Chemosphere 149 (2016) 146–153

Contents lists available at ScienceDirect

Chemosphere

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

# Study of metal transport through pine bark for reutilization as a biosorbent

R. Paradelo [a], [*], L. Cutillas-Barreiro [a], D. Soto-Gómez [a], J.C. Nóvoa-Muñoz [a], M. Arias-Estévez [a], M.J. Fernández-Sanjurjo [b], E. Álvarez-Rodríguez [b], A. Núñez-Delgado [b]

[a] *Universidade de Vigo, Departamento de Bioloxía Vexetal e Ciencia do Solo, Área de Edafoloxía e Química Agrícola, Facultade de Ciencias de Ourense, As Lagoas s/n, 32004 Ourense, Spain*

[b] *Universidade de Santiago de Compostela, Departamento de Edafoloxía e Química Agrícola, Escola Politécnica Superior, Campus Univ. s/n, 27002 Lugo, Spain*

## HIGHLIGHTS

- Potential use of pine bark as a biosorbent for Cu, Pb, Zn, Ni and Cd was evaluated in column experiments.
- The sequence of metal affinity for pine bark was the following: Pb > Cu ≈ Cd ≈ Ni > Zn.
- Pine bark removed 100% of the elements from 2.5 mM metal solutions.
- Metals were not detected in the outcoming solution until pine bark reached saturation.

## ARTICLE INFO

*Article history:*
Received 6 July 2015
Received in revised form
12 January 2016
Accepted 21 January 2016
Available online 6 February 2016

Handling Editor: X. Cao

*Keywords:*
Laboratory column
Organic matter
Sorption
Transport experiment

## ABSTRACT

The potential utilization of pine bark as a biosorbent for the treatment of metal-contaminated soils and waters has been evaluated in transport experiments using laboratory columns. Solutions containing the metals Cu, Pb, Zn, Ni or Cd, each one individually and at three different concentrations (2.5, 10 and 25 mM) were tested. Pine bark affected metal transport and the breakthrough curves, producing a reduction of their concentrations in the solution and a clear retardation with respect to an inert tracer. At metal concentrations equal to 2.5 mM, 100% of the assayed elements were removed from the solution in the pine bark column. At the 10 mM metal concentration, the percentage of metals retained fell to 38–67% of the amount added, whereas at the 25 mM metal concentration, only 16–43% was retained. In all cases, the highest retention capacity corresponded to Pb, and the lowest to Zn, whereas Cu, Cd and Ni produced intermediate comparable results. The analysis of the pine bark within the columns after the transport experiment showed that the metals entering the column adsorb progressively until a saturation concentration is reached in the whole column, and only then they can be released at significant concentrations. This saturation concentration was approximately 70 mmol $kg^{-1}$ for Cd, Ni and Zn, 100 mmol $kg^{-1}$ for Cu, and 125 mmol $kg^{-1}$ for Pb. Overall, our experiments have shown the high effectiveness of pine bark to retain the assayed metals in stable forms of low mobility.

## 1. Introduction

Currently, *in situ* bioremediation is seen as the least ecologically damaging and least expensive remediation technique for contaminated soils (Park et al., 2011), thus giving a growing interest in recycling organic residual materials with this aim. The main goal during bioremediation of metal-contaminated soils is reducing metal bioavailability, as these pollutants do not undergo microbiological or chemical degradation. Decreased bioavailability can be achieved by immobilization onto solid matrices with high affinity for these pollutants, and the same principle is valid for the treatment of contaminated wastewaters (Sud et al., 2008). Organic matrices increase metal immobilization mainly through adsorption and complexation reactions (Park et al., 2011). Some organic materials have high affinity for metal cations due to its composition, including cellulose, hemicelluloses, lignin, proteins, sugars and

---

[*] Corresponding author.
*E-mail address:* remigio.paradelo@uvigo.es (R. Paradelo).

http://dx.doi.org/10.1016/j.chemosphere.2016.01.087

other components with a variety of ligands or functional groups with metal binding capacity. Carboxyl, phenolic, hydroxyl, carbonyl, acetamide groups, alcohols and esters provide metal affinity through ion exchange, complexation and chelation (Harter and Naidu, 1995; Sud et al., 2008).

Organic materials of residual origin present several advantages, in addition to waste reuse and recycling, including low-cost, availability, efficiency and often possibility of regeneration of the sorbent and metal recovery (Bailey et al., 1999). Among residual materials that have been used for the treatment of contaminated soils and waters, previous studies have focused on manure (Chamon et al., 2005), composts from a variety of feed-stocks (Brown et al., 2003; Farrell and Jones, 2010; Paradelo et al., 2011) and wood barks from several species (Seki et al., 1997). Bark from *Pinus sp*. is one of the materials recently investigated with this objective (Gichangi et al., 2012; Cutillas-Barreiro et al., 2014). Pine bark is a by-product from the timber industry which is produced in huge quantities in some areas of the world, in particular where forest areas and wood production are relevant. Its high organic content and composition makes it potentially suitable for the treatment of soils and waters polluted with metallic cations. The high tannin and lignin contents of pine bark have been signalled as the main cause for its potential metal sorption capacity (Bailey et al., 1999). The polyhydroxy polyphenol groups of these molecules are thought to be the active species in the adsorption process: ion exchange takes place as metal cations displace adjacent phenolic hydroxyl groups, forming a chelate (Randall et al., 1974; Vazquez et al., 1994).

Batch-type experiments have been previously used to assay pine bark efficacy as regards heavy metal sorption (Cutillas-Barreiro et al., 2014), giving good results. However, laboratory column experiments are considered a further step to approach field conditions and the industrial use of pine bark as purging material. Another aspect to be taken into account is that transport experiments are required to characterize some water treatment processes, such as those affecting *in situ* groundwater decontamination tasks undertaken with permeable reactive barriers (Blowes et al., 2000).

In this work we have performed laboratory column experiments to study the effect of pine bark on the retention and transport of five metals (Cu, Pb, Zn, Cd, Ni), with the objective of shedding light on processes taking place when using pine bark to treat contaminated soils and waters.

## 2. Materials and methods

### 2.1. Pine bark

The pine bark used was a commercial product from Geolia (Madrid, Spain), ground and sieved through a 2-mm mesh prior to analysis. pH in water was determined in 1/2.5 solid/liquid suspensions using a glass electrode (Crison micro-pH 2001, Spain). Total organic C and N contents were determined using an elemental Tru Spec CHNS auto-analyser (Waltham, USA). Pine bark has an acidic pH (4.5), 486 g $kg^{-1}$ carbon, and low nitrogen concentration (0.08 g $kg^{-1}$). The levels of heavy metals in pine bark (determined using the X-ray fluorescence technique, Philips PW1710 diffractometer) are low (7 mg Zn $kg^{-1}$, 2 mg Ni $kg^{-1}$, 0.2 mg Pb $kg^{-1}$, 0.1 mg Cd $kg^{-1}$, <0.1 mg Cu $kg^{-1}$).

### 2.2. Transport experiments

Laboratory experiments were conducted to obtain breakthrough curves (BTC) of metal solutions flowing through pine bark columns. Solutions of $Ni(NO_3)_2\cdot 6H_2O$, $Cu(NO_3)_2\cdot 3H_2O$, $Pb(NO_3)_2$, $Zn(NO_3)_2\cdot 6H_2O$ or $Cd(NO_3)_2\cdot 4H_2O$ containing total concentrations of 2.5, 10 or 25 mM of Ni, Cu, Pb, Zn, or Cd, all of them present individually, were used for the experiments, with $NaNO_3$ 0.01 M as background electrolyte. The metal concentrations of the incoming solutions have been selected taking into account the metal retention capacity of the pine bark under batch conditions (Cutillas-Barreiro et al., 2014). All the experiments were conducted at $20 \pm 1$ °C in a thermostatized chamber.

Vertically-oriented columns were constructed using glass tubes, 60-mm long, with 10 mm inner diameter, and filled with moist pine bark. Pine bark was added incrementally, with depths of 1 cm, each addition followed by gentle tapping of the column to consolidate it and remove any air bubbles. The columns were weighed at this point to determine the mass of pine bark employed. At the input, the columns were connected to a peristaltic pump (Gilson Minipuls 3, USA) through 1/16-inch PVC tubing. The pump was connected through a three-way valve to the bottles containing deionized water or metal solutions. At the output, columns were connected to a fraction collector (Gilson FC 203 B, USA) through 1/16-inch PVC tubing. Experimental conditions for all columns are summarized in Table 1.

Once packed, columns were slowly saturated from the bottom with deionized water during a 3-day period, with water entering the columns at 2 mL $h^{-1}$ as incoming flow. After this period, the valve was switched and metal solutions were introduced in the columns, with a 2 mL $h^{-1}$ flow rate maintained for 8 h, approximately equivalent to four pore volumes (Table 1). Then, the valve was switched and deionized water was again introduced in the columns, with a 2 mL $h^{-1}$ flow rate maintained for a 24-h period. At this point, the column was weighed again to determine the pore volume. The outflow effluents were sampled every 40 min, both during the incoming metal–solution phase and during the incoming water phase. Cu, Pb, Zn, Ni and Cd concentrations were measured in each outflow sample, using flame atomic absorption spectroscopy (FAAS) (Thermo Solaar M series spectrometer, USA). A parallel experiment was carried out to determine the retardation factor of each metal within the column. With this aim, a 10 mg $L^{-1}$ solution of KBr was used as a solute tracer. The bromide ($Br^-$) in the effluent samples was measured in a segmented flow analyser (Bran Luebbe Auto Analyser 3).

The resulting breakthrough curves (relative metal concentration in the effluent vs. elapsed time) were plotted for all metals. Relative metal concentration ($C/C_0$) is calculated by dividing the metal concentration in the effluent ($C$) by the metal concentration in the input solution ($C_0$).

Curves were further studied using temporal moment analysis as described by Valocchi (1985), Stagnitti et al. (2000) and Kamra et al. (2001). Temporal moment analysis allows quantifying solute transport properties independently from an underlying mathematical model.

In solute transport studies, the solute breakthrough curve in dimensionless form is represented by

$$f(t) = C(z,t)/C_0$$

where $C_0$ is the initial solution concentration at time $t = 0$ and $z$ is the location. The moment-generating function for a continuous function $f(t)$ is

$$M_p = \int_0^\infty t^p f(t)dt$$

where the superscript $p = 0; 1; 2; 3 \ldots$ represents the zeroth, first, second, third moments, etc. The normalised moments, $\mu_p^{<n>}$, are