Removal of sodium and chloride ions from aqueous solutions using fique fibers (Furcraea spp.)

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ABSTRACT

Fique fibers obtained from the leaves of Furcraea spp., a highly abundant plant in the mountains of South America, may offer an alternative as biosorbents in desalination processes as they exhibit high removal capacities (13.26 meq/g for chloride ions and 15.52 meq/g for sodium ions) up to four times higher than exchange capacities commonly observed in synthetic resins. The ion removal capacity of the fibers was also found to be a function of the pH of the solution with the maximum removal of ions obtained at pH 8. Unlike most commercial ion exchange resins, our results suggest that fique fibers allow simultaneous removal of chloride and sodium ions.

Key words | biomaterials, biosorption, desalination, fique fibers, isotherms, kinetics

INTRODUCTION

The concentration of sodium ions in seawater is typically around 11 g/L while chloride concentration nears 20 g/L (Benjamin 2002). High salt concentrations cause corrosion in distribution pipes, damage soil and crops, and affect the ecology of water bodies. Therefore, desalination of waste streams with high salt concentration is required prior to their disposal into surface water bodies or their use in irrigation.

Desalination can be achieved using adsorption and ion exchange processes (Miller 2005). During adsorption, surface complexation reactions, including surface hydrolysis and the formation of coordinative bonds with ligands and metals, take place. Several materials capable of removing sodium and chloride by ion exchange or sorption have been recently developed. For example, ZnAl-NO3 layered double hydroxides have uptake capacities of up to 1.3 meq Cl−/g (Lv et al. 2009). The chloride uptake of Amberlite IRA-420, a commercial resin, can reach values of up to 4 meq/g (Carmona et al. 2008). Other commercial synthetic anion exchange resins exhibit typical uptake capacities ranging between 1 and 4 meq/g. Similar uptake capacities are found in commercial cation exchange resins (Zheng et al. 1996; Zhao et al. 2014).

Low-cost sorbents of biological origin, aka biosorbents, can also be used to remove ions and other contaminants from water (Veglio & Beolchini 1997; Bailey et al. 1999; Annadurai et al. 2003; Anirudhan & Radhakrishnan 2007). Anion exchange capacities of about 4 meq/g have been obtained using rice hull, sugarcane bagasse, pure cellulose, and pure alkaline lignin (Orlando et al. 2002). All biosorbents contain cellulose, hemicellulose, and/or lignin (Orlando et al. 2003). Several ion-binding mechanisms are known to occur during biosorption including ion exchange, complexation, chelation, physical adsorption, and microprecipitation among others (Volesky 2001; Gadd 2009).

Fique fibers are obtained from the leaves of Furcraea spp., a plant indigenous to the Andean region of Colombia in South America (Chacón-Patiño et al. 2006). Fique fibers are widely used to manufacture rope and crafts, and they are composed of cellulose (65%), hemicellulose (17.5%), lignin (14.5%), and other minor components including pectin and waxes (5%) (Castellanos et al. 2012). Due to the widespread availability, their low cost, high surface area, and high cellulose content, we decided to explore the feasibility of fique fibers for the removal of sodium and chloride ions from water. Desalination is a novel application for fique fibers.

EXPERIMENT

Fiber preparation and characterization

Raw fibers, obtained from a local market, were cut in pieces ranging between 0.2 and 0.8 mm in length, and soaked in...
ultrapure water and ethanol (90%) (Gurgel & Gil 2009). The fibers were oven-dried (105 °C, 12 h) and separated using a 850 μm sieve. Surface area, average pore size, and pore volumes of the fibers were determined with an Autosorb-iQ Automated Gas Sorption Analyzer (Quantachrome Instruments). The surface chemistry of the fibers was analyzed using a Fourier transform infrared spectroscope (FTIR) (Shimadzu IR Prestige-21, Japan). Field emission scanning electron microscopy (FESEM) analyses were carried on a FEI QUANTA FEG 650 instrument equipped with a Large Field Detector; samples were coated with a thin layer of carbon before analysis and the micrographs were taken at 10 kV.

Isotherms and sorption kinetics

Solutions of sodium chloride (1 × 10⁻³ to 0.9 M) were used to determine sorption isotherms. The initial pH of the solutions was adjusted, using nitric acid or potassium hydroxide, to 4, 6, and 8. Approximately 0.5 g of fibers were placed in 50 mL of the solutions and shaken for 2 h at 25 °C. Fibers were separated from the solution prior to measuring sodium and chloride concentrations by filtration (0.45 μm). The concentration of Na⁺ was measured according to method 3500-Na C (AWWA 1998) via atomic absorption spectrometry (Perkin Elmer Analyst 300 Spectrometer). The concentration of Cl⁻ was measured by using the selective ion method (ME 4500-Cl⁻) with a 187 pH/IonMeter (Metrohm, Switzerland). Final pH values were measured for all equilibrium experiments. Point of zero charge (PZC) was measured using the pH drift method as previously described (Bouatay et al. 2014). Values for the kinetic constants were obtained by measuring the concentration of dissolved ions at regular intervals during 120 minutes starting at initial concentrations of 0.9 and 0.5 M. All experiments were conducted in triplicate.

RESULTS AND DISCUSSION

Adsorption isotherms

Fique fibers exhibited removal capacities of up to 13 meq/g for chloride and 15 meq/g for sodium (Figure 1). These values are up to four times higher than exchange capacities commonly observed in materials of agricultural origin and synthetic resins (Zheng et al. 1996; Orlando et al. 2002; Carmona et al. 2008; Zhao et al. 2014). The removal efficiency of the fibers was found to be pH dependent with a maximum value obtained at pH 8, for both sodium and chloride. As expected, the ion removal process resulted in a decrease of the pH in the solution. The lowest pH reached in the solutions, initially containing 0.9 M NaCl and having a pH 8 at the beginning of the experiment, was 4.1. The pH reduction during adsorption was consistent with that of an ion exchange process characterized by a higher affinity for cations than anions. PZC of the fique fibers was 4.6. The PZC describes the condition when the electrical charge density of a surface is zero. Below this pH, the adsorbent is positively charged and attracts mostly anions. At higher pH, the surface becomes negatively charged and attracts mostly cations.

The removal of negatively charged ions by lignocellulosic materials can be attributed to the electrostatic interactions between the anions and the protonated carboxyl groups present on the lignin surface (Demirbas 2005; Albadarin et al. 2011). When functional groups such as carboxyl, phenolic, hydroxyl and carbonyl are protonated, the surface is surrounded by hydronium ions, and thus promotes the approach of negatively charged ions.

The heterogeneous surface of fique fibers provides significant amounts of micropores and cavities that facilitate surface reactions (Figure 2) (Chacón-Patío et al. 2013). Nitrogen adsorption and BET data fits indicates a pore volume of 0.030 cm³/g, with a surface area or 9.393 m²/g. The Freundlich isotherm was used to analyze the experimental results as this model applies well to solids with heterogeneous surfaces. The Freundlich isotherm follows the equation $q = k F C^2$, where $k_F$ describes the adsorption density under standard conditions, and the $n$ exponent represents the binding strength whereby the adsorption density changes as a function of aqueous concentration (Benjamin 2002). The best-fit of the experimental data at pH 8 to the Freundlich isotherm renders for chloride: $q = 0.0205 C_e^{0.961}, R^2 = 0.9798$; and for sodium: $q = 0.2443 C_e^{0.611}, R^2 = 0.9802$. The parameter $n$ was less than 1.0 in both cases, which is typical when the surface has an heterogeneous nature (Benjamin 2002). The Langmuir isotherm was also used to evaluate the experimental results, but $R^2$ values were much lower than those observed with the Freundlich isotherm, and are therefore not shown.

The sorption capacity (Freundlich constant, $K_f$) is an order of magnitude higher for sodium than for chloride. This observation supports the conclusion that fique fibers exhibit higher affinity for cations over anions. Higher removal of cations is expected due to the abundance of −OH and C−O−C bonds in the fique fibers as illustrated by the FTIR spectra (Figure 2, right) (Gañán & Mondragon 2002).
Kinetic experiments

The rapid uptake of sodium and chloride ions observed during the first 30 minutes of the reaction and the fact that equilibrium was reached within one hour (Figure 3) indicate that fique fibers are indeed suitable for desalination processes. The fast removal upon exposure was probably achieved as a result of strong electrostatic forces between the ions and the functional groups on surface of the fibers (Ahmad & Alrozi 2014). After the rapid removal, the process slowed down due to the diffusion of ions through the fibers' pores.

Figure 1 | Adsorption isotherms for the removal of sodium (top left) and chloride (top right) ions from NaCl solutions at 25 °C using fique fibers as biosorbents. Experimental results (markers) and modeled predictions (lines) using the Freundlich isotherms are shown along with error bars representing the standard deviation from triplicate experiments. Results are compared with data reported in the literature using different materials for the removal of sodium or chloride ions from water: chloride removal using a commercial Amberlite IRA 420 resin (Carmona et al. 2008) and ZnAl(NO3) double hydroxides (Lv et al. 2009); and sodium removal using Na1.6Al0.6Ti1.4(PO4)3 (NATP) (Zhao et al. 2014) and crystalline silicotitanates (Zheng et al. 1996). Sorption isotherm for sodium evaluated at initial pH of 4, 6, and 8 (middle left). Sorption isotherm for chloride evaluated at initial pH of 4, 6, and 8 (middle right). Final solution pH as a function of the equilibrium aqueous concentration of sodium for NaCl solutions with an initial pH of 8 and initial NaCl concentration of 0.9 M (bottom).
The Lagergren equation is commonly used to describe removal kinetics according to a pseudo-first-order kinetic model (Ünlü & Ersoz 2009), where \( q_e \) is the equilibrium concentration, \( q_t \) is the amount of solute removed at time \( t \), and \( K_{ads} \) is the adsorption constant (Figure 3). The resulting Lagergren fits render: chloride: \( \log (14.53 - q_t) = 14.53 - (0.0493/2.303)t \), \( R^2 = 0.979 \); sodium: \( \log (15.82 - q_t) = 15.82 - (0.0386/2.303)t \), \( R^2 = 0.989 \) at initial pH of 8 and initial NaCl concentration of 0.9 M. The good quantitative fit of the experimental data to the Lagergren model is an indication that the process does indeed follow pseudo-first-order kinetics. The pseudo-second-order kinetic model was also used to evaluate our experimental data, but \( R^2 \) values obtained were slightly lower than those obtained with the Lagergren model.

Our results suggest that fique fibers can simultaneously be used for the removal of chloride and sodium ions from water. However, results presented here are only from batch experiments, and further experiments need to be conducted to evaluate the efficiency of the removal process under continuous conditions. Also, it is unknown if the cutting, sieving, washing, and drying of the fibers is required prior to the removal process and it is necessary to conduct further experiments to optimize pretreatments for cost and quality.

**CONCLUSIONS**

Fique fibers were studied as potential biosorbents for the removal of sodium and chloride ions from water. Experimental results indicated that both ions were removed at high rates, reaching saturation within 60 minutes. The removal capacities were significantly higher than most removal capacity values reported in the literature (Orlando et al. 2002; Carmona et al. 2008; Lv et al. 2009), namely up to 15 meq/g for sodium and 13 meq/g for chloride. Fique fibers present an interesting alternative for water desalination, featuring high removal capacity in a material of agricultural origin. Furthermore, unlike most commercial ion exchange resins, our batch test results suggest that fique fibers allow simultaneous removal of chloride and sodium ions.

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