Studies On Technology Oriented Methods For Water Contaminants And The Geochemical Influences On Contaminated Plume

REFERENCES


Studies On Technology Oriented Methods For Water Contaminants And The Geochemical Influences On Contaminated Plume


Published and Communicated papers based on the studies carried out so far

PUBLISHED PAPERS


COMMUNICATED PAPERS


Pandey P.K., Verma Y., Choubey S., Pandey M., 2006. Fe(II) removal from the ground water and industrial effluent using a novel adsorbent. Communicated to Chemistry and Environment Cleared the first stage of editorial scrutiny and has been sent to reviewers.

Pandey P.K., Choubey S., Verma Y., Pandey M., 2006. Separation of binary mixture of Ni(II) and Cr(VI) by column sorption technique. Communicated to Water research, Elsevier. Cleared the first stage of editorial scrutiny and has been sent to reviewers.

contamination and its health effect in Southeast Asia at American Journal of Environmental Science. Cleared the first stage of editorial scrutiny and has been sent to reviewers.

**Paper presented at Conferences and symposium**


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Biosorptive removal of cadmium from contaminated groundwater and industrial effluents

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Abstract

The cadmium removing capacity of a biosorbent Calotropis procera, a potential wild plant, is reported here. The biomass was found to possess high uptake capacity of Cd(II). Adsorption was pH dependent and the maximum removal was obtained at two different pH i.e. pH 5.0 and 8.0. Maximum biosorption capacity in batch and column mode was found to be 40 and 50.5 mg/g. The adsorption equilibrium (90% removal) was attained within 5 min irrespective of the cadmium ion concentration. Interfering ions viz. Zn(II), As(III), Fe(II), Ni(II) interfered only when their concentration was higher than the equimolar ratio. The Freundlich isotherm best explained the adsorption, yet the monolayer adsorption was also noted after concentrations of Cd(II). The FTIR analysis indicates the involvement of hydroxyl (-OH), alkanes (-CH), nitrite (-NO2), and ethoxy group (-COO) chelates in metal binding. The complete desorption of the cadmium was achieved by 0.1 M H2SO4 and 0.1 M HCL. The C. procera based Cd(II) removal technology appears feasible.

Keywords: Biosorption, Biomass, Cadmium; Groundwater; Contaminated water

1. Introduction

This research has focused on the potential use of wild plant material as the biosorbent for the removal of cadmium ions in aqueous solution. Cadmium (Cd) removal from wastewater is of vital importance because of the ubiquitous presence of Cd(II) in various effluents. Many industries, especially electroplating, battery and plastic manufacturing release heavy metals such as cadmium and zinc in waste water. Similarly there are instances of the groundwater contamination with chromium, cadmium, mercury etc. from the industrial activities. One report from central-east Indian location showed the presence of Cd(II) in the acid mine drainage from a copper mine (Pandey et al., 2007).

Cadmium is a potent neurotoxic metal and permissible limits for cadmium in drinking water is 0.003 mg/L (Government of India, 2000). Cd(II) is among the most toxic metals and is known to cause renal dysfunction, bone degeneration, lung inefficiency, liver damage and hypertension in humans. On the basis of these adverse health effects, Cd(II) has been included in the red list of priority pollutants by the Department of Environment, UK (UK red list substances, 1991) and in the black list of EEC Dangerous Substance Directive (EEC black list substances). US Environmental Protection Agency has also classified Cd(II) as group B1 carcinogen (US Environmental Protection Agency, 1999). Cadmium has been designated as category 1 carcinogen by International Agency for Research on Cancer (IARC). Cadmium being one of the “big three” toxic metals, the other two being lead and mercury, is of profound concern as toxic contaminant of aqueous environment and becomes concentrated through out the food chain to the extent of posing serious threat to health.
Hence, the search for economic adsorption alternatives is highly imperative.

A wide variety of methods such as precipitation and co-precipitation, oxidation (Chiu and Hering, 2000), ion exchange (BAMWSP, 2001) and adsorption (Dambies, 2001) have been proposed for heavy metal removal from aqueous solutions. Current treatment processes for metal containing wastewaters are reported to exhibit reduced efficiency with low concentration. Significant research has been conducted on biomass for their metal sorption capacity (Martínez et al., 2006; Davis et al., 2003). The use of non-living biomass as metal binding compounds has the advantage of not being affected by high levels of contamination. Moreover, they require minimum care and maintenance and can be obtained more cheaply. Various biomass have been used, including seaweeds (Hashimi and Chu, 2004), sugar beet pulp, corncobs (Zacaria et al., 2002), husk of agricultural waste (Ahyalu et al., 2005), tree harks (Saeed et al., 2005), green coconut shell powder (Pino et al., 2006) brown marine macroalgae (Lodicio et al., 2005), yeast biomass (Yekta et al., 2005) and chitin based sorbents (Frosa et al., 2001; Benguella and Benaissa, 2002) for the removal of cadmium ions.

This work demonstrates the efficacy of Calotropis procera, a widespread perennial shrub for the removal of Cd(II) from wastewaters and industrial effluents. This perennial shrub plant is a soft-wooded, evergreen, plant known as Giant milkweed. Giant-milkweed roots were found to have few branches and reach depths of 1.7-3.0 m in Indian sandy desert soils. In ecological terms is regarded as an indicator of overgrazed land, being one of the few plants that goats and camels won't eat. Giant-milkweed is native to West Africa as far south as Angola, North and East Africa, Madagascar, the Arabian Peninsula, southern Asia, and Indochina to Malaysia. The species is now naturalized in Australia, many Pacific islands, Mexico, Central and South America, and the Caribbean islands. The aim of this study was to investigate the feasibility of this easily available plant biomass to sequester cadmium metal and hence, to remediate contaminated effluents and aqueous system.

2. Methods

2.1 Collection and preparation of unleached biomass (UBM)

A perennial shrub C. procera was selected for this study owing to its abundance and availability in Chhattisgarh region and in various other parts of the world. The white flowered variety is botanically known as C. procera and the other with lilac, rosy or purple tinted flowers as Calotropis gigantea. Both varieties belong to family Asclepiadaceae. The locally available plant biomass was harvested by manually removing from soil and the woody root part of the plant was taken and washed with deionized water to remove the foreign materials and dust. The biomass was dried initially in the sunlight and then in a hot air oven at 60°C. The dried biomass was ground in blender and screened through a 250-μm mesh to obtain a fine biomass for use in adsorption studies. Unleached biomass (UBM) processed as above was used as such without any acid leaching.

2.2 Preparation of the leached biomass (LBM)

The biomass utilized was reported to contain quercetin-3-rutinoside, a glucoside (C6H12O7) in the roots, stem, leaves, flowers and latex (HerbalCareIndia.com, 2007). The screened biomass as obtained in Section 2.1 was oven dried and treated with nitric acid. This step was necessitated for polymerization and insolubilization of the available functional groups and phenolic compounds which could have stained the treated water, otherwise. The acid leaching also helped to remove any previously adsorbed metals. It was presumed that such a treatment will enhance the uptake capacity of the biomass. Biomass was treated with 1:1 HNO3 for 3 h. After this the biomass was filtered out with filter paper (Whatman filter No. 40) and was washed with distilled water till the washing was neutral. The biomass was then dried in an oven at 50°C, overnight. The acid treatment of the biomass resulted into loss of about 40% of the dried initial weight of the biomass.

2.3 Chemicals

All chemicals used in the work were of analytical grade and obtained from Merck (India/Germany). All solutions were prepared with deionized and distilled water. All utensils and bottles utilized in the experiments were washed with 5% nitric acid solution and rinsed with distilled water. The cadmium stock solution, 1000 ± 5 mg/L, was prepared by dissolving a desired amount of Cd(NO3)2·4H2O (Merck, Germany) in deionized water and adjusting the pH to 5 with 0.5 M NaOH. The pH of the reaction mixture was further adjusted using either 0.1 M HCl or 0.1 M NaOH as per the need of the experiment. The other standards for calibration as well as cadmium solutions (0.5-20 mg/L) for batch experiments were prepared from the stock solution. The cadmium concentration in the filtrate was analysed by flame atomic absorption spectrophotometer (Chemito-201, with background correction facility) adopting the standard analysis procedure (APHA, 1992).

2.4 Adsorption experiment

Batch experiments were conducted to characterize the mechanism of binding between the biomass with heavy metals. As described previously, the biomass was chemically modified by treating it with acid. Appropriate quantity of the leached biomass (LBM, 5 g/L) of particle size 250 μm was weighed and placed in thoroughly cleaned plastic beakers. Cd(II) solution (50 mg/L) were added to the biomass containing beakers. Cd(II) solution was adjusted to
varying pH from 2.0 to 9.0 with 0.1 M NaOH and 0.1 M HCl. The reaction mixture was then agitated for half an hour at room temperature (28 °C). Simultaneously, beakers with similar metal ion concentration and double deionised water with no biomass were treated as control samples. The experiments were conducted at room temperature between 28 and 35 °C.

The column mode study was conducted at room temperature in a packed glass column of internal diameter 1.0 and 11.5 cm height. A 0.5 g of plant biomass was loaded in the column, above and below which glass beads up to 1 cm height were placed for the uniform flow of metal solution through biomass. The biomass was moistened with tap water before introduction of metal solution. Cadmium ion solution of varying concentration (5-500 mg/L) at optimum pH was run through the column and was allowed to drop down by the force of gravity, which was about 0.2–0.3 ml/min. The percentage removal of each cycle was calculated by periodically removing 2 mL of the solution.

The amount of metal taken up by biomass was calculated as the difference between the initial and the final concentrations of the metal in the aqueous solution. The metal binding experiment was followed by metal desorption studies.

2.5. Elution procedure

The optimal eluent for the sequestered cation must be effective and non-damaging to the biomass. Various eluting agents of 0.1 M concentration such as HCl, HNO3, H2SO4, NaOH, Na2CO3, and NaCl were investigated for their efficacy to recover adsorbed Cd(II) from biomass. About 1.25 g of the biomass was brought into contact with 250 ml of metal solution containing 50 mg/L Cd(II) for a time period of 60 min and then separated by filtering it through Whatman filter paper (No. 40). This Cd loaded biomass was treated with 15 ml of the eluting agent for 15 min at 30 °C. The biomass was removed by passing it through a filter paper in a batch system and the supernatant was analysed for Cd(II) concentration. The column mode involved one or more cycles of elution for complete desorption of adsorbed Cd(II) depending on the contaminants level. After desorption the biomass was washed with distilled water and oven dried to regenerate it for reuse in adsorption–desorption studies.

2.6. Quality assurance and quality check (QA/QC) procedure

For QA/QC checks the Merck certified standard was used for calibration of AAS. An average of at least six readings was taken for every experiment. The results that were within ±10% were accepted otherwise the experiment was repeated. For each parameter study at least triplicate experiments were conducted. NIST standard 1643e and 1641d were used to ensure the correctness of the results of the Cd(II) removal.

3. Results and discussion

3.1. Effect of pH on metal ion binding

It was found that the pH of the solution played an important role in Cd(II) uptake by the Calotropis biomass. The batch pH experiments, which were carried out at 35 °C using a 500 mg of unleached biomass (UBL) in metal solution of concentration 50 mg/L, showed that the optimal pH for maximum Cd(II) sorption was 5.9. The pH profiling (pH 2–9) showed that the Cd(II) sorption increased (from 35% to 72%) between the pH ranges of 2–5. An appreciable decrease in adsorption was noted after pH 5 which continued till pH 6.5, beyond which the adsorption again increased showing a maximum removal at pH 8 (72%). Hence, two adsorption peaks were established at pH of 5 and 8. The further increase in pH beyond 8 caused a decrease in the adsorption of Cd(II) ions. This trend can be explained based on the behaviour of Cd(II) in the aqueous system. For the Cd(NO3)2 system Cd(IV) was the dominant species up to pH 8 which was strongly adsorbed by biomass, however, above pH 8 the Cd(OH)2 becomes the dominant species which starts to precipitates in the manner concurrent with the increasing pH (Saes and Mesmer, 1976). The Cd(II) precipitates so formed are amphoteric in nature and at higher pH they form amionic complexes which are rejected by negatively charged biomass.

On the other hand the low pH i.e. higher H+ concentration of the solution had shown diminished adsorption of Cd(II) to the biomass, obviously due to the higher presence of competing ions. On starting with initial pH of 5 the solution pH rises to about 5.5, which indicates the probability of co-adsorption with some H+ ions onto the biomass. This explanation was confirmed by the adsorptive behaviour at pH 8 when such an increase in pH was not observed. Hence from the application point of view it was found judicious to utilize this biomass at the pH at 5.0 for industrial effluents and at pH 8.0 for the natural water.

3.2. Kinetic study of sorption

To determine the metal sorption kinetics about 500 mg biosorbent samples were exposed to 50 mg/L concentration of cadmium at pH 5.0 in batch process. The residual metal concentration in aqueous solution was measured after a contact time of 5 min onwards at 10, 20, 30, 60,120, 180, 240 and 300-min intervals. The results showed that about 90% of the adsorption was attained within 5 min and the further increase in contact time had negligible effect on overall percentage removal even till 24 h. Further, if left into contact with the adsorbate the percentage removal decreased to about 77% at 48 h. These observations prove that the adsorptive intensity of the biomass for the Cd(II) was rapid and strong. The kinetics of Cd(II) adsorption follows first order kinetics as derived by the following equation:
log\( (q_t - q) / q_e \) = \( \log q_e - (K_{ad}/2.303) \times t \)

where \( q \) is the amount of Cd(II) (mg/g adsorbent) removed at time \( t \), \( q_e \) is the amount of Cd(II) removed at equilibrium and \( K_{ad} \) is the rate constant of adsorption (min\(^{-1}\)). The lower adsorption rate constant \( K_{ad} \) of UBM (1.54 min\(^{-1}\)) compared to that of LBM (1.55 min\(^{-1}\)) can be explained by the lower availability of the active sites on UBM.

### 3.3. Metal binding capacity experiment

The metal removal from the solution generally takes place by the interaction of metal and active sites on the cell surface. The fresh biomass can be given several physical and chemical treatments to tailor the metal binding properties of biomass to specific requirement. Some reports on Juniperus monosperma adsorbents have revealed that heavy metal sequestration behavior was influenced and depended on the functional groups generated by the chemical modifications (Min et al., 2004; Shin and Rowell, 2005). In case of Calotropis biomass the acid leaching was found to increase the uptake capacity of the biomass by about 12%. For the determination of the initial Cd(II) concentration, the percentage removal was found to be about 70% for 250 mg/L of Cd(II) ions. Beyond this concentration, there was a continuous decrease in the uptake capacity. This decrease can be attributed to the non-availability of any more active sites.

Experiments conducted to find out the efficacy of batch and column mode of operation for the Cd(II) showed (Fig. 2) that the residual Cd(II) concentration in the solution treated by column mode were significantly lower than in batch mode. This result is encouraging for developing the column mode pilot scale removal plant for Cd(II) removal from the contaminated effluents.

### 3.4. Effect of co-ions on the percentage removal of Cd(II) ions

The presence of other metal ion can affect the removal of primary metal ion and may hamper the removal efficiency (Kim and Teo, 1994). Water often contains large number of ions coexisting, which may either enhance or depress the removal of the target ion. Hence, an extensive study on the uptake capacities of biomass was carried out in the presence of coexisting ions viz. Mg(II), Ca(II), As(III), Fe(II), Ni(II), Cr(VI), Pb(II), Hg(II), Zn(II) ions and anions like Cl\(^-\), SO\(_4\)\(^2-\), PO\(_4\)\(^3-\), F\(^-\). A binary combination study of Cd(II) with various competing ions shows that the metal affinity of the biomass for single metal ion system has been similar to that of mixed metal ion system in equimolar ratio. Beyond that there was an inhibition effect on the target ion removal efficiency with increasing concentration of the foreign metal ion. This may be attributed to the lower availability of the binding sites. Ca(II), Mg(II) and Cr(VI), marginally affected the Cd(II) uptake, the presence of other metals reduced the uptake capacity at their higher concentration (Figs. 3 and 4). Presence of some of the anions like Cl\(^-\) and PO\(_4\)\(^3-\) retarded the removal efficiency, whereas SO\(_4\)\(^2-\) and F\(^-\) did not affect the adsorption process even at high concentration (Figs. 5 and 6). Hence, the biomass appears quite selective for Cd(II) and the removal was free from interferences from many metals at the equimolar ratio at the reported working conditions. It is known that the greater the atomic weight, electronegativity, electrode potential and ionic size, the greater will be the affinity for sorption. In the case of present biomass the sorption mechanisms are a little more complicated. The cations like Fe(III) and Ni(II) with lower ionic radius and higher electronegativity have been found to be adversely affecting the Cd(III) removal only at a higher concentration.
concentration, whereas the Zn(II) was found to retarding the Cd(II) uptake even at a low concentration. The screening effect by the metals present in the solution appears to be a reason of the observed phenomena. Thus, in the optimized conditions the sorption of metal was a competitive process between the ions in solution and those sorbed on to the biomass surface. The exact mechanism could not be deduced by simple extrapolations.

3.5. Equilibrium studies

The percentage removal of Cd(II) ion by the biomass was calculated from the following equation:

\[ \%R = \frac{C_i - C_e}{C_i} \times 100 \]

where \( R \) is the removal, \( C_i \) and \( C_e \) are initial and equilibrium metal ion concentration in aqueous solution. In the batch mode the percentage of metal removal in the untreated biomass was found to be 88% for 50 mg/L Cd(II) which subsequently decreased with increasing concentrations. In contrast the treated biomass showed 100% removal of 50 mg/L of Cd(II). As the biosorption process involves mainly cell surface sequestration, cell wall modification can greatly alter the binding of metal ions. A number of methods have been employed for modifying the cell wall of biomass in order to enhance the metal binding capacity and to elucidate mechanism of binding. The sorption capacity of unleached and leached biomass was evaluated and the uptake values were calculated from the change in solution concentration using following equation:

\[ q = \frac{V(C_0 - C_e)}{M} \]

where \( q \) is the uptake, \( C_0 \) and \( C_e \) are the initial and final concentrations, \( V \) is the volume of solution and \( M \) is the mass of biomass used. From Fig. 1, it can be seen that the uptake capacity of native (UBM) and treated (LBM) biomass was not of very high order particularly at the lower Cd(II) concentration range. This indicates the possibility of the monolayer adsorption of the metal ions on the primary adsorption sites. However, it was noted that at higher Cd(II) concentrations, there was a steep rise in the adsorption. This increased capacity for Cd(II) sequestration can be explained perfectly by the multilayer adsorption phenomena. The unleached biomass (UBM) was found to uptake 40 mg/g Cd(II) at the initial adsorbate concentration of 500 mg/L. On the contrary, the leached biomass (LBM) showed maximum Cd(II) uptake of 51.5 mg/g at similar initial adsorbate concentration. On comparing the uptake capacity with other reported biosorbents (Table 1) it was noted that the present biomass fares quite well. The cheap and abundant availability of the biomass could make it a method of choice for large-scale operation.
The results obtained in these equilibrium experiments were studied for the applicability of adsorption isotherms. The Freundlich isotherm can be linearised to the following equation:

$$\log q = \log K_f + \left(\frac{1}{n}\right) \log C$$

where $K_f$ and $n$ are Freundlich constant.

Similarly, the Langmuir isotherm can also be linearised to following:

$$\frac{C}{q} = \frac{1}{K_m A_m} + \frac{C}{A_m}$$

where $K_m$ and $A_m$ are sorption constant and maximum sorption capacity. The equilibrium data analysis clearly showed the existence of multilayered adsorption pattern owing to the high Cu(II) uptake capacity as explained in the preceding paragraph. The best fitment of the Freundlich isotherm was proved by high correlation coefficient value ($R^2$) of 0.97, whereas the $R^2$ value was low (0.90) in case of the Langmuir isotherm (Table 2). Greater value of $1/n$ (0.197) for LBM as compared to UBM (0.19) signifies that the leached biomass adsorbed the metal ion more strongly than the unleached biomass. Hence, it can be deduced that the adsorption process begins with the initial monolayer coverage on the outer surface of the adsorbent, after which the sorption progresses to the multilayer dimensions, which causes the high observed sorption.

Table 1

<table>
<thead>
<tr>
<th>Bioreactors</th>
<th>Uptake capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moringa oleifera</td>
<td>6.5</td>
<td>Sharma et al. (2007)</td>
</tr>
<tr>
<td>Musa recta</td>
<td>6</td>
<td>Yan and Vinarsagavan (2001)</td>
</tr>
<tr>
<td>Juncus montanum</td>
<td>5.5</td>
<td>Shin (2005)</td>
</tr>
<tr>
<td>Pteridium death palm</td>
<td>9.5</td>
<td>Iqbal et al. (2002)</td>
</tr>
<tr>
<td>Crab shell</td>
<td>5.3</td>
<td>Kim (2001)</td>
</tr>
<tr>
<td>Calotropis procera (LBM)</td>
<td>50</td>
<td>Present work</td>
</tr>
<tr>
<td>Calotropis procera (UBM)</td>
<td>51.5</td>
<td>Present work</td>
</tr>
<tr>
<td>Sawdust</td>
<td>5</td>
<td>Meng et al. (2007)</td>
</tr>
<tr>
<td>Galium hilaire</td>
<td>5</td>
<td>Horsfall and Spill (2005)</td>
</tr>
<tr>
<td>Rice husk</td>
<td>12</td>
<td>Ajmal et al. (2003)</td>
</tr>
</tbody>
</table>

The results obtained in these equilibrium experiments were studied for the applicability of adsorption isotherms. The Freundlich isotherm can be linearised to the following equation:

$$\log S = \log K_f + \left(\frac{1}{n}\right) \log C$$

where $K_f$ and $n$ are Freundlich constant.

Similarly, the Langmuir isotherm can also be linearised to following:

$$\frac{C}{q} = \frac{1}{K_m A_m} + \frac{C}{A_m}$$

where $K_m$ and $A_m$ are sorption constant and maximum sorption capacity. The equilibrium data analysis clearly showed the existence of multilayered adsorption pattern owing to the high Cu(II) uptake capacity as explained in the preceding paragraph. The best fitment of the Freundlich isotherm was proved by high correlation coefficient value ($R^2$) of 0.97, whereas the $R^2$ value was low (0.90) in case of the Langmuir isotherm (Table 2). Greater value of $1/n$ (0.197) for LBM as compared to UBM (0.19) signifies that the leached biomass adsorbed the metal ion more strongly than the unleached biomass. Hence, it can be deduced that the adsorption process begins with the initial monolayer coverage on the outer surface of the adsorbent, after which the sorption progresses to the multilayer dimensions, which causes the high observed sorption.

The IR analysis of metal-loaded unleached and leached biomass samples confirms the presence of hydroxyl (-OH), alkane (-CH), nitrite (-NO$_2$), carboxyl group (-COOH) chelates in the biomass. The frequencies of vibration and their corresponding groups. This also shows that several functional groups are available on the surface of Calotropis for binding of Cu(II) ions. The strong absorption peak at frequency of 3416 cm$^{-1}$ represents -OH stretching which signifies their major involvement of hydroxyl group in the metal binding behaviour. The characteristic IR bands of carboxylate (-COO$^-$), which is a known heavy metal binding group, appeared around 1158-1250 cm$^{-1}$. The increase in pH on Cu(II) adsorption proved the major role of H$^+$ ion sequestration or the release of OH$^-$ radicals in this

Table 2

<table>
<thead>
<tr>
<th>Adsortent</th>
<th>Freundlich isotherm constant</th>
<th>Langmuir isotherm constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unleached biomass (UBM)</td>
<td>0.191</td>
<td>1.80</td>
</tr>
<tr>
<td>Leached biomass (LBM)</td>
<td>0.197</td>
<td>1.60</td>
</tr>
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Table 3

<table>
<thead>
<tr>
<th>No.</th>
<th>Metal loaded unleached biomass (UBM)</th>
<th>Metal loaded leached biomass (LBM)</th>
<th>Change in peak behaviour on leaching</th>
<th>JR peak range (cm$^{-1}$)</th>
<th>Functional group reported corresponding to the observed peak behaviour (Wilkinson, 2004)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1416</td>
<td>1406</td>
<td>Shift</td>
<td>1350-1360</td>
<td>-OH stretching</td>
</tr>
<tr>
<td>2</td>
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<td>2974</td>
<td>Shift</td>
<td>1350-1355</td>
<td>Alkanes -CH stretching vibration</td>
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<tr>
<td>3</td>
<td>3984</td>
<td>3984</td>
<td>Additional peak</td>
<td>1350-2555</td>
<td>Alkanes -CH stretching</td>
</tr>
<tr>
<td>4</td>
<td>1090</td>
<td>1090</td>
<td>Shift</td>
<td>1000-1660</td>
<td>-NO$_2$ stretchings</td>
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<tr>
<td>5</td>
<td>1158</td>
<td>1158</td>
<td>Shift</td>
<td>1000-1260</td>
<td>-CO stretchings, carboxyl acid</td>
</tr>
<tr>
<td>6</td>
<td>1361</td>
<td>1361</td>
<td>Shift</td>
<td>750-1750</td>
<td>Phenyl ring substitution band</td>
</tr>
</tbody>
</table>

Table 4

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<tr>
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adsorption process which was justified based on FTIR study.

3.7. Regeneration of spent biomass

The experiments detailed in the preceding sections on the effect of pH and of co-ions indicated that at lower pH the adsorption was inhibited, similarly the presence of some of the ligands like Cl\(^-\) and NO\(_3\)\(^-\) suppressed the percentage of metal adsorption from the solution. These observations suggested that desorption of the metal laden (spent) biomass could be accomplished at low pH in the presence of the aforesaid ligands. The tests for desorption of metal loaded biomass were conducted under batch condition. It was found that all major inorganic acids viz. HCl, H\(_2\)SO\(_4\) and HNO\(_3\) effectively desorbed the Cd(II) loaded on to the biomass. It was also found that a complete recovery of the cadmium can be achieved by 0.1 M H\(_2\)SO\(_4\) and 0.1 M HCl, while HNO\(_3\) could remove 95% of the adsorbed Cd(II) ions from the biomass. This regeneration using a dilute acid demonstrated the potential of reusing the biomass and/or desorbed metal. The regenerated biomass was used for two more cycles. The ultimately spent biomass could be disposed off as a hazardous waste.

3.8. Application of biomass for removal of cadmium from simulated systems

The studies conducted using synthetic metal ion solution (multi-component) revealed the practicability of the biomass as a potential sorbent for removal of Cd(II) from industrial wastes and also from contaminated groundwater. The metal ions and the range of concentrations chosen are representative of typical industrial waste and groundwater. Almost complete removal of the Cd(II) was noted in case of simulated waste water (pH adjusted) and groundwater. Table 4 shows the removal of Cd(II) in wastewater and groundwater in both the column and batch mode. The column mode was found suitable for the near-complete removal of Cd(II). Reuse of the biomass was found possible by desorbing the adsorbed Cd(II) following the method described in the regeneration experiment.

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Column mode adsorption experiment on simulated water with Cd(II) contamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>pH Cd(II)</td>
</tr>
<tr>
<td></td>
<td>(mg/L)</td>
</tr>
<tr>
<td>Multi-element standard</td>
<td>5.0</td>
</tr>
<tr>
<td>Wastewater</td>
<td>5.5</td>
</tr>
<tr>
<td>(without pH adjustment)</td>
<td>5.0</td>
</tr>
<tr>
<td>Groundwater</td>
<td>6.0</td>
</tr>
</tbody>
</table>

4. Conclusion

The present study shows that the *Calotropis* biomass could be successfully utilized for sequestration of Cd(II) from industrial effluents or contaminated groundwater. The use of leached biomass offers better sorption capacity (51.5 mg/g) than unleached biomass (40 mg/g). The FTIR studies show the involvement of -O-H stretching vibration, alkane -C-H stretching vibration, alkane -C-H stretching, -NO\(_2\) stretchings, -C-O stretchings, carboxalic acid, and phenyl ring substitution band. The increased efficacy of the LBM can be attributed to the generation of new adsorption sites in the leached biomass. The adsorption capacities were found to be pH dependent and maximum removal was at the pH of 5 and 8. The kinetics of adsorption was fast with >90% of the Cd(II) removal was achieved within 3 min and it followed first order model. The study of adsorption isotherm showed that monolayer adsorption (Langmuir isotherm) was followed at lower adsorbate concentration, whereas multilayer adsorption (Freundlich isotherm) was followed at higher concentrations. The higher correlation coefficients also prove that the Freundlich isotherm is the predominant mode of adsorption in case of the *Calotropis* biomass. The presence of common ions viz. Ca\(^{2+}\), Mg\(^{2+}\), Cl\(^-\), SO\(_4\)\(^2-\), PO\(_4\)\(^3-\) did not significantly interfere with metal adsorption even at higher concentrations. On the other hand ions viz. Zn(II), As(III), Fe(II), Ni(II) did interfere with adsorption when in concentrations higher than the equimolar ratio. The biomass was found to be amenable to regeneration by dilute mineral acids. The biomass was successfully used for Cd(II) removal from simulated waste water and contaminated groundwater. These results evince the possibility of the use of biomass for technological applications.

5. Unquoted references


References


Biosorptive removal of cadmium from contaminated groundwater and industrial effluents.

Pandey PK, Verma Y, Choubey S, Pandey M, Chandrasekhar K.

Centre for Environmental Science and Engineering, Department of Engineering Chemistry, Bhilai Institute of Technology, Durg, 491 002 CG, India.

The cadmium removing capacity of a biosorbent Calotropis procera, a perennial wild plant, is reported here. The biomass was found to possess high uptake capacity of Cd(II). Adsorption was pH dependent and the maximum removal was obtained at two different pH i.e., pH 5.0 and 8.0. Maximum biosorption capacity in batch and column mode was found to be 40 and 50.5mg/g. The adsorption equilibrium (90% removal) was attained within 5min irrespective of the cadmium ion concentration. Interfering ions viz. Zn(II), As(III), Fe(II), Ni(II) interfered only when their concentration was higher than the equimolar ratio. The Freundlich isotherm best explained the adsorption, yet the monolayer adsorption was also noted at lower concentrations of Cd(II). The FTIR analysis indicates the involvement of hydroxyl (-OH), alkanes (-CH), nitrite (-NO₂), and carboxyl group (-COO) chelates in metal binding. The complete desorption of the cadmium was achieved by 0.1M H₂SO₄ and 0.1M HCl. The C. procera based Cd(II) removal technology appears feasible.

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