



## Ion exchange prediction model for multi-metal systems obtained from single-metal systems using the macroalga *Pelvetia canaliculata* (*Phaeophyceae*) as a natural cation exchanger



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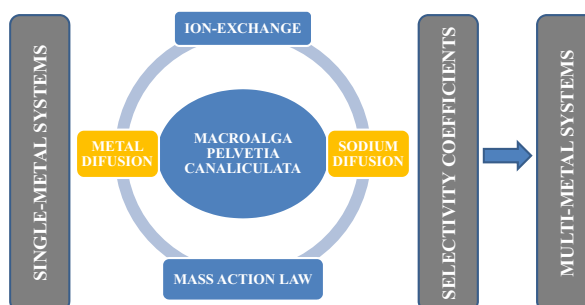
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### HIGHLIGHTS

- *Pelvetia canaliculata* showed to be a natural cation exchanger in multi-metal systems.
- Ion exchange prediction model for multi-metal systems from single-metal systems.
- Binding strength between transition metals and O donors increases as  $Zn \sim Cd < Cu < Pb$ .
- Competition between the transition metals occurs for the binding sites.
- Trapping of transition metals by biomass occurs by the release of sodium ions.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The aim of this study was to investigate the cation exchange capacity of the macroalga *Pelvetia canaliculata* (Linnaeus) Decaisne & Thuret in a multi-metal system containing  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$ . The Na-loaded alga was established as a cation exchanger, in which cadmium, lead, copper, zinc and hydrogen ions present in the liquid phase exchange with sodium ions bound to the functional groups on the algal surface, mainly weakly acidic carboxylic groups and strongly acidic sulfonic groups. A mass action law for the senary system ( $Na^+/H^+/Cd^{2+}/Pb^{2+}/Cu^{2+}/Zn^{2+}$ ) was able to predict the equilibrium data using the selectivity coefficients determined for the single-metal systems. Multi-metal equilibrium results, in agreement with the selectivity coefficients, showed a higher preference (affinity) of the biomass toward lead ions followed by copper, cadmium and zinc 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 chemical species in the liquid and solid phase. The results indicate that the biomass of *P. canaliculata* is an efficient natural cation exchanger for multi-metal systems.

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## Nomenclature

$a_p$	specific area of the thin plate particles (1/cm)	$\langle q_j \rangle$	concentration of species $j$ in the solid phase at time $t$ (mmol/g)
$C_H$	equilibrium concentration of protons in the liquid phase (mmol/L)	$q_j^*$	equilibrium concentration of species $j$ in the solid phase (mmol/g)
$C_T$	total concentration of species $j$ in the liquid phase (mEq/L)	$r_{cryst}$	Shannon crystal radii (Å)
$C_M$	equilibrium concentration of species $M$ ( $M$ : Cd <sup>2+</sup> or Pb <sup>2+</sup> ) in the liquid phase (mmol/L)	$r_{hyd}$	Nightingale hydrated ion radii (Å)
$C_{M_0}$	initial concentration of species $M$ ( $M$ : Cd <sup>2+</sup> or Pb <sup>2+</sup> ) in the liquid phase (mmol/L)	$R^2$	correlation coefficient
$C_j$	concentration of species $j$ in the liquid phase at time $t$ (mmol/L)	$R$	half of the thin plate thickness (cm)
$D_{h,j}$	coefficient of homogeneous diffusion inside the particle for each species $j$ (cm <sup>2</sup> /s)	$t$	time (s)
$k_{p,j}$	mass transfer coefficient for intraparticle diffusion of species $j$ (cm/s)	$V$	solution volume (L)
$q_M$	equilibrium concentration of species $M$ ( $M$ : Cd <sup>2+</sup> , Pb <sup>2+</sup> , Cu <sup>2+</sup> , Zn <sup>2+</sup> ) in the solid phase (mmol/g)	$\zeta_i$	parameter for total binding strength
$q_T$	total equilibrium concentration of species $M$ ( $M$ : Cd <sup>2+</sup> , Pb <sup>2+</sup> , Cu <sup>2+</sup> , Zn <sup>2+</sup> ) in the solid phase (mEq/g)	$X_m$	Pauling electronegativity
		$W$	mass of alga (g)
		$\alpha$	selectivity constant
		$\tau_{d,j}$	time constant for diffusion of ionic species into the particle (s)
		$\Delta X_m$	parameter for ionic bond character (electronegativity of the metal relative to oxygen)

## 1. Introduction

The presence of heavy metals in the environment has become a major threat due to their non-biodegradability and tendency to accumulate in living organisms, leading to high toxicity even in relatively low concentrations [1,2]. In particular, the accumulation of lead (Pb), cadmium (Cd), copper (Cu), zinc (Zn), nickel (Ni), chromium (Cr) and mercury (Hg) in soils, plants, rivers and groundwater has been extensively reported [3]. 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 environmentally-friendly technologies able to remove hazardous metals at low cost [3,4].

The biosorption process has received 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 means 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 reuse [5,6].

The main metal binding mechanisms are associated with surface complexation, ion-exchange and micro-precipitation, which can occur individually or in combination [4,6]. Many biomaterials, including bacteria [7], fungi [8], algae [1,9,10], industrial wastes [3], agricultural wastes [11,12] and polysaccharide materials, have been investigated as possible biosorbents for metal binding [13]. Among the biosorbents used for metal sequestration, algae are an inexpensive and readily available source of biomass [2].

The biosorption process using marine algae is associated with the interaction of the metal cations with functional groups present at the biosorbent surface, such as carboxylic, sulfonic, amine, and hydroxyl groups, which have different affinities for each metal ion, and competition between metals ions also occurs to the same active sites [14–16].

Brown algae are among the most promising biosorbents due to the density of carboxylic groups present in alginate (the main component of the cell walls), which is responsible for the high metal uptake capacity, and to their availability and abundance in oceans [17]. The marine brown macroalga *Pelvetia canaliculata* (Linnaeus) Decaisne & Thuret has demonstrated the ability to

remove efficiently metal ions from single-metal solutions in batch systems. The high sorption capacity of this brown alga has been attributed mainly to the presence of weakly acidic carboxylic groups and strongly acidic sulfonic groups [18,19].

In practice, industrial effluents rarely contain only one type of metal ion. Therefore, it is necessary to be able to predict the simultaneous biosorption of different metal ions present in real industrial wastewaters [15]. The use of biomaterials to bind metal mixtures has not been frequently reported and most of the studies involve single or binary metal systems [20].

Vilar et al. [16] studied the biosorption of the metal systems Pb<sup>2+</sup>/Cu<sup>2+</sup>, Pb<sup>2+</sup>/Cd<sup>2+</sup> and Pb<sup>2+</sup>/Zn<sup>2+</sup> using the alga *Gelidium sesquipedale*, an algal industrial waste and a waste-based composite material. They reported that the presence of Cd<sup>2+</sup> and Zn<sup>2+</sup> leads to a similar decrease in the Pb<sup>2+</sup> binding capacity and there is strong competition between Cu<sup>2+</sup> and Pb<sup>2+</sup> (the affinity to the binding groups increased in the following order Zn<sup>2+</sup> ~ Cd<sup>2+</sup> < Cu<sup>2+</sup> < Pb<sup>2+</sup>). Apiratikul et al. [21] tested the biosorption of binary systems (Pb<sup>2+</sup>/Cu<sup>2+</sup>, Pb<sup>2+</sup>/Cd<sup>2+</sup> and Cu<sup>2+</sup>/Cd<sup>2+</sup>) using a dried green macroalga *Caulerpa lentillifera* at different pH values and concluded that the presence of Pb<sup>2+</sup> decreased the sorption of Cu<sup>2+</sup> and Cd<sup>2+</sup> and vice versa, although to a lesser extent. Similarly, the sorption of Cd<sup>2+</sup> was more affected by the presence of Cu<sup>2+</sup>, than that of Cu<sup>2+</sup> by Cd<sup>2+</sup>. The competitive biosorption of Cd<sup>2+</sup> and Zn<sup>2+</sup> ions onto *Sargassum filipendula* was studied by Luna et al. [22] and the authors concluded that Zn<sup>2+</sup> had a notable effect on the Cd<sup>2+</sup> biosorption, but the interference of Cd<sup>2+</sup> in the sorption of Zn<sup>2+</sup> was considerably less intense. Binary and ternary systems of Ni<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> were investigated by Rodrigues et al. [23] using *Arthrospira platensis* and *Chlorella vulgaris* as biosorbents. The filamentous structure of *A. platensis* considerably reduces the surface area available for metal binding and it should be recognized as the principal cause of its lesser ability to remove metal ions when compared to *C. vulgaris*. The Pb<sup>2+</sup> removal efficiency and sorption capacity at equilibrium were not notably influenced by Ni<sup>2+</sup> or Zn<sup>2+</sup>, for both biosorbents, probably due to the biosorbent preference for Pb<sup>2+</sup>. In all binary systems, metals seemed to behave as antagonists. According to the authors, the adsorption mechanism involving ternary systems is much more complex than in dual systems, due to chemical interactions between the metal ions and the biomass.

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