Evaluation of *Posidonia oceanica* and organic sediment as biosorbents: Cu removal in fixed bed columns

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Abstract

In this work, fixed bed column experiments were performed with the aim of evaluating the Cu uptake capacity of two biosorbents. The marine phanerogam *Posidonia oceanica*, a waste from local beach cleaning practices at Denia (Spain), and locally available organic sediment, a highly mineralized peat from Torreblanca (Spain) were used. Column runs were carried out to determine the sorption isotherm. For this purpose, breakthrough curves up to the exhaustion point were obtained. Maximum uptake capacities were experimentally determined in 56.7 mg·g^{-1} and 43.3 mg·g^{-1} for *Posidonia oceanica* and organic sediment, respectively. High retention capacities indicate that these materials could be used as effective biosorbents for Cu removal. Langmuir equilibrium parameters were obtained for both biosorbents. A mass transport model including convection-dispersion and sorption processes under equilibrium or rate-controlled conditions has been developed to simulate column performance. Good compliance between experimental and modelling results was obtained.

Keywords: Cu, biosorption, Posidonia oceanica, organic sediment, column experiments, mass transport model.

1 Introduction

Biosorption has been revealed as a promising low-cost technology for heavy metal removal from water and wastewater. Many investigators have studied the sorption capacity of low-cost materials such as wood bark [1], peat [2, 3], lignin [4], agroindustrial wastes [5, 6] and different types of biomass [7, 8]. A major part of the literature data relating to the use of low-cost adsorbents for metal

removal has been obtained in batch mode. Application of a continuous flow system is still scarce [9-11], and extrapolation of batch results to the prediction of removal capacities in column systems should be carefully evaluated, since differences in contact and flow conditions can result in discrepancies. Limited data are also available on the rates of heavy metals sorption, in terms of intraparticle diffusion coefficients.

The main objective of this study was to investigate the adsorption characteristics of two biosorbent materials to evaluate their applicability for the removal of Cu. The marine phanerogam *Posidonia oceanica*, a waste from local beach cleaning practices at Denia (Spain), and locally available organic sediment, a high mineralized peat from Torreblanca (Spain) were used. The study was developed in laboratory fixed bed columns. To evaluate its practical application, several Cu concentration values were chosen to be representative of those in industrial wastewater. Column experiments were conducted to determine the breakthrough time and to evaluate the sorption capacity from the exhaustion point. Sorption data were used to calibrate Langmuir isotherms. After determining the viability of the application, the work has been focused on modelling the column data. A mass transport model including convection-dispersion and sorption processes under equilibrium or rate-controlled conditions has been developed. The hydrodynamic dispersion coefficient and the effective intraparticle diffusivity have been calibrated.

2 Material and methods

2.1 Materials

The marine phanerogam Posidonia oceanica, a waste coming from local beach cleaning practices, was offered from Denia Compost SA, a composting plant

Table 1: Physical and chemical properties of the sorbents.

		Organic Sediment	*Posidonia oceanica*
Elemental analysis[a], %	C	17.36	33.89
	H	1.89	4.68
	N	1.03	0.93
	S	1.10	0.18
Loss on ignition, %		29.8	83.6
pH_{ZPC}[b]		6.8	8.2
Specific surface area[c], $m^2\ g^{-1}$		1.3 ± 0.2	8.4 ± 0.9
Apparent density, $g\ dm^{-3}$		807.0	137.1

[a] Elemental Analyzer EA 1110 CE Instruments (Italy).
[b] Mass Titration [12].
[c] BET Surface, ASAP 2010 Micromeritics Instrument Corporation (USA).

located in Denia, Spain. The raw material was rinsed with tap water until constant conductivity was achieved. After rinsing with distilled water, it was oven dried. The organic sediment used in this study is a highly mineralized peat collected from the Torreblanca deposit located in Castellón, Spain. The distributing company (Infertosa, Spain) mixes the extracted material with nutrients to use as a commercial soil amendment. In this study, the commercial amendment was used. Before use, both materials were crushed and sieved to 0.5 – 2 mm particle size, oven dried and stored in a dessicator. The properties of the adsorbents are listed in table 1.

Both biosorbents were wetted before introducing them in the fixed bed column: suspensions of 50 g dm^{-3} in distilled water were shaken (180 rpm) at 20 ± 0.5ºC using a New Brunswick Scientific G25KC model incubator orbital shaker for 24 h. Cu solutions were prepared by dissolving sulphate salt ($CuSO_4 \cdot 5H_2O$) with distilled water. 1×10^{-2} mol dm^{-3} of NaCl was used as background electrolyte. Solutions of 1×10^{-1} mol dm^{-3} NaOH and 1×10^{-1} mol dm^{-3} HCl were used for pH adjustment and column regenerations. Reagents were analytical grade from Panreac.

2.2 Column set-up

For each biosorbent, column experiments with Cu concentration in the influent ranging between 1 – 60 mg dm^{-3} were carried out. Influent pH was maintained in 5.5 – 6 to avoid Cu chemical precipitation. Adsorption experiments were performed until exhaustion point. The biosorption process was carried out in Pyrex glass columns of 35 cm length and 1.0 cm inner diameter. Glass beads were introduced at the bottom of the column up to around 10 cm length. The biosorbent fixed-bed was wet packed up to a total length around 10 cm, except for the column runs with the organic sediment with Cu concentration in the influent lower than 10 mg dm^{-3}, for which the column length was selected at 5 cm due to the long duration of the experiments. The rest of the column was filled with glass beads to prevent the sorbent from floating. Columns were operated in the up-flow mode to avoid possible short-circuiting and channelling. The feed solution was pumped at ambient temperature (22 ± 1.0 ºC) through the column by a Watson-Marlow model 101 U/R peristaltic pump. Flow rate was adjusted to approximately 40 cm^3 h^{-1}. Effluent samples were collected each 2 or 4 hours, depending on the sorbent sorption capacity, by using an automatic fraction collector. The pH was measured using a WTW 340i model pHmeter with ± 0.01 accuracy. The samples were acidified with concentrated HNO_3, and stored for atomic absorption analysis. Cu concentrations were measured using Thermo S Series model S4 Atomic Absorption Spectrometer. Standard solutions of 1000 mg dm^{-3} of $Cu(NO_3)_2 \cdot 3H_2O$ in 0.5 N HNO_3 were used for calibration.

After the sorption period, columns were desorbed to recover the metals in a concentrated form and to regenerate the sorbent. Desorption of the columns was carried out by passing 0.05 mol dm^{-3} HCl. Bed porosity was determined at the end of each experiment resulting in the range of 0.84 to 0.94 for *Posidonia oceanica* and 0.62 to 0.67 for the organic sediment.

3 Results and discussion

3.1 Experimental results

Results of Cu sorption experiments are shown in fig. 1, in which breakthrough curves for each sorbent at different Cu concentration in the influent solution have been depicted. In these graphs, the normalized effluent metal concentration, C/C_0, versus the number of pore volumes (water bed volumes) treated is presented. The breakthrough curves showed a similar asymmetric shape, with early breakthrough and tailing, revealing non-ideal transport. The sorbents were wetted previously to the introduction in the column so the initial pH in the effluent was affected by the batch wetting, tending to the pH_{zpc} of the sorbents. The effluent pH evolved from an initial value in the range between 6.5 and 7 to a final value around 5.5-6.
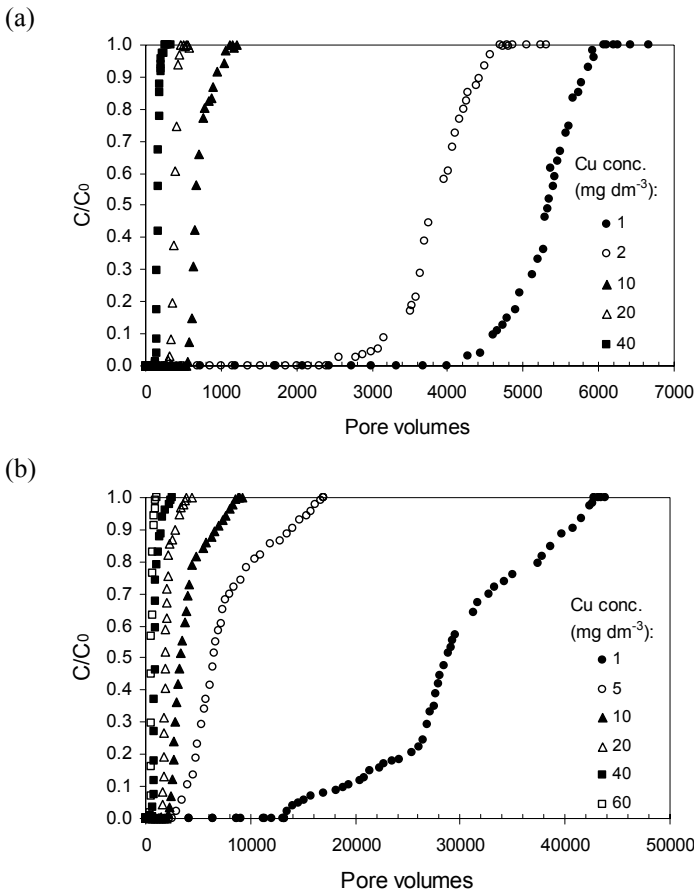
(a)

(b)

Figure 1:   Experimental breakthrough curves for Cu sorption onto: (a) *Posidonia oceanica*; and (b) organic sediment.

From fig. 1, it is clear that the number of pore volumes to reach breakthrough decreased with the increase in initial Cu concentration. Breakthrough pore volumes (defined at $C/C_0 = 0.05$) along with the corresponding hours of operation and the amount of Cu retained are shown in table 2 for each column run. The performance of both biosorbents for Cu removal is remarkable; both materials presented high retention capacity without detecting Cu in the effluent for a long period. Comparison between the two sorbents shows that *Posidonia oceanica* presents higher Cu uptake capacity expressed as mg of Cu retained per g of sorbent. However, the analysis of the pore volumes of treated wastewater to reach the column breakthrough indicates that the organic sediment presents the best performance for Cu removal, with more than 14000 pore volumes of water treated before Cu breakthrough occurred for an influent with Cu concentration of 2 mg dm^{-3}. This fact can be attributed to the much higher density of the organic sediment against the *Posidonia oceanica* one, which allows packing a greater quantity of biosorbent in the same volume of column bed. So, for the industrial application, the organic sediment provides longer time of operation before the exhaustion of the sorbent bed.

Table 2:   Cu uptake, pore volumes of treated water and operation time at breakthrough ($C/C_0 = 0.05$) for the tested biosorbents.

Cu conc. in the influent (mg dm^{-3})	Cu retained (mg g^{-1})	Pore volumes (cm^3)	Operation time (h)
Posidonia oceanica			
1.02[*]	34.95	4471.4	749.8
1.98[*]	35.61	3571.5	428.8
10.62[*]	44.61	575.7	103.1
20.07[*]	47.68	371.6	58.3
41.40[*]	46.75	166.9	25.0
Organic sediment			
1.05[§]	18.05	14669.9	933.0
5.02[§]	19.98	3478.3	202.9
10.38[§§]	25.83	2331.7	304.8
20.90[§§]	36.16	1631.9	197.4
40.20[§§]	29.96	717.1	88.0
59.95[§§]	32.99	466.8	62.2

[*]Amount of sorbent: approx. 1g.
[§] Packed bed length: 5 cm; amount of sorbent: approx. 2.2 g.
[§§] Packed bed length: 10 cm; amount of sorbent: approx. 5 g.

At the end of the sorption period, desorption of the columns was carried out by passing 0.05 mol dm^{-3} HCl to recover the metal. An average value of 95% of the Cu adsorbed was recovered, showing the reversibility of the sorption process onto the tested materials. The volumes of acidic solution used for the regeneration were 200-250 dm^{-3} in the case of *Posidonia oceanica* and 350-400 dm^{-3} for the organic sediment.

3.2 Sorption capacity

The total amount of metal retained in the column depends on the influent metal concentration and can be calculated from the area above the breakthrough curve up to the experimental column end point. The results are presented in fig. 2, as plots of solid-phase equilibrium metal concentration, q_e (mg g^{-1}), versus the liquid-phase metal ion concentration, C_e (mg dm^{-3}) has been plotted. Metal uptake increases as solution metal concentration increases, showing a typical Langmuir isotherm shape. The Langmuir model assumes that sorption process takes place onto a homogeneous surface and, at saturation, a monolayer of adsorbate is formed. Langmuir model is represented by the expression:

$$q_e = \frac{q_{\max} \, b \, C_e}{(1 + b \, C_e)} \qquad (1)$$

where $q_{\max.}$ is the maximum uptake (mg g^{-1}) and b (dm^{-3} mg^{-1}) is a constant related to energy of adsorption, which quantitatively reflects the affinity between the sorbent and the sorbate. Langmuir isotherm parameters, listed in table 3, have been determined by linear regression. Maximum uptake capacities were 56.7 and 43.3 mg g^{-1} for *Posidonia oceanica* and the organic sediment, respectively. Representative reported values of uptake capacities for Cu removal using different biosorbents in batch mode at similar pH conditions are: 30 mg g^{-1} onto sugar beet pulp [13], 19.5 mg g^{-1} onto cork biomass [14], or 42.92 mg g^{-1} onto grape stalks and 11.6 mg g^{-1} onto exhausted coffee [15]. The two bisorbents tested present a good adsorption capacity, indicating its great potential for the removal of Cu from wastewater.
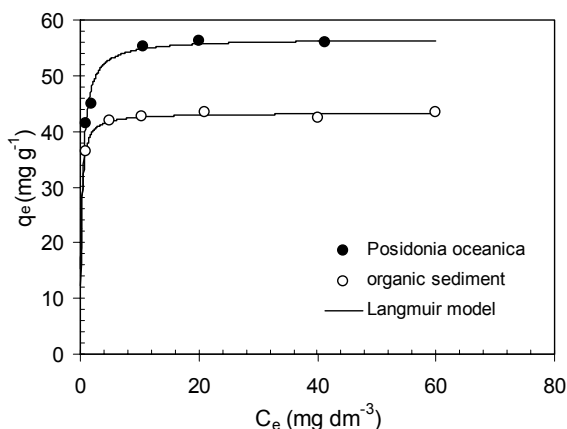

Figure 2:   Adsorption isotherms obtained in column experiments.

3.3 Mass transport modelling

Simulation of Cu transport experiments with *Posidonia oceanica* was carried out. In a first stage, simulations were performed assuming adsorption under

equilibrium conditions. For one-dimensional transport in the positive z direction with a steady-state flow, the convection-dispersion equation is [16]:

$$\theta \frac{\partial C}{\partial t} + \rho \frac{\partial q}{\partial t} = \theta D \frac{\partial^2 C}{\partial z^2} - \theta v \frac{\partial C}{\partial z} \tag{2}$$

where θ is the bed porosity, C is the solute concentration (kg m^{-3}), ρ is the bulk density of the porous media in the column (kg m^{-3}), q represents the adsorbed amount (kg g^{-1}), D is the hydrodynamic dispersion coefficient (m^2 s^{-1}) and v the average pore water velocity (m s^{-1}). For local equilibrium assumption, q is evaluated from the Langmuir isotherm.

Table 3:   Parameters for Langmuir isotherms.

Biosorbent	q_{max} (mg g^{-1})	b (dm^{-3} mg^{-1})	r^2
Posidonia oceanica	56.67	2.77	0.999
Organic sediment	43.29	5.47	0.999

The hydrodynamic dispersion coefficient was estimated from the local equilibrium modelling resulting in a value of 1 x 10^{-8} m^2 s^{-1}. In this condition, mass balances were accomplished with an average deviation of 1.7%. The simulated breakthrough curves do not represent the early breakthrough and tailing of the experimental data due to an over-prediction of the initial metal retardation. Such a discrepancy reveals that mass transfer limitations superposed on advective-dispersive transport cause the non-ideality of experimental transport.

Rate-controlled simulations assuming pore diffusion limitation were performed considering that the most important transport resistance lies in the solid phase rather than in the liquid phase. Pore diffusion has been modelled by first-order kinetics with a linear driving force. Thus, system equations for solute transport assuming pore diffusion mass transfer rate control are Eqn (2) plus

$$\frac{\partial q}{\partial t} = K_p \left(q_e^* - q \right) \tag{3}$$

where K_p is the first-order mass transfer coefficient (s^{-1}). In this case, q_e^* represents the adsorbed concentration at the external surface of the adsorbent, in equilibrium with the adsorbate solution concentration, and q represents the average adsorbed concentration.

Results of rate-controlled modelling for *Posidonia oceanica* are shown in fig. 3. The mass transport coefficient was estimated from transport simulations, with values from 5 x 10^{-6} s^{-1} to 6 x 10^{-5} s^{-1}. As can be observed, the predicted breakthrough curves matched the experimental data; therefore, the reported model parameters are useful for the evaluation of the breakthrough time to establish the operating conditions on an industrial scale.
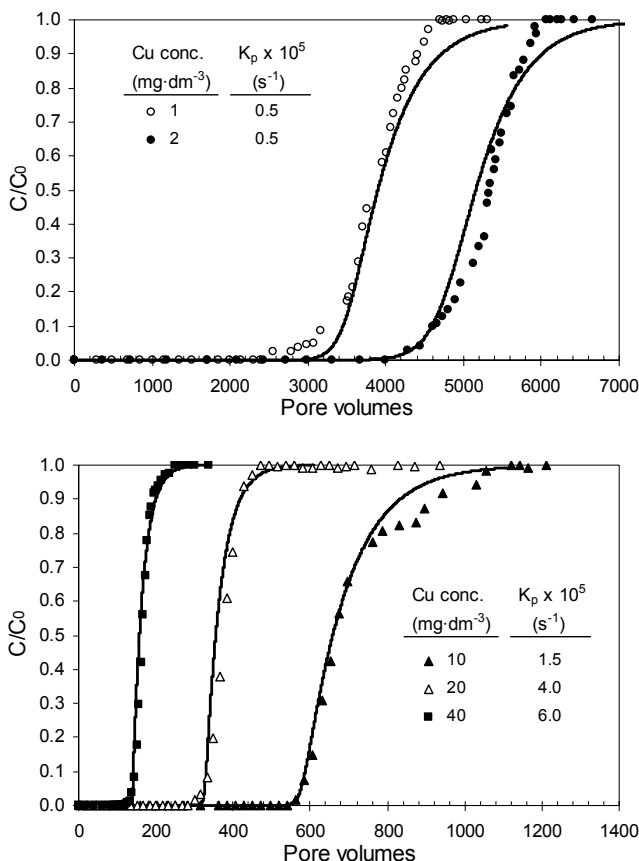
Figure 3:   Comparison of predicted and observed Cu breakthrough curves for *Posidonia oceanica.* Lines: predicted from pore diffusion rate control model.

4   Conclusions

The results indicate that *Posidonia oceanica* and the tested organic sediment are potentially useful biosorbents for Cu removal from wastewater. Other advantages of these biosorbents for removing Cu from acidic wastewater are the low cost, economic feasibility, suitable structural characteristics and the process reversibility in continuous operation. Although maximum Cu uptake was higher for *Posidonia oceanica*, the performance of the organic sediment for the same size of the sorption process unit allows maintaining the operation without detecting the metal ion in the effluent for longer time. A model to predict experimental breakthrough curves based in the assumption of pore diffusion rate control was successfully applied.

Acknowledgements

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