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Lead adsorption by silica-immobilized humin under flow and batch conditions: Assessment of flow rate and calcium and magnesium interference

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Abstract

Batch and column experiments were performed to determine the Pb(II) binding ability of silica-immobilized humin biomass under different conditions. Batch experiments were performed to determine the interference of Ca(II) and Mg(II) and column experiments were used to determine the effect of flow rate and the presence of Ca(II) and Mg(II) on the Pb(II) adsorption by the humin biopolymer. The results from the batch experiments showed that Pb binding decreased as the concentrations of Ca and Mg increased. At a concentration of 100 mM, the interference of Ca alone was 36%, while for Mg it was 26%; however, when both cations were present, the interference increased up to 42%. Column experiments were performed at flow rates of 1, 1.5, 2, and 3 mL min^{-1} using a 0.1 mM Pb(II) solution. The results showed that the highest Pb adsorption was obtained at the flow rates of 1 and 1.5 mL min^{-1}. The average Pb binding capacity at these two flow rates was 182.3 ± 0.7 μM Pb g^{-1}. In addition, a recovery of 99.5 ±0.3% was obtained. Immobilized humin exposed under flow conditions to Pb–Ca, Pb–Mg or Pb–[Ca + Mg] solutions (Pb used at 0.1 mM and Ca and Mg at 1 mM) showed a Pb binding capacity of 161 ± 5, 175 ± 5, and 171 ± 1 μM g^{-1}, respectively. In mixtures containing Pb–Ca, Pb–Mg and Pb–Ca–Mg, the Pb recovery was $89.8\% \pm 0.35$, $90.3\% \pm 0.43$, and $88.1\% \pm 0.5$, respectively. Pb recovery was performed using 30 bed volumes of 0.1 M HCl as stripping agent. The results of these experiments demonstrated that silica-immobilized humin biomass has the potential for Pb removal from aqueous solution even in the presence of 20 mM of calcium and magnesium.

Keywords: Humin-polymer; Lead; Column; Adsorption; Hard cations

1. Introduction

Adsorption is the partition of substances from the liquid phase onto the surface of a solid substrate. This process is called biosorption when a biomass is the solid substrate. Over the last two decades, scientists and engineers have studied the potential of several types of biomass for heavy metal removal from aqueous solutions. Recent studies have demonstrated that biomasses of algae, fungi, moss, peat moss, and humic substances are able to adsorb metals such as Pb from industrial effluents [1–9].

Humic substances (humin, humic and fulvic acids) are very complex compounds containing numerous functional groups, primarily carboxylic and phenolic groups [10]. Humin is insoluble at any pH value and it has the highest molecular weight and carbon content among the three humic fractions [10]. Moreover, humin is resistant to microbial degradation and is considered the final product of the humification processes [11]. ^{13}C NMR analyses of humic substances obtained from soil, sediments, and peat moss have shown that humin has a strong signal for paraffinic carbon. Other studies have demonstrated that these paraffinic groups contribute to humin insolubility [11,12].

Humin is a very porous substance with a large surface area. This characteristic is very useful in the adsorption process. Previous studies have demonstrated that humin can efficiently adsorb heavy metals in solution at pH 5 [13]. The studies also

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demonstrated that mechanisms such as electrostatic attraction, coordination and complexation, as well as ionic exchange, play a major role in the metal ion binding to dead biomass [1–4,10].

In the present research study, humin was immobilized in a silica matrix and packed into columns to evaluate its Pb removal and recycling capacity under different flow rates. Additionally, batch and column experiments were performed to evaluate the interference of the hard cations Ca(II) and Mg(II) on lead binding to immobilized humin.

2. Methodology

2.1. Humin extraction

Humin was extracted following the procedure previously described in the literature [8]. A fraction of 100 g of Canadian Sphagnum peat moss (Fisons Horticulture, Vancouver, BC, Canada) was dried at 51 °C for 72 h. The dried biomass was ground to a fine powder and sieved through the 80 mesh (0.177 mm) screen. Afterwards, the powder was washed twice with 0.01 M HCl and centrifuged for 5 min at 3000 rpm (Fisher Scientific, Marathon 6K). Subsequently, 500 mL of 0.1 M NaOH were added to the biomass and the pH of the solution was adjusted to 13.5 using 5 M NaOH. The solution was stirred for 48 h and centrifuged at 3000 rpm for 10 min. The humin fraction precipitated while humic acids remained in the supernatant. The humin fraction was washed twice with deionized (DI) water to eliminate the remaining alkalinity and freeze–dried on a Labconco freeze–dryer (Labcono, Kansas City, MO, USA) at -45 °C and 69×10^{-3} Mbar pressure for 48 h. The dried humin biomass was ground and sieved through a 100 mesh screen (149 μm size particle).

2.2. Immobilization of humin biomass

Humin biomass was immobilized following a similar procedure to the one previously reported [14]. Twenty gram of humin previously sieved through the 149 μm screen were washed twice with 0.01 M HCl and once with DI water. The washings were collected, evaporated, and weighed to record any loss of biomass. Three hundred milliliters of 5% H_2SO_4 were placed in a 2 L beaker and a solution of 6% Na_2SiO_3 was added until a pH of 2 was reached. Under continuous stirring, the washed biomass was added to the H_2SO_4/Na_2SiO_3 mixture and allowed to equilibrate for approximately 15 min. Additional sodium silicate solution was added until a pH of 7 was reached and the formation of the polymer achieved. The polymer gel was washed with DI water until washings were negative to the sulfates test (using $BaCl_2$ [19]. The polymer was dried overnight in an oven at 60 °C, ground using mortar and pestle, and sieved to pass the 20–40 mesh (0.841–0.420 mm) size.

2.3. Batch experiments for Ca(II) and Mg(II) interference on Pb(II) binding to humin biopolymer

The concentrations of Ca (from $Ca(NO_3)_2{\cdot}4H_2O$) and Mg (from $Mg(NO_3)_2{\cdot}6H_2O$) used in this experiment were 0, 0.1, 0.2, 1, 2, 10, 20, 100, 200, and 1000 mM. Pb was kept at a concentration of 0.1 mM. The concentration of Ca and Mg were chosen in order to test the binding ability of the biopolymer under light and heavy hardiness conditions. All the solutions were adjusted to pH 5. A portion of 500 mg of the biopolymer was washed three times with 0.01 M HCl and three times with double deionized (DDI) water to reduce any external source of Ca and Mg. The biopolymer was resuspended in 100 mL of DDI water to obtain a final concentration of 5 mg mL^{-1}, that was adjusted to pH 5 using HNO_3 and NaOH, as needed. Subsequently, aliquots of 4 mL of the suspension were transferred to 5 mL test tubes, centrifuged at 3000 rpm for 5 min, and the supernatants discarded. Subsequently, 4 mL of the metal mixtures were added to the respective reaction tubes, placed on a rocker, and allowed to react for 1 h. Afterward, the tubes were centrifuged for 5 min at 3000 rpm. The cations Ca, Mg, and Pb were determined in the supernatant using inductively coupled plasma/optical emission spectroscopy (ICP/OES). Each treatment was replicated three times for statistical purposes.

2.4. Column studies for Pb(II) adsorption by silica-immobilized humin

Column experiments were performed at pH 5, since de la Rosa et al. [13] reported that this is the optimum pH for Pb(II) binding to humin. A sample of approximately 1.5 mg of dry biopolymer was re-hydrated and 6 mL (one bed volume) of the re-hydrated polymer were loaded into columns of 15 cm × 1 cm i.d. After packing, the columns were washed with 0.01 M HCl to eliminate possible metal contamination. Subsequently, DI water adjusted to pH 5 was passed through the columns until washings had a pH of 5. Four columns at the flow rates of 1, 1.5, 2, and 3 mL min^{-1} were used to determine the effect of flow rate on Pb binding to the polymerized humin. A flow rate <1.0 mL min^{-1} was not employed to avoid a longer time of analysis. In summary, 500 bed volumes of a 0.1 mM Pb solution [from $Pb(NO_3)_2$] were passed through the columns at the respective flow rate and the effluents were collected. Pb content in the outlet solutions was determined by flame atomic absorption spectroscopy (FAAS) (Perkin-Elmer model 3110) at a wavelength of 283.3 nm. Three downflow sorption cycles were run on each column in order to determine the binding capacity of the polymer after the corresponding saturation and desorption cycle. Pb desorption was performed by passing 30 bed volumes of 0.1 M HCl through the saturated column. Subsequently, the corresponding effluents were collected and analyzed by FAAS to quantify the desorbed Pb ions and the percent of Pb recovery [19]. After every sorption/desorption cycle, the columns were washed with DI water adjusted to pH 5 on inverted flow, in order to destroy any preference channels that might have been formed. The washings were discontinued when the column reached a pH value of 5.

2.5. Column studies for Ca(II) and Mg(II) interference on Pb(II) binding to humin biopolymer

For the interference studies, three columns were packed as described in Section 2.3, and 500 bed volumes of the correspond-

ing solution were passed through each column (pH 5). In all the cases, the Pb concentration was maintained at 0.1 mM, while the solutions containing Ca, Mg, or both had 1 mM each. The flow rate was 2 mL min^{-1}, and all the solutions were prepared using DDI water.

2.6. Metal analyses using ICP/OES

The metal analyses for batch experiments were performed using an ICP/OES Perkin-Elmer Optima 4300 DV with an AS-90 plus auto sampler rack. The following parameters were introduced: nebulizer flow 0.7 L min^{-1}, radio frequency power 1300 W; sample introduction 1.45 mL min^{-1}; flush time 10 s; delay time 60 s; read time 10 s; wash time 45 s; replicates 3 (each sample was read three times). Standards were prepared from 4.8 mM (1000 mg L^{-1}) Pb(II), 2 M Ca(II), and 2 M Mg(II) stock solutions and diluted with 5% HNO_3. The calibration curves for metal determination using ICP were obtained with a blank and six different concentration points and the correlation coefficients (r^2) were 0.9999 or better. Samples were analyzed up to 500 bed volumes and the difference between metal concentration in the original solution and the metal concentration found in the effluent was assumed the metal bound to the column.

3. Results and discussions

3.1. Effect of flow rate on Pb(II) adsorption by silica-immobilized humin

Fig. 1 shows the breakthrough curves for Pb adsorption to silica-immobilized humin at different flow rates. Fig. 1a shows that at 1 mL min^{-1} flow rate, Pb appears in the effluent after 350, 380, and 315 bed volumes for the first, second, and third cycle, respectively. The capacity of the column to bind Pb at this flow rate had an average of 180 μmol Pb g^{-1} biomass (Table 1). Fig. 1b shows the breakthrough curves for three consecutive cycles at a 1.5 mL min^{-1} flow rate. This figure shows that Pb appeared in the effluent after 367, 340 and 400 bed volumes in the first, second, and third saturation cycles, respectively. Pb concentrations in the effluent at 500 bed volumes (for the first, second, and third cycle) were 48.3, 34.7, and 57.9 μM L^{-1} lower than the Pb concentration in the influent solution (103.0 ± 7.6 μM). According to the data presented in Table 1, at this flow rate the average capacity of the column was 180 μmol Pb g^{-1} biomass. Thus, the average capacity of three consecutive cycles was the same when the flow rates were 1 and 1.5 mL min^{-1}. Fig. 1c shows the breakthrough curve obtained using the 2 mL min^{-1} flow rate. The breakthrough point for the three cycles at this flow rate appeared to be the same (350 bed volumes). On the other hand, no significant difference ($P < 0.05$) was found in the Pb binding capacity of the column at this flow rate as compared to the capacity at 1 and 1.5 mL min^{-1} velocities (Table 1). No saturation of the column was observed since Pb concentration in the influent on the third cycle was 86 μM, while in the effluent it was 20 μM for the first two cycles and 23 μM for the third cycle. These results were similar to the ones reported by de la Rosa et al. [16]. Fig. 1d displays the breakthrough curves for the 3 mL min^{-1} flow rate. This figure shows that in the first and second cycle, Pb appeared in the effluent solution after 350 bed volumes. However, as observed with the other flow rates, even after 500 bed volumes the column was not saturated. The Pb concentrations found in the effluent in the first and second cycles were 52 and 53 μM lower, respectively, than the concentration in the fed solution (92 μM). In the third cycle, the breakthrough point started at 314 bed volumes, only 36 bed volumes earlier compared to the first and second cycles.

After 500 bed volumes the column was not saturated, since at this point the concentration of Pb in the effluent was 66 μM. In addition, the average binding capacity at this flow rate was of 170 μmol Pb g^{-1} (Table 1).

As data show, the capacity of the column to bind Pb at the different flow rates had small variations. Such variations may

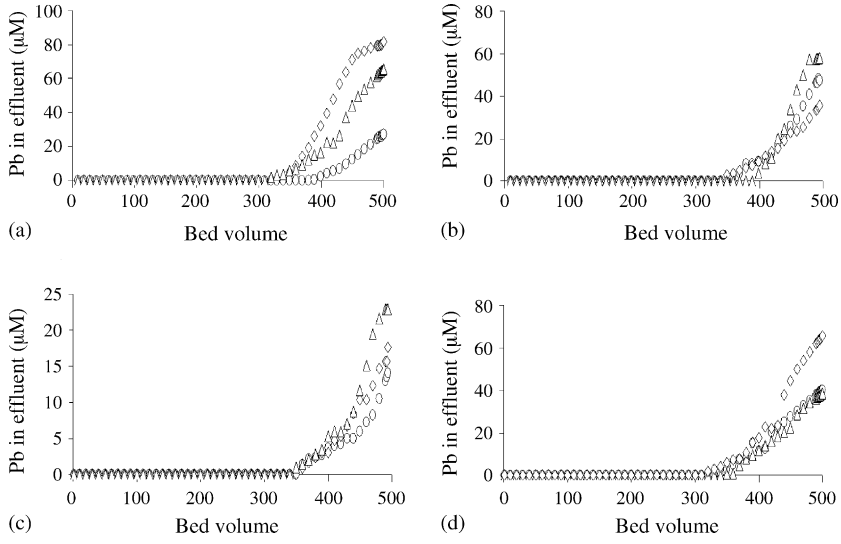

Fig. 1. Breakthrough curves for Pb(II) adsorption by humin biopolymer at different flow rates: (a) 1 mL min^{-1}; (b) 1.5 mL min^{-1}; (c) 2 mL min^{-1}; and (d) 3 mL min^{-1}. The Pb concentration in the influent was 100 ± 14 μM. Solutions were adjusted to pH 5: (◊) stands for first cycle; (◯) for second cycle; and (△) for third cycle.

Table 1
Lead adsorption capacity of silica-immobilized humin and percent of metal recovery at different flow rates

Flow rate (mL min^{-1})	Pb bound to humin biopolymer (μmol g^{-1})				Pb recovery (%)			
	1st cycle	Second cycle	Third cycle	Average ± S.E.	First cycle	Second cycle	Third cycle	Average ± S.E.
1	187	154	210	180 ± 13	99.9	98	99.7	99.1 ± 0.4
1.5	197	145	200	180 ± 15	100	99.8	99.6	99.8 ± 0.2
2	180	160	146	160 ± 8	99.4	98.1	99.2	98.9 ± 0.03
3	210	150	142	170 ± 17.8	92	91.7	91.9	91.8 ± 0.2

Each saturation cycle was run with 500 bed volumes of 0.1 mM Pb(II) solution adjusted at pH 5. A solution of 0.1 M HCl was used as stripping agent after each saturation cycle. Data are average ± S.E.

be attributed to small differences in metal concentration in the influent solution. In addition, variations in breakthrough points may be due to either uneven packed column or unequal flow patterns [15]. In this study, it was found that the columns never reached the saturation point. For this reason, it is possible to assume that the humin-immobilized biomass might be used for additional cycles.

Several studies have indicated that carboxyl groups and other proton exchanging moieties have important role in the metal binding process to biomasses. Thus, a decrease in pH to protonate Pb-carboxylate complexes has been recommended and used to recover Pb bound to the biomass [17,18]. According to this, the Pb bound to humin biopolymer was desorbed after each saturation cycle using 30 bed volumes of 0.1 M HCl and the results are given in Table 1. Table 1 shows that the percent of Pb recovered from the biomass under flow conditions had an average of 99.2% ± 0.2 for the first three flow rates, and 91% ± 0.2 for the 3 mL min^{-1} flow rate.

According to the results presented in Table 1, no significant difference ($P < 0.05$) was observed among the Pb binding capacity showed by the humin biopolymer at the four flow rates. However, the trend indicated that the binding capacity tends to decrease at higher velocity. The percentages of Pb recovered in the three cycles at each flow rate were similar, which indicates that HCl is a good stripping agent for Pb. Similar results have been reported by Chandra et al. using Indian Sarsaparilla and de la Rosa et al. using humic acids [18,19]. The results of the present study are comparable to those reported by Jalali et al. [20] for marine algae *G. canaliculata* and *G. corticata*, but smaller than those reported by the same authors for *U. lactuca* and other algal species. On the other hand, the amounts of Pb bound by immobilized humin were higher than those reported by Guangyu and Viraraghavan for *M. rouxii* [21], and Holan and Volesky [22] for *Ascophyllum nodosum*, *Sargassum natans*, *Fucus vesiculosus and Sargassum vulgare*. The information provided by the present research indicates that the preferential order for the flow rates studied was 1 mL min^{-1} = 1.5 mL min^{-1} ≈ 2 mL min^{-1} ≈ 3 mL min^{-1}.

3.2. Batch experiments for Ca(II) and Mg(II) interference on Pb(II) binding to silica-immobilized humin

Fig. 2 shows the results for the experiments on Ca and Mg interference on Pb binding to the silica-immobilized humin. The data showed that at concentrations up to 20 mM these hard

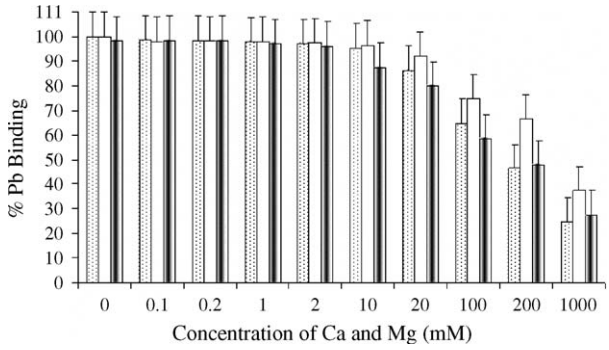

Fig. 2. Batch experiments for Ca(II) and Mg(II) interference on Pb(II) binding to humin biopolymer. Biomass was reacted with the mixtures Pb(II)–Ca(II) (⊡); Pb(II)–Mg(II) (▭); and Pb(II)–Ca(II)–Mg(II) (▮). Ca(II) and Mg(II) concentrations varied from 0 to 1000 mM each, while Pb(II) concentration was maintained at 0.1 mM. Solutions were adjusted to pH 5. Error bars represent ± S.E.

cations did not significantly interfere in the Pb binding to humin biopolymer ($P < 0.05$). As shown in Fig. 2, the percent of Pb bound decreased as the concentrations of Ca and Mg increased. At a concentration of 100 mM, the interference of Ca alone was 36%, while for Mg it was 26%; however, when both cations were present, the interference increased up to 42%. At a concentration of 200 mM the interference increased up to 52%, 35%, and 51%, when Ca, Mg or both cations were present, respectively. The interference on Pb binding was of 76%, 63%, and 73%, respectively in the presence Ca, Mg or Ca + Mg at 1000 mM each. The statistical analysis showed that Ca and Mg at 100 mM caused a significant interference ($P < 0.05$) on Pb binding to humin biopolymer. The data obtained herein also suggest that specially Ca (either alone or mixed with Mg) might cause most of

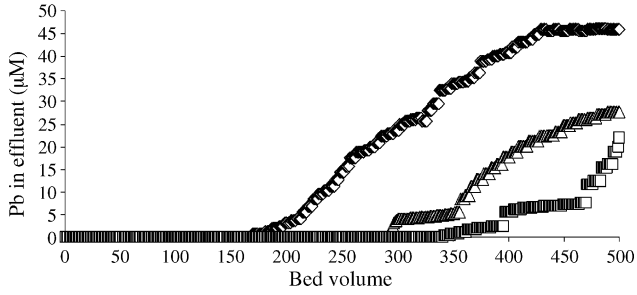

Fig. 3. Breakthrough curves for Ca(II) and Mg(II) interference on Pb(II) binding to humin biopolymer. The flow rate was 2 mL min^{-1}. The 0.1 mM Pb(II), 1 mM Mg(II), 1 mM Ca(II) solutions were adjusted to pH 5: (△) stands for Ca–Pb; (□) Mg–Pb; and (◊) for Ca–Mg–Pb.

Table 2
Binding capacity and percent of metal recovery for Pb(II) after three saturation cycle in presence of Ca(II), Mg(II), or both

Column	Pb bound to the biopolymer (μmol g^{-1})	Recovery of Pb (%)
Mg/Pb	175.5 ± 4.74	90.3 ± 0.43
Ca/Pb	161.1 ± 5.19	89.8 ± 0.35
Ca–Mg/Pb	170.8 ± 1.25	88.1 ± 0.54

The 0.1 mM Pb(II), 1 mM Mg(II), and 1 mM Ca(II) solutions were adjusted to pH 5, and a 1.5 mL min^{-1} flow rate was used. Data are average ± S.E.

the interference. It also might indicate the quantity of ions plays an important role in metal binding. Spinti et al. [6] using Sphagnum peat moss and Chandra et al. [18] using Indian Sarsaparrilla have reported similar results. The binding of different heavy metals to the functional groups present in the biomass might occur through an ion exchange reaction. In addition, Martell and Smith [23] have reported that some functional groups, such as carboxylates, have stability constants that cause a higher affinity for heavy metals than for harder cations.

3.3. Column experiments for Ca(II) and Mg(II) interference on Pb(II) binding to humin biopolymer

Column experiments were performed in order to determine the interference of Ca and Mg on Pb binding to the silica-immobilized biopolymer under flow conditions. Experiments were carried out using individual and combined solutions of 1 mM Ca and Mg, and 0.1 mM Pb, under a 1.5 mL min^{-1} flow rate. These parameters were chosen according to the best results obtained in the batch experiments described before. Fig. 3 shows the breakthrough curves for the mixtures Pb–Ca, Pb–Mg, and Pb–Ca–Mg.

As it was observed in the batch experiments, Mg showed a minimum effect on Pb binding since Pb appeared in the effluent after 350 bed volumes. However, for the Ca–Pb, and Ca–Mg–Pb mixtures, the breakthrough points appeared before 300 and 170 bed volumes, respectively. It was also found that after 500 bed volumes the column was not saturated because, at that point, the Pb concentration in the effluent was 48.30 μM for the three mixtures (see Fig. 3). This observation indicated that most of the interference for Pb binding was attributed to Ca, whose concentration was 10 times higher than Pb concentration. Table 2 summarizes the effect of Ca and Mg on Pb binding to humin biopolymer under flow conditions. As shown in this table, the average binding capacity was about 169.1 μmol g^{-1} and the percentage recovered varied from 88% to 90%. By comparing Figs. 1a–d and 2, it can be seen that Ca and Mg affected the Pb binding capacity of humin biopolymer when these elements were present at concentrations of 100 mM and above.

4. Conclusions

The average Pb binding capacity of immobilized-humin biomass under flow rates of 1 and 1.5 mL min^{-1} was of 182.3 ± 0.7 μM Pb g^{-1} with a recovery was of 99.5% ± 0.3. The retention capacity of the biomass was almost constant after three adsorption/desorption cycles, suggesting that the biopolymer might be used for additional cycles. It seems that Ca and Mg at low concentrations did not represent a major interference on Pb binding to the humin biopolymer. However, at 100 mM and above, this hard cations caused an important interference on Pb binding. The binding capacity of silica-immobilized humin has shown considerable advantage over other biosorbents treated alike. The results of this study showed that immobilized humin in a silica matrix might represent an inexpensive biosource for Pb removal from contaminated water, even in the presence of 20 mM of the hard cations Ca and Mg.

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