Use of residues from *Eucalyptus Globulus* as biosorbents for cadmium removal

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Abstract The present work studied the removal of cadmium from aqueous solutions by a series of batch sorption experiments using *Eucalyptus Globulus* bark and seeds as biosorbents. Both biosorbents showed good results in cadmium removal. The best results were obtained when working with a particle size < 75 µm, initial pH solution between 7.5 and 8.0, a mass-to-volume ratio of 18 and 12 g L^{-1} for the bark and seeds respectively. The Ho and McKay model explained well the biosorption kinetic results for both biosorbents. It was found that cadmium sorption on seeds was faster than that obtained on bark, with maximum cadmium capacity of 8.54 and 5.62 mg L^{-1} for the seeds ant bark respectively which indicates that the seeds presented better results. The experimental equilibrium data could be fitted well with both the Langmuir and Freundlich isotherm models.

Keywords: Cadmium removal, adsorption, wastewater, biosorbents

1. Introduction

Extractive metallurgical operations and mineral processing generate important amounts of liquid waste, with a high content of heavy metals. This is a serious environmental problem, especially in Chile, where a large amount of the world´s copper is produced (Hansen *et al*, 2010, Hansen *et al*, 2013). Toxic elements such as food chain accumulating heavy metals are present in these wastewaters (Naiya *et al*, 2009). Plants, animals and humans can be severely affected by the presence of cadmium, lead, copper, mercury and zinc (Demirbas, 2008). Exposure to high levels of cadmium can cause severe and life-threatening diseases and malfunctions (Chakravarty *et al*, 2010). Today, physicochemical methods are used to remove heavy metals from wastewater, such as precipitation, adsorption, solvent extraction, different membrane processes, ion exchange, filtration and electrochemical treatment (Barka *et al*, 2010). Compared to the aforementioned techniques, biosorption processes have certain advantages, being selective, of low cost and effective when removal of low concentrations of metals such as cadmium is required (Volesky, 2004). In addition, by using dead biomass of natural or agricultural waste as a biosorbent, it can be regenerated by reducing the amount of solid waste produced during the treatment, as compared, for example, with technologies such as chemical precipitation, which generates large amounts of sludge to be disposed (Arief *et al*, 2008). Therefore, in the treatment of wastewater, this technology offers an excellent and profitable alternative (Ghodbane *et al*, 2008). In the present study, *Eucalyptus Globulus* residues, mainly found in Central Chile, are studied as potential biosorbents to remove cadmium from liquid waste. These residues contain cellulose, hemicellulose and lignin – among others - with polyphenolic groups that are known to establish bonding to different metal cations (Taty-Costodes *et al*, 2008).

The objectives of this work were: (i) to study and analyze natural residues (*Eucalyptus Globulus* bark and seeds) as biosorbents for cadmium, (ii) to determine an adequate working particle size, initial pH, and mass/volume ratio, (iii) to find adsorption capacities for each case, (iv) to determine biosorption kinetics, (v) to determine equilibrium time, and (vi) to determine adsorption isotherms.

2. Experimental

2.1. Reagents

Solid $Cd(NO_3)_2 \cdot 4H_2O$ (analytical grade) was dissolved in distilled water to prepare the cadmium solutions. HCl or NaOH (both analytical grade) was added to this solution to reach the desired working pH.

2.2. Analytical

GF/A glass microfiber filter paper and a vacuum pump was used to filter each liquid sample. Chilean standard NCh 2313/10 Of. 96 was followed to determine the cadmium concentration in the filtrate (Atomic Absorption Spectrophotometry in flame). pH was measured with a combined pH electrode.

2.3. Adsorbent preparation

Eucalyptus Globulus residue samples of bark and seeds were collected in Laguna Verde, Valparaíso, Chile. After the sampling, the residues were first washed in tap water followed by a rinsing in distilled water. The clean residuals were dried at ambient air temperature (20-25 °C) for 24 hours and then dried until constant weight (at 50 °C). Each type of biosorbent was crushed, milled and sieved to obtain the particle size range needed for each experiment.

2.4. Experimental plan

Table 1 shows the experimental biosorption conditions. The analyzed parameters were: (a) particle size (PS) range, (b) initial pH, (c) mass/volume ratio (M/V), and (d) equilibrium time with the overall goal to determine adsorption capacities, kinetics and adsorption isotherms, using a batch method. Drops of 0.5 M HCl or 0.5 M NaOH were added to the solution to fix initial pH without affecting significantly the liquid volume of the liquid.

Table 1. Experimental biosorption conditions.

Type of experiment	Residue	Fixed parameter	Analysed parameter
PS	Bark and seeds	$[Cd]_0$: 100 mg L^{-1}, M/V: 6 g L^{-1}, pH: 5.5-6.0, time: 360 min	PS: <75, 150-212 and 355- 425 µm
Initial pH	Bark and seeds	$[Cd]_0$: 100 mg L^{-1}, M/V: 6 g L^{-1}, time: 360 min, PS: <75 µm	pH: 4.5-5.0, 5.5-6.0, 6.5-7.0 and 7.5-8.0
M/V ratio	Bark and seeds	$[Cd]_0$: 100 mg L^{-1}, pH: 7.5-8.0, time: 360 min, PS: <75 µm	M/V: 3, 6, 9, 12, 18 and 24 g L^{-1}
Biosorption kinetics	Bark	$[Cd]_0$: 100 mg L^{-1}, pH: 7.5-8.0, PS < 75 µm, M/V: 18 g L^{-1}	Time: 5, 10, 15, 30, 60, 120, 180, 360 and 1440 min
	Seeds	$[Cd]_0$: 100 mg L^{-1}, pH: 7.5-8.0, PS < 75 µm, M/V: 12 g L^{-1}	
Adsorptio isotherms	Bark	pH: 7.5-8.0, PS: < 75 µm, M/V: 18 g L^{-1}, time: 60 min	$[Cd]_0$: 25, 50, 75, 100, 200 and 400 mg L^{-1}
	Seeds	pH: 7.5-8.0, PS: < 75 µm, M/V: 12 g L^{-1}, time: 10 min	

Experiments were carried out in duplicate, at room temperature (20-25 °C) using an orbital shaker at approx. 140 rpm to maintain complete agitation. After evaluating the effect of PS, an adequate PS range was selected and used for determination of a suitable initial pH. Once the PS and initial working pH were chosen, the M/V (biosorbent mass-to-liquid volume) was evaluated. With the optimum parameters, the biosorption kinetics experiments were carried out and adsorption isotherms were determined. To analyze the three effects mentioned above, 250 mL of 100 mg L^{-1} cadmium solution was put in contact with the biosorbent during 6 h. Three PS ranges were used: <75 µm; 150- 212 µm and 355- 425 µm, with a mass/volume ratio of 6 g L^{-1} (1.2 g biosorbent in 200 mL solution) and an initial working pH in the range of 5.5-6.0. The study of the initial pH was carried out using four different pH ranges: 4.5-5.0, 5.5-6.0, 6.5-6.0 and 7.5-8.0 with M/V of 6 g L^{-1} and PS of <75 µm. Meanwhile, the effect of the mass/volume ratio (M/V) was carried out using 0.6, 1.2, 1.8, 2.4, 3.6 and 4.8 g biosorbent in 200 mL of solution using a particle size of <75 µm and an initial pH range of 7.5-8.0. For the equilibrium time and biosorption kinetics experiments, a cadmium solution of 100 mg L^{-1}, a particle size <75 µm, an initial working pH in the range from 7.5 to 8.0, and a M/V ratio of 18 and 12 g L^{-1}, for the bark and the seeds, respectively, were used.

3. Results and Discussion

3.1 PS, initial working pH and M/V ratio

PS is an important parameter for the biosorption process. In this work three different PS ranges were used, and Figure 1 shows the results. From the figure it is observed that the decrease in PS allows an increase in the retention of cadmium, as expected; with maximum retention values of 12.70 and 13.45 mg g^{-1}, for the bark and seeds respectively, at PS lower than 75 µm. Smaller PS means greater surface area of the particles and the sorption process is favored.

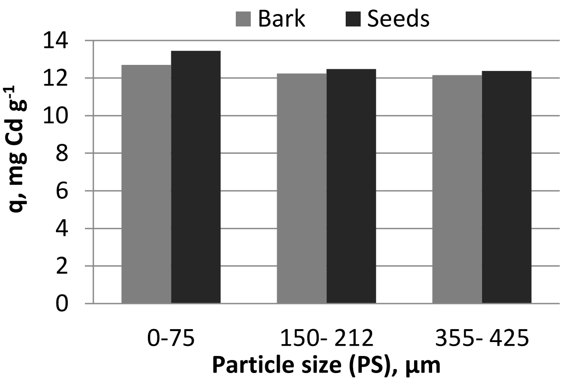

Figure 1. Particle size (PS) effect: $[Cd]_0$= 100 mg L^{-1}, M/V= 6 g L^{-1}, pH= 5.5- 6.0 and t= 360 min.

The performance of a biosorption process depends considerably on pH in the solution. In this work, four initial pH ranges were used. The results presented in Figure 2 indicate that the highest retention capacity is obtained for the initial pH range of 7.5-8.0, with a value of 12.78 and 15.59 mg L^{-1}, for the bark and seeds, respectively.

On the solid biosorbent surface, the slightly acidic ranges show a competition for the active sorption sites between excess hydronium ions (H_3O^+) and cadmium ions. The finding of the highest pH range as the optimum can be explained because when increasing the pH of the solution it will generate a greater amount of negatively charged active sites, increasing the attraction by electrostatic forces between them and the oppositely charged cadmium ions.

The M/V ratio can determine the retention capacity of a biosorbent in a solution with a controlled initial Cd concentration. In this study, the two optimal parameters - PS <75 µm and initial pH: 7.5-8 - obtained above were used.

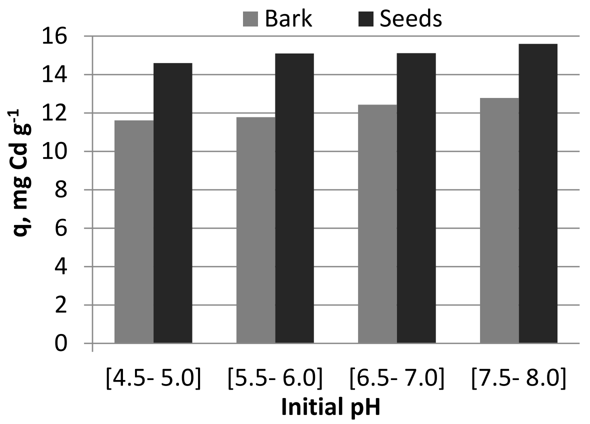

Figure 2. Initial pH effect: $[Cd]_0$= 100 mg L^{-1}, M/V= 6 g L^{-1}, Particle size <75 μm and t= 360 min.

Six different M/V ratio values were used: 3, 6, 9, 12, 18 and 24 g L^{-1}. Figure 3 and Figure 4 present the Cd removal as a function of M/V for bark and seeds, respectively, and indicates that the best removal is obtained with a M/V of 18 and 12 g L^{-1}, for the bark and seeds, respectively; with 90% removal of cadmium being the criterion chosen to determine the optimum ratio.

It could be seen that an increase in the M/V ratio generates more available active sorption sites, and therefore removal of cadmium is enhanced. In addition, the mass of cadmium adsorbed per mass of biosorbent is reduced with increasing biosorbent mass, and because of this, a decrease in retention capacity occurs.

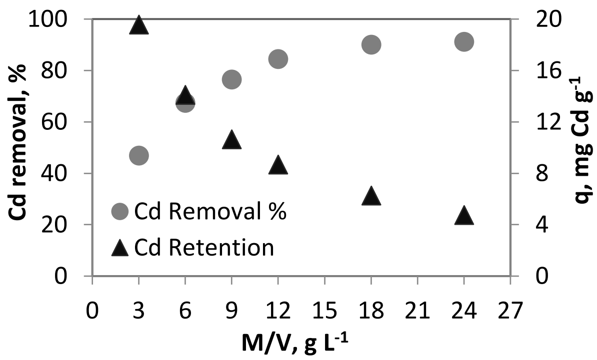

Figure 3. M/V ratio effect, bark: $[Cd]_0$= 100 mg L^{-1}, pH = 7.5-8.0, PS <75 μm and t= 360 min.

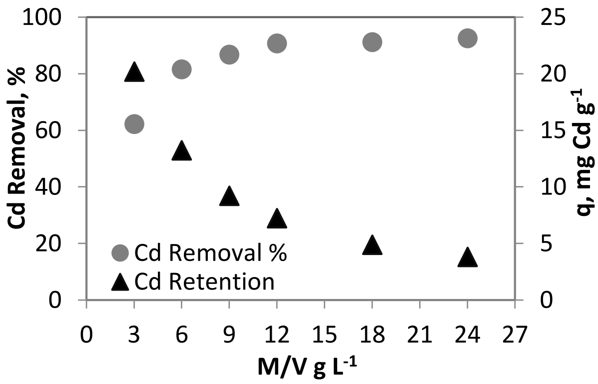

Figure 4. M/V ratio effect, seeds: $[Cd]_0$= 100 mg L^{-1}, pH = 7.5-8.0, PS <75 μm and t= 360 min.

4.2. Equilibrium time and biosorption kinetics.

The adsorption velocity – or how fast the contaminant is sorbed to the solid surface - is another crucial important factor to predict in the design of the system, thus knowing the contact time of the biosorbent and the dimensions of the reactor to be used (Sud *et al*, 2008).

For this experimental part, the three optimal parameters found in section 4.1 were used. The results are presented in Figure 5, where the retention reaches 90% of the equilibrium value after 5 min, for the two cases analyzed. It is observed that the optimal equilibrium times are 60 and 10 min, for the bark and seeds, respectively (using as a criterion the time in which 97% of equilibrium retention is obtained). When the experimental data were adjusted, the Ho and McKay model (Ho and McKay, 1999) showed better results (compared to a 1st order approach) for both bark and seeds, with R^2 = 0.9954 and R^2 = 0.9996, respectively. Table 2 shows the estimated parameters of the kinetic models.

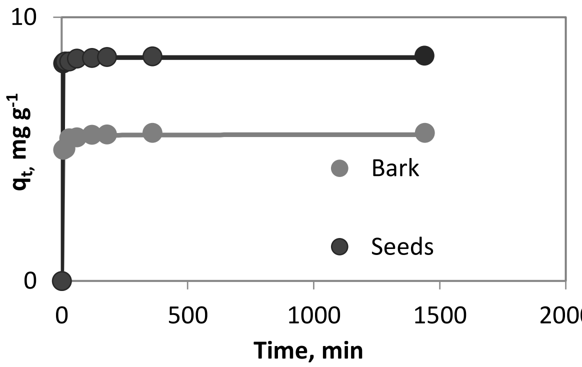

Figure 4. Determination of equilibrium time: $[Cd]_0$= 100 mg L^{-1}, pH = 7.5- 8.0, M/V= 18 g L^{-1} bark and 12 g L^{-1} seeds and PS <75 μm.

Table 2. Second order model coefficients and linear regression results and for bark and seeds.

Biosorbent	Bark	Seeds
R^2 1st order model	0.9851	0.9990
R^2 2nd order model	0.9954	0.9996
q_{eq} (mg g^{-1})	5.547	8.473
k (g mg^{-1} min^{-1})	0.2334	0.7098
k_{ad} (mg g^{-1} min^{-1})	7.182	50.953
Ho and Mckay model	$\frac{t}{q_t} = 0.180t + 0.1392$	$\frac{t}{q_t} = 0.118t + 0.0196$

4.3. Adsorption isotherms

Six initial concentrations of cadmium were studied (from 25 to 400 mg L^{-1}), using the four optimum parameters previously determined. These were: PS <75 μm, an initial pH range of 7.5-8.0, a M/V ratio of 18 and 12 g L^{-1} for the bark and the seeds, respectively, and a contact time for the bark of 60 min and 10 min for the seeds.

Figure 6 shows the Cd removal efficiency as a function of initial cadmium concentration. From the figure it is found that a low concentration of metal gives a cadmium cation amount similar to the active sites present in the biosorbents, it minimizes saturation and allows a better removal efficiency. Removals are high at initial concentrations lower than 100 mg L^{-1} of cadmium, with removal values of about 90% for both biosorbents;

considering that the optimal M/V ratios were found for 100 mg L^{-1} Cd initial concentration. At higher concentrations, a decrease in metal removal is observed because higher M/V ratios are required to not saturate the biosorbent. When working at concentrations higher than 100 mg L^{-1} of cadmium it would be advisable to find new optimal M/V ratios.

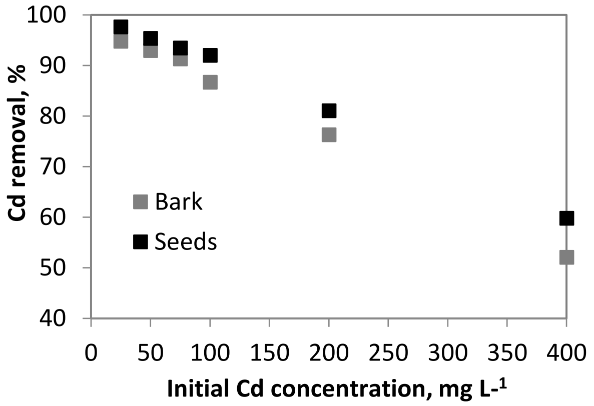

Figure 6. Cd removal % as a function of initial Cd concentration for bark and seeds.

When analyzing the Langmuir model maximum retentions, a higher value is obtained using the seeds compared to the bark. In the Freundlich model, the value of *n*, which is related to the distribution of metal-biosorbent bonds, represents a good adsorption if it is between 1 and 10. As shown in Table 3, which shows the Langmuir and Freundlich isotherm modelling data, the value is in that range for both biosorbents, showing favorable adsorption of the inorganic contaminant on the biosorbents used.

Table 3. Results of the adsorption isotherms.

Langmuir			Freundlich		
Parameter	Bark	Seeds	Parameter	Bark	Seeds
b [L mg^{-1}]	0,0573	0,0511	K_F [-]	2,013	3,7417
q_m [mg g^{-1}]	12,2219	26,0688	n [-]	2,968	2,7941
R^2	0,9795	0,9709	R^2	0,9695	0,9880

When adjusting the concentration and equilibrium retention data with the Freundlich and Langmuir models for adsorption isotherms, it could be observed that the Langmuir isotherm fitted better than the Freundlich model to the experimental data in the case of the bark. For the seeds, the behavior is reverse, but both models have a very good fit for both the bark and the seeds.

4. Conclusions

The bark and seeds of the species *Eucalyptus globulus* have a high affinity for cadmium, having high removal efficiency and adequate retention of the metal, with the seeds presenting the best results in the majority of the analyzed cases. An increase in biosorption is observed by decreasing the biosorbent particle size, and the use of a slightly basic initial pH increases retention. The increase of the M/V ratio generates an increase of available active sites, so the removal efficiency increases, but the retention decreases. The time to reach sorption equilibrium is low for both biosorbents, which offers advantages on an industrial scale.

Biosorption kinetics for both types of residues are well fitted with the Ho & Mckay model, and both the Langmuir and Freundlich isotherms are a good fit for experimental equilibrium data.

Therefore, it is recommended to use these types of natural waste for future work, because they are effective and economical interesting materials as biosorbents in the treatment of wastewater with cadmium.

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