



XXII CONGRESSO
BRASILEIRO DE
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23 a 26 de Setembro de 2018
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XVII ENCONTRO BRASILEIRO
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MARINE MACROALGA *PELVETIA CANALICULATA* AS A NATURAL CATION EXCHANGER FOR BARIUM REMOVAL

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ABSTRACT – *In this study, Ca-loaded macroalga Pelvetia canaliculata was investigated as a natural cation exchanger for barium removal. A mass action law was able to fit satisfactorily the equilibrium data for the ternary mixture ($Ba^{2+}/H^{+}/Ca^{2+}$), resulting in selectivity coefficients of $K_H^{Ba} = 6.88/0.41$ and $K_H^{Ca} = 3.08/0.03$, for carboxylic/sulphonic groups. In the packed bed column, the service capacity was 237 bed-volumes (BV), treating 14.2 L of influent with a feed concentration of 2.9 mEq Ba^{2+}/L , until the breakthrough point of 0.07 mEq Ba^{2+}/L . Elution efficiency near to 100% was achieved using 5 BV of 1.0 M HCl in counter-flow direction. A dynamic mass transfer model, considering equilibrium given by the mass action law, linear driving force (LDF) approach to describe the intraparticle mass transfer resistance and the stagnated film resistance described well the breakthrough profiles for all species obtained in a packed bed column.*

1. INTRODUCTION

Barium is a toxic metallic pollutant resulting from various industrial processes, with emphasis on the petrochemical, mining and nuclear industries. Barium contamination causes health damage: nausea, abdominal pain, muscular convulsions, cardiovascular problems, and paralysis of the peripheral nervous system. Therefore, minimizing barium contamination of water and soil sources has become a matter of environmental and public health concern.

In the last decades, the use of marine algae as natural cation exchange resins for heavy metals removal has been successfully highlighted in the literature (Zeraatkar *et al.*, 2016). However, in contrast to what happens with other metals (Cd, Cu, Ni, Pb, and Zn), studies on the use of marine algae for barium removal are scarce. Therefore, the present study aims to contribute to filling this gap.

2. MATERIALS AND METHODS



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The *P. canaliculata* (brown algae) was collected in Northern coast of Portugal, washed, dried and milled. The protonation of seaweed functional groups followed the procedure reported in Cechinel *et al.* (2016). Afterwards, the protonated biomass was converted into the calcium form, according to the methodology described by Mazur *et al.* (2017). This alga was denominated Ca-alga. Ba^{2+} solutions were prepared by dissolving a weighed quantity of $\text{Ba}(\text{NO}_3)_2$ (99%, Vetec) in ultrapure water.

The equilibrium and kinetic studies were carried out in Erlenmeyer flasks containing 50 mL of solution and 0.05 g of Ca-alga under constant stirring (130 rpm) and temperature (25 °C), at pH 5.3. For the Ba^{2+} equilibrium assays, initial barium concentrations from 5 to 300 mg/L were in contact with resin (1 g/L) for a period of 24 h (time required to reach equilibrium). Batch kinetic studies were performed with barium initial concentration of 200 mg/L ($[\text{Ba}^{2+}]_0$). Samples were collected at predetermined time intervals until equilibrium is reached. At the end of each experimental procedure, samples were filtered and the residual metal concentrations (Ba^{2+} and Ca^{2+}) were determined by atomic absorption spectrophotometry (AAS). A mass action law was used to describe the ternary ($\text{Ca}^{2+}/\text{H}^+/\text{Ba}^{2+}$) equilibrium cation exchange data as described by Mazur *et al.* (2017). A dynamic mass transfer model, reported in Mazur *et al.* (2017), was applied to predict the batch kinetic profiles for all species in solid and liquid phases.

An experiment in continuous mode was performed in a column made of borosilicate glass (2.5 cm inner diameter; 30 cm length). The column was packed with 31 g of Ca-alga resulting in a bed height of 23.5 cm. Barium solution ($[\text{Ba}^{2+}]_{\text{feed}} = 200 \text{ mg/L}$) was pumped up through the column (3 mL/min in upward flow). Column elution was performed with 1.0 M HCl solution (37%, Química Moderna), in downflow (6 mL/min). Samples were collected at predetermined time intervals and analyzed by AAS. A dynamic mass transfer model, considering the equilibrium given by the mass action law, a stagnated film and intraparticle mass transfer resistances, was used to predict the kinetic profiles for all species in a packed bed column. Equations (1), (2), (3), (4) and (5) represent, respectively, the mass balances in the liquid phase and initial and boundary conditions.

$$\frac{\partial C_{b,n}}{\partial t} = D_{ax} \frac{\partial^2 C_{b,n}}{\partial z^2} - u_i \frac{\partial C_{b,n}}{\partial z} - \frac{(1-\varepsilon)}{\varepsilon} \cdot \frac{\rho_{ap}}{f} \frac{d\langle q_n \rangle}{dt} \quad (1)$$

$$k_{f,n} a_p [C_{b,n} - C_{f,n}] = \frac{\rho_{ap}}{f} \frac{d\langle q_n \rangle}{dt} \quad (2)$$

$$\frac{d\langle q_n \rangle}{dt} = k_{p,n} a_p [q_n^* - \langle q_n \rangle] \quad (3)$$

$$t = 0; C_{b,n} = 0; \langle q_n \rangle = q_{n_0} \quad (4)$$

$$t > 0; \begin{cases} z = 0; C_{b,n} = C_{\text{feed},n} \\ z = L; \frac{\partial C_{b,n}}{\partial z} = 0 \end{cases} \quad (5)$$

where $C_{b,n}$, $C_{f,n}$ and $C_{feed,n}$ are, respectively, the concentration of species n (Ba^{2+} , H^+ or Ca^{2+}) in the liquid phase, stagnant film and feed (mEq/L); t is the time (min), D_{ax} is the axial dispersion coefficient (cm^2/s), z is the bed axial position (cm), u_i is the interstitial fluid velocity (cm/min), ε is the bed porosity, ρ_{ap} is the particle density (g/L , dry basis), f is the swelling factor, q_n^* is the equilibrium concentration, and $\langle q_n \rangle$ is the average concentration of species n at the solid phase, $k_{f,n}$ and $k_{p,n}$ are, respectively, the mass transfer resistance coefficients for species n in the film and for intraparticle diffusion (cm/s), a_p is the particle specific area ($1/\text{cm}$).

3. RESULTS AND DISCUSSION

Figure 1(a) shows that the maximum biosorption capacity for Ba^{2+} using Ca-alga at pH 5.3 was 1.8 mEq/g . The mechanistic model, based on the mass action law, was able to fit satisfactorily the equilibrium data for the ternary mixture ($\text{Ba}^{2+}/\text{H}^+/\text{Ca}^{2+}$). The selectivity coefficients obtained were $K_H^{\text{Ba}} = 6.88$ and $K_H^{\text{Ca}} = 3.08$ for carboxylic group and, $K_H^{\text{Ba}} = 0.41$ and $K_H^{\text{Ca}} = 0.03$ for sulphonic groups. According to Figure 1(b), the barium ions removal takes place by the release of calcium ions, initially bound to the functional groups present at the biomass surface, which indicates that the binding mechanism is an ion exchange process. The stoichiometric ratio between the Ca^{2+} (algal surface) and the Ba^{2+} (aqueous solution) is 1:1. The pH rose from 5.3 to 5.6, suggesting the uptake of small amounts of protons. Removal of Ba^{2+} ions is faster at the initial stage and gradually decreases with time until saturation (250 min). The proposed mass transfer model predicted well the kinetic profiles for all chemical species in the liquid and solid phases (Figure 1(b)).

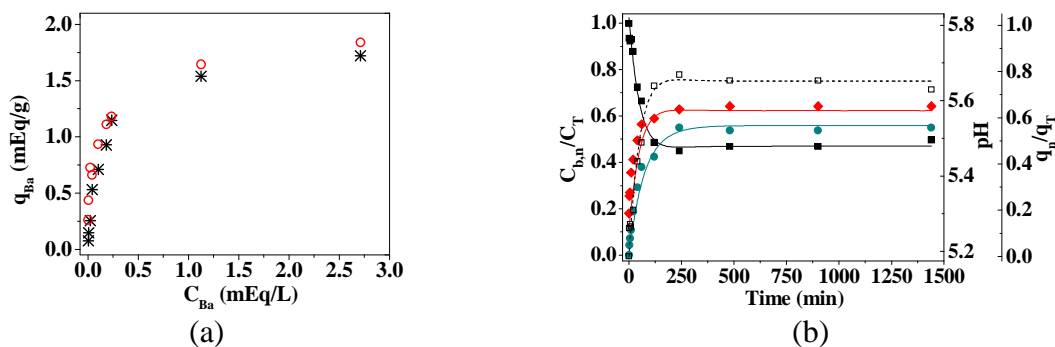


Figure 1 – (a) Equilibrium experimental data (*) and model prediction (○). (b) Kinetic experimental data (points) and model fittings (lines) for barium ion exchange: C_{Ba} (■), C_{Ca} (●), pH (◆) and q_{Ba} (□). C_T (overall concentration of species in the liquid phase (mEq/L)). q_T (overall amount of species sorbed per sorbent mass unit (mEq/g)).

Fig. 2a shows the breakthrough curves for all species in the liquid phase using a packed bed column. The length of the mass transfer zone (L_{MTZ}) was 10 cm (below the bed length (23.5 cm), resulting in a fraction of unused bed length (f_{LUB}) of 21%. The total capacity was near 1.8 mEq/g ($\sim 127 \text{ mg/g}$; 558 BV) which is in agreement with batch results. The bed packed with Ca-alga was able to treat 14.2 L of solution until reaching the breakthrough point, corresponding to a service capacity of 237 BV. The barium breakthrough point (5 mg/L) was established according to the CONAMA's discharge limit (Brazilian Legislation). The bed elution process occurred rapidly in the first 50 min of operation, corresponding to 96% elution using 5 BV of

1.0 M HCl in counter-flow direction (Figure 2(b)). The dynamic mass transfer model, presented in section 2, was able to predict satisfactorily the kinetic profile for all species in the continuous system, during saturation and elution steps.

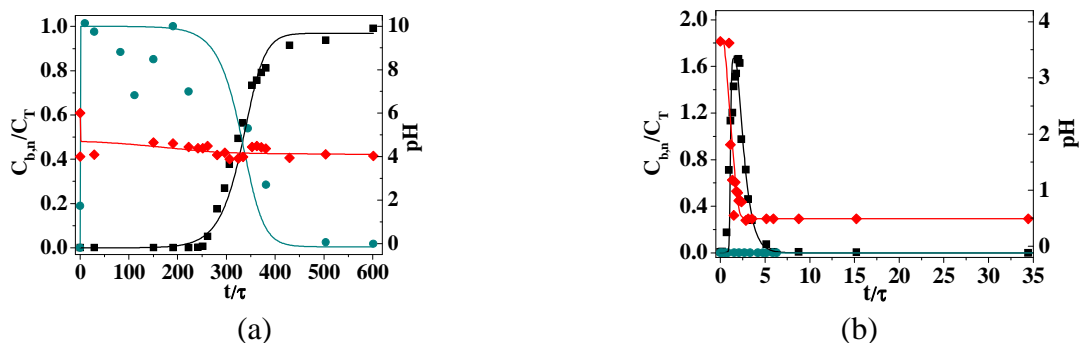


Figure 2 – Ion exchange column breakthrough curves for barium removal from aqueous solution: (a) saturation and (b) elution. Experimental: C_{Ba} (■), C_{Ca} (●) and pH (♦). Model lines: C_{Ba} (—), C_{Ca} (—) and pH (—).

4. CONCLUSIONS

The results obtained in this study indicate the *P. canaliculata* as a potential biosorbent for efficient barium removal. The mass action law model successfully fitted the ion exchange equilibrium data for the Ca-loaded *P. canaliculata* with the selectivity coefficients $K_H^{Ba} = 6.88$ and $K_H^{Ca} = 3.08$ for carboxylic groups and $K_H^{Ba} = 0.41$ and $K_H^{Ca} = 0.03$ for sulphonic groups. The service capacity for the fixed-bed system was 237 BV, being able to treat 14.2 L of influent until the breakthrough point. Column elution was fast and efficient. The proposed mathematical mass transfer models satisfactorily described the experimental data for the batch and the fixed-bed column configurations.

5. REFERENCES

- CECHINEL, MAP, MAYER DA, POZDNIAKOVA TA, MAZUR LP, BOAVENTURA AR, SOUZA AA, SOUZA SMAGU, VILAR VJP. Removal of metal ions from a petrochemical wastewater using brown algae as natural cation-exchangers. *Chem. Eng. J.*, v. 286, p. 1–15, 2016.
- HACKBARTH FV, GIRARDI F, SOUZA SMAGU, SOUZA AAU, BOAVENTURA AR, VILAR VJP. Marine algae *Pelvetia canaliculata* (Phaeophyceae) as a natural cation exchanger for cadmium and lead ions separation in aqueous solutions. *Chem. Eng. J.*, v. 242, p. 294–305, 2014.
- MAZUR LP, POZDNIAKOVA TA, MAYER DA, SOUZA SMAGU, BOAVENTURA AR, VILAR VJP. Cation exchange prediction model for copper binding onto raw brown marine macro-algae *Ascophyllum nodosum*: Batch and fixed-bed studies. *Chem. Eng. J.*, v. 316, p. 255–276, 2017.
- ZERAATKAR, AK, AHMADZADEHA H, TALEBI AF, MOHEIMANI NR, MCHENRY MP. Potential use of algae for heavy metal bioremediation, a critical review. *J. Environ. Manage.*, v. 181, p. 817–831, 2016.