CHEMICAL ENGINEERING TRANSACTIONS

VOL. 32, 2013

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at: www.aidic.it/cet

Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-23-5; **ISSN** 1974-9791

DOI: 10.3303/CET1332333

Determination of Optimal Operating Condition in Nanofiltration (NF) and Reverse Osmosis (RO) During the Treatment of a Tannery Wastewater Stream

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The aim of this work is the search the best operating condition in batch membrane processes in respect to fouling. The examined case is the purification of tannery wastewater.
In particular in this work, the treatment was performed by using two spiral wound membrane modules were used: nanofiltration (NF) and reverse osmosis (RO) membranes.
A modified version of the traditional method used to measure critical fluxes of membranes, that is the pressure cycling method, was applied to measure both the critical and the threshold flux on the nanofiltration membrane. Finally, the obtained results were compared from an economical point of view with a conventional biological process to validate the membrane plant as possible alternative to conventional process.

1. Introduction

Industrial wastewater treatment, such as those used for tannery wastewater, is complex due to the variety of chemicals added at different stages of processing of hides and skins. Major problems in tanneries are due to wastewater containing heavy metals, toxic chemicals, chloride, lime with high dissolved and suspended salts and other pollutants (Uberoi, 2003). The tanning process and the effluents generated have already been reported in literature (Wiegant et al., 1999, Sreeram and Ramasami, 2003, Stoop, 2003). Many conventional processes were carried out to treat wastewater such as biological process (Ahn et al., 1996, Vijayaraghavan and Murthy, 1997, Wiemann et al., 1998, Di Iaconi et al., 2003, Farabegoli et al., 2004), oxidation process (Sekaran et al., 1996, Dogruel et al., 2004, Sacco et al., 2012, de Caprariis et al., 2012) and chemical process (Di Iaconi et al., 2001, Orhon et al., 1998, Song et al., 2004) etc. Among these, physical and chemical methods are considered very expensive in terms of energy and reagents consumption (Churchley, 1994, Stern et al., 2003), and generation of excessive sludge (Chu, 2001). To reduce the production of sludge by the treatment of this wastewater combined or alternative systems must be explored**.** In particular, in this work, two spiral wound membrane modules were used: nanofiltration (NF) and reverse osmosis (RO). The goal of this approach is to insert membranes into the cycle of wastewater treatment in order to remove the entire chain of biological treatment and the resulting post physico-chemical residue with a significant reduction of sludge up to 95%.
A modified version of the traditional method used to measure critical fluxes of membranes, that is the pressure cycling method, was applied to measure both the critical and the threshold flux on the nanofiltration membrane in order to optimize the operating conditions.
Once obtained the critical and threshold flux values, this data was used as input for a batch membrane process optimization method developed previously by Stoller at al. (Stoller and Chianese, 2006, Stoller and Bravi, 2010, Stoller, 2009, Iaquinta et al., 2009, Stoller, 2008, Stoller, 2011). The output of the method indicates the optimal permeate feed flow rate which should be used during the batch in order to inhibit membrane fouling. Finally, the obtained results were compared from an economical point of view with a conventional biological process to validate the membrane plant as possible alternative to conventional process.

Please cite this article as: Sannino D., Sacco O., Chianese A., 2013, Determination of operating condition in nanofiltration (nf) and osmosis reverse (ro) during the treatment of a tannery wastewater stream, Chemical Engineering Transactions, 32, 1993-1998 DOI: 10.3303/CET1332333

2. Experimental

2.1 The wastewater stream

In general, tannery wastewaters are basic, have a dark brown colour and have a high content of organic substances that vary according to the chemicals used. The tannery wastewater was characterized by substantial organic matter content and high SS content, resulting in total COD_0 concentration of about 5000-6000 [mgL^{-1}] and a SS concentration of 985 [mgL^{-1}]. TKN, N-NH_3 and PO_4^{3-} averaged 112, 74 and 2.6 [mgL^{-1}], respectively. The pH of the tannery wastewater change from 3 to 7.7-7.9 after physical and chemical treatment. Sulfide and Total Chromium concentrations were 0.14 [mgL^{-1}], and 189 [mgL^{-1}], respectively, during the process feeding stages. It is also observed that tannery effluents are rich in nitrogen, especially organic nitrogen, but very poor in phosphorus. In addition to organic and nitrogen compounds, tannery wastewaters contain sulfide, chromium, which impart high antibacterial activity. Several problems have been encountered during the biological treatment of tannery wastewater because of high toxicity. The inhibition of biodegradation due to the presence of chromium and sulfides demonstrates the antibacterial activity. High concentrations of these constituents make the possible discharge of tannery wastewaters into water bodies problematic, as they cause eutrophication and other adverse environmental effects (Durai and Rajasimman, 2011). In the analyzed case the samples of a wastewater tannery collected after preliminary depollution treatments with an initial COD_0 content of 2020 [mgL^{-1}].

2.2 The lab scale plant

The used pilot plant is shown schematically in Fig. 1.

The plant consists of a 100 [L] feed tank FT1, in which the pre treated feedstock is carried. The centrifugal booster pump P1 and the volumetric pump P2 drive the wastewater stream over the used spiral wounded nanofiltration (NF) and osmotic reverse (RO) membrane, supplied by Osmonics, fitted in the housing M1, at an average flow rate equal to 600 [L h^{-1}], the maximum one that can be obtained constantly on this system (Stoller, 2011).

The membrane, model DK for NF (pore size equal to 0.2nm) and model SC for RO, respectively, were used for more than 1000 [h] of operation time. The active membrane area of the modules are equal to 0.51 [m^2]. 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 P_{EXT} over the membrane maintaining the feed flow rate constant with a precision of 0.5 [bar].

Both permeate and concentrate streams are cooled down to the 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 °C±1 °C.

After each experiment the membrane was rinsed with tap water at least 30 [min]. If not necessary, the membrane module was stored directly in the membrane housing filled with fresh tap water, else put in a fresh tap water filled external storage tank. The samples were analysed after the process to determine the change of COD by using the analytical spectrophotometrical procedure developed by Dr.Hach-Lange (Lasa100), using kit cells in the range of COD 1.000-10.000 and 100-2.000 [mg L^{-1}].

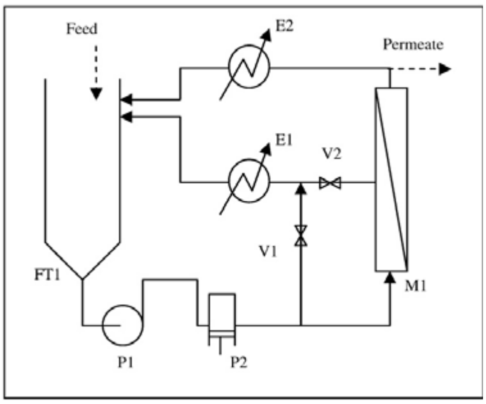

Figure 1: The scheme of the pilot plant

3. Results and Discussion

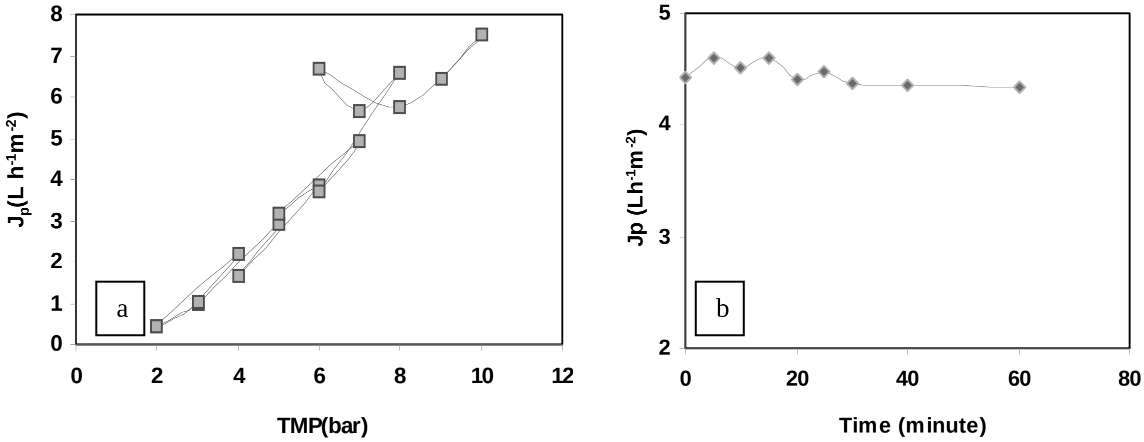

Figure 2:a) Threshold flux determination of tannery waste water using NF module b) Permeate flux profile operating condition 6 bar

The first objective was to identify the optimal operating conditions with the use of two different membrane modules. The critical flow was assessed by the procedure of variation of the operating pressure in steps for the spiral module (NF).After placing all the valves in the correct position the volumetric pump has been turned on, and the system was brought to a pressure of 2 [bar]. After a few minutes to allow stabilization the permeate flow rate was measured. Afterwards, the operating pressure was increased to 4 [bar], as proposed by the method step.

To make correct measurements of the permeate stream it is necessary to wait that the system reaches stable conditions, at each pressure value change. At a pressure value equal to 6 [bar] a deviation greater than 10% between the permeate fluxes before and after the pressure cycle was observed, therefore this value is the critical pressure (see Figure 2a).In Figure 2b, working at critical pressure over time, the flow rate of permeate remains constant, a sign that there is not short-term fouling triggering. The permeate of NF has a final COD_f of 102 [mg L^{-1}], corresponding to an overall reduction of 95% when compared to initial value of COD_0.For RO the osmotic pressure resulted to be equal to 9.71 [bar]. Later, a study to identify the critical flux through operating pressure stepping method was used.

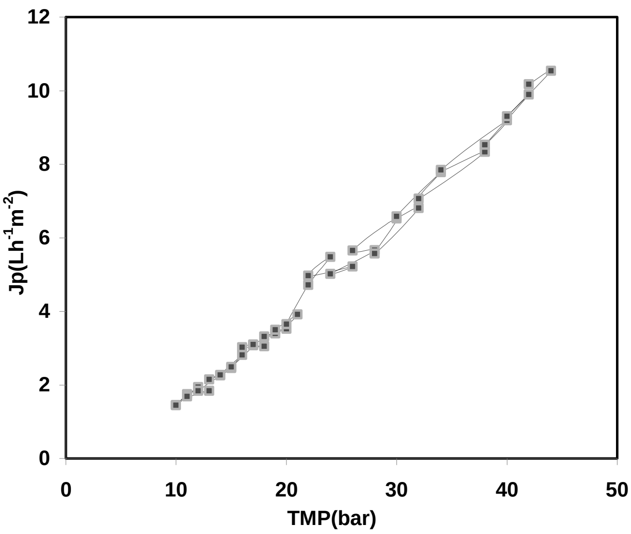

Figure 3: Threshold flux determination of tannery waste water using RO

After placing all the valves in the correct position the volumetric pump has been turned on, and the system was brought to a pressure of 10 [bar]. After a few minutes to allow stabilization the permeate flow rate was measured. Afterwards, the operating pressure was increased to 12 [bar], as proposed by the method step.
To make correct measurements of the permeate stream it is necessary to wait that the system reaches stable conditions, at each pressure value change (Figure 3).No critical points were identified, thus RO is not affected by fouling (Stoller et al., 2012, Ochando-Pulido et al., 2012). The RO membrane had a hydraulic permeability equal to 1.35 [L m^{-2} h^{-1} bar^{-1}].The tests were performed then performed at constant pressure and it is chosen to operate at 20 and 30 [bar]. The RO permeate has a final COD, respectively, 110 and 70 [mg L^{-1}], respectively accounting for 94.5% and 95.5%.

3.1 Operating conditions and cost evaluation

Both membrane modules used in this work allow to obtain a permeate quality compatible with discharge into the aquifer surface, with peak performance for RO used at high operating pressures (see Table 1).
The result shows that the permeate flow using high membrane area is still low, and thus it is convenient to use RO at high pressure values (see Table 1).

Table 1: operating conditions for membrane module of NF and RO

	RO			NF
Type	MAX	MED	MIN	
COD_0 (mg L^{-1})	2020	2020	2020	2020
COD_f (mg L^{-1})	50	60	110	100
ΔCOD%	97.5	97.0	94.5	95
Π (bar)	9.7	9.7	9.7	-
J_c (Lh^{-1} m^{-2})	13.03	8.6	3.8	4.38
m ($Lh^{-1}m^{-2}bar^{-1}$)	-	-	-	0.73
P_c (bar)	-	-	-	6
TMP (bar)	60	40	20	6
Area (m^2m^{-3})	77	116.28	232.16	232.557
Membrane number(m^{-3})	10	15	33	30

This is not the case for NF, were fouling is triggered and thus higher pressure values would lead to zero flux conditions quickly.The purification plant of the tannery waste water combined with the use of a membrane system is an experimental system, that presents items cost of construction and management that do not exist in an ordinary plant. The technical and economic data of existing treatment plants were compared with the results of this study. The costs of establishing and running were collected in categories: in the “construction” category (representing the investment costs) the costs for the purchase of membranes, of membrane housings, of the piping and the intake works and hydraulic return were considered; in the category “management” (representing the operational costs) the costs related to energy consumption were considered. In this way it is possible to think about different plant solutions, and compare them to a pre-existing plant.

3.2 Scheme

The scheme of the proposed process is to use membranes for the treatment of the wastewater stream which can be disposed at no cost in surface aquifers, and the nearby production of a small amount of concentrates, which has to be dried and disposed as chrome polluted special waste. The installation costs are reported at a flow rate of 340 [m^3h^{-1}], to a lifetime of 10 years, taking into account the replacement of the membrane modules every 2.5 years. The reference flow rate is equal to that of the plant connected to this research project. Management costs are considered costs related to the daily energy consumption of the pumps and the possible drying oven concentrated. For each cubic meter of wastewater treated 2.31 [€] of electric energy are required. The cost of living biological treatment, which is the part of the plant replaced by the membranes, are lower and comparable to those needed in treatment systems for municipal wastewater (0.40 [€m^{-3}]).In Table 2, the treatment costs were evaluated by taking into consideration different membrane plant design (e.g. reverse osmosis at different pressures). Membrane processes give rise to two different streams, a permeate that can be disposed at no cost in surface aquifers, and the concentrate containing chromium and therefore has to be treated as special waste after drying. At a first glance, the obtained results shows that using membrane processes did not reach any economical benefit, even if RO is used at its maximum pressure (representing the technical-economic optimal condition).On the other hand the reverse osmosis membrane is capable of retaining the 100% of bi- and trivalent metal ions, such as chromium, in the wastewater.

Table 2: Costs evaluation for different operating conditions

	RO			NF
Pressure (bar)	60	40	20	6
Costs relating to A				
Membrane (€ m^{-3})	0.227	0.340	0.748	0.680
Housing,Piping(€ m^{-3})	0.028	0.043	0.094	0.085
Current(€ m^{-3})	0.110	0.458	0.879	0.775
Current for evaporation(€ m^{-3})	0.145	0.145	0.145	0.145
Disposal and residual chromium(€ m^{-3})	0.460	0.460	0.460	0.460
Total costs (€ m^{-3})	0.97	1.44	2.32	2.14

Therefore the pre-treatment by means of flocculation, required in the conventional process, can be eliminated when using membranes. The alternative scheme of the process, shown in figure 4a, perform the direct treatment of the wastewater. In this case, the effluent has an initial value of the COD of about 5000 [mgL^{-1}], and as a consequence, if rejection values holds, the COD of the permeate will be equal to 125 [mgL^{-1}] .This value remains slightly below the legal value for the discharge in surface aquifer. For this reason, a safer approach is to provide the discharge of the purified wastewater into the municipal sewer system as a low cost, legal solution (see figure 4b). In Table 2 the costs related to the membrane system of reverse osmosis at high P were again evaluated. This time, the obtained results shows that the usage of membrane processes can lead to significant savings, in the order of 15%, in case RO is used at maximum pressure, representing the technical and economical optimum to treat tannery wastewater.
Better results may be obtained by using other membranes, commercially available, that support higher pressures (up to 120 [bar]).

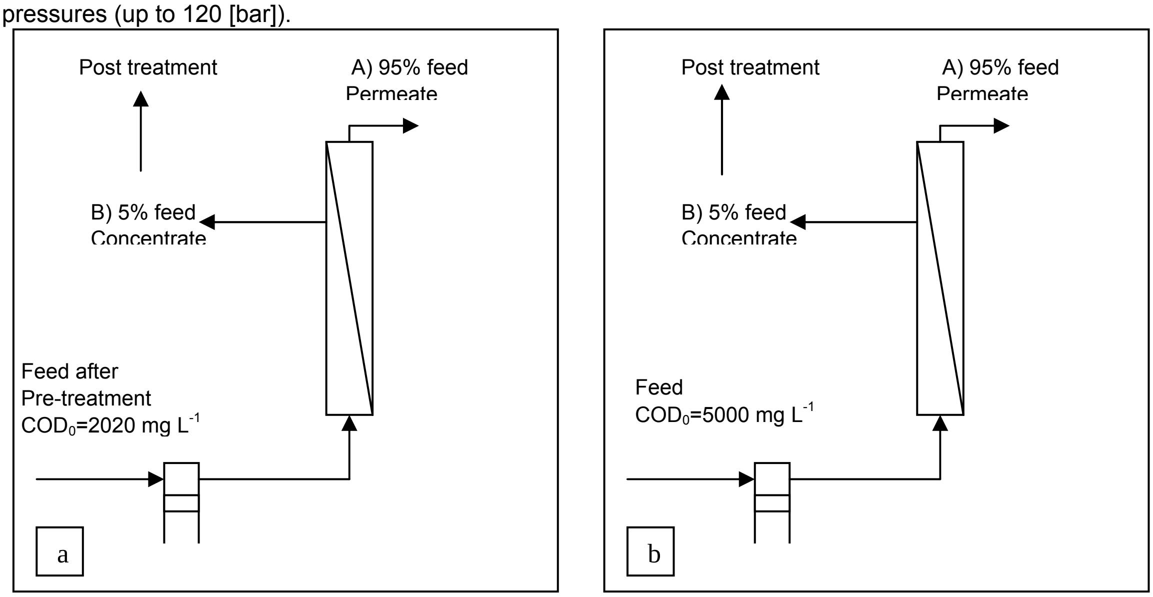

Figure 4: Flow sheet of two different configuration

4. Conclusions

The tannery wastewater was treated in a pilot scale membrane plant. At first a study of the critical flux was carried out to seek operating conditions inhibiting fouling. This was possible for nanofiltration (critical point found at 6 [bar]), but for reverse osmosis no critical flux has been found. For the latter membrane working at a pressure of 8-30 [bar] guarantee excellent results in respect to the COD_f values of 110 [mg L^{-1}] and 70 [mg L^{-1}], respectively: these values fall within the legal limits for discharge in aquifers.
Furthermore, the convenience to apply membranes in place of the existing conventional treatment plant for the treatment of this effluent was quantified in 15% total cost savings.

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