption site. As the pH increased, the adsorption surface becomes less positive and therefore electrostatic attraction between the metal ions and sporopollenin surface is likely to be increased. And also this may be further explained with the functional groups present on sporopollenin. Those functional groups should probably take part in metal uptake process by complexation which is pH-dependent, and the nature of the active sites and sorbate may change with pH [19]. The optimum pH values at which the maximum metal uptake could be achieved, were obtained as 5.0, 6.0 and 7.0 for Cu(II), Pb(II) and Cd(II) metals, respectively. For all subsequent experiments, these optimum pH values were used.

3.2. The effect of contact time and sorption kinetics

Metal ion uptake capacities were determined as a function of time to determine an optimum contact time for the adsorption of heavy metal ions on sporopollenin. Fig. 2 shows time course of the adsorption equilibrium of Cu(II), Pb(II) and Cd(II) metal ions onto sporopollenin. As it can be seen from the figure, there is a rapid uptake kinetics within 20 min and adsorption equilibria are attained within 1 h. It is also possible to say that adsorption equilibrium is attained within the first 30 min. Therefore 1 h of contact time was chosen as the optimum equilibration time for
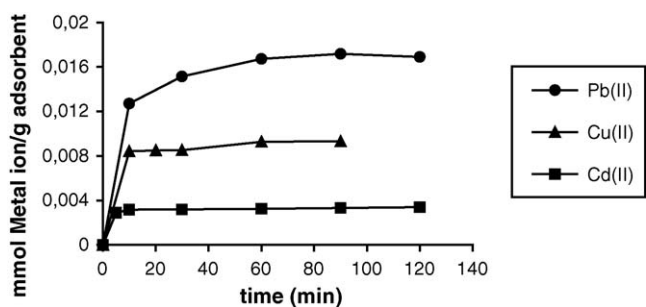
the experimental studies unless otherwise stated, to ensure that equilibrium condition was achieved. Kinetic characteristics in a chelating polymer depends not only on the presence of chelating functional groups on it but also depends on the accessibility of the functional groups without sterical hindrance which is greatly determined by the polymeric matrices. And the sorbents with the best characteristics are those based on hydrophilic macroporous structures [20]. Sporopollenin's porous, hydrophilic structure [21], which shows good permeability functionality depending on stokes' radius of the molecule [22], and easily available chelating functional groups on it are thought to be responsible for this rapid uptake kinetics.

There are several parameters which determine sorption rate, like structural properties of the sorbent (size, surface area, porosity), metal ion properties (e.g. hydrated ionic radius), initial concentration of metal ions, pH, temperature, chelate formation rate or presence of the competing ions [23]. Therefore, it is difficult to make a comparison between the sorbents. In our study, time required to attain equilibria for the adsorption of Cu(II), Pb(II) and Cd(II) metal ions onto sporopollenin is seemed to be suitable from kinetic considerations when compared with the results stated in the literature where time required to attain equilibrium ranged from 30 min to 7 h [24].

It is known that adsorption process could be dependent on and controlled with different kinds of mechanisms, like mass transfer, diffusion control, chemical reactions and particle diffusion. In order to clarify the adsorption process, several adsorption models were applied to evaluate the experimental data. For this purpose Lagergren's pseudo-first-order kinetic model, pseudo-second-order kinetic model and intra particle diffusion model were used.

3.2.1. First-order kinetics
The linearized form of the first-order rate equation by Lagergren and Svenska [25] is given as

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} \times t$$

where q_e and q_t are the amounts of the metal ions adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively and k_{ads} is the adsorption rate constant (min^{-1}). The plots of $\log(q_e - q_t)$
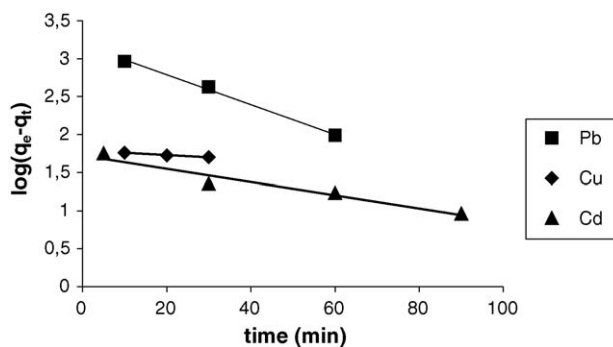

Fig. 2. Adsorption rates of heavy metal ions onto sporopollenin. [●, Pb(II)] $C_0 = 20$ mg L^{-1}, pH 6.0; [▲, Cu(II)] $C_0 = 8$ mg L^{-1}, pH 5.0; [■, Cd(II)] $C_0 = 18$ mg L^{-1}, pH 7.0; m(sporopollenin): 0.5 g; medium: 0.1 M acetic acid–acetate; temperature: 20 °C.

Fig. 3. Lagergren's pseudo-first-order plots for heavy metal ions on sporopollenin. [■, Pb(II)] $C_0 = 20$ mg L^{-1}, pH 6.0; [♦, Cu(II)] $C_0 = 8$ mg L^{-1}, pH 5.0; [▲, Cd(II)] $C_0 = 18$ mg L^{-1}, pH 7.0; m(sporopollenin): 0.5 g; medium: 0.1 M acetic acid–acetate; temperature: 20 °C.

Table 1
First-order, second-order and intraparticle diffusion rate constants

Metal	q_e(exp.) (mg g^{-1})	First-order rate constants			Second-order rate constants			Intraparticle diff rate constant	
		k_{ad} (min^{-1})	q_e(theor.) (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e(theor.) (mg g^{-1})	R^2	k_{id} (µg g^{-1} min$^{-1/2}$)	R^2
Cu	0.592	0.00668	0.0614	0.9788	0.735	0.605	0.998	3.12	0.9923
Pb	3.563	0.0456	1.54	0.9964	0.054	3.75	0.9996	181.64	0.9864
Cd	0.382	0.0200	0.0529	0.9444	3.07	0.374	0.9998	5.26	0.9919

versus t gives a straight line and the rate constants (k_{ads}) can be calculated from the slope. In Fig. 3 Lagergren's plots are given. In fact, it is required that calculated equilibrium adsorption capacity values, q_e(theor.), should be in accordance with the experimental q_e(exp.) values [26]. Experimental and theoretically calculated q_e values and coefficients related to Lagergren's plots are given in Table 1. As it can be seen from the results that the linear correlation coefficients, except for Pb, of the plots are not good and experimental and calculated q_e values are not in agreement with each other. So, these results suggest that the adsorption of Cu(II), Pb(II) and Cd(II) metal ions on sporopollenin is not a first-order reaction.

3.2.2. Second-order kinetics

Experimental data were also applied to the pseudo-second-order kinetic model which is given with the equation below:

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

where k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order adsorption reaction. Second-order kinetic is said to be applicable if the plot of t/q_t versus t shows linearity. Also this procedure is more likely to predict the behaviour over whole range of adsorption and is in agreement with chemical sorption being the rate-controlling step [26,27]. The graphical interpretation of the data for the second-order-kinetic model is given in Fig. 4. The rate constants (k_2), correlation coefficients of the plots together with the experimental and theoretical q_e values are given in Table 1. It is clear from these results that the correlation coefficients are very high and experimental and theoretical q_e values are in accordance with each other. These results sug-
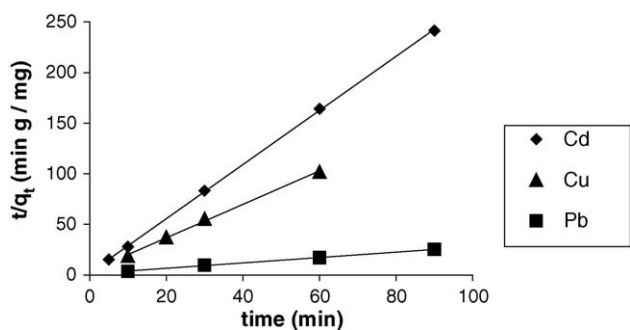
gest that the adsorption of the metal ions [Cu(II), Pb(II) and Cd(II)] on sporopollenin follows the second-order type kinetic reaction. This result can be expected because the ordinary type of exchange processes are more rapid and controlled mainly by diffusion, whereas, those in a chelating exchanger are slower and controlled either by particle diffusion mechanism or by a second-order chemical reaction [20]. Sporopollenin with its polymeric porous structure and chelating functional groups present on its surface most probably behaves like a chelating exchanger. Therefore second-order chemical reaction kinetics is expected to be followed in the adsorption processes.

3.2.3. Intraparticle diffusion

The adsorption process on porous sorbents generally described with four stages, and one or more of which may determine the rate of adsorption and amount of adsorption on the solid surface. Those stages are described as bulk diffusion, film diffusion, intraparticle diffusion and finally adsorption of the solute on the surface. Generally bulk diffusion and adsorption steps are assumed to be rapid and therefore not rate determining [19,28]. Mass transfer within the resin particles can be complex, as adsorption is inherently a transient process involving some short-range diffusion in both the fluid and adsorbed phases. For porous surfaces such as Al, Fe, and Mn oxides, where the average pore size is greater than or equal to 1.9 nm, the distribution falls into IUPAC classification of micro- and meso-pores which is based on gas liquid systems. However in the aqueous phase, pore surfaces are hydrated, resulting in potentially layers of water adsorbed to these pore walls. Therefore mesopores may act as micropores [29]. Both pore and surface diffusion may play a role in the liquid phase adsorption on macroporous adsorbents [30]. Since, because sporopollenin has a porous structure, kinetic studies have to be investigated to find out the effects of intraparticle diffusion to the adsorption process.

Intraparticle diffusion model is expressed with the equation given by Weber and Morris [31]:

$$q_t = k_{id} t^{1/2}$$

where q_t is the amount of metal ions adsorbed at time t (µg g^{-1}) and k_{id} is the intraparticle diffusion rate constant (µg g^{-1} min$^{-1/2}$). Plots of q_t versus t are shown in Fig. 5a and b.

As it can be seen from the figures that there is not a linear distribution of the points. For Cu(II) and Cd(II) the plots have an initial curved portion followed by a linear line and a plateau. Initial curved (as in the case for copper) or steep-sloped linear portion (as in the case for cadmium) was not observed for

Fig. 4. Pseudo-second-order plots for heavy metal ions on sporopollenin. [■, Pb(II)] $C_0 = 20$ mg L^{-1}, pH 6.0; [♦, Cu(II)] $C_0 = 8$ mg L^{-1}, pH 5.0; [▲, Cd(II)] $C_0 = 18$ mg L^{-1}, pH 7.0; m(sporopollenin): 0.5 g; medium: 0.1 M acetic acid–acetate; temperature: 20 °C.
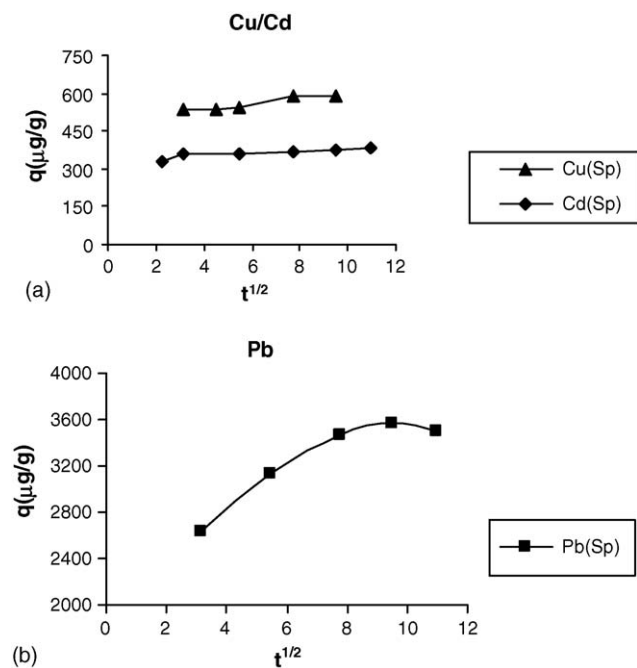
Fig. 5. Intraparticle diffusion plots for heavy metal ions on sporopollenin.

Fig. 6. Effect of initial concentration on heavy metal adsorption on sporopollenin. [$\bullet$, Pb(II)] pH 6.0; [$\blacktriangle$, Cu(II)] pH 5.0; [$\blacksquare$, Cd(II)] pH 7.0; m(sporopollenin): 0.5 g; t: 60 min; medium: 0.1 M acetic acid–acetate; temperature: 20 °C.

Pb(II). Initial curved or steep-sloped portion represents the bulk diffusion or exterior adsorption rate which is very high, the subsequent linear portion is attributed to the intraparticle diffusion and plateau portion represents the equilibrium. The intraparticle diffusion constants were calculated from the slopes of the linear portions of the curves and given in Table 1. The results showed that intraparticle diffusion, which may play an important role as a rate determining step in the adsorption process, was observed to be effective especially for the adsorption of Cd(II) and Cu(II). Intraparticle diffusion rate constant is much higher for Pb(II) with respect to Cd(II) and Cu(II) because of its relatively small hydrated radius. But because of the deviation of the curves from the origin and non-linear distribution of the plots, intraparticle diffusion cannot be accepted as the only rate-determining step for the adsorption of those target heavy metal ions onto sporopollenin. The same types of results are also given in some works [19,32].

3.3. Effect of initial concentration and sorption isotherms

The effect of initial concentrations on metal ion uptake was investigated by varying the initial concentrations of the metal ions at optimum pH values and 1 h of equilibration time. As it can be seen from Fig. 6 that, the adsorption capacities were increased with increasing the initial concentrations and reached a plateau which represents the maximum adsorption capacity of resin. This increase in loading capacity of the sorbent with relation to the metal ions concentration can be explained with the high driving force for mass transfer. In fact, the more concentrated the solution is the better the adsorption is.

Equilibrium adsorption isotherms relate the adsorbate concentration in the bulk and the adsorbed amount on the interface. The a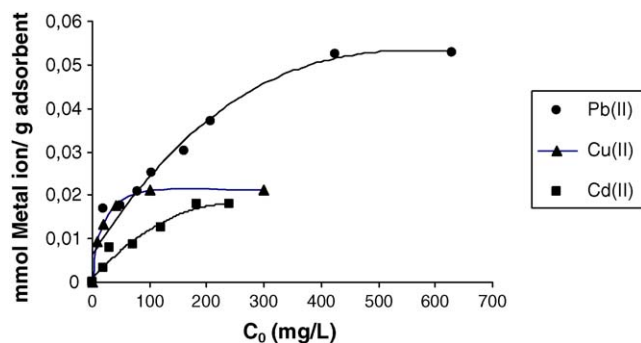nalysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes [33]. Experimental data obtained from the effect of initial concentration on adsorption capacity were evaluated with the three popular adsorption models which are Langmuir, Freundlich and D-R models. The linearized forms of the equations representing the models were used.

3.3.1. Langmuir isotherm

Langmuir isotherm which models the monolayer coverage of the adsorption surface. This model assumes that adsorption occurs at specific homogeneous adsorption sites within the adsorbent and intermolecular forces decrease rapidly with the distance from the adsorption surface. The Langmuir adsorption model further based on the assumption that all the adsorption sites are energetically identical and adsorption occurs on a structurally homogeneous adsorbent. Linearized form of the Langmuir equation based on those assumptions is given as [34]:

$$\frac{1}{q_e} = \frac{1}{Q^0} + \frac{1}{bQ^0C_e}$$

where q_e is the amount of solute adsorbed on the surface of the adsorbent (mmol g^{-1}), C_e is the equilibrium ion concentration in the solution (mmol L^{-1}), Q^0 is the maximum surface density at monolayer coverage and b is the Langmuir adsorption constant (L mmol^{-1}). The plots of $1/q_e$ versus $1/C_e$ give a straight line and the values of Q^0 and b can be calculated from the intercept and slope of the plots, respectively. Langmuir constants and correlation coefficients (R^2) are given in Table 2.

3.3.2. Freundlich isotherm

Freundlich equation is derived to model the multilayer adsorption and for the adsorption on heterogeneous surfaces. The Freundlich model is formulated as [35]:

$$q_e = K_F C_e^{1/n}$$

where q_e is the equilibrium solute concentration on adsorbent (mmol g^{-1}), C_e is the equilibrium concentration of the solute (mmol L^{-1}), K_F is the Freundlich constant (mmol g^{-1}) which indicates the adsorption capacity and represents the strength of the adsorptive bond and n is the heterogenity factor which

Table 2
Langmuir, Freundlich and D-R isotherm constants

Metal	Langmuir isotherm parameters			Freundlich isotherm parameters			D-R isotherm parameters			
	Q^0 (mmol g^{-1})	b (L mmol^{-1})	R^2	K_F (mmol g^{-1})	n	R^2	Q_m (mmol g^{-1})	k (mol^2 kJ^{-2})	E (kJ mol^{-1})	R^2
Cu	0.021365	7.575	0.9758	0.0195	3.25	0.9815	0.0499	−0.0032	12.5	0.9918
Pb	0.061989	2.068	0.9693	0.0411	2.36	0.975	0.197	−0.0053	9.71	0.9856
Cd	0.019812	2.343	0.9529	0.0146	1.69	0.9855	0.0790	−0.0057	9.37	0.9473

represents the bond distribution. A linear form of the Freundlich equation can be obtained by taking logarithms of the equation:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e$$

According to this equation the plot of the $\log q_e$ versus $\log C_e$ gives a straight line and K_F and n values can be calculated from the intercept and slope of this straight line, respectively. Experimental data obtained from the effect of initial concentrations to the adsorption of heavy metals on sporopollenin were also evaluated by applying this equation and related constants are given in Table 2.

On the comparison of the R^2 values given in Table 2, we can conclude that in all cases for the adsorption of target heavy metal ions to the sporopollenin Freundlich equation represents a better fit to the experimental data than the Langmuir equation. This result also predicts the heterogenity of the adsorption sites on sporopollenin. The Freundlich constant K_F indicates the sorption capacity of the sorbent. As it can be seen from Table 2, K_F values were found to be 0.0195, 0.0411 and 0.0146 mmol g^{-1} for Cu(II), Pb(II) and Cd(II), respectively. These adsorption capacities are comparable with some of those reported for other types of biomass (Table 3). n values are found to be greater than 1 in all cases. This result is most common and may be due to a distribution of surface sites or any factor that causes a decrease in adsorbent–adsorbate interaction with increasing surface density [36].

3.3.3. D-R isotherms

Langmuir and Freundlich isotherms do not give any idea about adsorption mechanism. D-R isotherm describes adsorption on a single type of uniform pores. In this respect the D-R

isotherm is an analogue of Langmuir type but it is more general because it does not assume a homogeneous surface or constant sorption potential [30]. In order to understand the adsorption type, D-R isotherms were obtained. The D-R isotherm which is given with the following equation:

$$Q = Q_m \exp(-k\varepsilon^2)$$

and linearized form of the equation is given as

$$\ln Q = \ln Q_m - k\varepsilon^2$$

where ε (Polanyi potential) is $[RT\ln(1+(1/C_e))]$, Q is the amount of solute adsorbed per unit weight of adsorbent (mol g^{-1}), k is a constant related to the adsorption energy (mol^2 kJ^{-2}) and Q_m is the adsorption capacity (mol g^{-1}).

The values of Q_m and k were calculated from the intercept and slope of the $\ln Q$ versus ε^2 plots and presented in Table 2. The mean free energy of adsorption (E) was calculated from the k values using the equation:

$$E = (-2k)^{-0.5}$$

The magnitude of E is useful for estimating the type of adsorption process. If this value is between 8 and 16 kJ mol^{-1}, adsorption process can be explained by ion exchange [30]. In this study, E values are calculated to be between the values of ion exchange. Therefore it is possible to say that adsorption mechanism of heavy metal ions (Cu(II), Pb (II) and Cd(II)) on sporopollenin can be explained with an ion-exchange process.

3.4. Thermodynamics of the adsorption

The effect of temperature on adsorption of heavy metal ions onto sporopollenin is shown in Fig. 7. Initial concentrations of

Table 3
Adsorption capacities of some adsorbents cited in the literature

Adsorbent	Adsorption capacities (mg g^{-1})			Reference
	Cu	Pb	Cd	
Aminated and protonated mesoporous aluminas	1.5–2.15	–	–	[3]
Sawdust	0.956	0.965	–	[37]
Activated carbon	–	2.95	–	[38]
Unexpanded perlite	1.01	–	–	[39]
Cocoa shell	–	6.2	–	[40]
Peach stone carbon	–	–	3.27	[41]
Almond shell carbon	–	–	2.7	[41]
Walnut shell	–	–	1.5	[42]
Waste tea			1.63	[42]
Sporopollenin	1.24	8.52	1.64	Present study

Table 4
Thermodynamic parameters for the adsorption of Cu(II), Pb(II) and Cd(II) on sporopollenin

Metal	C_0 (mg/L)	ΔH° (kJ mol^{-1})	ΔS° (J/K mol)	T (K)	ΔG° (kJ mol^{-1})	R^2
Cu	60	17.55	85.58	293	−7.54	0.943
				303	−8.38	
				313	−9.23	
				323	−10.09	
				338	−11.37	
Pb	20	31.97	150.98	303	−13.78	0.972
				313	−15.29	
				323	−16.80	
				338	−19.06	
Cd	20	13.99	76.64	298	−8.85	0.969
				303	−9.24	
				313	−10.00	
				323	−10.77	
				338	−11.92	

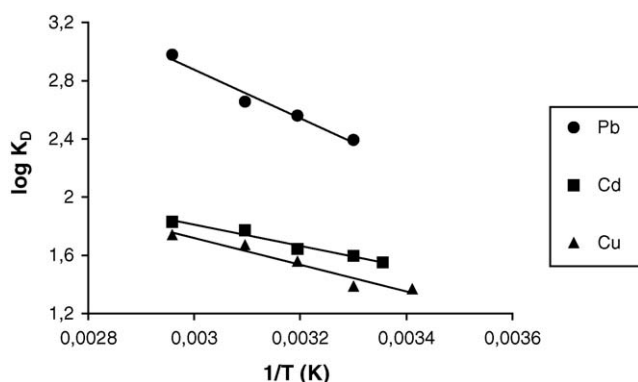
Fig. 7. log K_D–1/T graphs for the adsorption of Cu(II), Pb(II) and Cd(II) onto sporopollenin. [▲, Cu(II)] $C_0 = 60$ mg L^{-1}, pH 5.0; [●, Pb(II)] $C_0 = 20$ mg L^{-1}, pH 6.0; [■, Cd(II)] $C_0 = 20$ mg L^{-1}, pH 7.0; m(sporopollenin): 0.5 g; t: 60 min; medium: 0.1 M acetic acid–acetate.

Cu(II), Pb(II) and Cd(II) were taken as 60, 20 and 20 mg L^{-1}, respectively. The experiments were carried out at 298, 303, 313, 323 and 338 K and it was observed that the distribution coefficient values, K_D, increased with increase in temperature and that shows the endothermic nature of the adsorption (Fig. 7). Thermodynamic parameters like free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were estimated using the following equations. The Gibb's free energy change of the process is related to the distribution coefficient (K_D) by the equation:

$$\Delta G^\circ = -RT \ln K_D$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\log K_D = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT}$$

where K_D is the distribution coefficient (cm^3 g^{-1}), and R is gas constant (kJ mol^{-1} K^{-1}). According to the last equation given above the values of ΔH° and ΔS° can be calculated

from the slopes ($\Delta H^\circ/2.303R$) and intercepts ($\Delta S^\circ/2.303R$) of log K_D versus 1/T plots. The calculated values of thermodynamic parameters were given in Table 4. As it can be seen from Table 4 ΔH° values are found to be positive for all cases due to endothermic nature of the adsorption. Although there are no certain criteria related to the ΔH° values that define the adsorption type, the heat of adsorption values between 5.0 and 100 kcal mol^{-1} (20.9–418.4 kJ mol^{-1}), which are heats of chemical reactions, are frequently assumed as the comparable values for the chemical adsorption processes. ΔH° values were found as 17.55, 31.97 and 13.99 kJ mol^{-1} for Cu(II), Pb(II) and Cd(II), respectively. In the adsorption isotherms part, we described the adsorption mechanism of the target heavy metals ions [Cu(II),Pb(II) and Cd(II)] on sporopollenin with an ion-exchange process according to the calculated E values obtained from the D-R isotherms. But it is obvious from the ΔH° value obtained for Pb(II) that chemisorption also takes part in the adsorption process with chelating effects of the functional groups available on the surface of sporopollenin. Negative values of ΔG° indicates the spontaneous nature of the reaction. The reaction is favored and getting easier at higher temperatures. The values of ΔS° were found to be positive due to the exchange of the metal ions with more mobile ions present on the exchanger, which would cause increase in the entropy, during the adsorption process. Also, in the case of physisorption which may also contribute to the total adsorption process can cause increase in entropy because of the water molecules released from the hydrated ions or water molecules present on the surface during the adsorption process.

4. Conclusion

(1) Adsorption on sporopollenin can be expressed better with Freundlich type adsorption isotherms which shows the heterogenous characteristics of the adsorption sites on sporopollenin. Adsorption capacities order was found as Pb(II) > Cu(II) > Cd(II).

(2) Adsorption of heavy metal ions [Cu(II), Pb(II) and Cd(II)] onto sporopollenin was found to occur with an ion-exchange

process. But chelating effect of the functional groups on sporopollenin is also thought to take part in the adsorption process.

(3) The adsorption process was found to be endothermic, spontaneous and can be explained with pseudo-second-order type kinetic model due to polymeric structure of the sporopollenin. Intraparticle diffusion should also be taken into account but it was observed that intraparticle diffusion is not a rate-determining step.

(4) Sporopollenin as an ion-exchange resin can be used as a low-cost adsorbent for removal of heavy metal ions.

(5) Sporopollenin can also be used as a chelating resin for preconcentration and determination purposes in analytical applications.

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