

Recovery Of Chromium (Iii) By Polymer Enhanced Ultrafiltration

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The presence of high concentrations of chromium in the tannery wastewater is of concern due to high toxicity of this metal ion, since the tan process is a slightly effective process and needs a big consumption of chromium sulphate. The viability of recovering chromium (III) was studied by polymer enhanced ultrafiltration (PEUF). Four polymers with different structure, molecular weight and acid-basic equilibrium were tested at 40 and 60°C in order to investigate the sorption of chromium (III) ions onto the polymer chains: polyvinyl alcohol (PVA), polyacrylic acid-co-maleic acid (PACM), polyethylenimine (PEI) and ethoxylated polyethylenimine (EPEI). The reversibility of the polymer metal binding was studied by operating in a dead-end PEUF system. Alcohol groups did not cause binding, amino groups showed reversible binding, and carboxylic groups showed quasi irreversible binding.

Keywords: water-soluble polymers; membranes; metal ions; ultrafiltration

Introduction

In the tanning process specific reactions happen between the carboxylic groups of protein fibers of the skin and tanning agents. The product most often used for such purposes is chromium (III) sulfate. The presence of high concentrations of chromium in the tannery wastewater is of concern due to the toxicity of this metal ion. Several processes are used to reduce chromium discharge by the leather industry: chemical precipitation [1], solvent extraction [2], ion exchange [3], adsorption [4], membrane technology [5]. The use of membrane technologies applied to the leather industry represents an economic advantage, especially in the recovery of chromium from residual waters of leather tanning. Membranes act as a selective barrier that prevent the passage of the metal ions and allow a clean watery solution to be obtained. Ultrafiltration combined with water-soluble polymers has been shown to be a useful process for removing metal ions from pollutant wastewaters [6]. Metal-polymer bonds are generated by electrostatic attraction or electron coordination between electron donors and acceptors. High molecular weight polymers can complex a large number of metal ions [7]. These very soluble polymers are usually formed by ionized groups, such as carboxylic or amine groups [8]. The metal ion removal is based on the metal-polymer complexes, which are retained by the membranes, whereas the unbound metallic ions pass through the membranes. Different variables should be controlled in order to complex the metallic ion with the polymer: polymer nature, metallic ion concentration, pH, ionic strength, etc.

The interaction between metal ions and water-soluble polymers may also be considered an adsorption phenomenon of metal ions on the polymer chains. Analytical expressions for the corresponding retention profiles have been obtained considering the Freundlich and Langmuir isotherms [9]. Chromium (III) is a metal cation with a high tendency to form complexes with a variety of polymers. The literature shows that the quantity of chromium (III) bound to the polymer is pH-dependent.

The aim of this work is to establish the experimental conditions for the separation of chromium (III) in water by means of polymer enhanced ultrafiltration with polymers of different chemical composition. The adsorption and desorption of chromium (III) onto polymer chains at different experimental conditions (i.e., temperature; pH) are also reported.

Materials And Methods

Materials

Four commercially available water-soluble chelating polymers were used to remove the chromium (III) (Chromium sulphate, Fluka Chemika): polyvinyl alcohol (PVA) with an average molecular weight of 146000-186000 (87-89% hydrolyzed, Aldrich), polyacrylic acid-co-maleic acid (PACM) with a molecular weight of 70000 g/mol (50 wt.% in water, Rhom&Haas), polyethylenimine (PEI) with an average molecular weight of 60000 (50 wt.% in water, Aldrich), and ethoxylated polyethylenimine (EPEI) with an average molecular weight of 70,000 (35-40 wt.% in water, Aldrich). First, a fixed weight of the polymer was diluted to the required concentration with deionized and distilled water. The polymer solutions were dialyzed by a ceramic membrane with molecular weight cut-off of 15000 g/mol in order to eliminate low-molecular-weight molecules. All of the chemicals used were analytical or special grades. Chromium (III) concentrations were measured with an inductively coupled plasma spectrometer (ICPS-5000, Shimadzu Seisakusho).

Ultrafiltration devices

The sorption of chromium (III) onto the water-soluble chelating polymer chains at a fixed pH was studied by a dead-end ultrafiltration at room temperature (ca. 25°C). The dead-end ultrafiltration was performed using Ultrafree-CL Centrifugal Filter Units with a molecular weight cutoff (MWCO) of 5000 g/mol (Millipore Corporation) and the permeate was taken by the centrifugal force given by a centrifugal HERAUS programmed to work at a speed of centrifugation of 6000 r.p.m. In this operating condition, the general differential mass balance for a solute can be written as:

$$d(V_R \cdot C_R) = C_P \cdot dV_R \quad (1)$$

where C_R and C_P are the concentrations in the retentate and permeate, respectively, and V_R is the retentate volume that contains the concentrated solution. Assuming that the rejection is almost constant throughout the process, the concentration in the retentate is obtained by integrating eq. (1) with the initial condition $C_R = C_F$ when $V_R = V_F$:

$$C_R = C_F \cdot \left(\frac{V_F}{V_F - V_P} \right)^R \quad (2)$$

From eq. (2), the rejection for chromium (III) adsorbed to the polymer can be easily determined by linear regression in double-logarithm plot of C_R versus $(V_F/(V_F - V_P))$. All rejections were determined by this method using 6 different V_R values.

Experimental Procedure

Aqueous solutions of the polymers (1 wt.%, 50 ml) and the chromium (III) solution (2 mM, 50 ml) prepared to the required pH and ionic strength (50 mM NaCl) were mixed and kept stirring at 40 or 60°C for 24 hours to reach the equilibrium. The change in the pH of the solution was adjusted to the fixed value by adding a small amount of aqueous solution of sodium hydroxide or chloridric acid at intervals of about 2 h until no further change in pH of the solution was observed. To avoid any precipitation problems, pH variation was limited to pH = 5. The initial solution to study the adsorption process was prepared by quadrupled at pH = 1. After 24 hours, the pHs of the other three solutions were adjusted to 2.5, 3.5 and 5, and were mixed and kept stirring at 40 or 60°C for 24 hours to reach the new equilibrium. Finally, the retention in the dead-end ultrafiltration of the four samples (pH = 1, 2.5, 3.5 and 5) was determined by weighing the retentate and measuring the chromium (III) concentration. The desorption process was investigated by preparing four solutions at pH = 5 and following the same procedure.

Results And Discussion

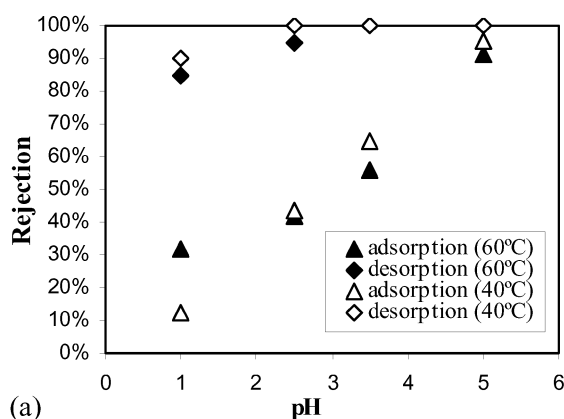
The target of the adsorption study is the determination of the polymer capacity to retain or adsorb chromium (III) ions according to the pH solution and sorption temperature. The chromium (III) rejection with PVA was null at all pHs, indicating that chromium (III) is not able to adsorb on the polymer surface, at least in the analyzed experimental conditions. Increasing the temperature of the adsorption process did not improve the retention of chromium (III). Therefore, the chromium ions do not interact with the free electrons of the atom of oxygen of the alcohol group. Some authors have modified the PVA to increase the affinity to join metal ions. Concretely they replace the hydrogen of the group alcohol with ionized groups with the pH, for example the phosphoric acid [10].

Figure 1(a) shows the evolution of the chromium (III) rejection with PACM as a function of the pH and temperature of the sorption process. Rejections are very different for adsorption and desorption processes, especially at low pH, rejection of the desorption process always being higher than the adsorption process. This hysteretic behavior reveals that the equilibrium between both sorption processes is not reached and desorption of chromium (III) is not completed, possibly due to the presence of an irreversible fraction of chromium (III) linked to the polymer.

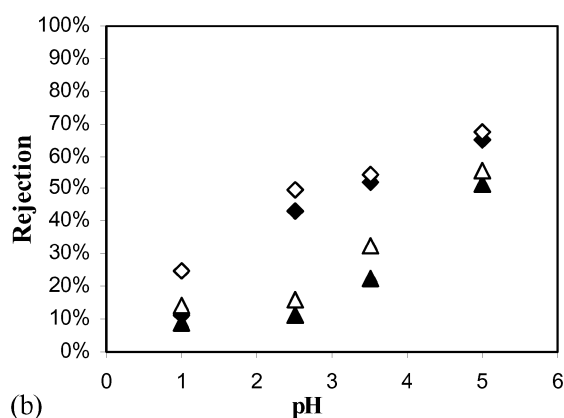
Rejections of adsorption process are significantly pH dependent. At pH = 1, the rejection of chromium reaches values of 10% at 40°C and 30% at 60°C. By increasing the pH, the rejection increases, reaching very high values (close to 100%) at pH = 5. Hence, the affinity between chromium ions and PACM increases with pH. On the other hand, the rejections of desorption process (obtained by decreasing the solution pH from pH = 5) decreases slightly with pH, such that the rejection at pH = 1 is of 85%.

The PACM is an anionic polyelectrolyte with carboxylic groups that dissociate at pH up to 4.5, it is then that the negative charges of the polymer interact with the positive charges of the metal ion. As the pH increases the carboxylic groups are more deprotonated and interactions with the chromium increase. Tomida et al. [11] determined that the carboxylic groups of the polyacrylic acid can link metal ions across the formation of electrostatic forces and of complexes by means of acid-base Lewis reactions. Both mechanisms take place in different magnitudes depending on the pH. At high pH, the contribution of the electrostatic

effect is stronger than at low pH, when the formation of complexes is of major importance. The carboxylic groups can act as monodentate and bidentate ligands, according to the number of oxygens that interact with the chromium (III). The negative charges provoke an electrostatic repulsion between polymer chains and, therefore, the metal ions join with one or two nearby groups. On the other hand, at low pH, the separation between chains decreases and the metal ions can be coordinated by two or four carboxylic groups of different nearby monomers. This behavior makes us suppose that the complexes formed between the carboxylic groups and the metal ion they are very stable and with a linkage of difficult desorption. Rivas et al., 1999, realized a conformational study of the complexes formed by PACM and the zinc (II) ion. They observed that zinc (II) joins two oxygens of the carboxylic group of the acrylic monomer and another ion joins the oxygens of a carboxylic group of the maleic monomer. This way, only a single carboxylic group of the unit of acid maleic in the copolymer takes part in the coordination.



(a)



(b)

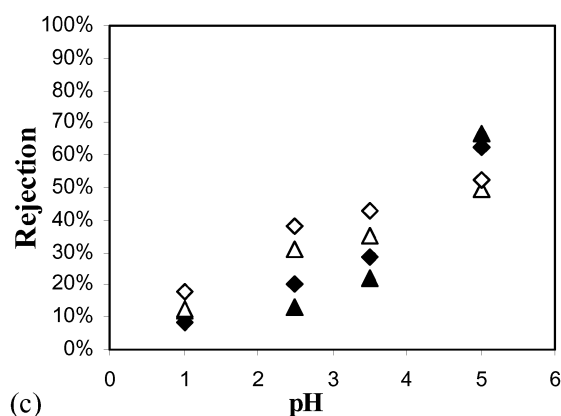


Figure 1 Effect of pH on the chromium (III) ions rejection with (a) PAAMA, (b) PEI and (c) PEIE. Triangles correspond to adsorption process at 60 °C (black) and 40 °C (white), and diamonds correspond to desorption process at 60 °C (black) and 40 °C (white).

Figure 1(b) shows the chromium (III) rejection adsorbed on the PEI at different pHs and temperatures. Again, it is observed that the rejections are very different for both processes. At low pH, 1 and 2.5, rejections do not reach 16% for a temperature of 40°C and of 8% at 60°C, while the PEI links significantly the chromium (III) at pH of 3.5 and 5, and the retention reaches 33 and 55% at 40°C, respectively. Temperature did not show a notable effect within the range from 40 to 60°C. At pH = 1, desorption process takes place and rejections reach values of 11% at 60°C and 25% at 40°C. PEI has a tendency to form stable complexes with the chromium (III), thus increasing the retention of the metal ion. The amino groups form stable complexes since the lone nitrogen pair binds the chromium (III) according to the acid and base Lewis theory. These complex bonds are significantly more selective than electrostatic interactions. Thus, Juang et al. [12] found that a metal ion preferentially binds to any amino groups of PEI but not to adjacent amino groups, as in the case of metal-PAA binding in the pH range lower than 4.0. At basic pHs, the affinity and stability of the interactions between metal ions and the PEI increase, and the rejection are higher than 85%. While, at acidic pHs, where the amino groups are protonated, the affinity for the metal ions is poor, the stability of the complex is low, and the rejection decreases significantly. Molari et al. [13] found that this polymer is able to complex metal ion at pH = 6 or higher, while desorption happens at pH < 3.

The chromium rejections with EPEI are shown in Figure 1(c). Hysteresis is also observed, although this is less significant, possibly due to the presence of alcohol groups which are not able to bind with chromium ions (as discussed above for PVA). This fact could mean that the equilibrium between both sorption processes is almost reached. Rejection shows pH dependence for adsorption and desorption processes, such that pH increased from 10% to 70% when pH was 1 and 5, respectively. Thus, the EPEI releases most of the chromium ions bound to the nitrogen atom.

The results discussed above allow us to deduce the best conditions to realize both sorption processes. The conditions to retain the greatest quantity of chromium (III) are obtained by

the polymer PACM, at pH = 5 and 40°C. Nevertheless, this acid polymer practically does not liberate chromium (III) joined previously to the carboxylic groups. Thus, the polymer that best realizes both sorption processes (adsorption and desorption) is the basic polymer EPEI, since the EPEI allows retention of the chromium (III) of approximately 70% at pH = 5 and 60°C, and permits liberation of most of the chromium (III) bound, resulting in a rejection lower than 10%, by means of reducing pH from 5 up to 1 at 60°C.

Conclusions

Sorption processes between water soluble polymers (PVA, PACM, PEI and EPEI) with chromium (III) ions were studied under the ultrafiltration technique and two operation modes. High chromium adsorption onto polymer surface was identified by high chromium rejection values. For dead-end mode, comparison of the four polymers showed that carboxylic groups formed stable and quasi irreversible bonds with chromium (III) ions. Amino groups adsorbed and desorbed these metals ions, while alcohol groups did not interact with chromium (III) ions. Therefore, EPEI was the polymer that best realized both sorption processes, since EPEI contains amino and alcohol groups in the molecular chains.

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References

1. Pansward T., O. Chavalparit, Y. Sucharittam and S. Charoenwisedsin, 1995, *Water Sci. Technol.* 31, 73.
2. Senthilnathan J., S. Mohan and K. Palanivelu, 2005, *Sep. Sci. Techno.* 40, 2125.
3. Kocaoba, S. and G. Akcin, 2004, *Adsorp. Sci. Technol.* 22, 401.
4. Covarrubias, C., R. Assiagada, J. Yanez, R. Garcia, M. Angelica, S.D. Barros, P. Arroya and E.F. Sousa-Aguilar, 2005, *J. Chem. Technol. Biotechnol.* 80, 899.
5. Ortega, L.M., R. Lebrun, I.M. Noël and R. Hauslera, 2005, *Sep. Purif. Technol.* 44, 45.
6. Sabaté, J., M. Pujolà and J. Llorens, 2002, *J. Membrane Sci.* 204, 139.
7. Koper, G, 2001, *J. Phys. Chem. B* 105, 6666.
8. Llorens, J., M. Pujolà and J. Sabaté, 2004, *J. Membrane Sci.* 239, 173.
9. Moreno-Villoslada, I. and B.L. Rivas, 2002, *J. Membrane Sci.* 208, 69.
10. Rivas, B.L., E. Pereira, P. Gallegos, D. Romper and K.E. Geckeler, 2004, *J. Appl. Polymer Sci.* 92, 2917.
11. Tomida, T., K. Hamaguchi, S. Tunashima, M. Katoh and S. Masuda, 2001, *Ind. Eng. Chem. Research* 40, 3557.
12. Juang R.S. and M.N. Chen, 1996, *Ind. Eng. Chem. Research* 35, 1935.
13. Molinari R., P. Augurio and T. Poerio, 2004, *Desalination* 162, 217.