EXTRACTION OF LEAD(II) AND CADMIUM(II) BY CROSS LINKED POLYSTYRENE THIOUREA

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The aim of this study is to investigate Lewatit TP 214, which is a chelating ion-exchange polymer containing chemically bonded thiourea group, for the sorption of Pb(II) and Cd(II) ions from aqueous solutions. The effects of parameters such as the concentration, pH, contact time, ionic strength and temperature have been investigated. The results showed more affinity of resin towards cadmium than for lead cations. Lewatit TP 214 exhibited a good sorption potential at initial pH values for Pb(II) and Cd(II) at room temperature. The extraction kinetics, for both Pb(II) and Cd(II), is best described by the pseudo second order model. This study showed that the diffusion of moving boundary particles fits well the experimental data ($r > 0.99$) for the sorption of both Pb(II) and Cd(II) ions. The Langmuir isotherm fits better with the obtained equilibrium data as compared to that with the Freundlich isotherm. The thermodynamic data for the sorption of Pb(II) and Cd(II), on the resin, indicate that the process is endothermic for Pb(II) while it is exothermic for Cd(II). The process showed negative ΔG values, indicating that the sorption of both Pb(II) and Cd(II) ions is spontaneous.

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Introduction

Heavy metals are significantly hazardous due to their toxicity even at very low concentration in water.[1] Exposure to lead and cadmium are old problems with modern prevalence, they are widely dispersed in the environment, and exposure to either element can give rise to a number of adverse health effects, due to their toxicity after accumulation in multiple body organs.[2] The main sources of these elements are metal plating industries, abandoned disposal sites, and mining industries.[3] The removal of heavy metals from waste waters can be carried out by a number of separation technologies, such as chemical precipitation,[4] membrane processes,[5,6] ion exchange,[7,8] adsorption,[9,10] and solvent extraction.[11-13] Nonetheless, many conventional technologies are inadequate, expensive or produce large amounts of sludge, which create disposal problems.[14] Moreover, they are not economical to reduce metal toxicity to extremely low levels, as required by the environmental regulations, which limits the usage of these technologies to drinking water purification.[14] Solid-phase extraction (SPE) is the most common technique used for metal pre-concentration in aqueous phase because of the advantages it offers, i.e. high enrichment factor, high recovery, rapid phase separation, low cost, reversible process and low consumption of organic solvents.[15,16] In SPE, the choice of an appropriate chelating agent is critical to obtain a full recovery and a high enrichment factor. For this reason, modification of resins with thiourea has been extensively investigated.[17-20] Lewatit TP 214 is a monospherical, macroporous chelating resin with thiourea groups and has a high affinity for metal cations.

The objective of this research is to carry out a comparative study on the solid-phase extraction of both Pb(II) and Cd(II) ions from aqueous solutions, using resin Lewatit TP 214. The effects of analytical parameters, such as the metal concentration in aqueous phase, pH level, contact time, ionic strength and temperature on the degree of extraction have been investigated.

Experimental

Reagents and Apparatus

Lewatit TP 214 (Bayer) is a chelating ion-exchange resin having thiourea as functional group in a divinylbenzene cross linked polystyrene matrix (Figure 1). All chemicals products used in this work were of analytical grade. Cadmium nitrate, lead nitrate, hydrochloric acid (37 %), sodium hydroxide (80 %) and 4-(2-pyridylazo)-resorcinol (PAR) were from Merck. Absolute ethanol, sodium chloride, potassium chloride and sodium nitrate were provided by Fluka. Acetic acid (100 %) and nitric acid (60 %) were obtained from Riedel-de Haen.

Stock and standard solution of Pb(II) and Cd(II) ions were prepared by dissolving an appropriate amount of their salts in distilled water. Solutions of lower concentrations were prepared by the dilution of stock solution.
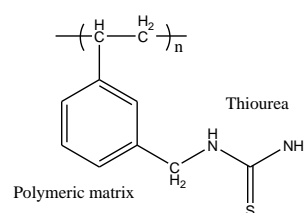

Figure 1. Structure of Lewatit TP 214 resin.

The sorption of Pb(II) and Cd(II) ions on Lewatit TP 214 resin was studied by the batch technique. A shaker (Haier model) was used for adsorption experiments except for temperature effect where a magnetic stirrer (RCT Basic IKAMAG Stirrer with ETS-D5 Temperature Controller) was used. All pH measurements were performed with a WTW 3310 Set 2 digital pH meter.

Sorption Studies

The sorption of lead and cadmium ions onto Lewatit TP 214 beads was investigated in solid-phase extraction from aqueous media in a batch system. Lewatit resin (0.050 g) was added to 5 mL of a solution containing metal cations, in a glass flask (25 mL) and the mixture was shaken for a suitable time. Then, the aqueous phases were separated from the chelating resin by filtration. The concentration of Pb(II) and Cd(II) ions, in aqueous phase, were determined , before and after sorption, at pH = 10 and 5.5 at λ_{max} = 525 nm and λ_{max} = 510 nm, respectively using a spectrophotometer (Analytik Jena Specord 210Plus) with PAR as complexant.[21,22]

Kinetic studies on the removal of Pb(II) and Cd(II) ions were carried out, with an initial ion concentration of 1.0×10^{-3} mol L^{-1} at room temperature. The effect of contact time on the sorption was studied up to 120 minutes, while other parameters, like the sorbent dosage, shaking speed (Ø) and pH were kept constant. The effect of the initial pH on the removal of Pb(II) and Cd(II) ions, was studied at pH 1.4 to 5.5 and 2.0 to 6.1, respectively. The pH was adjusted by adding appropriate quantities of HCl or NaOH solutions (0.01 mol L^{-1}). The percentage removal (φ) of Pb(II) and Cd(II) ions was determined by using Eqn. (1).

$$\varphi = \frac{C_0 - C_t}{C_0} 100, \% \qquad (1)$$

The amount of Pb(II) and Cd(II) ions uptakes at time t, q_t (mg g^{-1}), was calculated by Eqn. (2).

$$q_t = \frac{C_0 - C_t}{W} V \qquad (2)$$

where C_0 and C_t are the metal ion concentration in the beginning and at time t, respectively. V (L) is the volume of the solution, M (g mol^{-1}) is the molar mass of metal ion and W is the mass of the chelating resin used (g).

Results and Discussion

Effect of pH

The effect of the pH on the recovery of Pb(II) and Cd(II) ions was investigated in the pH range of 1.4 to 5.5 and 2.0 to 6.1, respectively, using 5 mL of each one of the solution of Pb(II) and Cd(II), and 0.050 g of Lewatit TP 214 resin. The results (Figure 2) indicated that the extraction yield for

Cd(II) continuously increased reaching a value of 60.4 % at pH 6.1, whereas that of Pb(II) was 52 % at pH 4.1 and thereafter it decreased. However, when the pH is lowered, the extraction yield decreases, and this may be attributed to the hydrogen ions which compete with the metal ions for the sorption sites in the chelating resin Lewatit TP 214.[23]

Effect of Contact Time

The effect of contact time is shown in Figure 3. The sorption of both Pb(II) and Cd(II) ions was rapid in the initial 15 min, and then the extraction yield increased slowly. The sorption process reached equilibrium at nearly 15 and 30 min, respectively, for the removal of Pb(II) and Cd(II) ions by Lewatit TP 214 resin. The % extraction yield, almost in equal proportions, was rapid in the beginning of the contact time. It is related to the availability of a larger number of active sites on the resin surface, which improved diffusion of metal ions to the surface.[24]
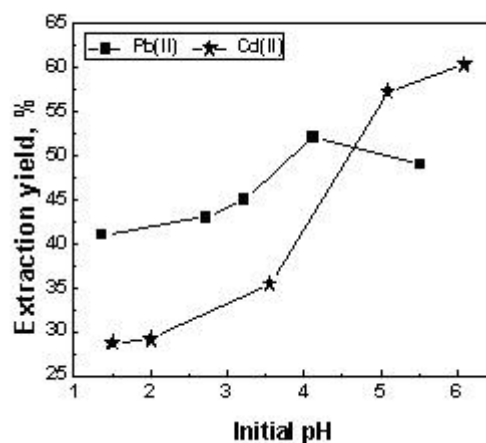
Figure 2. Effect of initial pH of solution on Pb(II) and Cd(II) ions extraction yield. [Pb(II)]$_0$ = 1.0 mM, [Cd(II)]$_0$ = 1.0 mM, W = 0.050 g, V = 5 mL and Ø = 250 rpm.
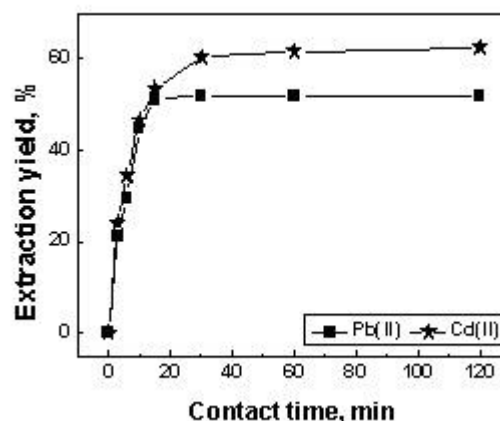
Figure 3. Effect of contact time on extraction yield of both Pb(II) and Cd(II) ions removal. [Pb(II)]$_0$ = 1.0 mM, [Cd(II)]$_0$ = 1.0 mM, W = 0.050 g, V = 5 mL, pH = 5.0 and Ø = 250 rpm.

Effect of the Initial Concentration of Metal Ions

The retention capacity of the chelating resin Lewatit TP 214 was determined by equilibrating 0.050 g of resin with 5 mL of the solution containing different concentrations (1.0 x 10^{-4} to 1.0 x 10^{-1} mol L^{-1}) of metal ions. For the removal of Pb(II), by Lewatit TP 214, the uptake (q_t) increased with the initial concentration of Pb(II) up to the maximum value q_{max} = 55.59 mg g^{-1} (Figure 4). The observed sorption capacity is higher than that of some of the other sorbent materials reported in literature, like phosphatic clay (35.83 mg g^{-1}),[25] chars from co-pyrolysis (1.87 mg g^{-1}),[26] Jordanian kaolinite (54.35 mg g^{-1}),[27] and carbon nanotubes coated with crystalline manganese dioxide nanoparticles (20.0 mg g^{-1}).[28] Figure 4 also shows that the sorption capacity for Cd(II) (81.75 mg g^{-1}) is much better than that for Pb(II) (55.59 mg g^{-1}), which means that resin Lewatit TP 214 can more efficiently remove Cd(II) present in aqueous solutions compared to other sorbent materials, for instance the adsorption of cadmium(II) on MnO_2-loaded resin (21.45 mg g^{-1}),[29] MnO_2 loaded D301 resin (77.88 mg g^{-1}),[30] and by the Amberlite XAD-7/Cyanex 921(13.0 mg g^{-1}).[31]

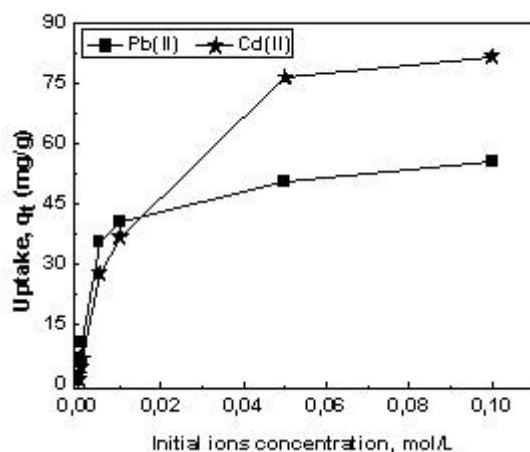**Figure 4.** Effect of initial Pb(II) and Cd(II) ions concentration on their sorption capacities by Lewatit TP 214 resin: $[Pb(II)]_0$ = 1.0 mM, $[Cd(II)]_0$ = 1.0 mM, W = 0.050 g, V_{sol} = 5 mL, $\emptyset$ = 250 rpm and pH $\cong$ 5.0.

Sorption Kinetics

In order to study the sorption mechanism of Pb(II) and Cd(II) ions onto Lewatit TP 214 resin, the pseudo first-order, pseudo second-order and second-order kinetic models were applied to the experimental data.[32] The linear form of the pseudo-first-order rate equation, given by Lagergren, is expressed as Eqn. (3),

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

where q_e and q_t are the respective amounts of metal ions (mg g^{-1}) sorbed onto the resin, at equilibrium and at time t, and k_1 is the first-order sorption rate constant (min^{-1}). The linear form of the pseudo-second order rate equation is given by Eqn. (4),

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

where q_{es} is the sorption capacity, calculated from the pseudo-second-order kinetic model (mg g^{-1}), and k_2 is the pseudo-second-order sorption rate constant (g mg^{-1} min^{-1}). The second order sorption kinetic rate equation is given by Eqn. (5).

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_3 t \qquad (5)$$

where k_3 (g mg^{-1} min^{-1}) is the second-order sorption rate constant.

The results of analysis in terms of the three equations are summarized in Table 1. The best correlation is obtained with the pseudo-second-order equation ($r > 0.99$). The plots of the sorption of Pb(II) and Cd(II) ions using the pseudo-second-order model are shown in Figure 5. From Table 2 and Figure 5, the equilibrium sorption capacity was calculated and was found to be close to the experimental value.

Table 1. Kinetic modelling of Pb(II) and Cd(II) ions sorption by Lewatit TP 214 resin

Models	Parameters	Pb(II)	Cd(II)
First-order rate model	q, calculated	15.01	6.69
	q, experimental	10.77	7.025
	$k_1(min^{-1})$	0.266	0.128
	r	0.971	0.998
Pseudo-second-order rate model	q, calculated	12.99	8.26
	q, experimental	10.77	7.025
	k_2(g mg^{-1} min^{-1})	0.015	0.027
	r	0.991	0.999
Second-order rate model	q, calculated	62.50	8.55
	q, experimental	10.77	7.025
	k_3(g mg^{-1} min^{-1})	0.056	0.041
	r	0.913	0.980

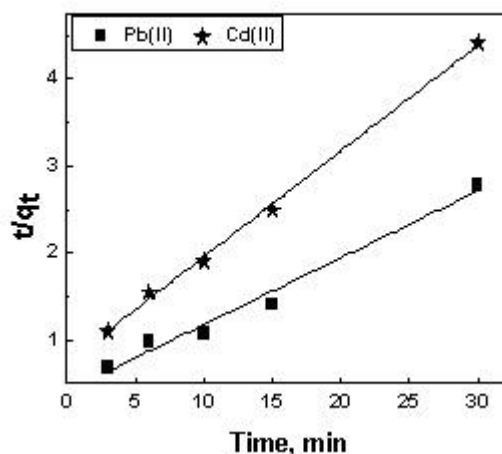**Figure 5.** Pseudo second-order plots for the Pb(II) and Cd(II) ions sorption by Lewatit TP 214 resin: $[Pb(II)]_0$ = 1.0 x10^{-3} mol L^{-1}, $[Cd(II)]_0$= 1.0 x10^{-3} mol L^{-1}, W = 0.050 g, V_{sol} = 5 mL, pH = 5.0 and $\emptyset$ = 250 rpm.

Diffusion Study

The sorption of Pb(II) and Cd(II) ions onto Lewatit TP 214 resin from their nitrate solutions may be considered as a liquid–solid phase reaction which includes several steps,[33-35] viz., (i) diffusion of ions from the solution to the resin surface, (ii) diffusion of ions within the solid resin, and (iii) chemical reaction between ions and the functional groups of resin. The transfer of ions can be described by means of Nernst–Planck equations which apply to the counter diffusion of two species in an almost homogeneous medium.[30] If the liquid film diffusion controls the exchange rate, the Eqn. (6) can be applied.

$$-\ln(1-F) = kt \qquad (6)$$

In case of diffusion of metal ions inside the resin, Dumwald-Wagner proposed a mathematical model,[35] which can be simplified into Eqn. (7).

$$-\ln(1-F2) = kt \qquad (7)$$

In both Eqns. (6) and (7), k is the kinetic coefficient or rate constant, which can be defined by Eqn. (8).

$$k = \frac{D_r \pi^2}{r_0^2} \qquad (8)$$

where F is is the fractional attainment of equilibrium at time t and is obtained by the ratio, $F = q_t/q_e$. D_r is the diffusion coefficient in resin phase and r_0 is the average radius of a resin particle.

When the adsorption of metal ions involves mass transfer accompanied by a chemical reaction, the process can be explained by the moving boundary model.[33] This model assumes a sharp boundary that separates a completely reacted shell from an unreacted core. This boundary advances from the surface toward the center of the solid with the progression of adsorption. In this case, the rate equation is given by Eqn. (9).

$$3-3(1-F)^{2/3} - 2F = kt \qquad (9)$$

The correlation data of Figures 6, 7 and 8 are summarized in Table 2 and showed that the film diffusion fits well the experimental data ($r = 0.999$) in Cd(II) sorption while the moving boundary diffusion is more adequate in Pb(II) ($r = 0.989$) sorption.

Table 2. The regression constants and regression coefficients of diffusion study for Pb(II) and Cd(II) ions onto Lewatit TP 214.

Metal		Film Diffusion	Intraparticle diffusion	Moving boundary
Pb(II)	K (min⁻¹)	0.0301	0.271	0.066
	r	0.978	0.967	0.989
Cd(II)	K (min⁻¹)	0.123	0.099	0.034
	r	0.999	0.997	0.997

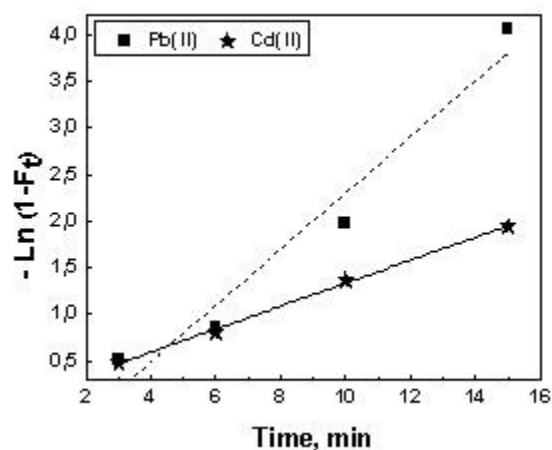**Figure 6.** Plot of film diffusion (Eqn. 6) for Pb(II) and Cd(II) ions sorption onto Lewatit TP 214 resin: [Pb(II)]₀ = 1.0 mM, [Cd(II)]₀ = 1.0 mM, W= 0.050 g, V_{sol} = 5 mL, pH ≅ 5.0 and Ø = 250 rpm.
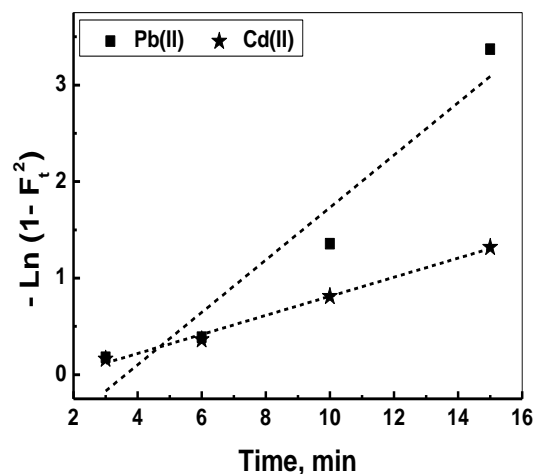

Figure 7. Plot of intraparticle diffusion (Eqn. 7) for Pb(II) and Cd(II) ions sorption onto Lewatit TP 214 resin. [Pb(II)]₀ = 1.0 mM, [Cd(II)]₀ = 1.0 mM, W = 0.050 g, V_sol = 5 mL, pH ≅ 5.0 and Ø = 250 rpm.
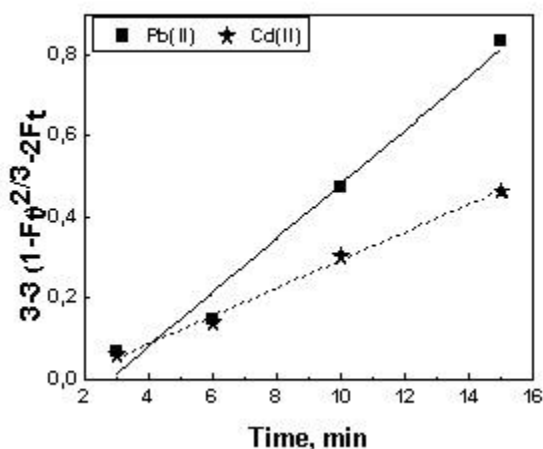

Figure 8. Plot of moving boundary model (Eqn. 9) for Pb(II) and Cd(II) ions sorption onto Lewatit TP 214 resin: [Pb(II)]₀ = 1.0 mM, [Cd(II)]₀ = 1.0 mM, W= 0.050 g, V_{sol} = 5 mL, pH ≅ 5.0 and Ø = 250 rpm.

Adsorption Isotherm

The equilibrium isotherm parameters often provide some insight into the sorption mechanism of the adsorbent. There are many equations for analyzing the experimental data for the adsorption equilibrium. In this work, the experimental results obtained were tested by the Langmuir and Freundlich isotherm models.[36,37] Their linear forms are expressed as Eqns. (10) and (11).

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad (10)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (11)$$

where C_e the equilibrium concentration, q_m the maximum sorption capacity, K_L the Langmuir constant which is related to the heat of sorption, n the constant indicating the Freundlich isotherm curvature and K_F the Freundlich sorption coefficient. The Langmuir and Freundlich plots are shown in Figures 9 and 10. The higher regression coefficients obtained for Langmuir model (Table 3) as compared to that for the Freundlich model indicates that the Langmuir model is applicable to this system. Thus the sorption of Pb(II) and Cd(II) by Lewatit TP 214 is of a monolayer-type, which agrees with a previous report.[38]

Table 3. Sorption isotherm models for Pb(II) and Cd(II) ions adsorption onto Lewatit TP 214 resin.

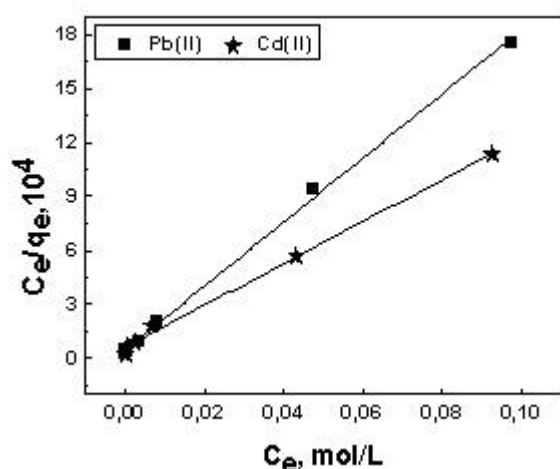| Metal	Langmuir Isotherm			Freundlich Isotherm		
	K_L	Q_m, mg g^{-1}	r	K_F	n	r
Pb(II)	395.55	56.18	0.999	231.44	2.34	0.957
Cd(II)	187.09	86.21	0.998	311.45	2.15	0.981

Figure 9. Langmuir isotherm for Pb(II) and Cd(II) ions sorption on Lewatit TP 214. W = 0.050 g, V_{sol} = 5 mL, pH $\cong$ 5.0 and Ø = 250 rpm.
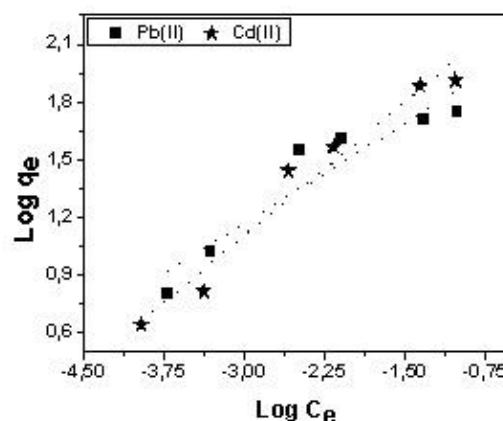

Figure 10. Freundlich isotherm for Pb(II) and Cd(II) ions sorption on Lewatit TP 214. W = 0.050 g, V_{sol} = 5 mL, pH $\cong$ 5.0 and Ø = 250 rpm.
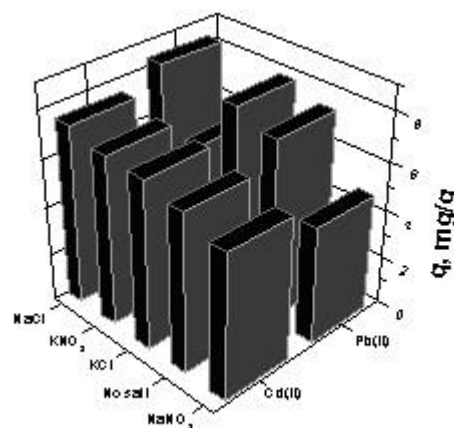

Figure 11. Effects of adding of an electrolyte on Pb(II) and Cd(II) ions sorption onto Lewatit TP 214 resin : $[Pb(II)]_0$ = 1.0 mM, $[Cd(II)]_0$ = 1.0 mM, [electrolyte] = 1.0 mol.L^{-1}, W = 0.050 g, V_{sol} = 5 mL and Ø = 250 rpm

Effects of Electrolytes

To study the effect of electrolytes on the sorption of Pb(II) and Cd(II) ions onto Lewatit TP 214 resin, 1 mol L^{-1} of each NaNO$_3$, NaCl, KNO$_3$ and KCl was added in separate experiments. The results are depicted in Figure 11. It was noted that the sorption of both Pb(II) and Cd(II) increased on the addition of KCl and NaCl. For Pb(II), the sorption increased from 7.50 to 8.06 and 8.36 mg g^{-1}, respectively. For Cd(II), it rose from 6.54 to 6.95 and 7.45 mg g^{-1} respectively. Addition of NaNO$_3$ (1 M) decreases the sorption of Pb(II) and Cd(II) to 4.84 and 5.96 mg g^{-1}, respectively, compared to the values obtained without electrolyte. It might be the consequence of difference in changes in hydration degree of cations take part in the sorption process. This is, however, depends on the concentration of the used electrolytes. Addition of KNO$_3$ increases Cd(II) sorption but reduces that of Pb(II) (see also section – *Effect of ionic strength*) .

Effects of Ionic Strength

To study the effect of ionic strength on Pb(II) and Cd(II) ions sorption onto Lewatit TP 214 resin, a series of batch experiments were carried using NaNO$_3$ at different concentrations (from 0.05 to 3 mol L^{-1}) as electrolyte. The solution ionic strength was set to have values ranged from 0.056 to 3.006 mol L^{-1}. The observed data are depicted in Figure 11. It was noted that both Pb(II) and Cd(II) ions sorption increased with increasing the solution ionic strength. For Pb(II) ions sorption the sorption capacity increases from 4.57 to 6.03 mg g^{-1} when NaNO$_3$ increased from 0.1 to 3 mol L^{-1} and for the Cd(II) ions sorption, the sorption capacity increases from 3.83 to 7.01 mg g^{-1} when NaNO$_3$ increased from 0.05 to 3 mol L^{-1} (Figure 12).
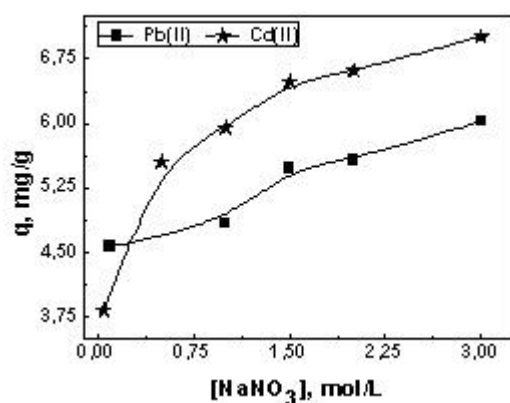

Figure 12. Effect of NaNO$_3$ concentration on Pb(II) and Cd(II) ions sorption onto Lewatit TP 214 resin: [Pb(II)]$_0$ = 1.0 mM, [Cd(II)]$_0$ = 1.0 mM, W = 0.050 g, V_{sol} = 5 mL and Ø = 250 rpm.

Effect of temperature

Few studies of effect of temperature changes have been carried out on chelating ion exchangers. Empirical studies show that temperature has a significant effect on retention in chelating exchange.[39] Thermodynamic parameters such as, the Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) have been determined for the present system.

Table 4. Thermodynamics parameters for sorption process of Pb(II) and Cd(II) ions on Lewatit TP 214 resin

Parameter	T, K	Pb(II)	Cd(II)
ΔH, kJ mol^{-1}		8.94	-51.65
ΔS, J mol^{-1} K^{-1}		32.51	-182.33
ΔG, kJ mol$^-$	T, K	Pb(II)	Cd(II)
	291	-	-1.41
	294	0.62	-
	298	-	-2.68
	308	-1.07	-4.51
	318	-	-6.33
	323	-1.56	-
	338	-2.05	-

A plot of ln K versus inverse of temperature is linear and the thermodynamic parameters were calculated by standard procedure (Table 4). A negative ΔG value indicates that the sorption of Pb(II) and Cd(II) ions with Lewatit TP 214 are spontaneous. These results show also that the sorption of Pb(II) ions onto Lewatit TP 214 is an endothermic process while that of Cd(II) ions is exothermic.

Conclusion

This work demonstrated the successful application of Lewatit TP 214 for an effective sorption and pre-concentration of lead and cadmium cations in batch mode. The experimental data showed that the sorption of Pb(II) and Cd(II) ions onto Lewatit TP 214 resin is highly affected by operational parameters, such as contact time, initial ion concentration, initial pH, ionic strength, and temperature. The maximum sorption of Pb(II) and Cd(II) ions was obtained at pH 4.1 and 6.1, respectively. The kinetic study showed an initial stage (the first 15 min) where the sorption reaction was fast for both cations (Pb(II) and Cd(II)), then the reaction rate decreased slightly until equilibrium was reached. The sorption capacity rose as the initial concentrations of lead and cadmium cations were increased. The sorption capacity of cadmium ions (81.75 mg g^{-1}) was better than that of lead ions (55.59 mg g^{-1}). The kinetic data were well described by the pseudo–second-order model ($r >$ 0.99). The diffusion study showed that the moving boundary diffusion fits well the experimental data ($r >$ 0.99). The observed equilibrium data showed a better fit with Langmuir isotherm model than with Freundlich model. This indicates that the sorption of Pb(II) and Cd(II) ions by Lewatit TP214 is of a monolayer-type. It was noted also that the sorption of Pb(II) and Cd(II) ions increased as the solution ionic strength went up. The thermodynamic study showed negative ΔG values, which indicates that the sorption of both Pb(II) and Cd(II) ions with Lewatit TP 214 is spontaneous. Moreover, this study showed that the sorption of Pb(II) ions onto Lewatit TP 214 is an endothermic process while that of Cd(II) is exothermic.

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