Performance of packed bed column using Chara aculeolata biomass for removal of Pb and Cd ions from wastewater

Article in Journal of Environmental Science and Health Part A · February 2017
DOI: 10.1080/10934529.2017.1282774

5 authors, including:

Najjapak Sooksawat
5 PUBLICATIONS 27 CITATIONS
SEE PROFILE

Metha Meetam
Mahidol University
13 PUBLICATIONS 273 CITATIONS
SEE PROFILE

All content following this page was uploaded by Najjapak Sooksawat on 16 March 2017.
The user has requested enhancement of the downloaded file. All in-text references underlined in blue are added to the original document and are linked to publications on ResearchGate, letting you access and read them immediately.
Performance of packed bed column using Chara aculeolata biomass for removal of Pb and Cd ions from wastewater

Najjapak Sooksawat, Metha Meetam, Maleeya Kruatrachue, Prayad Pokethitiyook & Duangrat Inthorn


To link to this article: http://dx.doi.org/10.1080/10934529.2017.1282774

Published online: 22 Feb 2017.
Performance of packed bed column using *Chara aculeolata* biomass for removal of Pb and Cd ions from wastewater

Najjapak Sooksawat\textsuperscript{a,b}, Metha Meetam\textsuperscript{b,c}, Maleeya Kruatrachue\textsuperscript{b,c}, Prayad Pokethitiyook\textsuperscript{b,c}, and Duangrat Inthorn\textsuperscript{c,d}

\textsuperscript{a}Department of Agricultural Engineering and Technology, Faculty of Agriculture and Natural resources, Rajamangala University of Technology Tawanok, Bangpra, Chonburi, Thailand; \textsuperscript{b}Department of Biology, Faculty of Science, Mahidol University, Bangkok, Thailand; \textsuperscript{c}Center of Excellent on Environmental Health and Toxicology (EHT), CHE, Ministry of Education, Bangkok, Thailand; \textsuperscript{d}Department of Environmental Health Sciences, Faculty of Public Health, Mahidol University, Bangkok, Thailand

\textbf{ABSTRACT}

Biosorption of Pb and Cd from aqueous solution by biomass of *Chara aculeolata* was studied in a continuous packed bed column. *C. aculeolata* in the fixed bed column is capable of decreasing Pb and Cd concentrations from 10 mg/L to a value below the detection limit of 0.02 mg/L. Selective uptake of Pb and Cd in a binary solution resulted in Pb having much higher relative affinity than Cd. The experiments were conducted to study the effects of column design parameters, bed depth, and flow rate on the metal biosorption. Pb uptake capacity of *C. aculeolata* increased with increased bed depth and decreased flow rate, while Cd uptake capacity increased with increased bed depth but remained constant at any flow rate. The Thomas model was found to be in a suitable fitness with the experiment data for Pb and Cd ($R^2 > 0.90$). The efficiency of biosorbent regeneration achieved by 0.1 M HCl was very high, that was, 98\% for Pb and 100\% for Cd in the third reused cycle. It can be concluded that *C. aculeolata* is a good biosorbent for treating wastewater having low concentrations of Pb and Cd contamination.

\textbf{Introduction}

Heavy metals can be released naturally from soil erosion and flooding, and anthropogenically by mining and metallurgical industries, municipal wastes and agricultural pesticides.\textsuperscript{[1,2]} The continuous discharging of industrial, domestic, and agricultural wastewater into surface water resources causes deposit of heavy metals in sediment, transfers them from one to another organism, which has the capacity to biomagnify them through food chain.\textsuperscript{[3]} Due to acute and chronic health effects to all life, heavy metals such as Pb and Cd are non-essential elements that are highly toxic. Excessive Pb can damage the central nervous system, kidney, hemopoiesis, heart and blood vessels, and internal secretion system of human beings.\textsuperscript{[4]} Exposure of 30–50 $\mu$g Cd per day increases risk of bone fracture, cancer, kidney dysfunction, and hypertension.\textsuperscript{[5]} As a result, many countries have set the acceptable regulatory standards for toxic metals. The US Environmental Protection Agency recommends that the concentrations of Pb and Cd in freshwater should be below 0.015 and 0.005 mg/L, respectively.\textsuperscript{[6]} In Thailand, the total permissible amounts of these metals are set higher at 0.2 and 0.03 mg/L for Pb and Cd, respectively.\textsuperscript{[7]}

Highly efficient metal removal technologies are needed to reduce the metal concentrations in wastewater. Chemical precipitation, reverse osmosis, and other conventional methods are inefficient when heavy metals are present at trace concentration in a large volume of solution.\textsuperscript{[8]} Biosorption exploits the ability of biomass to reduce heavy metal ions from aqueous solutions by physicochemical mechanisms. The role of various biomass such as aquatic plants, brown and green seaweeds by packed bed biosorption for the removal of heavy metal has been well documented.\textsuperscript{[9–11]} Since design procedures as well as process equipment for conventional activated carbon packed bed columns are readily available, biosorption for full-scale applications can in principle be implemented using the packed bed configuration.

*C. aculeolata* and *N. opaca* are the characean green algae and are among the most abundant macroalgae growing in a wide range of fresh and brackish water bodies.\textsuperscript{[12]} In eutrophication status of water bodies, the abundance of some Chara and Nitella species may reach a nuisance level, reduce other plant and animal diversity and have to be dumped by man-power or biological and chemical control, thus their massive growth yields regenerative source of abundant biomaterial.\textsuperscript{[13]} In our previous study, we showed that *C. aculeolata* and *N. opaca* had high ability to remove Pb and Cd from synthetic wastewater.\textsuperscript{[14]} In addition, dried biomass of *C. aculeolata* has maximum sorption capacity of 106.4 mgPb/g and 36.1 mgCd/g and that of *N. opaca* has 102.0 mgPb/g and 27.6 mgCd/g. In the present work, Pb and Cd biosorption by *C. aculeolata* and *N. opaca* were investigated in a packed-bed column. The effects of design parameters, such as flow rate, bed depth, influent concentration of Pb and Cd on biosorption, were examined. For a practical use, the metal biosorption behavior of *C. aculeolata* in three...
The biosorption saturation capacity of the system can be determined from the slope, and the point at the lowest usage rate was identified \cite{16} The usage rate and EBCT were in accordance with the equations (Eqs. (1) and (2)) as follows:

\[
EBCT = \frac{BV}{F} \quad (1)
\]

\[
Usage \ rate = \frac{M}{Vb} \quad (2)
\]

Where BV is bed volume (mL), F is flow rate (mL/min), M is sorbent mass (g) and \( V_b \) is volume at breakpoint of biosorption bed (\( V_b = 0.05 \ V_o \) (mL), and \( V_o \) is volume of clean effluent water (mL).

**Effects of flow rate and bed depth service time (BDST) on Pb and Cd biosorption**

To study the effect of flow rate on metal biosorption, metal solutions were passed through the column with flow rates of 20, 30, 40, and 60 mL/min. The BDST model was applied to determine the sorption capacity (Q) of metal ion by the biomass. The linear relationship between bed depth (Z) and BDST(Tb) was developed. When Tb was plotted versus Z, the sorption capacity of the system can be determined from the slope, and the rate constant (K) is from the intercept. The equation (Eq. (3)) is expressed as follows: \cite{16}

\[
Tb = \frac{QZ}{C1V} - \frac{1}{KC1} \ln \left( \frac{C1}{Cb} - 1 \right) \quad (3)
\]

Where Tb is BDST (h), Q is sorption capacity (mg/g), Z is bed depth (cm), \( C_1 \) is initial metal concentration (mg/L), \( V \) is linear velocity (cm/h), K is rate constant, and \( C_b \) is breakthrough metal ion concentration (mg/L).

**Effects of Pb and Cd concentrations on metal biosorption**

The sorption equilibrium in solution was studied with varying metal ion concentrations (5, 10, and 20 mg/L of Pb or Cd). The solution was passed through the 0.5-g packed column with a flow rate of 40 mL/min for Pb solution and the 1-g packed column at 20 mL/min for Cd solution. The effluents were analyzed for metal ion concentrations. Successful design of a column sorption process required prediction of the maximum equilibrium sorption capacity or breakthrough curve for the effluent. \cite{17} Various mathematical models can be used to describe the fixed bed adsorption. Among these, the Thomas model is simple and widely used by several investigators. \cite{11,17} The linearized form of Thomas model can be expressed as follows (Eq. (4)):

\[
\ln \left( \frac{Co}{Cb} - 1 \right) = \frac{KthQmM}{F} - KthCot \quad (4)
\]

Where \( C_0 \) is initial metal concentration (mg/L), \( C_b \) is metal concentration at breakpoint of biosorption (mg/L), \( K_{th} \) is Thomas model constant (L/mg.h), \( Q_{th} \) is maximum biosorption capacity (mg/g), \( F \) is volumetric flow rate (L/h), and \( t \) is time (h).
**Effect of binary metal solution on Pb and Cd biosorption**

For the determination of the synergistic/antagonistic effect of cations present in the metal solution effluent, 10 mg/L each of Pb and Cd were mixed and passed through 0.5 g and 1 g of C. aculeolata biomass in the packed column. The effluents were collected periodically and analyzed for Pb and Cd concentrations using FAAS as described previously.

**Reusability of C. aculeolata packed column**

To find the most effective desorbing agent for the elution of heavy metals from algal biomass, 2 g/L of dried C. aculeolata or 3 g/L of dried N. opaca was added to 50 mL of 10 mg/L of Pb or Cd solution in the batch system. The mixtures were shaken at 150 rpm, 25 ± 2°C for 3 h, and then filtered through 0.45-μm Whatman filter paper. The filtrates were analyzed for metal concentrations using FAAS. The metal removal percentage was determined (Eq. (5)). Pb and Cd laden biomasses were placed in various solutions of desorbing agents: 0.1 M HCl, 0.1 M HNO₃, 0.1 M CaCl₂, 0.1 M NaOH and 0.05 M nitritoltri acetic acid (NTA). The 0.1 M CaCl₂ solution was adjusted to pH 3 with HCl before use.¹¹ NaOH (0.1 M) was used as a control because it was used to dissolve NTA. The mixtures were shaken at 150 rpm, 25 ± 2°C for 3 h and filtered through 0.45-μm Whatman filter paper. The filtrates were analyzed for metal concentrations using FAAS. The metal desorption percentage was determined (Eq. (6)).

\[
\text{Metal removal} \%(\%) = \frac{M_{\text{adsorption}}}{M_{\text{total}}} \times 100 \quad (5)
\]

\[
\text{Desorption efficiency} \%(\%) = \frac{M_{\text{desorption}}}{M_{\text{adsorption}}} \times 100 \quad (6)
\]

Packed bed experiments were conducted at room temperature (25 ± 2°C) in glass columns of 1-cm diameter and 50-cm length. Two columns were packed separately with 0.5 g (bed volume of 1.93 mL) and 1.0 g (bed volume of 3.46 mL) of C. aculeolata dry biomass. 1,000 mL of 10 mg/L of Pb or Cd (pH 4) was pumped through the column at a flow rate of 40 mL/min or 20 mL/min, respectively, using a peristaltic pump. The effluent was collected and analyzed for Pb or Cd concentration using FAAS. For the desorption process, 1,000 mL of 0.1 HCl was used to rinse the Pb or Cd laden biomass. The desorbed and regenerated C. aculeolata column was used for two more cycles.

**Metal removal from municipal wastewater**

The municipal wastewater was collected from 3 wastewater treatment plants located in different areas, Din Daeng, Sripraya, and Nongkham, in Bangkok, Thailand. The water samples were analyzed for water quality (temperature, pH, dissolved oxygen (DO), biological oxygen demand (BOD), electrical conductivity (EC), alkalinity, total dissolved solid (TDS) and anions) prior to filtration; then, they were filtered to remove the solid sediment.¹⁸ The filtrate was then analyzed for Pb and Cd concentrations using FAAS.⁹,¹⁵ Because the original concentrations of Pb and Cd were very low to undetectable (<0.05 mg/L of Pb and <0.002 mg/L of Cd), standard solutions of Pb(NO₃)₂ and Cd(NO₃)₂ were added to the wastewater samples to bring the estimated final concentrations to 10 mg/L of Pb and 1.5 mg/L of Cd, which are fifty-fold greater than the accepted wastewater quality standard.¹⁹ The measurable concentrations of the metals in the modified water samples are shown in Table 1.

The study on metal removal from municipal wastewater was conducted at room temperature (25 ± 2°C) with the packed-bed column containing 0.5 g or 1 g of C. aculeolata dry biomass. 5,000 mL of municipal wastewater from each treatment plant (pH 4) was pumped through the column at the flow rate of 40 mL/min for Pb biosorption or 20 mL/min for Cd biosorption, using a peristaltic pump. The effluent was collected and analyzed for Pb or Cd concentration using FAAS.

**Results and discussion**

**Packed column study of Pb and Cd breakthrough curve by charophytes**

The breakthrough curve of Pb biosorption by C. aculeolata and N. opaca is shown in Figure 2. The result showed the ratio of effluent (C) and influent (C₀) Pb concentrations (C/C₀) obtained from experiment. According to the breakthrough curve, the breakthrough point is 5% effluent concentration of influent concentration. The exhaustion point is 70% effluent concentration of the influent Pb concentration by C. aculeolata and 90% effluent concentration of influent Pb concentration by N. opaca (Fig. 2). The breakthrough and exhaustion points of Pb sorption by C. aculeolata occurred in throughput volumes of 1,750 mL and 3,250 mL, respectively, whereas those by N. opaca were

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Collected area of municipal wastewater</th>
<th>Din Daeng</th>
<th>Sripraya</th>
<th>Nongkham</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water quality</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>28.25</td>
<td>28.75</td>
<td>29.25</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>7.67</td>
<td>7.49</td>
<td>7.53</td>
<td></td>
</tr>
<tr>
<td>EC (μs/cm)</td>
<td>1.625</td>
<td>2.865</td>
<td>0.5925</td>
<td></td>
</tr>
<tr>
<td>TDS (g/L)</td>
<td>0.865</td>
<td>1.53</td>
<td>0.315</td>
<td></td>
</tr>
<tr>
<td>DO (mg/L)</td>
<td>7.7</td>
<td>5.6</td>
<td>5.75</td>
<td></td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>20.4</td>
<td>15.95</td>
<td>16.2</td>
<td></td>
</tr>
<tr>
<td>Alkalinity as CaCO₃ (mg/L)</td>
<td>262.7</td>
<td>211.7</td>
<td>220.0</td>
<td></td>
</tr>
<tr>
<td>Metal ions (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>7.67</td>
<td>6.89</td>
<td>8.02</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>1.66</td>
<td>1.63</td>
<td>1.62</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>&lt;0.005</td>
<td>0.09</td>
<td>&lt;0.005</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.09</td>
<td>0.113</td>
<td>0.136</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>21.70</td>
<td>34.68</td>
<td>8.35</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>243</td>
<td>500</td>
<td>52.09</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>71.35</td>
<td>81.16</td>
<td>53.66</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>35.12</td>
<td>72.01</td>
<td>13.14</td>
<td></td>
</tr>
<tr>
<td>Anions (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl⁻</td>
<td>397.4</td>
<td>869.7</td>
<td>66.0</td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>2.0</td>
<td>1.8</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>13.4</td>
<td>11.8</td>
<td>24.1</td>
<td></td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>3.5</td>
<td>2.7</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>90.6</td>
<td>150.3</td>
<td>40.0</td>
<td></td>
</tr>
</tbody>
</table>

Abbreviations: EC (Electrical Conductivity), TDS (Total Dissolved Solid), DO (Dissolved Oxygen), BOD (Biological Oxygen Demand).

Limits of detection: Pb < 0.05 mg/L, Cd < 0.002 mg/L, Zn < 0.005 mg/L, Mn < 0.025 mg/L.

...
obtained at 500 mL and 2,750 mL, respectively. The effluent concentration ratio of N. opaca (C/Co = 0.90) was more than that of C. aculeolata (C/Co = 0.70). The phenomenon depended on the physical characteristics of N. opaca biomass (R² > 0.99 for the pseudo-first-order kinetic; data not shown), while that by C. aculeolata was of the physisorption through intraparticle diffusion (R² > 0.99 for the intraparticle diffusion model; data not shown). With the same bed depth of algal biomass, breakthrough volume for Pb by C. aculeolata was 3.5 times more than that by N. opaca, indicating a better property of C. aculeolata as biosorbent for Pb removal in packed column. In addition, very low bulk density of N. opaca (0.13 g/mL) compared with that of C. aculeolata (0.26 g/mL) and the cramped property of N. opaca when having the metal solutions passed was observed.

Effects of bed depth and the usage rate on Pb and Cd biosorption

The breakthrough curves for biosorption of Pb and Cd by C. aculeolata biomass at different bed depths are shown in Figure 2. Pb biosorption by C. aculeolata (algal weight of 0.5 g, bed volume of 1.93 mL and bed depth of 3.29 cm) and N. opaca (algal weight of 0.2 g, bed volume of 1.95 mL and bed depth of 3.3 cm) packed column. Experimental conditions: initial concentration of Pb or Cd of 10 mg/L, pH 4, and flow rate of 40 mL/min for C. aculeolata and 20 mL/min for N. opaca.

Figure 2. Pb biosorption by C. aculeolata (algal weight of 0.5 g, bed volume of 1.93 mL and bed depth of 3.29 cm) and N. opaca (algal weight of 0.2 g, bed volume of 1.95 mL and bed depth of 3.3 cm) packed column. Experimental conditions: initial concentration of Pb or Cd of 10 mg/L, pH 4, and flow rate of 40 mL/min for C. aculeolata and 20 mL/min for N. opaca.

In the present study, C. aculeolata biomass displayed much higher relative affinity for Pb than for Cd ions.

Effects of flow rate and BDST on Pb and Cd biosorption

The breakthrough curves for biosorption of Pb and Cd at different flow rates are shown in Figure 5a and b. In general, for both metal ions, the breakthrough curves were constant with increasing flow rates. For Pb sorption, the slow flow rate at 30 mL/min decreased the exhaust effluent concentration, indicating higher Pb uptake by the biomass (Fig. 5a). The Pb sorption capacity of the bed at different flow rates as calculated from the linear relationship between bed depth and BDST is shown in Table 2. The Pb uptake capacity by C. aculeolata biomass was slightly different between the flow rates of 40 and 60 mL/min. When the flow rate was decreased to 30 mL/min, the sorption capacity of the biomass increased to 352.9 mgPb/g. However, the rate constants...
which characterized the rate of Pb ion transfer from the fluid phase to the solid phase, were increased with the increased flow rate. For Cd biosorption, the flow rate had no effect on the breakthrough curves (Fig. 5b), indicating a rapid reaction between Cd ions and biosorbent with a wide range of flow rates (20–40 mL/min). At the flow rate of 40 mL/min, the sorption capacity and rate constant for Cd ion (38.37 mg/g and 1.66 L/mg h, respectively) were less than those for Pb ion (51.61 mg/g and 2.42 L/mg h, respectively). The results suggested that the rate of Pb transfer to biosorbent was faster than that of Cd.

**Effect of Pb and Cd concentration on metal biosorption**

The breakthrough curves for the effect of Pb or Cd concentration on metal biosorption of *C. aculeolata* biomass are presented in Figure 6a and b. The breakthrough volume was increased for both Pb and Cd ions at low concentrations. The breakthrough volumes of Pb sorption at initial Pb concentration of 5, 10, and 20 mg/L with flow rate of 40 mL/min were 3,250, 1,750, and 750 mL, respectively (Fig. 6a), and those for initial Cd concentration of 5, 10, and 20 mg/L with flow rate of 20 mL/min were 2,000, 1,000, and 750 mL, respectively (Fig. 6b). All breakthrough volumes of Pb were more than those of Cd. The maximum sorption capacity of Pb and Cd is shown in Table 3. The results indicated that when Pb and Cd concentrations increased, the maximum sorption capacities for both metal ions increased. At the same initial concentration, the maximum Pb sorption capacity was higher than that of Cd, indicating higher capacity of *C. aculeolata* biomass for Pb ion in the packed column.

**Table 2.** Biosorption capacity of Pb by *C. aculeolata* packed column at different flow rates.

<table>
<thead>
<tr>
<th>Flow rate (mL/min)</th>
<th>Q (mg/g)</th>
<th>K (L/mg h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>85.63</td>
<td>4.57</td>
</tr>
<tr>
<td>40</td>
<td>51.61</td>
<td>2.42</td>
</tr>
<tr>
<td>30</td>
<td>352.9</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Experimental conditions: algal weight of 0.5 g, bed depth of 3.29 cm, initial concentration of 10 mg/L, pH 4, and flow rates of 30, 40, and 60 mL/min. Abbreviations: Q (Adsorption capacity), K (Rate constant).

**Table 3.** Maximum adsorption capacity of Pb and Cd by *C. aculeolata* packed column.

<table>
<thead>
<tr>
<th>Metal</th>
<th>concentration (mg/L)</th>
<th>Q_m (mg/g)</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>5</td>
<td>42.99</td>
<td>0.923</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>105.63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>250.47</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>5</td>
<td>16.33</td>
<td>0.967</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>37.85</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>79.74</td>
<td></td>
</tr>
</tbody>
</table>

Experimental conditions: algal weight of 0.5 or 1 g, bed depth of 3.29 or 6.49 cm, initial concentration of 5, 10 and 20 mg/L of Pb or Cd, pH 4, and flow rate of 40 or 20 mL/min. Abbreviations: Q_m (maximum sorption capacity), R^2 (correlation coefficient).
Effects of binary metal solution on Pb and Cd biosorption

Effect of Cd ion on Pb biosorption is presented in Figure 7. The breakthrough curves for biosorption of single Pb ion and of the mixture (Pb and Cd) were different. The Pb breakthrough point of single Pb was 1,750 mL, whereas that in the mixed solution was 1,250 mL. The results indicated that Cd ion interfered with Pb biosorption. Similarly, the presence of Pb showed an antagonistic effect on Cd biosorption (Fig. 7). The Cd breakthrough point of single Cd was 250 mL, while that in the mixed solution was less than 250 mL. The effluent concentration of Cd in the binary solution was higher than that in the single Cd solution. This was due to the result of replacement of some Cd ions with Pb ions at the binding sites, resulting in the release of Cd ions into the solution.

Reusability of C. aculeolata packed column

Desorption study in batch system was conducted to identify an efficient desorbing agent. Figure 8 shows Pb and Cd desorption from metal-laden C. aculeolata biomass. HCl and HNO₃ gave high desorption percentage for both Pb (61.31 and 60.78%, respectively) and Cd (98.22 and 100%, respectively). The results indicated that they were effective agents for elution of Pb and Cd from algal biomass. NTA gave high desorption percentage for both Pb (61.31 and 60.78%, respectively) and Cd (98.22 and 100%, respectively). The results indicated that they were effective agents for elution of Pb and Cd from algal biomass. CaCl₂ could elute Cd from C. aculeolata biomass with relatively high percentage in comparison to the acids. The results of this study indicated that acids (0.1 M HCl and 0.1 M HNO₃) were more effective than the Ca salt and base (CaCl₂, NTA and NaOH) for elution of Pb and Cd ions from the algal biomass.

The algal packed column was tested for reusability using acids as desorbing agents. Table 4 shows the removal efficiency obtained in three sorption cycles with the original and regenerated biosorbent. After the first cycle, Pb sorption by C. aculeolata biomass was reduced to 98.03%, whereas Cd sorption by the biomass remained constant when the biomass was used in cycles 2 and 3. The results indicated the success of reusability of C. Aculeolata biomass as the biosorbent for removal of Pb and Cd ions.

In packed column study for Pb and Cd biosorption, many parameters such as particle porosity, surface area, bulk density, and swelling degree are very important in the modeling of breakthrough curves. [21] In the present study, C. aculeolata had higher bulk density than N. opaca, and it had a good property for metal sorption in the fixed bed column. Types and quantities of functional groups present on the surface of different biomass influence the sorption mechanisms of the biosorbents. They are the potential sites for metal sorption, and the uptake of metal depends on various factors such as abundance of sites, their accessibility, chemical state, and affinity between the sorption site and the metal ions. In algae, hydroxyl and carboxyl groups are very effective in capturing heavy metal ions due to their negative charges. [22] The functional groups present in protein, polysaccharide, fatty acid including P-O-C links of organic phosphate groups play important roles in metal sorption by the algal biomass. [21,23] In the present study, C. aculeolata were used to adsorb Pb and Cd due to its high maximum sorption capacity in batch (106.4 mgPb/g and 36.1 mgCd/g, respectively) and in fixed bed column (105.6 mgPb/g and 37.9 mgCd/g, respectively) relating to their highly abundant active sites.

Column parameters, bed depth and flow rate, affected the breakthrough curve of biosorption in this study. Biosorption kinetic and the characteristics of the biosorbent are related to biosorption reactions by the charophytes. The reaction of Pb biosorption in C. aculeolata was intraparticle diffusion of the ions to the active sites in the biomass. The pH and counterions can affect Pb solubility within the biomass. In the presence of phosphate and chloride, Pb solubility is limited, and the partition coefficient for Pb may reflect precipitation reaction rather than adsorption reaction. [24] Anionic substances such as phosphate, chloride, and carbonate are known to influence Pb

<p>| Table 4. Reusability of C. aculeolata packed column. |
|---------------------------|---------------------------|---------------------------|</p>
<table>
<thead>
<tr>
<th>Metal</th>
<th>Cycle</th>
<th>Removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>98.51</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>98.03</td>
</tr>
<tr>
<td>Cd</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>100</td>
</tr>
</tbody>
</table>

Experimental conditions: algal weight of 0.5 or 1 g, bed depth of 3.29 or 6.49 cm, initial concentration of 10 mg/L of Pb or Cd, pH 4, flow rate of 40 or 20 mL/min, and desorbing agent of 0.1 M HCl.
reactions either by precipitating the mineral or by reducing adsorption through complex formation.\cite{24} In this study, increase of bed depth with slow flow rate increased Pb uptake by C. aculeolata biomass. The increasing equilibrium solution concentration relates to decreasing Pb adsorption and tends to form metal ion complexation. For Cd, Zachara et al.\cite{25} reported that Cd formed monocalcogenate complexes in solution of low concentrations of CO$_3$. Based on CdCO$_3$ solubility, the formation of Cd(CO$_3$)$_{3}^{2-}$ and the increase of CdCO$_3$ solubility were found with the increase in CO$_3$ concentration. Since C. aculeolata biomass contains abundant CO$_3$, Cd sorption by the biomass might be Cd$^{2+}$-CO$_3^{2-}$ with strong interactions that could be eluted reversibly by some desorbing agents.

In the present study, Pb and Cd sorption by C. aculeolata biomass could be eluted from the metal-loaded biomass by some desorbing agents. The results suggested that pH of the desorbing agents affected the elution of both Pb and Cd from the algal biomass. Application of the biodegraded-chelating agent, NTA, is limited by its solubility in NaOH solution with the high pH. Lower pH, which increases metal solubility, increased desorption percentage of both metal ions. With high pH solution, the decrease in metal desorption efficiency is due to the formation of insoluble hydroxylated complexes of the metal ions. Pb is present as Pb(OH)$_2$ at pH above 6.\cite{26} Similarly, beyond pH 9, Cd precipitates as Cd(OH)$_2$.\cite{27} The efficient removal of sorbed metals from C. aculeolata biomass is important to determine its long-term use for repeated extraction-elution cycles. In this study, NTA was attractive for practical application due to its biodegradable property, while HCl was used as a desorbing agent due to its high desorption ability. The limitation of acid is its corrosion property, which could destroy the binding site structures for heavy metals.\cite{28} However, regeneration and reuse of biosorbent in a column are an economical method for removal of heavy metals from wastewater stream, and they require an effective and ecologically friendly desorbing agent.

**Metal removal from municipal wastewater**

To test metal removal from wastewater, Figure 9a and b show Pb and Cd biosorption from wastewater collected from 3 different wastewater treatment plants. In comparison with the synthetic metal solution, the breakthrough points for Pb and Cd biosorption from wastewater solutions were lower than those from the synthetic solution.

Study for Pb and Cd biosorption in municipal wastewater using a packed bed column, among 3 different wastewater resources, wastewater from Nongkhram district had lowest conductivity and contained less metal ions (K, Na, Ca, Mg) and anions (Cl$^-$ and SO$_4^{2-}$) than those from Din Daeng and Sriraya (Table 1). Therefore, the breakthrough curve for Pb biosorption of wastewater from Nongkhram district was close to that of the synthetic metal solution. Cd biosorption was strongly affected in both binary and municipal wastewater. The study on metal removal from real wastewater found the antagonism possibly by cation competition and anion complexation with Pb, Cd, and biomass in the biosorption process. The soluble and insoluble organic matter contents in the wastewater samples should be examined further to clarify their effect on the biosorption process as well. However, the present study demonstrated the practical use and ability of algal biomass for metal biosorption in the continuous flow using packed bed column.

**Conclusion**

Column study showed that C. aculeolata had good property for biosorption in a packed bed column. Column parameters such as bed depth, flow rate, and metal concentrations affected the breakthrough curve of biosorption by C. aculeolata, which were related to biosorption kinetic and sorbent characteristics, i.e. porosity and bulk density of the biomass. Although physical property of C. aculeolata biomass such as particle size, porosity and its chemical property (functional groups) which are the binding sites for heavy metals need further study to understand the mechanism of metal biosorption in C. aculeolata biomass, the present study showed the performance of packed bed column using C. aculeolata biomass for removal of Pb and Cd ions from the Pb–Cd binary solution and the real wastewater. The reusability of the packed bed column in the third reused cycle showed the ability to regeneration of biosorbent in 0.1 M HCl at high efficiency at 98% for Pb biosorption and 100% for Cd biosorption, respectively.

**Funding**

This research was supported by the grants from the Royal Golden Jubilee (RGJ) PhD Program under The Thailand Research Fund, Thailand; and in
part by the Center of Excellence for Environmental Health and Toxicology under Science and Technology Postgraduate Education and Research Development Office (PERDO), Thailand.

References


