Journal of Hazardous Materials 170 (2009) 845–854

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Chromium (III) uptake by agro-waste biosorbents: Chemical characterization, sorption–desorption studies, and mechanism

Garcia-Reyes Refugio Bernardo[a], Rangel-Mendez Jose Rene[a,*], Alfaro-De la Torre Ma. Catalina[b]

[a] *Division of Environmental Sciences, Instituto Potosino de Investigación Científica y Tecnológica, A.C., Camino a la Presa San José 2055, Col. Lomas 4ta. Sección, C.P. 78216, San Luís Potosí, S.L.P., Mexico*

[b] *Faculty of Chemistry Sciences, Universidad Autónoma de San Luís Potosí, Av. Dr. Manuel Nava 6, Zona Universitaria, C.P. 78210, San Luís Potosí, S.L.P., Mexico*

ARTICLE INFO

Article history:
Received 28 January 2009
Received in revised form 9 May 2009
Accepted 11 May 2009
Available online 19 May 2009

Keywords:
Agricultural residues
Functional groups
Equilibrium constants
Ion exchange
Complexation

ABSTRACT

Within their complex structure, agro-waste materials such as sorghum straw (SS), oats straw (OS) and agave bagasse (AB) have functional groups (i.e. carboxyl and phenolic) that play a major role in metals sorption. The advantages of these materials include availability, low-cost, and a reasonable metal sorption capacity. These agro-waste materials were chemically characterized by acid-base titrations and ATR-FTIR analyses in order to determine their functional groups, equilibrium constants, and surface charge distribution. Batch experiments were conducted at pH 3 and 4, at 25 °C and 35 °C to determine the biosorbents chromium (III) sorption capacity. Partially saturated biosorbents were desorbed with HNO_3, NaOH, and EDTA at different concentrations and temperatures (25 °C, 35 °C, and 55 °C). Finally, the chromium (III) sorption mechanism was discussed.

Agro-waste materials functional groups are associated, in part, to carboxyl and hydroxyl groups: these oxygen-containing sites play an important role in the chromium (III) removal. The maximum chromium (III) sorption capacity was 6.96, 12.97, and 11.44 mg/g at pH 4 for acid-washed SS, OS, and AB, respectively. The chromium (III) sorption capacity decreased at pH 3 because H^+ ions competed for the same functional groups. On the other hand, an increase in temperature enhanced both the biosorbents chromium (III) sorption capacity and their desorption by EDTA. The most probable chromium (III) sorption mechanisms were ion exchange and complexation.

The agro-waste materials studied herein efficiently remove chromium (III) from aqueous solution and, most importantly, EDTA can efficiently desorb Cr (III) from agro-waste materials at 55 °C.

1. Introduction

Heavy metal pollution is of great concern due to the human health problems that these cause when present in drinking water. In addition, heavy metals are non-biodegradable and can be bioaccumulated by organisms. Non-treated effluents from industries such as metallurgical, electronic, tannery, electro-plating, water cooling systems, among others can contaminate water systems with chromium, and other heavy metals.

This element is present in aqueous solutions mainly in the trivalent and hexavalent oxidation states. It is well known that trivalent chromium (Cr (III)) is an essential nutrient at trace concentration, and hexavalent chromium (Cr (VI)) is highly toxic and carcinogenic, but recently Suwalsky et al. [1] demonstrated that Cr (III) ions cause more structural perturbation in human erythrocyte membrane than Cr (VI). This structural perturbation, induced by Cr (III) ions, changes the biological membrane permeability affecting the functions of ion channels, receptors, and enzymes immersed in the erythrocyte membranes. In humans, Cr (III) can decrease immune system activity.

In Mexico, the maximum allowed concentration of chromium in drinking water is 0.05 mg/L [2]. In wastewater effluents, the allowed chromium concentration, on a monthly average, range from 0.05 to 0.1 mg/L depending on the final discharge site (i.e. river, lake, sea, etc.) [3]. Finally, wastewater discharges into municipal drainage cannot exceed 0.5 mg/L (monthly average) measured as Cr (VI) [4].

Due to the toxic effects of chromium, it is necessary to eliminate it from the contaminated effluents. Several alternatives to remove Cr (III) from effluents have been reported; for example, chemical precipitation, chemical oxidation-reduction, electro-chemical treatment, membrane separation processes, evaporation, adsorption, ion exchange, biosorption, among others [5–8]. In general, the first five treatment processes have considerable disadvantages such as incomplete metal removal, high priced equipment and/or expensive monitoring systems, high reactive requirements and/or energy, and toxic sludge production that needs to be confined [9–11].

---

* Corresponding author. Tel.: +52 444 834 2000; fax: +52 444 834 2010.
E-mail address: rene@ipicyt.edu.mx (R.-M.J. Rene).

0304-3894/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2009.05.046

Biosorption processes have advantages such as low-cost and locally available material, although they are sensible to pH and temperature changes. Some factors that influence the biosorbents metal sorption capacity are electric charge, type and quantity of chemical groups, pore size, surface area, temperature, and solution pH. Various biosorbents used to remove metals in aqueous solution are microorganism biomass [8,9,12], marine seaweed [7,13–18], agricultural by-products [19–24], chitin and chitosan [25–27], among others.

Agro-waste materials are mainly formed by such natural polymers as cellulose, hemi-cellulose, pectin and lignin. These components contain carboxyl functional groups linked together by calcium bridges which can play an important role in metal adsorption. For instance, researchers have found that divalent metal ions are exchanged by calcium ions present in agro-waste materials [28,29].

Mexico is a producer of sorghum (*Sorghum bicolor*) and oat (*Avena sativa*). The grains are used to prepare balanced food and sometimes the agro-waste materials (straw) are used for livestock. On the other hand, agave bagasse (*Agave salmiana*) is a waste generated in the industry of mezcal that produces ecological problems because it is burned or disposed of inappropriately. These agro-waste materials are locally available and could be used in adsorption processes, for example to remove Cr (III) from aqueous solution, but desorption studies are required to determine if these biosorbents can be regenerated and reused in order to make their application more attractive.

Therefore, the objectives of this research are to chemically characterize sorghum straw (*S. bicolor*), oats straw (*A. sativa*), and agave bagasse (*A. salmiana*), and also to explore their application for removing chromium (III) from water by sorption/desorption studies. An additional objective is to propose a sorption mechanism based on ion exchange.

2. Materials and methods

2.1. Biosorbents

Sorghum straw (SS), oats straw (OS) and agave bagasse (AB) were tested as biosorbents to remove Cr (III) from aqueous solution. Previous to the sorption experiments, the agro-waste materials were ground to obtain particles of about 1 mm, and then washed with de-ionized water (W) or hydrochloric acid (A) 0.01N. After the acid treatment, the biosorbents were washed with de-ionized water until obtaining a neutral pH. Finally, the biosorbents were dried in an oven at 50 °C for 24 h, and then stored in desiccators until the experiments were conducted.

Capital letters were used throughout the document to identify each biosorbent; for example, acid-washed agave bagasse is represented as AAB.

2.2. Chemicals

A stock solution of 500 mg/L was prepared by using $Cr(NO_3)_3{\cdot}9H_2O$ (A.C.S., Meyer). Appropriate dilutions were prepared to conduct sorption experiments with initial concentration of Cr (III) ranging from 5 to 100 mg/L. An EDTA salt (disodium salt, dehydrate cystal, A.C.S., J.T. Baker) was used to prepare 0.1 M and 0.05 M eluent solutions. In addition, 1.0N HNO_3 and 1.0N NaOH (both A.C.S., Fermont) solutions were used to regenerate chromium-loaded biosorbents. De-ionized water was used to prepare all solutions. Finally, chromium, calcium, and magnesium concentrations were measured by using an atomic absorption spectrophotometer, AAS (PerkinElmer, AAnalyst 400).

2.3. Surface charge distribution, functional groups, and equilibrium constants

Potentiometric titrations were conducted to determine the materials surface charge distribution. First, 125 mg of biosorbent were placed in 50 mL polyethylene vials. After that, 20 mL of 0.1N NaCl (A.C.S., Caledon) were added to the vial containing the biosorbent. Then a different volume of 0.1N NaOH or 0.1N HCl (both A.C.S., J.T. Baker) was added into each vial. Finally, 0.1N NaCl solution was used to complete 25 mL. Carbon dioxide free-solution was obtained by stripping with nitrogen gas. In the same way, a blank experiment (without biosorbent) was conducted. Solutions were kept at 25 °C and were manually shaken twice a day for a period of 5 days. Finally, the equilibrium pH of each experiment was measured (Thermo, Orion 4 STAR).

Additionally, to estimate the biosorbents functional groups and their equilibrium constants, the experimental data obtained from potentiometric titrations were processed according to the method proposed by Yun et al. [18].

2.4. Functional groups identification

Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) analyses (Thermo-Nicolet, Nexus 470 FT-IR E.S.P.) were used to identify the biosorbents functional groups, before and after the sorption–desorption processes.

Previous to ATR-FTIR analyses, biosorbents were dried at 50 °C for 24 h. Then the spectra were obtained in the range from 650 to 4000 cm^{-1} with 4 cm^{-1} resolution. The resulting spectra were the average of 32 scans. Finally, the spectra were used to identify the functional groups based on the characteristic transmittance peaks.

2.5. Chromium species in aqueous solution

The chromium speciation diagram was computed with the software Visual MINTEQ 2.51 [30]. This diagram was obtained for a chromium concentration of 100 and 357 mg/L of nitrates.

2.6. Adsorption experiments

The biosorbents Cr (III) sorption capacity (Q_e) was determined at different temperatures (25 °C and 35 °C) and pH values (3 and 4) in duplicate and the average values are presented. Samples of 100 mg of biosorbents were added to 100 mL of Cr (III) concentrations of 5–100 mg/L. These experiments were continuously stirred at 180 rpm. The solution pH was adjusted daily to pH 3 or 4 by adding 0.1N NaOH and/or 0.1N HNO_3 until the equilibrium was achieved. Aliquots (10 mL) were taken to measure the initial and the equilibrium chromium concentrations (C_e) by AAS.

2.7. Metal ions adsorbed and released

It is well known that heavy metal ions are exchanged by other ions (such as calcium, magnesium or H^+) in biosorption processes. To understand the Cr (III) sorption mechanism, batch experiments were conducted in triplicate to determine both the chromium adsorbed and the ions released (such as calcium, magnesium, and H^+) from the agro-waste materials.

Samples of 100 mg of biosorbent were added to 100 mL of Cr (III) solutions (initial concentration 20 mg/L) contained in Erlenmeyer flasks at 25 °C. These flasks were closed and continuously stirred at 180 rpm. For experiments with pH control, the solution pH was adjusted daily to pH 4 by adding 0.1N NaOH and/or 0.1N HNO_3 until the equilibrium was achieved. For experiments without pH control, the initial pH was fixed to 4 and the final pH was measured at the end of the experiment.