

COLOR REDUCTION IN TEXTILE EFFLUENTS BY MEMBRANES

A.A. ULSON DE SOUZA, J.C.C. PETRUS, F.P. SANTOS, H.L. BRANDÃO,
S.M.A. GUELLI U. SOUZA and L.N. JULIANO

*Mass Transfer Laboratory, Chemical and Food Engineering Department, Federal University of Santa Catarina,
C.P. 476, Florianopolis, SC, Brazil*

Tel.: (+55) (48) 3721-9448; Fax: (+55) (48) 3721-9687

augusto@enq.ufsc.br

Abstract - In this study, the efficiency of polymeric membranes in terms of reductions in color and chemical oxygen demand (COD) in textile industry effluents was investigated. Effluents containing different mixtures of dyes, taken from different processing stages, and some pure dyes in aqueous solution were used. Five membranes were used, three commercial ones produced by Osmonics (two nanofiltration M1 and NF-HL and one reverse osmosis SG) and two ultrafiltration (UF) membranes prepared in the laboratory using PES (polyethersulfone) named T1 and T2. Each membrane, due to its particular chemical nature and molecular weight cut-off (MWCO), had distinct values for permeate flux, and color, conductivity and COD reductions. After stabilization, the permeate flux varied from 20 to 71 L/h/m² and the dye retention from 81 to 100%. For aqueous solutions containing pure dyes, the permeate flux varied from 57 to 119 L/h/m², depending on the temperature used in the process. Membrane M1 showed a good performance; when considering the values for permeate flux (66 L/h/m²) and color reduction (99.3%).

Keywords - textile effluent, dye, polymeric membrane.

I. INTRODUCTION

The textile industry can be considered as one of the greatest consumers of water, due to the high consumption at different stages of the production process, it being necessary to adequately treat large quantities of effluents before their discharge to the environment. Some of these effluents are colored, despite containing only small amounts of dyes. These dyes are toxic and, in most cases, are not biodegradable or their biodegradation is difficult and they resist well physico-chemical treatment methods.

The presence of inorganic dyes in the effluents is the main reason for their non biodegradability and their removal from these effluents has been recently studied using biotechnological processes, adsorption, hydrolysis and, more recently, through nanofiltration or reverse osmosis microporous membranes, with removals of between 95 and 100% being achieved (Noël *et al.*, 2000; Cho *et al.*, 1999; Xu *et al.*, 1999).

With the popularization of membrane processes, such as reverse osmosis and nanofiltration, in various application areas, the cost of industrial units has been

reduced, making viable their use in processes which were previously economically unviable.

The removal of dyes from textile industry effluent, along with the removal of other contaminants in effluents from other industries, opens the possibility for water reuse. Depending on the treatment used and its efficiency in terms of reducing color, turbidity and chemical oxygen demand (COD), the water can be entirely or partially reused for the same process from which it originated or in other processes which use less clean water, such as for equipment cleaning or gardening.

The possibility for reuse has gained the attention of the industrial sector due to the imminent possibility for large consumers to be charged for water, even when they carry out their own collection. Considering the large volume of water consumed by the textile industries, there is a need to invest in adequate treatment technologies with a view to reuse, given the risk of becoming less competitive should a water charging system be implemented.

This study aimed to test ultrafiltration, nanofiltration and reverse osmosis polymeric membranes in the treatment of different effluents containing a mixture of dyes and of solutions containing a pure dye. The permeate flux, color reduction, turbidity and COD were evaluated.

II. MATERIALS AND METHODS

A. Membranes

Five membranes were used, three commercial ones produced by Osmonics (two nanofiltration M1 and NF-HL and one reverse osmosis SG) and two prepared in the laboratory from PES (polyethersulfone) named T1 and T2. These latter two were prepared from an 18% homogeneous solution of PES, with additions of PVP at 1% (T1) and 2% (T2) in N,N'-dimethylformamide. The solution was spread over the polyester-polypropylene (Viledon Filter – Carl Freudenberg) support and coagulated in water at a temperature of 20-22°C.

Analytical Methods

The soluble COD was determined according to a method of the "American Public Health Association – Standard Methods for the Examination of Water and Wastewater" (APHA, 1995) Method 5220 D. The conductivity was measured directly with a conductivitymeter at ambient temperature and expressed in mS/cm (Tecno-pen). The color was determined spectrophotometrically at 420nm (Shimadzu, model UV mini 1240) and

the pH with a digital pH meter (Quimis, modelo Q-400M2).

Effluents

Nine types of effluent were used, originating from the washing stages, after dyeing with dispersive and reactive dyes, and from the final stage of the process (a mixture of all the dyes used in one day of processing). The effluents used, along with the types of dyes and their concentrations, are described below. All the effluents contain salts (NaCl and NaOH), each at 4% concentration, for the fixation of the dyes in the fabrics.

Effluent 1

Terasil Flavine 86F - 0.06%
Teratop Blue B6E - 0.70%

Effluent 2

Dianix Yellow SE-gG - 0.17%
Escarlate Foron - 0.72%

Effluent 3

Terasil Yellow W-GGS - 0.06%
Terasil Red W-RS - 0.042%

Effluent 4

Cibacrone Red FNR - 0.04%
Cibacrone Yellow FN2R - 0.05%

Effluent 5

Remazol Gold Yellow RML - 0.05%
Remazol Blue BB - 0.04%
Remazol Turquoise Blue - 0.03%

Effluent 6 – Effluent originating from the equalizer tank. It contains a mixture of several dyes, used for synthetic fibers, of undefined composition since they originate from various waters from the washing of different fabrics.

Effluent 7 – Collected from the continuous washing, in the holding tank – soaping. The products used in the dye bath are: sodium silicate (60g/L); sodium hydroxide (8.4g/L); remazol yellow RR, remazol blue RR and remazol red RR at pH 12.3

Effluent E8 – Contains a mixture of several reactive dyes. The reactive dyes used in a concentration of 20g/L (total) were: remazol gold yellow RR; remazol bright red RGB, and remazol bright blue RN.

Effluent E9 - from the "cotton flow" dyeing process, comprising a mixture of reactive colorants: yellow remazol RR, intense red remazol RGB, blue remazol RR.

Pure dyes in aqueous solution (red 3BS, remazol blue RN and remazol black B) were also separately filtered.

Equipment used in the tests.

A filtration cell was used operating in perpendicular flux with filtration area of 15.9cm² and volume of 250mL. The cell was equipped with a magnetic stirring system, with water circulation in the outer sheath, under controlled temperature. The pressure was achieved through nitrogen introduced into the upper part of the

cell. A schematic diagram of the cell, which supports pressure of up to 30 bar, is shown in Fig. 1.

Methods

Firstly, the membranes were characterized through filtration with distilled water, in order to determine the pure water flux (PWF). In the filtration of the effluents and pure dyes different transmembrane pressures and operation temperatures were used. Before each filtration with water or effluent, always under magnetic stirring, the membrane was conditioned with distilled water, at the pressure to be used in each experiment, for at least 2 hours. After the processing of each sample, the membranes were cleaned using acid and alkaline solutions, alternating with rinsing until a permeate with neutral pH was obtained.

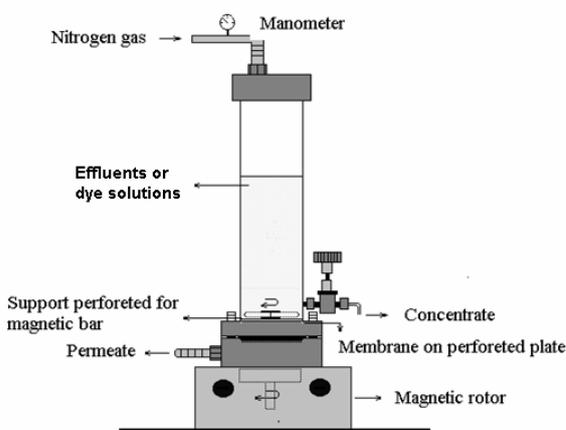


Figure 1 – Schematic diagram of dead-end stirred cell used in all experiments

III. RESULTS

A. Water Pure Flux (WPF) for Membrane M1

In Fig. 2, the permeate fluxes for Membrane M1 are shown at ambient temperature (20–22°C) and pressure intervals between 10 and 20 bar, as normally used in nanofiltration processes.

The fluxes obtained for Membrane M1 are to be expected for a nanofiltration membrane, due to its low porosity (Nyström *et al.*, 1995). It can be observed that all of the PWFs were proportional to the applied pressure and that they stabilized in the first few minutes of filtration and remained at the same intensity for at least 2 hours after the initial filtration. The fact that the permeate flux does not decrease as a function of time may be because the filtration was carried out with distilled water and, thus, without any solute or suspended material, and also because the membrane does not suffer compaction effects, at least at the pressure levels used, which would reduce its pores and consequently the permeate flux.

Performance of all membranes in the filtration of effluent E4.

The values for permeate flux, color reduction and electrical conductivity are shown in Table 1. According to

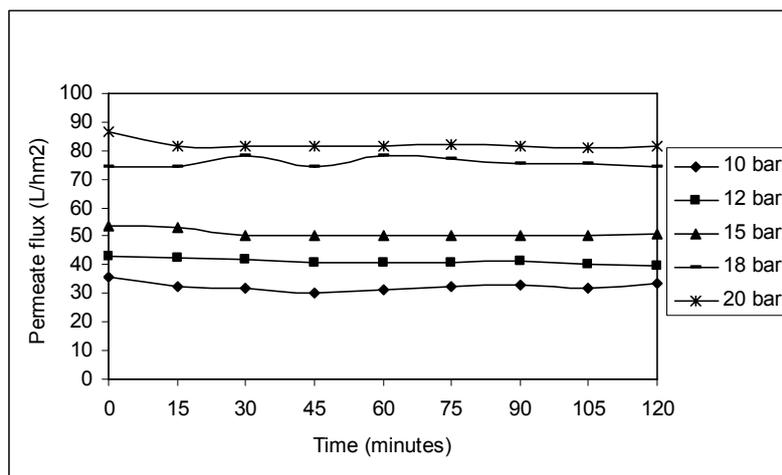


Figure 2 – PWF for Membrane M1 as a function of the different transmembrane pressures.

Table 1 – Performance of the membranes in the filtration of effluent E4 at 23°C

	Membranes						
	T2	T2	T1	M1	M1	NF-HL	SG
Pressure (bar)	10	20	10	10	20	10	10
Permeate flux (L/h/m ²)	45.8	69.9	27.0	30.5	64.5	58.8	9.6
Color retention (%)	91.0	90.5	96.9	97.6	99.0	99.6	99.9
Conductivity reduction (mS/cm) (%)	11.3	10.0	19.7	34.4	30.5	28.4	95.0

Table 2 – Performance of membrane M1 in the filtration of effluents E1, E2 and E3, at ambient temperature and a transmembrane pressure of 12 bar

Effluent	Permeate flux after stabilization (L/h/m ²)	Color reduction (%)	Conductivity reduction (mS/cm) (%)	COD reduction (%)
E1	21	84.5	44.6	65.9
E2	18	97.7	43.6	20.4
E3	23	98.8	50.1	18.2

Table 3 – Performance of membrane T2 in the filtration of effluent E4, at ambient temperature and a transmembrane pressure of 12 bar

Pressure (bar)	Permeate flux after stabilization (L/h/m ²)	Color reduction (%)	Conductivity reduction (mS/cm) (%)
10	43	95.6	11.2
15	63	91.3	7.3
20	68	90.7	10.0

the nature of each membrane used in the filtration, distinct values for permeate flux and color and electrical conductivity reductions were obtained. In general, the lowest permeate flux gave the greatest color and electrical conductivity reductions, for the same pressure, indicating a considerable reduction in the salts used in the fixing of color in the fabric.

The greatest retention of dyes and salts, as expected, occurred with the use of the reverse osmosis membrane (SG). Since the performance of a filtration unit is measured mainly by the permeate flux and retention of solutes, an optimum point has to be found where the greatest permeate flux and greatest retention are achieved. A higher pressure (20 bar), for the same membrane (T2 and M1), resulted in an increase in the permeate flux, but not with the same degree of color and electrical conductivity reductions.

Performance of membrane M1 in the treatment of effluents E1, E2 and E3

The permeate flux and color, conductivity and COD reductions for the different effluents filtered by membrane M1, are shown in Table 2. Although there were significant changes in the parameters color, conductivity and COD reductions, there was no notable difference in the permeate flux. The retention of color was greater for effluents E2 and E3 probably due to the nature of these dyes, particularly their molar mass and their possible interaction with the membrane.

Performance of membrane T2 in the filtration of effluent E4

The performance of membrane T2 in the filtration of effluent E4, as a function of pressure, is shown in Table 3. It can be observed that an increase in transmembrane pressure resulted in an increase in the permeate flux, but it had an adverse effect on color reduction.

It is known that the use of high pressures may reduce the retention rate of solutes by forcing them to permeate through the membrane, which does not occur

at lower pressures (Nyström *et al.*, 1995; Chen *et al.*, 1997). Even a color reduction of the order of 96% is not sufficient to discolor an effluent satisfactorily.

Effect of effluent dilution on permeate flux and color reduction

In order to determine the effect of effluent dilution on permeate flux and color reduction, a 1:5 dilution of effluent E5 was filtered through membrane M1 at different transmembrane pressures, and the results are shown in Table 4.

It was found that an increase in pressure increased the permeate flux and that the most concentrated effluent (without dilution) gave the greatest color reduction and, therefore, greatest dye retention. Normally, a greater concentration of solutes leads to a greater polarization by concentration which, during the filtration, may lead to a higher degree of membrane clogging, which results in a greater retention of solutes (Garba *et al.*, 1999). Regardless of these points, the level of color reduction was satisfactory for the three dilution processes.

Performance of Membrane M1 in the filtration of effluents E6, E7, E8 and E9

The performance of membrane M1 was determined through the filtration of different effluents, as shown in Table 5.

Membrane M1 had a good performance in terms of color reduction for all of the effluents and led to varied results in relation to the reductions in conductivity and COD, according to the distinct composition of each effluent. The reduction in conductivity, which is a consequence of the salt retention, varied greatly for the different effluents. Since a nanofiltration membrane separates monovalent from polyvalent ions, the former being more permeable, it appears that there is a greater concentration of polyvalent salts, in decreasing order, from effluents E6 to E9.

Influence of solution pH on the performance of membrane M1

Figure 3 shows the PWF at ambient temperature and a transmembrane pressure of 20 bar. The variation in pH may affect the permeability of the membrane by altering the interactions between the polymer chains of which it is composed. These alterations may increase or decrease the distance between the chains leading to an increase or

decrease in the permeability of the membrane. In this specific case, the greater the pH deviated from neutral, the greater the permeate flux.

It was noted that a 50% increase in the permeate flux through the adjustment of the pH gave a 50% reduction in the filtration area of an industrial unit required to process the same quantity of effluent. This represents an important reduction in the implantation costs of the system. It should also be considered that extreme pH values may lead to a destructuring of the membranes and changes in their properties, adversely affecting their solute retention levels.

Influence of the temperature of effluent E8 on the performance of membrane M1

Higher temperatures favor a greater permeate flux by reducing the viscosity of the solution to be filtered and increasing its diffusion through the membrane (Jiratananon *et al.*, 2000). In Fig. 4 the permeate flux for membrane M1 in the filtration of effluent E8, as well as the reductions in color, COD and electrical conductivity, are shown. There was an increase in the permeate flux with an increase in temperature, with no important change in the other parameters. Evidently, filtration at higher temperatures results in higher processing costs (Bowen and Mohammad, 1998).

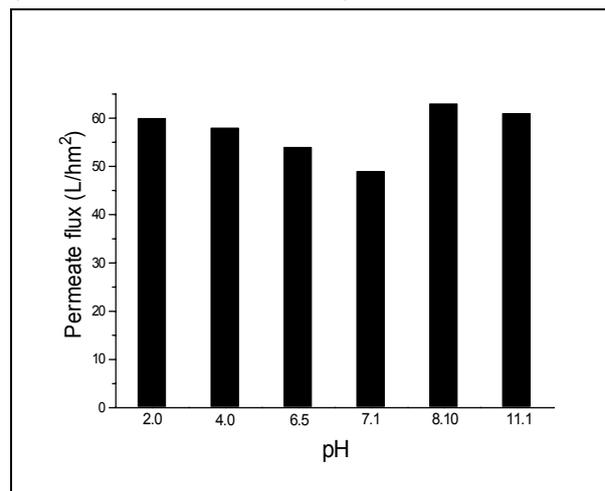


Figure 3 – PWF as a function of pH for membrane M1 and a pressure of 20 bar at ambient temperature.

Table 4 – Effect of the dilution of effluent E5 (1:5) on permeate flux and color retention for different transmembrane pressures

Pressure (bar)	Permeate flux after stabilization (L/h/m ²)	Color reduction (%)
15	24	98.7
18	72	99.3
20	74	99.2
20 (without dilution)	32	99.8

Table 5 – Performance of membrane M1 in the filtration of effluents E6, E7, E8 and E9 at ambient temperature and a transmembrane pressure of 20 bar

Effluent	Permeate flux after stabilization (L/h/m ²)	Color reduction (%)	Conductivity reduction (mS/cm) (%)	COD reduction (%)
E6	54	99.4	80.3	-
E7	30	99.5	67.9	87
E8	58	100.0	29.7	41.8
E9	44	99.7	2.3	77.1

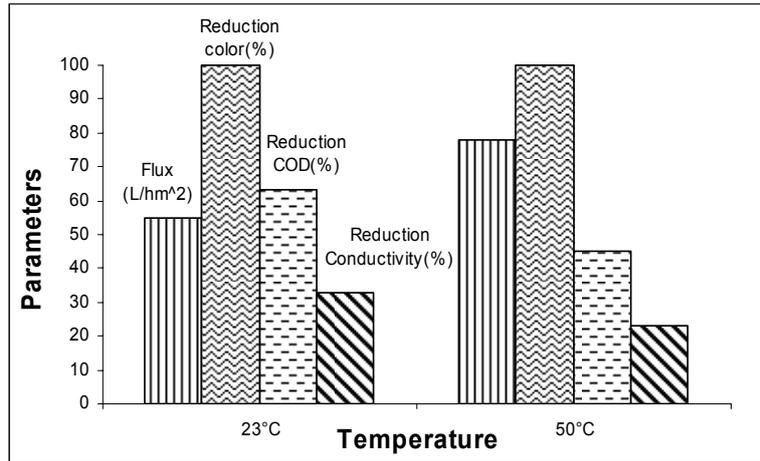


Figure 4 – Effect of temperature on the permeate flux and color, COD and electrical conductivity reductions for effluent E8, using membrane M1 and a transmembrane pressure of 20 bar at pH 12.9

In this case, the increase in permeate flux must be more significant than the increase in cost for the process to be economically viable. As with the pH, it should be considered that very high temperatures, normally above 60°C, may adversely affect the structure of the membranes with a gradual loss of their properties related to the permeate flux and solutes retention.

Influence of the temperature of effluent E9 on the performance of membrane M1

For effluent E9, a higher temperature resulted in greater permeate flux through membrane M1, with the advan-

tage of reducing the COD, the reductions in color and electrical conductivity remaining unchanged, as shown in Fig. 5.

Removal of pure dyes in aqueous solution

Filtration experiments were carried out with membrane M1 and pure dyes in aqueous solution. Three dyes were used: Remazol Red 3BS, Remazol Blue RN and Remazol Black B, all at a concentration of 100 ppm with a transmembrane pressure of 20 bar and temperatures of 23°C and 45°C. The results are shown in Figs. 6, 7 and 8

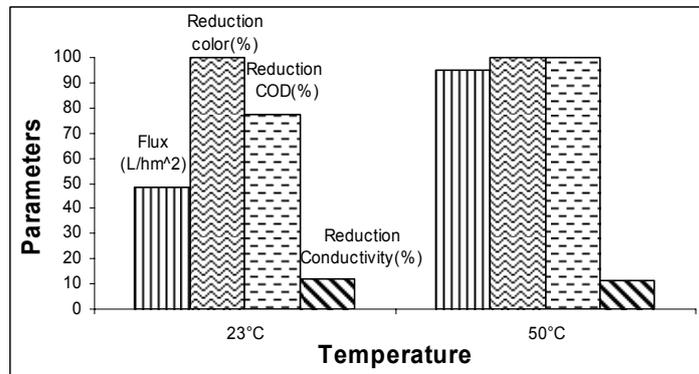


Figure 5 – Effect of temperature on permeate flux and color, COD and electrical conductivity reductions of effluent E9, using membrane M1 at a transmembrane pressure of 20 bar at pH 12.7

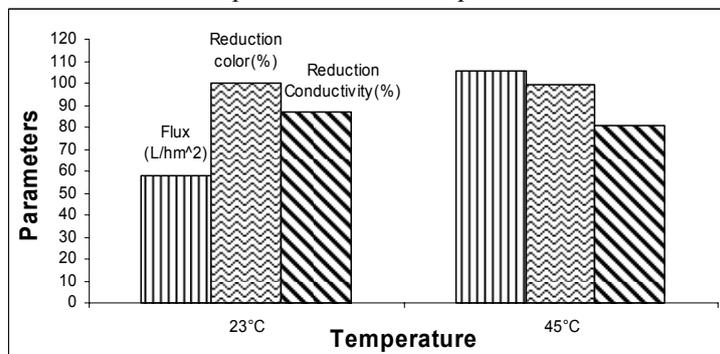


Figure 6 – Effect of temperature on the permeate flux and color and electrical conductivity reductions of a 100 ppm solution of the dye Remazol Red 3BS, using a transmembrane pressure of 20 bar at pH 6.9.

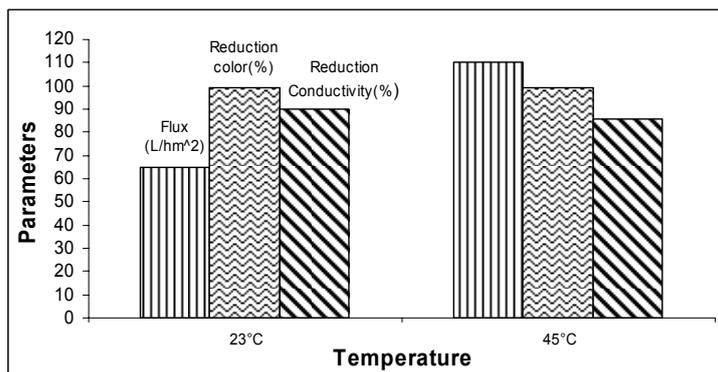


Figure 7 – Effect of temperature on the permeate flux and color and electrical conductivity reductions of a 100ppm solution of the dye Remazol Blue RN, using a transmembrane pressure of 20 bar at pH 7.2.

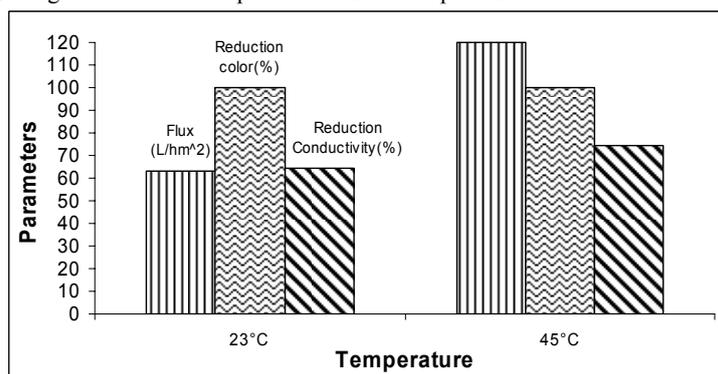


Figure 8 – Effect of temperature on the permeate flux and color and electrical conductivity reductions of a 100ppm solution of the dye Remazol Black B, using a transmembrane pressure of 20 bar at pH 6.5.

There was an important increase in the permeate flux with the increase in temperature from 23°C to 45°C for all of the dye solutions, without a significant change in the color and conductivity reductions.

As expected, it was observed that for both temperatures the permeate flux was higher than when the effluents were filtered (Fig. 4), due to their greater complexity in the presence of other dyes and the particulate material resulting from the fabric dyeing process.

IV. CONCLUSIONS

All of the membranes used in this study led to color and electrical conductivity reductions for all of the effluents tested, to degrees which varied according to the specific selective properties of each membrane. The membranes also showed a distinct permeate flux according to the temperature, pressure and effluent used. In general, membrane M1 had the best performance when considering dye retention and permeate flux. The results obtained indicate that membrane technology is promising in relation to the removal of dyes from textile industrial effluents, with a view to their reuse in the same process or in processes which require less clean water, such as initial washing processes, floor washing or gardening.

ACKNOWLEDGEMENTS

The authors are grateful to FINEP/CTHIDRO for financing Projeto AGUATEX, *Racionalização do Uso de Água nos Processos da Indústria Têxtil Catarinense* in partnership with the companies Buettner, Coteminas, Karsten, Menegotti Tapajós.

REFERENCES

- Bowen, W.R. and A.W. Mohammad, "A theoretical basis for specifying nanofiltration membranes," *Desalination*, **117**, 257-264 (1998).
- Chen, G., X. Chai, P. Yue and Y. Mi, "Treatment of textile desizing wastewater by pilot scale nanofiltration membrane separation," *J. Membr. Sci.*, **127**, 93-99 (1997).
- Cho, J., G. Amy and J. Pellegrino, "Membrane filtration of natural organic matter: initial comparison of rejection and flux decline characteristics with ultrafiltration and nanofiltration membranes," *Water Research*, **33**, 2517-2526 (1999).
- Garba, Y., S. Taha, N. Gondrexon and G. Dorange, "Ion transport modelling through nanofiltration membranes," *J. Membr. Sci.*, **160**, 187-200 (1999).
- Jiraratananon, R., A. Sungpet and P. Luangsowan, "Performance evaluation of nanofiltration membranes for treatment of effluents containing reactive dye and salts," *Desalination*, **130**, 177-183 (2000).
- Noël, I.M., R. Lebrun and C.R. Bouchard, "Electro-nanofiltration of a textile direct dye solution," *Desalination*, **129**, 125-136 (2000).
- Nyström, M., L. Kaipia and S. Luque, "Fouling and retention of nanofiltration membranes," *J. Membr. Sci.*, **98**, 249-262 (1995).
- Xu, Y., R.E. Lebrun, P.J. Gallo and P. Blond, "Treatment of textile dye plant effluent by nanofiltration membrane," *Sep. Sci. Technol.*, **34**, 2501-2519 (1999).

Received: November 7, 2007.

Accepted: May 7, 2008.

Recommended by Subject Editors Ana Lea Cukierman and Rubén Piacentini.