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Insights into trivalent chromium biosorption onto protonated brown algae *Pelvetia canaliculata*: Distribution of chromium ionic species on the binding sites

Vítor J.P. Vilar [a,*], José A.B. Valle [b], Amit Bhatnagar [a], João C. Santos [a], Selene M.A. Guelli U. de Souza [c], Antônio Augusto U. de Souza [c], Cidália M.S. Botelho [a], Rui A.R. Boaventura [a]

[a] *LSRE – Laboratory of Separation and Reaction Engineering, Associate Laboratory LSRE/LCM, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*

[b] *Fundação Universidade Regional de Blumenau, Departamento de Engenharia Química, Rua São Paulo, 3250, Itoupava Seca, 89.030-000 Blumenau, SC, Brazil*

[c] *Laboratório de Transferência de Massa, Departamento de Engenharia Química e Engenharia de Alimentos, Universidade Federal de Santa Catarina, PO Box 476, CEP 88040-900 Florianópolis, SC, Brazil*

HIGHLIGHTS

- ▶ Insights into Cr(III) biosorption onto protonated brown algae *Pelvetia canaliculata*.
- ▶ Carboxylic groups are the major binding sites present in the surface of biomass.
- ▶ Distribution of chromium ionic species in the solution and on the binding sites.

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ABSTRACT

In the present study, biosorption of trivalent chromium by protonated brown algae, *Pelvetia canaliculata*, was studied in batch system. FTIR analyses provided information about the possible binding groups present in the algae, as carboxylic, hydroxyl and sulfonate groups. Potentiometric acid–base titrations showed a heterogeneous distribution of two major binding groups, carboxyl and hydroxyl ones, following the Quasi-Gaussian affinity constant distribution suggested by Sips, which allowed to estimate the maximum amount of acidic functional groups ($2.26 \pm 0.02\ \text{mmol g}^{-1}$) and proton binding parameters ($\text{p}K'_{\text{H}} = 3.18 \pm 0.01; m_{\text{H}} = 0.78 \pm 0.03$) for an ionic strength of 0.2 M. The trivalent chromium removal was found to increase with pH and the maximum chromium uptake was observed at pH 4.0 ($\sim$0.6 mmol/g), corresponding to 1.34 meq/g, since at that pH, 25.8% of total chromium is in the Cr^{3+} form and 72.7% as $CrOH^{2+}$. An equilibrium model incorporating the hydrolysis reactions that chromium undergoes in the aqueous phase was able to predict the chromium biosorption at different pH values and chromium concentrations, enabling the prediction of the distribution of chromium ionic species on the binding sites. A mass transfer model provided a good representation of the chromium biosorption kinetics, resulting in intraparticle homogeneous diffusion coefficients of $4.6 \times 10^{-7}\ \text{cm}^2/\text{s}$ for Cr^{3+} and $1.8 \times 10^{-8}\ \text{cm}^2/\text{s}$ for $CrOH^{2+}$. The distribution of chromium ionic species in the solution and on the binding sites was also predicted by the kinetic model.

1. Introduction

Chromium is released into the environment by various industrial activities such as mining, iron sheet cleaning, chrome plating, leather tanning, dyes and pigments, steel and alloys production and wood preservation [1,2]. Chromium exists in several oxidation states (di-, tri-, penta-, and hexa-), but Cr^{6+} and Cr^{3+} are the most common forms present in the aquatic environment [3]. Cr^{3+} is an essential nutrient for humans and its shortage may cause heart related problems, disruptions of metabolisms and diabetes. However, the uptake of higher dosages of Cr^{3+} may cause harmful health effects such as skin rashes [4]. A long-term exposure to trivalent chromium is known to cause allergic skin reactions and cancer [5]. Due to the toxic effects of chromium on living organisms, US EPA has set the maximum Cr^{6+} concentration level in domestic water supplies at 0.05 mg/L, while total Cr is regulated below 2.0 mg/L [6].

Different technologies such as chemical precipitation [7], ion exchange [8], electrocoagulation [9], electrodialysis [10] and

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* Corresponding author. Tel.: +351 918257824; fax: +351 225081674.
E-mail address: vilar@fe.up.pt (V.J.P. Vilar).

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