Chromium (III) Sequestration by Oats Straw and Agave Baggasse: Sorption Mechanism

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Abstract

Agro-waste materials such as oats straw (OS) and agave baggasse (AB) have functional groups which are able to bind metal ions. The agro-waste materials studied in this research (acid washed) were chemically characterized and their chromium sorption and desorption capacity was obtained. HNO_3, NaOH and EDTA (at different concentrations and temperatures) were used to regenerate partially saturated biosorbents. Finally, the chromium (III) sorption mechanism was discussed.

The results demonstrated that OS and AB contain carboxyl and hydroxyl functional groups. The chromium (III) removed by acid washed OS and AB was 2.48 and 9.85 mg/g, respectively. Based on chromium (III) removed and ions released (mainly H^+ and Ca^{2+}) during the sorption process, it was suggested that the main sorption mechanism was ion exchange: for each mol of $CrOH^{2+}$ adsorbed 1 mol of Ca^{2+} and 2 mol of H^+ were released to the solution. On the other hand, the highest chromium desorption was obtained by using an EDTA solution at 55°C.

Oats straw and agave baggasse are capable of removing cations from aqueous solution. Preliminary results show that chromium (III), as $CrOH^{2+}$, is exchanged by Ca^{2+} and H^+ during the sorption process. In addition, an EDTA solution could be used to regenerate the chromium loaded biosorbents.

Keywords: Oats straw, Agave baggasse, Chromium (III), Sorption, Mechanism.

Introduction

Wastewater containing chromium is discharged from industries such as metallurgical, electronic, tannery, metal plating, among others. It is well known that hexavalent chromium is extremely toxic and carcinogenic. However, hexavalent chromium could be reduced to trivalent chromium by some microorganism or manganese oxide. Recently, Suwalsky *et al.* (2008) demonstrated that trivalent chromium exerts stronger structural effects than hexavalent chromium on the human erythrocyte membrane and membrane model. These new findings lead us to look for alternatives to remove chromium (III) from aqueous solution.

Biosorption is an emerging technology for treating water contaminated with heavy metal ions. For instance, seaweed biomass (Yun *et al.*, 2001; Cossich *et al.*, 2004), and agricultural by-products (Romero-Gonzalez *et al.*, 2006; Sawalha *et al.,* 2007 and 2008) have been used for removing chromium (III) from water.

Agro-waste materials components (cellulose, hemi-cellulose, pectin and lignin) contain carboxyl and hydroxyl functional groups which can be involved in metal binding (Reddad *et al.*, 2002). However, desorption studies are not often reported when agro-waste materials are used as adsorbents. In addition, the sorption mechanism is not well understood.

For that reason, the objectives of this research are to chemically characterize agro-waste materials (oats *sativa* straw (OS) and agave *salmiana* baggasse (AB)) locally available in Mexico, and to obtain the chromium (III) sorption/desorption capacity. Finally, the chromium (III) sorption mechanism was discussed based on results previously reported in literature and the ions released during the adsorption process.

Methodology

Agricultural residues such as oats *sativa* straw (OS) and agave *salmiana* baggasse (AB) were used as adsorbents after being hydrochloric acid (0.01 N) washed (A). These capital letters were used throughout the document to identify each biosorbent; for example acid washed agave *salmiana* baggasse is represented as AAB.
To obtain the agro-waste materials surface charge distribution, potentiometric titrations were carried out and to estimate the functional groups and equilibrium constants, the experimental data obtained from potentiometric titration were processed according to the method proposed by Yun *et al.* (2001). Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) was used to identify the biosorbents functional groups.

Batch sorption experiments were carried out to determine the chromium (III) adsorption capacity. Then regeneration of partially saturated agro-waste materials was carried out by using 100 mL of HNO_3 (0.1 and 1.0 N), NaOH (0.1 and 1.0 N) or EDTA (0.05 and 0.1 M) at 25, 35 and, in some cases, 55°C. The initial and equilibrium chromium and calcium concentration were determined by an atomic absorption spectrophotometer.

Results and discussion

The functional groups present in AOS and AAB were similar, although these exist in different amounts. The first functional group can be associated to carboxyl (pk_a value 3.8-4.1), these were confirmed by ATR-FTIR analyses at 1745, 1650, 1260, 1160, and 1060 cm^{-1} (Wade, 1993; Socrates, 1998). The second functional group cannot be associated to a specific group by the great amount of functional groups (amine, phosphoryl, amide, imidazol, etc.) associated to the pk_a values between 6.3 and 7.1. Finally, the third functional group can be associated to hydroxyl groups (pk_a 9.1-12.6) and these groups were confirmed by ATR-FTIR analysis in a broad band at 3350 cm^{-1}.

The pH_{PZC} was 3.2 and 3.5 for AOS and AAB, respectively. Because the adsorption experiments were carried out at pH 4, the agro-waste materials net surface charge posses a negative charge and, for that reason, cations metal could be adsorbed by electrostatic attraction. For instance, chromium species are positively charged at pH 4 as follows: Cr^{3+} (30%), $CrOH^{2+}$ (40%), $Cr_2(OH)_2^{4+}$ (26%) and $Cr_3(OH)_4^{5+}$ (4%). These species could be adsorbed in negatively charged functional sites (e.g. carboxyl groups).

The amount of chromium adsorbed and calcium released is showed in Figure 1. AOS adsorbed less chromium and released less calcium than AAB. These findings demonstrated that AOS contain less calcium than AAB, and these calcium released is directly related to the amount of chromium adsorbed. For example, for each mol of chromium (III) adsorbed 0.1 and 1.2 mol of calcium were released from AOS and AAB, respectively.

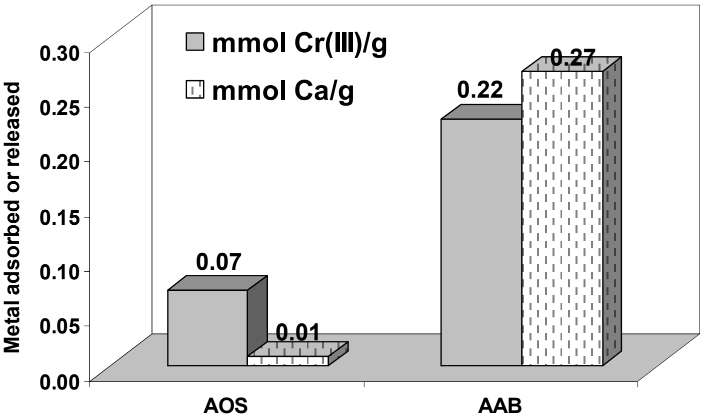

Figure 1. Chromium adsorbed and calcium released in agro-waste materials at pH 4 and 25°C.

However, the chromium adsorbed in AOS can not be explained by the release of calcium. For that reason, an additional adsorption experiment was carried out at the same conditions (25°C, 100 mg of AOS in 100 mL) but at pH without control (starting at pH 4) and initial chromium concentration of 100 mg/L. The initial and final pH was measured and then the amount of H^+ and chromium (III) ions was calculated. The molar ratio average, between H^+ released/chromium adsorbed, was 1.93 which suggested that $CrOH_2^+$ is preferentially adsorbed onto the agro-waste materials because when this specie is adsorbed, 2 mol of H^+ are released to the solution according to the following reaction (1):

$$2\{\equiv R\text{-}COOH\} + CrOH^{2+} \leftrightarrow \{\equiv R\text{-}COO\}_2\text{–}CrOH + 2H^+ \qquad (1)$$

In contrast, based on chromium (III) removed and calcium released during the sorption process (Figure 1), the adsorption mechanism could be:

$$\{\equiv R\text{-}COO\}_2\text{-}Ca + CrOH^{2+} \leftrightarrow \{\equiv R\text{-}COO\}_2\text{–}CrOH + Ca^{2+}$$

On the other hand, although the agro-waste materials presented less sorption capacity for chromium than seaweed biomass, activated carbons, or ion exchange resins, the agro-waste adsorbents are an available and cost-effective option for the removal of chromium (III) from aqueous solution. However, it is necessary to find a way to regenerate them and reuse them to make their application more attractive in real systems. In that sense, batch desorption experiments were carried out by using chromium partially saturated biosorbents. The chromium sorption capacity, at pH 4 and 25°C, was 9.9±1.0 and 2.5±1.0 mg/g for AAB and AOS, respectively. Chromium desorption results by HNO_3, NaOH and EDTA are given in Figure 2.

From Figure 2, it is clearly observed that the agro-waste materials regeneration was affected by both temperature and the eluent concentration. For instance, the regeneration by EDTA 1.0 M at 25 and 35°C was 32 and 39%, respectively, but at 55°C it achieved 63%. In addition, regeneration by EDTA did not cause initial weight lost as 1.0 N HNO_3 or NaOH (results are not shown).

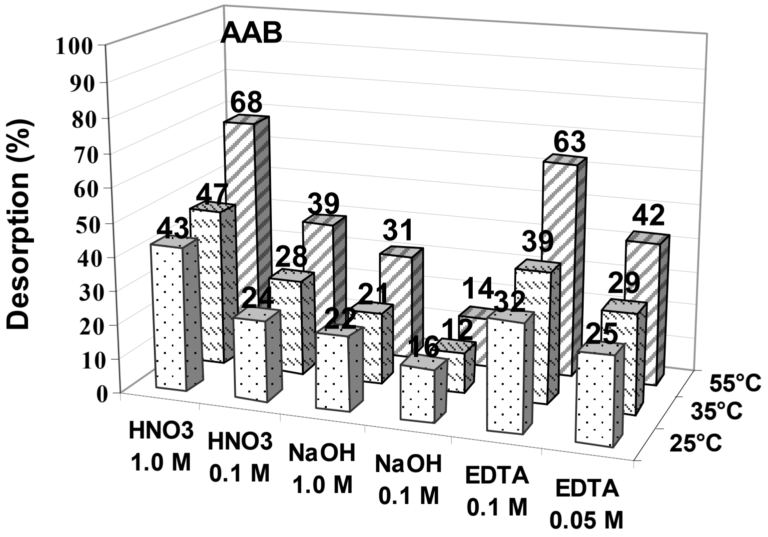

Figure 2. Chromium (III) desorption from AAB with different eluents and temperatures.

However, the low percentage of chromium desorbed by HNO_3 (1.0 N) at 25°C (see Figure 2) indicated that chromium (III) ions were covalently bound to the biosorbents functional groups (e.g. oxygen-containing sites). Finally, chromium desorption from agro-waste materials by EDTA at 55° presented an interesting option.

Conclusion

Oats straw and agave baggasse contain carboxyl and hydroxyl functional groups which are able to bind chromium (III) from aqueous solution. Preliminary results show that chromium (III), as $CrOH^{2+}$, is exchanged by Ca^{2+} and H^+ during the sorption process. In addition, an EDTA solution can be used to regenerate 63% of the chromium-loaded biosorbents without apparent modifications on the adsorbent.

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