Removal of lead from aqueous solutions using an immobilized biomaterial derived from a plant biomass

K. Chandra Sekhar a,∗ C.T. Kamala a, N.S. Chary a, A.R.K. Sastry b, T. Nageswara Rao b, M. Vairamani a

a Analytical Chemistry and Environmental Sciences Division, Discovery Lab (D-120), Indian Institute of Chemical Technology, Hyderabad 500 007, AP, India
b Organic Coatings and Polymers Division, Indian Institute of Chemical Technology, Hyderabad 500 007, AP, India

Received 26 August 2003; received in revised form 29 January 2004; accepted 29 January 2004

Abstract

Because of the severity of heavy metal contamination and potential adverse health impact on the public, a tremendous effort has taken place to purify waters containing toxic metal ions. Traditional methods which have been employed prove to be costly and prohibitive for low level waste remediation. Biosorption is presented as an alternative to traditional physicochemical means for removing toxic metals from ground and wastewaters. Most recently, plant based biomaterials have been of interest.

The bark of Hemidesmus indicus, an extensively available plant biomass commonly called as Indian sarsaparilla was used as biomaterial for removal of lead from aqueous streams. Batch experiments were carried out with immobilized biomass of H. indicus (IPBFIX) to optimize the experimental parameters like effect of contact time, initial metal concentration, initial IPBFIX concentration and co-metal ion effect on biosorption of lead from contaminated waters. Column experiments were performed under flow conditions for regeneration and recycle efficiency of IPBFIX and was found to be effective for three cycles. Elution experiments were carried out to remove lead ions from loaded IPBFIX and 100% elution was achieved with a 0.1 M HNO3 solution. The effectiveness of the IPBFIX for biosorption of lead ions was demonstrated using the wastewater samples emanating from a non-ferrous metal industry and the results are presented in this paper. The results from these studies will be useful for a novel phytofiltration technology to remove and recover lead from wastewaters and this can also be well adapted for secondary treatment or polishing of wastewaters. An attempt has been made to remove lead from the lead polluted waters (both ground and surface) from an industrially contaminated sites.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Lead; Immobilization; Biomass; Beads; Phytofiltration; Regeneration

1. Introduction

As today’s technology progresses, the natural environment suffers from the detrimental effects of industrial pollution. The natural process of transportation of metal ions between the soil and water consolidates metal contamination in high concentrations that affect the areas of natural ecosystems [1]. Industries such as smelters, metal refineries, and mining operations have been indicated as major sources of metal release into the environment [2–6]. Heavy metal contamination that does get into the environment could cause permanent negative ecological effects [7]. Many attempts have been made throughout the globe to clean heavy metal polluted groundwaters and soils. However, recent studies have shown that many of the treated polluted groundwater sites have not been restored back to drinking water standards [8]. Therefore, heavy metal contamination of the environment has become an area of increasing concern. The limitations of conventional groundwater remediation have spurred many investigations into alternative methods that are more cost effective. With the increase in environmental awareness and governmental policies, there has been a push toward development of new environmentally friendly ways to clean contamination by using low cost methods and materials.

Biological methods for remediation may provide the answer [9–11]. Among the various biological systems, dead systems offer many advantages over live systems because they do not fall prey to toxicological effects of high concentrations of contaminants and can be obtained inexpensively [12]. However, recovery of metal from loaded biomass is...
still cumbersome. Recently, plants have been studied for their ability to remove contaminants from the environment [13–19]. Researchers have recognized that immobilizing biomass in a granular or polymeric matrix may improve biomass performance and facilitate separation of biomass from solution [20,21]. The American Bureau of Mines has investigated the use of biomass immobilized in porous poly-sulfonate beads (BIOFIX) for extracting toxic and heavy metals from dilute waste streams [22]. Gardea-Torresdey et al. [23] have removed copper ions from aqueous solutions by silica immobilized Medicago sativa (alfalfa). Immobilized biomass appears to have a greater potential than raw biomass in packed bed or fluidized bed reactors with benefits such as control of particle size, better capabilities of regeneration, reuse and recovery without destruction of biomass beads [24–26].

Lead contamination of drinking water occurs as a result of corrosion and leaching from Pb/Sn soldered joints associated with the copper service lines commonly used in households plumbing [27]. Lead poisoning in human causes severe damage to the kidney, nervous system, reproductive system, liver and brain and causes sickness or death [28]. Severe exposure to lead has been associated with sterility, abortion, stillbirth and neonatal deaths [29]. The permissible limits for lead in drinking water given by US Environmental Protection Agency (USEPA) is 0.015 mg dm$^{-3}$ [30] and for wastewaters is 0.1 mg dm$^{-3}$ [2] given by both USEPA and Bureau of Indian Standards (BIS) [31,32]. Thus it becomes mandatory to pass through a 1 mm mesh and used for immobilization.

Immobilized biomass beads (IPBFIX) were prepared using immobilized Medicago sativa (alfalfa) biomass beads and to investigate the binding of Pb from representative wastewaters with biomass beads to determine optimal time required for control by immobilized $H. \text{indicus}$ biomass beads and to indicate factors that impact the sorption and elution characteristics of the beads. Laboratory batch experiments were performed with biomass beads to determine optimal time required for lead ion binding to the biomass, effect of varying IPBFIX loadings, initial lead ion concentration and effect of co-metal ions such as Zn and Cr. Column experiments were performed under flow conditions for regeneration of IPBFIX beads for their re-use. The elution experiments were carried out with varying concentration (0.025–0.2 M) of eluants such as HCl, HNO$_3$, EDTA, Na$_2$CO$_3$ and NaOH for elution of lead ions from the loaded IPBFIX. Biosorption experiments with IPBFIX for real-life samples from non-ferrous metal processing wastes was also carried out.

2. Experimental

2.1. Materials and methods

2.1.1. Chemicals and reagents

The stock solutions of Pb and other co-ions Zn and Cr were prepared by dissolving appropriate quantities of Pb(NO$_3$)$_2$, (Drug houses [INDIA] Pvt. Ltd., Graham Road, Mumbai), Zn(CH$_3$COO)$_2$ (Glaxo Laboratories IND Ltd., Mumbai) and K$_2$Cr$_2$O$_7$ (Ranbaxy Laboratories Ltd., Punjab) salts in 5% HNO$_3$, respectively. The pH of the working solutions was maintained with 0.01 M HNO$_3$ or NH$_3$ using an Elico pH meter (Elico Pvt. Ltd., India). All the chemicals used were of AR grade and deionized distilled water was used for all the experiments.

2.1.2. Preparation of biomass beads

Our previous experimental studies with raw biomass of $H. \text{indicus}$ have proved that the root bark of the plant is a potential biosorbent for lead ions [33]. $H. \text{indicus}$ commonly known as Indian sarsaparilla is taxonomically classified as a member of family Asclepiadaceae (Warrier, 1995). The biomass was oven dried at 100°C for 24 h and powdered to pass through a 1 mm mesh and used for immobilization.

Experiments using column set-up (Fig. 1) as per Reddy et al. [15] were conducted to determine the IPBFIX retention capacity for lead ions, elution of metal ions from loaded IPBFIX, and regeneration of the IPBFIX for its reuse. The results of such a study are useful for determining the basic engineering data, which is necessary for scaling up the process. Ten grams of IPBFIX (bed height 7 cm) was packed into the column having an internal diameter of 1.6 cm and a column height of 20 cm. One liter of solution containing 100 ppm of lead was passed through the column containing IPBFIX at a flow rate of 0.81 l/h for 24 h at the predetermined pH. The pH of the inlet metal solution was adjusted with 0.01 M HNO$_3$ or NH$_3$ using an Elico pH meter (Elico Pvt. Ltd., India). All the chemicals used were of AR grade and deionized distilled water was used for all the experiments.

2.1.3. Equilibrium experimental set-up

Equilibrium experiments were conducted with stoppered flasks in a mechanical shaker (Techno India Ltd.). One gram of IPBFIX was washed twice with 50 ml of 0.01 M HCl to remove any debris or soluble biomolecules that might interact with metal ions. Washings were collected, and IPBFIX was dried and weighed to account for any weight loss of the IPBFIX. The IPBFIX was then stirred with 100 ml of 100 ppm lead ion solutions at room temperature ($\pm 30$°C) at 300 rpm for 5 min. The pH of the lead ion solution was taken as it is (pH 1.8–2.0) as our earlier batch experimental studies with raw biomass of $H. \text{indicus}$ revealed that lead ion removal from aqueous solutions was independent of pH variation and hence no experiments were carried out with IPBFIX to study the effect of pH. After biosorption the samples were filtered and analyzed three times along with a control sample by AAS for lead [34].

Batch experiments were conducted to study the effect of various parameters on the biosorption of lead by the IPBFIX such as metal to IPBFIX contact period, IPBFIX loadings, initial metal ion concentration and co-metal ions.

2.1.4. Column set-up

Experiments using column set-up (Fig. 1) as per Reddy et al. [15] were conducted to determine the IPBFIX retention capacity for lead ions, elution of metal ions from loaded IPBFIX, and regeneration of the IPBFIX for its reuse. The results of such a study are useful for determining the basic engineering data, which is necessary for scaling up the process. Ten grams of IPBFIX (bed height 7 cm) was packed into the column having an internal diameter of 1.6 cm and a column height of 20 cm. One liter of solution containing 100 ppm of lead was passed through the column containing IPBFIX at a flow rate of 0.81 l/h for 24 h at the predetermined pH. The pH of the inlet metal solution was adjusted with 0.01 M HNO$_3$ or NH$_3$ using an Elico pH meter (Elico Pvt. Ltd., India). All the chemicals used were of AR grade and deionized distilled water was used for all the experiments.
continuously monitored and maintained constant automatically by the addition of 0.01 M NH₄OH or HCl. After the experiment, the concentration of metal ions in the solution was analyzed to determine the retention capacity of the IPBFIX. Elution of metal from loaded IPBFIX was carried out with 100 ml (at a flow rate of 1 ml/min) each of different concentrations (0.025–0.2 M) of HCl, HNO₃, EDTA, Na₂CO₃ and NaOH eluants. The eluted IPBFIX beads were washed twice with 500 ml of deionized water for regeneration. The regenerated IPBFIX beads were tested for lead uptake to determine the evolution of its retention capacity.

3. Results and discussion

3.1. Batch studies

3.1.1. Kinetic study for lead binding to the IPBFIX

The time dependency batch experiments were performed with varying the contact time of IPBFIX to lead ions from 5 to 120 min (5, 15, 30, 60 and 120 min). All other parameters such as IPBFIX concentration (1 g), volume of lead ion solution (100 ml) was kept constant. The experiments were conducted to determine the time required for IPBFIX beads to bind the lead ions. It can be seen from Fig. 2 that 99.2% lead ions are bound to the IPBFIX within 5 min of contact after which it increased marginally in 30 min and stabilized thereafter. The rapid binding of metal ions from solution compared to 15 min by pure biomass [33] could mean that the binding sites for lead are located on the H. indicus cell walls and also the immobilization did not alter the binding sites and instead enhanced the binding capacity of IPBFIX. Similar conclusions were obtained by Zhang and Majidi [35].

3.1.2. Effect of IPBFIX concentration

The percentage lead removal was studied with varying IPBFIX loadings from 0.1 to 2.5 g (0.1, 0.5, 1.0, 1.5, 2.0 and 2.5 g) and taking the pH of the metal solution as it is (pH ~ 2). The parameters such as contact time (5 min), volume of lead ion solution (100 ml), and initial lead ion concentration (100 ppm) were kept constant. The results of the experiment are presented in Fig. 3a and b. From the figure it is clear that by using 1 g IPBFIX, 100% of the metal can be removed whereas 2 g of the non-immobilized raw biomass required for the same amount of metal removal [33]. This may be explained due to the increase in surface area of the biomass due to immobilization. Experiments with control (the polymer used for immobilization) revealed no metal removal indicating the metal removal is only due to plant biomass. All these data obtained with simple experiments can be of great interest in scale-up process to optimize
3.1.3. Effect of initial metal ion concentration

The metal removal by IPBFIX corresponding to different initial metal concentrations (25, 50, 100, 250, 500, 1000, 2000, 4000, 5000 and 6000 ppm) are shown in Fig. 4a and b. The parameters such as contact time (15 min), volume of solution (100 ml) and IPBFIX loading (1 g) were kept constant. As can be seen from Fig. 4a, removal of lead ions is 99.8% till 1000 ppm concentration of lead ions in aqueous solutions. The binding sites are limited keeping IPBFIX loadings as constant. With increasing metal concentration, the percentage of metal removed stabilized and then decrease to 70 for 6000 ppm of lead ions in solution. In our earlier experiments with raw H. indicus biomass the percentage lead removal above 1000 ppm metal decreased due to slurry formation [33]. Thus by using IPBFIX the problem of slurry formation was avoided and the beads were stable for metal concentrations as high as 6000 ppm.

3.1.4. Co-ion effect

The co-ion experiments were conducted with 1.0 g of IPBFIX and a shaking time of 15 min and keeping the volume constant (100 ml). The results of the experiment are presented in Fig. 5. The results revealed that lead removal was not affected by any of the cations (Zn and Cr), however, the presence of co-ions enhanced Zn removal but decreased Cr removal. In the presence of co-ions in solution, chemical interactions between the ions themselves as well as with the biomass take place resulting in site competition [37,38]. Many of the functional groups present on the cell wall and the membrane are non-specific and different cations compete for the binding sites. It has been reported that metal removal is increased as the ionic radii of metal cations affect the ion-exchange and adsorption process [39]. The differences in the sorption affinities may also be attributed to differences in the electrode potentials of the various ions. The greater the electrode potential, the greater is the affinity for biomass [40,41]. The ionic radii and the electrode potentials of the metal ions are summarized in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Ionic charge</th>
<th>Ionic radius (Å)</th>
<th>Electrode potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb⁴⁺</td>
<td>+2</td>
<td>1.32</td>
<td>0.126</td>
</tr>
<tr>
<td>Zn⁶⁺</td>
<td>+2</td>
<td>0.74</td>
<td>0.783</td>
</tr>
<tr>
<td>Cr⁶⁺</td>
<td>+6</td>
<td>0.44</td>
<td>0.744</td>
</tr>
</tbody>
</table>

In multicomponent systems, the complex interactions of
several factors such as ionic charge, ionic radii and electrode potential will account for the differences in the metal removal capacity of the biomass. As a result, ordering of the metal ions based on a single factor is very difficult.

3.2. Column studies

3.2.1. Elution tests

Efficient removal of loaded metal from the IPBFIX biomass beads was necessary to ensure their long-term use for repeated extraction-elution cycles. A review of literature indicated that dilute mineral acids, ethylenediamine tetraacetic acid (EDTA), and caustic solutions [41] have been utilized to remove sorbed metal ions from microorganisms. These reagents were therefore evaluated for eluting sorbed metals from the IPBFIX beads.

Mineral acids evaluated as potential eluants included HNO₃ and HCl. Experimental conditions were maintained as explained in column set-up. Among the mineral acids 0.1 M HNO₃ was very effective eluant than HCl (Fig. 6). In the first 10 min of contact, 90% of elution occurred and complete metal elution (100%) was achieved within half an hour. EDTA was also evaluated as a potential metal eluant but is not as effective as HNO₃. The caustic solutions studied were NaOH and Na₂CO₃. Sodium carbonate was the most effective of the caustic eluants tested. A 0.1 M sodium carbonate eluted 75% of the metal. Among all the eluants used 0.1 M nitric acid proved to be the best eluant.

Table 2

<table>
<thead>
<tr>
<th>Number of cycles</th>
<th>Raw biomass</th>
<th>IPBFIX</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lead uptake (mg/g)</td>
<td>Lead elution (mg/g)</td>
</tr>
<tr>
<td>1</td>
<td>93.6 ± 3.9</td>
<td>90.2 ± 3.8</td>
</tr>
<tr>
<td>2</td>
<td>89.3 ± 1.8</td>
<td>85.3 ± 4.1</td>
</tr>
<tr>
<td>3</td>
<td>74.2 ± 3.2</td>
<td>70.2 ± 3.8</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Number</th>
<th>Sample label and composition</th>
<th>Pb (mg/g) removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw biomass</td>
<td>IPBFIX beads</td>
</tr>
<tr>
<td>Model solutions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Control composition (ppm): Pb = 1000</td>
<td>900 ± 10.8 (90)</td>
</tr>
<tr>
<td>2</td>
<td>Syn-1 composition (ppm): Pb = 1000; Zn = 5000; Cr = 1000</td>
<td>790 ± 8.6 (79)</td>
</tr>
<tr>
<td>3</td>
<td>Syn-2 composition (ppm): Pb = 2500; Zn = 2500; Cr = 500</td>
<td>1875 ± 14.3 (75)</td>
</tr>
<tr>
<td>4</td>
<td>Syn-3 composition (ppm): Pb = 5000; Zn = 1000; Cr = 2500</td>
<td>3300 ± 12.5 (66)</td>
</tr>
<tr>
<td>“Real-life” samples</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Real-1 composition (ppm): Pb = 26.04; Zn = 0.41</td>
<td>19.6 ± 0.02 (75.27)</td>
</tr>
<tr>
<td>6</td>
<td>Real-2 composition (ppm): Pb = 29.27; Zn = 0.94</td>
<td>18.4 ± 0.03 (95.87)</td>
</tr>
<tr>
<td>7</td>
<td>Real-1 + Cr and Zn composition (ppm): Pb = 0.013; Zn = 0.41; Cr = 1000</td>
<td>19.8 ± 0.013 (76.38)</td>
</tr>
<tr>
<td>8</td>
<td>K1 (surface waters): Pb = 20.7 ppm</td>
<td>16.09 ± 0.012 (79.3)</td>
</tr>
<tr>
<td>9</td>
<td>K2 (surface waters): Pb = 16.7 ppm</td>
<td>12.8 ± 0.013 (77.3)</td>
</tr>
<tr>
<td>10</td>
<td>K3 (groundwater): Pb = 33.2 ppm</td>
<td>8.81 ± 0.016 (75.3)</td>
</tr>
<tr>
<td>11</td>
<td>K4 (groundwater): Pb = 30.7 ppm</td>
<td>7.8 ± 0.015 (76.5)</td>
</tr>
</tbody>
</table>

Values in parenthesis are % lead removal.

3.2.2. Regeneration of loaded beads for its reuse

The batch laboratory experiments showed that IPBFIX has ability to bind lead and remove it from aqueous lead ion solutions, but batch system may not be practicable for removing lead ions from contaminated waters. Therefore, column experiments were performed to study the binding of lead ions to the IPBFIX beads under flow conditions.

Experiments were carried out using the conditions in column set-up for retention capacity of IPBFIX for lead ions and its regeneration trials and the results are presented in Table 2. From the results it is very much clear that elution of lead ions from IPBFIX is stable till three cycles when compared to the raw biomass. This suggests that the IPBFIX could be regenerated for use in continuous operation of
metal ion removal from aqueous solutions. The decreased efficiency of metal uptake and release by raw biomass could be due to physical damage to the biomass caused by the extended volumes of the eluant.

3.2.3. Analytical application

The studies reported here are conducted using model metal ion solutions. However, the metal ions at the range of concentrations chosen are representative of typical waste effluents emanating from various non-ferrous processing industries. Therefore results of this work have considerable practical implications. The results shown in Table 3 represent the comparison of metal removal in model co-ion solutions, real effluent collected from non-ferrous metal industry and also the ground and surface water samples collected from the lead contaminated sites of Kattedan Industrial Area, Hyderabad. As we did not get “real-life” effluent samples for Cr(VI) we have spiked Real-1 sample with Cr(VI). Table 3 clearly shows that IPBFIX is effective in lead ion removal when compared to raw biomass. The results from these experiments prove that IPBFIX can be used effectively for the removal of lead ions from aqueous systems.

4. Conclusions

The characterization of lead uptake by IPBFIX showed that the binding kinetics is pH independent up to pH 5.0 and occurs in less than 5 min. The binding of the lead ions is on the cell wall of the plant biomass but not on the polymeric material used for immobilization. The IPBFIX that was saturated with lead ions shows the remarkable ability for lead recovery by treatment with low concentrated nitric acid. Through column experiments it was shown that the IPBFIX was not only successful for effective lead removal but it was also reusable. These studies show that IPBFIX has the potential to be used as a biofilter for fast removal and recovery of lead ions from contaminated waters. This innovative technology provides a reusable material, which is environmentally friendly.

Acknowledgements

The authors are grateful to Dr. K.V. Raghavan, Director, Indian Institute of Chemical Technology (IITC), and Dr. V. Balaram, Head, Geochemistry Department, National Geophysical Research Institute (NGRI) for their encouragement and support in carrying out this work.

References
