

Evaluation of batch adsorption of chromium ions on natural and crosslinked chitosan membranes

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Abstract

Removal of chromium ions from aqueous solutions by using natural and crosslinked chitosan membranes was achieved using batch adsorption experiments. The effect of pH (6.0 and 2.0), concentration of chromium ions and crosslinking agents (glutaraldehyde: GLA and epichlorohydrin: ECH) on the adsorption properties of chitosan membranes was analyzed. The experimental equilibrium data was fitted to Langmuir and Freundlich models. Through the model curves, it was possible to observe that the amount of chromium ions adsorbed was significantly higher for crosslinked membranes compared to non-crosslinked chitosan. The maximum adsorbed amount was about 1400 mg g^{-1} for ECH-crosslinked chitosan at pH 6.0. The adsorption rates for crosslinked chitosan membranes with glutaraldehyde and epichlorohydrin were similar for natural chitosan. Desorption study using NaCl (1 mol L^{-1}) solution was performed on chitosan membranes, in order to recover chromium ions and to determine the suitable number of cycles for repeated use of these membranes without considerable decrease in their adsorption capacity. The desorption results showed that chromium ions could be more effectively removed at pH 2.0 than pH 6.0, mainly for ECH-crosslinked chitosan.

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1. Introduction

Contamination of water by heavy metals has become an increasing problem to the environment and health, once they are very toxic and non-biodegradable, even at low concentrations [1]. Chromium can be found in different oxidation states, however, the trivalent and hexavalent forms are the only stable forms frequently found in nature. High concentrations of chromium are lethal, mainly at high oxidation forms, i.e. the hexavalent form is more dangerous than the trivalent one [2]. Cr (III) is the most important and stable form and it is considered an essential nutrient. However, at high concentrations it can oxidate to Cr (VI) in alkaline solutions and also affect the human health.

Several methods are used for the removal of heavy metals from aqueous solutions, such as, ion exchange, reverse osmosis, adsorption, complexation and precipitation. Adsorp-

tion is considered an effective and economical method to remove pollutants from wastewater [3]. The adsorption capacity of several low-cost-adsorbents has been investigated, mainly using biopolymers, which are obtained from renewable sources and adsorb metallic ions selectively.

Chitosan, a biopolymer prepared through the deacetylation of chitin, which is the major component of crustaceans shells and the second most abundant biopolymer in nature, has been widely used for adsorption of heavy metal ions [4–10]. Its chelating properties are attributed to the amino and hydroxyl groups in chitosan chain, that therefore, can act as chelation sites for different metals [11]. Fig. 1 illustrates the molecular structure of chitosan.

Crosslinking of chitosan with epichlorohydrin (1-cloro-2,3-epoxipropane) [3,9,12,13] or glutaraldehyde (1,5-pentanodial) [9,10,14,15] has been proposed to improve pore size distribution, mechanical resistance, chemical stability and adsorption/desorption properties. These chemicals can attack the hydroxyl and amino groups as shown in Fig. 2.

The aim of this study was to compare the equilibrium and kinetic behavior of chromium ions adsorption onto natural and

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Nomenclature

| | |
|------------------|--|
| C_f | final Cr ions concentration (mg L^{-1}) |
| C_i | initial Cr ions concentration (mg L^{-1}) |
| K | Langmuir dissociation constant (L mg^{-1}) |
| K_F | Freundlich constant (L g^{-1}) indicating adsorption capacity |
| $1/n$ | Freundlich constants (dimensionless), indicating adsorption intensity |
| Q | adsorbed amount of Cr ions (mg g^{-1} chitosan) |
| Q_{max} | maximum adsorbed amount of Cr ions (mg g^{-1} wet chitosan) |
| R^2 | fitting coefficients |
| V | volume of Cr solution (L) |
| W | weight of adsorbent in wet base (g) |

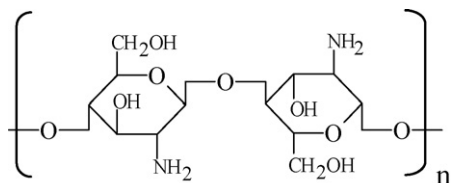


Fig. 1. Molecular structure of chitosan.

crosslinked chitosan membranes. The influence of the experimental conditions of chromium ion concentration, pH and the type of crosslinking were evaluated. The experimental equilibrium parameters were obtained by fitting the experimental data to Langmuir and Freundlich models. The kinetic data were obtained, in order to evaluate the adsorption rate. The chemical changes (chemical modification with crosslinking and adsorption process) were characterized by using Fourier-transformed infrared spectroscopy with attenuated total reflectance device (FTIR-ATR) and thermal gravimetric analyses (TGA and DSC). Adsorption/desorption cycles were experimented, in order to determine the suitable number of cycles for repeated use of

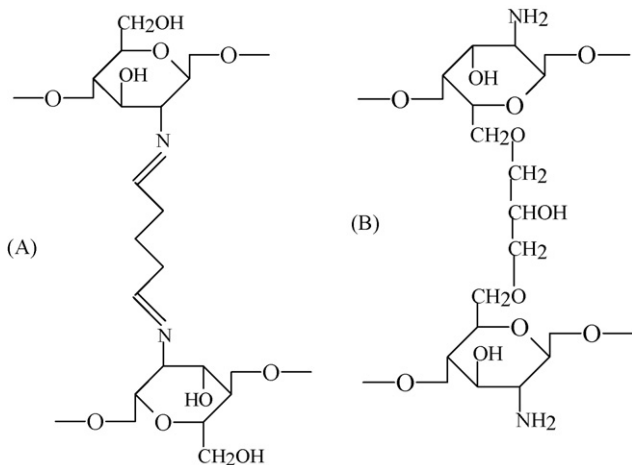


Fig. 2. Possible structures formed from crosslinking using glutaraldehyde (A) and epichlorohydrin (B).

these membranes without considerable loss in adsorption capacity with recovery of metallic species into a more concentrated solution form.

2. Materials and methods

2.1. Preparation and chemical modification of chitosan membranes

Raw chitosan was purchased from Sigma (USA), which was used to prepare a chitosan solution 2.5% (w/w) in acetic acid (3%, v/v). In order to obtain porous membranes, the chitosan solution was spread on a Petri dish. The dish was kept at 60°C until a reduction of 50% of its initial weight. The membranes were immersed in a solution of NaOH (1 mol L^{-1}) for 24 h to neutralize the amino groups. Afterwards, the membranes were exhaustively washed with distilled water until all alkali was removed and stored in water [16].

Natural (pristine) chitosan membranes underwent crosslinked by heterogeneous reaction in 0.75% (w/w) aqueous glutaraldehyde solution (3.0 g of wet chitosan membrane in 50 mL of glutaraldehyde solution) without agitation, at room temperature for 2 h, followed by rinsing with deionized water to remove the unreacted glutaraldehyde residue. To crosslink with epichlorohydrin, 3.0 g of wet natural chitosan membranes were immersed in 50 mL of epichlorohydrin solution 0.01 mol L^{-1} (prepared in NaOH solution 0.067 mol L^{-1}) at 40°C under continuous agitation for 2 h [13]. Afterwards, the membranes were rinsed with deionized water to remove unreacted epichlorohydrin.

Some parameters such as width, diameter and porosity for natural and crosslinked chitosan membranes were determined by Vieira and Beppu [9]. The water content in wet chitosan membranes was also determined, which was 93.9, 91.5 and 93.1% for natural and GLA- and ECH-crosslinked chitosan, respectively. This conversion factor was very important to calculate the equilibrium and kinetic adsorption results in dry base.

2.2. Adsorption and desorption experiments

Chromium solution was prepared by dissolving potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$ —Sigma 99.9%), obtaining a stock solution of chromium ions of 1000 mg L^{-1} . This solution was adjusted to the desired pH (2.0 or 6.0, using NaOH or H_2SO_4 solutions (0.1 mol L^{-1})) and was then diluted to obtain the standard solutions (250 – 1000 mg L^{-1}).

Batch kinetic experiments were carried out by soaking a known amount of wet weight of natural or crosslinked chitosan membranes in 50 mL of chromium solution (250 mg L^{-1}) at pH 6.0, 25°C and under stirring at 200 rpm. The samples were withdrawn at fixed time intervals and analyzed for chromium content determination. Small aliquots of solution were withdrawn for measurements to disturb the system as minimum as possible, and do not change the final volume of solution, influencing the real adsorption phenomenon. Chitosan adsorption capacity was calculated taking into account the variation of the chromium solution concentration in the fixed time intervals.

Total chromium concentration was determined by atomic absorption spectrophotometer (Perkin-Elmer Analyst 100) in air-acetylene flame, based on the radiation of chromium atoms in 357.9 nm. Hexavalent chromium content was determined spectrophotometrically at 540 nm after colorimetric reaction with 1,2-diphenylcarbazide [17]. The analyses of Cr (VI) were made just to verify the effect of pH (6.0 and 2.0) in chromium reduction and to analyze metal speciation, even though the main objective of this work was to remove all the chromium species from aqueous solution. Therefore, all results depict adsorbed/desorbed amounts of total chromium.

Batch equilibrium experiments were conducted by soaking known amount of wet weight of natural or crosslinked chitosan membranes (0.3 g in wet base) in 50 mL of chromium solution (ranging from 250 to 1000 mg L⁻¹) at pH (6.0 and 2.0), for 24 h at 25 °C under stirring. The time of 24 h was chosen based on results of chromium ions adsorption kinetics onto chitosan membranes. The concentrations of chromium ions in the supernatant were analyzed as described previously. The adsorption capacity of chitosan was calculated based on the difference of chromium concentration in bulk solution before and after adsorption.

The equilibrium isotherms were adjusted by Langmuir and Freundlich models, given by Eqs. (1) and (2).

$$Q = \frac{Q_{\max} K C_f}{1 + K C_f} \quad (1)$$

$$Q = K_F C_f^{1/n} \quad (2)$$

where Q is the amount of chromium ions adsorbed by the chitosan (mg g⁻¹), Q_{\max} the maximum amount adsorbed within a monolayer (mg g⁻¹), C_f the final chromium concentration (mg L⁻¹) and K (L mg⁻¹) is the Langmuir dissociation constant, which is related to the adsorption energy. K_F (L g⁻¹) and $1/n$ (dimensionless) are the Freundlich characteristic constants, indicating adsorption capacity and adsorption intensity, respectively. The Langmuir isotherm model assumes: monolayer adsorption on a surface with a finite number of identical sites, that all sites are energetically equivalent and that there is no interaction between adsorbed molecules. The Freundlich expression is an empirical equation based on adsorption on a heterogeneous surface.

Desorption study was performed using NaCl (1 mol L⁻¹) as an eluent solution. These experiments were performed immersing the chitosan membranes in 50 mL of NaCl solution for 24 h with stirring at 200 rpm. The bulk metal concentration in solution was measured as previously described. These experiments were performed in order to evaluate the possibility of concentrating chromium ions. The extent of desorption was calculated from Eq. (3).

$$\text{Desorption (\%)} = \frac{\text{desorbed amount of metal ions}}{\text{adsorbed amount of metal ions}} \times 100 \quad (3)$$

The adsorption and desorption capacity values were calculated either in wet and dry base. The reason for depicting the results in wet base is mainly due practical conditions, once this is the condition in which the adsorbent is prepared and stored. In addition, drying processes normally change important adsorbent

properties such as superficial area, crystallinity, etc. On the other hand, the dry base is more convenient for theoretical comparison among chitosan and its modifications.

2.3. Characterization of metal-chitosan complex

2.3.1. FTIR-ATR spectroscopy

FTIR experiments were performed by using ATR accessory. The attenuated total reflection device allows getting information about the surface chemical structure. As adsorption is a surface phenomenon, this technique is suitable to observe the chemical changes occurring on the surface induced by either chemical modification or by heavy metal adsorption. Infrared spectra were obtained by using chitosan films with 200 scans and 16 cm⁻¹ resolution, using the Nicolet Protegé 460 (650–4000 cm⁻¹) spectrophotometer with germanium crystal as the reflection element. The ATR (attenuated total reflection) device allows to get information about the surface. In order to get a precise information of chitosan–chromium interaction, dense chitosan films were used, as they provide a better contact between chitosan surface and the ATR element.

2.3.2. Thermo-gravimetric analyses

Thermo-gravimetric analyses were performed in order to characterize the water affinity on natural and crosslinked chitosan membranes and to study how these modifications can interfere in adsorption/desorption results. The measurements were performed using a Shimadzu TGA 50 equipment, with a heating rate of 10 °C min⁻¹, in a dynamic N₂ atmosphere on approximately 5.0 mg of sample. The samples were previously freeze-dried using the Freeze Dry System/Freezone 4.5 equipment under 35 × 10⁻³ mbar vacuum and -45 °C. The temperature range of 25–900 °C was used for TGA analyses.

2.3.3. Differential scanning calorimetry

DSC analyses were used to verify the energy changes of membranes after chemical modification and adsorption process. The measurements were performed using a thermic analyzer DSC 50—Shimadzu. Accurate 5.0 mg of each sample were encapsulated non-hermetically in aluminium pans, being afterwards scanned from 25 to 450 °C at a heating rate of 10 °C min⁻¹ in dynamic atmosphere of N₂ at 50 mL min⁻¹.

3. Results and discussions

3.1. Characterization of chitosan membranes

3.1.1. FTIR-ATR spectroscopy

Fig. 3(A–C) depicts the IR spectra for chitosan before and after adsorption. These figures show the chemical modifications of crosslinked chitosan and the modifications due to adsorption. When chitosan was crosslinked with glutaraldehyde, a reduction of the peak due to the presence of primary amine (1100 cm⁻¹) was observed, denoting that these groups were bound to glutaraldehyde molecules. A peak at 1655 cm⁻¹ is also observed, which may be related to the imine bonds (C=N) formed in the crosslinking process [15,18,19]. There is also

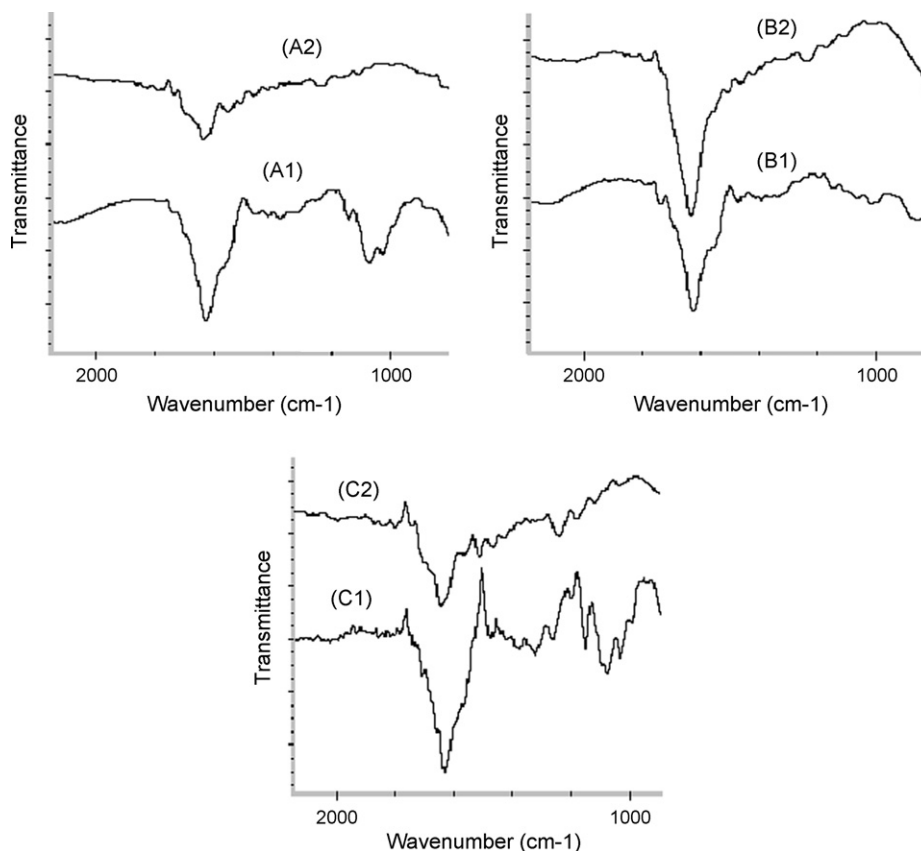


Fig. 3. FTIR-ATR spectra of natural (A1 and A2), glutaraldehyde-crosslinked (B1 and B2) and epichlorohydrin-crosslinked (C1 and C2) chitosan membranes, before and after chromium adsorption, respectively.

an evidence of the characteristic band related to free aldehydic group ($1700\text{--}1750\text{ cm}^{-1}$), which did not react with amino groups in the polymer. Especially in extensive crosslinks, the bifunctional glutaraldehyde molecules not necessarily have both aldehyde groups reacted with chitosan, and unreacted aldehyde functions may be available in the final crosslinked matrix.

Regarding the epichlorohydrin-crosslinked chitosan, an increase in the peak intensity between 1000 and 1300 cm^{-1} is noticed, indicating a C–O bond, typical of epichlorohydrin-crosslinking. For glutaraldehyde-crosslinked chitosan, a reduction in the peak intensity was observed for primary amine groups (1100 cm^{-1}), indicating that chromium adsorption affected the chemical bonds to amino groups. It is assumed that the nitrogen atoms should be the main adsorption sites for chromium. For epichlorohydrin-crosslinked chitosan, the transmittance was reduced at $1000\text{--}1300\text{ cm}^{-1}$, related to C–O stretching vibrations. These changes suggest the possibility that the oxygen atoms in the hydroxyl groups in epichlorohydrin-crosslinked chitosan were also involved in chromium adsorption.

3.1.2. Thermal analyses

3.1.2.1. TGA analysis. Fig. 4 shows the thermograms for natural and crosslinked chitosan before chromium adsorption. Fig. 5(a–c) presents the analysis after chromium adsorption for natural, glutaraldehyde-crosslinked chitosan and epichlorohydrin-crosslinked membranes, respectively.

The analysis of TGA curves (Fig. 4) allowed to observe that degradation in all samples occurred in two stages: the first peak refers to loss of water and the second refers to the sample degradation.

The first peak for the glutaraldehyde-crosslinked sample was greater than the others, indicating that the sample tends to keep less water and ends up releasing it more easily. This result shows that amino groups, which are hydrophilic, are really unavail-

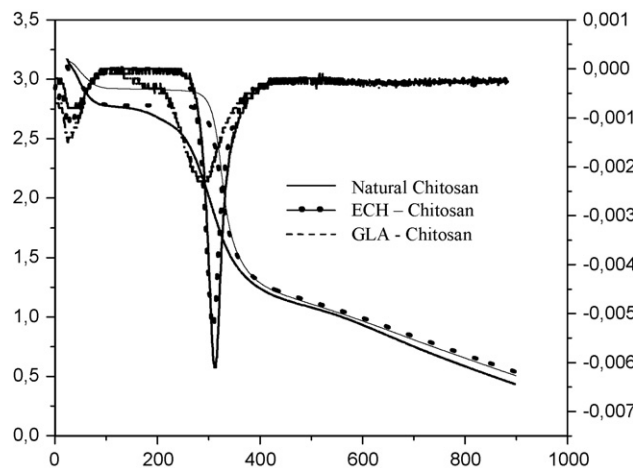


Fig. 4. Thermograms for natural and crosslinked chitosan before chromium adsorption.

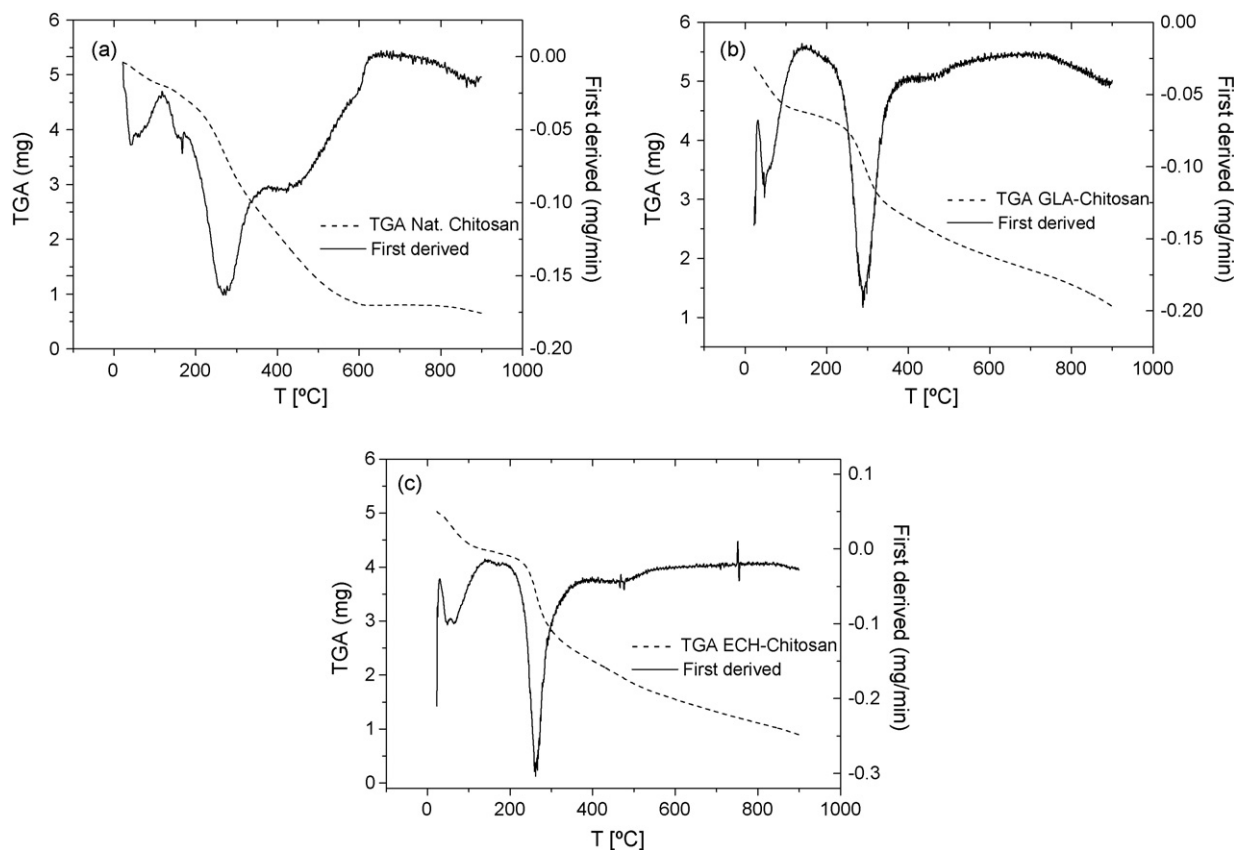


Fig. 5. (a–c) Thermograms after chromium adsorption for natural, glutaraldehyde-crosslinked and epichlorohydrin-crosslinked chitosan membranes, respectively.

able at glutaraldehyde-crosslinked chitosan, in accordance with FTIR-ATR results. Comparing natural with epichlorohydrin-crosslinked chitosan, there is similarity indicating the same hydrophilic nature with the blockage only in the hydroxyl groups.

From Fig. 5(a–c), thermal instability of the structures was observed after chromium adsorption with a degradation peak before of 300 °C, which is lower than the one observed to the sample before chromium adsorption, i.e. the metal incorporation in the chitosan structure reduced the thermal stability compared to that of pure chitosan. This result is different from that presented by Paulino et al. [20]. These authors showed that the incorporation of Pb^{2+} and Ni^{2+} on chitosan increased its thermal stability.

3.1.2.2. DSC analysis. Fig. 6(a–c) shows the endothermic and exothermic peaks for natural and crosslinked chitosan membranes. The thermograms are similar for natural and epichlorohydrin-crosslinked chitosan, but the glutaraldehyde-crosslinked sample presented a different behavior. In all cases, the endothermic peaks are related to water evaporation, presenting the lowest value for glutaraldehyde-crosslinked chitosan, associated to the low capacity of water absorption by the sample. The exothermic peaks are related to chemical degradation of the sample [21].

After metal adsorption, mainly for glutaraldehyde-crosslinked chitosan, the curves presented very close shapes

compared to those observed before adsorption. For natural and epichlorohydrin-crosslinked chitosan, the endothermic peaks referring to water evaporation were the biggest ones and the exothermic peaks due to degradation were relatively small.

Natural chitosan presented a significant reduction in the thermal stability after complex formation with chromium, presenting two exothermic peaks: the first peak was located at a temperature lower than that observed before adsorption, and the second one presented low intensity.

Sreenivasan [21] showed that the changes of thermal stability due to chelation for mercury, copper and iron ions on chitosan were endothermic transitions that occurred for each metal ion specifically involved in the complex formation.

3.2. Adsorptions equilibrium

In order to understand the species present in the aqueous solution, a distribution of chromium species as function of pH, for a defined metal ion concentration, was simulated using HYDRA (Hydrochemical Equilibrium-Constant Database) software [22]. Chromium speciation indicated that the majority of Cr (VI) exists in the form of $HCrO_4^-$ in the acidic region (pH 2.0) and as $HCrO_4^-$ (~75%) and CrO_4^{2-} (~25%) at pH 6.0. At pH 2.0, the majority of amino groups are protonated and, at pH 6.0, there are both NH_3^+ and NH_2 groups. These findings are very useful to describe if the adsorption mechanism would take place mainly by chelation or electrostatic interaction.

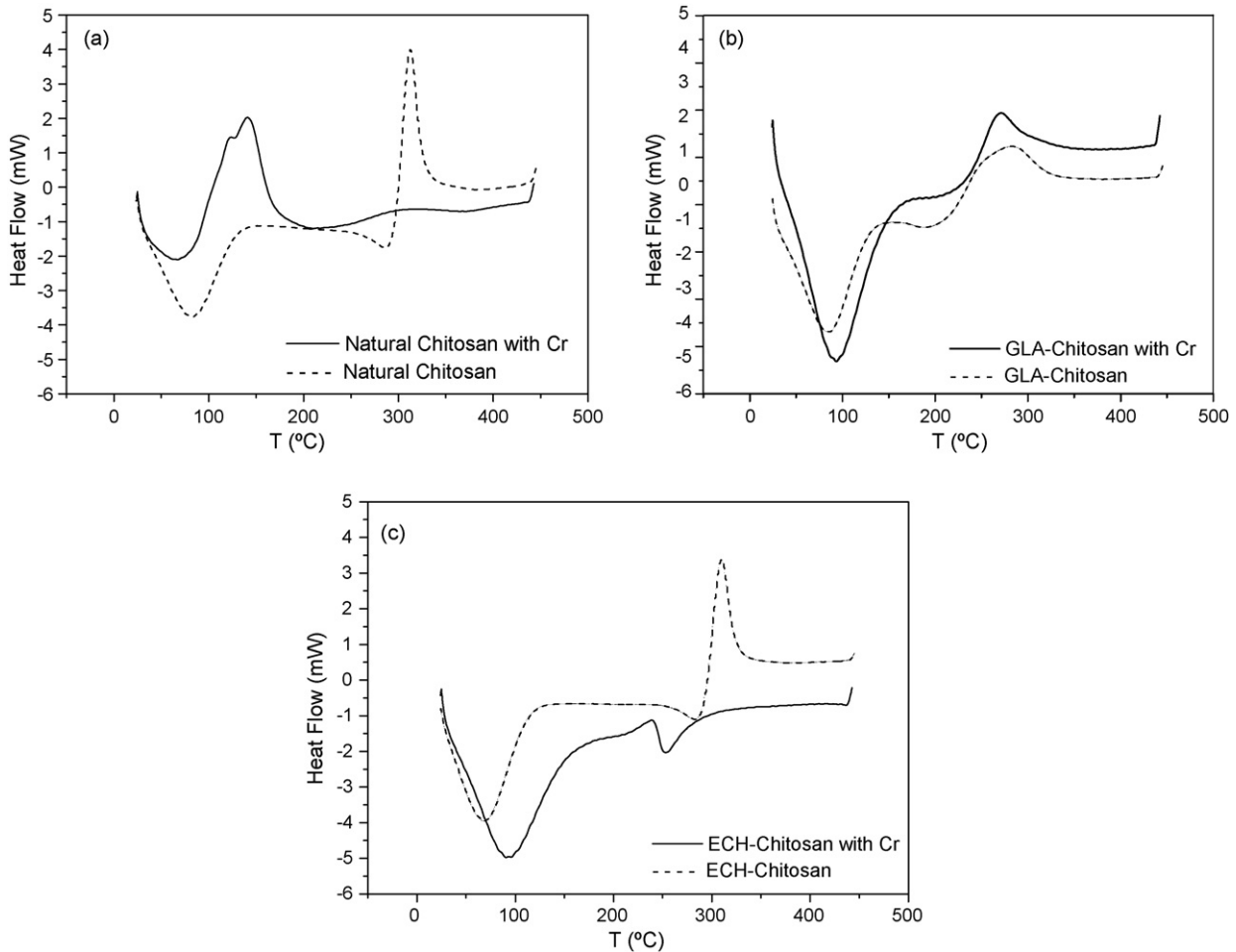


Fig. 6. DSC thermograms of natural (a), glutaraldehyde-crosslinked (b) and epichlorohydrin-crosslinked (c) chitosan membranes.

Langmuir and Freundlich models were used to describe the equilibrium data of total chromium adsorption on natural and crosslinked chitosan membranes. Figs. 7 and 8 depict the adsorption isotherms, at pH 2.0 and 6.0, fitted to Langmuir and Freundlich models, respectively, based on dry weight of chitosan. Table 1 presents Langmuir and Freundlich equilibrium constants and the corresponding R^2 fitting coefficients, which

were obtained through the application of least squares method for both models. The results are shown in dry and wet weight of chitosan (Table 1).

The Langmuir model presented a better fitting coefficient, except for epichlorohydrin-crosslinked chitosan at pH 6.0, indicating that adsorption take place preferably forming a monolayer, as assumed by this model.

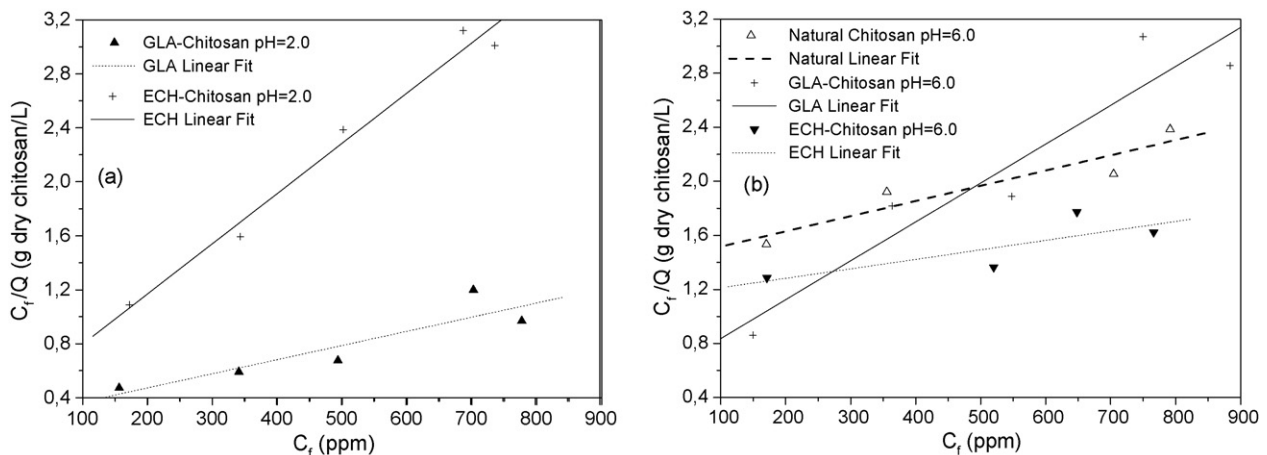


Fig. 7. Isotherms of chromium adsorption at pH 2.0 (a) and pH 6.0 (b) fitted to Langmuir model.

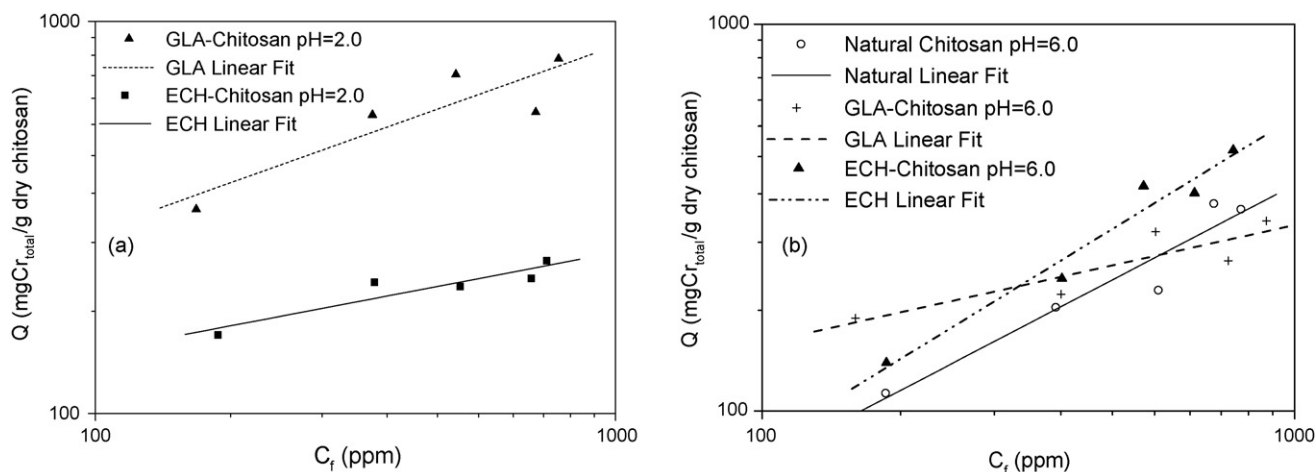


Fig. 8. Isotherms of chromium adsorption at pH 2.0 (a) and pH 6.0 (b) fitted to Freundlich model.

Evaluating the effect of pH (pH 6.0 and 2.0), it was observed that epichlorohydrin-crosslinked chitosan presented high adsorption capacity at pH 6.0 compared to pH 2.0, in contrast to glutaraldehyde-crosslinked chitosan.

For ECH-crosslinked chitosan, at pH 2.0, the majority of amino groups is protonated and the competition effect between the hydroxonium ions and chromium anions is higher than that observed at pH 6.0, indicating that in this condition, electrostatic interaction is more important for adsorption mechanism than chelation. At pH 6.0, there are both NH_3^+ and NH_2 groups and the adsorption phenomenon is controlled either by chelation and electrostatic interaction. These results are in accordance with Lee et al. [23] who studied the adsorption of hexavalent chromium by chitosan-based polymeric surfactants (CBPSs) and showed that the adsorption phenomenon is controlled by electrostatic interaction followed by colloidal precipitation.

At pH 6.0, GLA-crosslinked chitosan presented lower value of adsorption capacity than the ones calculated for natural and epichlorohydrin-crosslinked chitosan. This result means that the chromium adsorption occurs preferably with the amino groups of chitosan, once they are unavailable after the crosslinking reac-

tion. Monteiro and Airoidi [15] studied copper adsorption on natural and GLA-crosslinked chitosan. An increase in adsorption capacity compared to natural chitosan was observed, which was explained using DRX and FTIR techniques. After chemical modification, chitosan presented an increase in the accessibility of copper ion to chitosan amino groups, due a decrease in crystallinity of polymer chains. FTIR indicated that imine bond is also able to adsorb copper ions.

Bosinco et al. [24] evaluated the capacity of Cr (VI) adsorption as 76 mg g^{-1} for glutaraldehyde-crosslinked chitosan beads. Rojas et al. [25] found the value of 215 mg g^{-1} for glutaraldehyde-crosslinked chitosan flakes at pH 4.0. For non-crosslinked chitosan, Schmuhl et al. [26] and Udaybaskar et al. [27] evaluated the capacity, respectively, as 78 mg g^{-1} at pH 5.0 and 32 mg g^{-1} at pH 4.0 for chitosan powder.

3.3. Adsorption kinetics

Fig. 9 presents the chromium ion adsorption kinetic curves using natural and crosslinked chitosan membranes. Chromium solutions had an initial concentration of 250 mg L^{-1} and pH 6.0.

Table 1
Freundlich and Langmuir parameters for adsorption experimental data

| | pH | Freundlich model | | | Langmuir model | | |
|----------------------|-----|------------------|-------|-------|-------------------------------------|------------------------|-------|
| | | K_e | $1/n$ | R^2 | $Q_{\text{max}} (\text{mg g}^{-1})$ | $K (\text{L mg}^{-1})$ | R^2 |
| Dry base of chitosan | | | | | | | |
| Natural chitosan | 6.0 | 0.43 | 0.72 | 0.963 | 885 | 8.0×10^{-3} | 0.935 |
| GLA-chitosan | 2.0 | 1.52 | 0.47 | 0.892 | 950 | 4.0×10^{-3} | 0.902 |
| | 6.0 | 1.56 | 0.31 | 0.887 | 347 | 5.3×10^{-3} | 0.950 |
| ECH-chitosan | 2.0 | 1.65 | 0.25 | 0.925 | 270 | 8.7×10^{-3} | 0.990 |
| | 6.0 | 0.23 | 0.84 | 0.980 | 1420 | 6.2×10^{-4} | 0.801 |
| Wet base of chitosan | | | | | | | |
| Natural chitosan | 6.0 | 0.20 | 0.72 | 0.927 | 65.7 | 8.0×10^{-4} | 0.935 |
| GLA-chitosan | 2.0 | 2.81 | 0.47 | 0.796 | 81.1 | 4.0×10^{-3} | 0.902 |
| | 6.0 | 3.12 | 0.31 | 0.785 | 29.5 | 5.2×10^{-3} | 0.950 |
| ECH-chitosan | 2.0 | 3.10 | 0.25 | 0.855 | 18.6 | 8.7×10^{-3} | 0.990 |
| | 6.0 | 0.12 | 0.84 | 0.961 | 98.2 | 6.2×10^{-4} | 0.801 |

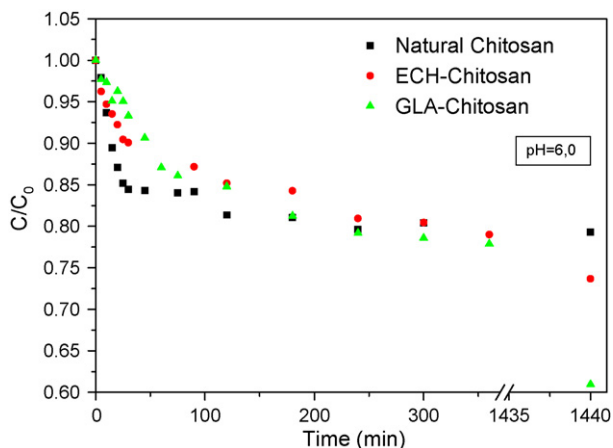


Fig. 9. Chromium ion adsorption kinetic curves for natural and crosslinked chitosan membranes.

Relatively slow kinetic rates of chitosan chromium system were observed. Chromium quantitative analyses may present errors that are significant when small differences of concentrations are being analyzed. This fact, associated with the slow adsorption kinetic rate of chromium (mainly near the equilibrium), may be the most significant sources of errors in our experiments.

Natural chitosan had a faster adsorption kinetic rate than that observed for crosslinked chitosan membranes. However, crosslinked chitosan membranes presented a higher adsorption capacity. Glutaraldehyde-crosslinked chitosan membranes required a longer period of time to achieve the adsorption equilibrium compared to the other two membranes. For the glutaraldehyde-chitosan system, there was a sharp decrease in the chromium concentration after 24 h, indicating that the system had not reached equilibrium yet. Hence, the absorption kinetic rates data obtained are promising to implement chromium ion removal processes utilizing chitosan membranes.

3.4. Desorption of chromium ions

The average percentage of chromium ion desorption using NaCl (1 mol L⁻¹) solutions are displayed in Table 2. At pH 2.0 epichlorohydrin-crosslinked chitosan membranes presented a high percentage of chromium ion desorption, although it had the lowest adsorption capacity compared to the other membranes.

Comparing the desorption and adsorption properties of the membranes, it is possible to infer about the metal-absorbent interactions. The adsorption of metal ions on chitosan may involve different mechanisms (chelation, ion exchange, elec-

Table 2
Desorption of chromium total ions in NaCl (1 mol L⁻¹)

| Sample | Desorption (%) | |
|------------------|----------------|--------|
| | pH 2.0 | pH 6.0 |
| Natural chitosan | – | 48.6 |
| GLA-chitosan | 40.32 | 35.71 |
| ECH-chitosan | 77.2 | 49.1 |

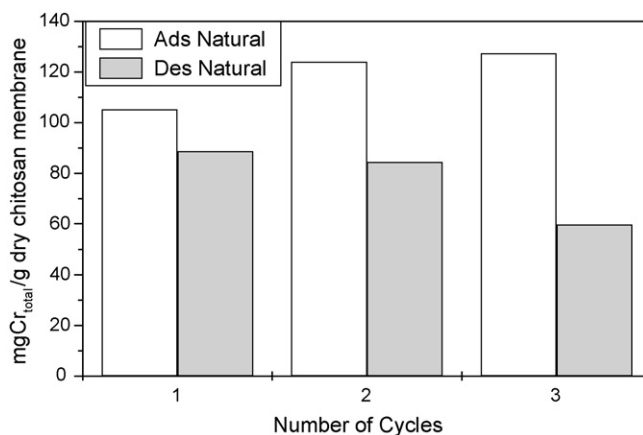


Fig. 10. Adsorption/desorption cycles on natural chitosan.

trostatic attraction, etc.), which depends on the composition of the solution, the pH and the speciation of metal ions [5]. These mechanisms may happen simultaneously. The electrostatic interactions of chitosan with metal ions are believed to be influenced by the degree of polymerization and deacetylation, and the distribution of acetyl groups along the polymer chain [5]. The desorption of chromium species using NaCl solution may be explained by electrostatic interaction between Cr species and the charged species from elution, through the compression of the electric double layer, which would weaken the interaction between chitosan and metal, promoting desorption.

Three adsorption/desorption cycles were evaluated and the amounts of chromium are shown in the Figs. 10–12 for natural and crosslinked chitosan membranes based on dry weight of chitosan. The chitosan membranes maintain the adsorption/desorption capacity for successive cycles. Glutaraldehyde-crosslinked chitosan presented small reduction in adsorption capacity after the first adsorption cycle. Natural chitosan have slight reduction in desorption capacity in the third cycle, despite the fact that the values obtained were very close between the different cycles, either for natural and crosslinked chitosan.

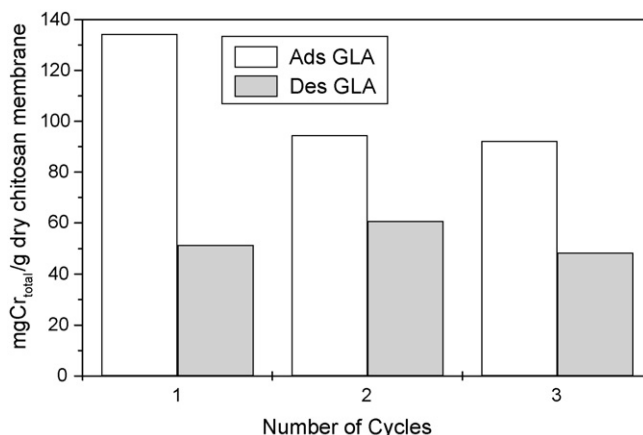


Fig. 11. Adsorption/desorption cycles on glutaraldehyde-crosslinked chitosan.

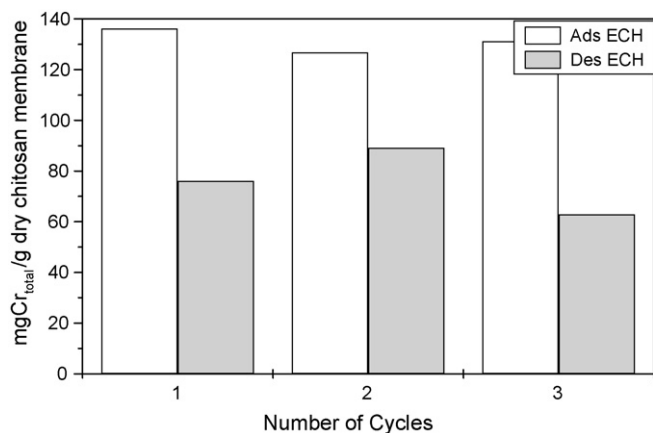


Fig. 12. Adsorption/desorption cycles on epichlorohydrin-crosslinked chitosan.

4. Conclusions

In this study, the feasibility of using natural and crosslinked chitosan membranes in chromium ions removal from aqueous solution was confirmed. The maximum adsorption capacity occurred in epichlorohydrin-crosslinked chitosan at pH 6.0, indicating that adsorption process occurs mainly in chitosan amino groups. The best desorption condition was obtained for epichlorohydrin-crosslinked at pH 2.0. At pH 6.0 the desorption percentage was similar in the three conditions. Chitosan membranes are favorable also for different adsorption/desorption cycles.

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