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Reuse of tannery wastewaters by combination of ultrafiltration and reverse osmosis after a conventional physical-chemical treatment

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Abstract

Due to the high conductivity of the global wastewater from a tannery industry, wastewater reuse is only possible if a reverse osmosis process is implemented in the wastewater treatment. The supernatant of a physical-chemical treatment is still very polluted, containing high COD values between 3000 mg/l and 4000 mg/l and conductivities of nearly 20 ms/cm. In this work, a combination of filtration, ultrafiltration and reverse osmosis is evaluated as treatment for the physical-chemically treated wastewater. Filtration was carried out using microfilters as a previous stage to ultrafiltration process. Ultrafiltration tests were performed in a laboratory plant. Organic membranes from Orelis with different cut-offs were tested to optimize the rejection and the permeate flux. Finally, the reverse osmosis step was carried out using an ESPA-1 membrane from Hydranautics. Results showed high COD values in ultrafiltration permeates (between 2000 and 3000 mg/l). A polyethersulfone membrane with cut-off of 30 kD was chosen for the pre-treatment of the reverse osmosis membrane. Permeate fluxes of the reverse osmosis membrane reached 40 l/(m^{2}h) at 30 bar. Though membrane fouling was not observed during RO experiments, an industrial scale plant should pay special attention to a probable flux decrease due to the scaling if a high conversion is aimed.

Keywords: Ultrafiltration, Wastewater reuse, Reverse osmosis, Tannery wastewater

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1. Introduction

Industrial wastewater reuse is becoming nearly a duty to contribute to water consumption reduction, due to the water scarcity in Mediterranean areas in Spain. Besides, the legal standards are becoming increasingly stringent. Thus, those industries with a great water and chemicals consumption are required to exhaustive wastewater treatment and water reuse.

Tanning industries use big quantities of water, approximately between 15 and 20 m^3 per tonne of raw skin. Their effluents are characterized by high COD, BOD and conductivity values. In Table 1, characteristics of the raw wastewater from a tannery that includes beamhouse operations, chrome tanning, dyeing and finishing of cattle hides are detailed. This characterization has been carried out after sulphide ions oxidation in the alkaline wastewaters (those coming from beamhouse operations).

As it can be observed, tannery wastewaters present COD and SS values approximately five times higher than municipal wastewaters and high salt concentrations similar to brackish waters.

In order to minimize the pollution of these wastewaters, some authors propose the adoption of integrated cleaner technologies [1] and the treatment, mainly by means of membrane technologies, of the waste streams from particular processes. It would drive to both water reuse and removal of pollutants that would not be included in the global wastewaters. In this way, Cassano and Molinari [2,3] studied experimentally the treatment of the unhairing waste stream (to separate by UF a protein concentrated stream from a permeate stream with sulphide ions and lime to be recycled to the unhairing drum), pickling waste stream (to reuse the pickling solution by means of a RO system) and chromium tanning effluent (to reuse water and chemicals by combining UF and RO). Galiana et al. evaluated the use of nanofiltration for pickling and tanning effluents in order to minimize the sulphate ions concentration in the global wastewaters [4]. It can be highlighted that chrome recycling by membranes is the most studied process to save water and chemicals in a tannery [5,6,7]

Table 1
Raw wastewater characterization from a tannery with beamhouse operations, and chrome tanning that produces leather from cattle hides

Parameter	Tannery effluent
COD, mg/l	5000–5500
BOD_5, mg/l	3000–3500
Suspended Solids (SS), mg/l	2500–3000
Cr^{3+}, mg/l	80–100
SO_4^{2-}, mg/l	1800–2000
Cl^-, mg/l	5000–6000
pH	8–9
Conductivity, ms/cm	10–12

However, the high polluted partial waste streams make difficult the membrane operation [8]. In addition; the reuse, recycling or valorisation of only one partial stream is not sufficient for the water reuse after a conventional treatment of global wastewaters.

Other authors suggest an integrated treatment of the global effluent for water reuse. The first step is a physical-chemical treatment of the wastewater in order to reduce the suspended solids considerably. This entails an important COD and BOD_5 reduction too. However, conductivity remains practically constant and not even a biological treatment could reduce it.

Only a few processes are able to separate salts from wastewater. Reverse osmosis will be more feasible than evaporation, ion exchange or nanofiltration, because of the conductivity value and the high chloride ion concentration of the wastewater.

Suthanthararajan et al. [9] propose an exhaustive tertiary treatment for the biologically treated wastewater from a tanning industry consisting of a sand filter, a photochemical oxidation step, a softener, chemicals dosage (acid, anti-oxidant and anti-scaling), cartridge filter, NF and RO. This proposed treatment showed obviously excellent results but from an economical point of view these costs can not been assumed by most of tanning industries.

On the other hand, the operation of a biological reactor for tannery wastewaters is sometimes difficult due to the high conductivity and the presence of chromium and organic substances coming from finishing operations, which can damage the reactor biomass. In this way, in the present work a tannery wastewater treatment consisting of a physical-chemical process (carried out at the factory), filtration, ultrafiltration and reverse osmosis is evaluated for water reuse (Fig. 1).

It is worth to mention that the combination of physical-chemical processes and membrane techniques has been proposed by some authors for other industrial wastewaters such as the textile wastewaters [10] and meat industry wastewaters [11]. They use a physical-chemical process in combination with NF in the first application and flotation, filtration, UF and RO in the second one.

2. Material and methods

This work was divided into three stages: wastewater characterization, UF and RO experiments.

2.1. Wastewater characterization

Integrated wastewater samples were taken from the tannery plant after being treated with a physical-chemical process. The main analysed parameters were COD, turbidity, pH, conductivity, total solids (TS), suspended solids (SS), sulphates, chlorides and colour. COD, sulphates and chlorides were determined with a Spectroquant Nova 60 from Merck, turbidity with D-112 apparatus from DINKO and both conductivity and pH were measured with CRISON instruments. Total solids and suspended solids were determined according to Standard Methods [12]. Colour was calculated with the Spectral Absorption Coefficients at three different wave lengths (436, 525 y 620 nm) according to Krull procedure et al. [13] using a UV-Visible spectrophotometer HP 8453.

2.2. UF experiments

Tannery effluent was treated physical-chemically in the industry and filtered at the laboratory with a 20 μm cartridge filter previously to UF experiments. They were performed in a laboratory plant. The scheme of the plant can be observed in Fig. 2. UF module was plane with an effective membrane area of 0.009 m^2. Four polyetersulphone (PES) membranes Iris 3029 from Rodia-Orelis of different cut-off (3, 10, 30 y 100 kDa) were tested at different transmembrane

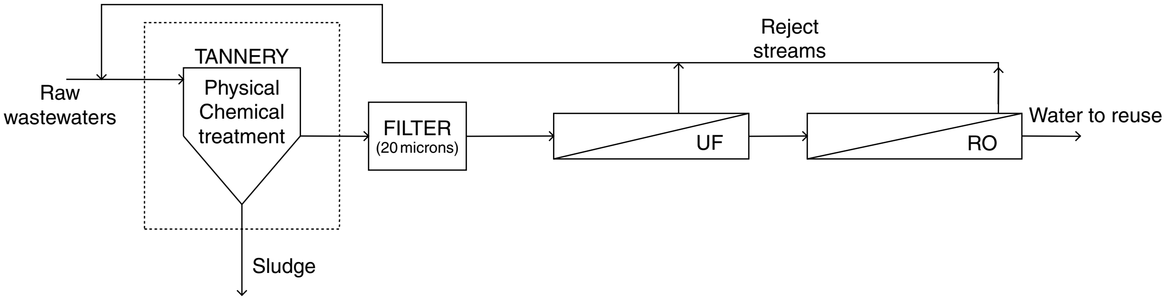
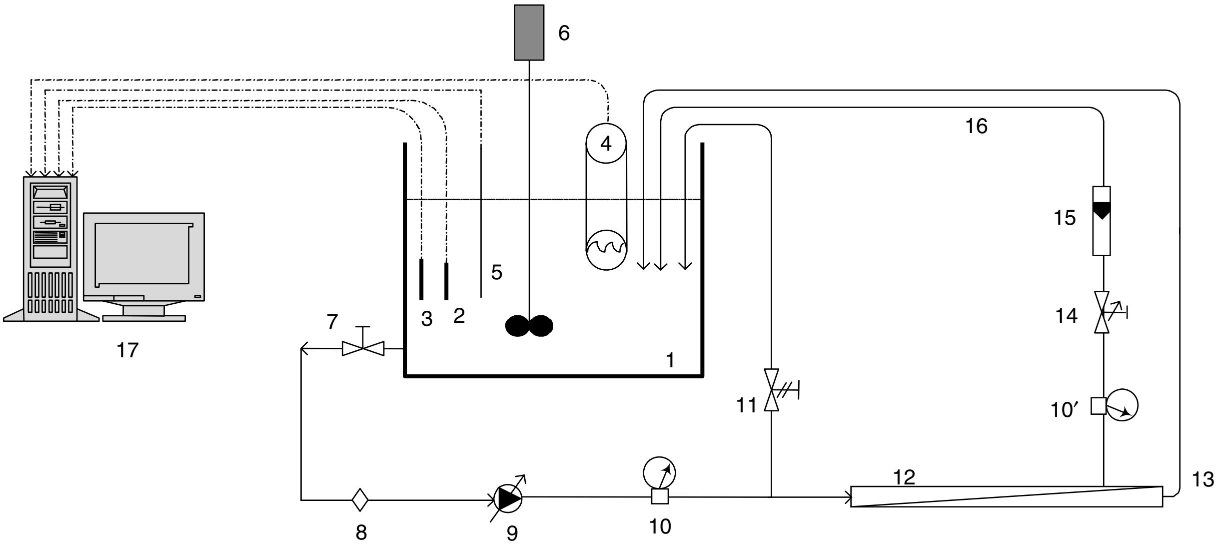


Fig. 1. Scheme of the proposed treatment.



1. Feed tank
2. Thermometer
3. Conductimeter
4. Heat exchanger
5. Level meter
6. Stirring
7. Valve
8. Filtration system 5 μm
9. Pressure pump
10-10′. Manometer
11. Security valve
12. NF module
13. Permeate stream
14. Regulation valve
15. Speed control
16. Rejection stream
17. PC

Fig. 2. UF pilot plant scheme.

pressures (1, 2 and 3 bar). For all tests the cross-flow velocity was 1.5 m/s and the temperature was held at 25°C. Permeate and reject streams were recycled to the feeding tank. Periodically permeate flux (J_P), conductivity and pH were determined. In addition, at the end of each experiment, COD, colour, suspended solids and turbidity were analysed.

2.3 RO experiments

Reverse osmosis experiments were performed in another laboratory plant equipped with a pressure vessel that contains one spiral wounded membrane element. The membrane tested was ESPA-1 from Hydranautics with an effective membrane area of 2.6 m^2. The operating conditions were three different transmembrane pressures (20, 25 and 30 bar), a feed flow rate of 400 l/h and a temperature of 25 °C. The laboratory plant can be observed in Fig. 3. Permeate and reject streams were recycled to the feeding tank. Permeate flux, TS, COD and conductivity were measured periodically.

3. Results and discussion

3.1. Wastewater characterization

Table 2 shows the characterization of the physical-chemically treated wastewater from the tannery. It can be observed that the COD and salts concentrations are considerably higher than those measured for a municipal wastewater.

Fig. 3. Photograph of the laboratory plant.

Table 2
Characterization of the physical-chemically treated wastewater from the tannery

Parameter	Feed stream
pH	7–9
Conductivity, ms/cm	10–13
COD, mg/l	2700–3600
Sulphates, mg/l	1300–2400
Chlorides, mg/l	2500–3000
TS, mg/l	11000–25000
SS, mg/l	500–800
Colour	0.9–2.0
Turbidity, NTU	65–95

3.2. UF experiments

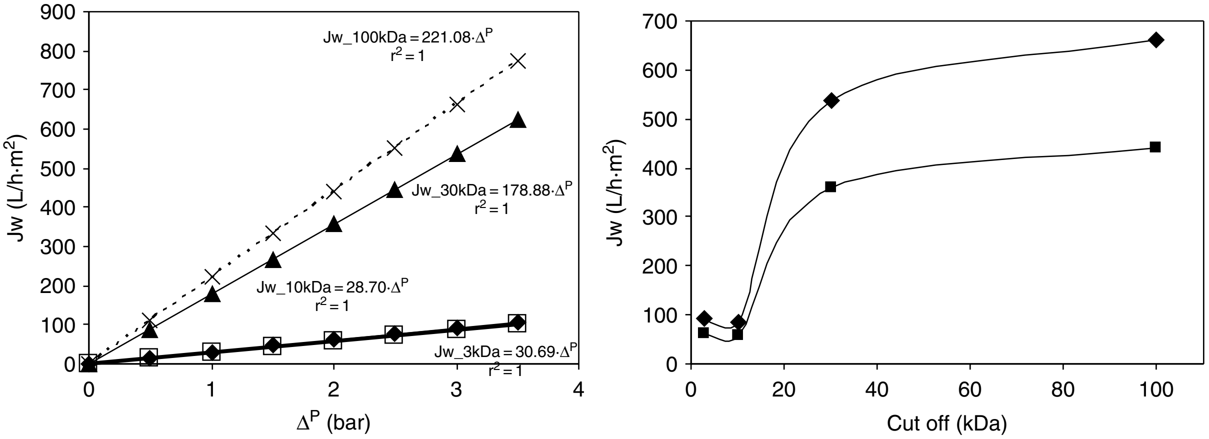
In the following paragraphs, results of UF experiments carried out with distilled water and tannery wastewater are shown.

3.2.1. Distilled water experiments Fig. 4a shows the measured fluxes at different transmembrane pressures for each membrane. As expected, the higher transmembrane pressure, the higher permeates fluxes were achieved. However, in Fig. 4b, it can be highlighted that given a transmembrane pressure, flux sharply increased from 10 to 30 kDa deviating from a lineal flux evolution with the membrane cut-off. The same evolution was observed for all transmembrane pressure tested.

3.2.2. Tannery wastewater experiments The best results in terms of flux and rejection were obtained at $\Delta P = 2$ bar and a cross-flow velocity of 1.5 m/s. Table 3 shows the characteristics of feed and permeate streams at these operating conditions. For all membranes, it can be observed an appreciable turbidity and colour drop after the UF process. Nevertheless, COD values hardly decreased (removal efficiencies were only around 15%). This result can be explained since COD was mainly soluble consisting in hydrolyzed proteins of low molecular weights. The presence of inorganic reduction agents could contribute to the high COD values too.

According to the results, the influence of the membrane cut-off on the COD separation was almost negligible. This fact determines the selection of a low fouling membrane for the RO step.

The variation of the fluxes with the operating time is shown in Fig. 5a. Fluxes were very low in comparison with those obtained with distilled water (Fig. 5b). While the permeate fluxes of the membranes of 3 and 10 kDa were very low from the beginning of the experiments (about 20 L/(m^2·h)), the



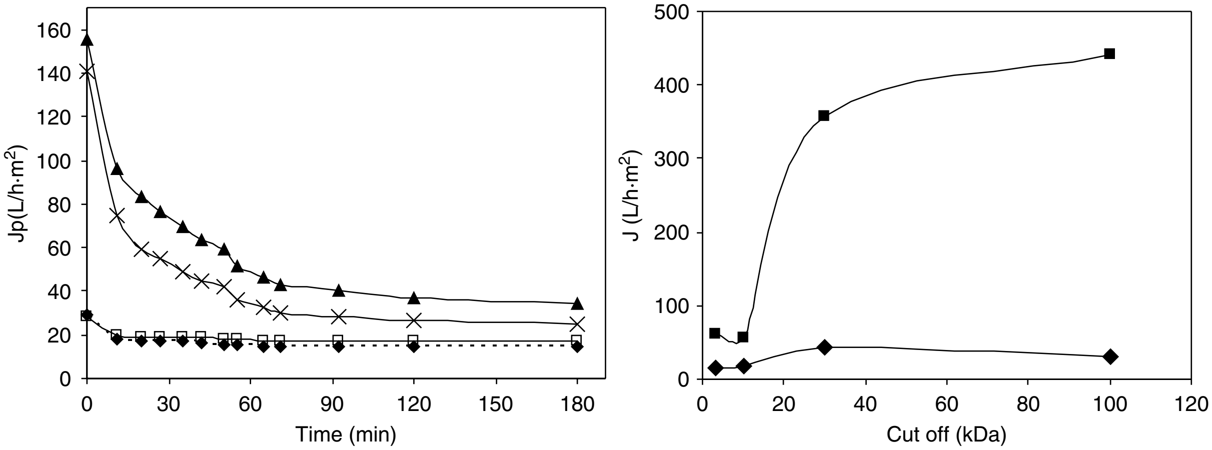
(a) ×100 kDa; ▲ 30 kDa; ☐ 10 kDa; ♦ 3 kDa.

(b) ♦ ΔP = 3 bar; ■ ΔP = 2 bar

Fig. 4. Distilled water fluxes at 25°C for UF membranes.

Table 3
Feed and permeate stream characteristics in UF experiments ($\Delta P = 2$ bar, pH = 8.10, v = 1.5 m/s and T = 25°C)

Sample	Conductivity, ms/cm	Colour	COD, mg/l	Turbidity, NTU
Feed	12.07	0.72	2531	53.22
Permeate 100 kDa	11.92	0.10	2259	5.70
Permeate 30 kDa	11.97	0.10	2133	6.82
Permeate 10 kDa	12.03	0.18	2222	8.02
Permeate 3 kDa	11.89	0.12	2197	6.30



(a) ×100 kDa; ▲ 30 kDa; ☐ 10 kDa; ♦ 3 kDa.

(b) ■ Distilled water; ♦ Tannery wastewater.

Fig. 5. Evolution of the permeate flux with the operating time.

Table 4
Feed and permeate characteristics in RO experiments (pH = 8.2 ΔP = 2 bar, v = 1.5 m/s)

Sample	Conductivity, ms/cm	TS, mg/l	COD, mg/l
Feed (30 kD)	12.00	8984	2210
Permeate 20 bar	0.17	100	41
Permeate 25 bar	0.19	112	49
Permeate 30 bar	0.19	108	50

permeate fluxes of 30 and 100 kDa membranes were high at the beginning and decreased very quickly, reaching a practically constant flux after 1 h.

The highest flux was achieved by the 30 kDa membrane. This flux was even slightly higher than that obtained with the 100 kDa. This behaviour can be explained by the effect of the solutes molecular size on the membrane fouling. The 100 kDa membrane rejected peptidic molecules that clogged the membrane pores, increasing the membrane fouling.

3.4. RO experiments

Table 4 shows the characterization of the feed and permeates streams for the RO experiments.

As expected, salts and COD rejections were higher than 98%. Permeates can be reused in the tannery, even in those processes that require the lowest salt concentrations like the dyeing one.

The evolution of the permeate fluxes with the time at three different transmembrane pressure in the RO tests can be observed in Fig. 6. For the three transmembrane pressures, the steady state was reached after a brief period of time, remaining the flux practically constant during the rest of the experiment. Since only a membrane element was used (the recovery was between 10 and 15%), the solutes concentration was not high enough to produce scaling and fouling problems in the experiments. At 30 bar, the permeate flux was nearly 40 l/(m^{2}h) at the steady state. Although, this value was considered appropriate, longer experiments should be carried out to study the membrane behaviour.

4. Conclusions

Due to the high chloride concentration of the tannery wastewater, a reverse osmosis process is necessary for water reuse in the factory. The high organic matter content in the tannery effluent requires an exhaustive pre-treatment before a RO process.

The combination of a physical-chemical treatment with ultrafiltration was not efficient to remove the soluble COD of the waste-

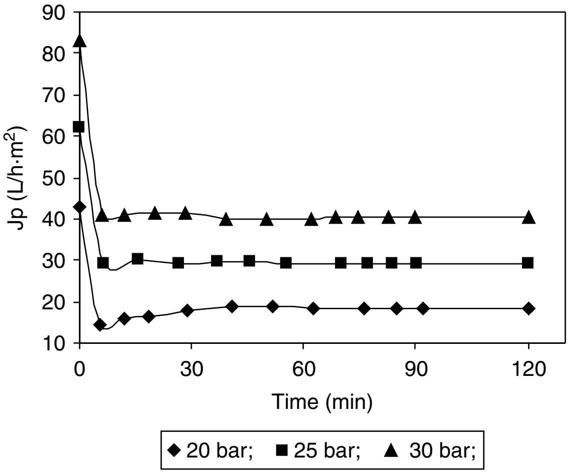


Fig. 6. Evolution of the permeate fluxes with the operating time at three different transmembrane pressure in RO tests.

water, remaining concentrations higher than 2000 mg/l in all tested UF membranes (3, 10, 30 and 100 kDa). Thus, the selection of the UF membrane was based on the permeate flux rate. For 100 kDa membrane, a higher fouling was observed due to the size of peptidic molecules in the wastewater that clogged the membrane pores.

As expected, the quality of the RO permeate was high enough even for its reuse in the tannery processes that require the lowest conductivity. In spite of the organic matter content of the UF permeates, no fouling problems were observed in the period study. However, longer experiments should be performed.

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