



MACRO-ALGAE *PELVETIA CANALICULATA* AS A NATURAL CATION EXCHANGER FOR METAL IONS REMOVAL AND SEPARATION: A CASE STUDY ON SENARY SYSTEMS ($\text{Na}^+/\text{H}^+/\text{Pb}^{2+}/\text{Cd}^{2+}/\text{Cu}^{2+}/\text{Zn}^{2+}$)

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ABSTRACT: The aim of this study was to investigate the cation exchange capacity of the macro-algae *Pelvetia canaliculata* (Linnaeus) Decaisne & Thuret for Cd^{2+} , Pb^{2+} , Cu^{2+} and Zn^{2+} removal from aqueous solutions. The competitive biosorption of cadmium, lead, copper and zinc onto brown alga from metals mixture was studied in a batch stirred system. Na-loaded algae was established as a cation exchanger, in which cadmium, lead, copper and zinc ions present in the solution exchange with Na^+ bound to the functional groups on the algae surface.

A mass action law for the mixture ($\text{Na}^+/\text{H}^+/\text{Cd}^{2+}/\text{Pb}^{2+}/\text{Cu}^{2+}/\text{Zn}^{2+}$) was able to predict the equilibrium data, where the selectivity coefficients showed a higher preference (affinity) of the biomass towards lead ions. A mass transfer model, considering equilibrium given by the mass action law, and a linear driving force model for intraparticle diffusion, was able to fit well the batch kinetic experimental data for all the species in the liquid and solid phase.

KEYWORDS: biosorption; macro-algae; metals; mass transfer model; ion exchange.

1. INTRODUCTION

Given the importance of controlling the pollution of water resources due to the indiscriminate disposal of heavy metals, there is a need to develop new friendly technologies able to remove those hazardous metals at low cost (Torab-Mostaedi et al., 2013; Oliveira et al., 2014). The presence of heavy metals in the environment has become a major threat due to their tendency to accumulate in living organisms because they are non-biodegradable, thus exhibiting high toxicity even in relatively low concentrations (Sarı et al., 2011; Abdel -Aty et al., 2013). The main metals that have received attention due to its accumulation in soils, plants, rivers and groundwater are lead (Pb), cadmium (Cd), copper (Cu), zinc (Zn), nickel (Ni),

chromium (Cr) and mercury (Hg) (Torab-Mostaedi et al., 2013).

The biosorption process has received a special attention in the last ten years as a low cost environmental friendly technology that uses raw biomass for the sequestration of heavy metals present in water. This method provides an effective mean of purifying metal containing wastewaters, besides simplicity of design and operation, fast adsorption and desorption kinetics, availability of biosorbents worldwide and the possibility of biomaterial reusability (Zouboulis et al., 2004; Vilar et al., 2012).

The biosorption process has been attributed to the interaction of the metal ions with the negatively charged functional groups present in the surface of the biomass, such as carboxylic and sulfonic groups (Gadd, 2009; Hackbarth et al.,



2014). The main binding mechanisms have been associated to surface complexation, ion-exchange, and micro-precipitation, which can occur individually or combined (Zouboulis et al., 2004; Oliveira et al., 2014). Many biosorbents including bacteria (Özdemir et al., 2009), fungi (Tunali et al., 2006), algae (Ibrahim, 2011; Dittert et al., 2012; Abdel -Aty et al., 2013), industrial waste (Torab-Mostaedi et al., 2013), agricultural wastes (Singh et al., 2006; Santos et al., 2011), and other polysaccharide materials had been investigated as possible biosorbents for metal binding (Vijayaraghavan; Yun, 2008). Among these biosorbents used for biosorption, algae are an inexpensive, readily available source of biomass (Sari et al., 2011).

The main objective of this work was to determine the cation exchanger capacity of Na-loaded *Pelvetia canaliculata* algae, for cadmium, copper, lead and zinc ions in aqueous solutions. An equilibrium ion-exchange model, considering two different binding sites, carboxylic and sulfonic groups, was developed to describe the equilibrium data for the mixture $\text{Na}^+/\text{H}^+/\text{Cd}^{2+}/\text{Pb}^{2+}/\text{Cu}^{2+}/\text{Zn}^{2+}$. A mass transfer model, considering intraparticle resistance was also developed to describe batch kinetic profiles for all the species in the liquid and solid phase.

2. EXPERIMENTAL METHODS

2.1. Biomass Preparation

The brown seaweed *P. canaliculata* (*Phaeophyceae*) was collected at Viana do Castelo ("Praia Norte" beach), Northern coast of Portugal, during May of 2012. The seaweeds were washed with tap water and afterwards with D.I. water to remove sand and excess salts, air-dried over two days, dried in an oven overnight at 45°C, and finally stored until use (raw biomass). Then the raw biomass was converted to the sodium ionic form (Na-biomass) by soaking it into 0.5 M NaCl solution for two 12 h-cycles under stirring. After each cycle, the old solution was replaced by a fresh one. Afterwards, the Na-loaded algae were rinsed with D.I. water until achieving a solution with low conductivity. Finally the algae were dried at 45°C in an oven for 24 h and stored until use.

2.2. Solutions 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. The pH of each test solution was adjusted to the required value with diluted HCl and NaOH solutions. 0.5 M of NaCl solution was prepared by dissolving NaCl salt (Merck) in deionized (D.I.) water.

2.3. Batch Sorption Studies

Sorption kinetics experiments were carried in 100 mL capped Erlenmeyer flasks containing 50 mL of a solution containing a equimolar concentration of Cd^{2+} , Cu^{2+} , Pb^{2+} and Zn^{2+} (initial concentration of each metal ≈ 0.5 mmol/L) and 0.025 g of biomass Na-loaded algae, which were placed inside a thermostatic cabinet, in order to ensure a constant temperature (25 °C), under constant orbital shaking (170 rpm) (VWR Advanced digital system), until equilibrium was achieved. After adjusting the initial metal solution pH to the predefined value, no further pH adjustment was done and pH was recorded during the experiment. Samples were collected (each Erlenmeyer flask corresponds to one sample) at predetermined time intervals, filtered by cellulose acetate membrane filters (Sartorius Stedim) and the residual contaminants (Cd, Cu, Pb or Zn) and the exchangeable metal (Na) concentrations were determined by atomic absorption spectrometry (AAS). The experiments were carried at an initial pH value of 4.0

Equilibrium studies were studied by varying the initial concentration of the four-metal solution (Cd^{2+} , Cu^{2+} , Pb^{2+} and Zn^{2+}) from 0.1 to 1.5 mmol/L. The initial pH of the metal mixture solution was 4.0. The equilibrium experiments were carried out in duplicate. The biomass (0.5 g/L) was added to 50 mL of the four-metal solution in a 100 mL Erlenmeyer flask, under constant stirring (170 rpm) using an orbital stirrer (VWR Advanced digital system), which was placed inside a thermostatic cabinet to ensure a constant temperature of 25 °C. After the system reached equilibrium, samples were collected, filtered (cellulose acetate membrane filters, Sartorius Stedim) and the residual cadmium, copper, lead, zinc and sodium concentrations were determined by AAS. The final pH value for each equilibrium point was registered.

2.4. Analytical Procedures

The concentrations of Cd^{2+} , Cu^{2+} , Pb^{2+} , Zn^{2+} and Na^+ in aqueous solution were determined by

AAS (GBC 932 Plus, Perkin Elmer) using deuterium background correction and a spectral slit width of 1 nm for Pb²⁺, 0.5 nm for Cd²⁺, Cu²⁺, Zn²⁺ and Na⁺. The working current/wavelength was adjusted to 3 mA/228.8 nm for Cd²⁺, 3.0 mA/324.7 nm for Cu²⁺, 5.0 mA/217 nm for Pb²⁺, 5.0 mA/213.9 nm for Zn²⁺ and 5 mA/330.4 nm for Na⁺, giving a detection limit of 0.04 mg/L for Cd²⁺, 0.2 mg/L for Cu²⁺, 0.2 mg/L for Pb²⁺, 0.07 mg/L for Zn²⁺ and 0.4 mg/L for Na⁺. In the analysis of Na⁺, KCl (0.38% (w/v)) was added respectively to minimize ionization interferences. The instrument response was periodically checked by using standard solutions.

3. RESULTS AND DISCUSSION

3.1. Ion Exchange Equilibrium for the Na⁺/H⁺/Cd²⁺/Pb²⁺/Cu²⁺/Zn²⁺ System

In our previous studies using ternary systems, Na⁺/H⁺/Cd²⁺, Na⁺/H⁺/Cu²⁺, Na⁺/H⁺/Zn²⁺ and Na⁺/H⁺/Pb²⁺, the maximum ion-exchange capacity for Cd²⁺ and Pb²⁺ was 1.25 mmol/g (Hackbarth et al., 2014), for Cu²⁺ 1.15 mmol/g and for Zn²⁺ 1.20 mmol/g (Girardi et al., 2014) using the macro-algae *P. canaliculata* Na-loaded. Hackbarth et al. (2014) combining potentiometric titration, FTIR and esterification techniques showed the presence of two major functional groups (acidic and basic functional groups) in the surface of the brown marine macro-algae *P. canaliculata*. The total number of exchangeable binding sites was found to be 2.50 ± 0.01 and 0.8 ± 0.1 mmol/g for acidic and basic functional groups, respectively. Hackbarth et al. (2014) showed that after biomass *P. canaliculata* esterification, the metal binding capacity decreased significantly, and concluded that the amount of sulfonic and carboxylic groups was ~1.0 mmol/g and ~1.5 mmol/g, respectively, which is in agreement with the total amount of sodium ions present in the surface of Na-loaded biomass (~2.5 mEq/g).

In the present study the maximum biosorption capacity for Cd²⁺ was 0.05 mmol/g, for Pb²⁺ 0.72 mmol/g, for Cu²⁺ 0.26 mmol/g and for Zn²⁺ 0.11 mmol/g, totalizing 2.28 mEq/g, which corresponds to the saturation of 91% of the binding sites. The total biosorption capacity achieved for the four-metal mixture is similar to that obtained using one-metal system (Girardi et al., 2014; Hackbarth et al., 2014).

The four-metal ion-exchange equilibrium indicates that the presence of one metal lowers substantially the binding capacity of the other metal, which means that competition to the binding sites occurs between the metals.

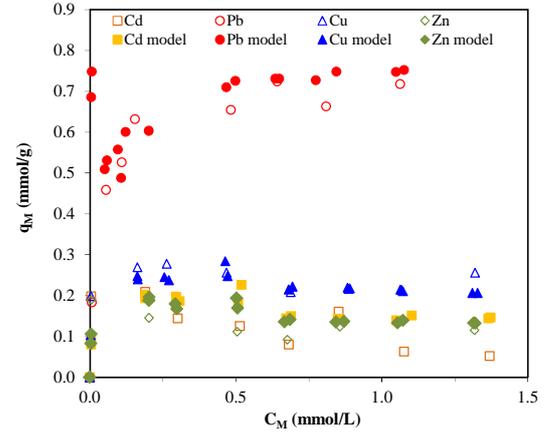


Figure 1. Ion exchange equilibrium for Na⁺/H⁺/Cd²⁺/Pb²⁺/Cu²⁺/Zn²⁺ system: experimental data and mass action law prediction

A mass action law, considering monovalent carboxylic and sulfonic functional groups initially saturated with sodium ions, and the exchange reactions with Cd²⁺, Pb²⁺, Cu²⁺, Zn²⁺ and H⁺, represented by Equations 1-5, was fitted to the batch ion exchange equilibrium data for the Na⁺/H⁺/Cd²⁺/Pb²⁺/Cu²⁺/Zn²⁺ system.

$$q_{H,i} = \frac{-\left(1 + \frac{C_{Na}}{\alpha_{Na,i}^H C_H}\right) + \sqrt{\left(1 + \frac{C_{Na}}{\alpha_{Na,i}^H C_H}\right)^2 + 8 \frac{C_T}{(\alpha_{Na,i}^H)^2 C_H^2} (\alpha_{Na,i}^{Cd} C_{Cd} + \alpha_{Na,i}^{Pb} C_{Pb} + \alpha_{Na,i}^{Cu} C_{Cu} + \alpha_{Na,i}^{Zn} C_{Zn})}}{4 \frac{C_T}{(\alpha_{Na,i}^H)^2 C_H^2 q_T}} \quad (1)$$

$$q_{Cd,i} = \frac{\alpha_{Na,i}^{Cd}}{(\alpha_{Na,i}^H)^2} \frac{C_{Cd}}{C_H^2} \frac{C_T}{q_{T,i}} q_H^2 \quad (2)$$

$$q_{Pb,i} = \frac{\alpha_{Na,i}^{Pb}}{(\alpha_{Na,i}^H)^2} \frac{C_{Pb}}{C_H^2} \frac{C_T}{q_{T,i}} q_H^2 \quad (3)$$

$$q_{Cu,i} = \frac{\alpha_{Na,i}^{Cu}}{(\alpha_{Na,i}^H)^2} \frac{C_{Cu}}{C_H^2} \frac{C_T}{q_{T,i}} q_H^2 \quad (4)$$

$$q_{Zn,i} = \frac{\alpha_{Na,i}^{Zn}}{(\alpha_{Na,i}^H)^2} \frac{C_{Zn}}{C_H^2} \frac{C_T}{q_{T,i}} q_H^2 \quad (5)$$

where $q_{M,i}$ is the concentration of species M (M: Cd²⁺, Cu²⁺, Pb²⁺ or Zn²⁺) in the solid phase for



each functional group i (mmol/g), α is the selectivity coefficients, C_M is the concentration of species M in the liquid phase (mmol/L), C_T is the total concentration of species j in the liquid phase (mEq/L), C_H is the concentration of protons in the liquid phase (mmol/L) and $q_{T,i}$ is the amount of binding sites ($i = 1$ – carboxylic groups; $i = 2$ – sulfonic groups) (mEq/g).

Figure 1 shows that the mass action law is able to fit well the equilibrium points for all the metal ions in the $\text{Na}^+/\text{H}^+/\text{Cd}^{2+}/\text{Pb}^{2+}/\text{Cu}^{2+}/\text{Zn}^{2+}$ system, considering the selectivity coefficients obtained for the ternary systems $\text{Na}^+/\text{H}^+/\text{Cd}^{2+}$, $\text{Na}^+/\text{H}^+/\text{Cu}^{2+}$, $\text{Na}^+/\text{H}^+/\text{Zn}^{2+}$ and $\text{Na}^+/\text{H}^+/\text{Pb}^{2+}$, at different pH values (Girardi et al., 2014; Hackbarth et al., 2014). Table 1 presents the selectivity coefficients for all exchange ion pairs and for the two functional groups, as also the correlation coefficient and the sum of squares of the residuals.

This means that the selectivity coefficients determined for one-metal system can be used for the equilibrium prediction in multi-metal systems.

The selectivity coefficients of the algae increase in the following order: $\text{Na}^+ < \text{H}^+ < \text{Cd}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+} < \text{Pb}^{2+}$ (for carboxylic groups) and $\text{Na}^+ < \text{H}^+ < \text{Zn}^{2+} < \text{Cu}^{2+} < \text{Cd}^{2+} < \text{Pb}^{2+}$ (for sulfonic groups) which indicates that carboxylic and sulfonic

groups have a higher preference (affinity) to Pb^{2+} (Table 1). The higher affinity of Pb^{2+} to sulfonic groups can be attributed to Hard and Soft Acid and Base theory (HSAB theory) (Pearson, 1963). Zinc and cadmium ions exhibit similar selectivity, which hinders the separation of each one in a multi metal system.

Through Figure 1, it can be seen that for low metal concentrations, the uptake capacity of Cd^{2+} , Cu^{2+} and Zn^{2+} is greater than for high metal concentrations; this occurs because for low metal concentrations, the amount of active sites are sufficient for the binding of the metal ions present in the solution. For high metal concentrations, all the binding sites will be occupied easily by the metal ions, and competition between the metal species for the same binding sites occurs. In this situation, lead ions have a higher affinity to the binding sites and will displace the copper, zinc and cadmium ions previously bound. This phenomenon is more pronounced for Cd and Zn. For the same equilibrium concentrations of metals (1.4 mmol/L each), approximately 58% of the binding sites are occupied by Pb, indicating that this metal has a higher affinity for the active site (Table 1). Therefore, Pb ions will preferentially adsorbed, even in the presence of Cd^{2+} , Cu^{2+} and Zn^{2+} ions.

Table 1. Ion exchange equilibrium model parameters.

Metal	Carboxylic groups			Sulfonic groups			R^2	S_R^2 (mmol/g) ²
	q_T (mmol/g)	α_{Na}^M	α_{Na}^H	q_T (mmol/g)	α_{Na}^M	α_{Na}^H		
Cd^{2+}		337			38			
Cu^{2+}		521			29			
Pb^{2+}	1.5	941	10	1	1695	22	0.918	1.2×10^{-2}
Zn^{2+}		341			11			

3.2. Ion Exchange Kinetics for the $\text{Na}^+/\text{H}^+/\text{Cd}^{2+}/\text{Pb}^{2+}/\text{Cu}^{2+}/\text{Zn}^{2+}$ System

Figure 2 show the ion exchange kinetic experimental data for system $\text{Na}^+/\text{H}^+/\text{Cd}^{2+}/\text{Pb}^{2+}/\text{Cu}^{2+}/\text{Zn}^{2+}$ ($[\text{Cd}^{2+}]_0 = [\text{Pb}^{2+}]_0 = [\text{Cu}^{2+}]_0 = [\text{Zn}^{2+}]_0 = 0.5$ mmol/L) at pH 4.0. Kinetic profile of all species in the liquid (protons, sodium, cadmium copper, lead and zinc ions) (Figure 2a) and solid phase (cadmium, copper, lead and zinc ions) (Figure 2b) is also represented.

The trapping of cadmium, copper, lead and zinc ions takes place by the release of sodium ions,

initially bound to the functional groups present at the surface of the biomass, which indicates that the binding mechanism is an ion exchange process with a stoichiometric ratio 2:1 between sodium and transition metals. Ion-exchange between protons and sodium ions also occurs, which is observed by the increase of pH.

The process of ion exchange reaches equilibrium in less than 150 minutes. Removals of 23%, 25%, 29% and 51% were obtained for Cd^{2+} , Zn^{2+} , Cu^{2+} and Pb^{2+} , respectively. These values are lower than those obtained by Hackbarth et al. (2014) and Girardi et al. (2014) in the single-metal systems using the same algae, collected in the same location

and season, indicating competition between metal ions for the binding sites. The uptake capacity for the multi-metal system increased in the following order $Zn < Cd < Cu < Pb$, which is in agreement with the selectivity coefficients, indicating that lead ions has a higher affinity for the active sites present in the biomass.

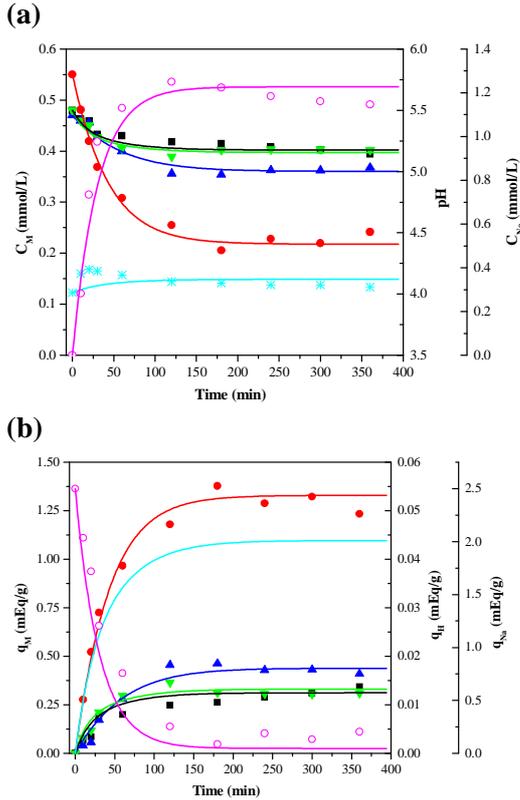


Figure 2. Experimental (points) and estimated (lines) ionic species concentration at the liquid (a) and solid (b) phase, for the multi-metal biosorption on Na-loaded algae at pH 4.0. ■ – Cd^{2+} , ● – Pb^{2+} , ▲ – Cu^{2+} , ▼ – Zn^{2+} , ○ – Na^+ , * – pH.

According to previous results (Costa et al., 2010; Bhatnagar et al., 2012; Hackbarth et al., 2014), the ion exchange process at batch system, assuming uniform dimensional thin plates particles, is controlled by the diffusive contribution of ionic species in the solid phase, given by a linear driving force model (Equation 7) (Glueckauf; Coates, 1947), where the relationship between the ions species at equilibrium is given by the mass action law (Equations 1-5).

$$\frac{d\langle q_j \rangle}{dt} = k_{p,j} \times a_p [q_j^* - \langle q_j \rangle]; \quad a_p = \frac{1}{R};$$

$$k_{p,j} \times a_p = \frac{D_{h,j}}{3R^2} = \frac{3}{\tau_{d,j}} \quad (7)$$

Initial conditions:

$$t = 0, C_H = 10^{(-pH_0 + 3)} \text{ mmol/L}, C_{Na} = 0 \text{ mmol/L}, C_{Pb} = C_{Pb,0} \text{ mmol/L}, C_{Cd} = C_{Cd,0} \text{ mmol/L},$$

$$\langle q_{Pb} \rangle = \langle q_{Cu} \rangle = \langle q_{Cd} \rangle = \langle q_{Zn} \rangle = 0 \text{ mmol/g}; \langle q_{Na} \rangle = 2.5 \text{ mmol/g.}$$

where $k_{p,j}$ is the mass transfer coefficient for intraparticle diffusion of species j (cm/s), $D_{h,j}$ is the coefficient of homogeneous diffusion inside the particle for each species j (cm^2/s), a_p the specific area of the thin plate particles (1/cm), $\tau_{d,j}$ is the time constant for diffusion of ionic species into the particle (s), q_j^* is the equilibrium concentration in the solid phase and R is half of the thin plate thickness (cm). The system of ordinary differential equations (ODE's initial value problem) was integrated in time using the solver LSODA (Petzold, 1983).

Figure 2 present the predicted concentration for all ionic species at the liquid and solid phase, which are in a good agreement with the experimental data.

Table 2 presents the intraparticle homogeneous diffusion coefficient (D_h) and diffusion time constant (τ_p) for Na-algae at pH 4.0 considering the thickness of the thin plate particles as 1.0 mm ($R = 0.05mm$).

In the multi-metal system, the diffusion time was lower than those reported by Hackbarth et al. (2014) and Girardi et al. (2014) for single-metal systems using the same algae, with exception for Cu^{2+} . This happens because in the multi-metal system, the total concentration of the metals ions is higher than that used in the single metal systems, and consequently the driving force is higher.

In general, the values of the homogeneous diffusivity of metal ions in the multi-metal system are higher than those determined in single-metal systems reported by Hackbarth et al. (2014) and Girardi et al. (2014), because the concentration



gradient in the multi-metal system is higher, reducing the resistance to mass transfer and increasing the diffusivity of homogeneous metal ions.

Table 2. Estimated parameters for the mass transfer model ($C_0 = 0.5$ mmol/L; $T = 25$ °C).

Ion	$k_p x a_p$ (1/min)	τ_d (min)	D_h (cm ² /s)*	S_R^2 (mmol/L) ²
Cd ²⁺	6.0×10^{-2}	50	3.4×10^{-9}	0.2
Pb ²⁺	1.8×10^{-2}	164	2.6×10^{-9}	0.2
Cu ²⁺	2.1×10^{-2}	142	3.0×10^{-9}	0.2
Zn ²⁺	5.3×10^{-2}	57	7.4×10^{-9}	0.2
Na ⁺	3.2×10^{-2}	92	2.7×10^{-9}	0.2
H ⁺	2.4×10^{-2}	127	3.3×10^{-9}	0.2

* $R = 0.05$ mm; $V = 0.05$ L; $W = 0.025$ g.

4. CONCLUSIONS

Considering that *P. canaliculata* is an abundant algae waste product on the beaches of Portugal, its recovery and use as a potential natural cation exchanger of heavy metals could represent an economically attractive industry for local economies.

This paper showed that sodium-treated *P. canaliculata* is a suitable cation exchanger for Cd²⁺, Pb²⁺, Cu²⁺ and Zn²⁺ ions. The release of sodium ions during the uptake of Cd²⁺, Pb²⁺, Cu²⁺ and Zn²⁺ ions revealed that the current biosorption mechanism involves ion-exchange. Apart from carboxylic groups, which can be considered the main chemical group responsible by the Cd²⁺, Pb²⁺, Cu²⁺ and Zn²⁺ sequestration, other chemical groups such as sulfonic groups also represent an important role in the transition metals binding. A mass action law for the multi-metal system, Cd²⁺/Pb²⁺/Cu²⁺/Zn²⁺/H⁺/Na⁺, was able to predict well the equilibrium data. Selectivity coefficients indicate a higher affinity of Pb²⁺ ions for the binding groups, followed by Cu²⁺, Cd²⁺ and Zn²⁺ ions. A mass transfer model, considering that the ion exchange limiting step is the intraparticle ion diffusion, was able to fit the concentration profile of all ionic species at the liquid and solid phases. The understanding of the ion-exchange process in multi-metal systems is essential for development of appropriate management strategies for wastewater treatment.

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