Sorption and Desorption of Chromium (III) from Aqueous Solution by Agro-Waste Materials

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Abstract

Agro-waste materials such as sorghum straw (SS), oats straw (OS) and agave baggasse (AB) contain several functional groups (carboxyl, carbonyl, acetamido, amino, hydroxyl, etc.) which are able to bind heavy metal ions present in aqueous solution. The major advantages of these materials are: low-cost, high efficiency and regeneration. The agro-waste materials studied in this research (water washed and acid washed biosorbents) were chemically characterized and their chromium sorption capacity was obtained. Also, the regeneration of partially saturated biosorbents was carried out by using HNO_3, NaOH and EDTA at different temperatures. Finally, the sorption mechanism of chromium (III) was discussed.

The results show that the main functional groups can be associated to carboxyl, nitrogen, and hydroxyl groups. In addition, acid treatment shifted the pH_{PZC} to acid pH values. The maximum chromium (III) sorption capacity, for acid washed OS, was 12.9 and 8.3 mg/g at pH 4 and 3, respectively: the sorption capacity decreased at pH 3 since H^+ ions competed with chromium (III) ions for the biosorbents sorption sites. On the other hand, the biosorbents regeneration increased with rising the temperature. Based on the ATR-FTIR spectra and previously results reported in literature, it was suggested that chromium (III) has special affinity for the biosorbents oxygen-containing sites.

In conclusion, the agro-waste materials studied herein could be used to remove chromium (III) and they can be efficiently regenerated by an EDTA solution at 55°C.

Keywords: Chromium (III), agro-waste materials, sorption, regeneration.

Introduction

Recently Suwalsky *et al.* (2008) demonstrated that trivalent chromium ions exert stronger structural effects than Cr (VI) on the human erythrocyte membrane and molecular models. This perturbation could affect the functions of ion channels, receptors and enzymes immersed in the erythrocyte membranes.

Biosorption process is a cost-effective alternative for the removal of chromium (III) from water. Some biosorbents that have been tested for the removal of Cr (III) from aqueous solution are marine seaweed (Yun *et al.*, 2001; Cossich *et al.*, 2004), agricultural by-products (Romero-Gonzalez *et al.*, 2006; Sawalha *et al.,* 2007), etc.

Agro-waste materials are mainly formed by natural polymers such as cellulose, hemi-cellulose, pectin and lignin. These components 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.

The objectives of this research are to chemically characterize and to obtain the chromium (III) sorption/desorption capacity by agro-waste materials (sorghum *bicolor* straw (SS), oats *sativa* straw (OS) and agave *salmiana* baggasse (AB)) available in Mexico.

Methodology

Agricultural residues such as sorghum *bicolor* straw (SS), oats *sativa* straw (OS) and agave *salmiana* baggasse (AB) were used as adsorbents after being de-ionized water washed (W) and 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 by adding 125 mg of biosorbent in 25 mL of solution at different pH. The ionic strength solution was fixed by NaCl solution (0.01 N). 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 by adding 100 mg of biosorbent in 100 mL of chromium (III) solutions (ranging from 5 to 100 mg/L) at 25°C. These materials were continuously stirred. The solution pH was adjusted daily to pH 3 or 4 by adding 0.1 N NaOH and/or HNO_3 until the equilibrium was reached.

Partially saturated biosorbents were obtained by adding 100 mg of biosorbent in 100 mL of chromium (III) solutions (20 mg/L) at pH 4 and 25°C. Regeneration of partially saturated biosorbents 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 concentration were determined by an atomic absorption spectrophotometer.

Results and Discussion

In general, the biosorbents functional groups 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. On the other hand, the acid treatment applied to the agro-waste materials reduced the amount of functional groups that have pk_a values around 7.0. Finally, the third functional group can be associated to hydroxyl groups (pk_a 9.1-12.6), these were confirmed by ATR-FTIR analysis in a broad band at 3350 cm^{-1}.

From the surface charge distribution curves, it was observed that the acid treatment, applied to the agro-waste materials, shifted the pH_{PZC} to acidic values (from pH 5.5 to 3.5 for WAA and AAB). In addition, acid treatment removed soluble material attached to the biosorbents surface such as carbonates, silicates, calcium, magnesium, etc.

The maximum chromium sorption capacity, at pH 4 and 25°C, obtained by the Langmuir model was 6.96, 12.97 and 11.44 mg/g for ASS, AOS and AAB, respectively. No significantly differences were observed between the chromium sorption capacity of water and acid treated adsorbents.

On the other hand, although the agro-waste materials presented less chromium sorption capacity 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 biosorbents partially saturated with chromium. These chromium-loaded biosorbents were obtained at pH 4, 25°C and 20 mg/L of initial chromium concentration. Desorption results from acid washed oats straw (AOS) by HNO_3, NaOH and EDTA are given in Figure 1. The eluents were selected according to the possible chromium-biosorbents interaction.
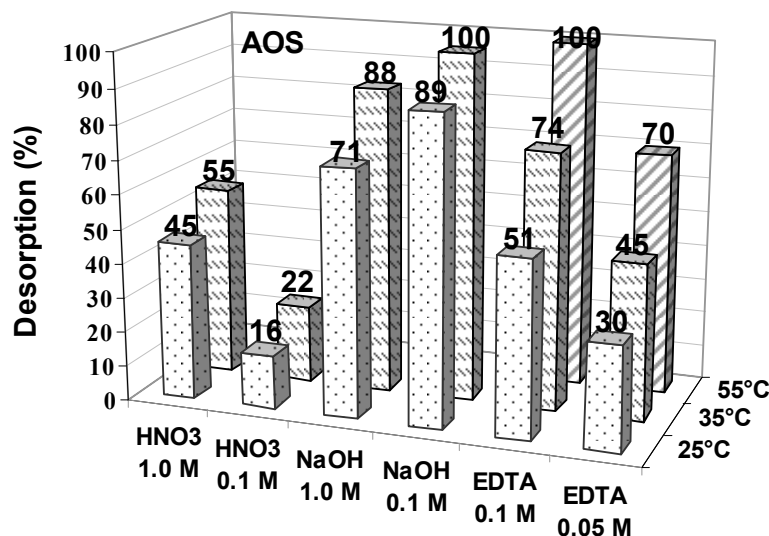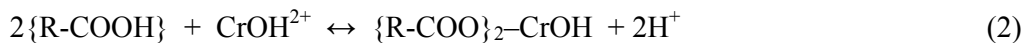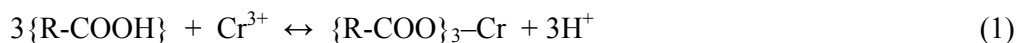

Figure 1. Chromium (III) desorption from oats straw acid washed at several eluents and temperatures. The chromium sorption capacity was 2.5±1.0 mg/g.

From Figure 1, it is clearly observed that the agro-waste regeneration was affected by temperature, for instance the regeneration by EDTA 1.0 M, at 25 and 35°C the chromium (III) recovered was 51 and 74%, respectively, but at 55°C the biosorbent was completely regenerated. In addition, regeneration by EDTA did not cause initial weight lost as HNO_3 or NaOH 1.0 N. The regeneration by HNO_3 (1.0 N) at 35°C was 55% which implied that the chromium ions were adsorbed on different functional groups including carboxyl groups. NaOH regeneration was better than HNO_3 (1.0 N) but produced more changes in the agro-waste materials.

Chromium (III) adsorption mechanism is not well understood due to the complex nature of the biosorbents. Nevertheless, some insights have been established. For example, Yun *et al.* (2001) demonstrated by potentiometric titration and FTIR analyses of seaweed biomass that trivalent chromium is adsorbed on carboxyl groups. In the same way, Sawalha *et al.* (2007), showed more evidences that the trivalent chromium adsorption was mainly due to carboxyl groups of chemically modified saltbush biomass (*Atriplex canescens*) by means of FTIR analyses and chemical modification. Finally, Ibánez and Umetsu proposed the following chromium sorption mechanism based on H^+ release when calcium-alginate beads were used as adsorbent:

$$3\{R\text{-}COOH\} + Cr^{3+} \leftrightarrow \{R\text{-}COO\}_3\text{–}Cr + 3H^+ \tag{1}$$

$$2\{R\text{-}COOH\} + CrOH^{2+} \leftrightarrow \{R\text{-}COO\}_2\text{–}CrOH + 2H^+ \tag{2}$$

Moreover, poly-nuclear chromium species are presented at pH 4, and then reaction (3) has to be considered as follows:

$$n\{R\text{-}COOH\} + Cr_2(OH)_2{}^{4+} \leftrightarrow \{R\text{-}COO\}_n\text{--}[Cr_2(OH)_2]^{(4\text{-}n)} + nH^+ \qquad (3)$$

However, the low percentage of chromium desorbed by HNO_3 (1.0 N) at 35°C (see Figure 1) indicated that chromium (III) ions first bind to carboxyl groups but form covalent bonds with their surrounding which contains oxygen-binding sites. For that reason, regeneration by EDTA (a chelating agent) at 55°C allowed to release the chromium from agro-waste materials.

Conclusion

Agro-waste materials contain carboxyl and hydroxyl functional groups which are able to bind chromium (III) from aqueous solution. In addition, agro-waste materials can be efficiently regenerated by an EDTA solution at 55°C without apparent changes in the structure. The possible chromium (III) sorption mechanism involved complexation on oxygen-containing groups.

Acknowledgements

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