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# 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

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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.

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## 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).

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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.

Finally, 10 mL aliquots were taken to measure the initial and final (at equilibrium) chromium, calcium and magnesium concentrations by AAS. The $H^+$ desorption capacity was calculated based on the initial and final pH measurements. In the same way, blank experiments (without chromium) were conducted to measure calcium, magnesium, and $H^+$ released.

### 2.8. Desorption experiments

Batch experiments were carried out in duplicate and the average values are presented to determine the Cr (III) desorption from agro-waste materials. Biosorbents were previously exposed to 20 mg/L of Cr (III) at pH 4 and 25 °C. Then 5 mL aliquots were taken to determine the initial and final (at equilibrium) concentrations. After that, chromium-loaded biosorbents were filtered and slightly rinsed with de-ionized water (at pH 4) to remove the excess of chromium solution. Then the biosorbent was added to 100 mL of $HNO_3$ (1.0N or 0.1N), NaOH (1.0N or 0.1N) or EDTA (0.1 M or 0.05 M) solutions. Regeneration experiments were continuously stirred at 180 rpm at selected temperatures (25 °C, 35 °C, or 55 °C) for 24 h. Finally, 5 mL aliquots were taken to measure the equilibrium chromium concentration by AAS.

Regenerated biosorbents were filtered, rinsed with de-ionized water (100 mL), dried at room temperature for 5 days, and weighed to obtain the mass lost after the regeneration step.

## 3. Results and discussion

### 3.1. Chemical characterization

Biosorbents have functional groups that play a major role in metal sorption. These groups can be dissociated or protonated depending on the solution pH. Yun et al. [18] developed a physical–chemical based method to estimate the functional groups ($b$, measure as mmol/g) and their equilibrium constants ($pK_a$). The experimental data obtained from potentiometric titration were processed according to this method. In most cases, the determination coefficient ($R^2$) was greater than 95% indicating that the estimated parameters ($b$ and $pK_a$) agreed with the experimental results. Table 1 shows the functional groups ($b$) and their equilibrium constants ($pK_a$). In general, the biosorbents functional group types were similar, although these were presented in different amounts.

**Table 1**
Functional groups ($b$, mmol/g) quantity and equilibrium constants ($pK_a$). Standard errors are given in parenthesis.

| Biosorbent | Functional group | $pK_a$ | $b$ (mmol/g) |
|---|---|---|---|
| WSS | Unknown | 7.00 (0) | 1.12 (0.3) |
| | Hydroxyl | 10.63 (0) | 1.15 (2.0) |
| ASS | Unknown | 6.61 (0) | 1.03 (0.2) |
| | Hydroxyl | 10.28 (0) | 1.29 (0.1) |
| WOS | Unknown | 7.04 (0) | 0.91 (0.2) |
| | Hydroxyl | 9.41 (0) | 1.12 (0.3) |
| AOS | Carboxyl | 3.79 (0.4) | 0.17 (0.2) |
| | Unknown | 6.33 (0) | 0.09 (0.2) |
| | Hydroxyl | 9.86 (0) | 1.20 (0.2) |
| WAB | Unknown | 6.90 (0) | 0.98 (0.5) |
| | Hydroxyl | 9.06 (0) | 0.22 (0.5) |
| | Hydroxyl | 12.58 (0) | 0.45 (0.6) |
| AAB | Carboxyl | 4.12 (0.1) | 0.31 (0.2) |
| | Unknown | 7.05 (0) | 0.58 (0.2) |
| | Hydroxyl | 10.97 (0) | 0.57 (0.2) |

The functional group with $pK_a$ ranging from 3.6 to 4.1 can be associated to carboxyl groups [18], which can be verified since it is well known that agro-waste materials contain pectin and hemicelluloses which have carboxyl groups in their chemical structure [29]. The latter was corroborated by ATR-FTIR spectra (Fig. 1A) since these provided transmittance peaks of around 1745, 1650, 1260, 1160, and 1060 $cm^{-1}$ attributed to carboxyl groups [31–33].

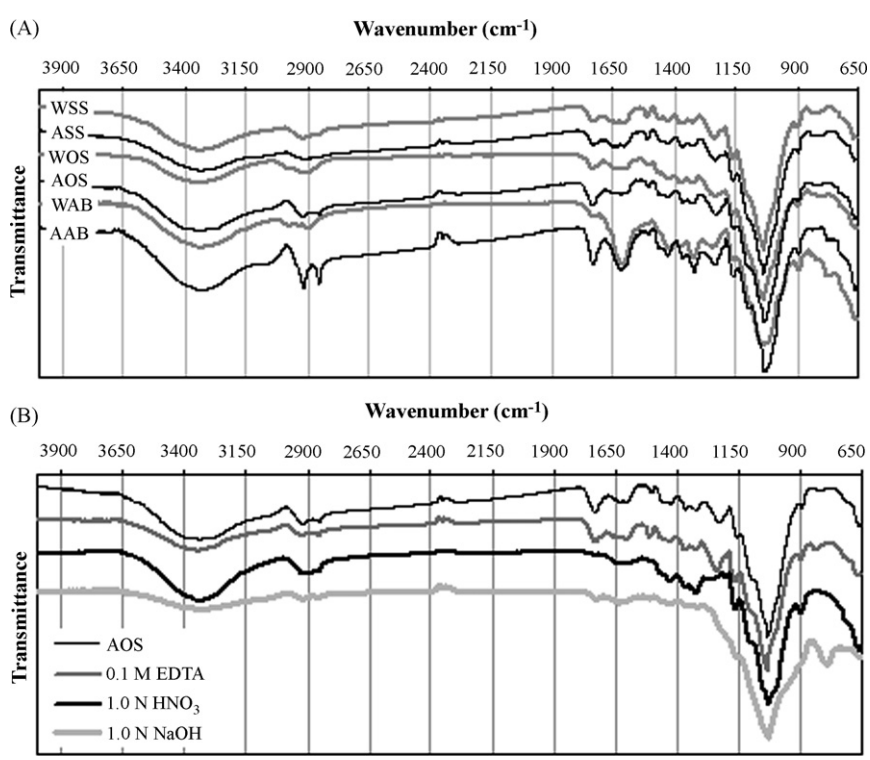


**Fig. 1.** (A) ATR-FTIR spectra of water-washed (grey line) and acid-washed (black line) agro-waste materials. (B) Acid-washed oats straw (AOS) spectra before and after being regenerated with EDTA, $HNO_3$, and NaOH.

Groups with p$K_a$ varying between 6.6 and 7.2 cannot be associated to a specific group because there are several types of functional groups such as amine, phosphoryl, amide, imidazol, etc. that have p$K_a$ values in this range. The analysis of the ATR-FTIR spectra (Fig. 1A) suggested that the agro-waste materials have amine groups related to transmittance bands at 1610 $cm^{-1}$ [31,33].

Finally, a third functional group can be associated to hydroxyl groups (p$K_a$ 9.06–12.58), which are present in the agro-waste materials components (e.g. cellulose, hemi-celluloses, pectin, lignin, etc.). These groups were confirmed by ATR-FTIR analyses (Fig. 1A) at transmittance peaks of about 3350 and 1060 $cm^{-1}$ [31–33].

Fig. 2 shows the surface charge distribution curves of agro-waste materials that are related to the type and quantity of surface functional groups. The slope changes of these curves indicated the dissociation of carboxyl, nitrogen, and hydroxyl groups which is directly related to their p$K_a$ value. Fig. 2 also shows that the acid treatment applied to the biosorbents moved the $pH_{PZC}$ (point of zero charge) to acid values. For instance, the water-washed SS, OS, and AB had a $pH_{PZC}$ of 6.0, 6.0, and 5.0, respectively, whereas the $pH_{PZC}$ of acid-washed SS, OS, and AB was 5.5, 3.2, and 3.5, respectively. If the sorption experiments were conducted at a pH higher than the $pH_{PZC}$ (where the net surface charge is negative) of the agro-waste materials, then positively charged metals ions would easily interact with the biosorbents surface.

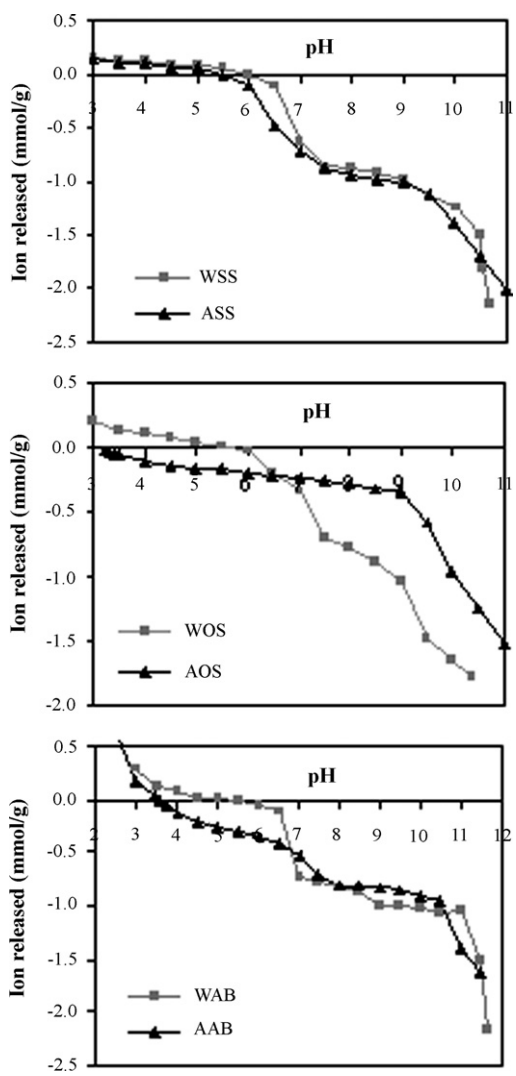


**Fig. 2.** Surface charge distribution curves of water-washed (solid symbols) and acid-washed (open symbols) agro-waste materials. The ionic strength was fixed with 0.1 N NaCl.

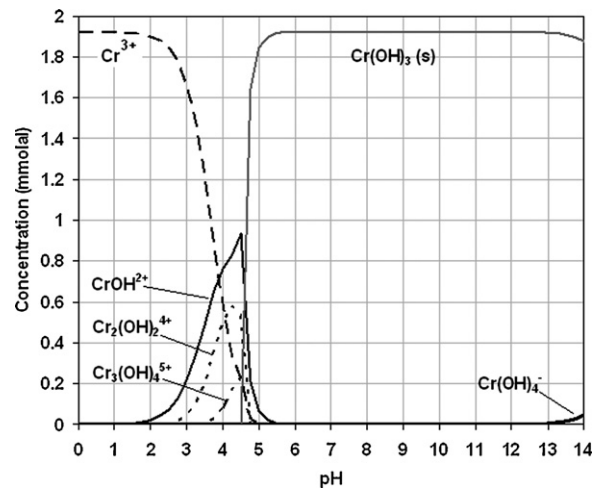


**Fig. 3.** Chromium (III) species in aqueous solution computed with VMINTEQ 2.51. This diagram was obtained for a chromium concentration of 100 and 357 mg/L of nitrates as $Cr(NO_3)_3$.

On the other hand, the acid-treated agro-waste materials contained fewer groups that have p$K_a$ values between 6.6 and 7.2 (see Table 1) in comparison with water-washed materials, suggesting salts dissolution. This fact was supported by the ATR-FTIR spectra of the water and acid treated biosorbents (see Fig. 1(A) WOS, AOS, WAB, AAB) because changes were observed between them at 1740 $cm^{-1}$. These can also be related to the surface charge distribution curve (Fig. 2) of the lower slope of both OS and AB at pH 6–8. The acid treatment applied to SS did not significantly affect the slope at pH 6.5–7.5 (Fig. 2) and the ATR-FTIR spectra (Fig. 1(A) WSS, ASS).

### 3.2. Chromium species in aqueous solution

The chromium speciation diagram (Fig. 3) shows the concentration of dissolved species and the pH at which hydrolysis occurs. At pH 3 the estimated dissolved species are $Cr^{3+}$ (87%), $CrOH^{2+}$ (11%) and $Cr_2(OH)_2{}^{4+}$ (2%), whereas at pH 4 the distribution of these species changes as follows: $Cr^{3+}$ (30%), $CrOH^{2+}$ (40%), $Cr_2(OH)_2{}^{4+}$ (26%) and $Cr_3(OH)_4{}^{5+}$ (4%). It is important to note that Cr (III) precipitates at pH 4.6 when the total concentration is 100 mg/L. In order to preserve the metal in solution, adsorption experiments were conducted at pH 3 and 4.

### 3.3. Adsorption experiments

Both Langmuir and Freundlich isotherms fitted reasonable well the experimental data (see Appendix A, Table A.1). In this case Langmuir isotherm, shown as a continuous line on Figs. 4 and 5, was selected to model the experimental results since this model gives useful information such as the maximum chromium sorption capacity ($Q_{max}$) and the isotherm constant ($b$) that is related to the affinity of the binding sites for metal ions.

Fig. 4 shows the Cr (III) adsorption isotherms onto agro-waste materials at 25 °C, pH 4, and pH 3. At pH 4, $Q_{max}$ obtained by the Langmuir model was 5.33 and 6.96 mg/g for WSS and ASS, respectively. Cano-Rodríguez et al. [19] reported that protonated sorghum biomass adsorbed 10 mg of chromium (III)/g at pH 4.5–5.0, which is 30% higher than the maximum chromium adsorbed by the ASS (6.96 mg/g) used in this study. This difference could be due to the pH at which the chromium adsorption experiments were conducted. For instance, at pH 5 the biosorbent possesses more dissociated

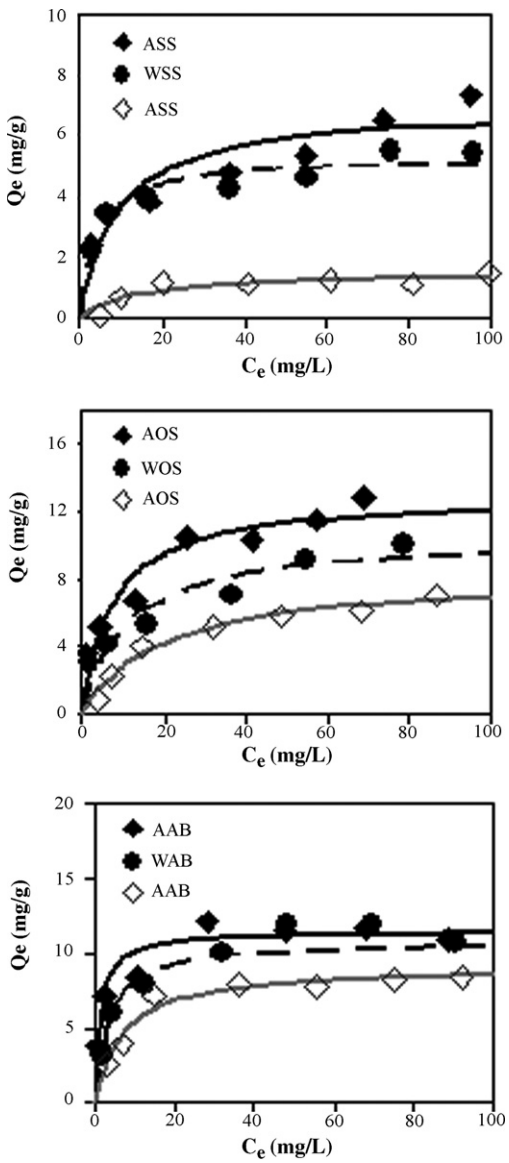


**Fig. 4.** Adsorption isotherms of chromium (III) onto agro-waste materials at 25 °C, pH 4 (solid symbols), and pH 3 (open symbols). Symbols represent the experimental measurements and the line the Langmuir model.

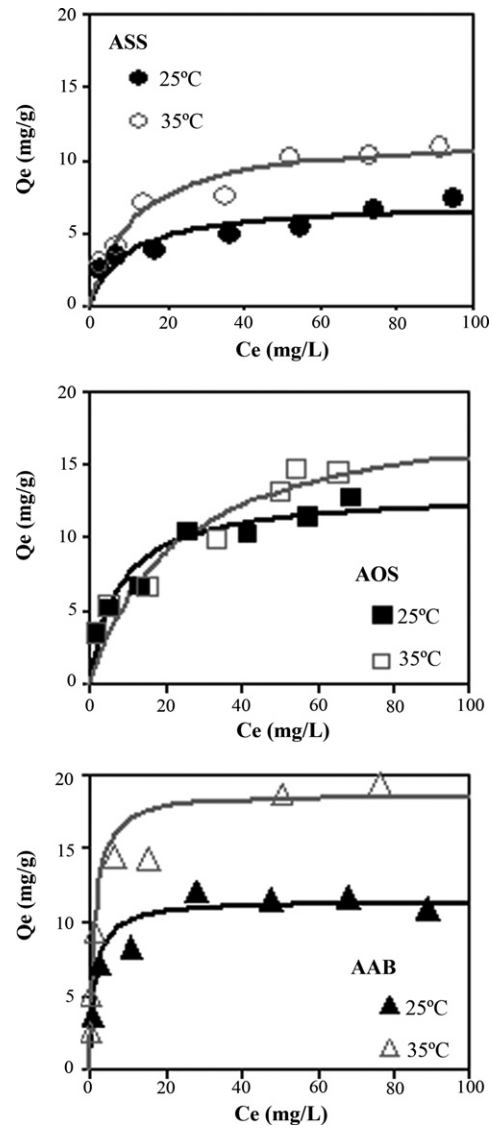


**Fig. 5.** Adsorption isotherms of chromium (III) onto acid-washed agro-waste materials at pH 4, 25 °C (black), and 35 °C (grey). Symbols represent the experimental measurements and the line the Langmuir model.

functional groups that can participate in the chromium sorption (i.e. carboxyl sites). In addition, according to the chromium speciation diagram (shown in Fig. 3) at pH 5, a solid phase would be formed in solution ($Cr(OH)_3$) and hence contribute to the chromium removal.

On the other hand, the maximum chromium sorption capacity for WOS and AOS at pH 4 and 25 °C was 10.55 and 12.97 mg/g, respectively. These results demonstrated that chromium sorption capacity was higher for AOS (12.97 mg/g) than ASS (6.96 mg/g). This difference could be due to the presence of more available carboxyl groups in AOS (see Table 1). These functional groups have been broadly studied and results reported in literature have demonstrated that metal cations have a high affinity for carboxyl sites [18,23,34,35].

In addition, the maximum chromium sorption capacity for WAB and AAB at 25 °C and pH 4 was 10.84 and 11.44 mg/g, respectively. Romero-Gonzalez et al. [21] reported a sorption capacity of 11.31 mg of chromium (III)/g of protonated Agave *lechuguilla* biomass at pH 4 and 22 °C, which agrees with our results although it is a different species.

Comparing the chromium sorption capacity ($Q_e$) among the agro-waste materials in this study, it is clear that AB and OS have higher $Q_e$ than SS (see Fig. 4), which is related to the concentration of carboxyl groups (see Table 1). Also the ATR-FTIR spectra obtained from AB and OS (Fig. 1A) showed stronger transmittance bands associated to carboxyl and amine groups (at 1750 and 1620 $cm^{-1}$) that are likely involved in the Cr (III) sorption.

In addition, the chromium sorption capacity of the acid-washed biosorbents was lower at pH 3 than at pH 4 (see Fig. 4), most probably due to the lower availability of active sites and the competition between $H^+$ and Cr (III) ions for the same sorption sites on the materials. This competition has been previously demonstrated in other studies [18,36].

Several research groups have tested a variety of adsorbents for the chromium (III) removal from aqueous solution, for instance seaweed biomass, agro-waste materials, and ion exchange resins (Table 2). Cossich et al. [13] reported that the water-washed seaweed *Sargassum* sp. biomass had very high chromium (III) sorption capacity (68.1 mg/g at pH 3.5) because all functional groups were kept in the biomass after being water-washed. In contrast, Yun et al. [18] reported a lower chromium (III) sorption capacity (20.5 mg/g

**Table 2**
Maximum chromium (III) sorption capacity ($Q_{max}$, mg/g) of various adsorbents.

| Adsorbent | Conditions | $Q_{max}$ (mg/g) | Reference |
|---|---|---|---|
| Sorghum biomass | pH 4.5–5.0 | 10.00 | [19] |
| Agave *lechuguilla* biomass | pH 4, 22 °C | 11.31 | [21] |
| Wheat straw | pH 4, 20 °C, $C_o$ = 200 mg/L | 6.75 | |
| Glass | | 7.31 | |
| Coir pith | pH 3.3, 27 °C, $C_o$ = 20 mg/L | 9.82 | [35] |
| Brown seaweed | pH 3.0, $C_o$ = 0–500 mg/L | 11.00 | |
| Biomass (*Ecldonia* sp.) | pH 3.5, $C_o$ = 0–500 ng/L | 20.50 | [18] |
| | pH 4, $C_o$ = 0–500 mg/L | 34.10 | |
| Seaweed biomass (*Sargassum* sp.) | pH 3.5, $C_o$ = 104–624 mg/L | 68.12 | [13] |
| Lewatit S 100 | pH 3.8, 25 °C, $C_o$ = 5.2–52 mg/L | 20.28 | [37] |
| Chelex-100 | | 1.55 | |
| Oats straw | pH 3, 25 °C, $C_o$ = 5–100 mg/L (acid-washed) | 8.32 | |
| Agave bagasse | | 9.06 | |
| Sorghum straw | | 5.33 | |
| Oats straw | pH 4, 25 °C, $C_o$ = 5–100 mg/L (water-washed) | 9.93 | This study |
| Agave bagasse | | 10.84 | |
| Sorghum straw | | 6.96 | |
| Oats straw | pH 4, 25 °C, $C_o$ = 5–100 mg/L (acid-washed) | 12,97 | |
| Agave bagasse | | 11.44 | |

at pH 3.5) for protonated seaweed biomass and that could be due to the acid treatment (2.0N $H_2SO_4$). The water-washed or acid-washed agro-waste materials studied herein did not show strong differences in the chromium sorption capacity as the seaweed biomass early mentioned. This was probably due to the mild conditions used in the acid treatment applied (25 °C and 0.01N HCl) in this research.

As shown in Table 2, the agro-waste materials have a lower chromium sorption capacity than ion exchange resins and seaweed biomass, but they are locally available and cheaper than ion exchange resins. For example, the cost of agro-waste materials locally is approximately 0.20 USD/kg.

Fig. 5 shows the effect of temperature in the chromium sorption capacity onto the acid-washed agro-waste materials. In general, an increase in temperature from 25 °C to 35 °C enhanced the chromium sorption capacity of the acid-washed agro-waste materials. In the case of AOS, the chromium sorption capacity did not increase at lower concentration than 40 mg/L. Romero-Gonzalez et al. [21] demonstrated the endothermic nature ($\Delta H$ = 52.77 kJ/mol) of chromium adsorption onto Agave *lechuguilla* biomass which could explain the increasing chromium sorption capacity by raising the temperature.

### 3.4. Adsorption mechanisms

The chromium (III) sorption mechanisms have not been clarified due to the complex nature of the biosorbents. Methodologies such as chemical modifications, FTIR (Fourier Transform Infrared), XPS (X-ray photoelectron spectra), among others, have been used to determine functional groups and at the same time to elucidate the biosorbents metal sorption mechanism [18,23,28,35,37]. Some of the functional groups that have been identified in biosorbents include: carboxyl, carbonyl, acetamide, amine, sulfonate, phosphate, phenolic, hydroxyl, etc., and the cations adsorption mechanisms that have been proposed for biosorbents include: chemical adsorption (complexes formation), ion exchange with cations such as calcium or magnesium, and physical adsorption by electrostatic interaction. For example, Yun et al. [18] demonstrated, by using potentiometric titrations and FTIR analyses of protonated brown seaweed *Ecklonia* sp. biomass, that carboxyl groups were the chromium-binding sites. In the same way Sawalha et al. [35] showed more evidence, by FTIR analyses, that the trivalent chromium adsorption was mainly due to carboxyl groups of chemically modified saltbush biomass (*Atriplex canescens*). On the other hand, Ibañez and Umetsu [34] demonstrated that the uptake of trivalent chromium by protonated dry alginate beads was coupled with a release of protons from the carboxyl groups, and the following ion exchange was proposed as the chromium sorption mechanism:

$$3\{\equiv R{-}COOH\} + Cr^{3+} \leftrightarrow \{\equiv R{-}COO\}_3{-}Cr + 3H^+ \quad (1)$$

$$2\{\equiv R{-}COOH\} + CrOH^{2+} \leftrightarrow \{\equiv R{-}COO\}_2{-}CrOH + 2H^+ \quad (2)$$

Moreover, when poly-nuclear chromium species are present at pH 4, reaction (3) has to be considered:

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

In contrast, Krishnani et al. [28] found that such divalent metals as $Cd^{2+}$, $Pb^{2+}$, $Zn^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Hg^{2+}$, $Co^{2+}$, and $Mn^{2+}$ can be adsorbed onto previously treated rice husks and that the metal adsorption capacity can be explained, in a high percentage, as ion exchange with calcium and, in the case of $Cd^{2+}$, $Pb^{2+}$, $Hg^{2+}$ with both calcium and magnesium. Also, Reddad et al. [29] demonstrated that the predominant sorption mechanisms for $Pb^{2+}$, $Cu^{2+}$, and $Zn^{2+}$ onto sugar beet pulp are both ion exchange with calcium and complexation. However, this ion exchange mechanism has not been studied for trivalent metal ions such as Cr (III).

In order to understand the chromium (III) sorption mechanism, as a whole, on agro-waste materials, batch experiments were conducted to determine the chromium (III) sorption capacity and the concentration of ions released (such as calcium, magnesium and $H^+$) as a consequence of the ion exchange mechanism.

Poly-galacturonic and hexuronic acids (present in pectin and hemi-celluloses) contain carboxyl groups linked together by calcium bridges, but once calcium is released to the solution, the carboxyl groups could be used by chromium (III) ions as adsorption sites.

Fig. 6(I) shows the chromium (III) adsorbed and the calcium released by agro-waste materials. Calcium released from AAB (0.211 mmol/g) was similar to the amount of Cr (III) adsorbed (0.207 mmol/g). These results suggested that calcium is released from the carboxyl moieties once chromium (III) species were adsorbed on it. In contrast, the calcium released/chromium (III) adsorbed (as a molar ratio) is about 0.64 when WSS, ASS and WOS are used as adsorbent which means that chromium was bound not only to carboxyl groups. The possible chromium (III) sorption mechanism that involves calcium release form carboxyl groups could be:

$$3\{\equiv R{-}COO\}_2{-}Ca + 2Cr^{3+} \leftrightarrow 2\{\equiv R{-}COO\}_3{-}Cr + 3Ca^{2+} \quad (4)$$

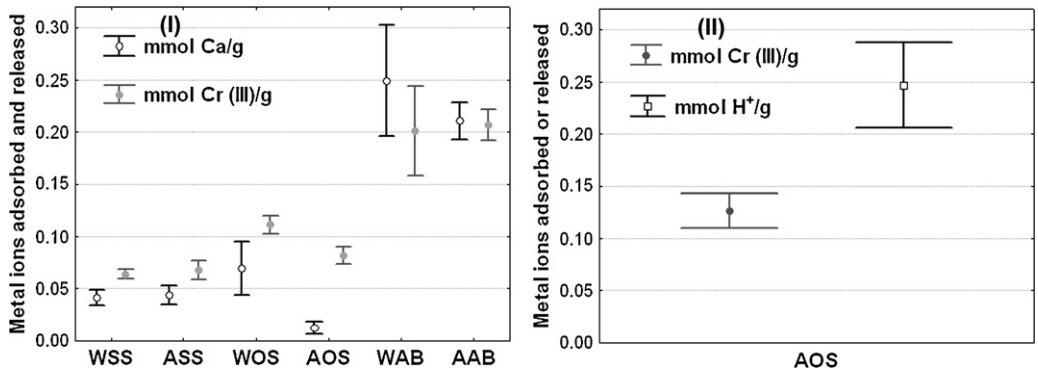


**Fig. 6.** Metal ions adsorbed and released when agro-waste materials are used as adsorbents. (I) Chromium adsorbed and calcium released from water-washed and acid-washed agro-waste materials at pH 4, 25 °C, and $C_o$ = 20 mg of Cr (III)/L. (II) Chromium adsorbed and $H^+$ released from acid-washed oats straw (AOS) without pH control at 25 °C, initial pH 4, and $C_o$ = 120 mg of Cr (III)/L. Symbols represent the average values and bar errors were built with a confidence interval of 95%.

$$\{\equiv R{-}COO\}_2{-}Ca + CrOH^{2+} \leftrightarrow \{\equiv R{-}COO\}_2{-}CrOH + Ca^{2+} \quad (5)$$

$$2\{\equiv R{-}COO\}_2{-}Ca + Cr_2(OH)_2{}^{4+} \leftrightarrow \{\equiv R{-}COO\}_4{-}Cr_2(OH)_2 + 2Ca^{2+} \quad (6)$$

However, the amount of chromium (III) adsorbed onto AOS cannot be explained as ion exchange with calcium (molar ratio 0.15). In order to quantify other ions released (e.g. $Ca^{2+}$, $Mg^{2+}$, $H^+$, etc.) when chromium is adsorbed onto AOS, experiments in triplicate without pH control were conducted and the results are presented in Fig. 6(II). The equilibrium pH was around 3.48 for these experiments. The molar average ratio between $H^+$ released/chromium (III) adsorbed is 1.95 which could suggest that $CrOH^{2+}$ was preferentially adsorbed onto AOS because of the release of 2 mol of $H^+$ to the solution according to reaction (2). In these experiments, calcium and magnesium ions were not detected.

Some studies have confirmed that oxygen-containing groups (e.g. carboxyl and phenolic) are involved in metal adsorption. For example, Manceau et al. [38] demonstrated that soil contaminated by lead was complexed to salicylate and catechol-type functional groups of humic substances. In another study, Park et al. [17] established that carboxyl and phenolic groups play a major role in the binding of the Cr (III) resulting from the abiotic reduction of Cr (VI) by the seaweed biomass. Yu et al. [24] proposed that $H^+$ ions (present in carboxyl and phenolic groups of maple sawdust) can be exchanged with metal cations ($M^{n+}$ and $M(OH)^{(n-1)+}$) in solution: when carboxyl groups are involved, the mechanisms are similar to reaction (1) and (2), whereas sorption on phenolic groups was reported as:

$$\{\equiv R{-}C_6H_5{-}OH\} + M^{n+} \leftrightarrow \{\equiv R{-}C_6H_5{-}O\}{-}M^{(n-1)+} + H^+ \quad (7)$$

$$\{\equiv R{-}C_6H_5{-}OH\} + M(OH)^{(n-1)+} \leftrightarrow \{\equiv R{-}C_6H_5{-}O\}{-}M(OH)^{(n-2)+} + H^+ \quad (8)$$

### 3.5. Desorption experiments

Metal desorption from biosorbents has not been well explored and for that reason it is necessary to study this process more in detail. In this research the chromium-loaded agro-waste materials were regenerated. Solutions of $HNO_3$, NaOH, and EDTA were used as eluents at different concentrations and temperatures (25 °C, 35 °C, and 55 °C). These eluents were selected aiming at an ion exchange process, between $H^+$ and $Na^+$ with Cr (III) species, or complexation (EDTA-Cr (III)). Figs. 7 and 8 show the chromium (III) desorption

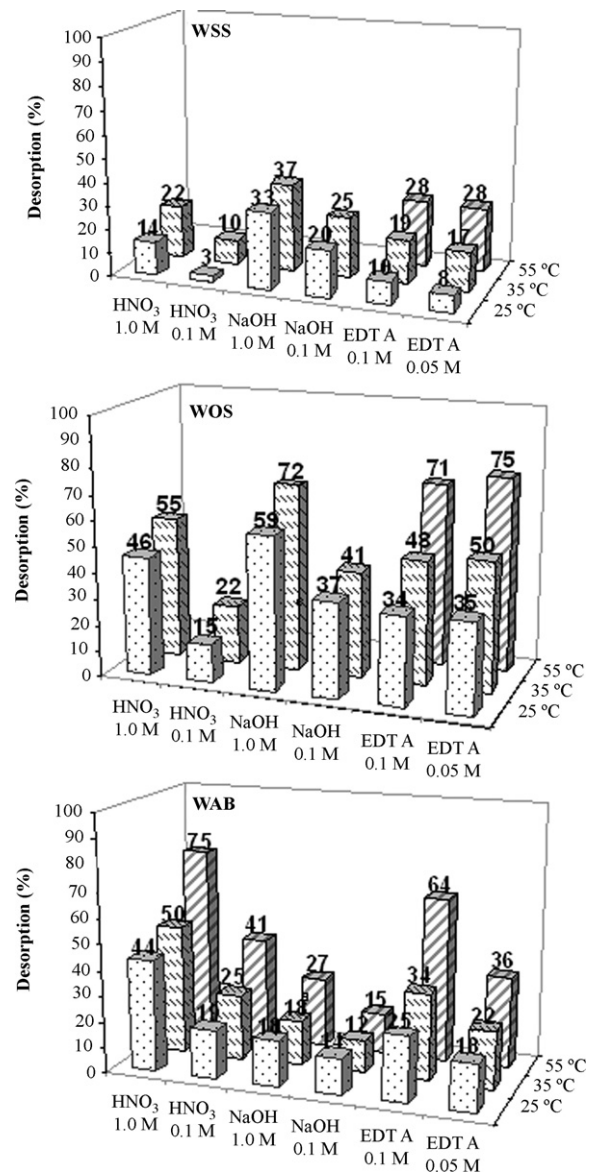


**Fig. 7.** Chromium (III) desorption after 24 h from water-washed agro-waste materials for several eluents and temperatures tested.

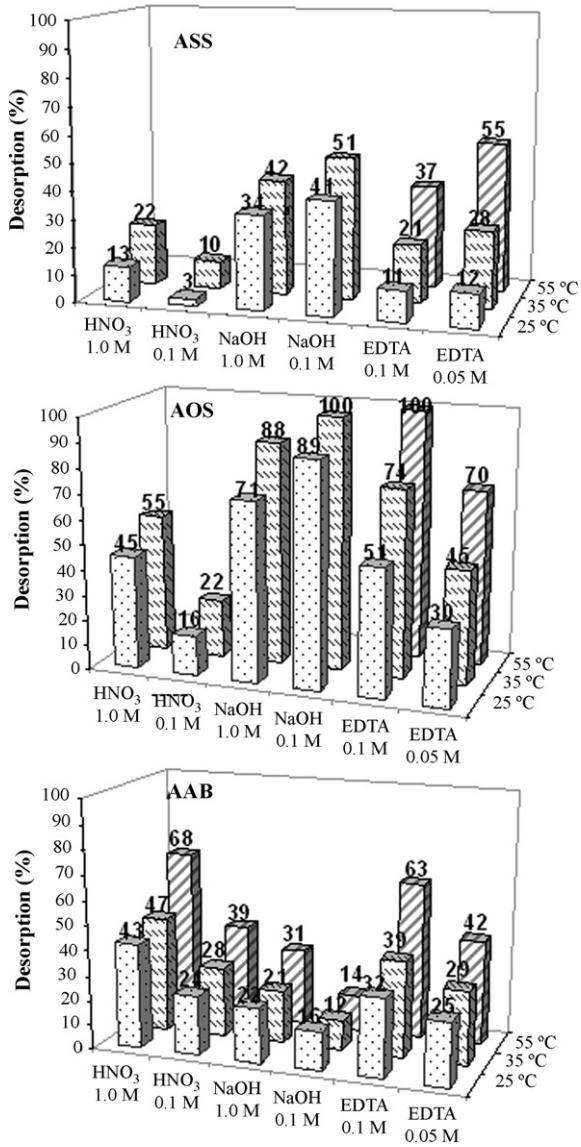


**Fig. 8.** Chromium (III) desorption after 24 h from acid-washed agro-waste materials for several eluents and temperatures tested.

from water-washed and acid-washed agro-waste materials, respectively.

It was thought that if Cr (III) was adsorbed on carboxyl-binding groups by electrostatic interaction, then acid solutions (e.g. $HNO_3$) would regenerate the chromium-loaded biosorbents since the concentration of $H^+$ increases (pH decreases and oxygen groups protonates) giving place to ion exchange with the chromium adsorbed as follows:

$$\{\equiv R{-}COO\}_3{-}Cr + 3H^+ \leftrightarrow 3\{\equiv R{-}COOH\} + Cr^{3+} \quad (9)$$

$$\{\equiv R{-}COO\}_2{-}CrOH + 2H^+ \leftrightarrow 2\{\equiv R{-}COOH\} + CrOH^{2+} \quad (10)$$

$$\{\equiv R{-}COO\}_4{-}Cr_2(OH)_2 + 4H^+ \leftrightarrow 4\{\equiv R{-}COOH\} + Cr_2(OH)_2{}^{4+} \quad (11)$$

However, the low Cr (III) desorption from agro-waste materials at 25 °C (lower than 46% for WOS when 1.0N $HNO_3$ was used) suggested that chromium ions form more stable chemical bonds (i.e. covalent coordinated bonds) with the biosorbents. This could be related to the increase in sorption capacity when the temperature rises (see Fig. 5).

For instance, chromium desorption from AAB with 1.0 M $HNO_3$ was 43%, 47%, and 68% at 25 °C, 35 °C, and 55 °C, respectively (see Fig. 8). However, the regeneration of AAB with 1.0 M $HNO_3$ at 55 °C caused 30% of initial weight lost (see Fig. 9), which suggested that the acid eluent hydrolyzed part of hemi-celluloses and dissolved some salts like calcium present in the agro-waste materials.

Conversely, the chromium desorbed with NaOH (1.0N) at 25 °C varied from 18% to 71% depending on the agro-waste material (see Figs. 7 and 8). However, the initial weight lost when 1.0N NaOH was used as eluent was higher (22–42%) compared to the regeneration with 1.0N $HNO_3$ (see Fig. 9). These results suggested that some components (mainly lignin and hemi-celluloses) present in the biosorbents could be hydrolyzed in an alkaline solution.

The most probable mechanism that could explain the chromium desorption with NaOH is illustrated in the following reactions:

$$2\{\equiv R{-}COO\}_3{-}Cr + 6Na^+ + 7OH^- \leftrightarrow 6\{\equiv R{-}COO\}{-}Na + Cr(OH)_4{}^- + Cr(OH)_{3(s)} \quad (12)$$

$$2\{\equiv R{-}COO\}_2{-}CrOH + 4Na^+ + 5OH^- \leftrightarrow 4\{\equiv R{-}COO\}{-}Na + Cr(OH)_4{}^- + Cr(OH)_{3(s)} \quad (13)$$

$$\{\equiv R{-}COO\}_4{-}Cr_2(OH)_2 + 4Na^+ + 5OH^- \leftrightarrow 4\{\equiv R{-}COO\}{-}Na + Cr(OH)_4{}^- + Cr(OH)_{3(s)} \quad (14)$$

The main specie formed by alkaline regeneration is $Cr(OH)_{3(s)}$ due to the high concentration of $OH^-$ (see Fig. 3), although $Cr(OH)_4{}^-$ is also formed but in less extend at high pH values. It is important to note that Cr (III) desorption by NaOH may be sub-estimated due to the presence of chromium precipitate as $Cr(OH)_{3(s)}$ (more experiments are needed to clarify this issue).

Moreover, it is important to mention that the regeneration effect is lessened when the eluent is diluted. For instance chromium (III) desorption was less than 10% by using mild acid (pH 2 or 3) or alkaline solutions (pH 11 or 12). These findings indicated that the Cr (III) desorption mechanism is not an easy task due to the agro-waste materials complexity.

Solutions of EDTA (0.1 and 0.05 M) were used to regenerate the chromium-loaded agro-waste materials. This eluent was chosen because it is well known that chromium (III) and EDTA ligand have the highest stability constants for the formation of complexes [39].

From Figs. 7 and 8, it is clearly observed that the regeneration with EDTA was affected by both temperature and the eluent concentration. For instance, the AOS regeneration with 1.0 M EDTA at 25 °C and 35 °C was 51% and 74%, respectively, but at 55 °C this biosorbent was completely regenerated (see Fig. 8). The higher chromium desorption with 1.0 M EDTA obtained at 55 °C suggested that the interaction Cr (III)-EDTA involved a chelate formation and an increase in temperature facilitated the chemical interaction between EDTA and Cr (III). Also when EDTA concentration was 0.05 M, the regeneration was reduced to 70% at 55 °C.

The possible chromium desorption mechanism by EDTA (where $M^+$ represents either $Na^+$ or $H^+$) could occur as follows:

$$\{\equiv R{-}COO\}_3{-}Cr + EDTA^{4-} + 3M^+ \leftrightarrow 3\{\equiv R{-}COO\}{-}M + \{Y{-}Cr\}^{-1} \quad (15)$$

$$\{\equiv R{-}COO\}_2{-}CrOH + EDTA^{4-} + 2M^+ \leftrightarrow 2\{\equiv R{-}COO\}{-}M + \{Y{-}CrOH\}^{2-} \quad (16)$$

$$\{\equiv R{-}COO\}_4{-}Cr_2(OH)_2 + EDTA^{4-} + 4M^+ \leftrightarrow 4\{\equiv R{-}COO\}{-}M + \{Y{-}Cr_2(OH)_2\} \quad (17)$$

In addition, the initial weight lost of acid-washed materials due to the regeneration with 0.1 M EDTA was much lower (0–9%) than

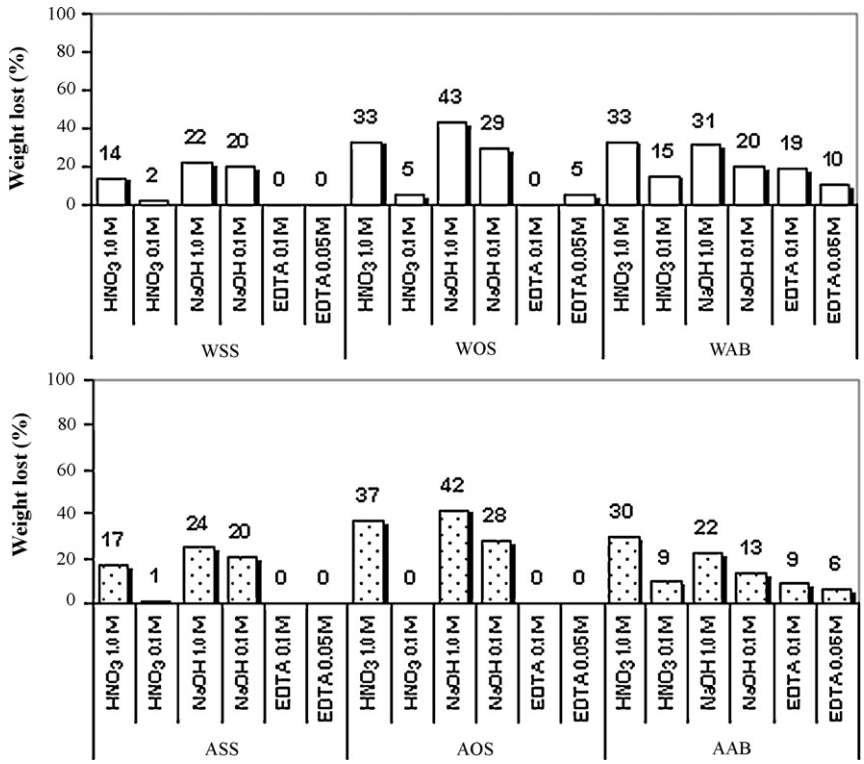


**Fig. 9.** Initial weight lost after the regeneration of agro-waste materials at the highest desorption temperature shown in Figs. 7 and 8.

what was obtained when 1.0N $HNO_3$ or 1.0N NaOH was used as eluent (see Fig. 9). This fact suggested that EDTA solutions produced fewer structural modifications in the biosorbents than the acid or the alkaline solutions; for example Fig. 1(B) shows that acid and alkaline solutions attacked the carboxyl groups (1740 $cm^{-1}$) conversely to EDTA solutions. In addition, alkaline and acid regeneration produced hydrolysis of the agro-waste materials confirmed by the initial weight lost, and the biosorbents color change. Therefore, based on the chromium desorbed and the initial weight lost, EDTA was the best option to regenerate the chromium-loaded agro-waste materials.

These results have demonstrated that the agro-waste materials studied herein have functional groups capable of removing Cr (III) from water. In addition, these materials will likely remove other heavy metal ions from aqueous solution (e.g. $Pb^{2+}$, $Cu^{2+}$, $Cd^{2+}$, etc.). Besides batch sorption/desorption experiments, sorption kinetics studies and sorption–desorption cycles in fixed-bed columns must be conducted to explore the feasibility of using these biosorbents in water treatment systems.

## 4. Conclusions

Functional groups such as carboxyl and hydroxyl are able to bind chromium (III) from aqueous solution. At concentrations below 20 mg of Cr (III)/L, agave bagasse has higher sorption capacity than oats and sorghum straw, which decreases at pH 3 since $H^+$ and Cr (III) ions compete for the biosorbents sorption groups. In addition, an increase in temperature from 25 °C to 35 °C enhances the chromium sorption in agro-waste materials because of the endothermic nature of the sorption process. Conversely, partially saturated agro-waste materials can be efficiently regenerated by an EDTA solution at 55 °C without apparent modifications on the biosorbents. Finally, based on the chromium sorption–desorption experiments, the possible chromium (III) sorption mechanisms onto agro-waste materials are ion exchange and complexation.

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## Appendix A.

See Table A.1.

**Table A.1**
Isotherm parameters estimated from experimental data of the chromium (III) adsorption on agro-waste materials.

| Biosorbent | Conditions | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|---|
| | | $Q_{max}$ | $b$ | $r^2$ | $k$ | $n$ | $r^2$ |
| WSS | pH 4, 25 °C | 5.329 | 0.233 | 0.95 | 2.047 | 4.604 | 0.97 |
| WOS | | 10.551 | 0.091 | 0.92 | 2.157 | 2.860 | 0.99 |
| WAB | | 10.837 | 0.271 | 0.99 | 4.006 | 3.997 | 0.95 |
| ASS | | 6.958 | 0.112 | 0.90 | 1.656 | 3.173 | 0.98 |
| AOS | | 12.974 | 0.136 | 0.94 | 3.297 | 3.163 | 0.98 |
| AAB | | 11.437 | 0.772 | 0.95 | 5.727 | 5.843 | 0.93 |
| ASS | pH 3, 25 °C | 1.553 | 0.069 | 0.91 | 0.273 | 2.764 | 0.85 |
| AOS | | 8.316 | 0.051 | 0.99 | 0.993 | 2.254 | 0.96 |
| AAB | | 9.064 | 0.150 | 0.98 | 2.800 | 3.895 | 0.92 |
| ASS | pH 4, 35 °C | 11.728 | 0.092 | 0.97 | 2.457 | 2.968 | 0.98 |
| AOS | | 18.951 | 0.046 | 0.95 | 2.120 | 2.158 | 0.98 |
| AAB | | 18.807 | 0.891 | 0.99 | 7.959 | 4.609 | 0.97 |

$Q_{max}$ (mg/g); $b$ (L/mg); $k$ ($L^{1/h}/mg^{1-1h}\,g^{-1}$); $n$, $r^2$ (dimensionless).

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