



MARINE MACROALGAE *PELVETIA CANALICULATA* AS CATION EXCHANGER FOR COPPER AND ZINC IONS REMOVAL FROM AQUEOUS SOLUTIONS

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ABSTRACT: The aim of this study was to investigate the cation exchange capacity of the macro-algae *Pelvetia canaliculata* for Cu²⁺ and Zn²⁺ removal from aqueous solutions. FTIR and potentiometric titration techniques allowed the identification and quantification of the major acid binding groups ([carboxylic] + [sulfonic groups] = 2.5 mEq/g) present in the surface of the natural cation exchanger responsible by Cu²⁺ and Zn²⁺ binding. Tests with the raw algae showed that sodium, potassium magnesium and calcium are easily replaced by copper and zinc ions. The selectivity coefficients of copper and zinc for carboxylic groups were much higher than for sulfonic groups. The selectivity coefficients of copper or zinc vs hydrogen were much lower than with sodium, indicating that hydrogens ions can compete for the same binding sites, decreasing strongly the copper and zinc ions removal at low pH values.

KEYWORDS: natural cation exchangers; macro-algae; functional groups; ion-exchange.

1. INTRODUCTION

Pollutants, such as heavy metals, are often released into aquatic environments as a result of anthropogenic activities, including mining and ore processing industry, metal processing, smelting industries, as also, textile, leather, microelectronics, fertilizers and pesticides industry (Patterson 1985; Volesky 2001). The high toxicity and cumulative effect of these heavy metals are often reported to have harmful effects to human health and other living beings (Alpatova *et al.* 2004). Copper and zinc ions are among the most common heavy metals present in these kinds of wastewaters. While the accumulation of copper ions in human body causes brain, skin, pancreas and heart diseases, the main symptoms of zinc poisoning are dehydration, electrolyte imbalance, stomachache, nausea, dizziness and incoordination in muscles (Jain *et al.* 2004).

Biosorption uses biological materials, which are abundant in nature, such as seaweeds and wastes, to concentrate and immobilize heavy metals (Vilar *et al.* 2008; Vilar *et al.* 2009; Vilar *et al.* 2012). The efficiency of the biosorption process for removal of metals is comparable to the ion exchange treatment even for low pH and high salinity (Vilar *et al.* 2009; Vilar *et al.* 2009; Bhatnagar *et al.* 2012). Effluents with metal ion concentrations in the order of ppb can be achieved using biosorption. While commercial ion exchange resins are rather costly, the price tag of biosorbents can be one tenth of that of the resin. Additional cost reduction results from the possible heavy metals recovery, since a high concentration ratio (>400) can be achieved using a fast desorption process with an acidic solution (nitric acid solution at pH = 1.0) (Vilar *et al.* 2007; Vilar *et al.* 2008; Vilar *et al.* 2009; Costa *et al.* 2010).

The major challenge of this work was to evaluate the cation exchanger properties of the



brown marine macro-algae, *P. canaliculata*, for copper and zinc ions, two of the major ions found in industrial metal processing wastewaters, removal from aqueous solutions. The ion exchange capacity, selectivity coefficients for the sodium loaded biomass, as also the intraparticle ionic diffusion coefficients were evaluated considering the ternary systems $\text{Na}^+/\text{H}^+/\text{Cu}^{2+}$ and $\text{Na}^+/\text{H}^+/\text{Zn}^{2+}$, which are important design parameters for an ion exchange treatment process. FTIR and potentiometric titration techniques, coupled with the information provided by the esterification of the binding sites, were used for the identification and quantification of the acid binding groups responsible by copper and zinc sequestration.

2. MATERIALS AND METHODS

2.1. Chemicals

Copper and zinc solutions were prepared by dissolving a weighed amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck > 98%) and ZnCl_2 (Merck > 98%) in ultrapure water. The pH of each test solution was adjusted (pH meter Hanna HI 4522) to the required value with HCl diluted solutions (Merck) and NaOH (Merck). 0.5 M of NaCl was prepared by dissolving sodium chloride (Merck with purity > 99.5%) in deionized (D.I.) water.

2.2. Biomass preparation

Biomass brown alga *P. canaliculata* was sun dried and washed with deionized water to remove the excess of salts and sand followed by drying overnight at 45 °C in an oven. The biomass was then milled (Retsch, ZM 100) and sieved (Retsch, AS 200) to obtain particles with a size of 1-2 mm and finally stored until used (raw biomass).

The prepared raw alga was subsequently converted to the sodium form using a 0.5 M sodium chloride solution (NaCl, Merck trademark), considering 2 washing cycles of 12 hours each under slow stirring. After each cycle, the old solution was replaced with a new fresh prepared solution. Subsequently, Na loaded algae was rinsed with ultrapure water in order to remove the excess of sodium ions in the surface of the biomass. Finally, the algae were dried at 45 °C for 24 hours and stored until used. The prepared algae will be named as sodium loaded algae.

2.3. Blocking of carboxylic and sulfonic groups present in the algae surface

Esterification of carboxylic groups was carried out by suspending 2 g of biomass in methanol (130 mL) and concentrated HCl (1.2 mL) and equilibrated for 6 h at 25 °C (Gardea-Torresdey *et al.* 1990). Then, the biomass was washed with D.I. water and dried at 45 °C for 24 h. For the esterification of sulfonic groups, 2 g of biomass was suspended in 130 mL of methanol and 1.2 mL of concentrated HCl and equilibrated for four cycles of 48 h, in continuous agitation, using fresh methanol/HCl solutions between cycles (Fourest and Volesky 1995).

2.4. Fourier transform infrared analysis (FTIR)

The identification of the functional groups on the surface of the biosorbent was performed by infrared spectroscopy using a Shimadzu FTIR IRAffinity. The algae were analyzed in the solid form using a diffuse reflectance accessory (Pike Technologies Inc., model TM EasiDiff). Spectra were registered from 4000 to 400 cm^{-1} .

2.5. Cation exchange kinetic and equilibrium studies

The cation exchange kinetic and equilibrium experiments were performed in closed 100 mL flasks containing 50 mL of Cu^{2+} or Zn^{2+} solutions (≈ 100 mg/L) and 0.05 g of raw or Na-loaded biomass (1 g/L). The flasks were placed inside a thermostatic refrigerator cabinet (Lovibond) in order to guarantee controlled temperature conditions (25 °C). The suspension was under orbital stirring (VWR Advanced digital system; 170 rpm) until reach equilibrium (24 h).

Copper and zinc exchange kinetic were also performed at three initial solution pH values (2.0, 3.0 and 4.0). After adjusting the desired initial metal solution pH, no further pH adjustment was done and pH was recorded during the experiment. Samples were collected (each erlenmeyer flask corresponds to one point of the kinetic experiment) at predetermined time intervals.

The experiments in equilibrium were carried out in duplicate with initial copper or zinc concentrations in the range of 40 – 360 mg/L, at three different initial pH values (2.0, 3.0 and 4.0). After adjusting the desired initial metal solution



pH, no further pH adjustment was done and pH was recorded for each equilibrium point

Samples (kinetic and equilibrium) filtered by cellulose acetate membrane filters (Sartorius Stedim, 45 μm porosity) and the residual metal concentration (metal contaminant (Cu or Zn) and the exchangeable metals (Ca, Mg, Na and / or K)) was determined by AAS (GBC 932 Plus).

2.6. Analytical procedures

The concentrations of Cu, Zn, Na, K, Ca and Mg in the aqueous solutions were determined by Atomic Absorption Spectrometry (AAS) (GBC 932 Plus) using deuterium background correction and a spectral slit width 0.5 nm for Cu, Zn, Ca, Na and K, and 1.0 nm for Mg. In the analysis of Ca and Mg, La_2O_3 solution (5.86 % (w/v)) was added to the solution (1 mL La_2O_3 per 10 mL solution) in order to minimize chemical interferences, while in the analysis of Na and K, KCl (0.38% (w/v)) and NaCl (0.50% (w/v)) were added respectively to minimize ionization interferences.

3. RESULTS AND DISCUSSION

3.1. FTIR analysis

FTIR spectrums of *P. canaliculata* biomass (Figure 1) in the raw or metal-loaded forms showed different absorption peaks, being possible to obtain information about the chemical bounds present in the surface of the biomass, and correlate with the functional groups responsible by the metal binding.

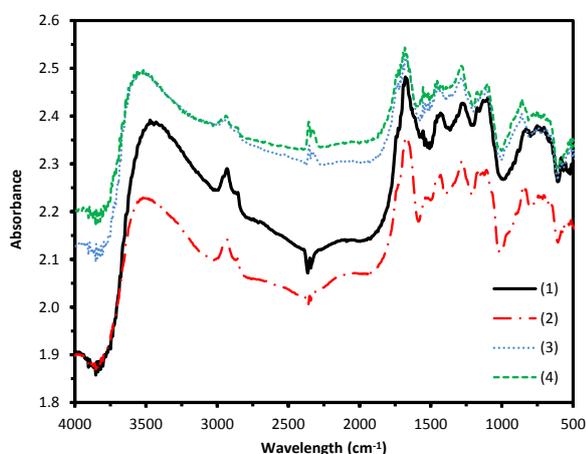


Figure 1. FTIR spectra of different forms of algae: (1) raw algae, (2) Na-loaded algae, (3) Na-loaded algae after copper sorption, (4) Na-loaded algae after zinc sorption.

The region between 3600 and 3200 cm^{-1} corresponds to hydroxyl stretches in several compounds, and N-H stretching bands (amines and amides in amino acids). This band is broad and strong (Figure 1) because of the high number and large density of hydrogen bonds, mainly hydroxyl in the polysaccharide pyranose rings (Shriner, Hermann *et al.* 2004; Oliveira, Hammer *et al.* 2014). FTIR spectrum shows a small shift in the band, which may be correlated with the interaction of cadmium and zinc ions with the $-\text{NH}_2$ groups (Subbaiah, Yuvaraja *et al.* 2011). The bands observed at about 2900 cm^{-1} could be assigned to the $-\text{CH}$ stretch of $-\text{CH}_3$ and $-\text{CH}_2$ groups (Sheng, Ting *et al.* 2004). The carbonyl stretching of carboxylic acids appears close to 1750 cm^{-1} (Costa, Vilar *et al.* 2010; Oliveira, Hammer *et al.* 2014). A band at 1420 cm^{-1} may be due to C-OH deformation vibration with contribution of O-C-O symmetric stretching vibration of carboxylate group (Mathlouthi and Koenig 1987). Carboxyl groups are the most abundant functional groups in polysaccharides and are the main functional groups involved in the biosorption of heavy metals with algae and other biomasses (Davis, Volesky *et al.* 2003; Volesky 2003; Mehta and Gaur 2005).

The band at 1260 cm^{-1} and 1160 cm^{-1} should be assigned to the presence of sulphate ester groups (S=O) which is a characteristic component in fucoidan (Vilar, Botelho *et al.* 2009; Synytsya, Kim *et al.* 2010; Gómez-Ordóñez and Rupérez 2011).

3.2. Blocking of sulfonic and carboxylic groups present at the biomass surface

Carboxylic and sulfonic groups were blocked, trying to elucidate the role of functional groups, present at the surface of the algae *Pelvetia canaliculata*, in the binding of Cu^{2+} and Zn^{2+} . The equilibrium uptake capacity for esterified algae was 43/18% (Cu^{2+}) and 55%/58% (Zn^{2+}) lower than un-esterified one (Na-loaded algae), respectively for pH 4.0 and 2.0, which indicates that carboxylic groups plays a major role in Cu^{2+} and Zn^{2+} sequestration. (Fourest and Volesky 1995) observed a correlation between the degree of blocking of carboxylic groups by esterification in *Sargassum fluitans* and the corresponding decrease in metal uptake.

Although the algae esterification procedure reduced substantially the metal sequestration



capacity, others functional groups present in surface of biomass were not blocked and are responsible for the remaining metal binding. Sulfonic groups, which are present in the sulphated polysaccharide fucoidan (Davis, Volesky *et al.* 2003), has been also reported as one of functional groups responsible by the metal binding principally at low pH values (Crist, Oberholser *et al.* 1992; Davis, Volesky *et al.* 2003; Murphy, Hughes *et al.* 2007; Oliveira, Jouannin *et al.* 2011; Plaza Cazón, Viera *et al.* 2013).

Considering the esterification and potentiometric titration results, and the data reported in a previous work (Hackbarth, Girardi *et al.* 2014), the amount of sulfonic and carboxylic groups can be assumed as ~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 (~2.45 mEq/g) and total amount of light metals in the raw biomass (~2.47 mEq/g).

3.3. Cation exchange kinetics with raw algae

The raw biomass was initially used to carry out the cation exchange kinetics using an initial concentration of 100 mg/L at pH 4.0, in order to evaluate the Zn²⁺ and Cu²⁺ removal mechanism. The release of light metal cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺) from biomass to the solution, as well the uptake of Cu²⁺, Zn²⁺ and H⁺ by the biomass was monitored.

It was found that the amount of Zn²⁺ and Cu²⁺ bound to the raw biomass of *P. canaliculata* was similar to the sum of the light metal released (Na⁺, K⁺, Ca²⁺ and Mg²⁺) from the biomass to the solution. According to the solution pH, the protons uptake was negligible. Hackbarth, Girardi *et al.* (2014) reported values of light metal concentrations of 0.72 mEq Mg²⁺/g, 0.65 mEq Na⁺/g, 0.56 mEq Ca²⁺/g and 0.54 mEq K⁺/g, for the same algae, collected in the same location and season. According to the cation exchange kinetics, potassium and sodium ions are released faster and in higher amounts than magnesium and calcium ions, which indicates that Cu²⁺ and Zn²⁺ exchanges more easily with Na⁺ and K⁺ than Ca²⁺ and Mg²⁺.

3.4. Cation exchange equilibrium with Na-loaded algae

The transition metal exchange easily and faster with sodium ions than others light metals and protonated biomass is not recommended to be used since metal cations present in solution will exchange with the protons on the surface of the resin, decreasing the solution pH and consequently competition for ion exchange sites will increase, affecting greatly the system efficiency.

Selectivity coefficients for the sodium loaded algae were determined for Cu²⁺, Zn²⁺ and H⁺, using ternary equilibrium studies at different pH values and transition metal (Cu and Zn) concentrations. A mass action law, considering monovalent carboxylic and sulfonic functional groups initially saturated with sodium ions, and the exchange reactions with Cu²⁺, Zn²⁺ and H⁺, represented by Equation 1, fitted well the experimental equilibrium data for both ternary systems, Na⁺/H⁺/Cu²⁺ or Na⁺/H⁺/Zn²⁺ resulting in the selectivity constants. A detailed description of the mass action law equation can be found in (Hackbarth, Girardi *et al.*, 2014.).

$$q_{M,i} = \frac{\alpha_{Na,i}^M \cdot C_M \cdot C_T}{(\alpha_{Na,i}^H)^2 \cdot C_H^2 \cdot q_{T,i}} \left\{ \frac{-\left(1 + \frac{C_{Na}}{\alpha_{Na,i}^H C_H}\right) + \sqrt{\left(1 + \frac{C_{Na}}{\alpha_{Na,i}^H C_H}\right)^2 + 8 \frac{\alpha_{Na,i}^M}{(\alpha_{Na,i}^H)^2} \frac{C_M C_T}{C_H^2}}}{4 \frac{\alpha_{Na,i}^M}{(\alpha_{Na,i}^H)^2} \frac{C_M C_T}{C_H^2} q_{T,i}} \right\}^2 \quad (1)$$

where, C_M is the concentration of species M (M : Cu²⁺ or Zn²⁺) in the liquid phase (mmol/L), C_H is the concentration of protons in the liquid phase (mmol/L), C_T is the total normality of the solution (mEq/L), C_{Na} is the concentration of sodium ions in the liquid phase (mmol/L), $q_{T,i}$ is the concentration of exchangeable binding sites (i stands for carboxylic or sulfonic functional groups), $q_{M,i}$ is the metal concentration in the solid phase for each functional group i (mmol/g), $\alpha_{Na,i}^H$ is the selectivity coefficient between sodium and protons for each functional group i (adimensional), and $\alpha_{Na,i}^M$ is the selectivity coefficient between sodium and species M for each functional group i (adimensional).

Selectivity coefficients indicate that Cu²⁺ replace easily Na⁺ than Zn²⁺ and H⁺, for both functional groups. Beyond that, copper and zinc ions have a higher affinity to the carboxylic groups, than to sulfonic groups.

The pH plays an important role on the metals uptake capacity, in which Cu²⁺ and Zn²⁺ sequestration increases strongly with the increase of pH, since at higher pH values, more ionized



functional groups are available for metal binding and competition for the active sites between H^+ and Cu^{2+} or Zn^{2+} decreases due to the lower H^+ concentration. Strong acid resins behave similarly to a strong acid, being highly ionized in both the acid ($R-SO_3H$) and salt ($R-SO_3Na$) form. The hydrogen and sodium forms of strong acid resins are highly dissociated and the exchangeable Na^+ and H^+ are readily available for exchange over the entire pH range. Consequently, the exchange capacity of strong acid resins is independent of solution pH. At pH of 2.0, the carboxylic groups are not ionized and consequently not available for the copper and zinc binding. The maximum uptake capacity of pH 2.0 is approximately 1.0 mEq/g for copper and zinc ions, which correspond to the total amount of strong acid sulfonic groups.

The selectivity coefficients obtained between zinc and protons ($\alpha_{H^+}^{Zn} = 3.4$ and $\alpha_{H^+}^{Zn} = 0.02$) and between copper and protons ($\alpha_{H^+}^{Cu} = 5.2$ and $\alpha_{H^+}^{Cu} = 0.06$), respectively for carboxylic and sulfonic groups, which were calculated by Equation 2, shows a higher influence of pH on the sorption capacity of zinc ions than copper ions, indicating that competition between zinc and protons is higher than between copper and protons.

$$\alpha_H^M = \frac{\alpha_{Na}^M}{(\alpha_{Na}^H)^2} \quad (2)$$

Similar effects were found by (Ucun, Aksakal *et al.* 2009) for the biosorption of copper and zinc using the biomass *Pinus sylvestris* L.

3.5. Cation exchange kinetics with Na-loaded algae

The ion exchange kinetic experimental initial data for copper and zinc were $[Cu^{2+}]_0 = 100 \text{ mg/L} = 3.15 \text{ mEq/L}$ and $[Zn^{2+}]_0 = 100 \text{ mg/L} = 3.06 \text{ mEq/L}$. The copper and zinc ion exchange kinetics were performed using Na-loaded algae at three different initial solution pH values (2.0, 3.0 and 4.0).

Sodium ions present in the solid phase are exchanged for copper, zinc and protons present in the liquid phase, showing the natural exchanger capacity of marine macro-algae. At high pH values, low concentration of H^+ , the exchange is mainly between sodium and copper or zinc ions. However, for low pH values, the high concentration of protons caused the rapid

displacement of sodium ions from biomass, which indicates that protons diffuse faster than copper or zinc ions. Furthermore, sodium ions were completely displaced from the biomass within the first 50 min for copper and zinc at pH 2.0. However, at pH 4.0, the sodium ion release was slower and mainly due to exchange with metal ions (Cu^{2+} and Zn^{2+}).

Table 1 shows the time constant of diffusion of the particles (τ_d) and the respective values of the coefficient of homogeneous intraparticle diffusion (D_h) for algae, considering the thickness of the thin plate particles of 0.1 mm. Thus, $R = 0.05 \text{ mm}$ and D_h is in the range of 4.4×10^{-9} and $1.2 \times 10^{-8} \text{ cm}^2/\text{s}$ for Cu^{2+} and Zn^{2+} , 4.8×10^{-9} and $7.5 \times 10^{-8} \text{ cm}^2/\text{s}$ for Na^+ and 1.5×10^{-9} and $8.0 \times 10^{-8} \text{ cm}^2/\text{s}$ for H^+ . From the kinetic profiles it can also be seen that hydrogen ions diffuse faster than sodium, copper and zinc ions, which is in agreement with the nightingale hydrated ion radii (r_{hyb}) (Marcus and Kertes 1969) (2.82 \AA for H^+ ; 3.58 \AA for Na^+ ; 4.19 \AA for Cu^{2+} and 4.30 for Zn^{2+}) and molecular diffusion coefficients given by Nernst-Haskell expression ($D_m = 7.2 \times 10^{-6} \text{ cm}^2/\text{s} - Cu^{2+}$, $6.9 \times 10^{-6} \text{ cm}^2/\text{s} - Zn^{2+}$, $1.3 \times 10^{-5} \text{ cm}^2/\text{s} - Na^+$, $9.3 \times 10^{-5} \text{ cm}^2/\text{s} - H^+$).

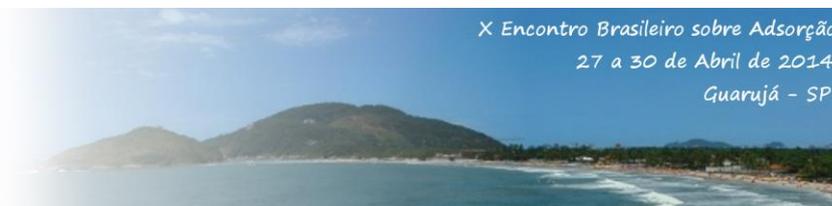
Table 1. Parameters estimated for the mass transfer model ($C_o = 100 \text{ mg/L}$, $T = 25 \text{ }^\circ\text{C}$).

Ion	pH	$k_p r_a r_p$ (L/min)	S_R^2 (mmol/L) ²	τ_d (min)	D_h (cm ² /s) [*]
Cu ²⁺	2.0	5.9×10^{-2}	0.20	51	8.1×10^{-9}
	3.0	3.2×10^{-2}	0.10	94	4.4×10^{-9}
	4.0	8.6×10^{-2}	0.33	35	1.2×10^{-8}
Na ⁺	2.0	15.3×10^{-2}	0.20	20	2.1×10^{-8}
	3.0	5.4×10^{-2}	0.10	55	7.5×10^{-9}
	4.0	3.5×10^{-2}	0.33	86	4.8×10^{-9}
H ⁺	2.0	9.1×10^{-2}	0.20	33	1.2×10^{-8}
	3.0	7.3×10^{-2}	0.10	41	1.0×10^{-8}
	4.0	1.1×10^{-2}	0.33	268	1.5×10^{-9}
Zn ²⁺	2.0	8.6×10^{-2}	0.09	35	1.2×10^{-8}
	3.0	4.3×10^{-2}	0.03	70	6.0×10^{-9}
	4.0	3.2×10^{-2}	0.26	93	4.5×10^{-9}
Na ⁺	2.0	15.5×10^{-2}	0.09	19	2.1×10^{-8}
	3.0	6.4×10^{-2}	0.03	47	8.9×10^{-9}
	4.0	4.3×10^{-2}	0.26	70	5.9×10^{-9}
H ⁺	2.0	5.7×10^{-2}	0.09	52	8.0×10^{-9}
	3.0	21.6×10^{-2}	0.03	14	3.0×10^{-8}
	4.0	3.8×10^{-2}	0.26	78	5.3×10^{-9}

* $R = 0.05 \text{ mm}$; $V = 0.05 \text{ L}$; $W = 0.05 \text{ g}$

4. CONCLUSION

The combination of FTIR and potentiometric titration techniques, jointly with the esterification procedures showed to be a powerful



tool for the identification and quantification of the major functional groups present in the surface of the brown marine macro-algae *Pelvetia canaliculata*. The natural cation exchange capacity of the macro-algae was attributed mainly to weakly carboxylic acid groups (COOH; 1.5 mEq/g) and strongly sulfonic acid groups (SO₃H; 1.0 mEq/g). The release of light metals during the uptake of Cu²⁺ and Zn²⁺ revealed that the current biosorption mechanism involves ion-exchange. The degree of dissociation of the weak acid groups is strongly influenced by the solution pH, affecting greatly the ion exchange capacity due to carboxylic groups for low pH values. Sulfonic groups are highly ionized in both the acid (R-SO₃H) and salt (R-SO₃Na) form, and consequently, the exchange capacity of strong acid resins is independent of solution pH. The maximum uptake capacity at pH 2.0 is approximately 1.0 mEq/g for copper and zinc ions, which correspond to the total amount of strong acid sulfonic groups. The high selectivity of these biomaterials indicates that they can be used for the recuperation of valuable metals present in different wastewaters. At pH 4.0, almost all binding sites were occupied by copper and zinc ions, achieving maximum uptake capacities near 2.4 mEq/g. A mass transfer model, using the mass action law to describe the ternary equilibrium, and considering a linear driving force model to describe the intraparticle mass resistance, was able to predict the kinetic profiles for both ternary systems, Cu²⁺/H⁺/Na⁺ or Zn²⁺/H⁺/Na⁺, in a batch system.

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