Environmental Technology & Innovation 11 (2018) 105–115

Contents lists available at ScienceDirect

Environmental Technology & Innovation

journal homepage: www.elsevier.com/locate/eti

Aluminum biosorption using non-viable biomass of *Pseudomonas putida* immobilized in agar–agar: Performance in batch and in fixed-bed column

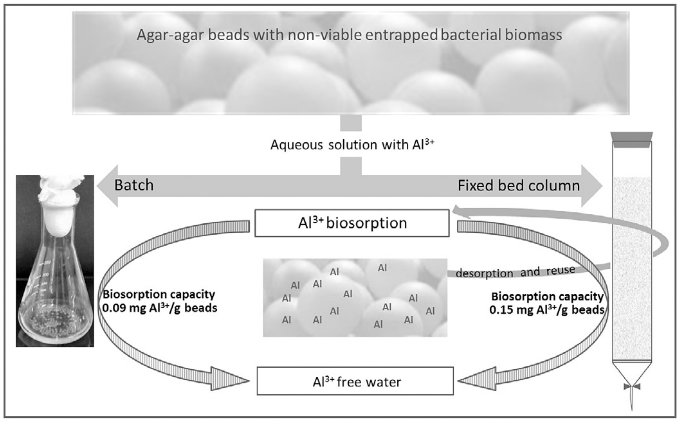
Paola S. Boeris, Andrés S. Liffourrena, Gloria I. Lucchesi *

Departamento de Biología Molecular. Facultad de Ciencias Exactas, Físico-Químicas y Naturales, Universidad Nacional de Río Cuarto, Río Cuarto, Córdoba, Argentina

HIGHLIGHTS

- Al^{3+} adsorption by non-living *P. putida* trapped in agar in batch and fixed-bed column.
- Biosorption capacity was higher in fixed-bed column than in batch experiments.
- Fixed-bed column was stable up to 12 successive adsorption/desorption cycles.
- Fixed-bed is a very good alternative for the removal of Al^{3+} from aqueous solutions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 January 2018
Received in revised form 20 April 2018
Accepted 10 May 2018
Available online 17 May 2018

Keywords:
Aluminum
Adsorption
P. putida
Fixed-bed column

ABSTRACT

Non-viable biomass of *Pseudomonas putida* immobilized in agar–agar was used as adsorbent to remove aluminum from aqueous solutions. In batch assays, adsorption equilibrium was reached after 45 min and 95% of 2.7 mg/L Al^{3+} were adsorbed. Immobilized biomass was packed to obtain a fixed-bed column and the dynamic behavior in continuous mode was established through breakthrough curves. At different flow rates (0.5 and 1.0 mL/min) the adsorption capacity of the column did not change, but removal percentage was higher at the lowest flow rate (64.92% and 44.34%, respectively). The fixed-bed column presented a higher biosorption capacity than that obtained in batch experiments (0.15 and 0.09 mg Al^{3+}/g beads, respectively), and showed stability for up to 12 successive adsorption/desorption cycles with negligible loss in adsorption efficiency. We concluded

* Correspondence to: Departamento de Biología Molecular, Facultad de Ciencias Exactas Físico-Químicas y Naturales, Universidad Nacional de Río Cuarto, CPX5804BYA Río Cuarto. Córdoba, Argentina.

E-mail address: glucchesi@exa.unrc.edu.ar (G.I. Lucchesi).

https://doi.org/10.1016/j.eti.2018.05.003

that this packed biosorbent could be a good alternative for the removal of Al^{3+} from aqueous solutions.

1. Introduction

At present, pollution by metal ions is a major environmental problem. Aluminum is generally complexed with minerals and inaccessible to living systems, but the advance of industrialization, linked to acid rain and a decrease in soil pH, has increased the leaching of the metal in groundwater (Tharmalingam et al., 2007 and citations therein; Auger et al., 2013), with a prevalence of harmful soluble species, such as the Al^{3+} cation (Garcidueñas Piña and Cervantes, 1996). It has also been described that the indiscriminate use of chemical fertilizers and agrochemicals causes acidification of soils, which leads to an increase in those aluminum forms that are toxic for plant growth (Kochian et al., 2005; Sukweenadhi et al., 2015).

Aluminum has been detected in drinking water (Kumari and Ravindhranath, 2012) and in effluents from a wide variety of industries, where it is used as raw material or as a component of final products (for e.g. in the manufacturing of packaging materials and domestic utensils, aeronautics, automobiles, pharmaceutical and medicine products) (Soylak et al., 1997; de Amorim et al., 2006; Tuzen and Soylak, 2008; Tassist et al., 2010). The aquatic toxicity of aluminum is strongly influenced by the species of metal, which in turn depends on the pH value of the solution. At pH values close to 4, most aluminum exists as free Al^{3+}, while at pH values greater than 7, insoluble hydroxylated forms are present (Garcidueñas Piña and Cervantes, 1996). Relatively insoluble aluminum hydroxy species tend to be less biologically available, and as a consequence, significantly less toxic than monomeric species or free metal ions (Dixon, 1997).

For a long time, Al^{3+} was considered harmless for living organisms. However, several studies have since shown its harmful effects (Mailloux et al., 2011; Tomljenovic, 2011). Particularly in humans, the accumulation of this metal in the brain has been related to neurodegenerative diseases such as Alzheimer's, Parkinson's and amyotrophic lateral sclerosis (Wong et al., 1998; Buratti et al., 2006). In plants, Al^{3+} released into the soil limits root growth and activates oxidative stress, leading to structural cell damage, lack of growth and lack of root development (Singh et al., 2017).

Metals are non-biodegradable species and their removal from wastewater can be carried out through various methods. Physico-chemical methods (ion exchange, chemical precipitation, electroflotation, osmosis) have several disadvantages: they need chemical additives, have a high energy requirement and a high operating cost, do not completely remove the metal, and produce toxic sludge and secondary pollution (Mittal et al., 2010; Gupta and Nayak, 2012; Devaraj et al., 2016). Compared to conventional techniques, biosorption is a potential alternative for toxic metal removal since it is an eco-friendly, efficient process that allows the removal of metal traces (Loutseti et al., 2009; Majumder et al., 2015; Abdolali et al., 2015; Rashid et al., 2016; Muñoz et al., 2016, Boeris et al., 2016; Zang et al., 2017; Muñoz et al., 2017; Barquilha et al., 2017; Abdolali et al., 2017). With biosorption, metals bind to different ligands present on the surfaces of biological materials (carboxyl, phosphate, amine, imidazel, thioether, sulfhydryl and hydroxyl groups). Biosorbents can be metabolically active or inactive biomasses of algae, fungi, yeast and bacteria, as well as industrial and agricultural wastes (Vijayaraghavan and Yun, 2008; Wang and Chen, 2009). When bacterial biomass is used as adsorbent, biosorption can be carried out with microorganisms in free condition (planktonic state) or immobilized in polymeric matrices (Vijayaraghavan and Yun, 2008). The use of immobilized biomass as an adsorbent has a number of advantages, such as its easy extraction from the effluent to be treated, its operational flexibility, its reusability, and its low operating costs. Additionally, the immobilized adsorbent can be packed in glass or PVC columns to create fixed-bed reactors (Vijayaraghavan and Yun, 2008; Majumder et al., 2015; Muñoz et al., 2016; Zang et al., 2017; Barquilha et al., 2017; Abdolali et al., 2017; Dhoble et al., 2017). The use of these columns allows continuous flow operations with high pollutant removal efficiency. Furthermore, the process can be scaled from a laboratory scale to a full or industrial scale (Vijayaraghavan and Yun, 2008; Barquilha et al., 2017).

In a previous study we demonstrated that metabolically active and inactive biomass of *Pseudomonas putida* A (ATCC 12633) is able to attach to Al^{3+}. Scanning electron microscopy (SEM) photomicrographs of non-living biomass exposed to Al^{3+} showed the presence of particles in the form of an irregular globule on the cell surface, indicative of the presence of metal. Moreover, by infrared spectroscopy analysis it was determined that the metal is adsorbed to amine, hydroxyl and phosphate groups on the cell surface, with the phosphatidylcholine content of the bacterial membrane being particularly important for adsorption capacity (Boeris and Lucchesi, 2012; Boeris et al., 2016). Using both biomass types, Al^{3+} adsorption was fast and stable in time, and efficient at pH 4.3 between 15 and 42 °C. However, non-viable biomass showed higher adsorption capacity than that determined for viable biomass (0.55 and 0.48 mg Al^{3+}/g adsorbent, respectively) (Boeris et al., 2016). The greater adsorption capacity of non-viable biomass was attributed to the fact that this biomass was obtained by autoclaving and, accordingly, the cells provided a larger available surface area and more surface binding sites (Errasquin and Vazquez, 2003).

Given the biosorption abilities of *P. putida* A (ATCC 12633) biomass in regards to aluminum ions, and the possible advantages offered by biomass immobilization to improve the biosorption process, in this study we evaluated Al^{3+} biosorption in batch experiments using non-viable *P. putida* biomass immobilized in agar–agar beads. Also, for the purpose of evaluating the biosorption process in continuous mode, a fixed-bed column was designed and the factors influencing its performance were analyzed.