

# Chromium recovery by membranes for process reuse in the tannery industry

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## Abstract

Leather tanning is a wide common industry all over the world. In leather processing, water is one of the most important medium, almost 40-45 L water kg<sup>-1</sup> raw-hide or skin is used by tanneries for processing finished leathers. The composition of tannery wastewater presents considerable dissimilarities in the concentration range of pollutants both of inorganic (chlorides, with concentration ranging from several hundred to over 10,000 mg L<sup>-1</sup> Cl<sup>-</sup>; sulphate (VI), ammonium ions and sulphide ions, exhibiting concentration that ranges from tens to several hundred mg L<sup>-1</sup>) and organic (the COD value is usually several thousand mg L<sup>-1</sup> O<sub>2</sub>). Throughout the years, many conventional processes have been carried out to treat wastewater from tannery industry: unfortunately, in this case, biological treatment methods give rise to an excessive production of sludge, whereas physical and chemical methods are too expensive in terms of energy and reagent costs. In this work, a membrane process based on NF membrane modules was adopted to treat the tannery feedstock after primary conventional treatment. In a first step, the determination of all boundary flux parameters, in order to inhibit severe fouling formation during operation, were performed. After this, experimental work was carried out to validate the approach. The target of water purification was reached, that is the legal discharge to municipal sewer system in Italy of 90% of the initial wastewater stream volume. This allows having an immediate cost saving of 21%. Moreover, the developed process leads to a second benefit, that is the production of 5% of the initial volume as a highly chromium-rich concentrate at no cost suitable to tannery process recycle and reuse. In this case, cost saving rates exceeds 40%. At the end, scale-up of the investigated process will be discussed from technical and economic point of view.

**Keywords:** chromium, tannery wastewater, reuse, recovery

## 1. Introduction

Throughout the years, many conventional processes have been carried out to treat wastewater streams such as

biological process, oxidation process and chemical process. Among these, physical and chemical methods are considered very expensive in terms of energy and reagents consumption (Bavasso, 2016; Di Palma, 2014, Di Palma, 2015; Gueye, 2016; Iaquinta, 2009; Ruzmanova, 2013). Moreover, biological treatment may lead to the generation of excessive sludges (Le Clech, 2006). Unfortunately, in the case of tannery wastewater streams, all previous statements apply, making chemical, physical or biological treatment methods too expensive in terms of energy and reagent costs. Therefore, the treatment of this wastewater needs technical reorganization, by combining and integrating alternative systems to the conventional ones. In particular, the use of membrane technologies applied to the leather industry represents an economic advantage, especially in the recovery of chromium from residual waters of leather tanning. Several studies showed that crossflow microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and supported liquid membranes (SLMs) can be applied successfully on wastewater treatment processes (Stoller, 2010, 2012; Ochando Pulido, 2014). In particular, in the leather industry, a recovery of chromium from spent liquors, the reuse of wastewater and chemicals of the delimiting/bating liquor, the reduction of the polluting load of unhairing and degreasing, the removal of salts, can put condition for their discharge and reuse. Reverse osmosis RO with a plate-and-frame membrane has been used as post treatment to remove refractory organic compounds (chloride and sulphate). The high quality of the permeate stream produced by the RO system with a plane membrane allowed the reuse of the tannery effluent within the production cycle, thus reducing groundwater consumption. In particular, in the membrane process described by the Authors, the tannery feedstock after primary conventional treatment was driven to an NF membrane.

## 2. Experimental setup

The pilot plant used is shown schematically in Figure 1.

The plant consists of a 100 liter feed tank, FT1, in which the pretreated feedstock is carried. The centrifugal booster pump, P1, and the volumetric pump, P2, drive the wastewater stream over the used spiral wounded

nanofiltration (NF model DK supplied by Osmonics) or reverse osmosis (RO model SC supplied by Osmonics) membrane, fitted in the housing, M1, at an average flow rate equal to 600 L h<sup>-1</sup>. The active membrane area of both the modules are equal to 0.51 m<sup>2</sup>. The maximum allowable operating pressure is equal to 32 bar and 64 bar for NF and RO, respectively. Acting on the regulation valves, V1 and V2, it is possible to set the desired operating pressure over the membrane with a precision of 0.5 bar, maintaining the feed flow rate constant. Permeate and concentrate streams are cooled down to the fixed feedstock temperature, mixed together and recycled back to the feedstock. In this way, the feedstock composition is kept constant during each experimental batch run. The temperature was controlled for all experiments at the value of 20 ± 1 °C. After each experiment, the membrane was rinsed with tap water for at least 30 min.

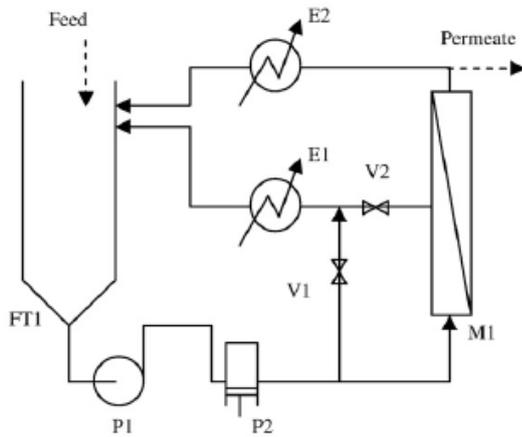


Figure 1. Scheme of the experimental setup

### 3. Results and Discussion

The first objective of this work was to identify optimal operating conditions for the two different membrane modules. The boundary flux (Stoller, 2014, 2016) was measured for the NF membrane only, since RO did not show significant fouling issues in the adopted pressure range. The measurements were performed by applying the pressure cycle step method and successive evaluation method, described in detail elsewhere, starting from a value of 2 bar (Stoller, 2015). Concerning the boundary flux,  $J_b$ , the following fitting equations apply (Stoller, 2014):

$$-dm/dt = \alpha; J_p(t) \leq J_b \quad (1)$$

$$-dm/dt = \alpha + b[J_p(t) - J_b]; J_p(t) > J_b \quad (2)$$

where  $m$  is the permeability of the membrane and  $b$  is a fitting parameter. Below boundary flux, no fouling is observed; therefore, a constant contribution to the fouling phenomena is absent ( $\alpha = 0$ ). This is not the case below the threshold flux value, where fouling is immediately observed ( $\alpha \neq 0$ ). Above boundary flux values, the fouling behavior sensibly increases, and fouling quickly starts to occur ( $\alpha \neq 0$ ). Of interest is Eq.(1), since operation should occur with no or a small amount of fouling. Eq.(1) can be discretized between  $t_1$  and  $t_2$ , equal to one pressure cycling period,  $\Delta t$ , and the following linear equation, hereafter marked by an asterisk, can be derived:

$$(-\Delta m/\Delta t)^* = \alpha; J_p(t) \leq J_{th} \quad (3)$$

As long as the adopted trans-membrane pressure (TMP) values remain below the threshold one, no effect on the changes of the permeability loss rate should be observed, thus resulting in a constant  $(-\Delta m/\Delta t)^*$  value. This value is the expected permeate reduction if Equation (3) holds, that is, at sub-boundary flux regimes, and must be compared to the measured one, hereafter reported as  $(-\Delta m/\Delta t)^\circ$ . The application of Equation (3) implies the knowledge of the “ $\alpha$ ” parameter value: in this work, this value was calculated at the lowest available TMP value, where chances to work at sub-boundary operating conditions are highest. Finally, by the application of the pressure cycling method, following conditions on the measured  $(-\Delta m/\Delta t)^\circ$  values are met:

$$(-\Delta m/\Delta t)^\circ > (-\Delta m/\Delta t)^* \quad (4)$$

The obtained results from the analysis were reported in Table 1. From the obtained results, the determination of the “ $\alpha$ ” parameter in Equation (1) at 2 bar was successful, since the permeability decline stays within the measured limits, even at higher TMP values, thus confirming that the reference was taken at sub-threshold flux operating conditions. A boundary flux point exists of 6 bar, where  $(-\Delta m/\Delta t)^\circ$  is starting to become higher than  $(-\Delta m/\Delta t)^*$ , equal to 4.4 L h<sup>-1</sup> m<sup>2</sup> and characterized by definition by a permeability loss of 14.124 × 10<sup>-5</sup> L h<sup>-2</sup> m<sup>-2</sup> bar. The permeate of NF has a final COD value of 102 mg L<sup>-1</sup>, corresponding to an overall rejection value of 95 %. The permeate characteristics are reported in Table 4. case of others, in particular, chromium and, possibly, other heavy metals. Therefore, RO must be applied to reach the targets of all parameters. The osmotic pressure of RO was equal to 9.71 bar and permeability equal to 0.364 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup>. The operating pressure relies only on economics. Since a capacity constraint exists on NF, given by the threshold flux, this latter aspect was taken into account, and as a consequence, a pressure of 22 bar is suggested for RO. In Figure 2, the obtained permeate flux profiles, with a target of 95% of recovery, were plotted at 6 bar and 22 bar for NF and RO, respectively. The characteristics of the obtained membrane permeate streams are reported in Table 2.

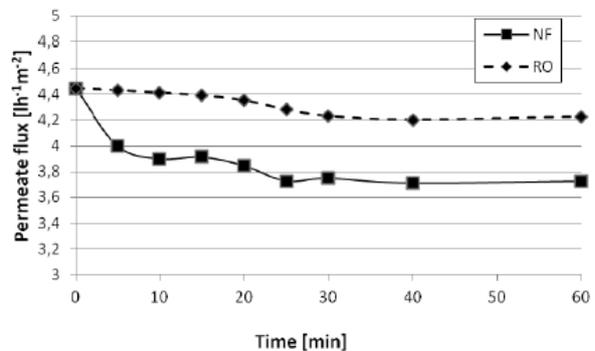


Figure 2. Plot of the NF and RO permeate flux as a function of operating time

It is possible to notice that, besides fouling, an additional sensible permeate flux reduction exists, due to the

operation in batch mode at a constant TMP value: the separation of the permeate stream leads to a solute concentration of the feedstock, and as a consequence, the membrane permeability decreases (Stoller, 2011; Ochando Pulido, 2016). The experimental work showed the feasibility of performing the secondary treatment of the tannery wastewater effluents by membrane technology. The proposed membrane plant is therefore composed of NF and RO membrane processes in series. The operating parameters are reported in Table 3. In order to check the economic feasibility of the membrane process, a cost estimation of the proposed treatment was carried out, and the results were compared to the cost required by an external wastewater treatment service, relying on conventional biological processes.

#### 4. Conclusions

The feedstocks' characteristics and membrane properties, as well as the operating conditions adopted, are hereafter

reported in Table 3. The boundary flux  $J_b$  was found to be  $4.4 \text{ L h}^{-2} \text{ m}^{-2}$ . Moreover, the sub-boundary fouling parameter  $\alpha$  was estimated to be equal to  $0.00014 \text{ L h}^{-2} \text{ m}^{-2} \text{ bar}^{-1}$ . In these conditions, the application of membrane technology appears to be advantageous for the tannery manufacturer, even if the economic benefit of chromium recovery is not taken into account: the treatment and discharge of the wastewater stream is solved, with a minimum total cost savings of about 21 %, if compared to the fixed fees of the external biological treatment plant. The treatment process by membranes limits the disposal of concentrates to external services to 5 %, permitting the discharge of 90 % of the initial wastewater volume in surface waters and reusing 5 % as chromium-rich concentrate at no cost.

**Table 1.** Boundary flux determination (in bold) for NF

TMP [bar]	$\Delta t$ [h]	$(-\Delta m/\Delta t)^{\circ}$ [ $10^{-5} \text{ L h}^{-2} \text{ m}^{-2} \text{ bar}$ ]	$(-\Delta m/\Delta t)^{*}$ [ $10^{-5} \text{ L h}^{-2} \text{ m}^{-2} \text{ bar}$ ]
2	1	14,124	14,124
3	2	5,817	14,124
4	3	6,394	14,124
5	4	12,191	14,124
<b>6</b>	<b>5</b>	<b>16,130</b>	<b>14,124</b>
7	6	16,847	14,124

**Table 2.** Characteristics of the permeate stream

	COD [ $\text{mg L}^{-1}$ ]	TTS [ $\text{mg L}^{-1}$ ]	$\text{NH}_4$ [ $\text{mg L}^{-1}$ ]	P [ $\text{mg L}^{-1}$ ]	S [ $\text{mg L}^{-1}$ ]	Cr [ $\text{mg L}^{-1}$ ]
Feed (raw WW)	2200	266	69	2,5	0,09	195
Discharge limits	160	80	15	10	1	2
NF Permeate	102	0	5,89	<2,5	0,09	7,92
RO Permeate	86	0	-	-	-	0,04

**Table 3.** Operating conditions of the proposed membrane plant; capacity equal to 646 m<sup>3</sup> h<sup>-1</sup>

Feedstock	Key parameter	COD	COD
	Value in feed stream	2.0 g L <sup>-1</sup>	0.1 g L <sup>-1</sup>
Membrane properties	Pretreatments	Primary treatment	Primary treatment + NF
	Membrane type	NF	RO
	Membrane model	SW	SW
	Membrane ID	DK	SC
	Membrane supplier	Osmonics	Osmonics
	Pore size	0.5 nm	-
	mw [L h <sup>-1</sup> m <sup>-2</sup> bar <sup>-1</sup> ]	2.500	0.364
Process properties	T [°C]	20	20
	v <sub>F</sub> [L h <sup>-1</sup> ]	600	600
	π [bar]	0.0	9.7
	Operation time [h]	4	4
	Operation cycles [-]	450	450
	R [%]	95.0	95.0
Boundary flux data	Boundary flux type	threshold	threshold
	α [L h <sup>-2</sup> m <sup>-2</sup> bar <sup>-1</sup> ]	0.00014	0.00000
	Δw% [%]	0.001	0.001
	J <sub>b</sub> [L h <sup>-1</sup> m <sup>-2</sup> ]	4.4	4.4
	TMP <sub>b</sub> [bar]	6.0	22.0
Results	Membrane area [m <sup>2</sup> ]	257280	
	Investment costs [€ m <sup>-3</sup> ]	1.44	
	Operating costs [€ m <sup>-3</sup> ]	0.36	
	Total costs [€ m <sup>-3</sup> ]	1.80	
Note	Cr is recovered back in the concentrate and might be used again in the tannery process.		

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