ADSORPTION OF HEAVY METAL IONS BY THE BIOMASS OF *SOLANUM ELAEAGNIFOLIUM* (SILVERLEAF NIGHTSHADE)

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ABSTRACT

A screening previously performed for metal concentration in desert plants indicated that *Solanum elaeagnifolium* (silverleaf nightshade) had the potential to be used as a biomaterial for heavy metal removal from contaminated soils and waters. The Pb(II), Cu(II), Ni(II), Cd(II), Zn(II), Cr(III), and Cr(VI) binding properties of native and NaOH-modified biomass of *Solanum elaeagnifolium* were studied. Batch experiments were conducted with oven-dried and ground leaves of *Solanum elaeagnifolium* to characterize the metal-binding properties. These experiments included pH profiles, time dependencies, and metal-binding capacities of the biomass. Results from this work have indicated that optimal metal binding occurred at pH 5.0 for Pb(II), Cu(II), Ni(II), Cd(II), Zn(II), and Cr(III) within a 10-15 minute time period. However, optimal Cr(VI) binding occurred at pH 2.0. Capacity experiments showed that native *Solanum elaeagnifolium* was able to bind the following amounts of metals in mg metal/g biomass: 20.6 mg Pb(II)/g, 13.1 mg Cu(II)/g, 6.5 mg Ni(II)/g, 18.9 mg Cd(II)/g, 7.0 mg Zn(II)/g, 2.8 mg Cr(III)/g, and 2.2 mg Cr(VI)/g. However, the NaOH-modified biomass of *Solanum elaeagnifolium* showed an increase in metal binding for most of the metal ions studied. By treatment with HCl, the bound-metal ions were recovered. These results indicate that the biomass of *Solanum elaeagnifolium* can be chemically modified with NaOH and can be used to remove several metal ions from aqueous solution. In addition, silica-immobilized *Solanum elaeagnifolium* was used in columns for flow studies which show that silverleaf nightshade could be used to remediate heavy metal-contaminated waters in a cost-efficient manner.

Key words: *Solanum elaeagnifolium, silverleaf nightshade, heavy metal binding, chemical modification*

INTRODUCTION

Natural waters have been found to be contaminated with several heavy metals arising mostly from mining wastes and industrial discharges (Grousset et al., 1999; Schalcsha et al., 1998). These metals are toxic in both their chemically combined forms as well as the elemental form (Manahan, 1993). Acute lead, cadmium, chromium, and copper poisoning in humans causes severe dysfunction in the renal, reproductive, and nervous systems (Berman, 1980; Yong et al., 1998). Besides, chronic exposure to these contaminants present even at low concentrations in the environment can prove to be harmful to the human health (Wyatt et al., 1998).

Currently used water treatment technologies involving chemical precipitation, evaporation, electrochemical treatment, and the use of ion exchange resins are expensive and sometimes ineffective, especially when metals are present in solution at very low concentrations (Volesky,1987; Yang et al.,1998; Ouki et al., 1997). An emerging field of interest is employing certain plants which possess the natural ability to uptake heavy metals for the remediation of the environment. Besides live plants, studies have demonstrated that non-viable plant biomass can effectively bind toxic metals and as such can be used to remove metals from solution (Seki et al., 1998). The unique ability of these plants to bind metals has been attributed to the presence of various functional groups

which can attract and sequester metal ions. This technology is attractive mainly because it is effective, environmentally friendly, and inexpensive. Several plants growing in different climatic regions have been studied for this purpose. A screening previously performed for metal concentration in desert plants indicated that *Solanum elaeagnifolium* (silverleaf nightshade) had the potential to be used as a biomaterial for heavy metal removal from contaminated soils and waters [Gardea-Torresdey et al., 1998a]. In this paper we examine the binding of Pb(II), Cu(II), Ni(II), Cd(II), Zn(II), Cr(III), and Cr(VI) to the *Solanum elaeagnifolium* biomass. Also, the recovery of these metals from the biomass using a dilute acid has been studied. In an attempt to remediate metal-contaminated waters, the ability of the *Solanum elaeagnifolium* biomass to bind metal ions was further investigated under flow conditions.

MATERIALS AND METHODS

*Plant (*Solanum elaeagnifolium*) Collection and Preparation of the Biomass*

The *Solanum elaeagnifolium* plants were randomly collected from a control site located approximately four miles from a smelter located in El Paso, Texas. This site is shielded from the smelter by a mountain, thus minimizing metal deposits in the soil by air pollutants. After collection of the plants, the leaves were plucked and washed with deionized water and subsequently dried in an oven at 60°C for one week. The dried leaves were ground and sieved through a 100-mesh Tyler screen and the fine biomass obtained was used in the experiments described below.

pH Profile for Metal Ion Binding

Batch pH profile experiments were conducted based on a procedure previously reported on (Gardea-Torresdey et al., 1998b). In summary, a 250 mg sample of the biomass was weighed and washed twice with 0.1 M hydrochloric acid (HCl) and once again with deionized water to remove any metals or soluble biomolecules present in the biomass. Fifty ml of 0.01 M HCl were added to the biomass to obtain a tissue concentration of 5 mg/ml. The pH of this suspension was adjusted to 2.0, and 2 ml aliquots of the suspension were added to three 5 ml tubes. Similarly, the pH of the suspension was adjusted to 3.0, 4.0, 5.0, and 6.0 and three, 2 ml aliquots were collected at each pH. The suspensions were centrifuged at 2800 r.p.m and the supernatants were collected in separate tubes. A metal solution of 0.1 mM concentration was prepared and the pH adjusted to 2.0, 3.0, 4.0, 5.0, and 6.0. At each pH, 2 ml of the metal solution were added to the respective biomass pellet and supernatant. In addition, 2 ml of the metal solution at each pH were added to three tubes for controls. All the tubes were reacted on a rocker for one hour. The tubes were then centrifuged at 2800 r.p.m. for five minutes, and the supernatants of the pellets were collected in separate tubes. After recording the final pHs of the tubes, the metal content was determined using flame atomic absorption spectroscopy.

Time Dependency for Metal Ion Binding

A 250 mg sample of the biomass was weighed and washed twice with 0.1M HCl and once again with deionized water. The biomass was suspended in 50 ml of 0.01 M sodium acetate to obtain a tissue concentration of 5 mg/ml. After adjusting the pH to 5.0, 2 ml of the suspension were transferred to 21 tubes—three tubes for each time interval of 5, 10, 15, 30, 60, 90, and 120 minutes. The tubes were centrifuged and the supernatants were discarded. Two ml of 0.3 mM metal solution (buffered to pH 5.0 with sodium acetate) were added to each pellet. All the tubes were reacted on a rocker for the specified time. The tubes were then centrifuged at 2800 r.p.m. for five minutes and the supernatants were analyzed by flame atomic absorption spectroscopy (Gardea-Torresdey et al., 1998b).

Metal-Binding Capacity Experiment

A 100 mg sample of the biomass was washed twice with 0.1 M HCl and once with deionized water. The washings were collected and dried in an oven to account for the loss of biomass, if any. Twenty ml of 0.01 M sodium acetate at pH 5.0 were added to the biomass. After adjusting the pH to 5.0, 2.0 ml of the suspension were transferred to three test tubes. The tubes were centrifuged and the supernatants were decanted. To each pellet, 2.0 ml of 0.3 mM metal solution (buffered to pH 5.0 with 0.01 M sodium acetate) were added. The tubes were placed on a rocker and reacted for 15 minutes. This process was followed by centrifugation and the supernatants were collected in three separate tubes. The process of adding the metal solution to the pellets, reacting and centrifuging them, and collecting the supernatants was repeated eight times. Flame atomic absorption spectroscopy was employed for analyzing the supernatants.

The metal-binding experiment was followed by metal-desorption studies. Two ml of 0.1 M HCl were added to each metal-laden pellet. The pellets were reacted with the acid for 15 minutes. The tubes were centrifuged and the supernatants were collected and analyzed for metal content using flame atomic absorption spectroscopy.

Chemical Modification of the Biomass with Sodium Hydroxide

Fifteen grams of the biomass were weighed and washed twice with 0.1 M HCl, followed by centrifugation at 2800 r.p.m. and then washed again with deionized water. The biomass was then reacted with 150 ml of 0.1 M sodium hydroxide (NaOH) for a period of approximately 24 hours. The reacted solution was centrifuged and the biomass was washed three times with deionized water. The washed biomass was subsequently lyophilized in a Labconco freeze dryer for three days.

Immobilization of the Biomass in Silica

The procedure followed herein has been previously reported (Gardea-Torresdey et al., 1998b). Approximately 10 grams of the biomass were weighed and washed twice with 0.1 M HCl and a third time with deionized water, followed by centrifugation after each wash. The supernatant from the washings was collected, dried, and weighed to account for the loss of biomass during

washing. One hundred and twenty ml of 5% sulfuric acid (H_2SO_4) were mixed with enough 6 % sodium silicate (Na_2SiO_3) to raise the pH of the solution to 2.0. At pH 2.0, the washed biomass was added to the solution and stirred for 10 minutes. An adequate amount of 6 % Na_2SiO_3 was then added to slowly raise the pH of the solution to 7.0. The resulting polymer gel was washed with water and oven dried at 60°C for approximately one week. The dried polymer was ground by mortar and pestle and sieved to obtain a particle size of that between 20 and 40 mesh.

Column Experiments

Approximately 3 ml of the silica-immobilized biomass were packed in a column. Prior to passing the metal solution through the column, the immobilized biomass was buffered to the required pH by passing several bed volumes (volume of the polymer in the column) of 0.01 M sodium acetate (at the optimum binding pH) through the column until the effluent obtained was at that pH (biomass conditioning). Three hundred bed volumes of 0.1 mM metal solution prepared in 0.01 M sodium acetate at optimum binding pH were passed through the column at a flow rate of 1 ml per minute. Two bed volumes, equivalent to approximately 6 ml, were collected in each test tube by using a fraction collector (Spectra/Chrom CF-1) and analyzed for metal content by flame atomic absorption spectroscopy.

Subsequently, the metal accumulated in the silica-immobilized biomass was recovered by passing 0.1M HCl through the column. Thirty bed volumes of the resulting effluent were collected and analyzed for metal content.

After recovering the metal from the polymer, the recyclability potential was determined by passing an equal number of bed volumes of metal solution through the column and recovering the metal in a similar manner. Three cycles were performed on each column for every particular metal ion.

Metal Analyses and Statistical Treatment of Data

A Perkin-Elmer model 3110 Atomic Absorption Spectrometer with deuterium background subtraction was used to analyze the effluents. The wavelengths used for copper, lead, nickel, cadmium, chromium, and zinc were as follows: 327.4 nm, 283.3 nm, 352.5 nm, 228.8 nm, 358.2 nm, and 213.9 nm, respectively. Known standards were used to calibrate the instrument and to keep a good quality control, our goal was to obtain a correlation coefficient value of as close to 1.0 as possible. The difference between the metal ion concentration of the control and that of the supernatant or effluent was used to determine the amount of metal bound to the biomass.

The batch experiments were performed in triplicate and the mean and the standard deviations were computed for each set of values. Error margins were determined by calculating the 95% confidence intervals.

RESULTS AND DISCUSSION

The effects of pH on the binding of different metal ions by the unmodified silverleaf nightshade

biomass is shown in Figure 1. The x-axis represents the pH and the y-axis represents the percentage of metal bound by the biomass. The 95 % confidence intervals are displayed by the error bars. With the exception of Cr(VI), the other six metals, Pb(II), Cu(II), Ni(II),Cd(II), Zn(II), and Cr(III) behave in a similar way. As the pH of the solution increases from 2.0 to 6.0, all these metals show an increase in binding to the biomass with optimum binding occurring between pH 5.0 and 6.0. This gives us an insight into the mechanism of the binding involved within the biomass. Previous studies have reported the binding of metals to some organic acids which contain carboxyl ligands (Korshin et al., 1998). Our results also suggest that to some extent carboxyl groups (-COOH) are responsible for the binding of metal ions. Reportedly, the ionization constants for a number of carboxyl groups range between 4 and 5 (Gardea- Torresdey et al., 1996c). At lower pHs, the carboxyl groups retain their protons reducing the probability of them binding to any positively charged ions. Whereas at higher pHs (above 4.0), the carboxyl groups are deprotonated and as such are negatively charged. These negatively charged carboxylate ($-COO^-$) ligands attract the positively charged metal ions and binding occurs. Thus, metal ion binding to the biomass is in essence an ion-exchange mechanism which involves electrostatic interaction between the negatively charged groups in the cell walls and metallic cations (Wase et al., 1997). However, in Figure 1 it is observed that the biomass binds more than 80% of Pb(II) at pH 3.0. and about 50% at pH 2.0. This suggests that besides carboxyl groups, other groups may also be involved in Pb(II) binding. In addition, the biomass binds more Cr(VI) at pH 2.0 compared to that bound at pH 5.0. In an attempt to gain an insight into the mechanism of Cr(VI) binding by the biomass, two processes have been hypothesized. First, because Cr(VI) occurs as an oxo-anion such as $(CrO_4)^{2-}$, $(HCrO_4)^-$,or $(Cr_2O_7)^{2-}$, binding at higher pHs where negatively charged carboxylate ions prevail is highly unlikely. Second, it has been reported that at lower pHs, Cr(VI) is reduced to Cr(III) by some biomasses (Krotochvil et al., 1998). This might explain the binding of Cr(VI) at low pHs. The percentage metal bound by the silverleaf nightshade biomass as a function of time is shown in Figure 2. Using the optimal binding pH from Figure 1, the metal solutions of Pb(II), Cu(II), Ni(II),Cd(II), Zn(II), and Cr(III) were buffered to a pH of 5.0, whereas the Cr(VI) metal solution was adjusted to a pH of 2.0. Although different metals bind to the biomass at varying degrees, little change is observed in the binding over time. Maximum binding of most of the metals occurs within the first 10-15 minutes and remains fairly uniform throughout the 120 minutes. The rapid binding of the metal ions to the biomass indicates that probably adsorption is taking place and the metal ions are bound to the cell walls. Additionally, metal adsorption may be characterized as a passive process because the plant tissues were inactivated. However, in Figure 2 a gradual increase in binding over time is observed for Cr(III). The unique behavior of Cr(III) with respect to the other metals may be explained on the basis of its size. Because Cr(III) has a relatively smaller ionic radius (0.62 A) compared to the other metal ions [ionic radii of Pb(II), Cu(II), Ni(II), Cd(II), and Zn(II) are 1.19 A, 0.73 A , 0.69

A , 0.95 A , and 0.74 A , respectively], it probably diffuses into the cell wall and hence requires more time to bind (Lide et al., 1994). Besides, its smaller size could make it available to other ligands which are inaccessible to bulkier metals.

The metal-adsorption capacity of the unmodified silverleaf nightshade biomass was determined at the optimal binding pH and time. The pH of the metal solutions was adjusted to 2.0 for Cr(VI) and 5.0 for the other metals. The metal solutions were reacted with the biomass until the biomass was completely saturated with the metal. The amount of metal bound by the biomass in mg metal/g biomass and in µmol metal/g biomass is summarized in Table 1. As can be seen from the table, the affinity of the biomass for different metals varies to a great extent. A significant amount of Pb(II), Cu(II), Ni(II),Cd(II), and Zn(II) are adsorbed by the biomass whereas the amount of Cr(III) and Cr(VI) adsorbed is much less.

From the pH profile experiments, it is clear that the binding of the metals drops significantly at low pHs. Therefore, we hypothesized that the metal ions can be recovered by decreasing the pH. A dilute acid (0.1M HCl), which would not degrade the biomass, was used for this purpose. The metal recovery data is also shown in Table 1. The percentage metal desorbed from the biomass varies from more than a 100% for lead to 41.13% for Cr(VI). Although Cr(III) is completely recovered, the low recovery of Cr(VI) may be due to the fact that it is reduced by the biomass to Cr(III) and is thus more strongly bound.

As discussed earlier, carboxylate ligands are believed to be responsible for metal binding by the biomasses. This means that metal binding can be enhanced by increasing the number of carboxylate ligands in the biomass. Interestingly, cellulose, hemicellulose, and lignin, which are major constituents of most plant tissues, contain methyl esters which do not bind metal ions significantly. However, these methyl esters can be modified to carboxylate ligands by treating the biomass with a base such as sodium hydroxide, thereby increasing the metal-binding ability of the biomass. The hydrolysis reaction of the methyl esters is as follows:

$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}OCH_3 + NaOH \rightarrow R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O^- + CH_3OH + Na^+$$

Therefore, by chemically modifying the biomass, we hypothesize to increase the number of carboxylate ligands which would enhance the binding ability of the biomass. The metal-binding capacities of the unmodified and NaOH-modified biomasses are compared in Table 2. More than a 100% increase in binding is observed for Pb(II) and an increase of approximately 72 % and 51% is observed for Zn(II) and Cu(II), respectively. From the enhanced binding demonstrated by the NaOH-modified biomass, it can be inferred that carboxylate ligands are involved in metal binding. However, no significant difference in Cd(II) binding is observed upon modification with

NaOH. This suggests that probably other ligands are involved in the binding of Cd(II) to the biomass. Also, as was expected, the amount of Cr(VI) bound by the biomass is not enhanced by modification with NaOH. This is because Cr(VI) exists as an oxo-anion and, therefore, cannot bind to the negatively charged carboxylate ligands.

The batch experiments have demonstrated the ability of these biomasses to bind various metals. However, it is not feasible to apply a batch system to the treatment of water. A practical approach to decontaminate metal-polluted waters with the biomass would be to pass the contaminated water through a column containing the biomass. In order to avoid clumping and to obtain a uniform flow rate, the biomass was immobilized in a silica matrix. The capacity of the silica-immobilized *Solanum elaeagnifolium* biomass to bind different metal ions in three subsequent cycles is shown in Figure 3. Three hundred bed volumes of the metal solution were passed through the column in every cycle. The individual metal ions are represented on the x-axis, while the y-axis represents the metal bound by the biomass in mg metal/g biomass. The three different patterns of the bars represent each of the three cycles. The amount of lead(II) bound by the *Solanum elaeagnifolium* biomass is comparatively higher than the other metals. Nevertheless, the biomass is capable of binding significant amounts of the other metals, especially in the first cycle. A small decrease in binding occurs for Ni(II) and Cd(II) in the second cycle. However, the decrease in binding in the second cycle for Pb(II), Zn(II), Cr(III), and Cr(VI) is more pronounced. On the other hand, the amount of copper bound in the first and second cycles is approximately the same. In fact, a slight increase in Cu(II) binding is observed in the third cycle. This may be because the column was being conditioned in the first two cycles and the binding sites were not completely exposed.

Figure 4 shows the percentage of metals recovered from the silica-immobilized *Solanum elaeagnifolium* biomass in the three subsequent cycles. One hundred percent of the bound Cu(II), Cd(II), and Zn(II) were recovered in the first cycle. However, the percentage of chromium (trivalent and hexavalent) recovered in the first cycle is less than 20% and even though an increase is observed in the subsequent cycles, the recovery is much less compared to the other metals. As discussed earlier, this may be due to the fact that chromium is diffused within the cell wall and as such is not easily recovered. Nevertheless, the fact that some of the Cr(VI) is recovered by passing an acid (pH-profile studies demonstrate that Cr(VI) binds at low pHs) indicates that probably Cr(VI) is reduced to Cr(III) by the biomass and it is, therefore, possible to recover it. A relationship between the amount of metal bound and that recovered is demonstrated in the case of Pb(II). Not all of the Pb(II) is recovered in the first cycle which may be the reason for the decrease in binding observed in the second cycle in Figure 3. As the recovery of Pb(II) increases in the second cycle (Figure 4), the amount of metal bound stays approximately the same in the third cycle (Figure 3). A similar dependency of the amount of metal bound on the percentage recovered is observed

for Ni(II). This is probably due to the fact that if all the metal is not recovered from the biomass, the binding sites are occupied and as a result a decrease in binding occurs in the subsequent cycles.

CONCLUSIONS

The inactivated biomass of *Solanum elaeagnifolium* was shown to be capable of binding several metals such as, Pb(II), Cu(II), Ni(II), Cd(II), Zn(II), Cr(III), and Cr(VI). Metal ion binding was rapid, indicating that the metals were probably adsorbed to the cell walls of the plant tissues. Also, metal ion binding was found to be pH-dependent suggesting the involvement of carboxyl groups present on the cell walls. Chemical modification of the biomass with NaOH enhanced the metal binding and further supported this hypothesis. Column experiments with the immobilized biomasses proved to be remarkably effective in the removal of metals from solution. Also, by recovering the metal ions from the biomasses using a dilute acid, we demonstrated the potential of reusing the metals. Recyclability results have shown that the column consisting of the immobilized biomass can be recycled and reused for a minimum of three times for all the metals studied. Once the metal is recovered, the immobilized polymer is biodegradable, causing no harm to the environment.

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Table 1. Metal adsorption capacity of the unmodified *Solanum elaeagnifolium* biomass and percentage of metal recovered after treatment with 0.1 M HCl.

Metal Ion	Amount of Metal Bound		95% C.I.	Percentage of Metal Recovered	95% C.I.
	mg Metal/g Biomass	µmol Metal/g Biomass			
Pb(II)	20.60	99.42	1.66	107.2	0.15
Cu(II)	13.14	206.92	0.92	88.65	0.12
Ni(II)	6.50	110.75	0.58	77.00	0.06
Cd(II)	18.94	168.53	2.71	53.79	0.10
Zn(II)	6.96	106.51	0.86	67.16	0.04
Cr(III)	2.78	53.41	0.18	109.7	0.29
Cr(VI)	2.16	41.62	0.30	41.13	0.23

Table 2. Comparison of the metal adsorption capacities of the unmodified and NaOH-modified *Solanum elaeagnifolium* biomasses.

Metal Ion	Amount of Metal Bound in mg Metal/g Biomass		% Increase in Binding
	Unmodified Biomass	NaOH Modified Biomass	
Pb(II)	20.60	46.79	127.14
Cu(II)	13.14	19.96	51.90
Ni(II)	6.50	7.55	16.15
Cd(II)	18.94	18.63	-1.64
Zn(II)	6.96	11.99	72.27
Cr(III)	2.78	3.24	16.55
Cr(VI)	2.16	1.83	-15.28

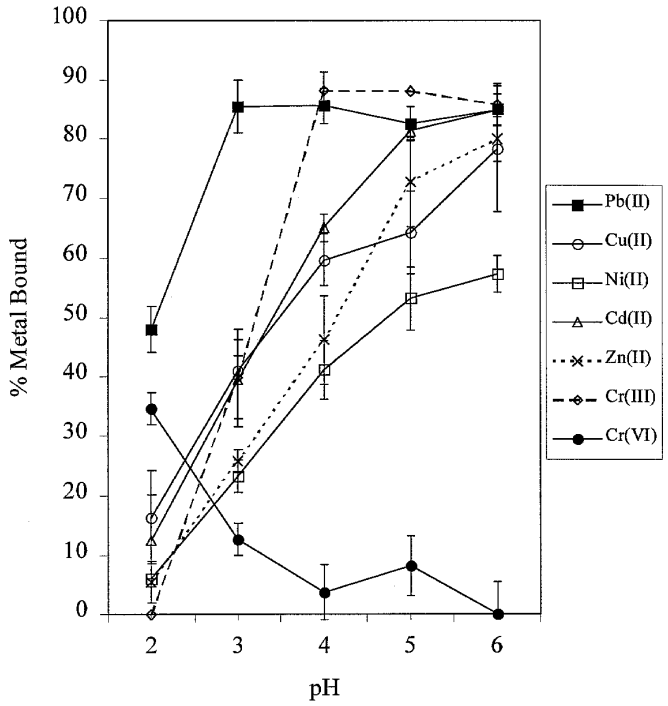

Figure 1. Effects of pH on the binding of lead(II), copper(II), nickel(II), cadmium(II), zinc(II), chromium(III), and chromium(VI) by the unmodified *Solanum elaeagnifolium* biomass. The x-axis represents the pH values studied and the y-axis represents the percentage of metal bound by the biomass.

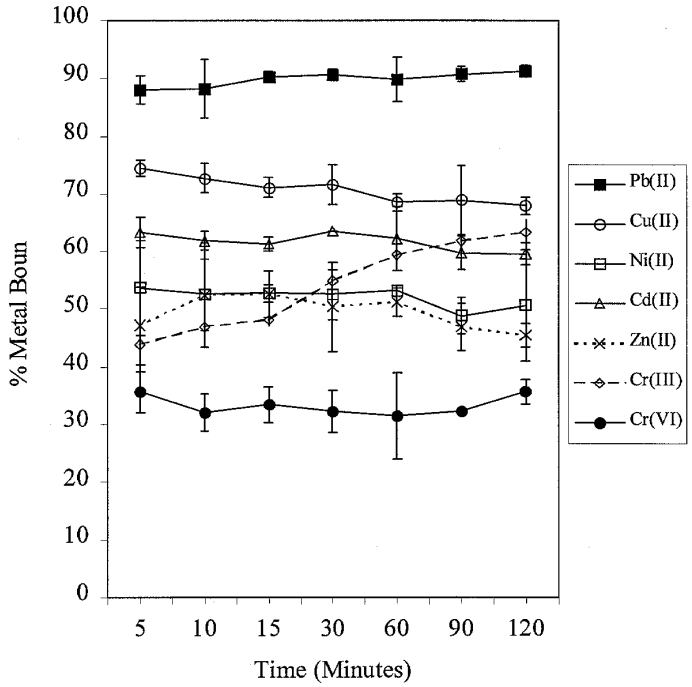

Figure 2. Percentage of different metals bound by the unmodified *Solanum elaeagnifolium* biomass as a function of time.

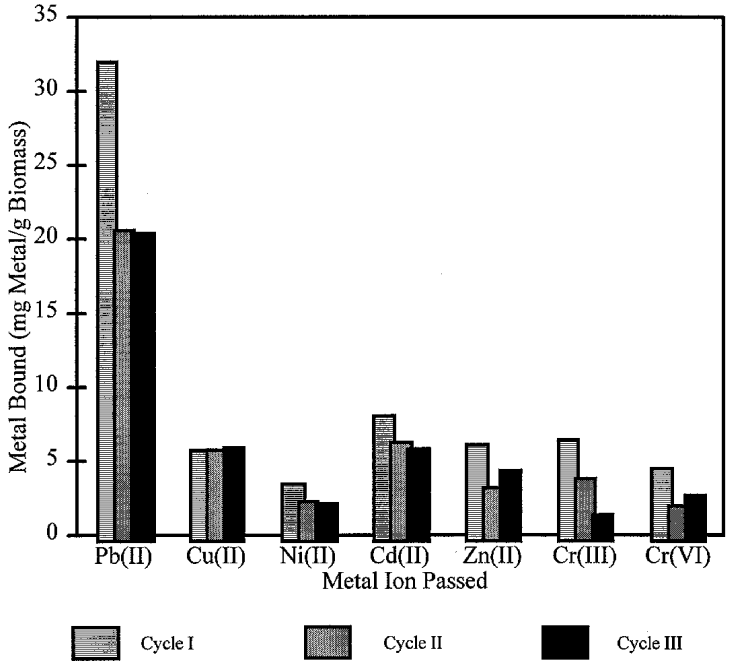

Figure 3. Capacity of the silica-immobilized *Solanum elaeagnifolium* biomass to bind different metal ions under flow conditions. A separate column was utilized for every metal and each column was recycled three times. The capacity of the biomass to bind metals in the three subsequent cycles is shown. The flow rate used was 1 ml/minute.

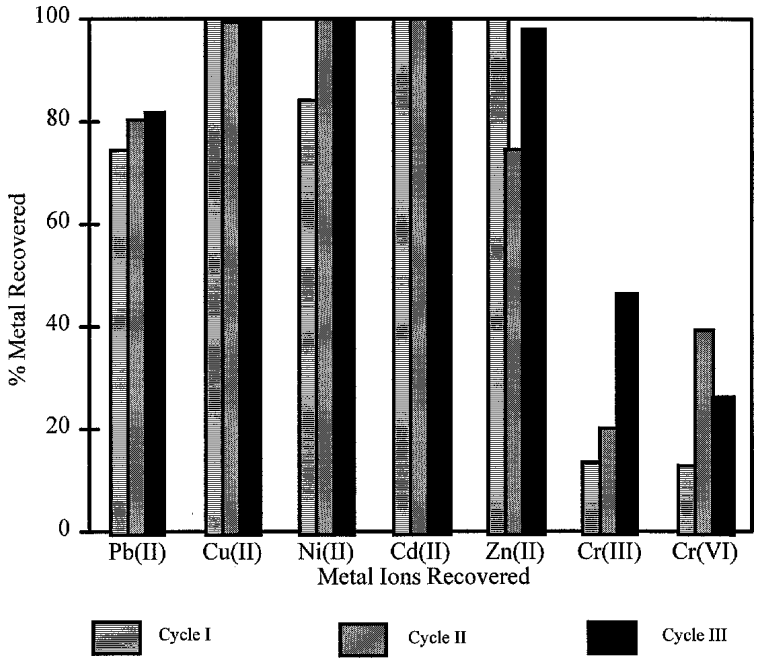

Figure 4. Percentage of metals recovered from the silica-immobilized *Solanum elaeagnifolium* biomass with 0.1M HCl, following the single metal-binding experiments under flow conditions. Metal recoveries from each of the three cycles are shown. The flow rate used was 1 ml/minute.