Adsorption (2009) 15: 75–80
DOI 10.1007/s10450-009-9152-2

Bioadsorption and ion exchange of Cr^{3+} and Pb^{2+} solutions with algae

Maria das Graças Nunes Matos · Vivian Gouveia Diniz · Cesar Augusto Moraes de Abreu · Augusto Knoechelmann · Valdinete Lins da Silva

Received: 9 November 2006 / Revised: 20 January 2009 / Accepted: 9 February 2009 / Published online: 24 February 2009

Abstract Heavy metals can be removed from effluents and recovered using physico-chemical mechanisms as biosorption processes. In this work "Arribada" seaweed biomass was employed to assess its biosorptive capacity for the chromium (Cr^{3+}) and lead (Pb^{2+}) cations that usually are present in waste waters of plating industries. Equilibrium and kinetic experiments were conducted in a mixed reactor on a batch basis. Biosorption equilibrium and fluid-solid mass transfer constants data were analyzed through the concept of ion exchange sorption isotherm. The respective equilibrium exchange constants ($K_{eqCr} = 173.42$, $K_{eqPb} = 58.86$) and volumetric mass transfer coefficients ($(k_{mCr}a)' = 1.13 \times 10^{-3}\ s^{-1}$, $(k_{mPb}a)' = 0.89 \times 10^{-3}\ s^{-1}$) were employed for the dynamic analysis of Cr and Pb sorption in a fixed-bed flow-through sorption column. The breakthrough curves obtained for both metals were compared with the predicted values by the heterogeneous model ($K_{eqCr} = 171.29$, $K_{eqPb} = 60.14$; $k_{mCr}a = 7.81 \times 10^{-2}\ s^{-1}$, $k_{mPb}a = 2.43 \times 10^{-2}\ s^{-1}$), taking into account the mass transfer process. The results suggest that these algae may be employed in a metal removal/recovery process at low cost.

Keywords Ion exchange · Algae · Chromium · Lead

1 Introduction

The presence of heavy metals in the environment at concentrations above critical values stipulated by national regulatory bodies is considered unacceptable. In the local context, heavy metals in various water bodies, such as industrial effluents or waste-water of cities with an ever-increasing population density. In that sense the water resources have been strongly attacked, mainly the estuarine environments by lack of adequate wastewater treatment.

The presence of heavy metals in the environment is of major concern because of their toxicity and threat to plant and animal life. Moreover, recovery of heavy metals from industrial waste streams is becoming increasingly important as society realises the necessity for recycling and conservation of essential metals (Hashim and Chu 2004). The employment of algae is having an increasing impact on environmental problems (Metaxa et al. 2006) and they are being used as biological pollution indicators of areas contaminated by heavy metals (Andrade et al. 2004; Topcuoğlu et al. 2003).

That ability is the basis of the processes developed to recover residual metallic ions (Burridge and Bidwell 2002; Davis et al. 2000; Lodeiro et al. 2006; Kalyani et al. 2004).

Several algae species are known for their ability to adsorb metal ions from solutions and have been used as biosorbents for recovery of metals from industrial effluents (Kuyucak and Volesky 1988), serving as toxic metal sequestrate (Mann et al. 1988; Deviller et al. 2005), or to recover precious metals (Madrid and Cámara 1997; Pawlik-Skowrońska 2002).

The free electrons of the amino acids present in algae give them the property of electrostatic bonding, which turns the assimilation of the metals very easy. These electrostatic attractions should occur with some metals like Ca and Na (Crist et al. 1988), via covalent bonds with Cu (Crist et al. 1994) and by redox reactions with certain noble metals (Guha et al. 2003; Zylkiewicz-Godlewska 2003). Considering the treatment of the effluents contaminated by chromium and lead, as in this work, aqueous solutions of these metals

M. das Graças Nunes Matos · V. Gouveia Diniz · C.A. Moraes de Abreu · A. Knoechelmann · V. Lins da Silva (✉)
Departamento de Engenharia Química, Universidade Federal de Pernambuco, R. Teresa Melia, s/n, 50740-521, Recife, PE, Brazil
e-mail: leaq_val@yahoo.com.br

were put in contact with "Arribadas" algaes, to bioadsorb them.

2 Material and methods

Bioadsorption experiments were conducted using separate solutions of Cr^{3+}, and Pb^{2+} in the form of $Cr(NO_3)_3{\cdot}9H_2O$ and $Pb(NO_3)_2{\cdot}3H_2O$, respectively. Metal concentrations were measured before and after the adsorption operations by Plasma Emission Spectroflame (ICP).

The "Arribadas" algaes were collected at Itamaracá Island, Pernambuco-Brasil, washed and dried in a greenhouse at $32.0 \pm 1°C$, crushed in a knife mill and screened to mesh size 100. Particles with diameter between 1.47×10^{-4} m and 2.97×10^{-4} m were selected for the experiments.

The prepared solutions using deionized water had an initial metal concentration in the range of 50 to 1000 mg L^{-1} and a pH of 3.0. An amount of 0.20 g of biomass was contacted with each metal solution. The mixture was stirred in a 125 mL Erlenmeyer for 24 hours of contact time, at $T = 25.0 \pm 1°C$, in order to be sure equilibrium between the algae and liquid was reached. The suspensions were filtered and the final chromium and lead concentrations in the filtrates were determined via ICP. The time evolutions were performed with 10 g of algae and 1.00 L of a chromium and lead solutions, at respective concentrations of 780 mg L^{-1} and 478 mg L^{-1}, and acidified to pH 3.0 with HNO_3. Solid algae was kept in suspension by constant stirring. 5 mL samples were taken at 0.5; 1; 5; 30; 60; 120; 180; 240; 300; 360; 420; and 480 min filtered through a millipore membrane and the respective chromium and lead contents determined in the solutions.

The rate studies were conducted in a glass tube with a height of 0.10 m and a diameter of 0.012 m, packed with 1.9 g of algae (dp $<$ 100 mesh). The chromium and lead solutions were pumped upwards through the algae bed by a peristaltic pump at a flowrate of 1.20 mL min^{-1}. The system was maintained at $T = 25.0 \pm 1°C$ while samples were taken at pre-established times at the top of the tube to evaluate the dynamic behaviour (breakthrough curves) of the bed.

3 Results and discussion

The results of the kinetic experiments in a batch system showed that after two hours the retained chromium and lead quantities in the algae were constant, 82.33 mgCr g^{-1} and 84.37 mgPb g^{-1} respectively. These adsorbed concentrations indicate equilibrium.

Possibly during the first 30 s, rapid superficial adsorption occurred, followed by a slower process, probably ion exchange when circa 99% of the chromium or 94% of the lead were retained on the solid. This fast metal removal from the solutions suggests that the main mechanism does not involve metabolic activity. Watson et al. (1989) noted also for the biosorption of strontium a fast metal retention by *M. luteus.* Yang and Volesky (1999) used biomass from *Sargassum* to remove uranium from waste. Experimental results obtained by Crist et al. (1990) indicate an external fluid-solid mass transfer step followed by an adsorption and/or ion exchange step. A proposed interaction mechanism (Crist et al. 1990) emphasizes the interactions of the sites on the algae surface which act as metal adsorbent. It is possible that initially, before the ion exchange, a fast adsorption step as a metal monolayer has occurred. Alginate is the main saccharide of the algae and it can be responsible for the adsorption of the solute through its polymeric chains on the solid surface.

Two models were analysed to represent the experimental results, one for the batch system and another one for the continuous fixed bed. For the experimental results in biosorption batch processes an equilibrium ion exchange mechanism was proposed while for kinetic experiments a Linear Driving-Force model with external fluid-solid mass transfer control was applied. For the continuous process a heterogeneous model, which considers interstitial plug flow and chromium or lead-algae mass transfer in the external layer, was proposed.

The chromium and lead exchanges with calcium of the algae (CaX_2) can be represented stoichiometrically by the following reactions:

$$2Cr^{3+} + 3(CaX_2) \leftrightarrows 3Ca^{2+} + 2(CrX_3)$$

$$Pb^{2+} + (CaX_2) \leftrightarrows Ca^{2+} + (PbX_2)$$

The high calcium concentration found in the solution in contact with the algae in kinetic experiments, indicates that the main phenomena in the chromium-algae and lead-algae bio interactions is ion exchange. Taking the stoichiometric ion exchange equations, the equilibrium constants were:

$$K_{eqCr} = \frac{[Cr^{3+}]_0(1 - [Cr^{3+}]^*/[Cr^{3+}]_0)^3(q^*_{Cr}/Q_{Cr})^2}{([Cr^{3+}]^*/[Cr^{3+}]_0)^2 Q_{Cr}(1 - \frac{3}{2}q^*_{Cr}/Q_{Cr})^3}, \quad (1)$$

$$K_{eqPb} = \frac{[Pb^{2+}]_0(1 - [Pb^{2+}]^*/[Pb^{2+}]_0)(q^*_{Pb}/Q_{Pb})}{([Pb^{2+}]^*/[Pb^{2+}]_0) Q_{Pb}(1 - q^*_{Pb}/Q_{Pb})}, \quad (2)$$

where $[Cr^{3+}]^*$, $[Pb^{2+}]^*$ and q^*_{Cr}, q^*_{Pb} are the chromium and lead equilibrium concentrations in the solution and retained by the algae, respectively. $[Cr^{3+}]_0$, $[Pb^{2+}]_0$ are the initial chromium and lead concentrations in the solution and Q_{Cr} and Q_{Pb} are the maximum adsorbed chromium and lead concentrations on the algae.

In Fig. 1 the chromium-algae and lead-algae equilibrium analysis are presented. Equations (1) and (2) expressed in their linear forms were fitted to the equilibrium data

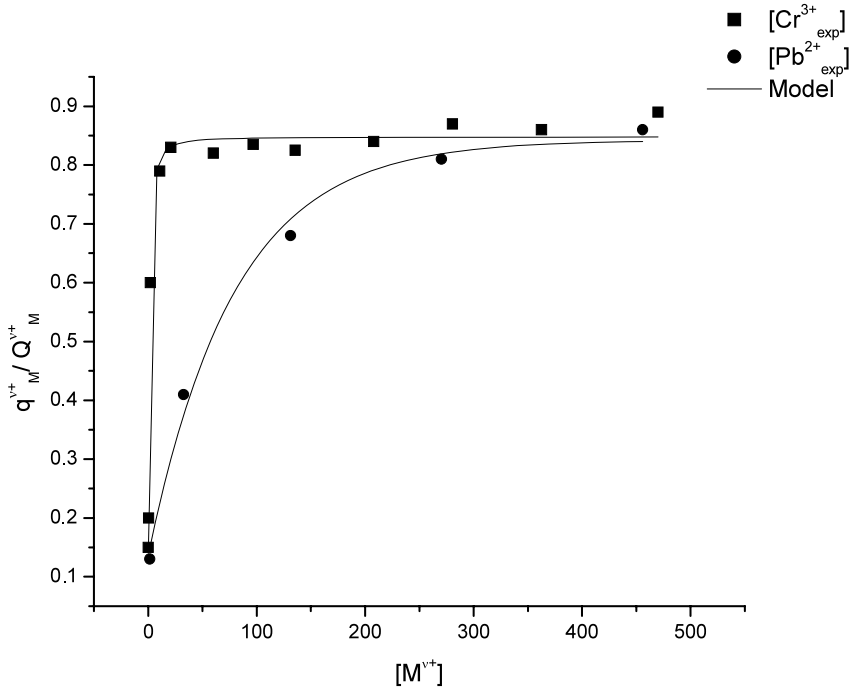

Fig. 1 Equilibrium curves. Arribadas algae (4 g L^{-1}) in chrome solution (780 mg L^{-1}), and in lead solution (478 mg L^{-1}); pH 3.0 and $T = 25.0 \pm 1°C$

and the equilibrium parameters constants and the maximum adsorbed concentrations on the algae were obtained as: $K_{eqCr} = 173.42 \pm 6.06$, $K_{eqPb} = 58.86 \pm 2.23$, and $Q_{Cr} = 83.29 \pm 3.49$ mgCr g^{-1}, $Q_{Pb} = 85.08 \pm 3.31$ mgCr g^{-1}.

Based on the order of external mass transfer fractions ($f_e = r_M L/k'_m[M^{\nu+}]$, $f_{eM} > 0.05$; Villermaux 1982), and considering Weisz's criterion ($\Phi'_M = r_M L^2/D_M[M^{\nu+}]$); for which $L = d_{palgae}/6$; and $d_{palgae} < 2.97 \times 10^{-4}$ m, hence $\Phi'_M < 0.23 \ll 1$), indicates that the pore diffusion is not limiting, and the rate was controlled by external mass transfer in the fluid. So, the kinetic analysis of the batch experiments, assuming that the process is controlled by the external fluid-solid mass transfer, can be presented by (3):

$$\frac{dq_M}{dt} = (k_{mM}a)'[M^{\nu+}] - [M^{\nu+}]^*;$$
$$M = Cr, Pb; \nu = 3, 2, \quad (3)$$

where $(k_{mM}a)'$ are the volumetric mass transfer coefficients.

The mass balance of the metal is expressed as:

$$-V_L \frac{d[M^{\nu+}]}{dt} = m_s \frac{dq_M}{dt} \quad (4)$$

where V_L and m_s were the volume of metal solution and mass of algae, respectively.

By combining (3) and (4), results (5):

$$\int_{[M^{\nu+}]_0}^{[M^{\nu+}]} \frac{d[M^{\nu+}]}{[M^{\nu+}]^* - [M^{\nu+}]} = (k_{mM}a)'t. \quad (5)$$

In Fig. 2 the values obtained from the model were compared with the experimental results, indicating that the processes are possibly controlled by the external mass transfer in the fluid.

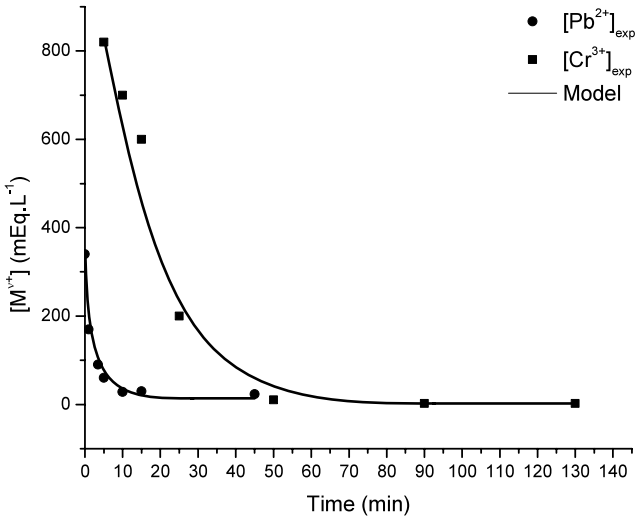

Fig. 2 Experimental kinetics results and simulated values of concentration of chrome and lead by model equations. Dried Arribadas algae (10 g L^{-1}) in chrome solution (780 mg L^{-1}) and in lead solution (478 mg L^{-1}); pH 3.0; $T = 25.0 \pm 1°C$

From this analysis the volumetric liquid-solid mass transfer coefficients, $(k_{mCr}a)' = (1.13 \pm 0.05)10^{-3}$ s^{-1} and $(k_{mPb}a)' = (0.89 \pm 0.03)10^{-3}$ s^{-1}, for the batch system, were obtained. The values of k'_m ($k'_{mCr} = (2.87 \pm 0.11)10^{-3}$ ms^{-1}; $k'_{mPb} = (2.81 \pm 0.93)10^{-3}$ ms^{-1}) were estimated by the Calderbank and Jones correlation (see (6); Smith 1970) employing the values of the diffusivi-

ties of the chromium and lead ($D_{Cr} = 8.11 \times 10^{-10}$ m^2/s; $D_{Pb} = 7.78 \times 10^{-10}$ m^2/s) calculated for ionic solutions by the Nernst-Haskell method (Perry and Green 1999), which are independent for any process.

$$k'_{mM}\left(\frac{\mu_L}{\rho_L D_M}\right)^{2/3} = 0.34\left(\frac{\Delta\rho\mu_L^g}{\rho_L^2}\right)^{1/3}, \quad (6)$$

where μ_L, ρ_L the viscosity and density of the liquid solution and $\Delta\rho = \rho_p - \rho_L$, with ρ_p the particle algae density.

Algae are typically filamentous, but for the sake of simplicity in this analysis, we consider the algae filaments to be massed together in a globular nearly spherical, tough certainly porous state.

Considering that the mass transfer in a batch system is distinctive from that of the flow in a fixed bed, the obtained values of the mass transfer coefficients had to be changed so that they could be applied to the continuous processes.

For the determination of the volumetric liquid-solid mass transfer coefficients (k_{mM}) for the continuous system one may employ the Ranz and Levenspiel correlation ($Sh_M = k_{mM} d_p D_M^{-1} = 2.0 + 1.8 Re^{1/2} Sc_M^{1/3}$; Kunii and Levenspiel 1989), where it is possible to employ the chromium and lead diffusion coefficients, previously determined.

By this methodology the fluid-solid mass transfer coefficients may be evaluated and used as a starting value which forms with the equilibrium constants a set of two parameters for each metal. These are used to optimise the chromium and lead concentration expressions at the outlet of the fixed bed.

In the continuous experiments 780 mg L^{-1} chromium and a 478 mg L^{-1} lead concentration solutions were continuously fed to the algae fixed bed with a constant flow of 1.20 mL min^{-1}. The metal concentrations at the outlet were measured as a time function.

The analyses of the bioretention processes in a fixed bed are achieved by fitting a dynamic model based on (7) and (8), considering transient flow, fast ion-exchange equilibrium and that the fluid-solid kinetics is controlled by external mass transfer.

$$\varepsilon v_L \frac{\partial[M^{\nu+}]}{\partial Z} + \varepsilon\frac{\partial[M^{\nu+}]}{\partial t} + (1-\varepsilon)\frac{\partial q_M}{\partial t} = 0, \quad (7)$$

$$(1-\varepsilon)\frac{\partial q_M}{\partial t} = k_{mM} a([M^{\nu+}] - [M^{\nu+}]^*). \quad (8)$$

Introducing the new variables $\zeta_M = k_{mM} a(\varepsilon V_L)^{-1} z$ and $\tau_M = k_{mM} a[K_{eqM}(1-\varepsilon)]^{-1}[t - (zV_L^{-1})]$ and applying Laplace's method, adopted by Hiester and Vermeulen (1952), he solution of this differential equation system is:

$$[M^{\nu+}] = [M^{\nu+}]_0\left\{1 - \int_0^{\zeta M} \exp[-(\zeta'_M + \tau_M)] \times I_0(2(\zeta'_M\tau_M)^{1/2})\mathrm{d}\zeta'_M\right\}u(\tau_M), \quad (9)$$

where $I_0[2(\zeta'_M\tau_M)^{1/2}]$ is the Bessel function of zero order and $u(\tau_M)$ the Heaviside function.

The results of the continuous experiments with the fixed bed may be compared with the values obtained from (9). This equation was employed to fit the experimental curves of the chromium and lead algae systems to curves obtained from the proposed model.

An objective function (F_{ob}) was defined ($F_{ob} = \sum_i ([M^{\nu+}]_{Thi} - [M^{\nu+}]_{Expi})^2([M^{\nu+}]_0)^{-1}$), for which a minimum is searched using the values of the ion-exchange equilibrium parameters K_{eqM} and of the volumetric mass transfer coefficients $k_{mM}a$. F_{ob} values of the order of 10^{-3} were considered in the final optimisations for the two metals, confirming the values of equilibrium parameters and giving definitive values for the mass transfer coefficients.

The optimised values ($K_{eqCr} = 171.29 \pm 3.46$, $k_{mCr}a = (7.81 \pm 0.27)10^{-2}$ s^{-1}, $K_{eqPb} = 60.14 \pm 2.41$, $k_{mPb}a = (2.43 \pm 0.08)10^{-2}$ s^{-1}) were employed in (9) representing the dynamic behaviour of the chromium and lead retentions in the fixed bed.

In Fig. 3 the simulations of the experimental breakthrough curves of the chromium and lead solution are shown.

Breakpoint and column saturation times for chromium in the fixed bed, derived from the model, are greater than those for lead biosorption. This behaviour may be explained in terms of the fluid-solid kinetics controlled by external mass transfer. The value of the coefficient of external mass transfer for chromium is circa three times that of the lead coefficient.

4 Conclusions

Biosorption tests with *Arribadas algae* to treat liquid effluents containing chromium and lead provided equilibrium and kinetics values for batch operations that were extended to the dynamic fixed bed process. Experimental evidence suggested that ion-exchange was the sorption mechanism. At 25.0°C, the equilibrium ion-exchange constants are $K_{eqCr} = 171.29$ and $K_{eqPb} = 60.14$, and the batch volumetric mass transfer coefficients are $(k_{mCr}a)' = 1.13 \times 10^{-3}$ s^{-1}, $(k_{mPb}a)' = 0.89 \times 10^{-3}$ s^{-1}. These values were used to characterize the continuous algae fixed bed process.

Dynamic experiments produced chromium and lead breakthrough curves at the outlet of the bed. Those were compared with the results of a heterogeneous model, which yielded values of the volumetric mass transfer coefficients

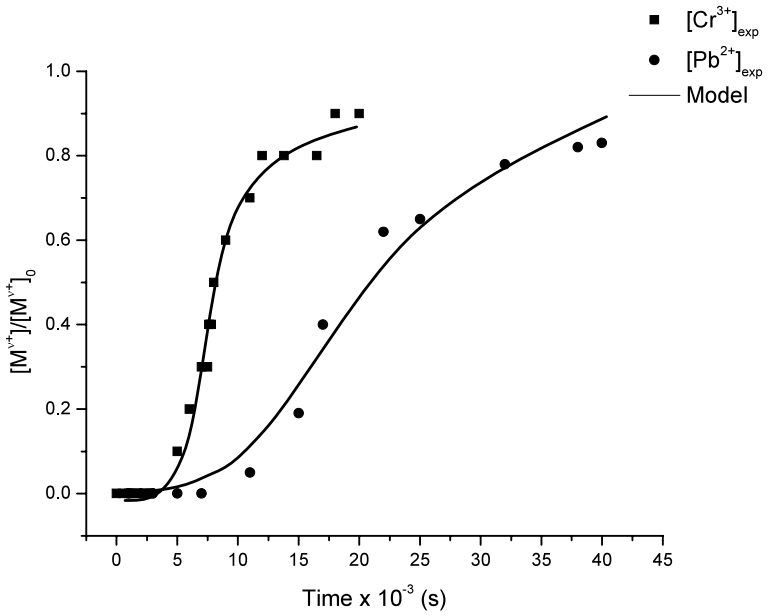

Fig. 3 Experimental and calculated (continuous heterogeneous model) breakthrough curves. Arribadas algae (10 g L^{-1}) in chrome solution (780 mg L^{-1}) and in lead solution (478 mg L^{-1}); pH 3.0; $T = 25.0 \pm 1$°C; flow of the liquid phase (1.2 mL min^{-1})

$k_{mCr}a = 7.81 \times 10^{-2}\ s^{-1}$ and $k_{mPb}a = 2.43 \times 10^{-2}\ s^{-1}$. These values are about 70× and 27× those in the batch experiments. It was determined for these experimental conditions that the processes were controlled by external mass transfer with fast ion-exchange equilibrium. Furthermore, the values of the mass transfer coefficients imply that the external mass transfer resistance in a fixed bed geometry is much lower than in an agitated batch-wise system, due to the greater shear stress at the liquid-solid interface.

Notation

a = interfacial area per unit volume (m^{-1})
d_{palgae} = particle diameter of algae (m)
f_{eM} = external resistance fraction
k'_{mM}, k'_{mCr}, k'_{mPb} = mass transfer coefficients (batch system) (ms^{-1})
$(k_{mM}a)'$, $(k_{mCr}a)'$, $(k_{mPb}a)'$ = volumetric mass transfer coefficients (batch system) (s^{-1})
k_{mM}, k_{mCr}, k_{mPb} = mass transfer coefficients (fixed-bed) (ms^{-1})
$k_{mM}a$, $k_{mCr}a$, $k_{mPb}a$ = volumetric mass transfer coefficients (fixed-bed) (s^{-1})
q^*_M, q^*_{Cr}, q^*_{Pb} = adsorbed concentration of metals (mg g^{-1})
t = time (s)
r_M = ionic exchange rate of metals ($g\ g^{-1}_{algae}\ s^{-1}$)
u (τ_M) = Heaviside function
w = weight (g)
D_M, D_{Cr}, D_{Pb} = diffusivities of metals ($m^2\ s^{-1}$)
F_{ob} = objective function
K_{eqCr}, K_{eqPb} = equilibrium constants of ionic exchange
L = characteristic length of particle (m)
m_s = mass of algae (g)
$[M^{\nu+}]$ = concentration of metals in solution (mg L^{-1})
$[M^{\nu+}]^*$, $[Cr^{3+}]^*$, $[Pb^{2+}]^*$ = equilibrium concentration of metals in solution (mg L^{-1})
$[M^{\nu+}]_0$, $[Cr^{3+}]_0$, $[Pb^{2+}]_0$ = initial concentration of metals in solution (mg L^{-1})
Q_M, Q_{Cr}, Q_{Pb} = maximum adsorbed concentration of metals (mg g^{-1})
Re = Reynolds number
Sc = Schmidt number
Sh = Sherwood number
V_L = volume of metal solution (L)

Greek letters

ε = bed porosity
ρ_p = particle algae density
ρ_L = solution density
ϕ'_M = Weisz's criterion
τ_M = time dimensionless variable
ξ_M = length dimensionless variable
μ_L = viscosity
ν = valence

Indexes

p = particle
s = solid
L = liquid
M = metal
Th = theoretical
Exp = experimental

Acknowledgements We would like to thank the Department of Chemical Engineering of UFPE (Pernambuco-Brasil), FACEPE (Fundação de Apoio à Pesquisa do Estado de Pernambuco), CNPq (Conselho Nacional de Desenvolvimento e Pesquisa do Brasil) for their support.

References

Andrade, L.R., Farina, M., Amado Filho, G.M.: Effects of copper on Enteromorpha flexuosa (Chlorophyta) in vitro. Ecotoxicol. Environ. Safety **58**, 117–125 (2004)

Burridge, T.R., Bidwell, J.: Review of the potential use of Brown algal ecotoxicological assays in monitoring effluent discharge and pollution in Southern Australia. Marine Pollut. Bull. **45**(1–12), 140–147 (2002)

Crist, R.H., Oberholser, K., Schwartz, D., Marzoff, J., Ryder, D., Crist, D.R.: Interaction of metals and protons with algae. Environ. Sci. Technol. **22**, 755–760 (1988)

Crist, R.H., Martin, J.R., Guptill, P.W., Eslinger, J.M., Crist, D.R.: Interaction of metals and protons with algae.2- Ions exchange in adsorption and metals displacement by protons. Environ. Sci. Technol. **24**(3), 337–342 (1990)

Crist, D.R., Grist, R.H., Martin, J.R., Watson, J.R.: Ions exchange systems in proton- Metals interactions with algal cells walls. FEMS Microbiol. Rev. **14**(4), 309–313 (1994)

Davis, T.A., Volesky, B., Vieira, R.H.S.F.: Sargassum seaweed as biosorbent for heavy metals. Water Res. **34**(17), 4270–4278 (2000)

Deviller, G., Palluel, O., Aliaume, C., Asanthi, H., Sanchez, W., Franco Navad, M.A., Blancheton, J.-P., Casellas, C.: Impact assessment of various rearing systems on fish health using multibiomarker response and metal accumulation. Ecotoxicol. Environ. Saf. **61**, 89–97 (2005)

Guha, H., Jayachandran, K., Maurrasse, F.: Microbiological reduction of chromium (VI) in presence of pyrolusite-coated sand by Shewanella alga Simidu ATCC 55627 in laboratory column experiments. Chemosphere **12**(1), 175–183 (2003)

Hashim, M.A., Chu, R.H.: Bisorption os cadmium by brown, green and red seawed. Chem. Eng. J. **97**(2–3), 245–255 (2004)

Hiester, Vermeulen: (Chem. Eng. Prog. 48, 505, 1952): In: Perry's Handbook, 7th edn. McGraw-Hill, New York (1999)

Kalyani, S., Srinivasa Rao, P., Krishnaiah, A.: Removal of nickel (II) from aqueous solutions using marine macroalgae as the sorbing biomass. Chemosphere **57**, 1225–1229 (2004)

Kunii, D., Levenspiel, O.: Fluidization Engineering. Wiley, New York (1989)

Kuyucak, N., Volesky, B.: Biosorbents for recovery of metals from industrial solutions. Biotechnol. Lett. **10**, 137–142 (1988)

Lodeiro, P., Barriada, J.L., Herrero, S., Vicente, R.M.E.: The marine macroalga Cystoseira baccata as biosorbent for cadmium(II) and lead(II) removal: kinetic and equilibrium studies. Environ. Pollut. **142**, 264–273 (2006)

Madrid, Y., Cámara, C.: Biological substrate for metal preconcentration and speciation. Trends Anal. Chem. **16**(1), 36–44 (1997)

Mann, H., Fyfe, W.S., Kerrich, R.: Proton-metal cation exchange in cell wall of *Nitella flexilis*. Toxic Assess **3**, 1–16 (1988)

Metaxa, E., Deviller, G., Pagand, P., Alliaume, C., Casellas, J.P., Blancheton, C.: High rate algal pond treatment for water reuse in a marine fish recirculation system: Water purification and fish health. Aquaculture **252**, 92–101 (2006)

Pawlik-Skowrońska, B.: Correlations between toxic Pb effects and production of Pb-induced thiol peptides in the microalga *Stichococcus bacillaris*. Environ. Pollut. **119**, 119–127 (2002)

Perry, R.H., Green, D.W.: Perry's Handbook, 7th edn. McGraw-Hill, New York (1999)

Smith, J.M.: Chemical Engineering Kinetics. International Student Edition, Tokyo (1970)

Topcuoğlu, S., Güven, K.C., Balkıs, N., Kırbaşoğlu, Ç.: Heavy metal monitoring of marine algae from the Turkish Coast of the Black Sea, 1998–2000. Chemosphere **52**(10), 1683–1688 (2003)

Villermaux, J.: Génie de la Réaction Chimique, Conception et Fonctionnement des Réacteurs. Technique et Documentation (Lavoisier), Paris (1982)

Watson, J.S., Scott, C.D., Faison, B.D.: Adsorption of strontium by immobilized microorganisms. Appl. Biochem. Biotechol. **20**, 699–709 (1989)

Yang, J., Volesky, B.: Biosorption of uranium on *Sargassum* biomass. Water Res. **33**(15), 3357–3363 (1999)

Zylkiewicz-Godlewska, B.: Biosorption of platinum and palladium for their separation/preconcentration prior to graphite furnace atomic absorption spectrometric determination. Spectrochim. Acta Part B: At. Spectrosc. **58**(8), 1531–1544 (2003)