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Lead uptake by algae *Gelidium* and composite material particles in a packed bed column

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ABSTRACT

Biosorption of lead ions was studied in a flow-through column packed with red algae *Gelidium* and a composite material (industrial algal waste from the agar extraction process immobilized with polyacrylonitrile). Experiments were performed in order to study the effect of important design parameters such as flow rate and influent pH. The breakthrough curves for lead and proton concentrations were obtained in saturation and elution studies. Macroscopically, when the flow rate increases, the residence time in the bed decreases, and the column saturation is faster achieved and the sharpness of the breakthrough curves increases. Microscopically, increasing the flow rate, the film diffusion resistance decreases. For higher values of the influent pH, the breakthrough time increases, due to the greater metal uptake capacity at the equilibrium. Considering the effectiveness of lead desorption from loaded biomass, we concluded that desorption was 100% effective and rapid, even for high values of the solid to liquid ratio, leading to high values of the concentration factor. The column packed with composite material was operated in two consecutive adsorption–desorption cycles, without any changes in the metal uptake capacity. A mathematical model based on external and intraparticle mass transfer was developed to simulate the breakthrough curves in the adsorption and desorption processes.

1. Introduction

In 1990, 5.627×10^6 tonnes of lead were consumed worldwide [1]. Mining, smelting and refining, as well as the manufacture of lead-containing compounds and goods, can give rise to lead emissions [2]. Traditional methods used to remove this toxic metallic ion from industrial wastewaters before discharge into natural water bodies, include coagulation and precipitation, ion-exchange, membrane separation and electrolytic technologies. Coagulation and precipitation processes lead to a high consumption of reagents and leave behind "hazardous sludge", which needs to be safely disposed off [3]. Ion-exchange (€20–40 kg^{-1}), activated carbon adsorption (€10–20 kg^{-1}) and membrane (€30–50 m^2) processes are expensive, particularly for large-scale clean-up operations, such as, for example, mining water treatment [3]. Those processes may also be ineffective for low metal concentrations (<100 $mg\,l^{-1}$) [3]. Alternative technologies are required to reduce toxic metal concentrations into environmental acceptable levels at affordable costs [3–5]. Biosorption, as it has been perceived so far, could be considered for its economic edge (€3–5 kg^{-1}) as a possible alternative technique for metal removal/recovery [3]. Biosorption is based on the passive sequestration by non-living biomass, containing many types of different chemically active groups that show some tendencies to uptake other chemical substances or ions, attracting them from solution and binding them to the biomass surfaces [3,6,7]. Biosorption of lead has been investigated using different kinds of marine algae, such as brown algae (*Sargassum hystrix*, *Sargassum natans*, *Padina pavonia*, *Fucus vesiculosus*, *Ascophyllum nodosum*), red algae (*Chondrus crispus*, *Galaxaura marginata*, *Palmaria palmate*, *Gracilaria corticata*, *Gracilaria canaliculata* and *Polysiphonia violacea*) and green algae (*Codium taylori*, *Ulva lactuca* and *Cladophora glomerata*) [8,9]. Other sorbents have been also applied, such as red mud-an aluminium industry waste [10], lignin obtained from black liquor-a paper industry waste material [11], waste brewery biomass [12], activated slag-a blast furnace waste [13] and others.

Biosorption of lead ions using red algae *Gelidium* and a composite material in a batch system was previously studied [14–16]. From these studies, it was concluded that biosorption of metal ions is due to negatively charged carboxylic groups present in the cell wall of the biosorbents at pH < 7. The mechanism of biosorption has been established as a combination of adsorption and ion-exchange between the metal cations present in solution and protons or other ions (Na^+, K^+) bound to carboxylic groups. For high proton

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Nomenclature

a_p	specific area for thin plates particles
C_b	metal concentration in the bulk (mg or mmol metal/l fluid)
C_{b_0}	initial metal concentration in the bulk (mg or mmol metal/l fluid)
C_E	feed concentration (mg or mmol metal/l fluid)
C_f	metal concentration in the film (mg or mmol metal/l fluid)
C_{final}	metal concentration in the solution at the end of the saturation or elution process (mg or mmol metal/l fluid)
C_H	equilibrium concentration of proton in the fluid phase (mmol proton/l fluid)
C_M	equilibrium concentration of metal in the fluid phase (mmol metal/l fluid)
C_T	total (lead + acid) liquid concentration (mmol/l fluid)
C_{T_0}	initial total (lead + acid) liquid concentration (mmol/l fluid)
C_{T_E}	total feed (acid) liquid concentration (mmol/l fluid)
d_p	particle diameter (cm)
D_{ax}	axial dispersion coefficient (cm^2/s)
D_h	homogeneous diffusion coefficient (cm^2/s)
D_m	molecular diffusivity of the metal ion in solution (cm^2/s)
k_f	film mass transfer coefficient (cm/s)
k_p	mass transfer coefficient for intraparticle diffusion (cm/s)
K_H	equilibrium proton constant (l fluid/mmol H)
K_M	equilibrium metal constant (l fluid/mmol M)
K_L	equilibrium constant of Langmuir (l fluid/mg M)
K_H^M	selectivity coefficient between ion M in the particle and H in solution
L	bed length (cm)
N_d	number of mass transfer units by intraparticle diffusion
N_f	number of mass transfer units by film diffusion
Pe	axial Peclet number based on the bed length
Pe_p	axial Peclet number based on the particle diameter (spherical) or width (thin plate)
pH_{SE}	pH of feed solution
pH_{CI}	initial pH of interstitial fluid inside the column
pH_{CF}	final pH of interstitial fluid inside the column
$\langle q \rangle$	average metal concentration in the solid phase (mg or mmol metal/g biomass)
q_E	solid phase concentration in equilibrium with C_E (mg or mmol metal/g biomass)
q_H	equilibrium concentration of proton in the biomass (mmol proton/g biomass)
q_M	equilibrium concentration of metal in the biomass (mg or mmol metal/g biomass)
q_{M_0}	metal concentration in the solid phase in equilibrium with C_{b_0} (mg or mmol metal/g biomass)
q^*	solid phase concentration in equilibrium with C_f (mg or mmol metal/g biomass)
Q_{max}	concentration of carboxylic groups or maximum capacity of biomass (mg or mmol/g biomass)
R	half of thickness of the thin plate (cm)
Sh	Sherwood number
t	time (s)
t_{Bp}	breakthrough time (s)
t_{st}	stoichiometric time (s)
T	temperature (°C)
u_i	interstitial fluid velocity (cm/s)
V_f	interstitial fluid volume (cm^3)
W	mass of biosorbent (g)
x	axial position normalized by the bed length
$\langle y \rangle$	dimensionless average concentration in the solid phase
y_b	dimensionless concentration in the fluid phase
y_f	dimensionless concentration in the fluid phase at the film
y_T	dimensionless total concentration in the fluid phase
y^*	dimensionless concentration in the solid phase at the particle surface
z	bed axial position (cm)

Greek letters

ε	porosity of the bed
τ	space time (s)
τ_d	time constant for intraparticle diffusion
τ_f	time constant for film diffusion
θ	dimensionless time
ρ_{ap}	apparent density of particles (g solid/cm^3 particle)
ξ	adsorber capacity factor for saturation
ξ'	adsorber capacity factor for desorption

concentration, the uptake capacity of metal ions decreases due to the competition with protons to the binding sites [14,15].

In this work, we investigated the performance of the same biosorbents to treat lead contaminated water in a packed bed column. The influence of the flow rate and pH of the feed stream on the breakthrough curve was analysed, as well as the possibility of regenerating the biosorbents. A mass transfer model was developed to describe the biosorption and desorption in the continuous packed bed column.

2. Materials and methods

2.1. Preparation of biosorbents

An algal waste from agar extraction industry was immobilized with an organic polymer (polyacrylonitrile-PAN) and used in this study as well as red algae *Gelidium*, which is the raw material for agar extraction. *Gelidium sesquipedale* is a red algae, harvested in the coasts of Algarve and São Martinho do Porto, Portugal. The industrial algal waste is composed essentially by 35% of algae *Gelidium* after agar extraction and 65% of diatomaceous earth used as filtration aid in the extraction process. To prepare the composite particles, fibrous PAN was first dissolved in dimethyl sulfoxide (DMSO) during 1–2 h. The powdered active component (industrial algal waste) was gradually added to PAN solution under stirring and the suspension mixed for about 30 min. Homogeneous suspension was then dispersed into water (coagulation bath) at room temperature. Beads formed in the water bath were washed with distilled water, separated by filtration on Buchner funnel and dried at about 30–40 °C. A more detailed description of the characteristics and preparation of both materials were presented in previous works [16,17].

2.2. Preparation of lead solution

Pb(II) solutions were prepared by dissolving a weighed quantity of anhydrous $PbCl_2$ (Merck-Schuchardt with purity >98%) in dis-