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Metal recovery from tannery effluent using nanofiltration process

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ABSTRACT

Most tannery industries use the chrome tanning process because of its easy use and excellent resulting leather properties. Nanofiltration is especially employed for softening industrial wastewater and for recovery of metal ions. The aim of this paper was to utilize nanofiltration NF90 technology as an environmentally sound and easy to use production system that minimizes pollutants in the wastewater of tanneries. Various effluent quality parameters were evaluated. Nanofiltration process was used for the removal of metals from the tannery effluent solution. Following the study of their transport through the membrane. NF90 membranes were able to retain ≥67% of the total mass of all metals present in the tannery effluent at pH = 1.2. The total mass of Ca retained exceeded 95.27% and Mg retained was 94.18%.

Keywords: Nanofiltration; Membrane; Recovery; Tannery effluent; Chromium

1. Introduction

Industrial waste is the most common source of water pollution in the present day, and it increases every year because most countries are industrialized. As a result, the environment is increasingly polluted by the waste generated by these industrial activities. The leather tanning industry has been investigated in terms of its environmental impact. Tanning is the most environmentally damaging operation in the leather manufacturing process. Agents such as chromium can be highly toxic and polluting [1–3].The oxidation states of chromium go from 2– to 6+. The less significant states of chromium are 1– and 2– and the most common are 2+, 3+ and 6+ [4].

The use of membrane-based separation processes can provide a technically and economically feasible solution as a clean treatment technology in recovering process water. Various membrane-based treatment processes, such as ultrafiltration and nanofiltration have been used to successfully remove Cr species from contaminated wastewaters [5].

Nanofiltration is a unique filtration process, intermediate between ultrafiltration (UF) and reverse osmosis (RO), for the highly specific separation of low molecular weight compounds such as minerals and salts from complex process streams [6–8]. Typical applications include washing of dairy products, recovery of metal ions, concentration and purification of soluble dyes and pigments [9,10].

The aim of this paper was to utilize nanofiltration NF90 technology as an environmentally sound and easy to use production system that minimizes pollutants in the wastewater of tanneries. Various effluent quality parameters were evaluated.

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2. Materials and methods

The reagents used were chromium(III) sulphate basic ($Cr_4(SO_4)_5OH_2$; 26% Cr_2O_3) from Fluka Analytical (Switzerland), magnesium chloride ($MgCl_2$; 99%) from Alfa-Aesar Kandel, Germany), calcium chloride 2-hydrate ($CaCl_2·2H_2O$; >99%), ammonium sulphate ($(NH_4)_2SO_4$; >99%) and sodium chloride (NaCl; 99.8%) supplied by AppliChem PanReac (Barcelona, Spain), hydrochloric acid (HCl; 35%–38%), potassium sulphate (K_2SO_4; >99%) and sodium hydroxide (NaOH; 98%) supplied by Sigma-Aldrich Chemicals (USA).

The nanofiltration membrane utilized was a polyamide membrane NF90 produced by the Dow Chemical Company, Midland, MI, USA. Inductively coupled plasma atomic emission spectrophotometry (ICP–AES) equipped with a radio-frequency (RF) generator of 40.68 MHz, A 1.00 m Czerny-Turner monochromator (sequential), an AS500 autosampler, and data acquisition software were used to determine the concentration of Ca, S, Mg, Na, K, and Cr. Ammonium content was determined colorimetrically using a Skalar SAN ++ segmented flow analyzer (Skalar Analytical B.V., AA Breda, The Netherlands). To monitor the pH of the aqueous solution during the experiments, the pH meter type CRISON from Spain is employed.

A synthetic solution with the same composition in the inorganic salts as the industrial effluent (Table 1) was prepared by dissolving the required compounds in deionized water, in order to investigate the performance of the membrane.

2.1. Experimental system

The experimental work was carried out in a laboratory test unit. A membrane area of 51.4 cm^2 was utilized in a dead-end stainless steel METCell NF test cell supplied by MET, UK. In this test cell, the membrane disc (NF90) was supported by a porous stainless-steel disc. The applied pressure was varied in the range of 20 to 40 bar using a pre-assembled gas unit (MET). Membrane permeability was monitored throughout the experiments and a new membrane disc was used whenever the membrane permeability deviated by more than 10% from its original value. The permeate was collected in containers during the experiment and the flux was monitored by recording the permeate weight with an electronic balance with an accuracy of 0.1 g.

Table 1
Characterization of synthetic tannery effluent

Parameter	Value
T, °C	20
pH	3.6
Conductivity, mS/cm	2.8
Cl^-, mg/L	746.1
NH_4^+, mg/L	48.4
Cr^{3+}, mg/L	50
Ca^{2+}, mg/L	81
K^+, mg/L	79.8
Mg^{2+}, mg/L	67.2
Na^+, mg/L	259
SO_4^{2-}, mg/L	1,203

2.2. Treatment of data

The permeate flux in L/(m^2·h) was calculated as follows [11]:

$$J = \frac{Q_P}{A} \tag{1}$$

where Q_p is the permeate flux (L/h) and A is the surface area of the membrane (m^2).

The hydraulic permeability of the membrane was calculated by measuring the permeate flux as a function of time and applying the Darcy equation [Eqs. (2) and (3)]:

$$L_p = \frac{J}{\text{TPM}} \tag{2}$$

$$\text{TMP} = \Delta P - \Delta\pi \tag{3}$$

where L_p (L/(h/m^2·bar)) is the hydraulic permeability of the membrane, TMP (bar) is the transmembrane pressure, ΔP (bar) is the applied pressure difference and $\Delta\pi$ (bar) is the osmotic pressure difference between the retentate and the permeate side (bulk solutions).

For dilute solutions, the van't Hoff equation can be used to calculate the osmotic pressure difference between the retentate and the permeate [Eq. (4)]:

$$\Delta\pi = RT\left(iC_F - i'C_P\right) \tag{4}$$

where R ((bar·L)/mol·K) is the gas constant and T (K) is the absolute temperature. C_F (mol/L) is the total feed molar concentration, C_P (mol/L) is the total permeate molar concentration and i, i are the van't Hoff factors of the feed and the permeate, respectively.

To calculate the osmotic pressure, chemical equilibrium diagrams were obtained using the software Make Equilibrium Diagrams Using Sophisticated Algorithms (MEDUSA) (version: Eq.calcs_32) [12].

The osmotic pressures of the feed and final retentate solutions and all sampled permeate solutions at the respective sampling times were estimated based on their analytically determined chemical compositions. Changes in osmotic pressure in the retentate were estimated from the respective instantaneous mass balances at the specific sampling times, considering negligible amounts of mass accumulated in the membranes.

The volume concentration factor (VCF) was calculated as the ratio of initial volume of feed divided by the retentate volume [Eq. (5)]:

$$\text{VCF} = \frac{\text{Volume}_{\text{initial}}\left(L\right)}{\text{Volume}_{\text{retentate}}\left(L\right)} \tag{5}$$

The contaminant removal (or apparent rejection (R)) was calculated as follows:

$$R = \frac{C_F - C_P}{C_F} \times 100\% \quad (6)$$

3. Results and discussions

3.1. Membrane permeability

Fig. 1 shows that the variation of the permeability through of the pressure can be described as a linear function, confirmed by the correlation coefficient which was greater than 0.978 at different pH values. It was observed that the fluxes increased with an increase in the pressures which was explained by the augmentation of the force applied to push the solution through the membrane. The slope of the equation refers to the permeability of the membrane and it depended on the molecule size. Compared to the membrane before the use a big decrease was seen in the permeability values after the passage of effluent through the membrane such as 7.171 to 0.839 (L/h·m^2·bar) at pH = 2.2 and 7.32 to3.971 (L/h·m^2·bar) at pH = 6.1.This decrease may have been due to the build-up of salts near at the membrane surface and severe internal fouling.

The degree of recovery of pure water permeability of the membranes after filtration tests with synthetic wastewater was evaluated and compared. The data are presented in Table 2. The highest recovery of hydraulic permeability of 54.249% was observed for NF90 at pH 6.1. This may

Table 2
Pure water membrane permeabilities for the NF90 membrane

pH	Pure water permeability L/(hm^2·bar)		Degree of recovery (%)
	Before (Lp_0)	After	
1.2	5.906	1.524	25.804
2.2	7.172	0.840	11.712
3.6	6.751	2.600	38.513
6.1	7.320	3.971	54.249

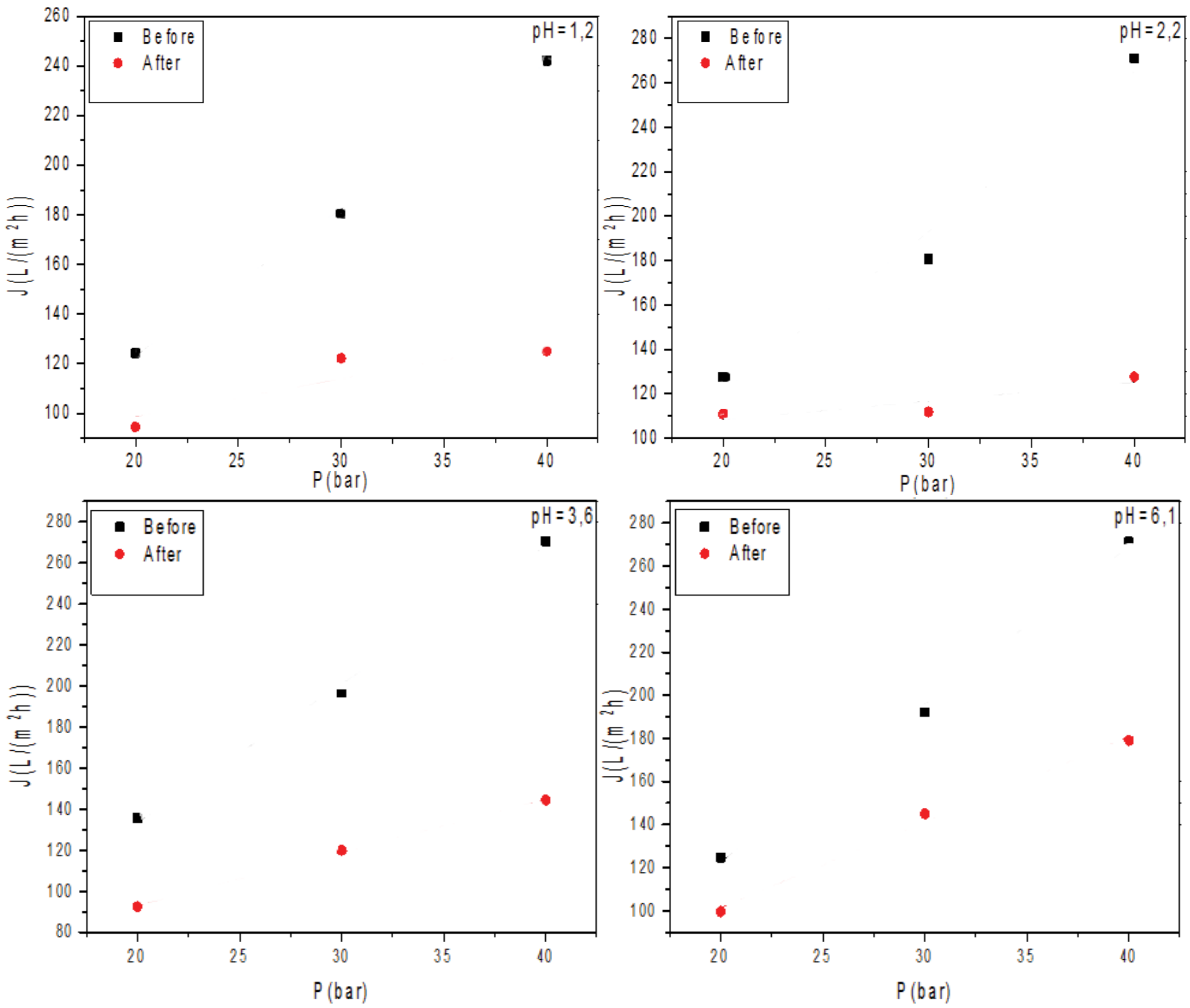

Fig. 1. Membrane permeability at different pH.

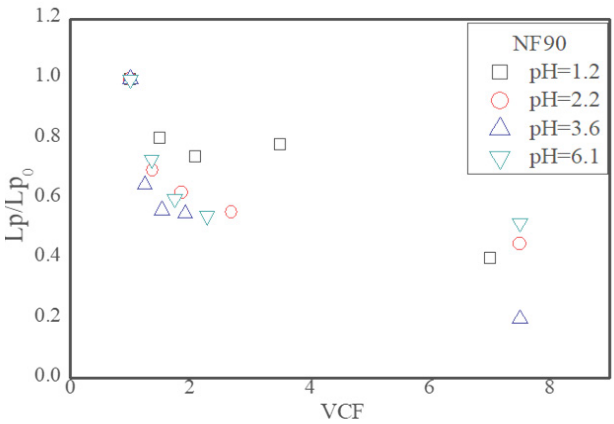

Fig. 2. Hydraulic permeabilities vs. volume concentration factors (VCFs) of a synthetic tannery effluent treated by NF90 at different pH values.

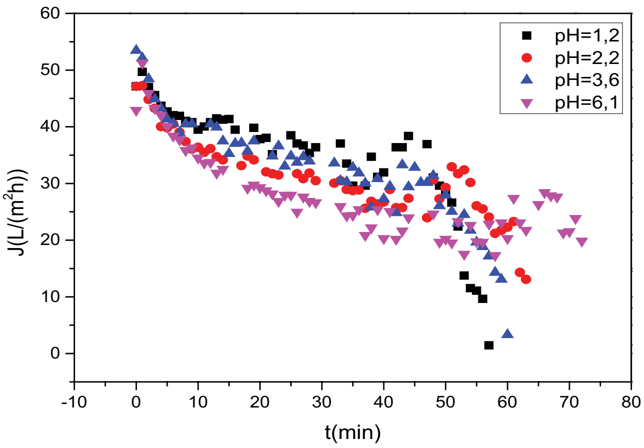

Fig. 3. Effluent fluxes during nanofiltration process.

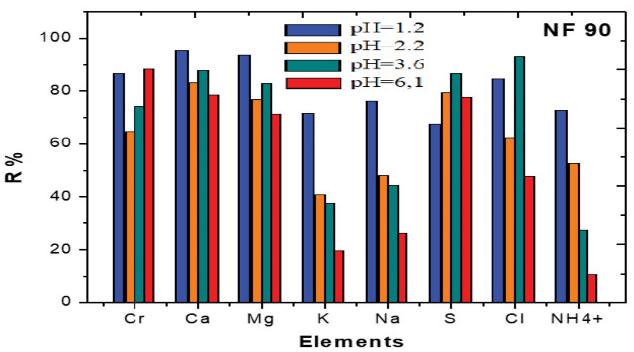

Fig. 4. Apparent rejections of the target compounds for the studied NF90 membrane.

have been due easier washing out of the retained deposited salts.

The effect of pH on membrane performance was also evaluated using the permeabilities Lp/Lp_0 (Fig. 2) at pH values between 1 and 6 through volumetric concentration factors VCF. The same behavior was observed except at pH = 1.2 which was a little high.

3.2. *Effluent fluxes through the nanofiltration membrane (NF90)*

Fig. 3 presents the variation of the effluent fluxes when the nanofiltration process was applied using NF90 membranes at different pH as a function of time. It can be seen that the fluxes had the same behavior by declining with time; it is usually associated with fouling and a decrease in usable TMP, which was due to increasing osmotic pressure in the retentate.

3.3. *Rejection after nanofiltration process*

The apparent residues of each compound (i.e., Cr, Ca, Mg, K, Na, S, Cl^- and NH_4^+) in the synthetic tannery effluents at a VCF of 8 in NF90 are shown in Fig. 4. As shown, the ions Na^+, K^+ and NH_4^+ were the least retained by the membranes, with apparent retention values below 30% at pH = 6.1 and reaching 70% at pH = 1.2. The lowest retention values may be due to the smaller size of these ions. The apparent rejection of Na^+ and K^+ appeared to decrease as the pH was varied from 1.2 to 6.1, suggesting an effect of positive charge in the rejection of cations. It was noted that the R% at pH = 1.2 was moderately high (66.65%).

The apparent rejections of the most toxic compound Cr exceed 86% at pH 1.2 and 6.1. Overall, these data are appropriate for Cr recovery and obtain permeate free of chromium, which can be directly discharged into the surrounding environment of the tannery plant according to the Algerian legislation [13], into the natural environment via Reghaia Lake.

4. Conclusions

Pressure driven processes are mature technologies with many successful applications in industrial water and wastewater treatment. The current work has shown that nanofiltration with NF90 membranes is a promising separation technique when applied to purification of tannery effluents containing chromium species. At pH = 1.2, NF90 membrane were able to retain ≥ 67% of the total mass of all metals present in the tannery effluent and 87.5% of chromium. This method of treating chrome tannery wastewater allows both for a reduction of chrome tannins in the tanning of skins and a reduction of salt consumption in the pickling of skins. An increase of pH solution and high concentration of salts near the membrane surface can cause fouling/scaling of the membrane.

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