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Applicability of nanofiltration in the recovery of chrome tanning wastewater

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Tannery industries generate high wastewater flow rates including high concentrations of organic matter and salts and other pollutants such as trivalent chromium (Galiana-Aleixandre, 2005).

The exhausted bath coming from chrome tannage contains about 30% of initial salt and it is normally sent to a cleaning-up plant. Here chrome salts end into the sludges creating serious problems for their disposal. Chrome recovery from tanning exhausted baths represents a significant economical advantage for leather industry in terms of its reuse and for the simplification of the polishing process of global wastewaters (Cassano, 2001).

There are different methods available to treat the chrome waste generated from chrome tanning process. Chemical precipitation, coagulation, solvent extraction and membrane process, ion exchange and adsorption methods are some of the concepts available to recover the chrome from the effluent (Kanagaraj, 2008).

Membrane technology, especially nanofiltration (NF) is considered a viable option for water treatment because of its efficiency for chrome removal. It can operate at low pressures and can provide a good permeation flow rate (Ortega 2005).

This study examined the technological benefits of membrane filtration for the recovery and reuse of chemicals from tannery process water. The objective of the present study was to investigate the suitability of applying nanofiltration system for recovery and reuse of quality water in tanning process. Therefore polyamide nanofiltration membrane was used for the Cr (III) and salt removal from the wastewaters of chrome tannage. Optimum operating conditions were determined for the nanofiltration membrane in the synthetic solution prepared similarly to the wastewater characterization. As a result of different flow, pressure and temperature tests, most suitable operating conditions, best removal and best reuse efficiency were found.

The membrane experiments were performed at a lab-scale plant. All the assays were performed with a cross-flow module having in an flat membrane test module. Effective surface area of membrane is 116 cm². XN 45 nanofiltation membrane were used All of them are polyamide thin film composite membrane and cut off 200Da.. The membrane was manufacture for Trisep Corparation (USA).

To determine the most suitable operating conditions for the nanofiltration membrane (XN45), synthetic solutions were prepared similar to the characteristics of wastewater generated from the chrome tanning process. These solutions comprise 5000 mg/L Cr(III) and 15000 mg/L NaCl. During the experiments, pressure was adjusted to 8, 12, 16, 20 bar, flow was adjusted to 1, 3, 5, 7 L/min and temperature was adjusted to 18, 22, 26, 30 °C. duration of the experiment was

taken as 4 hours and the supply volume was determined as 8 liter. The ph value was fixed at about 4. During the experiments, Cr(III), sodium and sulfate parameters were analyzed from the samples taken from the permeate and feed tank at certain intervals.

During different pressure (8, 12, 16, 20 bar) tests, it was observed that the flux loss of the membrane increased with the increase in the pressure (Ahmad et al. 2005). The highest flux loss was determined as 78.9% (57.5% concentration polarization and 21.4% pollution) at 20 bar. The highest VRF value was obtained at the same pressure as 1.53. High VRF value is the indicator of a high Cr(III) recovery in the feed tank. It was seen that the filtrate quality increased with the pressure rise. At the end of the experiment, the feed concentration of Cr(III) reached up to 7450 mg/L at 20 bar while the permeate concentration was 185 mg/L and removal efficiency of Cr(III) was 97.5%. Sodium and sulfate parameters were found to be respectively 20.4% and 95.60%.

Different flow (1, 3, 5, 7 L/min) tests showed that the most suitable flow rat was 7L/min for both flux loss and permeate quality. 71% flux loss was established during the test conducted with the flow of 7L/min. However, it was observed that increased flow reduced the concentration polarization and effect total flux loss positively (Benitez et al. 2008). The VRF value was obtained as 2. Cr(III) supply concentration in the synthetic wastewater was found to be 10350 mg/lL at the flow of 7L/min at the end of a 4-hour experiment. Filtrate concentration was 140 mg/L and the removal efficiency was 98.6%. Sodium removal efficiency was found to be 34.4% while sulfate removal efficiency was 96.5%.

Different temperature (18, 22, 26, 30°C) tests showed that flux loss increased with the temperature rise. Flux losses were found to be similar to each other and the highest flux loss was determined at 30°C (76.2%). At 18°C , 22°C and 26°C , concentration polarization and pollution affected the total flux loss similarly. At high temperatures, flux values showed increase, diffuse speed of the organic and inorganic matters increased but the removal efficiency decreased. Previous studies showed that nanofiltration membrane pores expanded with the temperature rise (Benitez et al. 2006). At 18°C , Cr(III) removal efficiency was 98.6%, sodium removal efficiency was 34.4% and sulfate removal efficiency was 96.53%.

Atomic Force Microscopy (AFM) measurements showed that NF(XN45) membrane had a rough structure (Kaya 2007). This caused high flux losses and accumulation of salt and chrome on the membrane surface. During the experiments conducted with NF(XN45) membrane, highest quality of permeate water and best Cr(III) removal were obtained at 20 bar pressure, 7L/min and 18 $^{\circ}$ C. Cr(III) supply concentration were raised from 5900 mg/L to 10350 mg/L. Approximately two-fold chrome recovery was achieved.

This study demonstrates the feasibility of using nanofiltration processes for the removal of chrome present in tannery effluents. The investigated 'clean technology' application of membranes brings the possibility of zero pollutant discharge closer to reality. The investigations carried out demonstrated clearly the benefits and economical feasibility of membrane applications for chemical recovery in the leather industry.

Key words: Nanofiltration, removal efficiency, flux, Cr(III)

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