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Pickling wastewater reclamation by means of nanofiltration

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Abstract

One of the main environmental problems of tannery industries is due to the liquid effluents generated in their processes. It contains high amounts of organic matter, sulphates and chlorides. In fact, the wastewater stream that comes from the pickling process can reach nearly 75 mS/cm of conductivity. The present work is focused on the reclamation of pickling wastewater after applying a nanofiltration (NF) process. The retentate stream, with a high sulphates concentration, can be reused in pickling baths whereas the permeate stream, with a high chlorides concentration, can be pumped to the soaking drums. In this work a detailed study of the use of the NF permeate stream in the soaking process and its effect on the quality of the final leather is performed. At the same time, a reduction of the salt content in the final tannery effluent is accomplished. NF experiments with pickling wastewater were performed in a laboratory plant equipped with a pressure vessel that contains one spiral wound membrane element (Desal-5 DK from GE-OSMONICS) with an effective membrane area of 2.51 m^2. The operating conditions of the experiments were a transmembrane pressure of 15 bar, 400 L h^{-1} of feed flow rate and a temperature of 25°C. It was studied the influence of the feed pH on the membrane performance (flux and salts rejection). The results showed that the maximum permeate flux was obtained at wastewater pH. The measured quality parameters of the final leathers soaked with NF permeates demonstrated that leathers did maintain the necessary quality for the final product.

Keywords: Tannery; Pickling wastewater; Nanofiltration; Reclamation wastewater

1. Introduction

Tannery industries require big quantities of water for their processes [1]. At the present, the water consumption to get finished leather from raw cattle hide can range between 20 and 30 L per kg of raw skin.

Pickling is one the tannery processes that precedes the tanning operation. In this step the hide is prepared for tanning. Thus, appropriate hide pH for tanning is set by the addition of acids,

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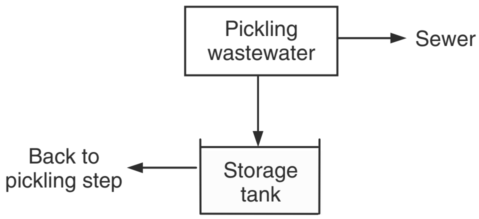

Fig. 1. Current pickling wastewater management.

mainly sulphuric acid. The addition of salts to the bath is necessary to avoid acidic hide swelling. After the process, a residual stream containing high salts concentrations is produced. Although most of the generated wastewater volume is reused in the pickling drum, an excess volume is produced, since the osmotic pressure leads to hide water loss. At the present, this excess wastewater volume is mixed with other residual streams from the tannery and discharged into the sewer. The Fig. 1 shows the current pickling wastewater management.

In this work the reclamation of pickling wastewater after applying a nanofiltration process is studied. According to the Fig. 2, the retentate stream, with a high salt concentration, could be reused in pickling baths whereas the permeate stream could be pumped to the soaking drums in the beamhouse operations. In this way, there would be no wastewater discharged from this process. It has to be mentioned that only a part of the total pickling effluent would be treated by NF. The treated volume would be calculated from a global mass balance so that the permeate volume could be equal to the excess one produced during the pickling operation.

The main objective of this work was a detailed study of the use of the NF permeate stream in the soaking process and its effect on the quality of the final leather. Besides, the NF membrane was tested at different feed pH to evaluate the influence of this parameter on membrane performance.

Nanofiltration has been studied as a process for treating tannery wastewater. Some authors propose individual treatments for each effluent generated. A. Cassano et al. applied NF membrane to the exhaust chromium tanning baths obtaining a concentrate solution that improved the characteristics of tanned and retanned skins compared to the skins treated with the traditional techniques [2]. M.V. Galiana-Aleixandre et al. studied the NF application for sulphate removal and water reuse of the pickling and tanning processes in a tannery. It was found that the recycling of the NF reject stream would avoid a pickling wastewater contribution to the sulphates load in the final effluent [3]. L.M. Ortega demonstrates the feasibility of using nanofiltration processes for the removal of chromium present in tannery effluents [4]. In former studies of this research group, B. Cuartas-Uribe et al. studied the influence of chlorides concentration using a simulated pickling wastewater in order to reuse the chloride concentrate stream (permeate) in the pickling process demonstrating that NF is a suitable technique to separate sulphates from a simulated pickling wastewater [5].

Several authors have studied the influence of pH on NF membrane performance. In this way, Szoke et al. worked on nanofiltration of mixtures

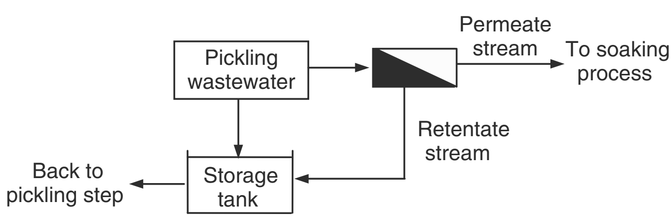

Fig. 2. Proposed pickling wastewater management.

of movalent and divalent ions at various pH (3–10). The authors detected a minimum chloride ions rejection at the isoelectric point of the membrane but they observed a lower sulphate rejection at pH values lower than the isoelectric point. In this case, the tested salt concentrations were lower than 600 mg/L [6].

Only few authors have reported about NF experiments with acidic conditions [7]. Qin et al. carried out experiments with town water solutions, NaCl and $NaNO_3$ after lowering the pH with HCl and HNO_3 [8]. The authors tested a Desal-5 membrane and concluded that feed pH had a substantial influence on ions rejection. The minimum ions rejection was reached very close to the membrane isoelectric point. Nevertheless, Hagmeyer and Gimbel obtained the minimum ions rejection at pH 5 with the same membrane (Desal-5 DK), one pH unit higher than the corresponding one to the isoelectric point. These authors worked with mixtures of NaCl and Na_2SO_4 solutions [9].

2. Materials and methods

2.1. Pickling wastewater characterization

The analysed parameters were conductivity, pH, sulphates, chlorides and organic matter concentration. Conductivity and pH were measured with CRISON instruments. Sulphates and chlorides were analysed according to the Standard Methods [10] and the organic matter concentration (in terms of COD) with Spectroquant Nova 60 from MERCK.

2.2. Nanofiltration experiments

2.2.1. Experimental set-up and membrane

Membrane experiments were performed in a pilot plant designed at the Polytechnic University of Valencia (Fig. 3) equipped with a spiral wound membrane module. The feed tank (60 L) included a stirrer to homogenize the feed solution and a level switch that enables continuous operation of the pilot plant. As temperature affects permeate flux, this variable was held constant by a cooling system. A 60 micron prefilter was placed upstream in order to reduce the particles pass into the system. Next to the feed pump exit there was a security valve that limited the maximum operating pressure in the pilot plant. Two manometers at each side of the membrane module were used to measure the transmembrane pressure. A flow meter was located in the retentate stream to measure the retentate

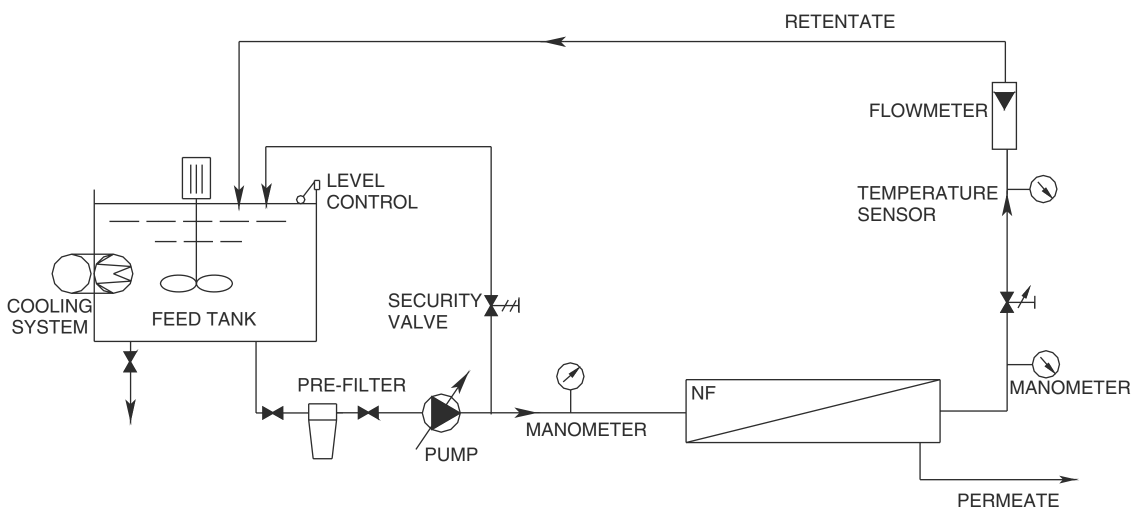

Fig. 3. Nanofiltration pilot plant diagram.

Table 1
Desal-5 DK membrane characteristics

Characteristics	
Material	Aromatic polyamide
Type	Thin film composite
Cut-off (g mol^{-1})	150–300
pH operating range	2–11
Maximum operation pressure (MPa)	3.45
Maximum temperature (°C)	50
Free chlorine tolerance (mg L^{-1})	<0.1
% R $MgSO_4$	98.5
Isoelectric point	4.0

volumetric flow rate. The valve located next to the flow meter was used to regulate the trans-membrane pressure.

The membrane tested was Desal-5 DK from GE-OSMONICS because it is a low fouling membrane and can operate at low pH values (see Table 1). It consists of a thin polyamide layer over a polysulphone microporous interlayer. On the bottom, a polyester non-woven layer supports the other layers. The total effective membrane area is 2.51 m^2. The main characteristics of this membrane are shown in Table 1.

2.2.2. Permeability test

First of all, the membrane permeability coefficient was determined. For that, experiments at different transmembrane pressures 1.0, 1.5 and 2.0 MPa were carried out using distilled water as feed. The feed flow rate was set at 400 L h^{-1} and the temperature was kept constant at 25°C.

2.2.3. Nanofiltration experiments for pickling wastewater

It was studied the influence of wastewater pH on the permeate flux, J_P (L m^{-2} h^{-1}), and apparent salt rejection coefficients, R_i (%) for sulphate and chloride ions. So, the wastewater pH (feed) was modified between 3 and 5 by addition of a NaOH solution. For each test, the operating conditions were the following: a transmembrane pressure of 1.5 MPa and a feed flow rate of 400 L h^{-1}. Also, the temperature was kept constant at 25°C. Both streams (permeate and retentate) were recycled back to the feed tank in order to keep a constant feed concentration.

Permeate fluxes and apparent salt rejection coefficients were measured when steady state was achieved. Apparent solute rejection coefficient (R_i) was calculated according to Eq. (1), where $C_{i,p}$ and $C_{i,m}$ are the solute concentrations in the permeate and feed streams, respectively.

$$R_i = \left(1 - \frac{C_{i,p}}{C_{i,m}}\right) \cdot 100 \qquad (1)$$

2.2.4. Membrane cleaning

After each run the membrane was cleaned. The procedure consisted in circulating chemical products solutions (acid and basic) in the system and then rinse it using distilled water without applying any pressure and increasing the feed flow rate in order to eliminate the organic and inorganic substances that clogged the membrane.

After that, the water permeability coefficient of the membrane was determined in order to check the membrane fouling state. The complete procedure is detailed in Table 2.

Table 2
Membrane cleaning procedure

Step	Time (min)	Solution
Rinsing	40	Distilled water
Basic cleaning	20	Sodium hydroxide at pH = 10
Rinsing	40	Distilled water
Acidic cleaning	20	Chlorhidric acid at pH = 4
Rinsing	40	Distilled water

Fig. 4. Laboratory drums for the skin samples soaking.

2.2.5. Soaking experiments

In a laboratory drums (Fig. 4), some small skin samples were soaked using the permeate volume collected. Previously, the permeate pH was adjusted between 7 and 9 with a NaOH solution.

Table 3 shows the quality parameters measured for the final leathers and their standard procedures. These parameters were measured for both the small samples leathers soaked with NF permeates and the leathers using the current soaked water.

Table 3
Leather quality parameters and their standard procedures

Parameter	Standard procedure
Thickness (mm)	UNE 59003
Water absorption (%)	UNE 59028
Time of water permeability (h)	UNE 59028
Grain stretch (mm)	UNE 59025
Migration, no rough	UNE-ISO 15701
Flex resistance dry (n° cycles)	UNE 59029
Flex resistance wet (n° cycles)	UNE 59029
Rub fastness dry (greyscale)	UNE-ISO 15701
Rub fastness wet (greyscale)	UNE-ISO 15701
Tear strength (N)	UNE 59024
Elongation (%)	UNE 59005
Tensile strength (N/qmm)	UNE 59005
pH-index	UNE-ISO 4045
Water vapour permeability, [mg/(cm^2 h)]	UNE 59009
Water vapour index (%)	UNE 59009

Table 4
Effluent characterization

Parameter	Pickling wastewater
Conductivity (mS cm^{-1})	70–75
pH	2.9–3.3
Sulphates (g L^{-1})	6.0–6.2
COD (g L^{-1})	5.0–5.5
Chlorides (g L^{-1})	58–70

3. Results

3.1. Pickling wastewater characterization

The main characteristics of the pickling wastewater are shown in Table 4.

It can be observed that the conductivity of this stream is very high. It is mainly due to the chlorides which are added as salts to avoid acidic hide swelling. The low pH value is caused by the acids, especially sulphuric acid, added during this step to prepare the hide for tanning.

3.2. Permeability coefficient

The membrane behaviour with the distilled water in terms of permeate flux at three different transmembrane pressures is depicted in Fig. 5.

As expected, the flux was proportional to the transmembrane pressure applied across the membrane (solution-diffusion model). The slope of the straight line corresponds with the permeability coefficient. For this membrane, the permeability coefficient value is 5.81 L m^{-2} h^{-1} bar^{-1}.

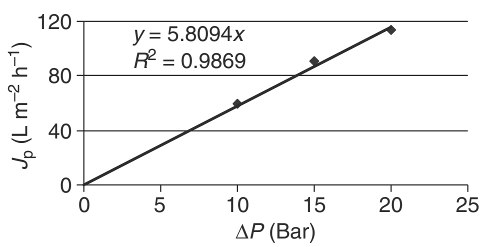

Fig. 5. Distilled water permeability for Desal-5 DK.

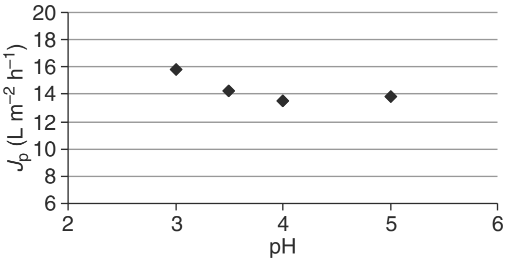

Fig. 6. Influence of pH on permeate flux.

3.3. Nanofiltration experiments for pickling wastewater

Fig. 6 shows the influence of wastewater pH on permeate flux. The depicted values show the permeate flux at the steady state conditions. For the pH values tested, the lowest flux was reached at the isoelectric point (pH = 4). For pH 3.5 and 5 the flux values were quite similar to pH = 4 and only varied between 3 and 5%, respectively. Only at pH = 3 the maximum flux was obtained and the difference between the rest flux values was close to 15%.

Fig. 7 shows the Pareto chart for the permeate flux variable. Pareto chart displays a frequency histogram where the length of each bar is proportional to the absolute value of the estimated effect of pH and chloride concentration on permeate flux. The cross line indicates the significance of each parameter.

It can be observed that pH did not affect the flux significantly, from a statistical point of view.

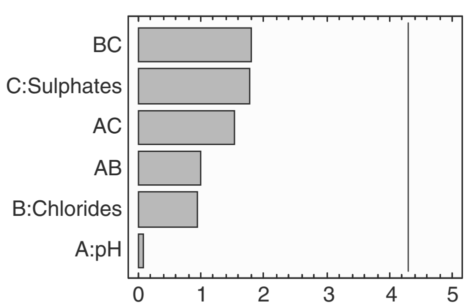

Fig. 7. Standardized Pareto chart for flux permeate.

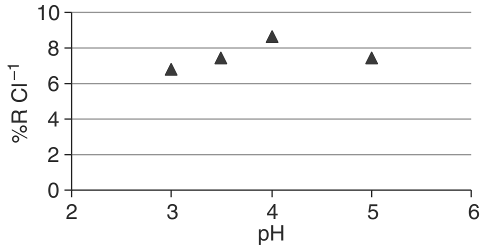

Fig. 8. pH influence on chloride rejection.

According to Figs. 6 and 7 flux permeate was not dependent on the pH values. This behaviour can be explained due to the high ionic strength of the wastewater.

Figs. 8 and 9 show the influence of pH on chloride and sulphate rejections, respectively. For all pH tested the rejections for chlorides were lower than 9% whereas for sulphates ions the rejections were higher than 97%.

Fig. 10 (a) and (b) shows the Pareto chart for the ion rejection variable for chlorides and sulphates, respectively. It can be observed that pH did not affect the ion rejection significantly, from a statistical point of view.

The Donnan effect plays an important role in retaining salts in the nanofiltration process but its effect decreases with increasing ionic strength of the feed stream to the membrane. Thus, the high chlorides concentration in the feed contributes to decrease the rejection values.

Related to the organic matter, its removal was in all cases around 40%, what means that the pH did not affect the COD removal.

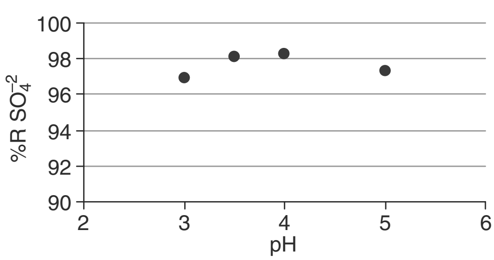

Fig. 9. pH influence on sulphates rejection.

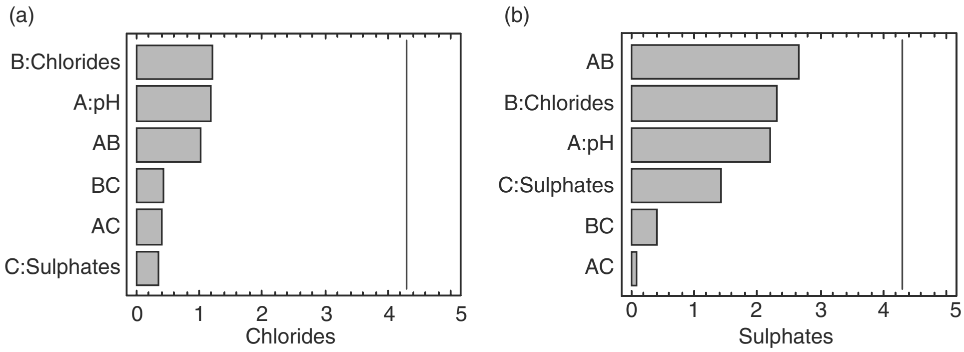

Fig. 10. Standardized Pareto chart for ions rejection.

3.4. Cleaning process

The loss in the permeability coefficient due to the membrane fouling made necessary a cleaning after each run. The membrane was cleaning according to the procedure explained in section 2.2.4. After the cleaning process the permeability coefficient was 4.91 L m^{-2} h^{-1} bar^{-1}. This permeability coefficient reduction suggested that the membrane achieved an irreversible fouling.

3.5. Soaking experiments

Table 5 shows the required quality values for each parameter and the measured values of some finished leather samples. The leather sample A was treated in the first soaking step using the current soaking water whereas the leather samples B, C and D were soaking in the same step using the NF permeate.

Results of the Table 5 show that the measured parameter values for all samples were very

Table 5
Measurements of leather quality parameters

Parameter	Control value	Sample A	Sample B	Sample C	Sample D
Thickness (mm)	1.3	1.3	1.3	1.3	1.3
Water absorption (%)	Max 15	10	11.2	9.1	12
Time of water permeability (h)	Min 3	>3	>3	>3	>3
Grain stretch (mm)	>8.0	9.2	8.1	8.5	8.9
Migration (no rough)	Min 4	4	4	4	4
Flex resistance dry (n° cycles)	50,000	OK	OK	OK	OK
Flex resistance wet (n° cycles)	10,000	OK	OK	OK	OK
Rub fastness dry (greyscale)	>4	4	4	4	4
Rub fastness wet (greyscale)	>3–4	4	4	4	4
Tear strength (N)	≥50	80	75	72	70
Elongation (%)	38–70	45	48	50	60
Tensile strength (N/qmm)	>18	20	22	25	26
pH-index	3.5–6.5	3.8	3.9	4	3.9
Water vapour permeability [mg/(cm^2 h)]	Min 5	6	5.5	5.6	5.5
Water vapour index (%)	Min 15	20	18	19	18

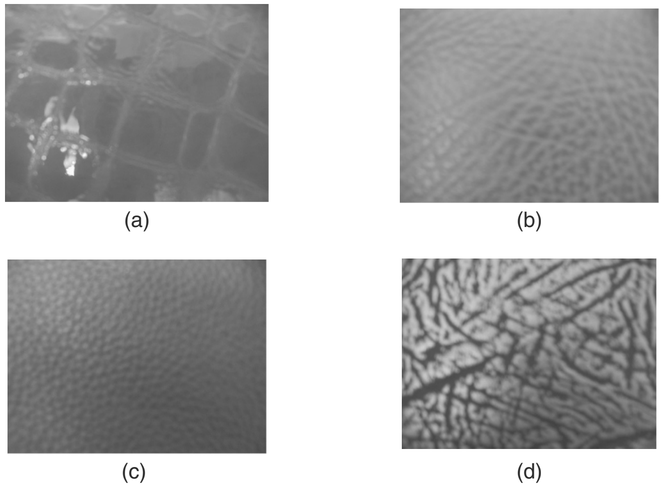

Fig. 11. (a) Sample A, (b) Sample B, (c) Sample C, (d) Sample D.

similar. Thus, the NF permeate use for the first soaking step led to leather with the necessary quality for the final product.

In the Fig. 11 (a)–(d) some of the final leather samples can be observed. No differences between samples A, B, C and D were found.

4. Conclusions

According to the results, the influence of the tested pH was not significant for both flux permeate and ion rejections. For that, it is considered that the optimal operating pH for treating pickling wastewater by nanofiltration is the wastewater pH. In addition, at this pH value it is not necessary to add chemical products (to modify the pH) that would increase the final operation cost.

The application of the NF process in this case demonstrated the feasibility of using both permeate and retentate streams. The NF permeate could be applied to the first soaking process obtaining a good final leather quality. The retentate stream, with high salts content, is recycled back to the pickling storage tank in order to be reused in pickling process.

Further pilot plant experiments should be performed in order to evaluate the membrane fouling and its behaviour when the feed concentration increases.

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