

# CHROMIUM (III) RECOVERY BY POLYMER-ENHANCED ULTRAFILTRATION USING A WATER SOLUBLE CHITOSAN DERIVATIVE AS MACROLIGAND

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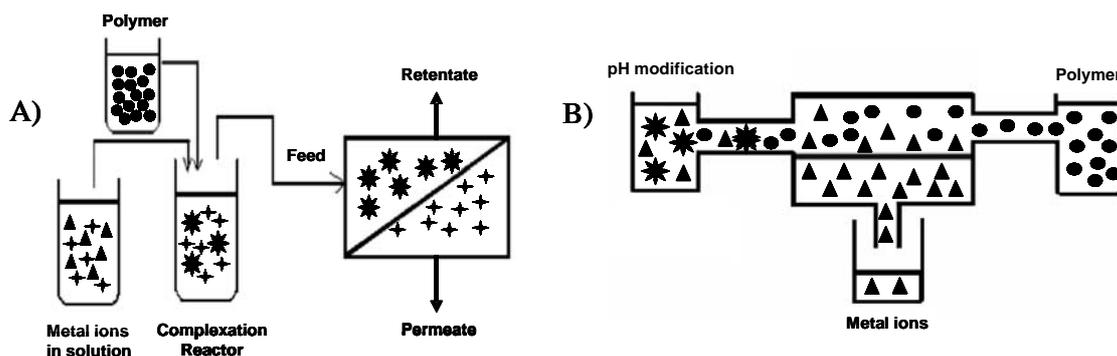
## Abstract

The Polymer Enhanced Ultrafiltration Process (PEUF) is a suitable technique for separating metal ions combining the principles of the ultrafiltration with ion complexation by soluble macroligands. The macromolecule must have a high complexation capacity and selectivity toward a metal ion, and the molecular weight must be bigger than the membrane molecular weight cut-off. In this way, the metal ion is selectively retained by the membrane as a complex. Chitosan is an aminopolysaccharide that has been widely used as solid sorbent for metal ion recovery and more recently it has been used in PEUF, in a dissolved form in acidic solutions. In neutral or alkaline milieu, chitosan precipitates causing membrane fouling. As an alternative, in this work a water soluble chitosan derivative is proposed. The synthesis and characterization of chitosan sulphate (ChS) are presented, as well as its application to chromium(III) recovery by PEUF. The synthesized product presents a high solubility in water in the studied pH range (1-13). The ChS was characterized by FTIR, <sup>13</sup>C-RMN, potentiometric titrations and elemental analysis. The obtained product presents a 1.2 sulfonation degree. Sulfonation occurs selectively on the OH groups of chitosan (preferably on the C<sub>6</sub>), leaving the amine group free for chromium complexation. The pH, metal concentration, and polymer concentration were the main parameters studied in PEUF. In ChS absence, chromium passes freely through the membrane at pH 2-5 (for higher pH values chromium precipitates). In the case of Cr(III) solutions in presence of ChS, the chromium remains in solution in the studied pH range (1-13). At pH 1, the Cr(III) is not retained efficiently (7 %), but the retention increases with the pH, reaching a total retention from pH 6 to 13.

## Introduction

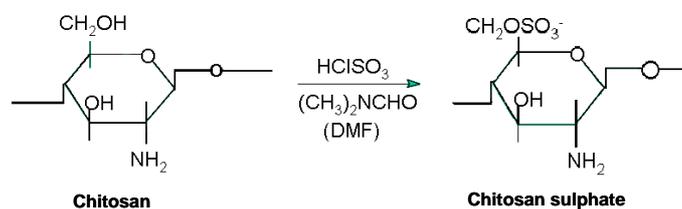
Nowadays, the threat of environment contamination by heavy metals is well known, therefore the legislation is getting more strict regarding metal discharge in water streams <sup>1,2</sup>. The conventional methods employed for removal of heavy metal ions from industrial wastewaters, such as: chemical precipitation, ionic exchange, adsorption and liquid-liquid extraction, present several limitations since they are expensive and/or incapable to remove heavy metal ions at trace levels, they require additional steps or they can present slow kinetics <sup>3</sup>. Besides, some techniques as the chemical precipitation produce residual sludge that requires storage and transportation to adequate places for their confinement, which generate additional costs. The evolution of industrial wastewater

processes has conducted to development of new separation processes or alternative methods more efficient, simple and competitive. One of the techniques that has shown good results for the separation of metal ions contents in industrial wastewater is the Polymer Enhanced Ultrafiltration Process (PEUF). This technique is based on the complexation of metal ions with water soluble polymers, followed by a physical separation through a ultrafiltration membrane <sup>4</sup>. This kind of membranes is typically used to retain macromolecules from a solution, the lower limit being solutes with molecular weights of a few thousand Daltons. The metal ion-polymer complex is retained and the free ions pass through the membrane. Subsequently, the bounded ions can be recovered destabilizing the complex by means of pH modification (Figure 1). The advantages of this method are the low requests of energy, the low cost <sup>5</sup> and the high metal ions removal efficiency from diluted solutions due to the effective binding power of the water soluble polymers <sup>5</sup>.



**Figure 1 :** PEUF process A) Metal ion separation. B) Polyelectrolyte recovery.

A large quantity of water soluble polymers has been utilized in the PEUF processes: synthetic polymers such as polyethylenimine (PEI) <sup>6</sup>, copolymers of 1-vinyl-2-pirrolidone) <sup>7</sup>, acrylamide derivatives <sup>7</sup> and natural polymers such as chitosan (Ch) <sup>6, 8</sup>. Chitosan is a partially acetylated glucosamine biopolymer, which is obtained mainly by chitin deacetylation. Chitosan is used for metal ions adsorption in near-neutral solutions <sup>9,10</sup>. This biopolymer also can be used in its dissolved form for the metal recovery by PEUF processes <sup>6, 8</sup>. Chitosan is soluble in most mineral and organic acids (with the exception of sulphuric acid). In fact, chitosan is soluble in acidic solution due to amine protonation, but when the pH is increased approaching the amine deprotonation zone, the polymer precipitates, causing the membrane fouling. To use chitosan in PEUF, in a wide pH range, it is necessary to increase solubility leaving free the amino groups. To reach this goal, the selective modification of the OH groups of chitosan has been proposed. This group is modified introducing sulphate groups, obtaining thus chitosan sulphate (Figure 2), which presents a greater solubility in a wide pH range.



**Figure 2 :** Chitosan sulphate synthesis.

This work presents the results obtained in Cr(III) recovery by PEUF using chitosan sulphate as macroligand. Metal recovery was investigated in static regime on a wide pH range (1 - 13), using a polyethersulphone membrane. Chitosan sulphate (ChS) was synthesized and characterized in our laboratory. The effect of the membrane modification was studied. The membrane was modified by consecutive permeations of ChS solutions. Besides, Cr(III) concentration was varied to analyse the complexation effect of ChS.

## Material and Methods

### Material

Chitosan was supplied by Aber Technology; (Plouvien, France); it is characterized by a 87 % deacetylation degree and a molecular weight of 125 KDa. Other reagents were: acetic acid (Fisher), methanol and toluene analytical grade (Karal), dimethylformamide (DMF, Sigma Aldrich) and chlorosulphonic acid (Aldrich).

The membrane used in the PEUF process is a polyethersulphone membrane (PES) (Alfa Laval, Canada) with a molecular weight cut-off of 10 KDa. The PES membranes have very good thermal, mechanical and chemical stability<sup>11</sup>. The PEUF experiments of Cr(III) were performed using an Amicon 8200 ultrafiltration module. The model Cr(III) solutions were prepared with water Milli Q and CrCl<sub>3</sub>.6H<sub>2</sub>O (Sigma). The pH of the solutions was controlled with NaOH and HCl 0.1, 1 and 3 M; and pH variations were monitored using a potentiometer (Corning pH/Ion meter 450).

### Synthesis and characterization of chitosan sulphate.

The technique proposed by Hayashi<sup>11</sup> was modified for the ChS synthesis. Dry chitosan (1 g) was dissolved in a 1% HAc solution (50 mL) and later precipitated with a 0.25 M NaOH solution (50 mL). The gel was subsequently washed with water and filtered to neutral pH. Immediately after, the water excess was removed by pressing with paper filter. Precipitated chitosan was treated with methanol for 2 days. Later, it was filtered and pressed again to remove methanol excess and, finally, chitosan was treated with dimethylformamide (DMF) for 2 days and the DMF excess was removed, obtaining a DMF-impregnated chitosan gel (DMF-Ch). DMF (5 ml) was placed in a three mouths flask, in a cold bath (0°C) and HClSO<sub>3</sub> (4 mL) was added drop to drop, producing a sulphonating complex. This complex was dissolved in toluene (40 g) and the DMF-Ch was added. The sulphonation reaction was carried out with continuous agitation for 4 h, leaving in rest for 12 h more. The obtained ChS is a brown gummy paste that was washed with methanol obtaining a beige paste. The product was dissolved in a pH 12 water solution; it was purified by UF using a 10 KDa membrane, for 3 consecutive times, to remove low molecular weight fractions. The water was evaporated by heating (45-50 °C), obtaining dry ChS thin layers. Finally, the product was characterized by FTIR (Perkin Elmer Model Spectrum One), <sup>13</sup>C-NMR (Varian Model Gemini 2000, 300 MHz), elemental analysis (Fisons Model EA 1108) and potentiometric titration (Metrohm, Model Tritino 716 DMS).

### Cr(III) PEUF

The Cr(III) PEUF were carried out at room temperature, with or without ChS in solution, in order to observe the influence of the ChS in solution on the Cr(III) permeation, in a wide pH range (1-13). Firstly, the membrane was washed, three times with water for 1 hour. Subsequently, the Cr(III) solution ultrafiltration was carried out at 50 psi (3.4 atm). The concentrations were in the range 2-50 ppm for Cr(III) and 100-1000 ppm for ChS. A 90 mL volume was used as feed solution, obtaining 40 mL of retentate and 50 mL of permeate. These volumes allow an easy management, recovery and analysis. The chromium analysis was carried out by flame atomic absorption spectrometry (Perkin Elmer model 3110) or by ICP-AES (Jobin-Yvon JY 2000, France). The specific parameters determined in Cr(III) PEUF were Cr(III) rejection, Cr(III) permeation and permeate flux. The Cr(III) recovery was determined by mass balance considering the concentrations of permeate and retentate with respect to the concentration of feed solution, in order to verify the possible occurrence of chromium loss by precipitation or accumulation on the membrane. Before and after the permeation of Cr(III) solution, water was permeated to verify possible variations of membrane permeability. The influence of low-molecular weight complexing agents in Cr(III) permeation was studied by adding 0.1 M acetic acid and controlling the pH to 5.

The membrane was modified by three consecutive permeations of 1000 ppm ChS solutions at pH 5. After membrane modification, the Cr(III) permeation was carried out with and without ChS in solution, in a similar way to permeation with a non-modified membrane.

## Results and Discussion

### Chitosan sulphate synthesis and characterization

The FTIR spectra showed bands at 804 and 1240  $\text{cm}^{-1}$  characteristic of the bonds C-O-S and S=O, due to sulphate groups added to the molecule (Figure 3). The  $^{13}\text{C}$ -NMR spectrums only showed the sulphonation of C<sub>6</sub> groups on chitosan molecule, the amino groups remaining free and available for metal ion complexation (Figure 4).

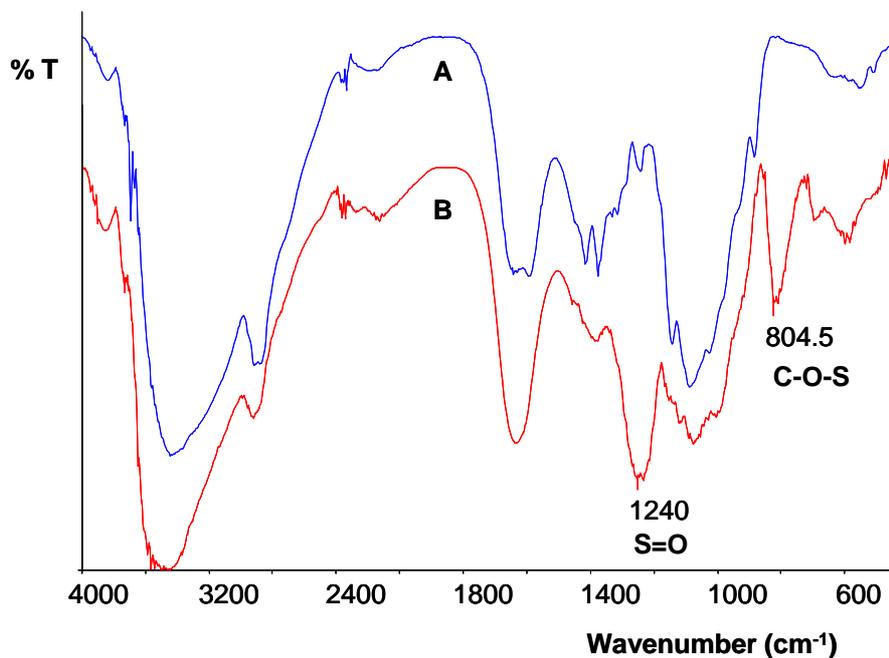


Figure 3 : FTIR spectra of chitosan (A) and chitosan sulphate (B).

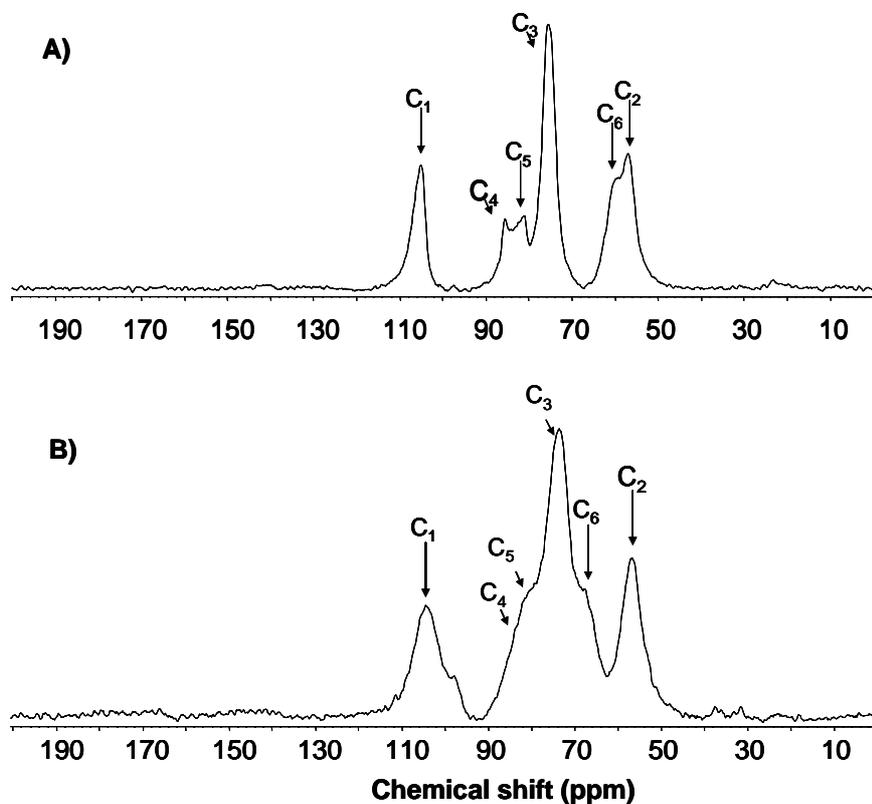


Figure 4 :  $^{13}\text{C}$ -NMR spectra of chitosan (A) and chitosan sulphate (B).

The elemental analysis showed a content of C, H, N and S of 22.7, 3.8, 4.4 and 12.0 %, respectively, with a substitution degree of 1.2. The potentiometric titration revealed a  $pK_a$  of 8.22 and 77.5 % of protonable amino groups. The product solubility was increased in all studied pH range (1-13), due to the insertion of sulphate groups.

#### Cr(III) recovery by PEUF using chitosan sulphate

The preliminary studies of the Cr(III) rejection at pH 5 with a non-modified membrane (Figure 5) show that, in the absence of ChS in solution, the membrane itself is incapable of rejecting the metal ion. On the contrary, when ChS is present in solution, a significant chromium rejection increment (72 %) is observed. These results show that at pH 5, Cr(III) complexation by the ChS is significant, in spite of the fact that, in these conditions, the majority of the amino groups of the ChS are protonated, avoiding the effective metal ion complexation. Besides, they show that the ChS has been correctly sulphonated on the hydroxyl groups, leaving the amino group free to be utilized as complexant in the PEUF.

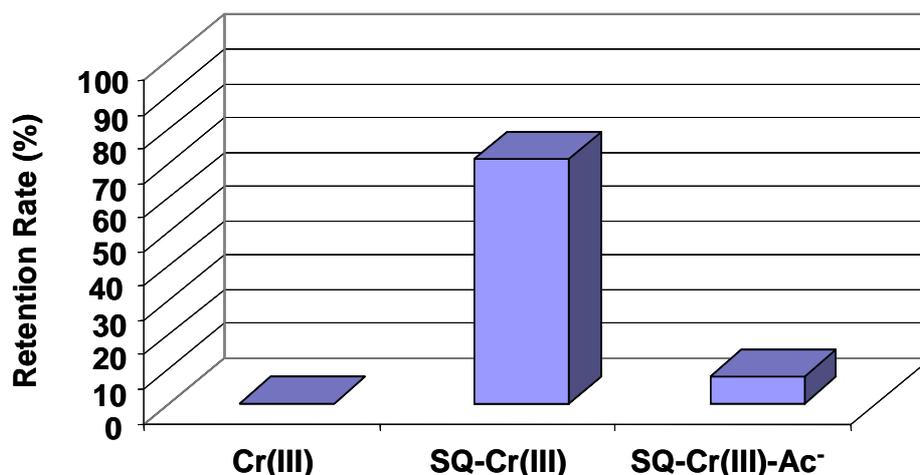


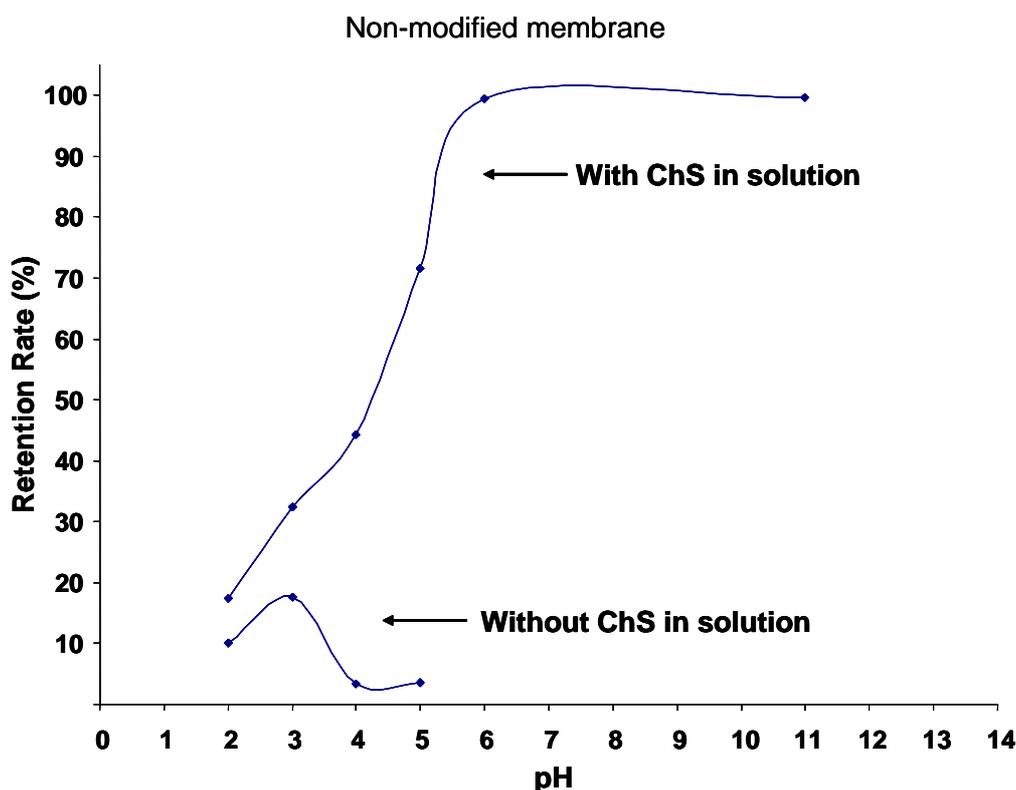
Figure 5 : Cr(III) rejection. pH 5 (non-modified membrane).

In the presence of complexing agents of low-molecular weight (such as acetate ions), Cr(III) rejection does not exceed 8%. This means that the complexation of Cr(III) by acetate ions limits the formation of Cr(III)-chitosan complexes. The Cr(III)-acetate complexes characterized as low-size molecules can pass through the membrane. In all these cases, the mass balance on Cr(III) (recovery  $\approx 100\%$ ) indicates that metal ion loss due to insoluble hydroxides formation or to ChS-Cr or Ac-Cr complex retention on the membrane is not significant.

In the absence of ChS, permeation flux remains constant in all the experiments ( $49.7 \text{ L m}^{-2} \text{ h}^{-1}$ ). These fluxes are similar to those obtained with the solvent (water) before and after chromium solution permeation. In the case of Cr(III) solution permeation in presence of ChS, a continuous decrease of flux was observed during the solution permeation due to polyelectrolyte interactions with the membrane. This is a normal phenomenon in the permeation processes with this kind of membranes. The presence of the polyelectrolyte causes the membrane fouling. However, when the solvent (water) is permeated again, the membrane is washed and the flux is increased reaching the original values.

#### pH effect on the Cr(III) rejection by PEUF

To continue with the analysis of Cr(III) rejection by PEUF using the ChS, a systematic study of pH effect was carried out. Firstly, Cr(III) PEUF was studied with a non-modified membrane, for Cr(III) solutions without ChS, varying the pH from 2 to 5. At higher pH, the chromium hydroxides formation and the subsequent deposit on the membrane cause problems in solution permeation. Subsequently, the study was continued with Cr(III) solution in presence of ChS, at pH 2-11 (Figure 6). For each case (modified and non-modified membrane), the same membrane was used all along the study of pH effect.



**Figure 6 :** Cr(III) rejection with and without ChS in solution (non-modified membrane).

The results obtained with Cr(III) solutions in the absence of ChS show low metal ion rejection ( $\approx 3\%$  at pH 4 and 5). Nevertheless, at pH 2 and 3, this value increases to 10 and 18 %, respectively. This fact can be attributed to a possible membrane protonation due to the acidic solution. Under these conditions, the Cr(III) can be partially rejected by electrostatic repulsions. The mass balance on Cr(III) (recovery  $\approx 100\%$ ) shows that the metal is not accumulated on the membrane. The water and Cr(III) solution permeation fluxes remain constant.

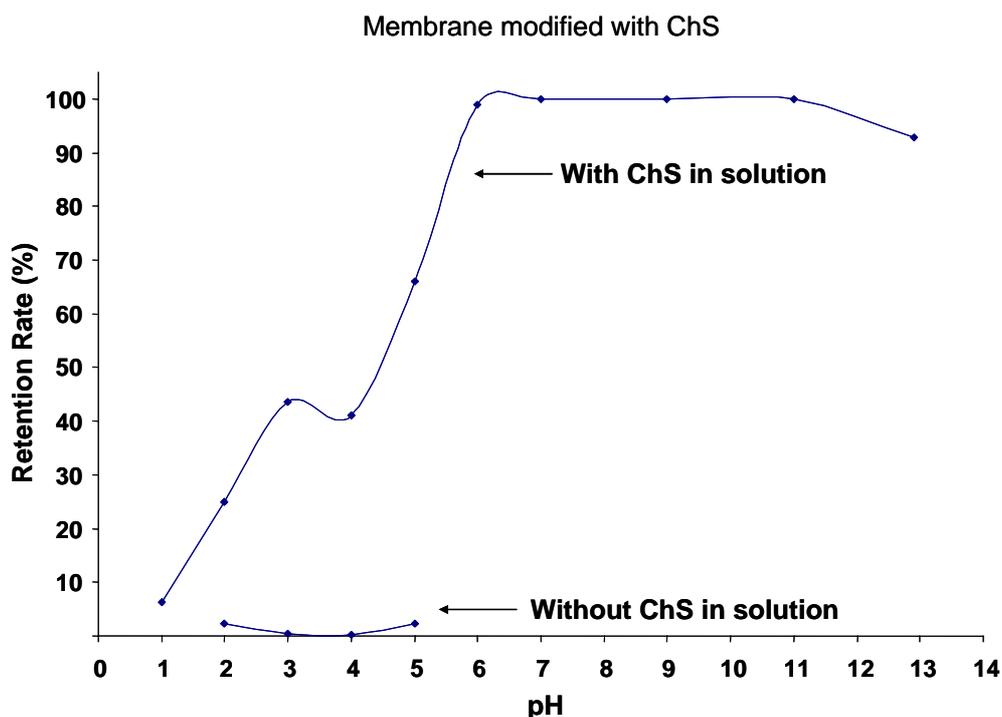
In the case of Cr(III) solution permeation with ChS in solution, the results show that, even in very acidic solutions (pH 2), the Cr(III) rejection is significant (17%). Decreasing the pH limits the possibility for chitosan to complex Cr(III); the remaining recovery activity is probably due to the effect of membrane charge. The Cr(III) rejection increases with the pH, reaching 100 % at pH 6. The total Cr(III) rejection is maintained until pH 11, showing the high Cr(III) complexation power of ChS. The mass balance on Cr(III) (recovery  $\approx 100\%$ ) again indicates that the metal is not accumulated on the membrane. The permeation flux gradually diminishes with the complex solution permeation (74 %) due to polyelectrolyte accumulation on the membrane.

The membrane modification effect on the Cr(III) rejection was studied under the same conditions as previously described. Cr(III) solutions were used with and without ChS in solution, in a pH range from 1 to 13 (Figure 7).

In the absence of ChS, the retention of Cr(III) by the modified membrane is negligible. These results indicate that ChS deposited on the membrane has not a significant influence on Cr(III) rejection. The mass balance on Cr(III) (recovery  $\approx 100\%$ ) indicates that there is not appreciable metal ion loss. The water and Cr(III) solution permeation fluxes remain constant.

The Cr(III)-ChS solution permeation through a membrane modified with ChS shows that Cr(III) rejection is very low (7%) at pH 1, but it increases with the pH, reaching 100 % at pH 6. This value is maintained until pH 11 and diminishes a little at pH 13 (93%).

The mass balance on Cr(III) (recovery  $\approx 100\%$ ) indicates that Cr(III) loss is negligible, even at basic pH, verifying again that the complexation of Cr(III) by ChS prevents the formation of chromium hydroxides. Again, the flux diminishes with the permeation of solution containing the polyelectrolyte.



**Figure 7 :** Cr(III) rejection with and without ChS in solution (modified membrane).

#### Influence of Cr(III) and ChS concentration.

This study was carried out with different Cr(III) concentrations (2-50 ppm), varying the ChS concentration (100, 200, 500 and 1000 ppm), so that the molar ChS/Cr ratio varied between 1.83 and 18.3. For lower molar ratios, the Cr(III) precipitates at alkaline pH, depending on its concentration. The permeations were carried out at pH 10.5, since at this pH the Cr(III) is efficiently retained and the formation of Cr(III) hydroxides remains negligible in the studied concentrations range.

In all these cases, the Cr(III) rejections were very high ( $\approx 100\%$ ), even for the lowest molar ChS/Cr ratio (1.83). These results indicate that ChS has a high complexation capacity, avoiding chromium permeation and chromium hydroxide precipitation.

#### **Conclusions**

The synthesized chitosan sulphate presents a high solubility in water in the studied pH range (1-13) and shows a high Cr(III) complexation capacity. The used membrane is incapable to retain efficiently the Cr(III) in absence of ChS. Nevertheless, in presence of ChS in solution, the Cr(III) is totally retained between pH 6 and 11. The Cr(III) permeation and the chromium hydroxide precipitation are avoided due to the high Cr(III) complexation power of the chitosan sulphate. The Cr(III) rejection is total ( $\approx 100\%$ ), even for chromium concentrations of 50 ppm, with 500 ppm ChS (pH 10.5).

The membrane modification with ChS does not affect significantly the behavior of Cr(III) permeation, obtaining similar results of Cr(III) permeation of Cr(III) with non-modified membranes. Nevertheless, the ChS sorption on the membrane causes a decrease of the permeate flux.

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