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Sorption of hazardous metals from single and multi-element solutions by saltbush biomass in batch and continuous mode: Interference of calcium and magnesium in batch mode

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ABSTRACT

Batch studies were performed to determine the interference of calcium (Ca) and magnesium (Mg) on the sorption of Cu(II), Cd(II), Cr(III), Cr(VI), Pb(II), and Zn(II) [from $CuSO_4$, $K_2Cr_2O_7$, $Pb(NO_3)_2$, $Cr(NO_3)_3$, $ZnCl_2$, and $Cd(NO_3)_2$] by saltbush (*Atriplex canescens*) biomass. The results demonstrated that Ca and Mg at concentrations of at least 20 times higher than the concentration of most of the target metals did not interfere with the metal binding. The data show that the batch binding capacity from a multimetal solution at pH 5.0 was (μmol/g) about 260 for Cr(III) and Pb, and about 117, 54, and 49 for Cu, Zn, and Cd, respectively. The use of 0.1 M HCl allowed the recovery of 85–100% of the bound Cu, Cr(III), and Pb, and more than 37% of the bound Cd and Zn. The column binding capacity for Pb was about 49 μmol/g from both the single and multimetal solutions, while it was, respectively about 35 and 23 μmol/g for Cr(III). The binding capacity for Cu and Zn from the single and multimetal column experiments was 35 μmol/g and less than 10 μmol/g, respectively. The stripping data from the single column experiment showed that 0.1 M HCl allowed the recovery of all the bound Cu and Zn, 90% and 74% of the bound Pb and Cr(VI), respectively, and less than 25% of the bound Cd and Cr(III), while the stripping from the multimetal experiment showed that 0.1 M HCl allowed the recovery of all the bound Cu and about 74%, 54%, 43%, and 40% of the bound Pb, Zn, Cd, and Cr(III), respectively.

1. Introduction

Water pollution, mainly caused due to mining, metal refinement, and other industrial activities threatens ecosystems and human health. Frequently, evaporative ponds and industrial effluents contain organic substances or heavy metals associated with hard cations such as calcium (Ca) and magnesium (Mg), that eventually reach bodies of water (Davydova, 2005; Dopp et al., 2004; Nadal et al., 2004; Pyatt et al., 2005; Rai et al., 2002). Although current water remediation technologies have proven to be efficient, a relatively new technology, bioremediation, is shown to have some advantages (Gardea-Torresdey et al., 2004; Khan et al., 2004; Mattina et al., 2003; Volesky, 2001, 2003). Biomasses used for water bioremediation bind different ions based on the type of ligands (Keasling et al., 1998; Davis et al., 2003; Gardea-Torresdey et al., 2004), the relative affinity of ions for the available ligands, and particular conditions or components (Arthur et al., 1974). For example, studies have shown that the arsenic sorption by sorghum biomass (*Sorghum bicolor*) is enhanced by iron salts but reduced by $MgSO_4$ (Cano-Aguilera et al., 2005). Other studies have shown that Ca and Mg ions at certain concentrations increased about 50% and 30%, respectively, the binding of Au(III) to hops biomass (Lopez et al., 2004). However, Ca and Mg reduced the binding of Cd(II), Cu(II), Cr(III), Ni(II), Pb(II), and Zn(II) by African alfalfa biomass (Gardea-Torresdey et al., 1997). Ca and Mg ions also reduced the binding of Co(II) by *Oscillatoria angustissima* biomass (Ahuja et al., 1999), but did not interfere with the binding of several heavy metals by chemically modified Marine brown algae biomass (Yoo et al., 1997). Likewise, Ca(II) and K(I) did not interfere with the biosorption of Cd by *Chlamydomonas reinhardtii* (Adhiya et al., 2002).

Previous experiments have shown that the bound metals can be recovered from the biomass using different stripping agents (Gardea-Torresdey et al., 1997; Horsfall and Abia, 2003). Stripping agents such as sodium citrate (Gardea-Torresdey et al., 2002), nitrilotriacetic acid (Lister and Line, 2001), ethylenediaminetetraacetic acid (Hashim et al., 2000), $NaHCO_3$ and Na_2CO_3 (Bai and

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Abraham, 2003) desorb metals by complexation chelation; sulfide desorbs by precipitation (Crist et al., 1994); and HCl, H_2SO_4, and NaOH desorb by ion exchange (Gardea-Torresdey et al., 1996; Lister and Line, 2001; Iqbal et al., 2002; Bai and Abraham, 2003). Previous studies have shown that carboxyl groups on saltbush biomass play a significant role in the binding of heavy metals (Sawalha et al., 2005, in press), which suggests that acidic stripping agents are a good option for recovering the bound metals from the biomass.

Saltbush plants are very abundant in the Southwestern Texas, USA. Previous results have shown that the aboveground biomass of saltbush plants can be used to remove heavy metals from aqueous solutions free of hard cations (Sawalha et al., 2005, in press). In addition, isotherm studies suggested that saltbush biomass has a high capacity of metal removal (Sawalha et al., 2006, 2007). The objectives of the present investigation were (1) to determine the metal binding capacity of saltbush biomass from single and multimetal solutions spiked with Ca and Mg, (2) to evaluate the removal of metals under flow conditions by the polymerized saltbush biomass, and (3) to determine the recovery of the bound metals by using HCl as stripping agent. For column experiments the biomass was immobilized on silica gel. Metal determinations were performed by using flame atomic absorption spectroscopy (FAAS) and inductively coupled plasma-optical emission spectroscopy (ICP-OES).

2. Methodology

2.1. Biomass collection and preparation

The saltbush (*Atriplex canescens*) biomass was collected from a site without previous report on metal contamination around El Paso, Texas area, where the saltbush grows wildly. The biomass was collected and prepared as previously described (Sawalha et al., 2005, in press). Briefly, the shoot biomass was washed with tap water, separated into stems, leaves and flowers, oven dried, and ground to pass through a 0.149 mm (100 mesh) sieve.

2.2. Interference of Ca and Mg on metal binding in batch conditions

The Ca and Mg interference on the binding of Cu(II), Cd(II), Cr(III), Cr(VI), Pb(II), and Zn(II) was performed as stated by Gardea-Torresdey et al. (1997). For each of the studied metals, a sample of 250 mg of saltbush leaf biomass was washed once with 0.01 M HCl and twice with deionized water (DI). The washings were evaporated to calculate the biomass loss. A slurry (5 mg/ml) of the washed biomass was prepared using DI and adjusted to the previously determined optimum pH (pH 2.0) for the biomass to be equilibrated with Cr(VI) and pH 5.0 for the other elements (Sawalha et al., 2005, in press). A sample of 2 ml of the biomass suspension was transferred into each of three test tubes, centrifuged at 3000 rpm (Fisher Scientific 8 K, Houston, TX) and the biomass pellets were saved for further analysis. Solutions at 0.1 mM of Cd, Cu, Cr(III), Cr(VI), Pb, and Zn were prepared from $CuSO_4$, $K_2Cr_2O_7$, $Pb(NO_3)_2$, $Cr(NO_3)_3$, $ZnCl_2$, and $Cd(NO_3)_2$. The metal solutions were spiked with Ca and Mg (as nitrate salts), at the concentrations of 0.0, 0.1, 0.2, 1.0, 2.0, 10.0, 20.0, 100.0, 200.0, and 1000.0 mM each.

For each of the studied metal, aliquots of 2 ml were taken from each of the metal/hard cation solutions and transferred to three tubes containing the washed saltbush biomass. The tubes containing biomass–metal solutions were reacted for 10 min in a specimix (Thermolyne M26125, Dubuque, IA). Controls of the respective metal solutions were retained with each of the three reaction replicates. After 10 min, the samples were centrifuged at 3000 rpm for 5 min and the supernatants were transferred to clean tubes for metal quantification.

2.3. Batch multimetal binding capacity studies

The multimetal binding capacity studies were performed as described by Munoz et al. (2002). The saltbush biomass was washed, suspended in DI, pH adjusted and centrifuged as described above. Triplicate 10 mg biomass pellets were reacted with a 2-ml multimetal solution containing 0.3 mM of each of the metal ions in 0.01 M sodium acetate. After equilibrating the mixtures for 10 min, the samples and controls were centrifuged and the decanted supernatants were stored for metal analysis. The biomass pellet was reacted in each tube with fresh multimetal solution for another cycle. This was repeated for 10 cycles or until the biomass became saturated. The samples were centrifuged and the supernatants were analyzed using an inductively coupled plasma/optical emission spectrometer (ICP-OES) Perkin Elmer Optima 4300 DV (Perkin Elmer, Shelton, CT). The biomass was kept for stripping studies. The same procedure was repeated using Cr(VI) instead of Cr(III) in the metal mixture, adjusting the pH as described above. The amount of metal bound in each cycle was considered to be the difference between the metal concentration in control solution and supernatants after centrifugation. The binding capacity was calculated to be the total amount of metal bound in 10 cycles divided by the biomass dry weight.

2.4. Recovery of the adsorbed metals

In order to remove the bound metal ions from the biomass, each of the metal loaded biomass pellets was equilibrated with 2 ml of 0.1 M HCl for 10 min, centrifuged, and the supernatants retained for metal quantification (first desorption cycle). The pellets were exposed again for 10 min to 2 ml of 0.1 M HCl to remove any remaining metals, centrifuged, and the supernatant was analyzed for metal determination (second desorption cycle). The percentage of metal recovery was calculated by dividing the total amount of metal stripped from both cycles over the total amount of metal bound.

2.5. Column experiments

To avoid columns clogging when performing the binding under flow conditions, the biomass was immobilized on silica as described before (Gardea-Torresdey et al., 1998; Tiemann, 1998). Briefly, samples of 5 g of biomass were washed once with 0.01 M HCl and twice with DI. A volume of 75 ml of 5% H_2SO_4 was mixed with enough volume of a 6% sodium silicate (Na_2SiO_3) solution until the pH became 2.0. Five grams of the washed biomass were added to the silica solution and stirred for 15 min. After that, the 6% Na_2SiO_3 solution was added slowly to raise the pH to 7.0. At this pH, the solution started to form a polymer. The polymer was washed several times to remove any soluble salt by adding 500 ml of DI and allowing the silica-immobilized polymer to settle. The resulted biopolymer was dried overnight at 60 °C in an oven (Isotemp oven, Fisher Scientific). The silica-immobilized biomass was shaken with a spatula when it was semi-dry to avoid having a very solid product. The biopolymer was then ground, sieved to a mesh size of 20-40 (0.841-0.420 mm) and packed into columns. The size of the packed biopolymer (in this experiment was 6 mL) was defined as the bed volume. The column was preconditioned by passing a 0.01 M solution of sodium acetate, buffered at pH 5.0, at a flow rate of 2 ml/min, until the pH of the effluent was 5.0 (the optimum pH). The flow rateof 2 ml/min was previously determined as the optimum for Pb binding (Contreras et al., 2006).

2.6. Single and multimetal binding by the immobilized saltbush

For the single metal binding studies, 127 bed volumes of 0.1 mM metal solution in 0.01 M sodium acetate (pH 5.0) were passed

through the column at a flow rate of 2 ml/min. In the case of Cr(VI), only 59 bed volumes were passed. The bed volumes were collected and kept for metal quantification using flame atomic absorption spectroscopy (FAAS, Perkin Elmer 3110, Shelton, CT, USA).

For the multimetal solution, 158 bed volumes containing Cu, Cd, Cr(III), Pb, and Zn at 0.1 mM each, in 0.01 M sodium acetate, were passed through the column at a flow rate of 2 ml/min. The bed volumes were collected and analyzed using ICP-OES. In both the single and multimetal studies, a sample of 6 ml from the metal solutions (controls) was kept for metal quantification. The difference in the amount of metal in the control and the effluent was considered as the amount of metal bound. Each experiment was run in triplicate.

2.7. Recovery of hard cations from the column

The bound metals were stripped out by passing 15 bed volumes of 0.1 M HCl throughout the column at a flow rate of 2 ml/min. Each bed volume was collected and analyzed by FAAS for single metal binding and by ICP-OES for multimetal binding. The amount of metal recovered in all bed volumes was assumed as the total amount of metal recovered from the column.

2.8. Metal analyses

The calibration coefficients (r^2) obtained from four calibration standards for all analyses (FAAS, and ICP/OES) were 0.999 or better. The wavelengths (nm) used for the metals were; Cu, 224.7, Cd, 228.8, Cr, 257.7, Pb, 220.3, and Zn, 213.8. The operation parameters for the ICP/OES were: plasma flow, 15 L/min; auxiliary flow, 0.2 L/min; nebulizer flow, 0.7 L/min; pump rate, 1.5 ml/min; and radio-frequency power, 1500 W. Sometimes samples were diluted to fit in the calibration range. Confidence intervals of 95% were calculated for the results.

3. Results and discussion

3.1. Calcium and magnesium interference results

The percent of metal bound from single metal solutions at various concentrations of combined Ca and Mg is shown in Fig. 1. The binding of Cr(III) and Pb was not affected by combined concentrations of Ca and Mg lower than 4 and 40 mM, respectively. However, when the concentration of Ca + Mg reached 200 and 2000 mM, the binding of Cr(III) and Pb decreased about 40% and 70%, respectively. Gardea-Torresdey et al. (1997) reported a similar trend in the binding of Cr(III) and Pb by African alfalfa biomass at pH 5.0. The binding of Cd occupied the third position after Cr(III) and Pb. Concentrations of Ca + Mg between 0.0–0.4 mM did not affect the Cd binding. However, when the concentration of Ca + Mg was between 2.0 and 4.0 mM, the binding of Cd was reduced by about 50%. Furthermore, when the Ca + Mg concentration was at 20.0 mM and above, the Cd binding was reduced by about 60%. The Cu binding was in the fourth position. The binding of this metal increased up to about 20% when the hard cation concentrations increased from 0.00 to 400.0 mM. Even at the maximum concentration of hard cations, the Cu binding was still higher than the binding from the plain Cu solution (no hard cations). It is hypothesized that the increase in Cu binding when the solution contained hard cations was due to the fact that one or both of the hard cations bound at certain locations on the biomass, attracted OH groups from the solution. This could increase the negative charge around those binding sites, attracting more Cu ions. Such behavior was suggested before to explain the increase in the arsenic binding to the open-celled cellulose sponge in the presence of Fe(III) (Munoz et al., 2002). In addition, functional groups other than carboxyl groups might be involved in the Cu binding.

The binding of Zn was not affected by hard cation concentrations equal to or lower than 2.0 mM. When the hard cation concentrations were higher than 4.0 mM, the binding of Zn was reduced by about 70%. Saltbush biomass presented the lowest binding for Cr(VI) (about 20% for hard cation concentrations between 0.0 and 4.0 mM). Nonetheless the decrease in the Cr(VI) binding was less than 10% at hard cation concentrations higher than 200.0 mM. It is very likely that at high concentrations, Ca and Mg occupy most of the binding sites in the biomass, thus reducing the binding of other metals. The fact that the saltbush biomass was able to bind significant amounts of heavy metals from solutions containing 100- or 1000-fold hard cation concentrations suggests that saltbush biomass selectively binds the heavy metals. A possible reason for this selectivity is the higher stability constants of heavy metals complexed with sulfates, amines, and carboxylates, compared to the stability constants of the same ligands complexed with Ca and Mg (Arthur et al., 1974).

3.2. Batch multimetal binding results

The percentage of metal bound by saltbush biomass at each reaction cycle is shown in Fig. 2. This figure shows that the percent of metal bound per cycle decreased as the number of cycles increased. This could be explained by a reduction in the number of available ligands after each cycle. The unsmooth trend shown by each metal binding profile could be explained by the substitution of

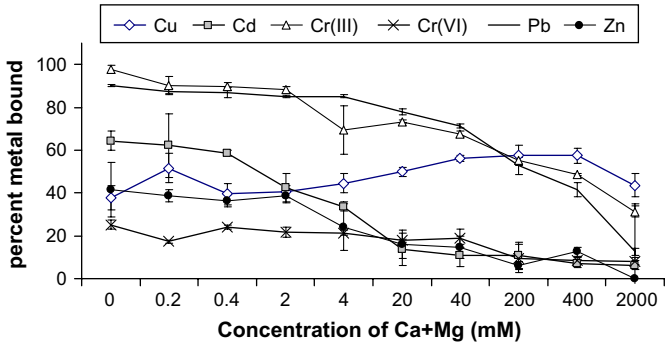

Fig. 1. Batch interference of combined calcium and magnesium on the binding of Cu, Cd, Cr(III), Cr(VI), Pb, and Zn by saltbush leaf biomass. The metal concentration was 0.1 mM and the solution was adjusted to pH 2.0 for Cr(VI) and pH 5.0 for the rest of the metals. The reaction time was 10 min. Error bars represent 95% confidence intervals, $\alpha = 0.05$; $n = 3$.

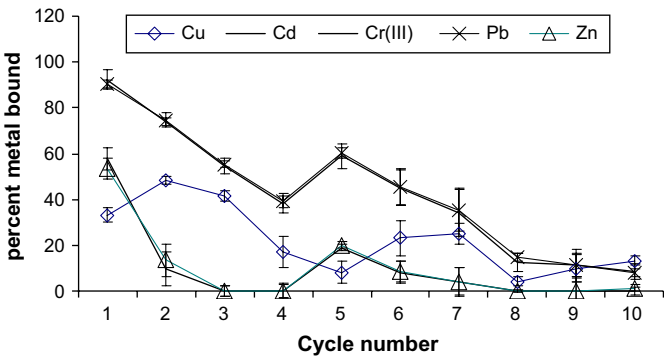

Fig. 2. Batch binding of Cd, Cu, Cr(III), Pb, and Zn by saltbush leaf biomass from a multimetal solution. The metals were mixed at 0.3 mM and the solution adjusted to pH 5.0; the reaction time was 10 min. Error bars represent 95% confidence intervals, $\alpha = 0.05$; $n = 3$.

metals on the biomass, produced by the binding affinity and metal concentration. The preferential order of metal binding from the multimetal solution presented in Fig. 2 is more clearly described using the capacity expressed in μmol/g, as shown in Table 1.

Table 1 (multimetal binding capacity without hard cations at pH 5.0) shows that saltbush had the highest binding capacity for Cr(III) and Pb (about 260 μmol/g), followed by Cu, Cd, and Zn (117, 49, and 54 μmol/g, respectively). Alfalfa biomass had similar multimetal capacity for Cd and Zn, but higher capacity for Cu; while for Pb, alfalfa biomass was able to bind only 168 μmol/g (Gardea-Torresdey et al., 1999). Since it was not possible to detect the amount for each of the Cr species in the solution using the ICP-OES, the binding experiment was performed again with Cr(VI) instead of Cr(III) in the multimetal solution adjusted at pH 2.0 (Sawalha et al., 2005). The data from this experiment are shown in Fig. 3. As seen in this figure, the percentages of metal bound were much lower compared to the values obtained at pH 5.0. The reason for this could be that at pH 2.0 most of the carboxyl groups were protonated and not available for metal binding. In addition, at low pH values, the protons at high concentration compete with the metals for the available binding sites (Hashim et al., 1997; Kuyucak and Volesky, 1988; Yun et al., 2001). However, at pH 2.0, the saltbush biomass still bound about 50 μmol/g of Pb and Cr(VI) (Table 1), followed by about 23 μmol/g for Cu and 13 μmol/g for each of the Cd and Zn. The leaps in cycles 6, 8, and 10 could be due to a displacement of heavy metals by protons in solution after certain degree of metal saturation onto the biomass. After the ion elution, the sites were free again for new ions to be bound by the biomass. It has been shown that Pb can replace Ca in the cell wall of *Pycnoporus sanguineus* biomass after the binding (Mashitah et al., 1999). Gardea-Torresdey et al. (1999) have reported that the ion exchange constants of metals to replace Ca in peat moss was in the order Pb >> Cu > Cd > Zn > Ca > Mg. This possibly could be a reason for having the highest binding for Pb with saltbush biomass in the presence of Ca and Mg. In general, the results show that the binding for Cr(III) and Pb was higher than the binding of Cd, Cu, and Zn. The higher stability constants for many Pb and Cr(III) complexes with carboxylic group might explain part of these results (Arthur et al., 1974). Another reason could be the different numbers of available

Table 1
Metal binding capacity and recovery from multimetal and single metal solution by saltbush biomass

	Capacity (μmol/g)	Recovery (%)
Multimetal (pH 5.0)		
Cu	117.3 ± 1.5	100.0 ± 9
Cd	49.1 ± 1.8	36.9 ± 10
Cr(III)	260.1 ± 2.3	85.8 ± 2
Pb	263.1 ± 1.7	84.5 ± 1
Zn	54.0 ± 1.7	41.1 ± 12
Multimetal (pH 2.0)		
Cu	22.8 ± 1.5	39.6 ± 5
Cd	13.4 ± 1.1	17.3 ± 6
Cr(VI)	49.7 ± 1.5	100.0 ± 22
Pb	50.2 ± 0.5	100.0 ± 15
Zn	12.9 ± 1.3	18.7 ± 5
Single metal (pH 5.0)[a]		
Cu	107.0 ± 1.7	64.9
Cd	102.3 ± 0.3	84.7
Cr(III)	436.5 ± 2.3	72.2
Cr(VI)	1.9 ± 8	Did not strip
Pb	137.7 ± 1.6	87.3
Zn	56.9 ± 1	45.7

In all cases the metals were at 0.3 mM. The binding data are from 10 binding cycles. The stripping was performed with 0.1 M HCl in two cycles. The equilibration time was 10 min/cycle. The data are average of three replicates/cycle ± 95% confidence intervals.

[a] Data added for comparison (Sawalha et al., 2005, 2006, 2007).

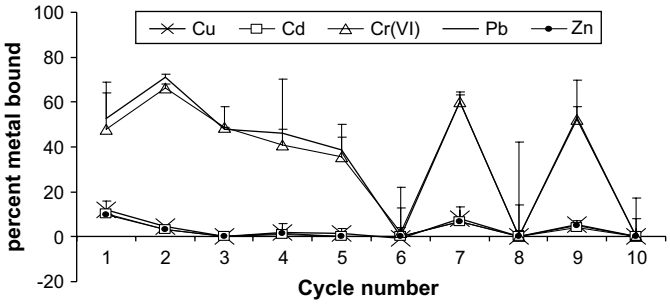

Fig. 3. Batch binding of Cd, Cu, Cr(VI), Pb, and Zn by saltbush leaf biomass from a multimetal solution. The metals were mixed at 0.3 mM and the solution adjusted to pH 2.0; the reaction time was 10 min. Error bars represent 95% confidence intervals, $\alpha = 0.05$; $n = 3$.

ligands towards which each metal had the affinity to bind. For a comparison, the single metal capacity and recovery results that were discussed in previous studies (Sawalha et al., 2005, 2008, in press), were added to Table 1. As explained before, the performance of the biomass with single metal experiments was either similar or better than the performance with multimetal solutions, except for Pb.

3.3. Batch multimetal stripping

The recovery of metal ions from the biomass is shown in Table 1. The data showed that all the Cu bound to the saltbush biomass from the multimetal solution at pH 5.0 was stripped out using 0.1 M HCl. The recovery for both Cr(III) and Pb was about 85%, while for Cd and Zn it was about 37% and 41%, respectively. The recovery of metals from the multimetal binding experiment at pH 2.0 was 40% for Cu and less than 20% for Cd and Zn. It is hypothesized that most of the binding sites had highest affinity for the metals when the amount of metal bound was small. On the other hand, it was possible to recover all the bound Cr(VI) and Pb. The fact that the stripping of these two ions was higher when bound at pH 2.0 compared to pH 5.0 might indicate the involvement of different functional groups at pH 2.0, since most of the carboxyl groups are protonated at this low pH.

3.4. Single and multimetal column binding results

The binding of each of the studied metals from a single metal solution under flow conditions at pH 5.0 is presented in Fig. 4. The

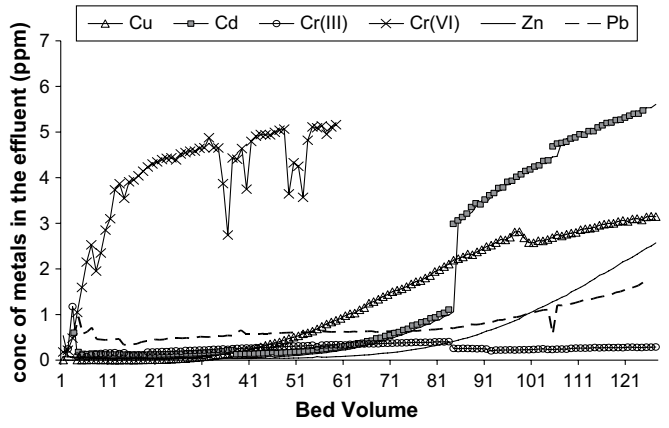

Fig. 4. Breakthrough curves for the adsorption of Cd, Cu, Cr(III), Cr(VI), Pb, and Zn by silica-immobilized saltbush leaf biomass. The influent solutions contained single metals at a concentration of 0.1 mM each. The flow rate was 2 ml/min. Solutions were adjusted to pH 5.0. For Cr(VI), 59 bed volumes were collected, and 127 for the other metals.

figure shows that almost all the Cr(III) in the solution was removed by the immobilized biomass. The Cr(III) in the effluent was less than 0.3 ppm through 127 bed volumes. The concentration of Pb and Zn was lower than 1 ppm after 100 bed volumes. On the other hand, Cd and Cu reached an effluent concentration of 1 ppm after 83 and 61 bed volumes, respectively. The column did not uptake most of the Cr(VI), which had a concentration lower than 1 ppm only in the first three cycles.

The calculated binding capacity for each metal in the single metal column experiment is shown in Table 2. These capacities were (μmol/g) about 49, 35, 35, 32, 22, and 3.8, for Pb, Cu, Cr(III), Zn, Cd, and Cr(VI), respectively. This single metal column capacity trend is very similar to the capacity trend presented in Table 1 for the multimetal batch capacity. Other studies have shown that under flow conditions, hops biomass had a binding capacity of 358.1 μmol of Pb per gram of biomass (Gardea-Torresdey et al., 2002). For humin biomass, the highest Pb adsorption was about 4.2 μmol of Pb per gram of biomass (Contreras et al., 2006).

For most of the studied metals, the immobilized biomass bound less from the multimetal solution than from single metal solutions. Fig. 5 shows that the binding data for all metals in the solution, except for the Cr(III) ion, started to breakthrough at earlier number of bed volumes compared to the single metal column binding. While the concentration of Cr(III) in the effluent was nearly constant in all the collected bed volumes, the Pb concentration in the effluent was more than 1 ppm after about 85 bed volumes. For the rest of the metals, the concentration increased to 1 ppm after 21 bed volumes. The calculated capacity values showed similar results for Pb in the multimetal and single metal column experiments. The Cr(III) binding capacity from the multimetal solution was about 12 μmol/g lower, compared to the single metal solution, while the calculated capacities for Cd, Cu, and Zn were, respectively, 4.5, 5, and 6 times lower than the values from the single metal experiment. The saltbush biomass metal preference follows the order $Pb > Cr(III) > Cu > Zn \approx Cd$. The results could be due to different metal binding affinities towards the same or different ligands present on the biomass surface. The fact that the highest binding capacity from the multimetal solution corresponded to Pb and Cr(III) could be explained by the high stability constants of these metals with many ligands containing carboxyl groups (Arthur et al., 1974). Zhang and Banks (2006) have shown that the biomass of sphagnum moss, the brown seaweed *Ascophyllum nodosum*, the waste biomass from the preparation of sunflower oil, and the biomass of whole maize plants bound Pb at the most, followed by Cu, Ni, and Zn. The results of the present study have shown that immobilized saltbush biomass can be used to remove Pb and Cr(III) from either single or multimetal solution. It may also be an option for the removal of Cu, Cd and Zn from single metal solution.

3.5. Column stripping results

The metal recovery from the immobilized biomass treated with single element and multielement solutions is shown in Tables 2 and 3, respectively. As shown in Table 2, all the bound Cu and Zn, about 90% of the Pb, 75% of the Cr(VI), and less than 25% of the bound Cd and Cr(III) were recovered using 15 bed volumes of 0.1 M HCl solution. Table 3 shows that all the bound Cu, about 74%, 54%, and 40-43% of the bound Pb, Zn, and Cd and Cr(III), respectively, were removed from the biomass treated with the multimetal solution, using 0.1 M HCl. It was previously proposed (Sawalha et al., 2005, in press) that carboxylic groups play the major role in the binding of Cd and Cr(III) with saltbush biomass. Mehta and Gaur (2005) have reported that lowering the pH of the metal loaded biomass allowed recoveries that exceed 90% of the bound metals. Additional experiments using other striping agents are required to determine the best way to recover Cd and Cr from the immobilized saltbush biomass.

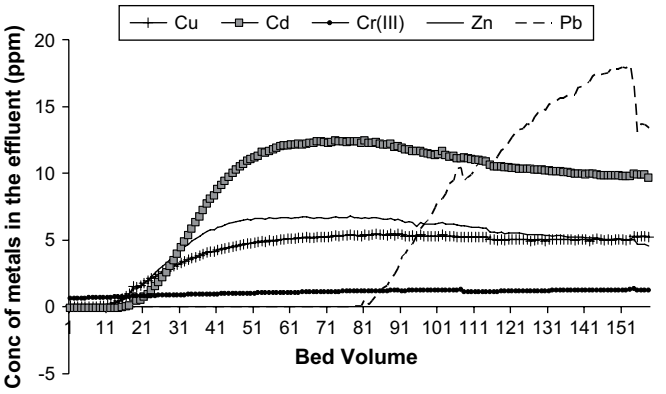

Fig. 5. Breakthrough curves for Cd, Cu, Cr(III), Pb, and Zn adsorption by silica-immobilized saltbush leaf biomass. The solution contained a mixture of all metals at the concentration of 0.1 mM each. The flow rate was 2 ml/min. The solution was adjusted to pH 5.0, and 158 bed volumes were collected.

4. Conclusions

The results from the Ca and Mg interference experiment demonstrated that the binding of Cr(III) and Pb was not affected by combined concentrations of Ca and Mg lower than 4.0 and 40.0 mM, respectively. However, the binding of Cr(III) and Pb decreased about 40% and 70% when the concentration of Ca + Mg reached 200.0 and 2000.0 mM, respectively. Concentrations of Ca + Mg between 0.0–0.4 mM did not affect the Cd binding. However, when the concentration of Ca + Mg was between 2.0 and 4.0 mM, the binding of Cd was reduced by about 50%. The binding of Cu increased up to about 20% when the concentration of Ca + Mg increased from 0.0 to 400.0 mM. Even at the maximum concentration of Ca + Mg, the Cu binding was still higher than the binding from the plain Cu solution (no hard cations). The binding from the multimetal solution also showed that saltbush biomass had a higher binding capacity for Cr(III) and Pb compared to the Cu, Cd, and Cr(VI). The stripping studies showed that 85-100% of the bound Cu, Cr, and Pb and about 37% of the bound Cd and Zn could be recovered using 0.1 M HCl. Saltbush demonstrated that it can be used for the selective removal of heavy metals from solutions even when Ca and Mg exist in the solution at high concentrations. However, more studies need to be done in order to determine the applicability of this biomass in wetlands, reactors or any other application.

Table 2
Capacity and recovery from the silica-immobilized saltbush column treated with single metal solution at a flow rate of 2 ml per min

Metal	pH	Capacity (μmol metal/g biomass)	Recovery (%)
Cu(II)	5.0	34.8	106.1
Cd(II)	5.0	22.3	18.6
Cr(III)	5.0	35.0	24.2
Cr(VI)	2.0	3.8	75.0
Pb(II)	5.0	48.9	90.0
Zn(II)	5.0	32.46	113.9

Table 3
Capacity and recovery from the silica-immobilized saltbush column treated with a multimetal solution adjusted at pH 5.0 and a flow rate of 2 ml per min

Metal	Capacity (μmol metal/g biomass)	Recovery (%)
Cu(II)	7.0	113.3
Cd(II)	5.2	43.3
Cr(III)	22.6	40.0
Pb(II)	49.2	73.6
Zn(II)	5.3	53.89

Column studies suggested that immobilized saltbush can be used to significantly romove Pb and Cr(III) from either single or multimetal solution. It can be also a good option for the removal of Cu, Cd and Zn, mainly from single metal solution. HCl demonstrated to be a very good stripping agent for the recovery of Cu, Pb, and Zn from the immobilized saltbush biomass.

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