Cadmium biosorption by non-living aquatic macrophytes

*Egeria densa*

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**ABSTRACT**

In this work the removal potential on Cd$^{2+}$ by the non-living *Egeria densa* biomass has been studied. The influence of the metal solution pH, the plant drying and the metal solution temperature, and biosorbent grain size was previously studied in batch systems. The cadmium adsorption rate has increased when the pH was increasing, but at pH 5, the cadmium precipitation has begun to occur, avoiding such high pH values in other tests. The cadmium removal was around 70% at 30°C biomass dried and solution temperatures, assuming as the best temperature conditions. No significant influence was observed in cadmium removal due to the grain size effect. The biosorption kinetic data were well fitted by a pseudo-second order model. The equilibrium time in experiments was around 45 min with a 70% Cd removal. The equilibrium data at pH 5 were described rather better by the Langmuir isotherm than the Freundlich one, with an adsorption rate and maximum metal content values of 0.40 L g$^{-1}$ and 1.28 meq g$^{-1}$, respectively, for Langmuir model. The kinetic parameter values are near to other biosorbents, indicating that the macrophytes *E. densa* could be used as biosorbent material in industrial effluent treatment system.

**Key words** | biosorption, Cd$^{2+}$, *Egeria densa*

**INTRODUCTION**

The pollution of water with heavy metals has been of great concern, due to their toxic nature and other adverse effects (Davis et al. 2003; Von der Heyden & New 2004; Pandey et al. 2007). Among the most toxic heavy metals, cadmium is known to cause renal dysfunction, bone degeneration, lung inefficiency, liver damage and hypertension in humans. Cadmium has been designated as category I carcinogen by International Agency for Research on Cancer (IARC). Even in low concentrations, that metal is toxic for diverse organisms including human beings (Hussein et al. 2004).

Cadmium is often detected in industrial wastewaters, which originate from metal plating, battery and pigment manufacture, printing and photographic industries, etc. (El-Sherif et al. 2008). In metal-contaminated wastewater treatments, several conventional methods such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, reverse osmosis, solvent extraction, ion exchange and evaporation have been applied, in order to reduce the high metal concentration. However, when the most of these methodologies are applied in low metal concentration effluent treatments, they could have high chemical costs or low removal efficiencies, low selectivities, high-energy requirements, and generation of secondary toxic slurries.

On the other hand, the biosorption technique has been applied in order to remove or reduce low metal concentration in wastewaters, showing a high efficiency (Kratochvil & Volesky 1998). Based on this technique, non-living plants can be used for heavy metal removal due to the low costs, free availability and easy regeneration. In this way, *Egeria densa* is an aquatic macrophyte
species commonly found in the tropical region and it can be used as biosorbent.

The industrial potential of the biosorption depends on many factors, such as biosorption capacity, efficiency and facility of metal recovery and, mainly, equivalence with the performance and cost of traditional processes (Liu et al. 2007). For the use in industrial applications and its corresponding equipment design, the biosorbent performance must be investigated and compared with other technologies. This kind of study has been reported for many biological materials such as bacteria (Chubar et al. 2008, Georgieva 2008), seaweed (Cruz et al. 2004; Chojnacka et al. 2005; Romera et al. 2008), green algae (Al-Rub et al. 2006), fungus (Ozsoy et al. 2008), and aquatic macrophytes (Saygideger et al. 2005).

In this work, the non-living aquatic macrophytes-based cadmium removal potential was investigated using the E. densa. The cadmium concentration values used in this work were similar to that found in industrial wastewaters originated from battery industry among others. For that, several adsorption kinetic and equilibrium experiments were performed, in order to obtain the best experimental conditions. The adsorption equilibrium and kinetic parameters for E. densa were estimated by some available models.

MATERIAL AND METHODS

Biomass sampling

Aquatic macrophytes E. densa were collected from artificial ponds in Aquiculture Advanced Research Center, which is located near to Toledo city at the Brazilian Paraná state west region. After that, aquatic plants were washed in tap water, and rinsed many times with deionized water. In laboratory, a part of them was dried at room temperature (30°C), while the other one was dried using an electrical oven at 50°C. All samples were ground using steel-knives electrical mill, and sieved to different fraction sizes and stored for posterior analysis.

Chemicals

The chemicals used were of analytical-reagent grade. Deionized waters were also used as dilution media. Several stock solutions of Cd in deionized waters were prepared, ranging from 4.0 to 8.0 meq L\(^{-1}\), from their water-soluble metallic salt (CdCl\(_2\)·H\(_2\)O, Merck pro analysis) and stored in 1-L volumetric flasks for posterior metal adsorption experiments. Solutions of NaOH (1 M) and HCl (1 M) were also used as pH adjustment. Based on a cadmium standard solution (1.0 g L\(^{-1}\) for AAS, Merck), different diluted-Cd concentrations ranging from 0.1 to 1.5 mg Cd L\(^{-1}\) were also prepared and used to obtain the calibrate curve for Atomic Absorption Spectrometer (AAS).

Cadmium concentrations

At each non-living macrophytes biomass-based metal adsorption experiment, the mean Cd concentration in the 0.45\(\mu\)m-membrane filtrated liquid phase was determined, using a previously calibrated AAS (AA 932-GBC, Analitica).

Preliminary tests

In order to find the pH value at which the metal precipitation occurs, we used a 1 L cadmium solution on 6.23 meq Cd\(^{2+}\) L\(^{-1}\) distributed in small aliquots, duplicated, with pH adjustment varying from 3 to 8 by the addition of NaOH and HCl solutions into each sample. The metal precipitation test was performed without shaking and room temperature by 48 h. Afterwards, the precipitate was separated from the metal solution through a 0.45\(\mu\)m pore size cellulose nitrate membrane-based vacuum filtration system. The cadmium concentration in each filtrate was measured by AAS.

In order to improve the biosorption kinetic and equilibrium experimental conditions, the temperature effect on plant drying was tested using two temperatures: 30 and 50°C, while the solution temperature effect was evaluated at four controlled temperatures, ranging from 25 to 45°C and using as biosorbent only those 30°C dry plants. For both tests, a volume of 50 mL Cd\(^{2+}\) solution was put into 125 mL Erlenmeyer flask, containing 250 mg dry plant. The mixtures were agitated on a rotary shaker for 12 h and at each setting temperature. Afterwards, the residual cadmium solution was separated from
the biosorbent using a vacuum filtration system and the cadmium concentration in it was measured by AAS.

The biosorbent grain size effect was also studied, using three grain fraction sizes between 0.1 to 0.6 mm and a mixture of them. This test was carried out at the same procedure for temperature effect test, but in this test, a 30°C cadmium solution controlled temperature and 12 h contact times were used. All preliminary tests were carried out by duplicate.

**Kinetic test**

For kinetic experiments, a 250 mg dry biomass was added to a 50 mL metal solution on approximately 4.0 meq Cd²⁺ L⁻¹ at 5 initial pH. The mixtures were agitated on a shaker at 30°C constant controlled temperature. The solution pH monitoring was carried out during the sorption experiments and the pH adjustment to 5 was made, as required. The adsorption experimental times were set up at least nine short contact times, ranging from 0 to 60 min, in order to determine the equilibrium time. In this way, a whole sample was taken at each setting time and the liquid phase was separated from the adsorbent using a vacuum filtration system. Afterwards, initial and final cadmium concentrations in each liquid phase were determined by AAS.

**Equilibrium concentration**

In order to obtain the equilibrium concentration and to assess the pH effect, several batch Cd²⁺ sorption experiments using the dry *E. densa* were carried out using a constant volume of 50 mL cadmium solution on different Cd²⁺ concentrations (from 4 to 8 meq L⁻¹) in contact with different amounts of biosorbent mass, varying from 20 to 550 mg. All equilibrium sorption experiments were carried out by duplicate. The suspensions were agitated on a rotary shaker at 30°C controlled temperature, monitoring and adjustment of pH at 4 and 5, during a 12 h contact time. Afterwards, the liquid phase was separated from the suspension using a vacuum filtration system, measuring the initial and equilibrium cadmium concentrations by AAS.

**RESULTS AND DISCUSSION**

**Preliminary tests**

The pH-based Cd precipitation data was fitted by a Logistic-type function, with a good correlation coefficient (0.9968) and residual $\chi^2$ (0.0016), as can be seen in Figure 1, allowing finding the limit pH before the metal precipitation. As pH threshold was found around the value of 5.2, when the cadmium precipitation starts to happen. Consequently, all next cadmium sorption experiments were performed adjusting the pH below this threshold, avoiding the no acceptable pH region.

In both dry temperature tested, it was achieved exactly the same cadmium removal percent near to 70%, suggesting that this previous biosorbent treatment is not important in order to increase the metal removal in a significant way. Consequently, in this work, a room temperature (30°C) was used for all cadmium sorption experiments and other tests, in order to simplify the plant dry procedure.

In the interval from 25 to 45°C controlled temperatures, the highest cadmium removal percent was observed to occur at 30°C solution temperature, corresponding to 70% Cd removal, which was approximately 15% above the others one. Based on this previous result, the 30°C
solution temperature was set up for all next cadmium sorption experiments.

On the other hand, the cadmium-sorption experiments based on the different *E. densa* grain fraction sizes have shown small differences (less 5%) when the removal of cadmium ion was compared among grain sizes tested. For practical purpose, the grain size effect might be considered as negligible and consequently grains without previous size separation after grounded process were chosen, allowing obtaining a 70%-mean cadmium removal.

**Kinetic test**

The dry *E. densa* biomass-based biosorption kinetic data using Cd$^{2+}$ solutions at pH 5 was fitted by a Logistic-type function, with good correlation coefficient (0.99936) and reduce $\chi^2$ (0.0017), as shown in Figure 2, allowing observing its quick metal biosorption behavior in short contact time, and finding the metal removal rate and equilibrium time. As can be seen in Figure 2, the biosorption process has increased sharply at contact times less 5 min and slowed gradually as equilibrium was approached, resulting an equilibrium time around 45 min, with a 70%-Cd$^{2+}$ removal. This kind of behavior is typical for a strong metal biosorption, which is characterized by no energy exchange reaction and thus the metal removal is assigned to a purely physical–chemical interaction between the surface in the biosorbent mass and the metal solution (Cruz et al. 2004).

The kinetic results in the present work were significant in order to apply this kind of biosorbent in effluent treatment system, when they are compared with other works or biosorbents recently studied, for example, in the same experimental conditions such as temperature, pH, initial metal concentration and biosorbent mass in the non living *Sargassum filipendula* based-cadmium adsorption experiment (Fagundes-Klen et al. 2007), wherein it was obtained a 70%-cadmium removal and reached the equilibrium time between 1 and 2 h, which was almost two times contact time higher than in the present work. Moreover, using plants such as *Bifurcaria bifurcata*, *Saccorhiza polyschides*, *Pelvetia caniculata*, *Ascoplyllum nodosum*, *Laminaria ochroleuca* (Lodeiro et al. 2005) as biosorbent, the cadmium removal and equilibrium time have been reported as being around 50% and 3 h, respectively. Indeed, these results demonstrate that the aquatic macrophytes *E. densa* has a great cadmium removal potential in comparison with other plants. Due to its low equilibrium time, the *E. densa* as biosorbent could reduce the mass transfer zone in a continuous system for lower dimensions than other biosorbents or take the biosorption-based effluent treatment systems for a long using time.

**Adsorption kinetic**

For all the cadmium sorption data, obtained below pH 5, the cadmium concentration in solid phase in time, labeled as $q_t$, was calculated from the initial concentration ($C_0$, in meq L$^{-1}$) and the final concentration ($C_t$, in meq L$^{-1}$) in time, accumulated onto the *E. densa* biomass, using the Equation (1).

$$q_t = \frac{V(C_0 - C_t)}{m_s}$$

where $V$ is the volume of the solution and $m_s$ the biosorbent mass (dry weight).

In order to analyze the sorption kinetics of cadmium, the pseudo-first order and pseudo-second order kinetic models were applied to the data. A simple pseudo first-order equation, which was proposal by Lagergren is
described by Equation (2) (Ho & Mckay 1998; Bhattacharyya & Sharma 2005). A plot of log\((q_{eq} - q_t)\) versus \(t\) would provide a straight line for first order adsorption kinetics, which allows to obtain the adsorption rate constant \((K_1)\) (Ozsoy et al. 2008).

\[
\log(q_{eq} - q_t) = \log(q_{eq}) - \left(\frac{K_1}{2.303}\right)t
\]  

(2)

where \(K_1\) is the rate constant of the pseudo first-order adsorption process \((\text{min}^{-1})\), \(q_{eq}\) and \(q_t\) \((\text{meq Cd}^{2+} \text{ g}^{-1})\) are the adsorption amounts at equilibrium and in time, respectively.

On the other hand, the Ho’s second-order rate equation, which has been called a pseudo-second order kinetic expression, has also been applied widely (Ho & Mckay 2000; Ho 2005) and described by Equation (3). For this case, the experimental data was convenient to plot as \(t/q_t\) against \(t\), which showed a linear tendency of the data and allowed the sorption rate constant, \(K_2\), to be determined quite simply,

\[
\frac{t}{q_t} = \frac{1}{K_2q_{eq}^2} + \frac{1}{q_{eq}}t
\]  

(3)

where \(K_2\) is the rate constant of sorption \((\text{g meq}^{-1}\text{min}^{-1})\).

The experimental data, at 30°C and pH 5, were found to best follow the second order kinetic model, according to the good correlation coefficient value \((r^2 = 0.9968)\), and both experimental and modeling results are shown in Figure 3. Hence, based on the second order kinetic model, it was possible to determine the \(q_{eq}\) adjustable parameter as being equal to \(1.025 \pm 0.002 \text{meq Cd}^{2+} \text{g}^{-1}\), and the sorption rate constant \((K_2)\) whose value was \(0.826 \pm 0.051 \text{g meq}^{-1}\text{h}^{-1}\).

**Equilibrium concentration**

Despite the original development, the Langmuir adsorption isotherm has traditionally been extend to empirically describe equilibrium relationships between a bulk liquid phase and a solid phase, in order to quantify and contrast the performance of different biosorbents (Davis et al. 2003). The traditional form of the Langmuir adsorption isotherm is represented by the Equation (4).

\[
q^* = q_{\text{max}}\left(\frac{bC^*}{1 + bC^*}\right)
\]  

(4)

where \(q^*\) is the uptake \((\text{meq Cd}^{2+} \text{g}^{-1})\) and \(q_{\text{max}}\) is the maximal uptake \((\text{meq Cd}^{2+} \text{g}^{-1})\) of the biosorbent. \(C^*\) is the final equilibrium solution Cd\(^{2+}\) concentration \((\text{meq Cd}^{2+} \text{L}^{-1})\) and \(b\) is a adjustable parameter \((\text{meq Cd}^{2+} \text{L}^{-1})\) corresponding to the ratio between the Cd adsorption and desorption rates.

On the other hand, the empirical Freundlich isotherm has also been employed to quantify the equilibrium biosorption system of cadmium and described by the Equation (5).

\[
q^* = a(C^*)^n
\]  

(5)

where \(a\) and \(n\) are empirically determined constants, with \(a\) being related to the maximum binding capacity, and \(n\) related to the affinity or binding strength (Weber 1985; Tsezos 1990).

**Sorption isotherm**

The typical favorable-type Langmuir and Freundlich isotherms, represented by the Equations (4) and (5) with
two adjustable parameters, were assumed to model the E. densa-based Cd equilibrium biosorption data. The metal adsorption modeling parameters for each isotherm type were obtained by a minimization procedure employing the SIMPLEX algorithm, developed by Nelder & Mead (1965). The adsorption experimental data for cadmium ion on ground dry E. densa corresponding to pH 4 and 5 are shown in Figures 4 and 5, respectively, including the both Langmuir and Freundlich isotherms. From the correlation coefficient and $\chi^2$ values of each model, the data were fitted better for the Langmuir isotherm which is rather better than Freundlich one in order to characterize the E. densa biomass as a new metal adsorbent. Consequently, the empirical Freundlich model was not a good isotherm to fit the present data since it exhibits rather higher relative-to-data difference and worse fitting statistical parameters than the Langmuir isotherm, although the Freundlich model is often employed for metal adsorption from liquids.

The curves drawn in Figures 4 and 5 were made using the couple of adjustable Langmuir ($q_{\text{max}}$, $b$) and Freundlich ($a$, $n$) parameters, which are summarized in Table 1. In comparison between Langmuir parameters for both pH, it was possible to find the best maximal cadmium content in E. densa, corresponding to $q_{\text{max}}$ value of 1.28 meq g$^{-1}$ at pH 5. Nonetheless, similar result was obtained by Fagundes-Klen et al. (2007), using the marine algae Sargassum filipendula, whose maximum cadmium content in it was 1.26 meq g$^{-1}$. In comparison, this is an almost identical value for that corresponding adjustable Langmuir parameter associated to the E. densa, at the same experimental conditions, indicating that the E. densa is an alternative biosorbent with a great metal removal capacity.

Based on the low ratio between the adsorption and desorption rates values (0.4 L meq$^{-1}$), which is one of adjustable Langmuir parameter, the low equilibrium time (45 min) and the quick cadmium removal rate (62% in 5 min), they suggest that the E. densa based-Cd removal could be not only associated to one main mechanism, but it might be a consequence there being others simultaneously competitive mechanisms within of this new kind of biosorbent, such as exchange ion, complexation, quelation, inorganic precipitation, and coordination, including also the adsorption mechanism. Nonetheless, the occurrence of all these mechanisms inside the E. densa heterogeneous biological structure could have an increasing of adsorption capacity of the E. densa, working nor as a weak adsorbent neither as a strong one, as shown by the Langmuir isotherms in Figures 4 and 5. From these adsorption results, the E. densa as biosorbent can be used into effluent treatment systems due to great adsorption potential.

<table>
<thead>
<tr>
<th>pH</th>
<th>$q_{\text{max}}$ (meq g$^{-1}$)</th>
<th>$b$ (L meq$^{-1}$)</th>
<th>$a$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.96 ± 0.05</td>
<td>0.39 ± 0.05</td>
<td>0.29 ± 0.02</td>
<td>0.45 ± 0.04</td>
</tr>
<tr>
<td>5</td>
<td>1.28 ± 0.05</td>
<td>0.40 ± 0.06</td>
<td>0.42 ± 0.05</td>
<td>0.42 ± 0.04</td>
</tr>
</tbody>
</table>

Figure 4 | Cadmium sorption isotherm for E. densa at pH 4. Solid and dotted curves are calculated with the Langmuir and Freundlich equations, respectively.

Figure 5 | Cadmium sorption isotherm for E. densa at pH 5. Solid and dotted curves are calculated with the Langmuir and Freundlich equations, respectively.
CONCLUSIONS

In this work, the biosorption-based removal of Cd divalent ions by non-living aquatic macrophytes *E. densa* was studied as possible metal clean up from industrial effluents. The results from the preliminary tests can be summarized as follows:

i. The pH threshold for cadmium precipitation was 5.2.
ii. A good cadmium removal percent was obtained without an artificial thermal treatment-based dried biomass of *E. densa*.
iii. Maximal cadmium removal was achieved at 30°C solution temperature.
iv. Grains of dry biomass without previous size separation after the grinding process are also satisfactory for cadmium sorption experiments.

Moreover, from the kinetic test, due to its low equilibrium time, the *E. densa* as biosorbent could take a reduction of effluent treatment continuous system dimensions. Nevertheless, whereas on its good characteristics on cadmium removal such as low equilibrium time, quick cadmium removal rate, and maximal cadmium uptake similar or better than other biosorbent, the *E. densa* can be considered as alternative biosorbent toward the implementation of biosorption technology in industrial and environmental remediation.

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