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Removal of vegetable tannins to recover water in the leather industry by ultrafiltration polymeric membranes

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A B S T R A C T

The leather tanning industry consumes large amounts of water and produces, consequently, significant volumes of wastewater with high concentration of chemicals and organic matter. One of the main chemicals present in effluents is the vegetable tannin, which causes a severe environmental impact. With the aim of predicting the performance in chemicals separation of two ultrafiltration (UF) polymeric membranes (OT050 and GR60PP) for potential use in the purification of the waste stream of vegetable tanning liquors, a synthetic wastewater was prepared. Trials were carried out at laboratory scale using a flat cell with an effective area of 0.004 m^2. The effect of transmembrane pressure in the permeate flux was studied. Flux decline, fouling resistance and fouling index of the membranes were analyzed. The efficiency of different membranes was assessed using the rejection coefficient for tannins, non-tannins and total solids. Analysis of the wastewater treated by UF showed 83% of tannin retention and a recovery of the water flux after cleaning the membrane GR60PP with water of 41–45%. The rejection coefficient observed for the GR60PP membrane was higher than for the OT050. There are no previous studies related to the removal of vegetable tannins in exhausted vegetable tanning bath by using UF polymeric membranes. This study sets a precedent because the results obtained are very promising regarding permeate flux and rejection observed.

Keywords: Tannery wastewater; Ultrafiltration; Water reuse; Fouling; Resistance

1. Introduction

The leather tanning industry consumes in average between 25 and 80 m^3 of water per ton of processed raw material and produces, consequently, large amounts of wastewater. This industry is characterized as being one of the most polluting industries, which can be mainly attributed to the overuse of chemicals and organic substances resulting from the processing of skins (Cassano et al., 2001). The sole tanning liquor, after its proper working cycle, represents the largest volume of wastewater discharge to the tannery global effluent.

Tannins (Quebracho, Mimosa, Almond, Tara) are the chemicals primarily used during the vegetable tanning stage. These are polyphenolic compounds with high molecular weight, from 500 to 20,000 Da (Cassano et al., 2003; Lofrano et al., 2007). The presence of tannins in wastewater can cause many problems associated with environmental pollution, effluent treatment and especially in the primary treatment (Cassano et al., 2003). This is because the efficiency of the flocculation/coagulation stage decreases due to the presence of vegetable tannins, are highly soluble in water (Scholz and Lucas, 2003) an extra high dose of metal coagulant is needed for the efficient settling, which is accompanied by the introduction of metal pollutants. On the other hand, as tannins inhibit the growth of microorganisms becoming toxic to activated sludge, the biodegradability of wastewater from tanneries depends directly on tannin concentration (He et al., 2007). Thus, it is necessary to study new methods to reduce the amount of tannin present into the wastewater.

At the present time, the possible methods for tannin removal from effluents are: chemical oxidation, flocculation, adsorption, ion exchange, ozonolysis and biological techniques (Anirudhan and Ramachandran, 2006; Liu et al., 2010; Walker and Weatherley, 1998).

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All of them are highly developed though they involve the addition of chemical reagents, high costs and cause an environmental impact. A possible alternative is the implementation of membrane technology. In recent years, processes with membranes have been increasingly used in several industrial applications and in wastewater treatment (Conidi et al., 2011; Huang et al., 2011; Mousa, 2007). In comparison with other concentration and separation systems, the main advantage of the membrane processes is that the concentration and separation is achieved in most cases without a state change and the use of chemicals or thermal energy (Baker, 2004; Bergamasco et al., 2011), and for all these reasons the membrane technology is friendly to the environment.

By reviewing most of the previous relevant literature, we can affirm that there are very few references in the treatment of exhausted vegetable tanning liquors using ultrafiltration (UF). Permeate reuse was reported in a study conducted on a pilot plant using UF tubular inorganic membranes, while the retentate was not reused because of its high concentration of insolubles (Cassano et al., 2001). It is important to emphasize that inorganic membranes are still under development and are more expensive than the polymeric ones. Other authors reported good results when they used nanofiltration (NF) for the treatment of these effluents (Aloy and Vulliermet, 1998; Cassano et al., 2003; Molinari et al., 2004), although the operating conditions were more extreme. There are also reports regarding biological treatments with tannin effluents using membrane bioreactors (MBR) (Munz et al., 2009). At present, it has been reported that the use of membrane technology was successful for the treatment of effluents generated at different stages of the leather industry. As example, UF was used for the unhairing, liming and dyeing stages (Alves and Silva, 2006; Brites Alves and Norberta de Pinho, 2000; Mendoza-Roca et al., 2010), whereas microfiltration (MF) was used for the delimiting – bating stage (Gallego-Molina et al., 2012).

Studies that use membrane technology in the leather industry reported major fouling problems due to the high concentration of organic matter in the effluents (Gallego-Molina et al., 2012; Mendoza-Roca et al., 2010). Some authors proposed to recover the permeate flux by implementing cleaning methods whether chemical or at high pressures, obtaining good results (Fababuj-Roger et al., 2007; Galiana-Aleixandre et al., 2011; Lee et al., 2009; Mendoza-Roca et al., 2010; Ortega et al., 2005).

The aim of this study was to evaluate the performance of different commercial polymeric UF membranes, in terms of the operating conditions, fouling, and the selectivity of the UF process, to treat an exhausted synthetic vegetable tanning liquor from the leather industry. The importance of this study is set precedents in regard to removing tannins using UF polymeric membranes, and also it represents a preliminary study for future researches.

2. Materials and methods

2.1. Characteristics of synthetic wastewater

A waste liquid stream from exhausted vegetable tanning bath was sampled, monthly for 1 year, in order to evaluate the efficiency of UF membranes in the removal and recovery of tannin. The effluent from a vegetable tanning industry processing bovine hides located in the Province of Salta, Argentina, was selected.

The physicochemical characterization was carried out by the determination of density using a hydrometer (FITE S.A., Argentina), pH at 25 °C by an Altronix pH-meter TPX1, conductivity was measured at 25 °C with a Parsec conductimeter, total and insoluble solids according to the standard methods (APHA-AWWA-WEF, 1882), tannins (T) and non-tannins (NT) by the Filter Method. Briefly, this method involves the passage of tannin solution through powder of pre-chromed skin or Freiberg powder. The determination of the concentration of tannins and non-tannins are calculated gravimetrically. This method has a high sensitivity and is widely used in the tanning industry. All these analyses were performed in our laboratory and in the lab of ARLEI S.A. Tannery, Salta, Argentina.

Table 1 – Physicochemical characterization of real and synthetic wastewater.

Parameter	Real	Synthetic
Density (°Bè)	4.00 ± 0.03	4.43
pH	3.18 ± 0.05	4.93
Total solids (% w/w)	6.07 ± 0.23	3.04
Insoluble solids (% w/w)	0.10 ± 0.02	0.00
Tannins (% w/w)	3.93 ± 0.35	2.48
Non-tannins (% w/w)	2.13 ± 0.15	0.56
T/NT	1.84 ± 0.06	4.43
Fat (% w/w)	0.14 ± 0.01	–
Conductivity (μS/cm)	25,200 ± 0.31	24,900

According to the characteristics of the real effluents, synthetic wastewater was prepared using leather tanning agents from quebracho colorado of Unitán S.A. company (UNITAN:website, 2014), which has a concentration of 72 ± 2% (w/w) of tannin, 9% (w/w) moisture, and impurities which are identified as NT. Tap water (electrical conductivity 362 μS/cm; pH 7.3) was used for the preparation of the synthetic wastewater, which is common practice in tannery industry. The wastewater was used for all the studies that were carried out (Table 1).

2.2. Membranes and laboratory scale filtration system

Two different types of UF commercial membranes were used. The characteristics of these membranes, according to the manufacturer are listed in Table 2.

The water contact angle was measured at room temperature using a goniometer (Standard Goniometer with DRO Pimage Standard, model 200-00, Ramé-Hart Instrument Co.). The porosity was determined according to Chakrabarty et al. (2008). The cross-sectional morphologies of membranes were examined using scanning electron microscopy (SEM), JEOL equipment, model JSM-6480 LV. The samples were fractured in liquid nitrogen and sputter-coated with gold.

The experiments were performed in a laboratory-scale cross-flow membrane system (Fig. 1) using synthetic wastewater as a model for tanning effluent. The operation time was 250 min. The feed solution (5 L) was pumped to the UF cell by a piston pump (Interpump Fe-5102 Model) and the operating pressure was controlled by regulating valve. Assays were carried out at two different transmembrane pressures (TMP): 2.5 bar and 5 bar. The UF cell used was rectangular and flat, made of stainless steel, with membrane effective surface of 0.004 m^2. The retentate stream was recycled to the feed tank, while the permeate stream was collected separately and not recirculated to the storage vessel. The UF was carried out until the retentate volume was minimum and the volume of accumulated permeate was close to 200 mL (the volume reduction factor was closed to one). The sampling was conducted in the feed tank and permeate flux stream.

Prior to tests, the membranes were washed with distilled water and compacted by filtering tap water, under a pressure of 5.5 bar, until a constant flux was achieved. The compaction step allows to obtain a stable membrane structure.

After the experiment with the synthetic wastewater, the fouled membrane was cleaned by rinsing with tap water at atmospheric pressure and room temperature for 1 h. That is, a

Table 2 – Characteristics of UF membranes.

Specification	GR60PP	OT050
Manufacturer	Danish Separation Systems	Pall Life Sciences
Material	Polysulfone	Modified Polyethersulfone
Thickness	185 ± 0.74 μm	104 ± 0.56 μm
Molecular weight cut-off	25 kDa	50 kDa
Water contact angle	67.4 ± 0.8	68.9 ± 0.1
Porosity	25.3 ± 0.49%	32.1 ± 1.02%
Operating pressure	<8 bar	<6 bar
Operating pH	2–12	1–14
Maximum temperature	75 °C	55 °C

backwashing is not used and no chemicals were added. Then, the water flux was measured under the same operating conditions (T = 25 °C; feed flow rate = 48 L/h; TMP = 2.5 bar and 5 bar) to determine the hydraulic permeability (L_p).

2.3. Analysis of resistances

The clean tap water flux was determined in stable conditions of temperature (25 °C) and feed flow rate of 48 L/h at different values of transmembrane pressure (TMP). The L_p of the membrane was determined by measuring the water flux (J_w) at different TMP. The water flux was calculated using the following equation:

$$J_w = \frac{\Delta P}{\mu R_m} \quad (1)$$

where J_w is the clean water flux (m^3/m^2 s), ΔP is the transmembrane pressure (Pa), μ is the viscosity of water (Pa s) and R_m is the intrinsic hydraulic resistance of the clean membrane (m^{-1}).

Subsequently, the performance of the membrane was assessed with the synthetic wastewater at 25 °C. The fouling of the membranes was determined by the resistance in series model (Dal-Cin et al., 1996; Fersi et al., 2009; Muthukumaran et al., 2011). The UF flux is expressed in terms of the transmembrane pressure difference (ΔP) and the total fouling resistance, according to:

$$J_p = \frac{\Delta P}{\mu R_t} \quad (2)$$

where J_p is the permeate flux with synthetic wastewater (m^3/m^2 s) and R_t is the total fouling resistance (m^{-1}), which includes three resistances:

$$R_t = R_m + R_{ef} + R_{if} \quad (3)$$

R_m is the intrinsic resistance of the membrane, R_{ef} is the reversible fouling resistance resulting from concentration polarization and the formation of the cake layer, and R_{if} is the irreversible fouling resistance due to pore plugging and the adsorption of material on the membrane pores.

The different resistances can be estimated based on

$$R_t = \frac{\Delta P}{\mu J_p} \quad (4)$$

$$R_m = \frac{\Delta P}{\mu J_w} \quad (5)$$

$$R_{if} = \frac{\Delta P}{\mu J_{fw}} - R_m \quad (6)$$

$$R_{ef} = R_t - \frac{\Delta P}{\mu J_{fw}} \quad (7)$$

where J_{iw} represents the initial water flux before the filtration step with the synthetic wastewater and J_{fw} is the water flux after the rinsing step of the membrane with water, all in (m^3/m^2 s).

The fouling index (I_f) was calculated taking into account the values of water permeability before and after the treatment

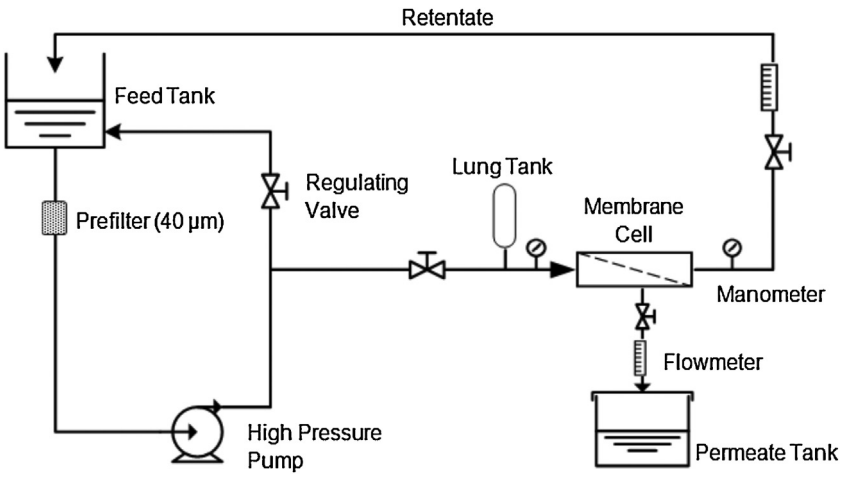

Fig. 1 – Schematic diagram of the experimental set-up.

of synthetic wastewater according to Mänttäri and Nyström (2007)

$$I_f = \left(1 - \frac{L_{pf}}{L_{fi}}\right) \times 100 \quad (8)$$

where L_{pi} and L_{pf} are the water permeability before and after the treatment of synthetic wastewater (L/m^2 h bar).

The selectivity of the UF membranes was determined by assessing the observed rejection coefficient R_{obs} for tannins, non-tannins and total solids, according to:

$$R_{obs}(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (9)$$

where C_P and C_F (% w/w) are the concentrations of a specific component in permeate and feed, respectively.

3. Results and discussion

3.1. Real and synthetic wastewater

Previous to UF experiments with the synthetic wastewater, the membranes were compacted with tap water and permeability of the virgin or cleaned membranes was measured. In all trials membranes were used previously compacted.

The wastewater from a local tanning industry and the synthetic wastewater prepared to simulate that were characterized previous to the study of the UF process (Table 1). The synthetic effluent used in all tests of filtration tests had a tannin concentration of 40.5 g/L. In addition, synthetic wastewater had a much lower percentage (26%) of NT than the real spent liquor. This occurs because during the tanning process, the skins adsorbed tannins and consequently increased the percentage of insoluble substances (salts, sulfates, among others) identified as NT, whereas in the synthetic solution the only substances identified as NT are impurities contained in commercial tannin. These compounds called non-tannins consist of different types of carbohydrates, organic acids, simple phenols with molecular sizes lower than tannins, salts present in the vegetal tissue and from water used during for the tannin extraction process, proteins and lignin compounds (UNITAN:website, 2014).

Although there was fat in the real tannin effluent, it was not added to the synthetic wastewater in order to avoid the interference during the filtration process to avert confusions while understanding the fouling process and focus our study on the interaction between tannins and membrane. On the other hand, percentage of fat on the real effluent was very low.

3.2. Membrane characterization

Both membranes have nearly the same hydrophobicity. They differed in pore size, porosity, intrinsic structure and material of the membrane (Table 2).

High linear correlation (R^2 = 0.964 for GR60PP and R^2 = 0.989 for OT050) between the tap water flux and the TMP (Fig. 2) was found. The slope of the line corresponds to the hydraulic permeability to pure water (L_p), which characterizes the membrane in the filtration process. It was 132.30 L/m^2 h bar for the OT050, whereas of only 33.52 L/m^2 h bar for the GR60PP. This can be attributed to the larger porosity of the OT050 membrane, which is 27% higher than that of GR60PP (Table 2).

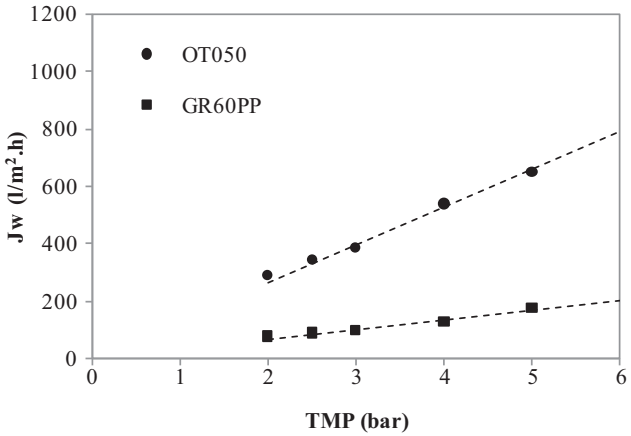

Fig. 2 – Influence of transmembrane pressure (TMP) on the tap water flux (J_w) of UF membranes (T = 25 °C; feed flow rate = 48 L/h).

Water permeability values reported in this study coincide with numerous values reported in the literature for similar UF polymeric membranes (Bhattacharya et al., 2005; Cassano et al., 2007, 2011; Galanakis et al., 2010; Mohammadi and Esmaeelifar, 2005). However, in many cases, there are differences in hydraulic permeability values reported by other authors (Cruz, 2012; Galanakis et al., 2010). Possible explanations for these differences in pure water permeabilities may be differences in compaction procedures of the membrane, the use of tap water, the module configuration used and the representativeness of the small membrane sheets used.

For a given value of TMP, lower water flux was observed for the lowest MWCO membrane. Thus, a higher value of R_m could be expected for GR60PP compared to OT050, which was confirmed by analyzing the resistances.

3.3. Flux decline

Previous to UF experiments with the synthetic wastewater, the virgin membranes were compacted with tap water and the permeability of the virgin or cleaned membranes was measured. In all trials membranes were used previously compacted.

The evolution of the synthetic wastewater flux over time at two different TMP was evaluated for each membrane (Fig. 3). All filtration tests were performed until flux reached a pseudo-steady state. A sharp flux decline was observed at the initial stage, which continued decreasing over time. Subsequently, a final stage was observed where the flux reached a pseudo-steady state at approximately 60 min and at 100 min for GR60PP and OT050, respectively. The initial stage of the filtration tests was different for both membranes. A greater flux decline was reported for OT050 membrane due to its greater MWCO, porosity and hydraulic permeability.

In trials with synthetic wastewater at 5 bar, the flux decline was 58.3% for GR60PP and 64.1% for OT050. Flux decline can be attributed mainly to fouling phenomenon, due to tannin adsorption, cake formation as well as pore blocking. The rejected particles accumulated near the membrane surface forming a cake layer that assisted in tannin removal and increased permeate flux resistance. This is because vegetable tannins are miscible with water and form polydisperse solutions, partly of colloidal type. In the effluent, labile aggregates form non-associated molecules with approximately spherical shape with 14–40 Å diameter. Besides colloidal particles,

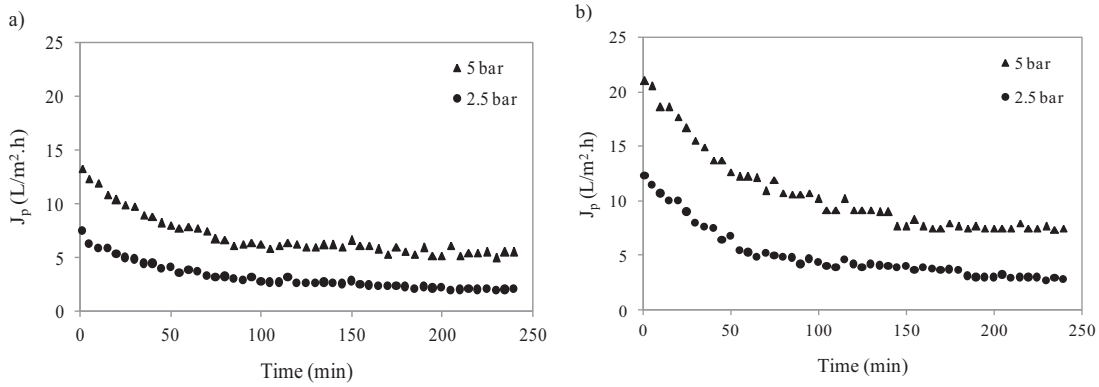

Fig. 3 – Permeate flux of synthetic wastewater during the experimental time using different pressures (a) membrane GR60PP and (b) membrane OT050 (T = 25 °C; feed flow rate = 48 L/h).

deposits of 6–13 μm particle diameter occur commonly in vegetable tannins (Bienkiewicz, 1983). Fouling causes must be taken into account when selecting the best membrane for a particular application (Salahi et al., 2010).

The average permeate flux for OT050 membrane was 10.68 ± 0.54 L/m^2 h at 5 bar and 5.06 ± 0.35 L/m^2 h at 2.5 bar; whereas for GR60PP membrane was 7.03 ± 0.29 L/m^2 h at 5 bar and 3.21 ± 0.18 L/m^2 h at 2.5 bar. These values can be compared with those observed by Cassano et al. (2003), who reported an average permeate flux of 12.5 L/m^2 h for a NF membrane (Nitto Denko NTR 7410 S4F), using exhausted vegetable tanning liquors from an Italian tannery.

When comparing the permeate fluxes of water with the initial and final permeate fluxes of synthetic wastewater was observed a large difference between the values obtained. It is important to remark that the values for the initial fluxes obtained in this work are comparable to those from other authors when they used similar effluents (Cassano et al., 2003; Molinari et al., 2004). Indeed, Molinari et al. (2004) reported a permeate flux of water of 55 L/m^2 h, at TMP 10 bar for NF membrane NF 70, while in trials with the effluent from exhausted tanning baths, the initial permeate flux was 8.00 L/m^2 h and the final permeate flux was 2.24 L/m^2 h at TMP 5 bar.

Taking into account the obtained results of the average permeate fluxes, it is important to highlight that UF membranes have a high potential for the treatment of exhausted vegetable tanning liquors compared to NF membranes. This is mainly due to the fact that UF membranes require low operating pressures which results in low investment and operating costs.

3.4. *Effects of TMP on the permeate flux*

The evolution of the pseudo-steady state permeate flux with the TMP in the experiments carried out with UF membranes was analyzed (Fig. 4). As expected, both membranes showed a linear flux increase with the TMP, characteristic of low MWCO membranes having a less severe fouling phenomenon (Minhalma and dePinho, 2001).

A low flux increase was observed for GR60PP membrane. This might have been due to the high solids retention on the membrane surface attributed to its lowest pore size. These observations were consistent with other studies that evaluated the performance of UF membranes with other effluents (Benítez et al., 2009; Mohammadi and Esmaeelifar, 2004; Muthukumaran et al., 2011).

3.5. *Cleaning with water*

Following synthetic wastewater experiments, the membranes were cleaned using tap water (at room temperature) as feed solution to remove the polarization and cake layer. Then, the water permeate flux was measured again in order to determine the membrane fouling and thus, the different resistances of the filtration process.

Fig. 5 shows tap water permeate flux at a TMP of 2.5 bar and 5 bar for UF membranes: (1) virgin, (2) after the treatment with synthetic wastewater and (3) after the cleaning stage with water at room temperature and atmospheric pressure for 1 h. A loss of the water permeate flux (above 80%) was determined after trials with the synthetic effluent. The subsequent incorporation of a cleaning stage for membranes allowed a water flux recovery of about 36–45% of the original value. According to the results obtained, a better flux recovery was achieved for GR60PP membrane due to its morphological characteristics as discussed above.

These results confirmed that the resistance caused by cake layer formation was significant in all cases. There are many studies that analyzed various ways of reducing the effect of membrane fouling, which proposed different pre-treatment and cleaning methods (Gao et al., 2011; Lau and Ismail, 2009; Nigam et al., 2008). For UF membranes (Membrane IRIS 3605, MWCO 40,000 Da) used in the leather industry, Mendoza-Roca et al. (2010) reported a greater recovery (83%) of the water flux

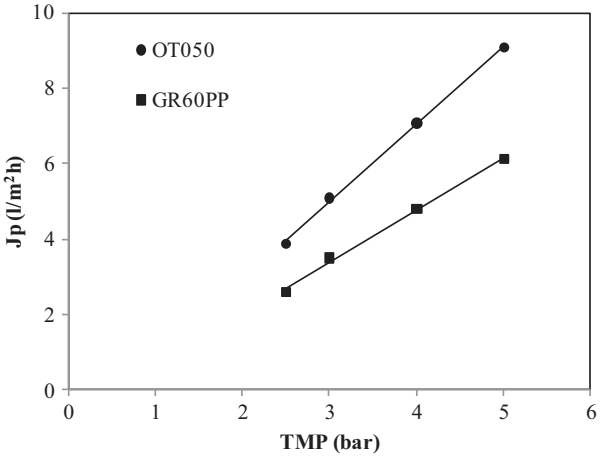

Fig. 4 – Influence of transmembrane pressure (TMP) on pseudo-steady state flux (J_p) for UF membranes (T = 25 °C; feed flow rate = 48 L/h).

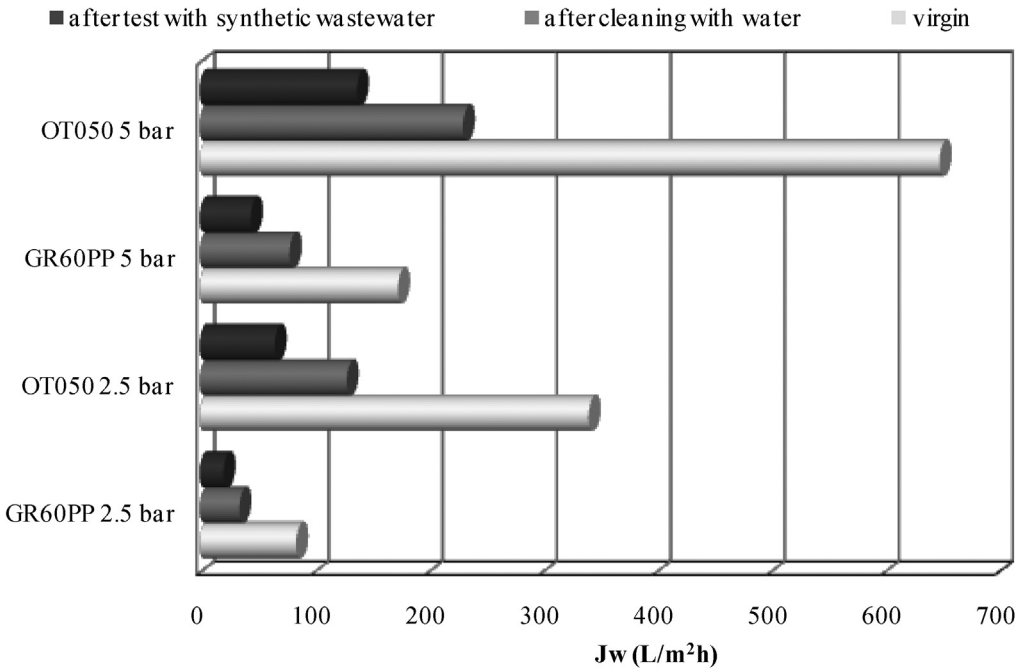

Fig. 5 – Tap water permeate flux (J_w) at TMP 2.5 bar and 5 bar for UF membranes: (1) virgin, (2) after the treatment with synthetic wastewater and (3) after the cleaning stage with water (T = 25 °C; feed flow rate = 48 L/h).

by performing a chemical cleaning with sodium hypochlorite (concentration: 1000 mg/L). For the treatment of exhausted vegetable tanning liquors with NF membranes (NTR 7410 S4F and Desal 5), Cassano et al. (2003) and Aloy and Vulliermet (1998) also reported a good flux recovery (approximately 60%). These authors carried out more complex cleaning methods using alkaline, enzymatic and acid solutions.

The cleaning method proposed in this study is simpler than the ones reported by other authors; however it allowed the flux recovery easily and mainly without the addition of chemicals. This cleaning method is environmentally friendly, which is particularly important for the leather tanning industry, typically characterized by a high consumption of chemicals. Besides, this method involves a low cost, which is essential for its implementation at the industrial level.

3.6. *Analysis of resistances*

The fouling index for UF membranes, based on water permeability before and after the treatment of synthetic wastewater, was determined (Table 3). Under the same operating conditions, OT050 membrane had a higher I_f than GR60PP. These results confirmed a greater fouling of OT050, perhaps due to the membrane structure, porosity, MWCO and the interaction between tannins and the membrane material. In a recent article Koo et al. (2012), reported that the tendency toward fouling of the membrane is not due only to the hydrodynamic conditions and feed water composition, but also to the pore size, the material and the hydrophobicity of the membrane.

Table 3 – Relative fouling index (I_f) and hydraulic permeability of UF membrane before (L_{pi}) and after (L_{pf}) the treatment of synthetic wastewater.

Membrane	L_{pi} (L/m² h bar)	L_{pf} (L/m² h bar)	I_f (%)
GR60PP	33.52	8.88	73.5
OT050	132.20	27.36	79.3

The resistance values in each trial performed with UF membranes, according to the resistance in series model, enables the investigator to evaluate the fouling mechanism of the membranes (Table 4).

It can be noted, in general terms, that the reversible resistance contributed in 91–97% to the total resistance, whereas the irreversible resistance was only a small fraction (1–5%). These results confirmed that the fouling of the membranes was mainly due to concentration polarization and the adsorption of organic matter on the membrane surface and the subsequent cake layer formation. The R_{if} values indicated that after cleaning with water, small particles stayed adsorbed within the membrane structure blocking the pores. In a recent study, Yao et al. (2010) investigated the performance of two MF membranes (PVDF and PC from the Millipore Corporation) versus different ratios of proteins and polysaccharides. They found that the resistance of the cake layer was the main contribution to fouling on both membranes. Our results allowed us to confirm that during filtration tests with organic solutes and polymeric membranes, the decrease of the membrane performance was principally due to cake layer formation.

Regarding the effect of TMP, the R_{if} value increased proportionally to the driving force. This was ascribed to the fact

Table 4 – Resistances obtained from the UF experiments under two different TMP (2.5 bar and 5.0 bar) with synthetic wastewater.

Resistances	GR60PP		OT050	
	2.5 bar	5.0 bar	2.5 bar	5.0 bar
R_t ($\times 10^{-14}$ m^{-1})	3.86	3.31	2.59	2.22
R_m ($\times 10^{-14}$ m^{-1})	0.12	0.12	0.03	0.03
R_{ef} ($\times 10^{-14}$ m^{-1})	3.57	3.06	2.51	2.14
R_{if} ($\times 10^{-14}$ m^{-1})	0.16	0.17	0.05	0.06
R_m/R_t (%)	3.1	3.5	1.1	1.4
R_{ef}/R_t (%)	92.7	91.4	97.0	96.1
R_{if}/R_t (%)	4.2	5.1	1.9	2.5

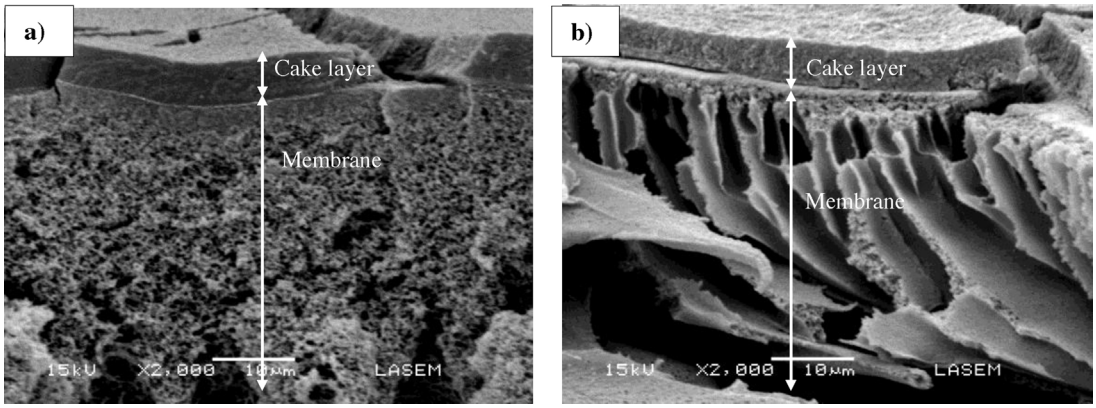

Fig. 6 – Cross-sectional SEM images of UF membranes after filtration of synthetic wastewater for 4 h and subsequent washing with tap water for 1 h; (a) membrane GR60PP and (b) membrane OT050.

that vegetable tannins have a wide molecular weight distribution of 500–20,000 Da (Cassano et al., 2003; Lofrano et al., 2007). Thus, the increase of pressure forced a greater percentage of particles to pass throughout the membrane and increase pore blockage. A higher R_m value was also observed for GR60PP due to its higher thickness and lower porosity and pore size (Table 2).

The images obtained by SEM after the filtration of synthetic wastewater for 4 h (Fig. 6) showed that there was a great difference between the morphology of the membranes. OT050 membrane had finger-like pores, which offered a lower permeate flow resistance. The GR60PP, on the other hand, had a highly porous structure which exhibited greater tortuosity, offering greater flow resistance. These were the main factors responsible for the intrinsic membrane resistance. At the same time, the SEM images confirmed the formation of a compact cake layer on the membrane surface of 5.20 ± 0.04 μm for GR60PP and of 6.13 ± 0.13 μm for OT050.

In a recent study on tannery effluents, Gallego-Molina et al. (2012) reported that reversible resistance due to cake formation could be removed by backwashing, whereas irreversible fouling required a chemical washing. Our study confirmed that for the UF membranes studied, irreversible resistance represented only 1–5% of the total resistance. Therefore, performing a chemical cleaning was not justified considering the major operational and environmental drawbacks.

3.7. *Rejection coefficients*

The rejection ratios observed for T, NT and TS were calculated for the different UF membranes (Fig. 7). The OT050 membrane showed lower rejection of all the assessed components in comparison to GR60PP. These results could be attributed to the morphological structure of the membrane, highest MWCO and to the chemical interaction between the solutes and the membrane material.

Regarding UF retentions, the tannin rejections (74% and 83% for OT050 and GR60PP membranes at 5 bar, respectively) were much higher than expected considering the molecular weight distribution of vegetable tannins (500–20,000 Da) and the MWCO of the membranes (Table 2). The high rejection observed for both membranes could be based on the size exclusion mechanism separation and could be attributed to particular properties of vegetable tannins extracts. They are well miscible with water to form polydisperse solutions, partially of colloidal type. In aqueous solution, labile aggregates are formed from non-associated molecules (Bienkiewicz, 1983; Cassano et al., 2003) and during the filtration the larger particles are deposited forming a cake layer that contributes to enhance the rejection (Bienkiewicz, 1983). The cake layer probably acts as a selective skin which might be responsible for the separation mechanism.

Similar removal efficiencies were obtained with the UF membranes of polyethersulfone: PW and PT by Benítez et al. (2009) in purification of cork processing wastewater, reported Robs for tannins above 70%. In addition, these values are also comparable with those reported by other authors that used different NF spiral membrane modules (thin film composite, TFC S2540 and NF 45-2540), and reported R_{obs} for tannins above 90%, although they reported lower permeate flux since they used exhausted tanning liquors (Molinari et al., 2004). To the best of our knowledge there are no previous studies related to the removal of vegetable tannins of tannery industry by using UF polymeric membranes, therefore this study sets a precedent because the results obtained are very promising regarding permeate flux and rejection observed. Feed and permeate streams for GR60PP membrane in the experiment with synthetic wastewater at 5 bar after 4 h are shown in Fig. 8.

In a review, Cassano et al. (2001) reported the potential of membrane processes in the treatment of aqueous solutions from the leather industry, emphasizing the importance of including membrane processes within the industry and the feasibility of recovery and recycling of various chemicals used in tanneries.

Other authors performed a techno-economic evaluation on using MF, UF, NF and RO membranes for recovery and reuse of chemicals from tanneries, reporting significant saving of

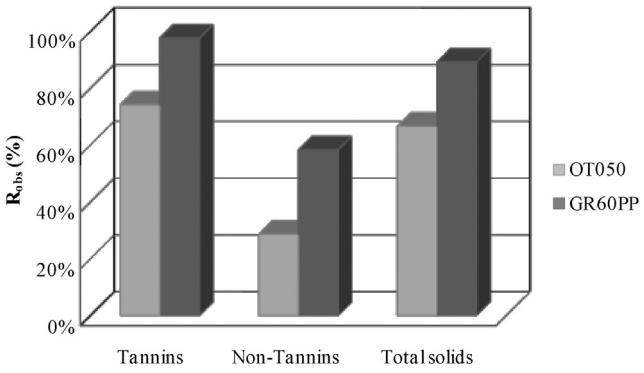

Fig. 7 – Observed rejections (R_{obs}) for GR60PP and OT050 membranes in the experiment with synthetic wastewater at 5 bar for 4 h.

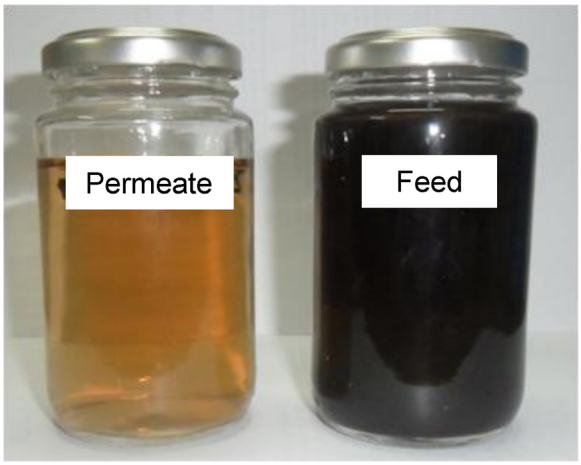

Fig. 8 – Photograph of feed and permeate streams for GR60PP membrane in the experiment with synthetic wastewater at 5 bar after 4 h (T = 25 °C; feed flow rate = 48 L/h).

chemicals and the reduction of environmental impact (Scholz and Lucas, 2003).

4. Conclusions and perspectives

Experimental results on laboratory scale trials showed that both UF membranes presented similar hydrophobicity, though they differed in their morphological structures and porosity. The hydraulic permeability of GR60PP was lower.

The flux of the membranes declined with time similarly due to fouling during UF of synthetic wastewater, used as a wastewater model, coming from the sole vegetable tanning. Several factors contributed to membrane fouling. The resistance-in-series model was applied and allowed us to identify the reversible resistance as the predominant factor in flux decline. The inclusion of a simple cleaning stage with water at room temperature and atmospheric pressure allowed the recovery of about 36–45% of the initial water flux. The rejection coefficient observed for tannins, non-tannins and total solids was higher for GR60PP membranes, although this membrane presented a lower flux consistent with its lower porosity, pore size, molecular weight cut off and intrinsic structure. The permeate fraction obtained with both membranes showed very low tannin concentration.

Summarizing, the tannin recovery by UF membranes and the reuse of the retentate and permeate streams within the same tannery is technically feasible and will probably result in a reduction of production costs. Furthermore, tannin recovery makes these processes considerably more environmentally friendly. We conclude that removal of tannins from wastewater effluents from the tanning process by membrane could be a useful additional treatment step in water purification plants encountering these effluents. Additional studies with real wastewater and the calculation of benefit/cost are required before making a final decision in terms of incorporating membrane technology in the tanning industry.

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