

Application of Nanofiltration and Reverse Osmosis for Tanning Wastewater

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ABSTRACT: The aim to achieve in this study is to recover the Cr(III) and process waters used in the wastewaters of chrome tanning operation by membrane process during leather production. In the treatment alternative contains, cartridge filter, nanofiltration (NF(NP10)), nanofiltration NF(XN45) and reverse osmosis RO(ACM2) membranes. The raw chrome wastewater from the cartridge filter was given to NF(NP10) membranes with 3 different pressures (12bar, 16bar, 18bar). In this alternative, the most appropriate pressure is determined as 20 bar and the COD, Cr(III) and SS values were detected as, in order, 65%, 49% and 87% for the removal efficiency. 2,7 times more concentration for Cr(III) was achieved in the NF (XN45) membrane, which was used after NF(NP10) membrane and COD, SS, SO₄⁻², Na⁺ and conductivity parameters showed removal efficiencies as, 75%, 89%, 95%, 38% and 16%. The permeate from RO(ACM2) membrane was decreased to the discharge criteria's; (Cr(III):2 mg/L, COD: 200 mg/L). As a result, the investment and the process cost of these membranes are more feasible.

Key words: Nanofiltration, Reverse osmosis, Cr(III), Removal efficiency, Cost

INTRODUCTION

Leather production involves a complex sequence of chemical reactions and mechanical processes. Amongst these, tanning is the most important stage giving the hide or skin the required stability. The major environmental impacts of leather production originate from liquid, solid and gaseous emissions resulting from the consumption of rawhides/skins, energy, chemicals and water. (Joseph et al. 2009) Tannery industries generate high wastewater flow rates including high concentrations of organic matter and salts and other pollutants such as trivalent chromium (Galiana-Aleixandre et al., 2005; Oral et al., 2007). In order to provide an estimate of the amount of water involved in the process, the latest studies by official organizations estimate that approximately 6 Mt of bovine salted raw hides are tanned yearly worldwide. Approximately 90% of these hides are tanned using chrome in accordance with the pollution values from tannery processes under conditions of good practice there is an average estimation that chrome tanning results in approximately 11 million m³ of contaminated water yearly, containing

approximately 0.22 Mt of salt and approximately 0.02 Mt of Cr(III) (Morera et al., 2007).

There are different methods available to treat the chromium 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 chromium from the effluent (Kanagaraj et al., 2008; Fabbicino et al., 2013).

In recent years, membrane technologies have been developing rapidly and their cost is continuing to reduce while the application possibilities are ever extending. The main advantage of a membrane based process is that concentration and separation are achieved without a change of phase and without use of additional chemicals or thermal energy, thus making the process energy-efficient and ideally suited for recovery applications (Chandan Das et al., 2007). Cassano et al. (2001-2007) reported a general overview of the potential of membrane processes in the treatment of aqueous effluents coming from the leather industry. They used an integrated membrane scheme

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(UF followed by NF polymeric membranes) to recover and concentrate the chromium exhaust tanning baths. This process also permits the reuse of the permeate from NF in the pickling phase considering the high content of chlorides in the solution. The flux in the NF membrane is about 86% after 1 h at 16 bar and then remained approximately constant for the following 2 h. NF was tested for the recovery of trivalent chromium in the residual tanning floats Suthanthararajan *et al.*, (2004) Pre-treated effluent was subjected to pilot scale membrane system consisting of nanofiltration and reverse osmosis. About 98% removal of total dissolved solids was obtained while permeate recovery was about 78%. The treated water was finishing process of tanning [9]. Scholz and Lucas (2003) studied the technological and economic benefits of membrane filtration for the recovery and reuse of chemicals from tannery process water. Taleb Ahmed *et al.* (2004, 2006) proposed the combination of a physicochemical treatment and nanofiltration to eliminate chromium from the tanning wastewater. Galiana-Aleixandre *et al.* (2005) studied the NF application for sulphate removal and water reuse of the pickling and tanning processes in a tannery. Other studies for chromium recovery from tannery effluents have also been reported in the literature (Shaaalan *et al.*, 2001; Guo *et al.*, 2006; Purkait *et al.*, 2009; Religa *et al.* 2013). In the literature, it is discussed not only about the chromium minimization in the final wastewater by direct reuse of the exhausted tanning bath (spent liquor), but also about the treatment of the washing wastewater by membranes and the further reuse of the rejection stream. Thus, Cassano *et al.* (2007) applied an integrated membrane process (ultrafiltration, nanofiltration) for the chromium recovery from tanning effluents (Vicenta *et al.*, 2010). The objective of the present study was to investigate the suitability of applying nanofiltration and reverse osmosis systems for recovery and reuse of chromium (III) ions and quality water in tanning process from treated tannery effluent. In the first stage, the study went on to estimate two different polymers cross-flow nanofiltration as a possible process for the recovery of chromium (III) ions. Also after the nanofiltration membrane, reverse osmosis membrane was used in order to investigate the recovery of water and salt. Such a distribution of components of chromium tannery wastewater will enable for direct re-use of both retentate and permeate. The proposed solution apart from reducing consumption of the chromium tannins, minimizing the concentration of chloride ions in wastewater and total consumption of process water.

MATERIALS & METHODS

The wastewater used in this study was collected from leather producing process located in Bursa-

Turkey. The wastewater was preserved in containers in dark at 4 °C. The main physicochemical characteristics of chrome tanning wastewater was given in Table 1. All the assays were performed in a flat membrane test module in a laboratory-scale membrane system. The module is constituted by a unit, designed for a maximum operating pressure of 40 bar, that allows us to obtain data concerning the behaviour of the membranes in cross-flow conditions with a reduced surface area (116 cm²), feed flow rate of 7 L/min. Schematic diagram of the experimental set-up is given in Fig. 1. The feed stream was pumped from the feed tank to the feed inlet of membrane cell. A portion of the solution permeated through the membrane and flowed into the permeate carrier. The concentrate stream flowed back to the feed tank.

Table 1. Characteristics of the chrome tanning wastewater

Parameter	Unit	Value
pH	-	4.13
Cr(III)	mg/L	6,358
Suspended Solids (SS)	mg/L	980
Chemical Oxygen Demand (COD)	mg/L	5,970
Sulfate (SO ₄ ⁻²)	mg/L	30,625
Sodium (Na ⁺)	mg/L	27,728
Conductivity	ms/cm	79.3

A heat exchanger in the feed vessel was used in all filtration experiments to control the temperature at 18°C±0.5. The raw chrome wastewater was filled into feed tank of experimental set-up. The experiment started and the wastewater circulated for a given period. Membrane cell used consists of two elements (cell body and cell holder). Hydraulic pressure was applied to the top of the holder. This pressure causes the piston to extend downward and compresses the cell body against the cell holder. A single piece of rectangular membrane was installed in the bottom cell body with a feed spacer. During the nanofiltration and reverse osmosis experiments, the weight of permeate was monitored by weighting permeate collected in permeate carrier as a function of time.

Membrane performance was measured in terms of membrane rejection (*R*) and permeate water flux (*J_w*). Rejection is a measure of solute separation by the membrane and is defined as, $R = (1 - C_p/C_f) \times 100$, where *C_p* and *C_f* are the Cr(III), COD, SS, SO₄⁻², Na⁺ and conductivity concentrations in the permeate and feed streams, respectively. Three membranes were used NF(NP10), NF(XN45) and RO(ACM2). NF(NP10) is polyethersulfone membrane and others polyamide thin film composite membrane. The membranes were provide

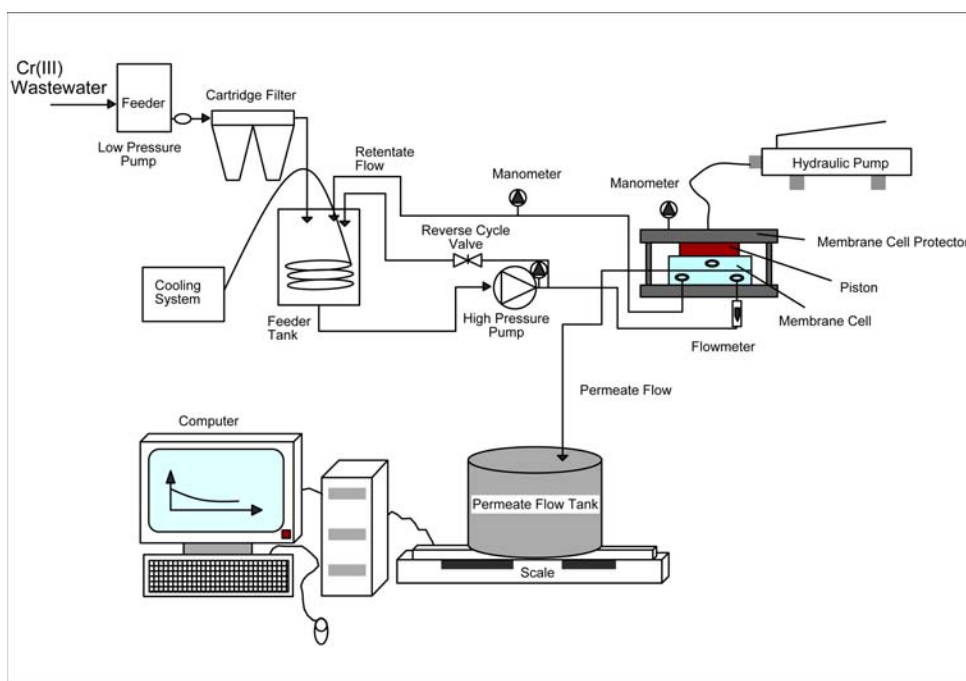


Fig. 1. Laboratory-scale membrane system

for Micro Nadir and Trisep. Cr(III), COD, pH, SS, SO_4^{2-} , Na^+ and conductivity measurements were carried out on the all samples (feed, permeate and retentate streams at each operating conditions) for the characterization and treatment studies. COD (using closed reflux method), SO_4^{2-} and SS analyses were carried out according to Standard Method 2540 (1998). ATI UNICAM 929 AA Spectrofotometer was used for Cr(III) measurements. pH measurement was done by using PT-10 Sartorius pH meter. Electrical conductivity and temperature which exists in feed water were detected with a JENWAY Conductivity Meter 4310 and for the detection of sodium a Flame Photometer has been used.

RESULTS & DISCUSSION

Chrome tanning wastewater was treated with 3 different cartridge filters with pore diameters of 50 μm , 10 μm and 5 μm . Analysis of the filtered wastewater showed that 39% removal efficiency was achieved in the SS parameter. Thus, by reducing the sediment load of chrome tanning wastewater which is this treatment alternative, the operating lifespan of the NF membranes used for pretreatment was prolonged. In addition, 22%, 19% and 20% removal efficiencies were achieved in COD, Cr(III) and SO_4^{2-} parameters, respectively; Na^+ and conductivity removal efficiencies were much lower, at 2% and 1.5%. It operated with polyethersulfone nanofiltration membrane (NF (NP10)) with 1000 Da MWCO value, which is used for pretreatment. Tests were conducted at 7 L/min. flow, 20°C temperature, pH

4 and at three different pressures: 12 bar, 16 bar and 20 bar. These tests continued for 4 hours. Aloy and Vulliermet (1997) tested the nanofiltration of tannery waste discharges for the recovery of trivalent chrome from the effluents. The experiments were run at transmembrane pressures between 10 and 20 bar. It is noteworthy that chromium reuse implies sulfate reuse, since the tanning agent is chromium sulfate. A time-based flux change graphic of permeate water obtained from the NF(NP10) membrane is given in Fig. 2. The adherence mechanism of ions by nanofiltration membranes is explained by electrostatic interaction between these ions and the surface load of the membrane (Mulder, 1996; Scott, 1996). As Ortega et al. (2005) stated, removal efficiencies of pollutants in the membrane are related to the load of membrane. The pH value of the solution contributes to positive and negative load of the membrane. When $\text{pH} > \text{I}_p$ is (isoelectric point), the membrane is negatively charged and when $\text{pH} < \text{I}_p$, the membrane is positively charged. In another study, isoelectric point of FM NP010 membrane was found to be "0" below pH 4.2. The results showed that this membrane was positively loaded below pH 4.2 and negatively loaded above pH 4.2. Nevertheless, at a pH near the isoelectric point, the pore size of membrane can not be reduced and therefore water flux is increased (Koschuh et al., 2005; Boussu et al., 2007). For this reason, tests were done by setting the pH of chrome wastewater to 4 when using the NP010 membrane.

As seen in Fig. 2, flux values increased with increasing pressure, on the basis of Darcy's law. Flux values were found to be 18 L/m².h at 12 bar, 19 L/m².h at 16 bar and the highest flux of 21 L/m².h was achieved at a pressure of 20 bar. Initial flux values decreased with time, as the wastewater has a high levels of conductivity value, ions and organic components.

As seen in Fig. 3, tests with the NF(NP10) membrane under different pressures displayed that the best removal efficiencies for all parameters were obtained at a pressure of 20 bar. While pollution parameter removal efficiencies increased with increased pressure, it was also stated, in the literature, that the pollution layer on the membrane squeezed and

increased (Benitez and Acero Leal, 2008). Removal efficiencies for SS and Cr (III) parameters were 87% and 49%, respectively. It was seen that SS concentration decreased to 78 mg/L and Cr(III) concentration decreased to 2627 mg/L level in the solution (Table 1). These values are similar to those reported by Cassano et al. (1997). They calculated polysulfone UF membrane with 20 kDa MWCO as 84 % and SS and Cr(III) removal efficiencies as 28%. In the NF(NP10) membrane, COD removal is typical for the nanofiltration membrane (Boussu *et al.*, 2007) and it was found as 65% at a pressure of 20 bar. The upper layer of the NF(NP10) membrane is too hydrophobic; therefore, there is an interaction between the membrane surface and pollutants. Conductivity removal

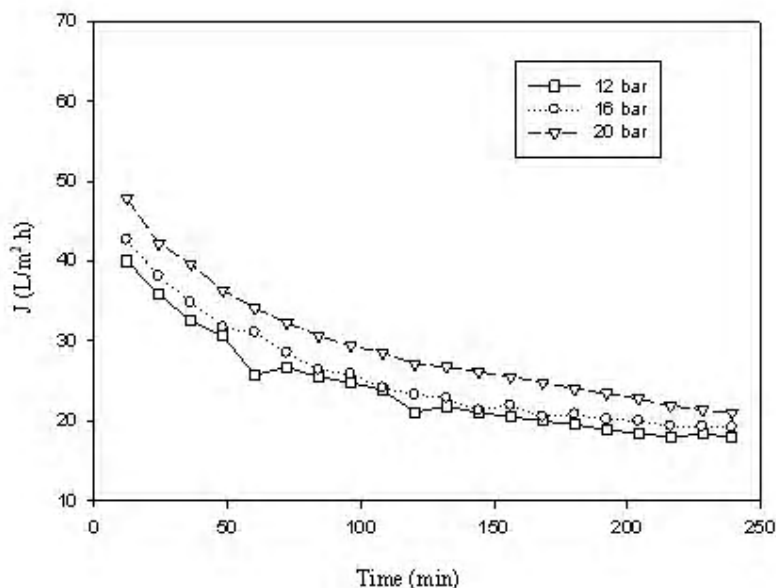


Fig. 2. Demonstration of time-based flux change of permeate water obtained from the NF(NP10) membrane

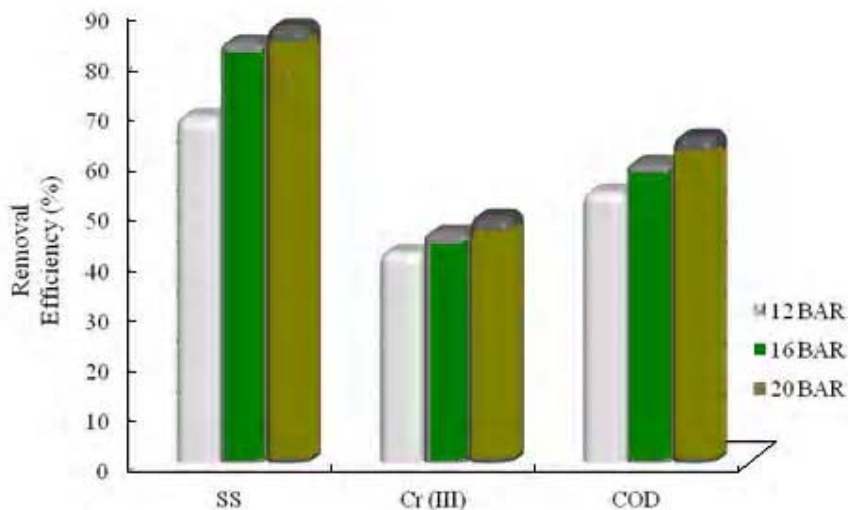


Fig. 3. SS and Cr(III), COD removal efficiencies obtained under different pressures in the NF(NP10) membrane

efficiency in the NP010 membrane was 6% and Na⁺ removal efficiency was very low, at 11% at a pressure of 20 bar (Table 2). It is known that, in salt removal with nanofiltration, the MWCO value is as important as the membrane load (Kaya, 2009). The very high MWCO value of the NP010 membrane and a low load density prevented the removal of NaCl. Removal efficiency of SO₄²⁻ was 41% and permeate concentration was seen to decrease until about 14,455 mg/L. Table 2 shows composite permeates obtained from chrome tanning wastewater, pre-filtered using a NF(NP10) membrane with cartridge filter at 3 different pressures (12, 16 and 20 bar).

Permeate obtained from the NF(NP10) membrane was transferred to the NF(XN45) membrane. The flow obtained by treating permeate wastewater from the NF(NP10) membrane then passing it through the NF(XN45) membrane, is given in Fig. 4.

Tests were done under suitable conditions that were provided after synthetic studies. Test conditions of 20 bar pressures, 18°C temperature, pH 4, 7 L/min flow, 0.7 m/sec cross flow rate, 4 hours test duration and 8 liters of feed volume were taken as constant (Kiril Mert and Kestioglu 2012).

While initial feed volume for the NF(XN45) membrane was 8 L, it decreased to 3.2 L at the end of the test. VRF value was 2.5. Flow rate reached steady state of 54 L/m² after 200 minutes (Fig. 4). The increase in VRF value obtained from the NF(XN45) membrane increased the chrome concentration in feed tank was also high.

As seen in Fig. 5, while initial Cr(III) concentration in the feed tank was 2627 mg/L, this value increased up to 7092 mg/L. Cr(III) concentration permeate value was 97 mg/L. The removal efficiency reached from 96% to 99% over time. Thus, Cr(III) quantity increased 2.7 times based on the initial feed concentration.

As seen in Table 3, removal efficiencies for COD and SS parameters were 75% and 89%, respectively. Thus, COD and SS values in the NF(XN45) membrane permeate water were reduced to 408 mg/L COD value and 9 mg/L SS value. In addition, it was seen that removal efficiencies in the NF(XN45) membrane were very close to the results reported by Cassano et al. (1996) using a nanofiltration membrane (65% COD, 100% Cr(III), 89% SS). Almost 95% removal efficiency was achieved for SO₄²⁻. Cuartas-Uribe et al. (2005) and Galiana-Aleixandre et al. (2005) reported removal efficiency of nearly 99% for SO₄²⁻. The lowest removal parameters were for Na⁺ and conductivity 38% and 16%. The fact that the Cr(III) level is very low and there is high conductivity in the composite permeate were obtained from the NF(XN45) membrane. This treatment alternative shows that it can be used in tanning, which is done before the re-tanning process.

Permeate obtained from the NF(XN45) membrane was transferred to the RO(ACM2) membrane. Tests were done under suitable conditions gained. Tests were performed under conditions of 21 bar pressure, 20°C temperature, pH 4, 7 L/min flow, 0.7 m/sec cross flow rate, 4 hours test duration and 8 liters of feed volume were taken as constant. The flow figure obtained by treating permeate water through the NF(XN45) membrane and then the RO(ACM2) membrane is shown in Fig. 6. The test results showed that flow rate decreased from 28 L/m².h to 12 L/m².h.

The time-based permeate and feed concentration change of Cr(III) after treating the NF(NP10) membrane permeate water with the RO(ACM2) membrane is shown in Fig. 7. The permeate obtained from the NF(XN45) membrane contained 105 mg/L. Cr(III). The subsequent treatment with the RO(ACM2) membrane achieved 100% Cr(III) removal. After treating the permeate water with the RO(ACM2) membrane, which was obtained from the NF(XN45) membrane, 96% COD removal efficiency was achieved. The resulting COD concentration of 16 mg/L from 408 mg/L was below COD discharge criteria. Na⁺ removal efficiency was nearly 96%. Similarly, Suthanthararajan et al. (2004) reported 94% Na⁺ removal efficiency using a polyamide reverse osmosis membrane.

The results from the RO(ACM2) membrane showed that Cr(III), conductivity and SS concentrations were completely removed (Table 4). Thus, as Fababuj-Roger et al. (2007) stated, permeate water has a very high quality. Further, as it has low conductivity value, which means it can be re-used in the tanning process. The concentrate part will be given back so as to be used in tanning process because it enables sulfate and sodium chloride to be recycled.

As seen in this treatment flow scheme given in Fig. 7, after experimental studies using NF(NP10), NF(XN45) and RO(ACM2) membranes, the number of membranes and membrane costs were calculated; the results are given in Table 5. Flow value for the NF(NP10) membrane was 18 L/m².h, NF(XN45) flow rate was 54 L/m².h, and RO(ACM2) flow rate was 12 L/m².h. In order to treat leather tanning wastewater containing 200 m³/G, the following total membrane areas were required: 463 m², 138 m² and 144 m². It was calculated that 12 membranes with an area of 39 m² were needed for the NF(NP10) membrane, 7 membranes were sized for the NF(XN45) membrane and 5 membranes were sized for the RO(ACM2) membrane. System costs of the NF(NP10), NF(XN45) and RO(ACM2) membrane systems were 4700 €, 23000 € and 13000 €, respectively. Unit membrane price was 900 € for the NF(NP10), 900€ for the NF(XN45) membrane, and 260€ for the RO(ACM2) membrane.

Table 2. Analysis and efficiencies of solution obtained from chrome leather tanning wastewater filtered using NF(NP10) membrane

NF(NP10) Membrane	Parameter	NF(NP10)		12 BAR		16 BAR		20 BAR	
		Cartidge Filter Feed (mg/L)	Feed (Cartidge Filter Exit) (mg/L)	NF(NP1 0) Permeate (mg/L)	NF(NP1 0) Removal Efficienc y (%)	NF(NP1 0) Pemeate (mg/L)	NF(NP1 0) Removal Efficienc y (%)	NF(NP1 0) Permeate (mg/L)	NF(NP1 0) Removal Efficienc y (%)
		COD	5,970	4,657	2,142	54	1,862	60	1,630
Cr(III)	6,358	5,150	2,987	42	2,781	46	2,627	49	
SS	9,80	598	185	69	96	84	78	87	
SO ₄ ²⁻	30,625	24,500	16,170	34	15,680	36	14,455	41	

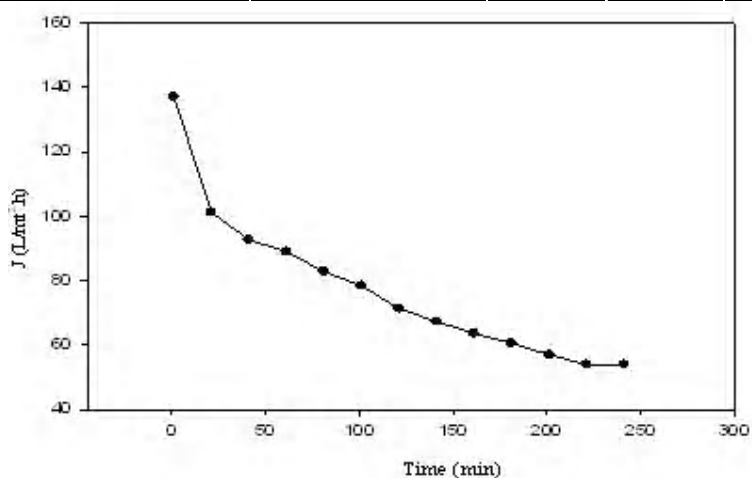
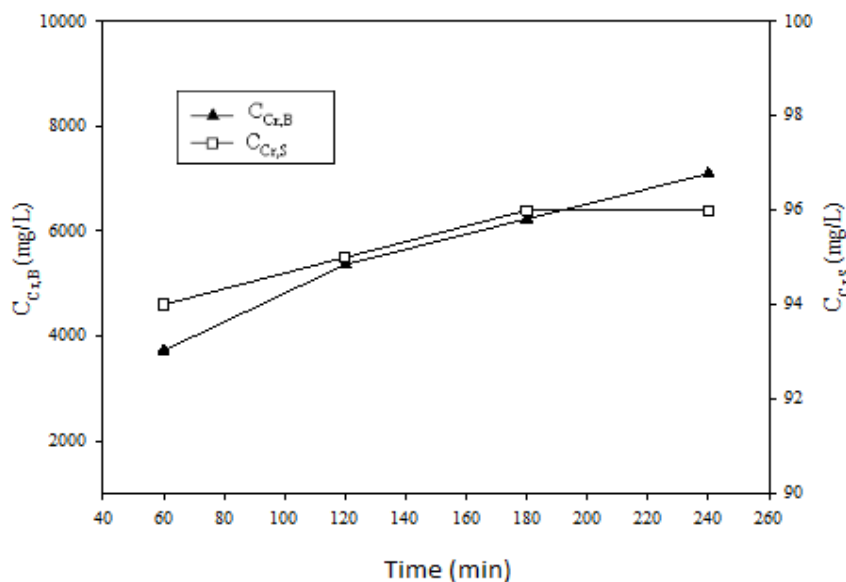


Fig. 4. Time-based flow change obtained by treating NF(NP10) permeate water with NF(XN45) membrane



(C_{Cr,B}: Cr(III) Concentration in Feed Water, C_{Cr,S}: Cr(III) Concentration in Permeate Water)

Fig. 5. Time-based change in permeate and feed concentration of Cr(III) after treating NF(NP10) membrane permeate water with NF(XN45) membrane

Table 3. Analysis values and removal efficiencies of filtration of permeate obtained from chrome tanning wastewater passing through membrane NF (XN45)

Parameter	NF(XN45) Feed (mg/L)	NF(XN45) Permeate (mg/L)	NF (XN45) Removal Efficiency (%)
COD(mg/L)	1,630	408	75
Cr(III) (mg/L)	2,627	105	96
SS	78	9	89
Na ⁺ (mg/L)	24,844	15,403	38
SO ₄ ⁻² (mg/L)	14,455	723	95
Conductivity (ms/cm)	73.4	61.6	16
pH	4.62	4.42	-

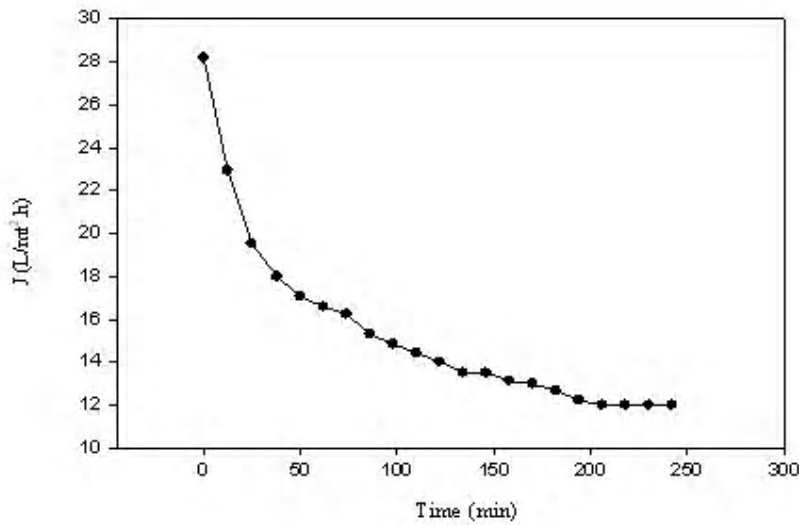


Fig. 6. Time-based flow rate change after treating NF(XN45) permeate water with RO(ACM2) membrane

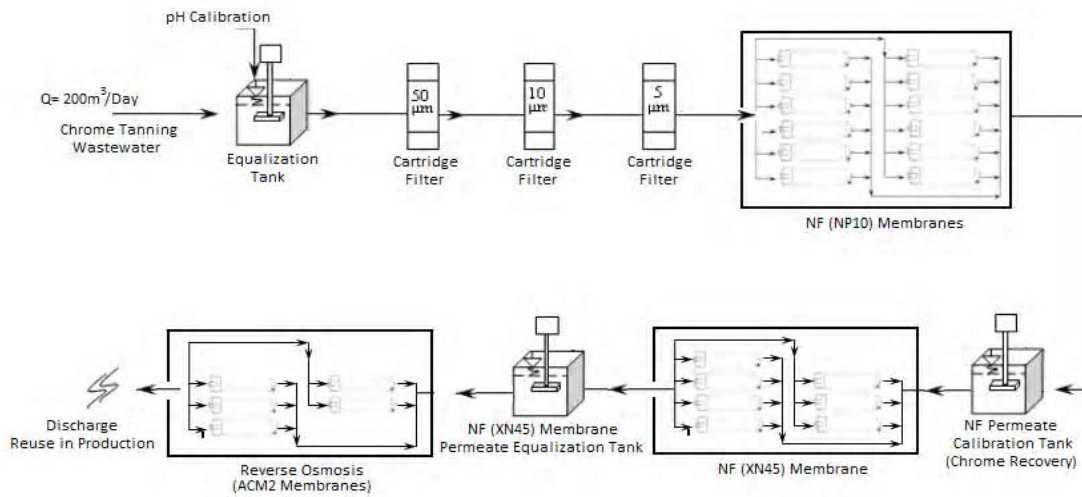


Fig. 7. Schematic showing of treatment alternative

Table 4. Analysis values and removal efficiencies of filtration obtained from chrome tanning wastewater passing through RO (ACM2) membrane

Parameter	RO(ACM2) Feed (mg/L)	RO(ACM2) Permeate (mg/L)	RO(ACM2) Removal Efficiency (%)	Discharge Criterian (Anonymous, 2004)	
				2 hour	24 hour
COD(mg/L)	408	16	96	200	300
Cr(III) (mg/L)	105	-	100	3	2
SS(mg/L)	9	-	100	-	-
Na ⁺ (mg/L)	15,403	616	96	-	-
SO ₄ ⁻² (mg/L)	723	7	99	-	-
Conductivity (ms/cm)	61.6	-	100	-	-
pH	4.42	6.27	-	6-9	6-9

Table 5. Economic feasibility of the treatment alternative

MEMBRANES	NF(NP10)	NF(XN45)	RO(ACM2)
Optimum Conditions			
Pressure (bar)	10	20	21
Recovery (%)	90	60	60
Technical Conditions			
Area (m ²)	463	138	144
Flow (L/m ² .h)	18	54	12
Membrane Quantity	12	7	5
Membrane Equipment Cost Membrane Equipment Cost			
System cost of spiral wound membrane, € (NF(NP(10),NF(XN45), TO(ACM2))	27,000	23,000	13,000
Cost of spiral wound membrane, €/year	10,800	6,300	1,300
Other investments, €		24,125	
Tubing Cost, €		8,712	
Total Membrane Cost, €/year (NF(NP10)+NF(XN45)+ (ACM2))		18,400	
Total Investment,		177,237	
Process Cost			
Energy Cost, €/year		21,769	
Other annual process costs, €		59,925	
Total Process Cost/year		100,094	
Total Process Cost, €/m³		1.86	
Annual Saving, €		23,6104	
Saving, €/year		154,410	
Saving, €/m ³		2.87	
Pay-back, months		8	

Total investment cost of the NF(NP10), NF(XN45) and RO(ACM2) membrane systems was 51237€, including tubing costs and other investment costs.

**(Cartridge filter lifespan was taken as 2 weeks, membrane change was taken as 3 times a year, cleaning chemicals were used once a week and the facility was assumed to work 296 work days in a year). Energy

cost, which was calculated within the operating cost of this treatment alternative, was determined according to the appropriate pressure for the membrane systems and assessed according to pump powers. Pressure pumps with 11 kW, 11 kW and 11kW pump powers, respectively, were chosen for the NF(NP10), NF(XN45) and TO(ACM2) membrane systems. Additionally,

within the membrane systems, energy costs were calculated for existing feed pumps (1.1kW), dosage pumps (0.2 kW) and balance tank mixers (5 kW). While calculating energy cost, the unit electricity cost was taken as 0.08€/kW, as in the first purification alternative. For other annual operating costs, cartridge filter change cost was calculated based on two changes per week. Membrane change cost was also calculated, which was assumed to be 3 times a year. Total operating cost was calculated as 1.86 €/m³. After the treatment alternative, nearly 42 m³/G of water was recycled and annual recycling saving was estimated as 18,076 €. Similarly, it was calculated that with the NF(XN45) membrane, 223 kg of Cr₂O₃ can be recycled. It was also calculated that an annual saving of 218,028 € is generated using this recycling process. In these calculations, a value of 1 €/kg was used for Cr₂O₃. Net annual saving was 154,410 €, corresponding to 2.87 € per m³. When the alternative wastewater purification was used for the real application, it showed that the facility can amortize its annual operating cost in nearly 8 months.

CONCLUSION

Alternative treatment consist of nanofiltration NF(NP10), nanofiltration NF(XN45) and reverse osmosis RO(ACM2) membranes.

The following conclusions can be drawn from the results of this study:

- Tests at 3 different pressures (16, 18, 20 bar) for the NF(NP 10) membrane showed that the most appropriate pressure was 20 bar. At this pressure, removal efficiencies for SS and Cr (III) were 87% and 49%, respectively; removal efficiency for COD was 65%, and removal efficiency for SO₄⁻² was 41%.
- Cr(III) removal efficiency for the NF(XN45) membrane was nearly 99%. Cr(III) quantity increased 2.7 times compared to initial feed concentration. In COD, SS, SO₄⁻², Na⁺ and conductivity parameters, removal efficiencies were 75%, 89%, 95%, 38% and 16%, respectively.
- As a result of treating the NF(XN45) membrane permeate water with the RO(ACM2) membrane, the membrane permeate water was treated to the discharge criteria (Cr(III):2 mg/L, COD: 200 mg/L).
- Sizing and cost analyses for chrome tanning wastewater containing 200 m³/G Cr(III) showed that the facility can amortize its annual operating cost in 8 months.

In short, the experimental results show that pressure-driven membrane operations, integrated into some phases of the tanning process, reduce the environmental impact; simplify the wastewater

deputation processes; permit easy reuse of sludges; reduce disposal costs; and result in a saving of chemicals and water .

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