Comparative analysis on efficiency of reverse osmosis and alkaline precipitation to remove hazardous substances in a tanning wastewater

B H Hintermeyer1,2 R A Curvale2,3 A Pérez Padilla3 and E L Tavani2*

1Facultad de Ingeniería y Ciencias Económico-Sociales de la Universidad Nacional de San Luis, 25 de Mayo 384, (D5730EKQ) Villa Mercedes, San Luis, Argentina
2Centro de Tecnología de Recursos Minerales y Cerámica (CETMIC), Comisión de Investigaciones Científicas de la Provincia de Buenos Aires, CONICET, Camino Centenario y 506, C.C. 49, (B1897ZCA) M.B. Gonnet, Argentina
3Instituto de Investigaciones en Tecnología Química (INTEQUI), Facultad de Química, Bioquímica y Farmacia de la Universidad Nacional de San Luis, CONICET, Chacabuco 915, (D5700BWS) San Luis, Argentina

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Reverse osmosis (RO) with polyamide membrane of spiral wound and precipitation with commercial sodium carbonate were studied to remove hazardous substances [chromium(III), sulfate, chloride and sodium] contained in a tanning wastewater. RO removed chromium(III) very efficiently (99.83%) and with lower but appreciable yields the other three constituents of liquid effluent. Major inconvenience of RO was fast decrease of permeate flux due to insufficient transmembrane pressure used. In turn, 99.71% of chromium(III) was separated with precipitation. Contents of sulfate, chloride and sodium remained without noticeable changes in filtrate liquid. Main physicochemical features of concentrate obtained at the end of RO and of precipitates produced for different reaction times were established.

Keywords: Alkaline precipitation, Chromium(III), Reverse osmosis (RO), Tanning wastewater components

Introduction

For 1 kg of processed hide, 3.0-5.0 l of tanning wastewater is produced. This liquid effluent has only chromium(III) [Cr(III)] since tannage process does not generate Cr (VI). Most abundant species in tanning liquor prepared with commercial salt [basic Cr(III) sulfate] is [(H2O)2Cr(OH)(SO4)(OH)Cr(H2O)3]2+1-3, a Cr(III) dimer with two hydroxo bridges and a sulfate bridge. Major components of tanning wastewater are: Cr(III), 0.6-2.5; sulfate, 10-20; sodium, 12-21; chloride, 9-26; fats, 1-3; and proteinaceous materials (PM), 1-4 g l-1. Liquid effluent composition varies with type of leather to be produced and with procedure employed for its manufacture4-10. Cr(III) is necessary, in small amounts, for certain biological activities. Cr(VI) (in minimum conc.) causes adverse effects on human health11-14. Separation of tanning agent is commonly carried out in industry by alkaline precipitation1,15-17. Reverse osmosis (RO)18,19 and biosorption20 are acceptable alternatives. Membrane process appears as the most promising by recycling Cr(III) contained in wastewater. Alkaline precipitation makes it possible to treat a considerable effluent volume and to remove large amounts of tanning agent. Substances mainly used to promote precipitation are calcium hydroxide, sodium hydroxide, magnesium oxide, sodium carbonate or calcium magnesium carbonate (dolomite). RO process with polyamide membrane of spiral wound has shown effectiveness in retaining Cr(III) plus sulfate, chloride and sodium. These ions also have harmful consequences on human health.

In present study, RO with polyamide membrane of spiral wound and alkaline precipitation with sodium carbonate were used to clean a tanning wastewater, comparing both technologies in terms of rejection for Cr(III), sulfate, chloride and sodium. Likewise, products obtained in each case were analyzed in order to reuse the tanning agent.

Experimental Section

Materials

Wastewater was collected from a single tannage industrial process performed with basic Cr(III) sulfate
(bascity 32-34%). Treatment started with removal of fats and PM via sieving followed by ultrafiltration. Sieves utilized were 20 (841 µm), 200 (75 µm) and 325 mesh (45 µm). Ultrafiltration tests were carried out with a Pellicon Cassette filter and polysulfone membrane PTHK00005 of 100,000 NMWL, under a transmembrane pressure of 1.5 atm. Membrane (active area, 0.46 m²) can be operated from pH 2.0 to 12.0.

Reverse Osmosis (RO)
Tests of RO were made using an Osmo Econopure 19E-HR500 equipment with polyamide membrane of spiral wound Osmo 192-HR, 1.5 m² active area and operable between pH 2.0 and 12.0. Tanning wastewater (24 l) without suspended solids was treated applying 15 atm (max. transmembrane pressure admitted by equipment) at 25-32°C. To evaluate membrane behavior, 10 samples (1.8 l) from permeate and 10 samples (0.075 l) from concentrate were extracted (aliquots chosen arbitrarily). Concentrations of Cr(III), sulfate, chloride and sodium were analyzed in these 20 aliquots. Cleaning of ultrafiltration and RO membranes was performed with H₃PO₄ solution at pH 2.0-2.5, NaOH solution at pH 11.0-11.5 and sodium lauryl sulfate solution 0.1% w/w. All these solutions were prepared with distilled water free of salts and chlorine. Cleaning was finished when initial permeate flux was recovered using distilled water as feed.

Alkaline Precipitation
Cr(III) precipitation was carried out in closed flasks with mechanical stirring (150-200 rpm) and reflux by adding commercial sodium carbonate to tanning wastewater (0.5 l) without suspended solids. In each test, a stoichiometric amount of sodium salt (1666 mg) was used to produce complete precipitation of Cr(III). After heating effluent at 80°C and without interrupting reactor stirring, carbonate was added for < 1 min. Once reaction ended, supernatant was separated from precipitate by filtration with filter paper Schleicher & Schuell (S&S) white ribbon and red ribbon. Precipitates were dried at room temperature.

Methods
Tests were duplicated for reproducibility. Cr(III) was measured by atomic absorption (AA) with air-acetylene flame at λ = 589 nm. AA/AE tests were carried out using a Jarell Ash instrument. Chloride was measured by Mohr volumetric method with silver nitrate. Sulfate valuation was made by gravimetry and barium chloride was added for precipitation. Fats were analyzed by extraction with dichloromethane and subsequent solvent evaporation at 40-60°C until a constant weight was achieved. Total nitrogen was obtained by Kjeldahl method (TNK), while amount of proteins was established multiplying TNK by the factor 5.51.

X-ray diffraction (XRD) was performed with a Philips 3 kW X’Pert equipment, Cu Kα radiation and Ni filter. Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) were carried out simultaneously in a Netzsch STA 409 equipment, with heating rate of 10°C min⁻¹. Sample was placed in a platinum crucible. Reference substance employed was α-Al₂O₃ (α-alumina) and tests were made under nitrogen dynamic atmosphere (flow rate, 0.0131 min⁻¹). Cr species in solution were identified by absorption within visible range (340-800 nm) by means of a Hewlett Packard 8453 spectrophotometer. Osmotic pressure measurement for permeates and concentrates was performed with a 5500 Wescor Vapor Pressure Osmometer.

Results and Discussion
Pretreatment of Tanning Wastewater by Sieving and Ultrafiltration
Presence of fats and PM in tanning wastewater evidences degradation produced in collagen molecule during transformation process of animal hide to leather. Fats released contaminate Cr(III) obtained by alkaline precipitation. PM involves very small skin pieces and denaturalized proteins. Proteins contained in the feed of RO are an adverse factor because they (in min. conc.) form layer of rejected molecules on membrane surface (gel layer), which adds an additional resistance to water transport through membrane, decreasing yield of RO. Denaturalized proteins (size, < 150 nm) may be separated by ultrafiltration. Values from original effluent and after sieving were: 1.18, 0.53 g l⁻¹; and PM, 1.33, 0.76 g l⁻¹, respectively. Removal of substances was completed by ultrafiltration. Chemical analysis of liquid effluent so obtained (pH 3.4) is as follows: Cr(III), 1.09; sulfate, 10.36; sodium, 11.10; chloride, 9.57; fats, 0.20; and PM, 0.40 g l⁻¹.

Reverse Osmosis (RO)
Performance of polyamide membrane of spiral wound used was analyzed in terms of permeate flux (J), effective
Permeate flux expresses solvent rate (water) transported per unit of active membrane area and its value (1 h⁻¹m⁻²) was established according to \( J = \frac{\Delta V_p}{\Delta t S} \), where \( \Delta V_p \) (l) is permeate volume that passes through membrane during a time \( \Delta t \) (h) and \( S \) is active membrane area (1.5 m²). For calculation of each \( J \), time required to obtain \( \Delta V_p = 1.8 \) l was measured. This operation was repeated 10 times. Total permeate volume (Vpt) after last measurement was 18.0 l and it represents a volume reduction% of 75% (Vpt/Initial \( \times 100 = 75\% \)). At 15 atm for three aliquots [initial (1), medium (5) and final (10)], \( J \) and volume reduction% were found as follows, respectively: initial, 2.57, 7.5; medium, 1.93, 37.5; and final, 1.03 l h⁻¹m⁻², 75%. Maximum permeability was 2.57 l h⁻¹m⁻² and it decreased during the last stages of RO process. Flux \( J \) evolution was examined as \( J = K(\Delta P - \Delta \pi) \), where \( \Delta \pi \) is transmembrane pressure, \( \Delta \pi \) is osmotic pressure gradient and \( K \) is water permeability coefficient (1 h⁻¹atm⁻¹m⁻²). Maximum \( \Delta P \) allowed in present study (15 atm) was higher than \( \Delta \pi \) only at the beginning of treatment, for example \( \Delta \pi \) stage 1 = 12.9 atm. \( \Delta \pi \) increases during the course of treatment, reaching an unfavorable state from stage 5 (\( \Delta \pi \) = 14.9 atm). To confirm that permeate volume produced does not affect the process yield, a new test with 100.0 l of liquid effluent was performed. Flux \( J \) was 2.25 l h⁻¹m⁻² after producing 20.0 l of permeate (vol reduction% = 20.0%; \( \Delta \pi = 14.2 \) atm). If such value is compared with 1.03 l h⁻¹m⁻² obtained for 18.0 l of permeate when feed was 24.0 l (vol reduction% = 75.0%; \( \Delta \pi = 15.8 \) atm), it is possible to assure that the behavior observed is due to low \( \Delta P \) applied in this study.

Rejection (separation) \( R \) (%) of a tanning wastewater component is relative change in its concentration from feed to permeate and for each species \( i \) is \( R_i(\%) = \left(1 - \frac{C_{f i}}{C_{p i}}\right)100 \), where \( C_i \) (g l⁻¹) is concentration of species \( i \) in permeate and \( C_{fi} \) (g l⁻¹) is concentration of same species in feed (tanning wastewater or concentrate). Cr(III) had highest rejection (Fig. 1) and its change was minimal in 18.0 l of permeate (av content, 1.9 mg l⁻¹; av rejection, 99.83%). Sulfate removal was very important and its variation with the permeate volume acquired certain relevance at the end of treatment (av content, 0.75 g l⁻¹; av rejection, 92.76%). Monovalent ions showed lowest removals among four effluent components analyzed and its variation with the volume reduction% was higher for chloride (av content, 6.10 g l⁻¹; av rejection, 36.26%) than for sodium (av content, 4.03 g l⁻¹; av. rejection: 63.69%).

Polyamide semipermeable membrane does not impede totally Cr(III) transport by diffusion nor by convection. When system is maintained at rest, the only mechanism that happens is diffusion. In order to emphasize this situation, experiment was interrupted for 17 h and then renewed with the methodology used previously. Diffusion valuation was performed on three permeate aliquots: i) that obtained before temporary cessation; ii) that produced after beginning the treatment again; and iii) with the equipment operating in a normal way. Cr(III) content and test time to achieve each permeate aliquot were, respectively: before break, 0.30 mg l⁻¹, 30 min; with system at rest, 1.19, mg l⁻¹, 17 h 40 min; and after break, 0.69 mg l⁻¹, 40 min.

Analysis included another test, in which flux was reduced to half. With such procedure, more time is required to produce the same permeate volume. A \( \Delta P \) of 13 atm instead of 15 atm was used, maintaining other operative variables constant. Flux up to collecting 1.8 l permeate was 1.30 l h⁻¹m⁻² and Cr(III) content 0.67 mg l⁻¹; this concentration was higher than the one obtained with 15 atm (0.30 mg l⁻¹). Summarizing, flux \( J \) not only determines membrane productivity but it also affects permeate quality.

**Alkaline Precipitation**

Tanneries performing alkaline precipitation as treatment of tanning wastewater frequently use a filter press to retain solid phase. S & S white ribbon filter
performed with stoichiometric amount at 80°C for 12 h. Analysis of filtrate liquid coming from a precipitation with chloride, sulfate and sodium in the supernatant. Chemical precipitation was obtained by increasing reaction time. The Cr(III) content was 99.00% in first 2 h of reaction. A higher Cr(III) separation was achieved at 80°C with stoichiometric amount of salt and variable reaction times (2, 4, 6, 8, 10 and 12 h). Cr(III) separation in final concentrate is not used; 80°C was selected because even in the industry, a high temperature to make wastewater treatment practical and economical is common. Reaction times were shortened considerably. Rejection of each species were: Cr(III), 0.0032, 99.71; sulfate, 10.23, 1.25; sodium, 10.03, 9.64; and chloride, 9.24 g l⁻¹, 3.45%, respectively. Comparison of these values with their initial contents reveals that precipitation produces a good separation of Cr(III), while chloride, sulfate and sodium remain in filtrate liquid without noticeable changes. Some reactions that occur during Cr(III) precipitation are irreversible; for example, when carbonate anion is combined with protons (hydronium) of liquid medium: $\text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{H}_3\text{O}^+ \rightarrow \text{CO}_2^\uparrow + \text{H}_2\text{O}$. Consequently, at the end, alkali is not recovered. This is a fundamental difference with respect to RO, since with such technology the use of a chemical reagent is not required.

Physicochemical Features of Final Concentrate

Physicochemical characterization of final concentrate (stage 10) obtained by RO supplies relevant information to implement the most effective methodology to reuse tanning agent. Therefore, chemical composition of final concentrate was determined and found as follows: Cr(III), 2.24; sulfate, 26.74; sodium, 18.95; and chloride, 12.47 g l⁻¹. Absorption spectrum of tanning wastewater at 20°C has bands at 417 and 578 nm, suggesting the presence of a dimer with hydroxo and sulfate bridges. It is well known that solution color allows differentiating when dimer is formed by a hydroxo bridge (green) or two hydroxo bridges (blue). Hence, two hydroxo bridges and a sulfate bridge participate in dimer formation. Sulfate anion content in concentrate increased with the permeate volume achieved (stage 1, 10.03 g l⁻¹; stage 5, 13.67 g l⁻¹ and stage 10, 26.74 g l⁻¹); this situation favors its insertion into Cr(III) complex ion. In its visual aspect, concentrate color changed from blue (stage 1) to dark green (stage 10). Light green suggests a Cr:SO$_4^{2-}$ ratio of 2:1 and dark green a ratio of 1:1. Then, ionic species is a dimer with two bridges (a hydroxo and a sulfate) between central cations plus a sulfate anion as monodentate ligand (Cr:SO$_4^{2-}$ ratio of 1:1).

Proposed route to recycle Cr(III) in final concentrate was as solvent of the tanning salt marketed in solid state. In this study, organic ligand chosen to form soluble complex ion of Cr(III) was formic acid. Liquor prepared to reuse tanning agent. Therefore, chemical composition of final concentrate was determined and found as follows: Cr(III), 2.24; sulfate, 26.74; sodium, 18.95; and chloride, 12.47 g l⁻¹. Absorption spectrum of tanning wastewater at 20°C has bands at 417 and 578 nm, suggesting the presence of a dimer with hydroxo and sulfate bridges. It is well known that solution color allows differentiating when dimer is formed by a hydroxo bridge (green) or two hydroxo bridges (blue). Hence, two hydroxo bridges and a sulfate bridge participate in dimer formation. Sulfate anion content in concentrate increased with the permeate volume achieved (stage 1, 10.03 g l⁻¹; stage 5, 13.67 g l⁻¹ and stage 10, 26.74 g l⁻¹); this situation favors its insertion into Cr(III) complex ion. In its visual aspect, concentrate color changed from blue (stage 1) to dark green (stage 10). Light green suggests a Cr:SO$_4^{2-}$ ratio of 2:1 and dark green a ratio of 1:1. Then, ionic species is a dimer with two bridges (a hydroxo and a sulfate) between central cations plus a sulfate anion as monodentate ligand (Cr:SO$_4^{2-}$ ratio of 1:1).

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out by means of shrinkage temperature (Ts), which is a measure of structural stability of leather in wet state and its value has been used to determine effectiveness of tanning agent\textsuperscript{2,3}. Average values\textsuperscript{29} of Ts were: original cattle hide, 62±2°C; leathers obtained with commercial solid salt dissolved in concentrate, 103±2°C; and leathers obtained with commercial solid salt dissolved in water, 103±2°C.

Most abundant electronic structure of Cr(III) complex ion in a tanning liquor prepared from commercial salts is a dimer with two hydroxo bridges and a sulfate bridge. Meanwhile, species present in final concentrate is a dimer with a hydroxo bridge, a sulfate bridge and a sulfate anion in position of monodentate ligand. This is not an important difference if Cr(III) amounts of concentrate are compared with commercial tanning salt used for liquor preparation.

Physicochemical Features of Alkaline Precipitates

Precipitates produced under different reaction times had very similar physicochemical features. Cr(III) content of filtrate liquid decreased from 10.9 mg l\textsuperscript{-1} for 2 h to 3.2 mg l\textsuperscript{-1} for 12 h. Difference between both values can be considered scarce when trying to establish the cation percentage removed (precipitated) taking into account its initial concentration in the effluent of 1090 mg l\textsuperscript{-1}. However, difference is highly relevant and this justifies the use of prolonged reaction times when comparing Cr(III) content that remains dissolved in all tests. Chemical analysis of precipitate obtained with stoichiometric amount of alkali at 80°C for 12 h is as follows: Cr(III), 21.22; sulfate, 3.95; sodium, 3.39; chloride, 4.10; calcium, 2.62; weight loss at 250°C, 28.80; and weight loss between 250-700°C, 22.60 % w/w.

Presence of calcium was explained by basifying agent (calcium magnesium carbonate) utilized in tannage process, from which wastewater was collected. Basifying agents increase pH during tannage process to favor fixation of Cr(III) to collagen\textsuperscript{10}. XRD analysis of precipitates showed only a crystalline substance, calcium sulfate hydrate (CaSO\textsubscript{4}.2H\textsubscript{2}O). Referring to Cr(III) and sodium, they would be forming amorphous solids. DTA showed that hydration water loss occurs by means of two endothermic reactions, at 143-144°C for Cr(III) amorphous polymers and at 164-165°C for calcium sulfate hydrate. These phase transformations appear concluded at 250°C. DTA peaks indicating changes in the sample were not observed between 250 and 700°C, although weight loss was important. Such behavior would be produced because transformations did not happen at a single temperature, which is consistent with the absence of an atomic arrangement of long range in Cr(III) amorphous polymers. Tanning agent reuse requires the precipitate dissolution through sulfuric acid and formation of Cr(III) dimer with two hydroxo bridges and a sulfate bridge. A high acidity residual (pH < 2.0-3.0) of final solution is not suitable for tannage process, so that it should be neutralized.

Conclusions

Significant amounts of fats (83.05%) and PM (69.92%) present in liquid effluent were separated via sieving followed by ultrafiltration. RO process with polyamide membrane of spiral wound removed: Cr(III), 99.83; sulfate, 92.76; sodium, 63.69; and chloride, 36.26%. Cr(III) concentration in total permeate volume was 1.9 mg l\textsuperscript{-1}. With respect to permeate flux, its initial value was low, observing an appreciable decrease during the last stages of treatment. Precipitation with commercial sodium carbonate produced a removal of 99.00% of Cr(III) dissolved when reaction was carried out for 2 h with stoichiometric amount of alkali at 80°C, resulting a cation concentration of 10.9 mg l\textsuperscript{-1} in filtrate liquid. Cr(III) separation was 99.71% for 12 h and its concentration in filtrate liquid decreased to 3.2 mg l\textsuperscript{-1}. Rejections of other three components for 12 h were: sulfate, 1.25; sodium, 9.64; and chloride, 3.45%. Cr(III) carrier species in final concentrate was a dimer with a hydroxo bridge and a sulfate bridge plus a sulfate anion as monodentate ligand. All precipitates had similar content of Cr(III). Precipitate composition corresponding to the longest test (12 h, stoichiometric amount of alkali, 80°C) was: Cr(III), 21.22; volatile substances, 51.40; and neutral salts, 14.06% w/w. This study suggests that RO is the most effective technology to get a greater removal of hazardous substances and that the reuse of final concentrate is easier if it is compared with alkaline precipitate. However, low permeate flux must be improved to employ the membrane process at industrial scale.

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