

ION-EXCHANGE BREAKTHROUGH CURVES FOR SINGLE AND MULTI-METAL SYSTEMS USING MARINE MACROALGAE *PELVETIA CANALICULATA* AS A NATURAL CATION EXCHANGER

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ABSTRACT – In this work, the single and multi-metal ion exchange, $\text{Na}^+/\text{H}^+/\text{Cd}^{2+}$, $\text{Na}^+/\text{H}^+/\text{Pb}^{2+}$, $\text{Na}^+/\text{H}^+/\text{Cu}^{2+}$, $\text{Na}^+/\text{H}^+/\text{Zn}^{2+}$ and $\text{Na}^+/\text{H}^+/\text{Cd}^{2+}/\text{Pb}^{2+}/\text{Cu}^{2+}/\text{Zn}^{2+}$, has been studied in a continuous mode using a fixed-bed column packed with Na-loaded macroalgae *Pelvetia canaliculata* as the cation exchanger. The breakthrough curves for all the systems studied were obtained using initial metal concentrations of 20 mg/L. A mass transfer model, including the mass balance to the packed bed column, mass balance to the thin plates algae particles, assuming a LDF model, and complementary equations (as mass action law equilibrium relations, initial and boundary equations), was able to fit well the experimental data. An overshoot in the outlet of Cd and Zn concentrations was observed for the multi-metal system and explained by competitive uptake with Pb and Cu ions. Desorption using 0.1 M HNO_3 as eluent was fast and effective. Finally, an ion-exchange pilot plant was tested for the treatment of a multi-metal synthetic solution using the natural macroalgae.

1. INTRODUCTION

Contamination of aqueous environment by heavy metals has become a major threat due to their high toxicity for living organisms including human beings. Among heavy metals in wastewaters, cadmium, lead, copper and zinc are considered having a high priority due to their toxicity and high disposal rate, thus, removal of these metals of industrial effluents is mandatory (Kosasih et al., 2010; Hackbarth et al., 2014). A large number of industries including, petroleum refining, battery manufacturing, plating, mining, electroplating, metal processing, textile, tanneries, paint manufacture, pesticides, pigment manufacture, are sources of heavy metal contamination (Vilar et al., 2008). Therefore, there is a need to develop feasible processes and new friendly technologies able to remove those hazardous metals at low cost from industrial effluents (Torab-Mostaedi et al., 2013).

Macroalgae biomass is largely employed as a biosorbent material mainly due to its renewable

source, it is available in large quantities, its processing is relatively cheap and simple, avoids any secondary contamination of water and performs well (Al-Homaidan et al., 2013). The ability of macroalgae to adsorb metals can be explained by its nature. Macroalgae is a material bearing a variety of functional groups such as amino, carboxylic and sulfonic. Such a complex chemical structure enables a number of mechanisms to be involved in a metal sorption process, i.e. ion-exchange with ions such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , H^+ (Kuyucak; Volesky, 1989). Of the various types of algae, brown seaweed *P. canaliculata* (*Phaeophyceae*) has been identified for its high sorption capacity, showing up a natural cation exchanger, mainly associated to weakly acidic (carboxylic groups) and strongly acidic (sulfonic groups) functional groups (Hackbarth et al., 2014).

Numerous studies of metal biosorption in batch regime have been reported in the literature; however, the use of biosorbents to adsorb metal mixtures in packed bed column has not been frequently reported. In most practical applications the separation and purification processes which utilize adsorption technology involves continuous flow columns operations. This type of system allows to treat large volumes of water, although limited by the retention capacity of the biosorbent (Naddafi et al., 2007).

The objective of this work is to study the continuous biosorption and desorption of single and multi-metal systems, $\text{Na}^+/\text{H}^+/\text{Cd}^{2+}$, $\text{Na}^+/\text{H}^+/\text{Pb}^{2+}$, $\text{Na}^+/\text{H}^+/\text{Cu}^{2+}$, $\text{Na}^+/\text{H}^+/\text{Zn}^{2+}$ and $\text{Na}^+/\text{H}^+/\text{Cd}^{2+}/\text{Pb}^{2+}/\text{Cu}^{2+}/\text{Zn}^{2+}$, onto Na-loaded algae *P. canaliculata*, as natural cation exchanger, in a packed bed column. A mass transfer model was applied to describe the biosorption and desorption in the continuous packed bed column. Finally, an ion-exchange pilot plant was tested for the treatment of a multi-metal synthetic solution using the natural macroalgae.

2. EXPERIMENTAL METHODS

2.1. Preparation of biosorbent

The brown seaweed *P. canaliculata* (*Phaeophyceae*) was used in this study. The characteristics and preparation of material was presented in a previous work (Hackbarth et al., 2014).

2.2. Solution preparation

Cd^{2+} , Cu^{2+} , Pb^{2+} and Zn^{2+} solutions were prepared by dissolving a weighed quantity of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma Aldrich), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$ and ZnCl_2 (Merck) in ultrapure water. 0.5 M of NaCl solution was prepared by dissolving NaCl salt (Merck) in deionized (D.I.) water.

2.3. Column experiments

Column experiments were conducted in a glass column (Sigma C 5794) with 2.5 cm inner diameter and 25 cm length (*L*) packed with algae *P. canaliculata* particles. Adjustable plungers, with 20 μm selective filters, were attached to the top and bottom of the column. The metal solution (≈ 20 mg/L) was pumped down flow through the column at a determined flow rate (*Q*) using a peristaltic pump (Gilson Minipuls 2). The flow rate was frequently measured during the experiment.

Samples from the column outlet were collected regularly by a programmable fraction collector (Gilson FC 203B Fraction Collector) and analyzed by atomic absorption spectrometry. The pH was continuously recorded at the column outlet. All experiments were carried out at 25 °C. After column exhaustion the loaded biomass was regenerated using 0.1 M HNO₃.

3. RESULTS AND DISCUSSION

The biosorbent surface characterization by potentiometric titration, infrared spectrometry and esterification techniques revealed the presence of two types of functional groups, acidic (carboxylic and sulfonic) and basic (hydroxyl) groups in the surface of the marine macroalgae *P. canaliculata*. Hackbarth et al. (2014) and Girardi et al. (2014) reported a total of acidic binding sites of 2.5 mEq/g (Carboxylic: 1.5 mEq/g; Sulfonic: 1.0 mEq/g). Beyond that, using a mass action law to describe the ion-exchange equilibrium data, the following selectivity constants were obtained: $\alpha_{Na}^{Cd} = 337$, $\alpha_{Na}^{Pb} = 941$, $\alpha_{Na}^{Cu} = 521$, $\alpha_{Na}^{Zn} = 341$, $\alpha_{Na}^H = 10$ for carboxylic groups and $\alpha_{Na}^{Cd} = 38$, $\alpha_{Na}^{Pb} = 1695$, $\alpha_{Na}^{Cu} = 29$, $\alpha_{Na}^{Zn} = 11$, $\alpha_{Na}^H = 22$ for sulfonic groups. The metal affinity towards the *P. canaliculata* biosorbent decreases in the following order: Pb > Cu > Zn > Cd. The maximum biosorption capacity was 1.25 mmol/g for Cd²⁺ and Pb²⁺, 1.15 mmol/g for Cu²⁺ and 1.20 for Zn²⁺ using the Na-loaded macroalgae *P. canaliculata*, which indicates that almost all acidic binding groups are saturated.

3.1. Na⁺/H⁺/Cd²⁺, Na⁺/H⁺/Pb²⁺, Na⁺/H⁺/Cu²⁺ and Na⁺/H⁺/Zn²⁺ Systems

Figure 1 (a – d) presents the ion-exchange column breakthrough curves for the four ternary systems studied: Na⁺/H⁺/Cd²⁺, Na⁺/H⁺/Pb²⁺, Na⁺/H⁺/Cu²⁺ and Na⁺/H⁺/Zn²⁺, using the Na-loaded algae *P. canaliculata*. Biosorption of metal ions by Na-loaded algae *P. canaliculata* is accomplished by the release of sodium ions, due to the ion exchange mechanism. The increase on pH at the initial part of the experiments suggests desorption of alkaline species from the algae surface. The solution pH decreased until achieve the pH value of the feed solution. The proton concentration front maintains itself constant, until the metal and sodium ions front reaches the end of the column. Despite the higher H⁺ diffusivity, H⁺, Na⁺ and M²⁺ concentrations fronts move at the same velocity, since solution electroneutrality must be maintained. However, the pH breakthrough time can be lower due to dispersive effects. In these kinds of systems, the pH breakthrough curve may be used as an indicator of metal breakthrough, which is a simple method of ending a column cycle since monitoring pH is easier than monitoring metal concentrations.

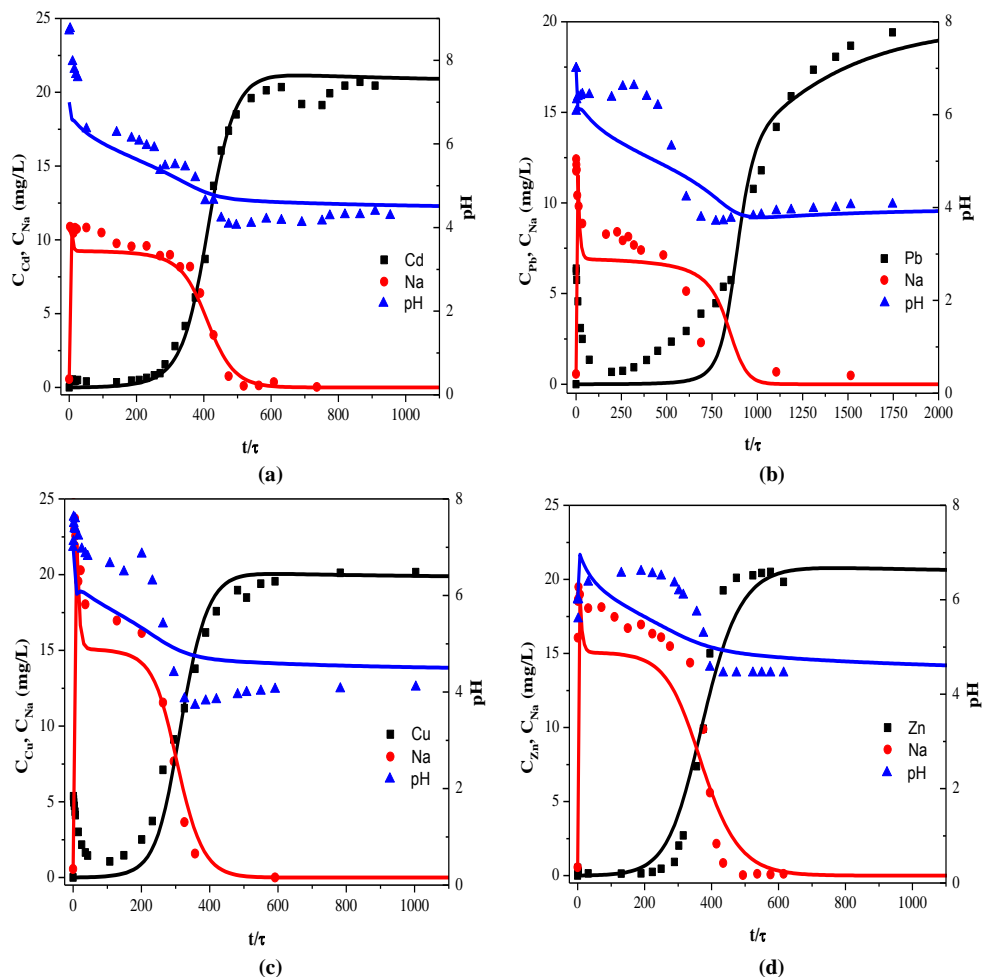


Figure 1 – Experimental breakthrough curves for the systems $\text{Na}^+/\text{H}^+/\text{Cd}^{2+}$ (a), $\text{Na}^+/\text{H}^+/\text{Pb}^{2+}$ (b), $\text{Na}^+/\text{H}^+/\text{Cu}^{2+}$ (c) and $\text{Na}^+/\text{H}^+/\text{Zn}^{2+}$ (c) with the mass transfer model curves (—). Operation parameters: for Cd^{2+} $Q = 20.5$ mL/min; pH = 4.4; for Pb^{2+} $Q = 17.1$ mL/min; pH = 4.0; for Cu^{2+} $Q = 25.0$ mL/min; pH = 4.4; for Zn^{2+} $Q = 24.6$ mL/min; pH = 4.4.

The breakthrough time for zinc, copper, cadmium and lead are approximately 36, 38, 42 and 85, respectively. However, the feed metal concentration, in terms of mmol/L, was different for each ternary systems, $\text{Pb}^{2+} < \text{Cd}^{2+} < \text{Zn}^{2+} \approx \text{Cu}^{2+}$ ($[\text{Cd}] = 0.18$ mmol/L; $[\text{Pb}] = 0.10$ mmol/L; $[\text{Cu}] \approx [\text{Zn}] = 0.31$ mmol/L).

The length of the mass transfer zone (L_{MTZ}) values are 25, 25, 19 and 12 cm and the fraction of unused bed (LUB) values are 71, 79, 63 and 35% for Cd^{2+} , Pb^{2+} , Cu^{2+} and Zn^{2+} , respectively. This means that a mass transfer zone cannot be formed for Cd^{2+} , Pb^{2+} and Cu^{2+} , because the L_{MTZ} value is higher than the column length (17.5, 15.6 and 15.5 cm, respectively), resulting in a very high non-used bed fraction. Similar results were obtained by Costa et al. (2010) and Vilar et al. (2008). In order to achieve better results, the length of the column should be two or three times longer than the MTZ.

Figure 1 b-c shows a premature breakthrough of lead and copper ions, which can be mainly associated to “preferred pathways” through the bed, leading to the occurrence of channeling effects. Normally, in order to avoid wall effects, column-to-particle diameter ratios higher than 30-50 must be used. In our case, considering that the equivalent spherical diameter of the algae thin plate is 1 mm, which corresponds to a column-to-particle diameter ratio of approximately 25. Beyond that, algae particles length is very heterogeneous, which difficult the correct bed packing leading to channeling effects, and consequently to a high fraction of non-used bed.

The uptake capacities at the end of the experiments were 0.68 mmol Cd/g, 0.88 mmol Pb/g, 0.99 mmol Cu/g and 0.92 mmol Zn/g (pH \approx 4.0). Comparing the uptake capacities obtained in the packed bed system and those at batch system, there is a difference of 36, 15, 12 e 14% for Cd²⁺, Pb²⁺, Cu²⁺ and Zn²⁺, respectively, which are associated to the problems reported above. In future works, in order to increase the bed utilization, columns of greater length and smaller algae particles must be used in order to avoid preferential paths.

In order to predict the breakthrough curves for the ternary systems, a mass transfer model was fitted to the experimental results. The mass transfer model was developed considering the following assumptions: (i) the process occurs in isothermal conditions; (ii) axial dispersed plug flow of the fluid phase; (iii) adsorption equilibrium in the solid/liquid interface is described by the mass action law; (iv) internal mass transfer resistance described by a linear driving force model (LDF). The Cd²⁺, Pb²⁺, Cu²⁺ and Zn²⁺ breakthrough curves obtained with the mass transfer model and also the predicted profiles of pH and sodium ions are presented in Figure 1 (a – d). The mass transfer resistance for each species used for simulation was those obtained from the batch kinetics. A small Peclet number was used for simulation indicating a high axial mixing, which reduces the efficiency of separation. The high axial dispersion or longitudinal mixing can be attributed to the high liquid velocity and low column-to-particle diameter ratio used in this study. Considering that 36, 15, 12 and 14% of the capacity of the column was not saturated with Cd²⁺, Pb²⁺, Cu²⁺ and Zn²⁺, respectively, it can be observed that the model adequately predicts the experimental results (Figure 1 (a – d)). The mass transfer model can thus be used to predict the breakthrough curve for adsorption of metal ions in a fixed-bed column.

Desorption experiments were also performed (data not showed) by using HNO₃ 0.1 M, showing a fast and 100% efficient process, achieving a maximum metal concentrations of approximately 2.8, 3.8, 1.5 and 1.8 g/L at the outlet of the column at the 6.5, 3.0, 4.0 e 8.0 min of operation for cadmium, lead, copper and zinc ions, respectively. This indicates the possible reuse of biomass in consecutive adsorption/desorption cycles.

3.2. Na⁺/H⁺/Cd²⁺/Pb²⁺/Cu²⁺/Zn²⁺ System

Figure 2 (a) presents the breakthrough curves for a six-component system (Na⁺/H⁺/Cd²⁺/Pb²⁺/Cu²⁺/Zn²⁺), considering also the profile of pH and concentration of counter-ion (sodium).

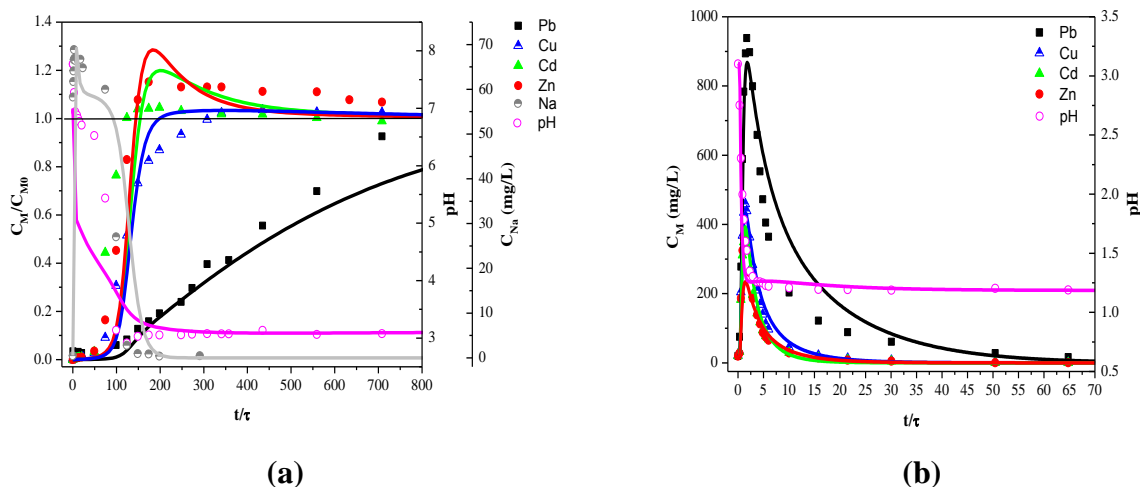


Figure 2 – Experimental breakthrough curves for the system $\text{Na}^+/\text{H}^+/\text{Cd}^{2+}/\text{Pb}^{2+}/\text{Cu}^{2+}/\text{Zn}^{2+}$ (a) and elution curves (b), with the mass transfer model curves (—). Operation parameters: for saturation $Q = 20.6 \text{ mL/min}$; $\text{pH} = 3.1$; and for elution $Q = 22.5 \text{ mL/min}$; $\text{pH} = 1.2$

The uptake capacities at the end of the experiments were 0.10 mmol Cd/g , 0.25 mmol Pb/g , 0.35 mmol Cu/g and 0.20 mmol Zn/g ($\text{pH} \approx 3.0$). It can observe that when four-metals coexisted, the adsorption capacity per metal ion decreased when comparing with single metal system. This was due to the competition between the different metal for the same active binding sites. However, the total biosorption capacity achieved for the four-metal mixture is similar to that obtained using one-metal system.

In the sorption process, Cd and Zn break through the column faster than Cu and Pb, which is in agreement with the selectivity coefficients, indicating the higher affinity of lead ions to the binding sites, followed by copper and cadmium and zinc. A significant overshoot in the outlet Cd and Zn concentration was observed and explained by competitive adsorption between all the metal ions, whereby the higher Pb affinity for the biosorbent displaces bound Cd and Zn ions. The amount of Cd^{2+} , Pb^{2+} , Cu^{2+} and Zn^{2+} bound to the biomass was similar to the sum of sodium released from the biomass, which indicates that the binding mechanism is an ion exchange process.

Figure 2 (a) illustrates the breakthrough curves simulated for all ionic species ($\text{Na}^+/\text{H}^+/\text{Cd}^{2+}/\text{Pb}^{2+}/\text{Cu}^{2+}/\text{Zn}^{2+}$) involved in the process. The mass transfer model was able to describe well all the species involved in the process, even taking into account that *P. canaliculata* is a natural material with a high heterogeneity of binding sites and the system under study involves six species.

Figure 2 (b) presents cadmium, lead, copper and zinc elution curves and the pH profile. Desorption experiments were also performed by using HNO_3 0.1 M . Desorption of biomass was an efficient and fast process. The mass transfer model simulated elution curves (Figure 2 (b)) for the four-metal solutions were obtained and are in a good agreement with the experimental data.

3.3. Ion-exchange pilot plant

The vast majority of scientific publications display studies on the removal/recovery of metals from aqueous solution containing only one or two metal species and using laboratory scale prototypes.

In order to evaluate the potential of macroalgae *P. canaliculata* for the treatment of metal containing wastewaters at pilot plant scale, preliminary tests were performed using a multi-metal system ($\text{Cd}^{2+}/\text{Pb}^{2+}/\text{Cu}^{2+}/\text{Zn}^{2+}$) and raw algae. Figure 3 (a) presents the breakthrough curves for the four metal ions. The feed rate used was approximately 190 mL/min with a feed concentration of ≈ 20 mg/L of each metal and $\text{pH} \approx 4.0$. An overshoot for Cd, Zn and Cu concentration can be observed in Figure 3, suggesting competition between Pb and others metals for the binding sites. The biosorption capacities obtained in the pilot plant were lower than those obtained in laboratory scale, since the experiment was interrupted before the complete saturation of the column. Desorption of all metals was 100% efficient and fast using a 0.1 M HNO_3 solution (Figure 3 (b)).

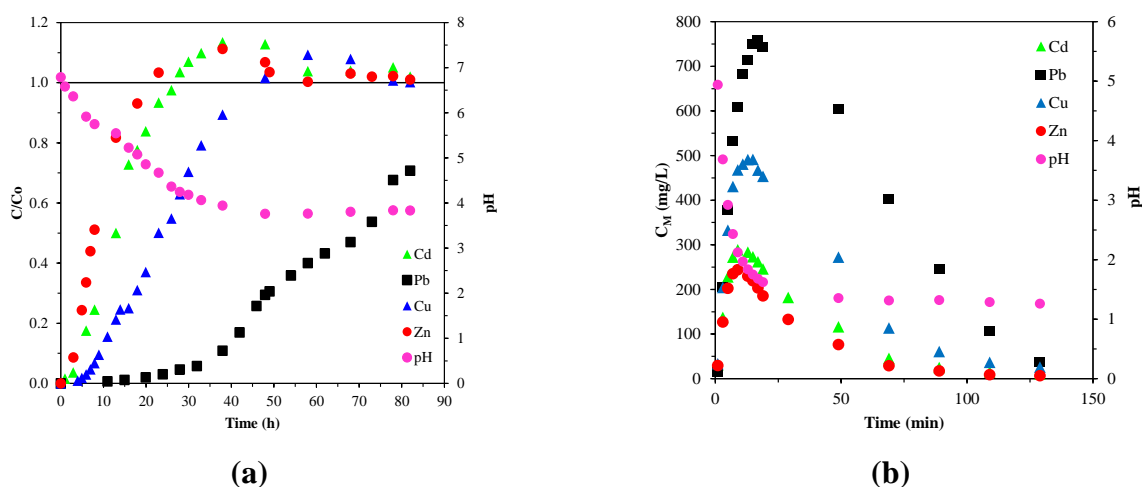


Figure 3 – Experimental breakthrough curves for the system $\text{Cd}^{2+}/\text{Pb}^{2+}/\text{Cu}^{2+}/\text{Zn}^{2+}$ (a) and elution curves (b) on a pilot plant using raw algae. Operation parameters: for saturation $Q = 190$ mL/min; $\text{pH} = 3.8$; and for elution $Q = 190$ mL/min; $\text{pH} = 1.3$

The lack of information on multi-metal systems and at pilot plant scale is the main drawback for real applications of the biosorption technology. These preliminary tests show that the pilot plant is a good tool to study the application of these raw materials, as a low cost sorbents, alternative to ion exchange resins and activated carbon sorbents.

4. CONCLUSIONS

This study investigated the ion exchange process between the cations Cd^{2+} , Pb^{2+} , Cu^{2+} , Zn^{2+} and Na^+ in a fixed-bed column packed with Na-loaded macroalgae *P. canaliculata*. Experimental data for ternary and senary metal biosorption ($\text{Na}^+/\text{H}^+/\text{Cd}^{2+}$, $\text{Na}^+/\text{H}^+/\text{Pb}^{2+}$, $\text{Na}^+/\text{H}^+/\text{Cu}^{2+}$, $\text{Na}^+/\text{H}^+/\text{Zn}^{2+}$ and $\text{Na}^+/\text{H}^+/\text{Cd}^{2+}/\text{Pb}^{2+}/\text{Cu}^{2+}/\text{Zn}^{2+}$) in a packed bed column revealed that the binding mechanism is an ion

exchange process. Algae *P. canaliculata* is an adsorbent comparable in terms of adsorption capacity to others adsorbents and also presents a good performance for multi-metal systems. Mass transfer model for the biosorption and desorption was applied for the design of continuous biosorption processes in a packed bed column. These models were able to predict the experimental data for biosorption and desorption steps of ternary and senary systems. The desorption step was efficient and fast, using a 0.1 M HNO₃ solution as eluent.

5. REFERENCES

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