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Valorization of biosorbent obtained from a forestry waste: Competitive adsorption, desorption and transport of Cd, Cu, Ni, Pb and Zn

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ABSTRACT

Bark from *Pinus pinaster* is one of the most abundant forestry wastes in Europe, and among the proposed technologies for its reutilization, the removal of heavy metals from wastewater has been gaining increasing attention. In this work, we have studied the performance of pine bark for heavy metal biosorption on competitive systems. Pb, Cu, Ni, Zn and Cd sorption and desorption at equilibrium were studied in batch experiments, whereas transport was studied in column experiments. Batch experiments were performed adding simultaneously different concentrations (0.08–3.15 mM) of two or more metals in solution to pine bark samples. Column experiments were performed with 10 mM solutions of two metals or a 5 mM solution of the five metals. In general, the results under competitive conditions were different to those obtained in monoelemental experiments. The multi-metal batch experiments showed the adsorption sequence Pb ≈ Cu > Cd > Zn > Ni for lower metal doses, Pb > Cu > Cd > Zn > Ni for intermediate doses, and Pb > Cu > Cd ≈ Zn ≈ Ni for high metal doses. Desorption followed the sequence Pb < Cd < Cu < Zn < Ni for the lowest metal doses, and Pb < Cu < Zn < Cd < Ni for the highest ones. The bi-metal batch experiments indicated that Cu and Pb suffered the highest retention, with high capacity to displace Cd, Ni and Zn from adsorption sites on pine bark. The transport experiments produced comparable results to those obtained in the batch experiments, with pine bark retention capacity following the sequence Pb > Cu > Zn > Cd > Ni. The presence of a second metal affected the transport of all the elements studied except Pb, and confirmed the strong influence of Pb and Cu on the retention of the other metals. These results can help to appropriately design decontamination systems using this forestry waste.

1. Introduction

Soil and water pollution due to high concentrations of heavy metals has greatly increased in the last decades, mainly due to more intensive industrial and agricultural activities, thus causing environmental and public health issues. In view of that, finding effective, low-cost and environmentally sound decontamination systems to retain those pollutants and waste water recycling is of great interest (Gupta et al., 2012).

Diverse bioadsorbent materials have been used for soil and water decontamination (Gupta et al., 2013; Asfaram et al., 2015); in particular, for heavy metals they have been used seaweed (Kratochvil et al., 1998), olive pomace (Pagnanelli et al., 2003), orange peel with Fe_2O_3 nanoparticles (Gupta and Nayak , 2012), forest by-products and waste (Seco-Reigosa et al., 2013), mussel shell (Fernández-Pazos et al., 2013; Ramírez-Pérez et al., 2013), activated sludge (Hammaini et al., 2007), alumina-coated carbon nanotubes and modified active carbon (Gupta et al., 2011; Ghaedi et al., 2015), or eucalyptus bark (Sarin and Pant, 2006),

The world land surface covered by pine trees is very relevant, and in particular that corresponding to *Pinus pinaster* is estimated to be around 4.4 million ha, most of them (4 million ha) located in Spain, Portugal, France, Morocco, Italy, Turkey, Greece and Tunis (Sanz, 2006). In Spain, 27.7 million ha are devoted to forest, with *P. pinaster* representing 20% of the total existences (151 million m^3) (Ministry of Agriculture, Food and Environment, 2011). *P. pinaster* is the coniferous tree with highest bark generation potential (up to 22% of the total volume of the trunk). Only in Galicia (NW Spain),

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about 350,000 t of *Pinus pinaster* bark are produced yearly, most of them being used to produce energy (Jerez et al., 2009).

Given the importance of the volume of bark generated by the forestry industry, intense research is currently taking place to develop new options for reutilization of this waste. Lignocellulosic wastes such as pine bark have been proposed for use as biosorbents in the removal of metals and metalloids from contaminated waters and wastewaters, because the polyhydroxy polyphenol groups present in tannin and lignin have a high potential sorption capacity by ion exchange and chelating processes (Randall et al., 1974; Bailey et al., 1999; Vazquez et al., 1994). Bioadsorbent materials can immobilize heavy metals present in polluted systems, which is essential to maintain environmental sustainability, bearing in mind that those pollutants are not biodegradable, and they can enter the food chain and accumulate in living organisms. Diverse waste materials have been proposed for use as biosorbents, including ascidian, microalgae, agave bagasse, barley straw, coconut shell, corn cob, eucalyptus bark, oak leaves, olive stone, rice straw, rice husk, or wheat straw (Kurniawan et al., 2006; Abdul Jaffar ali et al., 2015; Kim et al., 2015; Suresh Kumar et al., 2015; Rosales et al., 2015; Abdolali et al., 2016). Recent studies have investigated the potential of pine bark to adsorb metallic cations (Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+} and Hg^{2+}) in aqueous solutions (Nehrenheim and Gustafsson, 2008; Blázquez et al., 2011; Cutillas-Barreiro et al., 2014), showing its efficacy to treat industrial polluted waters. In view of that, pine bark could be an interesting bioadsorbent to be used as a low-cost alternative to more costly technologies traditionally employed to retain heavy metals in polluted soil and water. Additionally, this use would facilitate an environmentally sound recycling for a by-product.

Most studies focusing on heavy metal immobilization using pine bark are performed adding each metal individually, in experiments dealing with adsorption-desorption, in batch systems (Gundogdu et al., 2009; Cutillas-Barreiro et al., 2014) or, less frequently, in column systems (Long et al., 2014; Paradelo et al., 2016). However, competence for adsorption sites may cause drastic changes in adsorption processes, as have been shown for soils and soil components (Arias et al., 2002; Serrano et al., 2005). Nevertheless, there are little information about adsorption of heavy metals on pine bark in multimetal systems, what is important for utilization in multi-metal removal. Taking into account that metal pollution can take place affecting to various pollutants simultaneously, it is interesting to perform studies focusing on multi-metal systems. Consequently, in this work we used batch-type experiments to study the competitive adsorption and desorption of Cd, Cu, Ni, Pb and Zn on pine bark, both in bi-metal and multi-metal systems. Furthermore, studies using columns to characterize retention and transport of heavy metals through pine bark can complement batch-type experiments, giving results closer to field conditions, so we have also investigated metal transport through pine bark in column experiments. Both kinds of experiments could give useful results to program the appropriate design of pine-bark-based pollution treatment systems.

2. Materials and methods

2.1. Characterization of the adsorbent material (pine bark)

The pine bark used in this work was a commercial product from Geolia (Madrid, Spain). Previously to be analyzed, it was ground and sieved through a 2-mm mesh. It was characterized for pH in water, measured in 1/2.5 solid/liquid suspensions using pH-meter (Crison micro-pH 2001, Spain); C and N, using the elemental Tru Spec CHNS auto-analyzer (Waltham, USA); total concentrations of Na, K, Ca, Mg, Cd, Cu, Ni, Pb and Zn, using the X-ray fluorescence technique (Philips PW1710 diffractometer, The Netherlands); surface area, by using a surface area and porosity analyzer (Micromeritics model ASAP 2020, USA); lignin, glucan, xylan, galactan, arabinan, mannan, and acetyl groups contents, by means of the NREL/TP-510–42618 method.

Pine bark presented a surface area of 0.36 g m^{-2}, an acidic pH (4.5), and its carbon and N concentration were 48.6% and 0.008%, respectively. The levels of heavy metals were low, with the highest concentration corresponding to Zn (7 mg kg^{-1}). Regarding the composition of the organic matter, 47.9% was lignin, while glucan was 18.6%, and the sum of xylan + galactan + arabinan + mannan + acetyl groups was 14.7%.

2.2. Adsorption/desorption: batch experiments

2.2.1. Adsorption-desorption experiments in multi-metal systems

Triplicate 0.5 g pine bark samples were added with 10 mL solutions containing simultaneously Cd, Cu, Ni, Pb and Zn, applied as nitrate salts ($Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Pb(NO_3)_2$, $Zn(NO_3)_2 \cdot 6H_2O$ or $Cd(NO_3)_2 \cdot 4H_2O$) in various concentrations (concretely 0.08, 0.16, 0.39, 0.79, 1.57 and 3.15 mM for each metal) to different samples, using $NaNO_3$ 0.01 M as background electrolyte. The resulting suspensions were shaken for 24 h, then centrifuged at 4000 rpm for 15 min at room temperature (20 °C ± 2 °C), and finally filtered through acid-washed filters. The amount of each metal adsorbed was calculated as the difference between the concentration of metal added at the start and that remaining in dissolution when the equilibrium was reached. The concentrations of Cd, Cu, Ni, Pb and Zn were determined in the equilibrium solutions using atomic absorption spectroscopy (Thermo Elemental Solaar M5 spectrometer, USA), and pH was determined using pH-meter (Crison micro-pH 2001, Spain).

Experimental data were adjusted to a Freundlich equation for multi-metals, as follows:

$$\left(X^{Cu}+X^{Cd}+X^{Ni}+X^{Pb}+X^{Zn}\right) = K\left(C^{Cu}+C^{Cd}+C^{Ni}+C^{Pb}+C^{Zn}\right)^{n}$$

where X is the total amount of metals adsorbed (mmol kg^{-1}), C is the concentration in the equilibrium (mM), and K and n are constants (Freundlich coefficients).

Desorption experiments were carried out immediately after the adsorption trials. To do that, the centrifuged solid residues derived from the adsoption phase were weighed to determine the amount of occluded solution, then re-suspended by adding 10 mL of a 0.01 M $NaNO_3$ metal-free solution, which was allowed to equilibrate shaking for 24 h. Following equilibration, the suspensions were centrifuged for 10 min at 4000 rpm and filtered as in the adsorption phase. The amounts of interstitial Cd, Cu, Ni, Pb and Zn were determined by calculating the difference in weight; interstitial quantities of Cd, Cu, Ni, Pb and Zn, as well as their concentrations in the supernatant, were considered to estimate the quantity of metals desorbed. Additionally, pH was determined using pH-meter. The pH after 24 h contact was 3.9 ± 0.4.

2.2.2. Adsorption/desorption experiments in bi-metal systems

Triplicate 0.5 g pine bark samples were added with 10 mL solutions containing 0.79 mM of a metal (Cd, Cu, Ni, Pb or Zn) and variable concentrations (from 0 to 3.15 mM) of another metal within the same group (Cd, Cu, Ni, Pb or Zn), then following the procedure previously described for the multi-metal systems. The pH after 24 h contact was 4.0 ± 0.5. The percentage reduction of metal adsorption for each of the five metals was calculated as follows:

$$R.\,P. = \frac{C_0 - C_x}{C_0}100$$

where *R.P.* is the percentage reduction of metal adsorption, C_0 is the concentration of adsorbed metal (mmol kg^{-1}), when this metal is alone, and C_x is the concentration of adsorbed metal (mmol kg^{-1}),