Industrial Crops and Products 43 (2013) 200–206

Contents lists available at SciVerse ScienceDirect

Industrial Crops and Products

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

Chemical characterization of raw and treated agave bagasse and its potential as adsorbent of metal cations from water

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ARTICLE INFO

Article history:
Received 1 February 2012
Received in revised form 7 June 2012
Accepted 14 June 2012

Keywords:
Agave bagasse
Chemical characterization
Bioadsorption
Heavy metals
Mechanism

ABSTRACT

Lignocellulosic materials have a very complex configuration that contains a variety of active sites capable, in some cases, of adsorbing contaminants from water. Agave bagasse is a sub-product from the alcohol industry that has been very little studied, but that could have the potential to remove a variety of contaminants from aqueous solutions.

Raw and modified *Agave salmiana* bagasse were characterized, before and after they were tested to remove metal cations, by acid–base titrations, elemental analysis and ATR-FTIR. HCl, HNO_3, NaOH, tartaric, citric and oxalic acids were used to modify bagasse to determine if its concentration of active groups could be improved. These materials were then tested for the removal of Cd(II), Pb(II) and Zn(II) ions from water at pH 5, and desorption studies were performed at pH 2 and 4 at 25 °C.

The characterization techniques mainly identified carboxyl, hydroxyl, sulfur and nitrogen containing groups in bagasse. It was clear that mainly the carboxylic groups were responsible for metal uptake. Raw bagasse has an adsorption capacity of about 8, 14 and 36 mg g^{-1} for zinc, cadmium and lead, respectively, and this was improved about 27–62% upon modification with HNO_3 and NaOH. Treatments with citric, oxalic and tartaric acid did not have a significant effect in adsorption capacity.

Raw agave bagasse has a very acceptable adsorption capacity of metal cations and it can approximately be regenerated in a 45%, since the biosorption mechanism involves ion exchange and complexation.

1. Introduction

Research in removal of heavy metals from aqueous streams by natural biosorbents has been conducted for several years. This technique has shown to be very promising over conventional treatment methods because of its low cost, high efficiency, easy regeneration of biosorbents, and possibility of metal recovery. The native exchange capacity and general sorption characteristics of these materials derive from their constituents: cellulose, hemicelluloses, pectin, lignin, and proteins; which contain a variety of functional groups that can adsorb certain contaminants in water (Devaprasath et al., 2007).

Agricultural waste materials are abundant and have been proved to be good low cost adsorbents due to their easy conversion to a value-added product. These biosorbents, mostly lignocellulosic residues, have a comparable metal adsorption capacity (mg g^{-1}) to other natural sorbents (Garg et al., 2008; Lee and Rowell, 2004; Miretsky and Fernandez Cirelli, 2010; Ngah and Hanafiah, 2008; Zhu et al., 2008). Agave bagasse (*Agave salmiana*) is an abundant lignocellulosic waste material at the alcohol industry: as an example, about 350 000 tons per year are generated in the mescal industry in Mexico. This residue produces ecological problems due to its low natural degradation rate, and because it is commonly eliminated by burning, thereby becoming a source of atmospheric pollution. Recent studies by our research group have indicated that agave bagasse has a higher adsorption capacity for Cr(III) than sorghum or oat straw (Garcia-Reyes and Rangel-Mendez, 2009; Garcia-Reyes et al., 2009; Krishnani and Ayyappan, 2006). These results have encouraged us to continue exploring the potential of agave bagasse to remove contaminants from water, such as Cd, Pb, and Zn that are usually found in wastewater (Garg et al., 2008; Lee and Rowell, 2004). Moreover, the concentration of binding sites in agave bagasse could be increased, considering that the natural adsorption capacity of some lignocellulosic materials has been improved with treatments or modifications that include basic solutions (NaOH, Na_2CO_3, and $Ca(OH)_2$), mineral and organic acid solutions (HCl, HNO_3, H_2SO_4, tartaric acid, citric acid, and formic acid), organic compounds (formaldehyde, CH_3OH, and epichlorohydrin), and oxidizing agents (H_2O_2, K_2MnO_4, and propylene oxide) (Fourest and Volesky, 1996; Gardea-Torresday et al., 2004; Ngah and Hanafiah, 2008). For the purpose of this study, agave bagasse was treated with mineral acids

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http://dx.doi.org/10.1016/j.indcrop.2012.06.049

(HCl and HNO_3), NaOH, and organic acids (tartaric, citric and oxalic acid).

Therefore, the aim of this work is to determine the chemical properties of raw and modified agave bagasse and to find out their potential to remove Cd(II), Pb(II), and Zn(II) from water. The results reported herein also suggest possible biosorption mechanisms of metal cations.

2. Materials and methods

2.1. Materials

Agave bagasse (*A. salmiana*) was collected from a local distillery in San Luis Potosi, Mexico. The bagasse was ground to a particle size of approximately 1 cm long and then rinsed several times with distilled water to remove impurities. It was dried overnight in an oven at 60 °C, and then, stored in polyethylene bags. The adsorbent thus obtained was designated as raw agave bagasse (RAB).

The bagasse was modified as follows: 25 g of RAB was soaked in 350 mL of 0.01, 0.505, or 1 M NaOH solution for 6 h at 25 °C. Excess of NaOH was removed by rinsing with deionized water until a neutral pH was attained. The bagasse was then dried overnight in an oven at 60 °C. The resultant material was designated as Na-AB. The same protocol was followed when treating bagasse with HCl and HNO_3, and treated samples were designated as HC-AB and HN-AB respectively.

The tartaric acid (L-$C_4H_6O_6$, Fermont) modification was conducted by a method previously described by Wong et al. (2003).

Na-AB, HC-AB and HN-AB were added separately to a 0.01 or 2 M organic acid solution at a ratio of 2 g of material/100 mL solution. Each mixture was stirred and heated for the time and temperature established by a fractional factorial experimental design (see Supplementary information Table S1). Finally, the treated material was left to cool, washed several times with distilled water until a neutral pH was attained, and dried overnight in an oven at 60 °C. These adsorbents were designated as TNa-AB, THC-AB and THN-AB: where T signifies tartaric acid treatment.

The same procedure was followed when raw agave bagasse was treated with tartaric, oxalic or citric acid. These samples were named T-AB, Ox-AB and Cit-AB respectively.

2.2. Adsorption equilibrium experiments

Individual stock solutions of 100 mg L^{-1} were prepared with analytical grade $Cd(NO_3)_2{\cdot}4H_2O$ (Fluka Chemika), $Pb(NO_3)_2$ (Sigma–Aldrich) and $Zn(NO_3)_2{\cdot}6H_2O$ (J.T. Baker). Samples of either 0.08 or 0.04 g of raw or modified agave bagasse were added to 40 mL of an individual metal solution (1–100 mg L^{-1}) in conical-bottom polypropylene tubes. The solution pH was adjusted daily to 5.0 ± 0.25 using 0.1 N HNO_3 or NaOH. Experiments were monitored until equilibrium was achieved, which was determined when the concentration of adsorbate in solution remained constant. An alternative adsorption experiment was performed by contacting 0.08 g of RAB and an equimolar solution of Cd(II), Pb(II) and Zn(II) (1:1:1, 3.86×10^{-4} M). All of the experiments were conducted in duplicate.

The concentrations of metal ions were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) with a Varian 730-ES spectrophotometer. The adsorption capacity of the biosorbents (q_e, mg g^{-1}) was calculated as follows:

$$q_e = \frac{V(C_0 - C_e)}{w} \quad (1)$$

where V is the total solution volume, w is the amount of adsorbent, and C_0 and C_e are the initial and final (or equilibrium) metal concentration, respectively.

2.3. Desorption experiments

Agave bagasse materials were saturated with 80 mg L^{-1} of Cd(II), Pb(II) or Zn(II) at pH 5 and 25 °C until equilibrium was achieved. They were then filtered and slightly rinsed with deionized water to remove any excess metal solution. The materials were then added to 40 mL of deionized water at initial pH of 2 or 4, and stirred for 72 h at 25 °C. The pH of each solution was adjusted daily to 2 or 4 using 0.1 N HNO_3. Finally, the concentration of metals, Ca, Na and K ions released was determined by ICP-OES and the desorption capacity was calculated by mass balance.

2.4. Biosorbent characterization

Attenuated total Fourier transform infrared spectroscopy (Thermo Nicolet 6700 ATR-FT-IR) was used to determine both active groups and changes in vibrational frequencies in the functional groups of the raw and modified bagasse. The spectra were obtained within the wavenumber range of 600–4000 cm^{-1}, with a 4 cm^{-1} resolution. The influence of atmospheric water and CO_2 was always subtracted.

2.5. Potentiometric titrations

Potentiometric titrations were carried out with an automatic titrator (Mettler-Toledo T70) and with an InLab DG111-SC pH electrode (Mettler-Toledo). A sample of 0.1 g of raw, pretreated or modified agave bagasse was dispersed in a 50 mL solution of 1 mM NaCl as background electrolyte. Titration was carried out by stepwise addition of 0.001 mL of 0.1 N NaOH to the flask while the solution was stirred under a N_2 atmosphere to exclude CO_2. After each addition of titrant, the system was allowed to equilibrate until a stable pH value was obtained.

2.6. Elemental analyses

Elemental analyses of dried agave bagasse samples were performed using an Elemental Combustion System (COSTECH instruments). Samples of raw, treated or modified agave bagasse were ground to fine powder and 8 mg of each material (dry basis) were weighed on tin capsules and placed into the elemental furnace. The samples were burned in an excess of oxygen, and the mass of these combustion products (NO_2, CO_2 and H_2O) were used to calculate the percentage of C, H and N contained in each sample. The O content was calculated by difference to 100%, considering the ash content of each material.

3. Results and discussion

3.1. FTIR analysis of agave bagasse

The ATR-FTIR spectra of saturated materials are shown in Fig. 1. The characteristic absorption bands in RAB indicated the presence of protonated carboxylic groups or ester groups around 1725 cm^{-1}, as well as alkyl chains (—CH_3 and —CH_2) and —OH groups at 2940–2846 and 3360 cm^{-1}, respectively. Bands at 1410 and 1020 cm^{-1} confirmed the presence of acidic groups due to C—O and O—H of aliphatic and phenolic structures respectively. These bands could be related to cyclic structures, such as cellulose or lignin. A new band close to 1530 cm^{-1} appeared when RAB is pretreated with acid or alkali solutions. This peak showed the presence of a carboxylate anion ($(COO)_2^-$) stretch vibration, and demonstrates the conversion of a salt or ester group to a carboxylic acid