Fluoride removal by aluminum-modified pine sawdust: Effect of competitive ions

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ABSTRACT

The removal of fluoride from aqueous solutions by pine sawdust chemically modified with aluminum in batch systems was investigated. The loading process of aluminum in this biomaterial was achieved by the hydrolysis of metal salts. The kinetics and sorption capacities of the unmodified and modified pine sawdust were evaluated. The effect of different parameters such initial fluoride concentration, pH and contact time was studied on the sorption process. Since the presence of other ions may affect the sorption of fluoride, some studies of binary or multiple systems have simulated a real natural water effluent. The aim of this study was the evaluation of competitive ions in the sorption of fluoride using pine sawdust in fluoride (F^-) single systems and F^-/HCO_3^- and F^-/SO_4^{2-} binary systems. Batch-type contact experiments were performed to evaluate the kinetics and equilibrium fluoride sorption, all at 25 °C, 100 rpm and pH values adjusted to 6, 7 and 8 depending on the conditions of the binary or single systems. It was found that the Lagergren model described the F^- sorption kinetic data and the Langmuir and Freundlich equations described the equilibria of the sorption binary systems. These results suggested that the sorption mechanism was chemisorption on a heterogeneous material. The pH effects governing sorption capacities were also evaluated, showing a decrease as pH value rises, indicating that this sorption process is highly pH-dependent. The physical characterization of the biosorbent after fluoride removal by infrared analyses showed fluoride removal in different functional groups on the surface of the modified and unmodified biosorbents. The point of zero charge and co-existing ions affected the efficiency of defluoridation significantly. The pine sawdust showed a high affinity for fluoride ions compared with conventional adsorbents; therefore, it can be considered as a good low cost biosorbent for the defluoridation of water.

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1. Introduction

The presence of certain anionic species or trace elements can be considered as water pollutants when they exceed certain levels. Furthermore, bioaccumulation becomes an environmental problem when their concentrations affect human health and ecosystems (Manahan, 2007; Lito et al., 2012). Fluoride is a persistent and non-degradable poison that accumulates in soil, plants, wildlife and humans and that can be enriched in natural waters by geologi-

cal processes. The problem is more acute in rural and small urban communities, particularly in third world countries.

Fluoride, although one of the most reactive elements in the periodic table, is perhaps the only element whose deficiency (<0.5 mg/L) and presence in excess (>1.5 mg/L) in drinking water can provoke serious health problems (Nazeeb and Ravikumar, 2013). Due to its high concentration in intake (food, drink or medication) or exposure in any activity for long periods of time, fluoride causes fluorosis (dental and skeletal damage), nerve damage (impacts on IQ and behavior), endocrine affectations (hormonal) and damages to other organs (digestive system, immune system, etc.) (Ghosh et al., 2013; Lito et al., 2012).

In Mexico, the prevalence and incidence of fluorosis have increased during recent years. Hence, the physicochemical characteristics of soil and water are crucial for research on this topic, especially due to the high levels of fluoride in the northern, central and western parts of the country. Recent studies have demonstrated the presence of fluorides in the state of Michoacan, particularly in water wells and springs in the communities nearby Cuitzeo Lake such as Los Azufres, Araró, Huingo and El Hervidero. Those places show a fluoride concentration ranging from 0.2 to 17 mg/L (Alfaro et al., 2002; Alarcón Herrera et al., 2013), above the maximum permissible level set by the World Health Organization of 1.5 mg/L.

There are different methods for the treatment of water and wastewater with high levels of fluoride, including electrochemical methods, oxidation-reduction methods, filtration, precipitation, semipermeable membranes and ion exchange. The problem is that these processes can be complicated and expensive, with low selectivity and capacity and complicated operation and maintenance (regeneration and cleaning). In addition, they can generate secondary waste that is difficult to treat or dispose. Therefore, it is desirable to conduct research to find low cost methods that can be easily applied, particularly for water defluoridation in developing countries (Lito et al., 2012).

Biosorption is one method for water defluoridation, and the use of natural biosorbents is of great importance in the development of new technologies for the treatment of water in underdeveloped communities. However, the presence of other ions may affect the biosorption of trace elements. Therefore, studies of binary or multiple systems have simulated a real natural water effluent (Ayoob and Gupta, 2009; Chen et al., 2010).

Biosorption depends on the operating conditions of the removal process such as the biosorbent mass, concentration of pollutants, operating mode, characteristics of biosorbent functional groups (e.g. texture) and solution chemistry (e.g. temperature, pH, ionic strength). Based on this fact, biosorption mechanisms can occur simultaneously and specifically with lignocellulosic precursors. Agricultural residues are used as effective biosorbents due to their lignocellulosic structure and the large number of functional groups (e.g. alcohols, aldehydes, ketones, carboxylic/phenolic groups) since they have the capacity to sequester and accumulate ions by electron donation (Barathi et al., 2013).

Cellulose is a natural polysaccharide endowed with intramolecular hydrogen bonding and good stability. The small size of fluoride, its high electronegativity and its behavior as a strong base also make it compatible with metal ions such as aluminum. Taking advantage of this fact, cellulose biopolymer has been explored as an effective matrix for the impregnation of aluminum through electrostatic interaction with the hydroxyl groups in cellulose. These groups could also be used for the adsorption of anions through hydrogen bonding interactions on the surface of the biopolymer.

However, almost any kind of adsorbent shows different fluoride adsorption capacities when used for the defluoridation of drinking water as well as for the removal of fluoride ions from aqueous solutions in the presence of competitive ions. For instance, Chen et al. (2010) observed that fluoride adsorption was reduced in the presence of phosphate and sulfate ions and increased slightly in the presence of chloride and nitrate ions when using granular ceramic as an adsorbent. Strong interferences on fluoride removal in the presence of phosphate and sulfate ions when iron and aluminum-based mixed hydroxides were used as adsorbents has also been reported, while the presence of carbonate showed less interference (Sujana and Anand, 2010). Moreover, the presence of chloride ions significantly diminished the fluoride adsorption capacity, while the presence of nitrate and sulfate ions did not show any significant effect on fluoride removal, using an iron-modified natural zeolitic tuff (Velazquez-Peña et al., 2015).

Therefore, the aim of this study was the evaluation of competitive ions on the biosorption of fluoride using pine sawdust (*Pinusmichoacana*), in fluoride single systems and F^-/HCO_3^- and $F-/SO_4^{2-}$ binary systems. In order to achieve a better removal, natural sawdust (SwtN) was conditioned and modified with aluminum chloride ($AlCl_3$) to simulate an alumina compound that is effective in the removal of trace elements. Due to its high electronegativity and small ionic size, the fluoride ion is classified as a hard base, which has a strong affinity towards metal ions including Al(III) and Fe(III).

2. Materials and methods

2.1. Biosorbent preparation and modification with Al

Treated and untreated pine sawdust biosorbents were used in this study for the biosorption experiments. Pine sawdust (*P. michoacana*) was collected from a local wood mill. It was sieved, and the 0.5 mm grain size fraction was selected to carry out the tests. This fraction was then washed thrice with water to remove dust and water-soluble impurities. After treatment, the sawdust was dried in an oven at 60 °C for 24 h and then placed in a desiccator for further treatment. This material was identified as SwtN.

Pine sawdust was modified with aluminum in order to evaluate its fluoride sorption capacity after this treatment. This modification of the biosorbent was carried out by the following procedure: 10 g of SwtN was put in reflux with 250 mL of $AlCl_3$ 0.05 M solutionat pH 3.5 for 3 h. The mixture was allowed to cool and it was put in reflux again for another 3 h with fresh solution. Then, the modified sawdust with $AlCl_3$ (Swt-Al) was filtered and washed several times with distilled water to eliminate any excess aluminum and chloride ions from the material; the modified material was allowed to dry, and it was stored in a desiccator. This method was carried out according to those reported previously (López-Leal et al., 2012; Marín-Rangel et al., 2012).

2.2. Chemical characterization of the biosorbent

Moisture, ash, extractives, lignin, cellulose and holocellulose were determined by TAPPI methods (TAPPI, 2000). The pH value of the pine sawdust was determined using the method reported by Sandermann and Rothkamm (1959).

2.3. Scanning electron microscopy (SEM)

Samples of SwtN, Swt-Al and fluoride-loaded aluminum-modified sawdust (SwtF) were covered with copper and analyzed using a JSPM-5200 scanning electron microscope and a JEOL JSM-7600F FEG-SEM microanalysis detector in order to observe the surface morphology of the samples and obtain semi-quantitative elemental analysis.

2.4. Fourier transform infrared spectroscopy (FTIR)

FTIR analyses were carried out on SwtN, Swt-Al and SwtF. For the measurement, 0.3 g of dry KBr was mixed with 0.02 g of each sawdust sample and then compressed with a 3-ton force for 1 min. The samples were analyzed in a Bruker Tensor 27 FTIR spectrophotometer. The frequency range used was between 200 and 4000 cm^{-1}.

2.5. Point of zero charge (PZC)

The PZC was determined by measuring the zeta potential of Swt-Al using a Zeta-Meter System 3$^+$. Different solutions of the biosorbent at various pH values, ranging from 3 to 10, were prepared by adjusting pH with 0.01 M HCl and 0.01 M KOH solutions.