

SEPARATION OF THE CHROMIUM(III) PRESENT IN A TANNING WASTEWATER BY MEANS OF PRECIPITATION, REVERSE OSMOSIS AND ADSORPTION

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Abstract— The separation of the chromium(III) dissolved in a tanning wastewater was studied by means of precipitation with calcium carbonate, reverse osmosis with polyamide membrane and adsorption on activated carbon. All tests were carried out at laboratory scale with a wastewater obtained from a unique typical tannage process. In a first stage, the original effluent was treated by sieving and ultrafiltration to perform a partial removal of fats and denaturalized proteins. The separation of chromium(III) by precipitation, reverse osmosis and adsorption was performed with the tanning wastewater so treated. The precipitation efficiency was determined by taking into account the chromium(III) content of the supernatant with the reaction time and with the alkali amount added. The polyamide membrane behavior used was established by the permeate flux and by the rejection of each species. The adsorption valuation involved the determination of the adsorbed amounts of chromium(III), sodium, chloride and sulfate. Under optimum conditions established for each process, the following results were obtained: a supernatant with less than 3.0 mg L⁻¹ of chromium(III) by precipitation, a permeate with less than 2.0 mg L⁻¹ of chromium(III) by reverse osmosis and an equilibrium solution with less than 6.0 mg L⁻¹ of chromium(III) by adsorption. To conclude, the main physicochemical characteristics of the three processes used to remove chromium(III) dissolved in the industrial effluent were analyzed.

Keywords— chromium(III); tanning wastewater; precipitation; reverse osmosis; adsorption.

I. INTRODUCTION

The separation of chromium(III) dissolved in a tanning wastewater and the subsequent discharge of the effluent treated are complementary activities in the leather industry that demand a very important attention of the productive sector (Heidemann, 1993; Alexander *et al.*, 1992; Rutland, 1991; Prasad, 1991; Bienkiewicz, 1983). The environmental impact produced by the chromium discharge from tanneries has been subject of extensive scientific and technical dispute, without the existence of a unique criterion at the present time for fixing regulatory limits. Thus, diverse countries of the world have established total chromium maximum values that vary

between 0.05-10 mg L⁻¹ for discharges into water bodies (direct discharge) and 1-50 mg L⁻¹ for discharge into sewage systems (indirect discharge) (Bosnic *et al.*, 2000).

Besides the place in which the discharge of liquid effluents containing chromium is made, it results useful to consider the metal oxidation state. Although chromium(III) oxidation to chromium(VI) occurs under environmental specific conditions (Milačić and Stupar, 1995; Eary and Rai, 1987; Bartlett and James, 1979), special attention is devoted to this transformation because chromium(VI) causes adverse effects for the human health (Committee on Biologic Effects of Atmospheric Pollutants, 1974). Even when the tanning wastewater has chromium only in trivalent form since the tannage process does not generate chromium(VI), some countries fixed regulatory limits for the two species. This criterion appears from the assumption that the oxidation would be produced during storage and subsequent treatment of the liquid effluent to reduce its total chromium content. In Buenos Aires Province, Argentine district with an important activity of tanneries, maximum values established are the same for both types of discharge but they differ with the oxidation state: 0.2 mg L⁻¹ for chromium(VI) and 2.0 mg L⁻¹ for total chromium.

The most important processes to remove the chromium(III) from the tanning wastewater are: precipitation, reverse osmosis and adsorption. The chromium(III) precipitation is frequently carried out in tanneries. Substances used habitually to promote the precipitation are: calcium hydroxide, sodium hydroxide, magnesium oxide or calcium magnesium carbonate. The liquid effluent is heated at 60-90 °C and after the addition of the alkaline substance (denominated in generic form "alkali") it is maintained with stirring at pH 7.0-9.0. With this methodology, a supernatant free of chromium(III) (with abundant calcium/sodium or magnesium chloride) and a precipitate of chromium(III) hydroxide (containing diverse impurities) are obtained.

The added alkali determines the formation of reaction products that affect the later chromium(III) reuse. When the precipitation is carried out with calcium hydroxide (or carbonate), the sulfate present in the tanning wastewater is combined with the alkaline cation to form calcium sulfate. The anion of the organic acid (formic,

acetic or lactic) used as chromium(III) complexing agent, also reacts with the alkali. Both reaction products together with fats and denaturalized proteins, substances released from the skin in significant amounts during the tannage process, are the main impurities that co-precipitate with chromium (Rutkouski *et al.*, 1998; Toprak, 1994). Calcium salts are harmful for the leather (Christner, 1993), while fats and denaturalized proteins difficult the tannage process (Heidemann, 1991). An adequate selection of operative variables (ratio alkali-effluent and reaction time) allows to control the calcium co-precipitation. The effluent ultrafiltration before alkali addition was the alternative used to decrease the presence of fats and denaturalized proteins in the chromium(III) precipitate (Fabiani *et al.*, 1996).

The alkaline substance is not recovered at the precipitation end, so it is necessary to have a continuous provision of such raw material. In order to select the alkaline substance, it is useful to take into account the cost as the easiness for its obtention, storage and manipulation. The calcium (magnesium or sodium) carbonate has these conditions although its reaction with the chromium(III) occurs less directly than with hydroxide or oxide. Of the three alkalis, the calcium carbonate requires larger attention in the selection of operative variables for the precipitation process.

Recently it was established that the chromium(III) separation by reverse osmosis has some significant operative advantages with relation to the precipitation with alkalis (Pérez Padilla and Tavani, 1999; Aloy and Vulliermet, 1998, Galán *et al.*, 1991). Reverse osmosis is a process in which a semipermeable membrane is used to retain species of low molecular weight and a pressure is applied as driving force to revert the solvent natural tendency of passing from a more diluted solution to another more concentrated one. The phase that passes through the membrane is named "permeate" and contains water with very small amount of dissolved salts. Meanwhile, the phase that does not pass through the membrane is called "concentrate" and has almost the totality of dissolved salts (Medina San Juan, 2000; Fariñas Iglesias, 1999; Cheryan, 1998). The semipermeable membrane is a thin film that is constructed by different materials and it is assembled in order to support a high transmembrane pressure. Important removals of chromium(III) dissolved in tanning wastewaters were obtained with a polyamide semipermeable membrane (Pérez Padilla and Tavani, 1999; Galán *et al.*, 1991).

The presence of proteins in the industrial effluent affects the permeate flux obtained by reverse osmosis. When the protein concentration in the feed is high, a layer of rejected molecules is formed over the membrane surface (gel layer). Such gel layer adds an additional resistance to the mass transport through the membrane, causing a lower permeate flux (Kerkhof, 1998; Fernández-Sempere *et al.*, 1996). The previous removal of proteins must be made to avoid this problem. A separation higher than 75% of protein materials contained in the tanning wastewater was obtained by sieving and

ultrafiltration (Pérez Padilla and Tavani, 1999).

The adsorption is a process that makes it possible the accumulation of a liquid or gas (adsorbate) on the surface of a solid (adsorbent). When the adsorption is used for the removal of substances dissolved in a liquid medium, acceptable results are obtained with solid adsorbents of high specific surface. The soluble substance is accumulated on the solid surface from the liquid that surrounds it. Thus, a change in the concentration of some system components is originated by effect of such mass transfer between both phases. During the treatment of the tanning wastewater, the chromium(III) is transported from the liquid medium to the solid surface through the respective interface. The reagent addition is not necessary to perform the adsorption.

Chromium(III) adsorption was made only at laboratory scale up to the present time. Acceptable results were achieved with several adsorbents: synthetic zeolite in its sodic form (Barros *et al.*, 2003), activated carbon (Leyva-Ramos *et al.*, 1995) and smectite (natural clay) (Volzone and Tavani, 1995). Tests were carried out by using solutions prepared with nonhydrated chromium(III) nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) for the synthetic zeolite and the activated carbon, while a tanning wastewater was used for the smectite. The higher adsorption was obtained with the synthetic zeolite in contact with a solution whose concentration was 260 mg L^{-1} of chromium(III). Notwithstanding the higher yield of the synthetic zeolite, it was considered as appropriate to analyze the behavior of the activated carbon because it is an adsorbent widely used in applications of the environment (LaGrega *et al.*, 1994).

The quantitative comparison of chromium(III) separation processes must be made with a unique tanning wastewater. The presence of other substances in solution can originate interactions among the diverse species present in each case and they can change the physicochemical behavior of the system. Consequently, the comparison performed by using different solutions has inherent errors and results useful only as a qualitative reference. According to the mentioned facts, the purpose of this work was to study the chromium(III) separation from the same tanning wastewater by precipitation with calcium carbonate, reverse osmosis with polyamide membrane and adsorption on activated carbon.

II. EXPERIMENTAL

The wastewater was obtained from a typical tannage process. It was established that by means of a combined operation of sieving (sieves N° 20, 200 and 325) followed by ultrafiltration (filter Pellicon Cassette with polysulfone membrane PTHK00005 of 100.000 NMWL), fats and denaturalized proteins are removed efficiently from the effluent. The tanning wastewater had initially 1.18 g L^{-1} of fats and 1.33 g L^{-1} of denaturalized proteins. After sieving, such values were reduced to 0.53 g L^{-1} of fats and 0.76 g L^{-1} of denaturalized proteins. Removal of mentioned substances was completed by ultrafiltration. Chemical analysis of tanning wastewater after using both operations for separa-

tion of fats and denaturalized proteins is shown in Table 1. Chromium was found in the liquid effluent only in trivalent state.

Table 1. Chemical analysis of the tanning wastewater with low content of fats and denaturalized proteins

Component	g L ⁻¹
Chloride	9.57
Sulfate	10.36
Sodium	11.10
Chromium(III)	1.09
Fats	0.20
Proteins	0.40
pH	3.42

The chromium(III) precipitation was carried out at ~80 °C in closed flasks with mechanical stirring and reflux by addition of commercial calcium carbonate (Anedra, item 6452) to 0.5 L of the tanning wastewater. The process evolution was analyzed in two different ways. Firstly, the precipitation was performed as a function of reaction time for the alkali stoichiometric amount. Secondly, the alkali amount was the process variable but now, reaction time was maintained constant. Results obtained are shown in Figures 1 and 2. The alkali was added in a period of time shorter than 1 min once the effluent was at 80°C. During the corresponding time for each test, such temperature and an energetic stirring of the liquid medium (180-230 rpm) were maintained.

The stoichiometric amount of calcium carbonate ($r=1.00$) necessary to obtain the complete precipitation of chromium(III) was calculated from the chemical composition of the effluent. Alkali amounts used for precipitation tests were: $r=0.75$ (1179 mg); 1.00 (1572 mg) and 1.25 (1965 mg). When the precipitation was finished, the suspension was cooled abruptly up to surpass slightly the room temperature. Then, the supernatant was separated from the solid phase by filtration with paper Schleicher & Schuell white ribbon (type 589/2) and red ribbon (type 589/5). Precipitates obtained were dried at room temperature for their evaluation by means of chemical analyses, X-ray diffraction (XRD), differential thermal analysis (DTA) and thermogravimetric analysis (TGA).

Tests of reverse osmosis were carried out with an equipment Osmo Econopure 19E-HR500 with polyamide membrane Osmo 192-HR (high rejection) of spiral wound, 1.49 m² surface and operable between pH= 3.0 and 11.0. The design characteristics of the equipment used allowed us to work with a maximum transmembrane pressure of 15 atm and with recycling flow of 300 L h⁻¹. A 24 L volume of the tanning wastewater with low content of fats and denaturalized proteins was treated using 15 atm at 25-32 °C. The membrane behavior was established from the permeate flux (J) and the rejection (R) of the system majority components. In order to value both aspects, 10 permeate samples of 1.8 L and 10 concentrate samples of 0.075 L were extracted (aliquots chosen arbitrarily). All solutions were analyzed to determine the concentrations of chromium(III),

sodium, chloride and sulfate.

The cleaning of the membranes of polysulfone (ultrafiltration) and polyamide (reverse osmosis) was made with: water free from salts as well as chlorine, H₃PO₄ solution at pH 2.0-2.5, NaOH solution at pH 11.0-11.5 and sodium lauryl sulfate solution 0.001 w/w.

The determination of the chromium(III) adsorption isotherm was performed with commercial activated carbon (Anedra, item 6494). Previous to its use, the adsorbent was washed with distilled water and dried in furnace at 105 °C for 24 h. In all tests, the adsorbent was dispersed in distilled water (5% w/w) and under this condition it was added slowly to nine solutions that had different chromium(III) content: 30 (A), 60 (B); 90 (C); 130 (D); 170 (E); 260 (F); 430 (G); 690 (H) and 1090 (I) mg L⁻¹.

Solutions A–H were prepared by dilution of the original effluent with distilled water without changing the proportion of its components. In order to carry out each dilution, the distilled water volume present in the activated carbon dispersion was taken into account. Meanwhile, the most concentrated solution (I) was obtained by distillation at reduced pressure ($p < 50$ mmHg and 30 °C) of the original effluent until collecting a liquid volume equal to the distilled water of the dispersion.

Adsorptions were made with a ratio activated carbon/aqueous solution of 2.5 g L⁻¹. These suspensions were stirred and maintained at constant temperature (30 °C) for 60 min. Once the contact time was finished, the adsorbent was separated from the corresponding equilibrium solution by filtration with paper Whatman 40. Then, the adsorbent was washed with distilled water to remove soluble salts. Solids so obtained were dried at room temperature for their chemical analysis. The physicochemical characterization of the original effluent and equilibrium solutions was performed by chemical analysis and pH measurement.

Chemical analyses were carried out by atomic absorption/emission (AA/EA), volumetry and gravimetry. Analyses by AA/EA were made with a Jarell Ash instrument. Chromium(III) was determined by atomic absorption when the concentration was lower than 10 mg L⁻¹ and by volumetry for concentrations higher than such value. Chromium(VI) presence was analyzed by colorimetric measurement in the original effluent as well as in solutions obtained from each process (Keith, 1996).

Analyses by XRD were performed with a Philips 3 kW X'Pert equipment, using Cu K α radiation and Ni filter. Thermal analyses (DTA and TGA) were carried out simultaneously in a Netzsch STA 409 equipment, with a heating rate of 10 °C min⁻¹. Samples were placed in platinum crucibles, α -Al₂O₃ (α -alumina) was used as reference substance and tests were made in nitrogen dynamic atmosphere with a flow rate of 0.013 L min⁻¹. The pH was measured by means of two pH-meters: Radiometer PHM201 with combined electrode pH3005 (precipitation-adsorption) and Orion 720-A with electrode Ross EL 81 (reverse osmosis).

The physicochemical characterization of the activated carbon involved the valuation of specific surface BET, pore volume and point of zero charge (PZC). Specific surface BET was measured with a Micromeritics Accusorb 2100E equipment by means of nitrogen adsorption. The pore volume was evaluated with the porosimeter Carlo Erba, model Porosimeter 2000, by mercury intrusion. PZC was determined by a method very similar to that one used to study a clay by Avena and De Pauli (1998). Activated carbon aliquots of 0.5 g were dispersed in 100 mL of a KCl solution, at different electrolyte concentrations: 0.01; 0.1 and 1.0 M. For each KCl concentration, 0.1 M HCl or 0.1 M KOH was added in an alternate way up to obtain a starting pH ca. 3 or 10. The pH so obtained gradually changes with time and the two curves that show these variations asymptotically approach to a limit value, which corresponds to the PZC. Values measured by this method were 8.5, 8.3 and 8.2 for 0.01, 0.1 and 1.0 M KCl solutions, respectively. The other physicochemical characteristics of the activated carbon were: $573 \text{ m}^2 \text{ g}^{-1}$ of specific surface BET- N_2 and $1.58 \text{ cm}^3 \text{ g}^{-1}$ of pore volume.

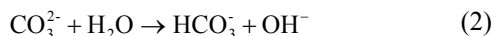
III. RESULTS AND DISCUSSION

A. Precipitation with calcium carbonate

Calcium carbonate is a salt scarcely soluble ($K_{sp} = 4.8 \times 10^{-9}$), which in aqueous medium is dissociated in carbonate and calcium ions. The reaction between the carbonate anion and an acid substance occurs with release of carbon dioxide.



When calcium carbonate is added to the tanning wastewater its reaction with protons (hydronium) of the medium and the belonging pH increase are produced. The carbonate anion excess that remains in the effluent is combined with water and a slightly basic reaction of the liquid phase occurs (Eq. (2)). Subsequently, hydroxyls formed during hydrolysis are bound with chromium(III) and they produce the cation precipitation. Chromium(III) hydroxide has an extremely low solubility ($K_{sp} = 6.3 \times 10^{-31}$), in consequence, chromium(III) initially dissolved precipitates as hydroxyls are formed. This sequence of reactions is maintained while there is chromium(III) to be removed from tanning wastewater. The release of carbon dioxide and the fast combination of hydroxyls formed determine a shift to the right (Le Châtelier principle) of the two reactions in which the carbonate anion participates. In this way, new hydroxyls are surely formed.



The separation (removal) R of a tanning wastewater component is the relative change in its concentration from the effluent (before treatment by alkaline precipitation) to the supernatant. The R value for each species i was determined with the expression

$$Ri(\%) = \left(1 - \frac{C_{si}}{C_{wi}}\right) 100 \quad (3)$$

where: C_{si} (g L^{-1}) is the concentration of the species i in

the supernatant and C_{wi} (g L^{-1}) is the concentration of the same species in the tanning wastewater. Table 2 shows separations of chromium(III), sulfate, sodium and chloride for a precipitation performed with the stoichiometric amount of commercial calcium carbonate at 80°C and 12 h. The chromium(III) was the unique system component that changed its concentration in a substantial way during the precipitation. Whereas, the other three system components had small separations and their concentrations in the supernatant were similar to the ones of the tanning wastewater.

Table 2. Separations of chromium(III), sulfate, sodium and chloride for a precipitation carried out with the stoichiometric amount of commercial calcium carbonate at 80°C and 12 h.

Component	R%
Chromium(III)	99.73
Sulfate	12.74
Sodium	6.22
Chloride	3.24

Figures 1 and 2 show the variation of the chromium(III) content of the supernatant with the reaction time for the alkali stoichiometric amount $r = 1.00$ and with the alkali amount added for a constant reaction time of 2 h. A significant decrease of chromium(III) content of the supernatant was achieved with a prolonged reaction time, for example 2.9 mg L^{-1} at 12 h (Fig. 1). In order to evaluate the effect of the alkali amount added on the chromium(III) removal, tests were made with different ratio (r) alkali–effluent using with each value a same reaction time.

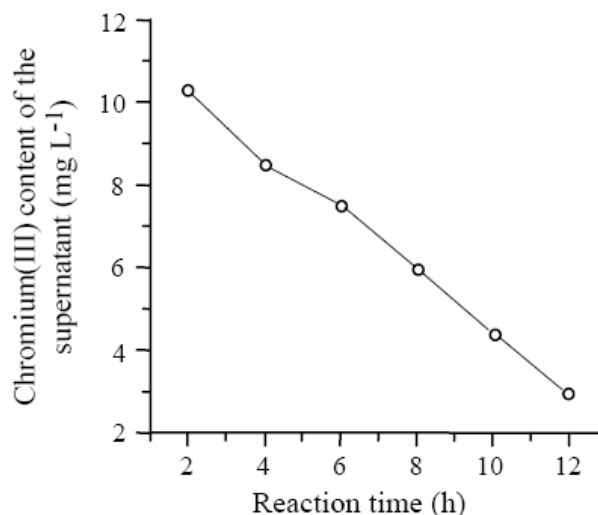


Figure 1. Chromium(III) content of the supernatant in relation to the reaction time for $r = 1.00$

Figure 2 shows that chromium(III) content of the supernatant had a minimum decrease ($\sim 13\%$) when r increased from 1.00 to 1.25 for a reaction time of 2 h. The analysis of precipitates obtained under these operative conditions revealed a higher presence of calcium when $r = 1.25$ was used (Table 3). A similar behavior was established for a reaction time of 4 h, in which the chromium(III) content of the supernatant decreased from 8.5 ($r = 1.00$) to 7.6 mg L^{-1} ($r = 1.25$) and the pre-

precipitated calcium amount increased from 12.55 ($r=1.00$) to 14.09% w/w ($r=1.25$). These results show that when increasing the ratio alkali–effluent from 1.00 to 1.25 a reaction time slightly lower is necessary to achieve equal chromium(III) removal, with the inconvenience that the calcium precipitation increases.

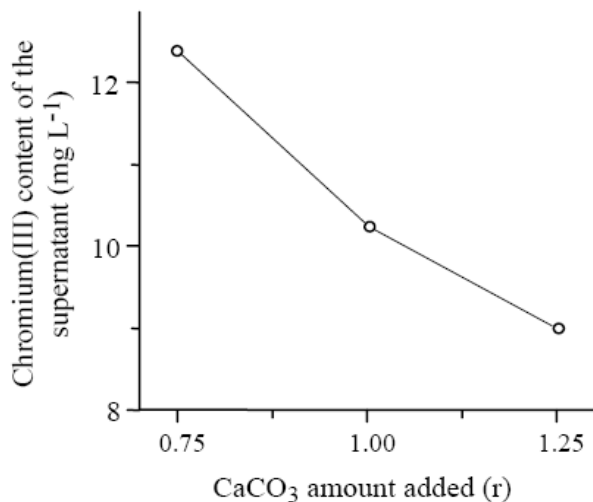


Figure 2. Chromium(III) content of the supernatant in relation to the alkali amount added for $t=2$ h at $80\text{ }^{\circ}\text{C}$.

The analysis by XRD of precipitates allowed us to identify the calcium sulfate hydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) as unique crystalline substance. The weight loss obtained at $250\text{ }^{\circ}\text{C}$ was $\sim 25\%$ w/w (DTA-TGA). Such weight loss would correspond to hydration (combined) water released from calcium sulfate hydrate and chromium(III) hydroxide.

Precipitate separation performed by filtration with paper Schleicher & Schuell white ribbon was incomplete in some supernatants, for this reason the chromium(III) content had an appreciable variation for tests carried out under the same operative conditions. In such cases, a substantial improvement was achieved in the precipitate separation when a second filtration was made using paper red ribbon. With this consecutive filtration, a variation of results lower than 1 mg L^{-1} of chromium(III) was obtained for duplicated tests.

B. Reverse osmosis with polyamide membrane

The permeate flux J ($\text{L m}^{-2}\text{h}^{-1}$) is the rate of solvent (water) transported per unit of membrane surface and its value was calculated with the equation

$$J = \frac{V}{tS} \quad (4)$$

where: V (L) is the permeate volume that passes through the membrane during a time t (h) and S is the membrane effective surface (1.49 m^2). In order to calculate each J value, the required time to obtain $V=1.8\text{ L}$ of permeate was measured. The calculation of J flux with this methodology does not consider the permeate volume obtained in previous measurements and its possible effect on the membrane fouling. Taking into account this situation, each J_n value was expressed as a function of the permeate total volume obtained up to that meas-

urement ($V_{\text{permeate}} = V_1 + V_2 + \dots + V_n$). Ten (10) determinations of permeate flux were made during treatment of 24 L of tanning wastewater. The permeate total volume obtained after the last measurement was 18 L ($10 \times 1.8\text{ L}$) and represents 75% of the effluent initial volume. Figure 3 shows the J flux variation as a function of the permeate volume.

Table 3. Chemical analysis of precipitates obtained with $r=0.75$, 1.00 and 1.25 of calcium carbonate for a constant reaction time of 2 h at $80\text{ }^{\circ}\text{C}$.

Component	$r=0.75$ ^(a)	$r=1.00$ ^(b)	$r=1.25$ ^(c)
	% w/w		
Chromium(III)	14.11	12.97	12.25
Sulfate	13.90	14.11	15.53
Sodium	6.78	7.39	7.80
Chloride	3.11	3.35	3.48
Calcium	10.34	12.39	13.82

Weight of each precipitate: (a) 3818 mg; (b) 4162 mg; (c) 4411 mg

The permeate flux was low and decreased during the test. The highest decrease was observed when the permeate volume raised from 7.2 to 12.6 L ($J=2.26-1.46\text{ L m}^{-2}\text{h}^{-1}$), while the other flux values showed lesser changes. With the purpose to verify that the J flux decrease was produced by the membrane fouling, the concentrate was replaced by distilled water without performing other system modifications. Under these conditions, the distilled water flux was near 0.4 times the value measured at the treatment beginning by reverse osmosis. The permeate flux recovery was achieved after performing the membrane chemical cleaning.

Membranes are not completely semipermeable, and this fact produces the occurrence of alternative mechanisms that make it possible the solute passage to permeate. Consequently, the permeate can have a content of ions larger than the expected one. The rejection (separation) R of the membrane for each species i is referred to the same concept mentioned in alkaline precipitation, this is the relative change in the solute concentration from the feed to the permeate. For its calculation, equation (3) is used, indicating with C_{pi} (g L^{-1}) the concentration of species i in the permeate and C_{fi} (g L^{-1}) the concentration of the same species in the feed (tanning wastewater or concentrate) ($R_i = (1 - C_{pi}/C_{fi})100$).

The rejection of a chemical species during treatment by reverse osmosis is a function of the chemical affinity of the solution components and the membrane, of the solutes-solvent interaction and of the obtained permeate volume. According to these facts, it was possible to determine the rejection of chromium(III), sodium, chloride and sulfate as a function of the permeate volume. Table 4 shows the rejections for the aliquots 1 (treatment beginning: 1.8 L permeate), 4 (40% treatment: 7.2 L permeate), 7 (70% treatment: 12.6 L permeate) and 10 (treatment end: 18.0 L permeate).

The chromium(III) was the system component that presented the highest rejection and remained almost unchanged with the permeate volume. The sulfate rejection was very important and its variation with the per-

meate volume acquired a certain relevance at the treatment end. Monovalent ions had a lower rejection between the four system components that were analyzed and their variation with the permeate volume was more important for the chloride than for sodium.

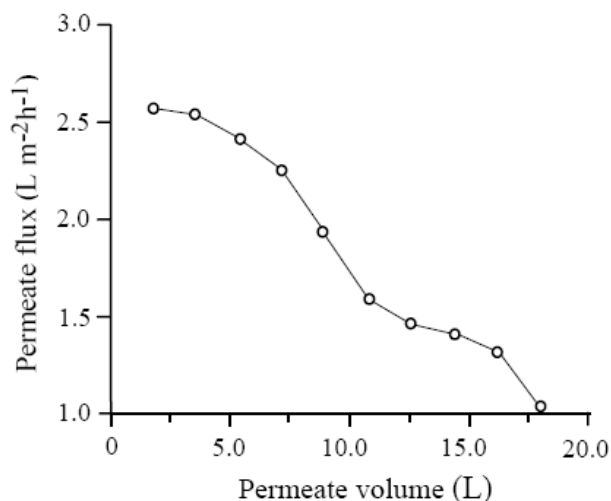


Figure 3. Evolution of permeate flux as a function of the permeate volume.

Table 4. Rejections of chromium(III), sulfate, sodium and chloride for aliquots of the reverse osmosis treatment.

Aliquot	Rejection %			
	Chromium(III)	Sulfate	Sodium	Chloride
1	99.97	98.01	85.55	68.90
4	99.94	97.06	71.87	50.67
7	99.88	95.27	68.00	35.08
10	99.81	92.86	67.02	21.41

C. Adsorption on activated carbon

An adsorption isotherm describes the ratio between the adsorbed amount of a substance and its equilibrium concentration at a constant temperature. Figure 4 shows the chromium(III) adsorption isotherm on commercial activated carbon at 30 °C. Such isotherm describes an irregular behavior with the cation concentration in the equilibrium solution. In the first part of the curve (diluted equilibrium solutions), a quick rise of the adsorbed chromium(III) on activated carbon is observed while its equilibrium concentration increases. For concentrated equilibrium solutions (second part of the curve), the increase tendency is reverted resulting in a decrease of the adsorbed chromium(III). In order to evaluate this behavior, the pH of the successive aliquots A–I before and after each adsorption was measured (Table 5).

The pH increase of the equilibrium solutions with respect to the one corresponding initial solutions constitutes an experimental evidence that besides the chromium(III) adsorption, a concentration decrease of protons (hydronium) in the liquid medium occurred. Such decrease would be produced by the adsorption of protons on the activated carbon. Although equilibrium solutions A–E had a high pH, the chromium(III) precipitation was not observed after finishing the respective adsorption tests.

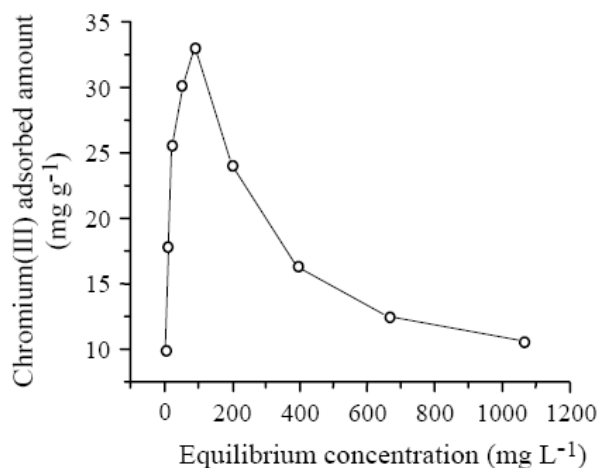


Figure 4. Chromium(III) adsorption isotherm at 30 °C on activated carbon.

Table 5. pH of solutions before (initial) and after (equilibrium) of each adsorption test at 30 °C

Solution	pH solution	
	Initial	Equilibrium
A	3.96	7.67
B	3.72	7.14
C	3.69	6.89
D	3.67	6.27
E	3.65	5.58
F	3.63	5.21
G	3.55	4.83
H	3.50	4.39
I	3.42	4.00

The formic acid (HCOOH) was the complexing agent added in the tannage process from which the wastewater used was collected. This monocarboxylic acid has a very important dissociation degree to pH > 6.0 ($K_d = 1.77 \cdot 10^{-4}$). The HCOO⁻ anion coming from the dissociation is exchanged with water ligand present initially in the chromium(III) complex ions. The new species so formed are sufficiently stable and their average life is higher than 6 h when the sulfate anion is as bridge between two chromium(III). The chromium(III) dimer with a sulfate bridge and two hydroxo bridges is the majority species present in the tanning liquor (Heidemann, 1993; Bienkiewicz, 1983). Due to the stabilizer effect of the formate, a quick cation precipitation was not produced as it would be expected at high pH values. After maintaining at rest the totality of equilibrium solutions for 7 days, the formation of chromium(III) precipitates occurred in the five samples of higher pH (A–E).

The insertion of hydroxyl groups into the chromium(III) coordination sphere is favored with the pH increase of the liquid medium. This insertion mechanism comprehends the decomposition of a water molecule in a hydroxyl and a proton. The hydroxyl remains in the complex ion, while the proton is released to the liquid medium ($-H_2O \rightarrow -OH + H^+$). In general, the referred hydroxyl ligand formation is sufficiently rapid and such group serve as hydroxo bridge between two

chromium(III) cations. The prosecution of this decomposition reaction leads to the chromium(III) precipitation (Heidemann, 1993; Bienkiewicz, 1983).

Adsorption of sodium, sulfate and chloride were determined in all activated carbon samples. Table 6 shows the amounts of each ionic species that were retained in samples A (lower chromium(III) concentration in the equilibrium solution), E (maximum chromium(III) adsorption) and I (higher chromium(III) concentration in the equilibrium solution). The chromium(III) adsorption was included in three aliquots as reference value.

The sulfate adsorption was significant and showed a variation with its equilibrium concentration similar to the one of chromium(III). In this case, it must be taken into account that the sulfate anion is a species present in the liquid medium that can enter also into the chromium(III) complex ion (Heidemann, 1993; Bienkiewicz, 1983). Then, it was supposed that the sulfate anion is part of complex ions with positive net charge and that such cationic species are absorbed on the activated carbon.

The sodium adsorbed amount was negligible in all activated carbon samples. The different adsorption of chromium(III) and sodium was explained from the density of superficial electric charge of each complex ion present in the liquid medium (cation electric charge/cation external surface, coulombs nm^{-2}). By means of specific studies, it was established that at low pH the chromium(III) complex ion was adsorbed partially dehydrated (with lesser water molecules than in the soluble complex ion) (Koppelman *et al.*, 1980). On the basis of such interaction mechanism, the fixation of chromium(III) would be carried out through a partial substitution of the water ligand by the surface electric charge of the activated carbon.

Table 6. Adsorbed amounts of chromium(III), sulfate, sodium and chloride on activated carbon, expressed in mg g^{-1} of adsorbent

Activated carbon	Chromium(III)	Sulfate	Sodium	Chloride
	mg g^{-1}			
A	9.8	2.3	0.5	0.4
E	33.1	10.1	0.5	0.6
I	10.6	9.1	0.7	0.9

In the dimer with two hydroxo bridges and a sulfate bridge (most abundant species of the tanning wastewater), each chromium(III) has a positive electric charge +1 ($1.60 \cdot 10^{-19}$ coulombs) (Heidemann, 1993) and its separation from the adsorbent surface could be considered as equivalent to the dehydrated cation radius 0.053 nm. Meanwhile, the sodium cation has an electric charge +1 ($1.60 \cdot 10^{-19}$ coulombs) and the dehydrated cation radius is 0.098 nm. The comparison of these values allows us to state that the density of surface electric charge of chromium(III) ($\sim 4.53 \cdot 10^{-18}$ coulombs nm^{-2}) triplicates in excess the one of sodium ($\sim 1.32 \cdot 10^{-18}$ coulombs nm^{-2}). This density difference could justify the highest chromium(III) adsorption on activated carbon.

The chloride adsorbed amount was very similar to the one of sodium. Taking into account this similarity, it

is possible to assume that the chloride retention would be made through an association with such cation. The presence of sodium soluble salts on the activated carbon was discarded since the adsorbent was washed with distilled water before performing each chemical analysis.

PZC supplies an alternative explanation about the irregular form of chromium(III) adsorption isotherm on activated carbon. PZC value changed with the support electrolyte concentration used for the measurement. When increasing the support electrolyte concentration, the PZC shifted to lower pH value. In clay minerals, this behavior is attributed to the combined effect of variable charges and structural negative charges (Avena and De Pauli, 1998). The activated carbon has variable electric charges resultant of the association–dissociation of amphoteric surface groups (Babić *et al.*, 1999) and oxygen–free $C\pi$ sites that can adsorb protons from solution (Leon y Leon *et al.*, 1992). With a practical criterion, it can be stated that the type of electric charge present in the activated carbon could have certain resemblance with that of clay minerals.

The adsorption of protons on $C\pi$ sites changes the pH in an ostensible way in the most diluted equilibrium solutions (Table 5). It is well known that the net charge on the carbon surface is positive at a solution pH lower than that corresponding to the PZC and is negative at a solution pH higher than PZC (Ayranci and Bayram, 2005). The adsorption of protons causes that more diluted equilibrium solutions (A–E) take a pH near to PZC of activated carbon, favoring the chromium(III) adsorption just as it was observed in the first part of the curve. The contrary case corresponds to more concentrated equilibrium solutions (F–I), whose pH are found far away from the PZC and under this condition the chromium(III) adsorption decreases. The PZC selection to make each comparison was made taking as reference the value determined with the KCl electrolyte concentration nearer to the respective equilibrium solution.

The maximum adsorption of chromium(III) per gram of activated carbon was 33.1 mg (solution E) and according to this value 32.9 g of adsorbent are required to treat each liter of the tanning wastewater. On the other hand, 5.5 mg L^{-1} was the lowest chromium concentration in an equilibrium solution (solution A). A new adsorption test ($30 \text{ }^\circ\text{C}$, 60 min) was carried out with a ratio activated carbon/aqueous solution of 35 g L^{-1} , determining that the chromium(III) final content in the equilibrium solution was 5.7 mg L^{-1} . Separations calculated applying Eq. (3) are indicated in Table 7.

Table 7. Separations of chromium(III), sulfate, sodium and chloride by adsorption on activated carbon with a ratio adsorbent/aqueous solution of 35 g L^{-1} .

Component	R %
Chromium(III)	99.48
Sulfate	7.82
Sodium	1.62
Chloride	1.58

IV. CONCLUSIONS

The content of fats and denaturalized proteins of the tanning wastewater was reduced considerably by sieving and ultrafiltration. The diverse aspects affecting the separation of the chromium(III) dissolved in the effluent partially free from fats and denaturalized proteins were analyzed by means of precipitation with calcium carbonate, reverse osmosis with polyamide membrane and adsorption on activated carbon.

The chromium(III) precipitation was higher than 99.73% and the cation final content in the supernatant was lower than 3.0 mg L⁻¹. In such supernatant the concentrations of sodium, chloride and sulfate were maintained almost without changes with relation to the tanning wastewater.

The separation (rejection) of chromium(III) by reverse osmosis with polyamide membrane varied between 99.97 (treatment beginning) and 99.81% (treatment end), thus obtaining a cation average content in the permeate lower than 2.0 mg L⁻¹. A separation quite appreciable of the three ionic species present in the permeate was also produced with a yield lower than the one of chromium(III). The rejection was: sulfate > sodium > chloride. The principal inconvenience of reverse osmosis was the quick decrease of the permeate flux; this fact would be produced by the membrane fouling.

The lowest chromium(III) content in an equilibrium solution was 5.5 mg L⁻¹ (R= 99.48%), while the other ionic species remained without important changes. The maximum adsorption of chromium(III) was 33.1 mg per gram of activated carbon, so more than 30 g of adsorbent were necessary to perform the treatment of each liter of the tanning wastewater used.

ACKNOWLEDGEMENTS

Authors thank Ing. D. Squarisi (Universidad Tecnológica Nacional) by the supply of the tanning wastewater. This work was financially supported by "Comisión de Investigaciones Científicas de la Provincia de Buenos Aires" and "Facultad de Química Bioquímica y Farmacia de la Universidad Nacional de San Luis".

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Received: October 25, 2006.

Accepted: May 22, 2007.

Recommended by Subject Editor Ricardo Gómez.