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ORIGINAL PAPER

Mercury and lead sorption properties of poly(ethyleneimine) coated onto silica gel

Bernabé L. Rivas · Bruno Urbano · S. Amalia Pooley · Ingrid Bustos · Néstor Escalona

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Abstract In this article, we studied the sorption properties of poly(ethyleneimine) coated on silica gel for metal ions with impact on the environment, such as Zn(II), Cd(II), Hg(II), and Pb(II). The experiments were carried out by batch procedure and the effects of pH, concentration, and temperature were evaluated. In addition, the selectivity was studied for binary, ternary, and quaternary metal ion mixtures. Mercury and lead showed promising results, achieving higher than 65% of sorption after only 1 h of contact. Under competitive conditions, resin presented high selectivity toward Hg(II) reaching 91 and 87% of retention respect to total amount of ions for binary and quaternary mixtures, respectively. The effect of time on Pb(II) and Hg(II) sorption was studied by batch procedure and the experimental data were adjusted to pseudo-first-order, pseudo-second-order, and intra-particle diffusion models. Pseudo-second-order model presented good agreement for Pb(II) sorption, while pseudo-first-order model fits better to Hg(II) sorption. Intra-particle diffusion model showed that sorption process is controlled mainly by film diffusion.

Keywords Chelating resin · Selectivity · Mercury · Adsorption · Kinetics

Introduction

Heavy metal pollution in water concern to worldwide due the toxic effect on humans. They are introduced into the environment during industrial processes, refining of ores, mining, disposal of industrial and domestic waters, etc. Therefore, the removal of metal ions has attracted considerable interest for many applications. Currently, there are several technologies available to remove metal from aqueous

B. L. Rivas (✉) · B. Urbano · S. Amalia Pooley · I. Bustos · N. Escalona
Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile
e-mail: brivas@udec.cl

sources, such as differential precipitation, solvent extraction, distillation, ion exchange, flotation, and filtration membranes, etc. [1, 2].

In the area of ion exchange process, the separation of desired metal ions by chelating resins from a solution containing various metal ions, the selectivity is one of the most important challenges. The choice of ligand introduced into the resin plays a significant role in achieving the selectivity. The high metal ion selectivity of chelating exchangers is attributed not only to electrostatic forces, but also to coordination bonds in metal chelating groups [3–5].

Poly(ethyleneimine) is well known for its metal chelation potentialities [6–11]. On the other hand, silica gel offers good enough stability to solvents and pressure to be used in column systems, wide scales of porous volume, specific area, available sizes, and availability for immobilizing organic molecules [12]. Therefore, the combination of chelation properties of polymers and mechanical properties of silica, lead to a desire material with the ability to adsorb heavy metal selectively, with specific area, the accessibility, swelling properties, and finally, allows a faster achievement of equilibrium sorption.

The aim of this article is to examine the sorption properties of poly(ethyleneimine) coated on silica gel. The sorption of Zn(II), Cd(II), Pb(II), and Hg(II) were evaluated as function of pH, concentration, temperature, in order to determine the condition necessary to a good performance of resins. Besides, competitive and non competitive conditions were performed to study the selectivity of polymer material. Finally, kinetic studies were carried out and experimental data were fitted to appropriate kinetic models, such as pseudo-first- and pseudo-second-order models.

Experimental

Materials

A commercial poly(ethyleneimine) coated onto silica gel (40–200 mesh, Aldrich) was purchased from Aldrich and used as received. Sorption experiments were carried out using the following nitrate salts: $Hg(NO_3)_2{\cdot}H_2O$, $Pb(NO_3)_2$, $Cd(NO_3)_2{\cdot}4H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, all salt were obtained from Merck Company. For resin elution experiments, nitric acid (65%, Riedel-de Haen), hydrochloric acid (37%, Merck), perchloric acid (60%, Merck), sulfuric acid (95–99%, Merck), and thiourea (Merck) were used.

Characterization

Evaluation of functional groups of resins were carried out by Fourier transformed infrared spectroscopy (FTIR) and the spectrum was obtained in a Perkin Elmer 1760-X spectrometer with Fourier transform, range of 4000–400 cm^{-1}, using KBr pellets. The adsorbent analyzed by scanning electron microscopy (SEM) a SEM-PROBE CAMECA, model SU-30 in order to determine surface characteristics of gel resins. The concentrations of metal ion were measured in Unicam Solaar 5M

atomic absorption spectrometer (the quantification limit for Pb(II) and Hg(II) were 0.19 and 0.40 mg L^{-1}, respectively).

Sorption experiments

All sorption experiments were carried out using the batch procedure. In a glass tube, 50 mg of poly(ethyleneimine)-silica were added and contacted with 5 mL of an aqueous solution of metal ion. In order to study the effect of pH in sorption, the pH of solutions was previously adjusted using diluted nitric acid and sodium hydroxide solutions with accuracy of ±0.1 using a Jenway pH-meter. The mixtures were placed in shaker, equipped with thermoregulated bath at 25 °C and 140 rpm. After 1 h of contact, the mixtures were filtered, and washed with bi-distilled water at the same pH and solutions were collected in a calibrated flask to further metal ion concentration measurements. The effect of concentration was studied by the same procedure described above, using metal ion solution of different concentrations prepared in different molar ratios. In a similar way, the maximum retention capacity was determined using a concentration of 1 g L^{-1} of metal ion. The solution (25 mL) was contacted with 0.5 g of resin, once mixture was filtrated, the resins is again contacted with 25 mL of solution. This procedure was carried out three times for each metal ion.

Sorption experiments were also carried out under competitive conditions in order to study the selectivity of resins. The mixtures were prepared using 50 mg of resins per each 5 mL of metal ion solution and contacted for 1 h.

The regeneration of resins was studied by elution experiments using different eluents, such as hydrochloric acid, nitric acid, and perchloric acid, among others. Loaded resins obtained from the maximum retention experiments were selected to regeneration experiments, and eluents were used at different molar concentrations.

Equilibrium and kinetics

The effect of time was studied by batch experiments for Hg(II) and Pb(II) ions. A set of test tubes with 50 mg of resins and 5 mL of metal ion aqueous solution at appropriated pH were placed in a bath shaker at 25 °C and 140 rpm. The tubes were removed from the bath at different time intervals and handled according to procedure described above. Once the metal ion concentrations were determined, the retention capacity was plotted versus time. The experimental data were analyzed and fitted to kinetic model based on solute concentration as pseudo-first- and pseudo-second-order models.

Results and discussion

Sorption experiments

The effect of pH is an important factor in sorption process of metal ions. Hydronium concentration can change the properties of adsorbent and the speciation of metal ion

Table 1 Metal ion uptake of Pb(II), Cd(II), Zn(II), and Hg(II) at different pH and molar ratio of ligand/ion at 20:1

Metal ion	pH	Retention (mmol M^{n+}/g_{resin})	Retention (mg M^{n+}/g_{resin})	Retention (%)
Pb(II)	3.0	0.006	1.30	16.1
	5.0	0.021	4.47	45.8
	5.0[a]	0.019	3.94	68.3
	6.0[b]	0.018	3.77	20.7
Zn(II)	3.0	0.000	0.00	0.00
	5.0	0.015	0.99	35.5
	6.0	0.015	0.20	35.5
Cd(II)	3.0	0.016	1.79	18.3
	5.0	0.016	1.80	40.8
	6.0	0.018	1.99	45.4
Hg(II)	1.0	0.008	1.60	20.6
	2.0	0.023	4.60	63.8

[a] Molar ratio of 40:1

[b] Molar ratio of 10:1

in solution, affecting the performance of adsorbent. Table 1 presents the retention values for several metal ions at different pH and it is observed that uptake is higher as the pH increase. Poly(ethyleneimine) possess basically only one functional group that are able to interact with metal ions (amine function), which at low pH can be protonated causing the electrostatic repulsion of positive metal ions (Pb^{2+}, $PbNO_3^+$, Cd^{2+}, $CdNO_3^+$, etc.), after which the hydronium concentration decrease the unprotonated amino groups that are able to interact with metal ions. Lead and mercury present the highest retention (>60%), specifically the maximum retentions were found at pH 2 and pH 5 for mercury and lead, respectively.

It is well known the high affinity of Hg(II) toward mercapto compounds [13], however, also it has been observed affinity toward functional groups with amino functions such as diethanolamine, dimethylamine, and *N*-methyl-D-glucamine through N···Hg coordinative interaction or by ion exchange of $Hg(NO_3)_4^{2-}$ species in highly acidic solution [14]. This interaction can explain the high retentions observed in poly(ethyleneimine) for Hg(II) ions. In case of Pb(II) ions, it is expected that interaction also occurs through coordinative interaction, due to the protonated condition of amino function at pH 5 (linear PEI has a pKa = 8.8) [15].

Table 2 shows the effect of concentration on sorption properties of poly(ethyleneimine)-silica resin for Hg(II) and Pb(II). Concentration is an important variable to evaluate in a sorption process, because changes in concentration of effluent can affect the performance of sorption process. In order to study the change in metal ion uptake with concentration, the sorption was evaluated at different functional group/metal ion ratios (mol) for 1 h of contact. The metal ion selected for experiment were Hg(II) and Pb(II) due to the high retention observed at pH 5 and 2, respectively. The Hg(II) presents similar retention values when its concentration increase (except for a ratio 20:0.5), suggesting that resins have reached saturation state (~50% of retention). In case of Pb(II), a maximum retention is observed when concentration ratio is 40:1, reaching retention over 80% similar to the results observed in Table 1.

Table 2 Concentration effect of Pb(II) and Hg(II) on metal ion uptake

Metal ion	Molar ratio	Retention (mmol M^{n+}/g_{resin})	Retention (mg M^{n+}/g_{resin})	Retention (%)
Hg(II)	20:0.5	0.001	0.26	7.8
	20:1	0.018	3.72	49.8
	20:2	0.037	7.54	49.7
	20:4	0.078	15.71	50.1
Pb(II)	40:0.5	0.005	1.10	73.6
	40:1	0.010	2.09	82.3
	40:2	0.020	4.21	62.4
	40:4	0.024	4.96	40.6

The temperature is other variable that affects the sorption process, producing effects on retention capacity, ionization degree, etc. The temperature affects mainly ion exchange systems with low ionization; thus, ion exchange resins with weakly acid–base functional groups are affected, which is the case of polyethyleneimine with weakly basic groups on its main chain (amino). Figure 1 shows the temperature effect on retention for Pb(II) and Hg(II) at pH 5 and 2, respectively, using the molar ratios with higher retention. Pb(II) does not present significant changes when temperature of contact was increased, however, mercury retention experiment was observed as temperature increases from 20 to 35 °C and the retention also increase from 0.019 to 0.026 mmol/g resin, corresponding to an increment of 20.7% of retention. The result can be explained considering that an increase on temperature also increase the kinetic energy of metal ion, promoting the diffusion of metal ions and favoring the exchange process [16].

Selectivity

In a water treatment process generally the effluent consist in a mixture of different metal ions, and the selectivity is an important issue to take into account. Functional group such as sulfonate are found in most of the ion exchange resins used, however, its selectivity is low compared with other functional groups containing nitrogen, sulfur, or oxygen atoms in the ligand function. In order to evaluate the selectivity of poly(ethyleneimine)-silica resins, experiments were carried out in different conditions; binary, ternary, and quaternary mixtures of metal ions (Table 3). The experiment in presence of Hg(II) were carried out at pH 2, while the experiment using a ternary mixture at pH 5. It is observed that for all mixtures containing Hg(II) ions, the resin present a high selectivity toward mercury. The most promissory result were for binary mixtures, Hg(II)–Cd(II) and Hg(II)–Zn(II), where mercury retention with respect to total amount of metal ion reached 91 and 84%, respectively. It is important to note that for quaternary mixture, Hg(II) retention was higher than 87%, confirming the high selectivity of poly(ethyleneimine) toward mercury ions. In case of ternary mixture, the resins showed a high retention for Zn(II) compared with other metal ions present in the mixture. This is an unexpected result considering the high retention of Pb(II) observed under non competitive conditions, however, it has been reported that Zn(II) presents a high affinity toward amino functions [17].

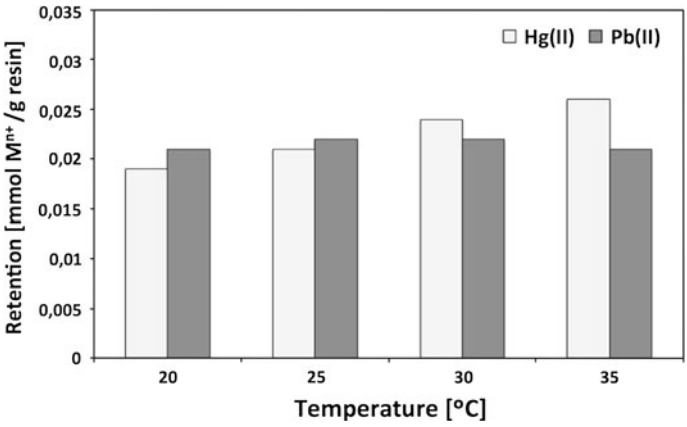

Fig. 1 Effect of temperature on Hg(II) and Pb(II) sorption

Table 3 Selectivity experiment for different mixtures

Mixture	Metal ion	Retention (mmol M^{n+}/g_{resin})	Retention (mg M^{n+}/g_{resin})	Retention A[a] (%)	Retention B[b] (%)
Binary	Pb(II)	0.011	2.32	29.3	37.1
	Hg(II)	0.019	3.80	51.5	62.9
Binary	Cd(II)	0.002	0.19	6.6	8.2
	Hg(II)	0.019	3.81	51.5	91.8
Binary	Zn(II)	0.003	0.22	9.7	15.2
	Hg(II)	0.019	3.80	51.5	84.8
Ternary	Cd(II)	0.001	0.07	3.6	4.9
	Zn(II)	0.008	0.55	29.8	69.2
	Pb(II)	0.003	0.65	26.2	25.8
Quaternary	Cd(II)	0.002	0.19	4.7	4.0
	Zn(II)	0.001	0.09	3.8	3.4
	Pb(II)	0.002	0.49	6.2	5.5
	Hg(II)	0.038	7.64	85.0	87.1

[a] Retention of single metal ion respect to initial concentration

[b] Retention respect to total amount of metal ion retained

Elution experiments

Once resins have reached its saturation of metal ions, the elution of metal ion retained lead to regeneration of resin, and then enabling the reuse of ion exchange resins. For this purpose, it is necessary to use a suitable eluent, which in case of a cation exchange resins, like poly(ethyleneimine) must be a strong acid. Table 4 summarizes the elution percentage of Hg(II) and Pb(II) using different acids and concentration. In case of mercury elution experiments, other eluent reagents were

Table 4 Elution experiments of Hg(II) and Pb(II)

Eluent	Eluent concentration (mol/L)	Hg(II) elution (%)	Pb(II) elution (%)
HCl	1	16.7	12.0
	4	30.5	11.7
HNO_3	1	30.2	11.2
	4	35.5	12.2
$HClO_4$	1	33.3	11.7
	4	28.5	10.4
NH_2SNH_2	0.5	39.3	–
	1	35.2	–
NH_2SNH_2:HCl	0.5:0.5	63.2	–
	1:1	51.1	–
	4:4	60.1	–
H_2SO_4	1	54.9	–
	4	63.1	–

evaluated; such is the case of thiourea, sulfuric acid, and a mixture of thiourea–hydrochloric acid. For Hg(II) elution experiments, results indicate when concentration of eluent increase the percentage of elution is higher. This is an expected result, as the concentration increase the gradient concentration of H^+ also increase allowing the desorption of Hg(II) bonded ions. The best performance of resin regeneration was found when the eluent consist in a mixture of thiourea and hydrochloric acid (0.5 M:0.5 M) reaching a 63% of elution. This result can be explained considering the high affinity of mercury and mercapto groups [13], leading a synergic effect between acid and thiourea. In case of Pb(II) ions, the eluent used shows a low elution with the acids used in experiment.

Sorption kinetics

The evaluation of kinetics sorption process is an important issue before to scale up an industrial process. In this study, kinetic experiments were carried out by batch procedure for a period of 24 h using poly(ethyleneimine)-silica resin and Hg(II) and Pb(II) as solute. Experiments were carried out according to the results obtained from previous sorption studies. Pb(II) sorption was studied at a molar ratio of 40:1 at pH 5, while Hg(II) sorption at a molar ratio of 20:1 at pH 2.

Several kinetic models have been used to determine the rate constants of different systems. The most used kinetic models are those based on the decrease of active sites available to interact with solute (adsorption capacity). The models have been successful used to determine rate constant and are characteristic of the sorption process, if it is described by pseudo-first-order model [18], pseudo-second-order model [19].

Figure 2 shows the effect of time on retention capacity for both metal ions and it is observed that Pb(II) reach the maximum retention at lower times than Hg(II),

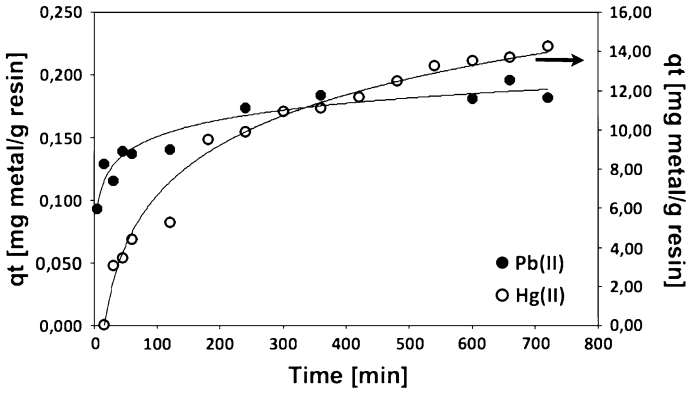

Fig. 2 Effect of time for Hg(II) and Pb(II) sorption by poly(ethyleneimine)-silica resins

indicating that sorption is more efficient. However, the retention capacity of resins for Hg(II) is higher, increasing continuously with time.

The effect of time on sorption uptake was evaluated by different kinetic model in order to provide useful information about process.

Lagergren proposed the first order model for describing the adsorption process of solid–liquid systems. The model based on solute concentration is called pseudo-first order and its linear form is formulated as below:

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

where q_e (mg/g_{resin}) and q_t are the amount of metal ion adsorbed at equilibrium and at time t, respectively. The slope taking from a plot of $\log(q_e - q_t)$ versus t, allows to determine the rate constant k_1 (1/min). On the order hand, Ho proposed the pseudo-second-order model, also based on solute concentration and considering the decrease of adsorption capacity. The kinetic model can be expressed as below:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2}$$

Integrating and assuming boundary conditions, the rearranged linear form of pseudo-second-order model is obtained:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where q_e and q_t are the metal ion amount adsorbed (mg/g_{resin}) at equilibrium and at time t, respectively, $h = kq_e^2$ is the initial sorption of metal ion [mg As(V)/g_{resin} min], and k_2 is the rate constant of sorption (g_{resin}/mg min).

Figure 3 shows the curves of pseudo-first- and pseudo-second-order models fitted to experimental data and Table 5 summarized the kinetic parameters obtained. In case of Pb(II) results, Lagergren pseudo-first order presented a low agreement between experimental data and the model, confirmed by the correlation coefficient ($r^2 = 0.9120$), besides, the calculated equilibrium sorption capacity was quite

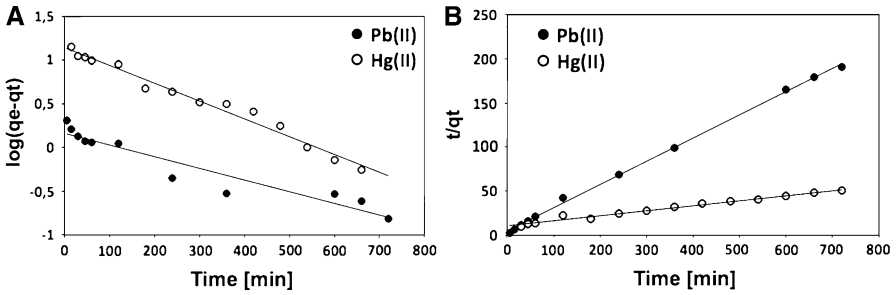

Fig. 3 Kinetic models adjusted to experimental data of Pb(II) and Hg(II) sorption by poly(ethyleneimine) coated on silica particles: **a** pseudo-first-order and **b** pseudo-second-order models

Table 5 Kinetics parameters for Pb(II) and Hg(II) sorption

Parameters	Pb(II)	Hg(II)
$q_{e,exp}$ (mg metal ion/g_{resin})	3.92	14.26
Pseudo-first order		
$q_{e,cal} \times 10^{-3}$ (mg metal ion/g_{resin})	8.16	13.96
$k_1 \times 10^{-3}$ (1/min)	2.99	4.60
r^2	0.9120	0.9798
Pseudo-second order		
$q_{e,cal}$ (mg metal ion/g_{resin})	3.79	17.69
$k_2 \times 10^{-3}$ (g_{resin}/mg metal ion min)	14.4	0.295
h (mg metal ion/g_{resin} min)	0.206	0.0923
r^2	0.9985	0.9814

different from the experimental value. On the other hand, the sorption of Hg(II) presented better agreement with higher correlation coefficient ($r^2 = 0.9798$), and the calculated sorption capacity presents a similar value compared with experimental value. Better agreements were found when experimental data were adjusted to pseudo-second-order model. The correlation coefficients increased compared with pseudo-first-order model and calculated sorption capacity of Pb(II) was almost the same as experimental value, specifically for Pb(II).

Equation 3 can be rearranged in order to obtain the time needed for a sorption fraction [20], for example, the half-life of sorption ($t_{0.5}$) when $q_t = 0.5q_e$ can be obtained by the next equation:

$$t_{0.5} = \frac{1}{k_2 q_e} \tag{4}$$

The half-life sorption of Pb(II) and Hg(II) by poly(ethyleneimine)-silica are 0.018 and 0.19 min, respectively. This indicated that sorption of Pb(II) is faster than Hg(II) which is confirmed by the values of rate constant in Table 5.

In addition to kinetic models, the diffusion rate of solute can be studied by other models based on diffusion laws (e.g., Fick law), which is the case of intra-particle diffusion model [21, 22]. This model take into account the diffusion of Pb(II) within

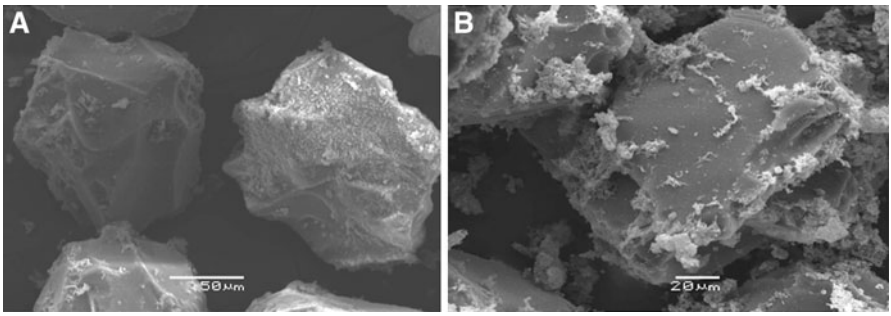

Fig. 4 Scanning electron micrographs of **a** poly(ethyleneimine)-silica and **b** poly(ethyleneimine)-silica after sorption of Pb(II)

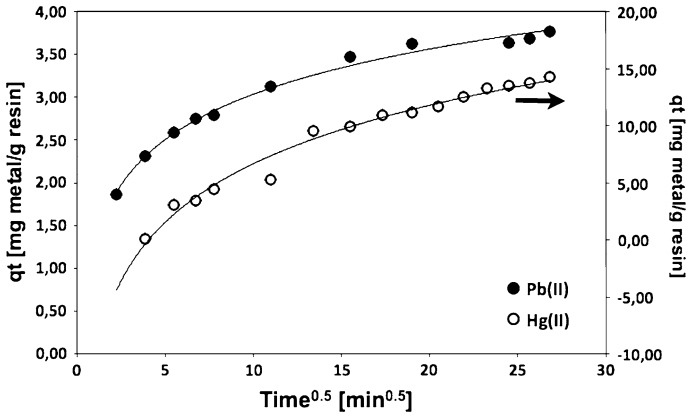

Fig. 5 Intra-particle diffusion model for Hg(II) and Pb(II) sorption by poly(ethyleneimine)-silica resins

the pores of adsorbent. The commercial poly(ethyleneimine)-silica used for sorption possess a uniform surface, no roughness, and without pores, and then is expected that sorption should be controlled by film diffusion, namely the diffusion of Pb(II) ions by the surrounding liquid film of adsorbent (Fig. 4). However, the water absorption capacity of poly(ethyleneimine)-silica was 16.4 mg H_2O/g resin, then it is possible for the diffusion of ions through the pores of resins due to the water absorption. In order to confirm if intra-particle diffusion controls the sorption process, the experimental data were plotted according to intra-particle diffusion proposed by Weber and Morris (q_t vs. $t_{0.5}$), which in ideal case should be a straight line passing through origin. Figure 5 shows the intra-particle diffusion curves for Hg(II) and Pb(II) sorption, and it is observed that curves did not cross the origin and present an intercept in y axis, indicating that exist an initial uptake. In addition, the curves do not represent a straight line confirming that sorption process is not intra-particle diffusion controlled and suggesting that process is governed by film diffusion with a rapid uptake at the first minutes of contact.

Conclusions

Sorption of poly(ethyleneimine)-silica resins were evaluated for Zn(II), Cd(II), Pb(II), and Hg(II) metal ions in aqueous solution. The resins showed good performance for Hg(II) and Pb(II) sorption when the molar ratio ligand/metal ion was 40:1 and 20:1, respectively. For competitive conditions, resins presented high selectivity toward Hg(II) ions, reaching a 87% of retention respect total amount of metal ion in case of a quaternary mixture. The effect of time on sorption showed that Pb(II) adsorption is faster than Hg(II), lead needs less time to reach the *plateau.* Pseudo-first- and pseudo-second-order models were fitted to experimental data and correlation coefficient indicated that pseudo-second-order model fits better compared with pseudo-first-order model, with correlation coefficient higher than 0.98. Besides, the half-time sorption demonstrated that Pb(II) sorption is more efficient than Hg(II) sorption.

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References

1. Letterman RD (1999) Water quality and treatment, 5th edn. McGraw-Hill, Inc, New York
2. Davis ML (2010) Water and Wastewater Engineering, 1st edn. The McGraw-Hill Companies Inc., New York
3. Smith SD, Alexandratos SD (2000) Ion Selective Polymer-Supported Reagent. Solvent Extr Ion Exch 18:779–807
4. Dabrowski A, Hubicki Z, Podkoscielny P, Robens E (2004) Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. Chemosphere 56(2):91–106
5. Pustam AN, Alexandratos SD (2010) Engineering selectivity into polymer-supported reagents for transition metal ion complex formation. React Funct Polym 70:545–554
6. Moreno-Villoslada I, Gonzalez F, Jofre M, Chandıa P, Hess S, Rivas BL (2005) Complexation Behavior of Cu2 + in the Presence of Iminodiacetic Acid and Poly(ethyleneimine). Macromol Chem Phys 206:1541–1548
7. Nonogaki S, Makishima S, Yoneda Y (1958) Polyvalent Anion-Exchange Resins Composed of Cross-Linked Polyethyleneimine Complexes of Heavy Metals. J Phys Chem 62(5):601–603
8. Rivas BL, Maturana HA, Peric IM, Fierro AM (1995) Modified poly(ethyleneimine) supports for vanadium, molybdenum, and rhenium removal. Polym Bull 35(3):337–343
9. Bartulín J, Maturana HA, Rivas BL, Peric IM (1984) Synthesis of strong basic resins for uranium recovery (part II). Polym Bull 12(2):189–193
10. Rivas BL, Moreno-Villoslada I (1998) Poly[acrylamide-*co*-1-(2-hydroxyethyl)aziridine], an efficient water soluble polymer for selective separation of metal ions. J Appl Polym Sci 69:817–824
11. Rivas BL, Geckeler KE (1992) Synthesis and metal complexation of poly(ethyleneimine) and derivates. Adv Polym Sci 102:173–183
12. Jal PK, Patel S, Mishra BK (2004) Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions. Talanta 62:1005–1028
13. Martell AE, Hancock RD (1996) Metal complexes in aqueous solution. Plenum Press, New York
14. Zhu X, Alexandratos SD (2005) Affinity and selectivity of immobilized *N*-methyl-D-glucamine for mercury(II) ions. Ind Eng Chem Res 44:7490–7495
15. Amara M, Kerdjoudj H (2004) Separation and recovery of heavy metals using a cation-exchange resin in the presence of organic macro-cations. Desalination 168:195–200
16. Ivanov V, Timofeevskaya V, Gorshkov V, Drozdova N (1996) The role of temperature in ion exchange processes of separation and purification. J Radioanal Nucl Chem 208(1):23–45

17. Ghoul M, Bacquet M, Morcellet M (2003) Uptake of heavy metals from synthetic aqueous solutions using modified PEI–silica gels. Water Res 37(4):729–734
18. Ho YS, McKay G (1998) The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat. Can J Chem Eng 76(4):822–827
19. Ho YS, McKay G (1999) Pseudo-second order model for sorption processes. Process Biochem 34:451–465
20. Ofomaja AE (2010) Biosorption studies of Cu(II) onto Mansonia sawdust: process design to minimize biosorbent dose and contact time. React Funct Polym 70(11):879–889
21. Wu F-C, Tseng R-L, Juang R-S (2009) Initial behavior of intraparticle diffusion model used in the description of adsorption kinetics. Chem Eng J 153:1–8
22. Ofomaja AE (2010) Intraparticle diffusion process for lead(II) biosorption onto mansonia wood sawdust. Bioresour Technol 101:5868–5876