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Evolution of Membrane Performance During the Ultrafiltration of Reactive Black 5 Solutions: Effect of Feed Characteristics and Operating Pressure

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In the present work, the feasibility of the ultrafiltration (UF) technology for the removal of a hazardous azo reactive dye, Reactive Black 5 (RB5), was studied. A tubular UF ceramic membrane was used to filter RB5 aqueous solutions. Solutions at different feed concentrations (50, 100, 500 mg/L) and temperatures (25, 30, 35, 40 ºC) were tested in order to observe the influence of these two parameters on the evolution of permeate flux and dye rejection with operating time. Moreover, the effect of transmembrane pressure (TMP) was also studied by performing essays at different operating pressures (1, 2, 3, 4 bar). Additionally, membrane performance was also evaluated by means of the average permeate flux and the cumulative flux decline.
The results showed that both the productivity and the permeate quality improved by increasing feed temperature and decreasing feed concentration. On the other hand, an increase in TMP led to an increase in permeate flux. However, in this case the flux decline was more pronounced and the retention of dye decreased. Finally, the relatively high dye rejections obtained are an indicator of the suitability of UF technology for the removal of RB5 from aqueous solutions as a pretreatment of other membrane processes to textile water reuse.

1. Introduction

Water demand and wastewaters generated by textile industry have been increasing proportionally, making this sector one of the main sources of severe environmental problems worldwide (Khouni et al., 2011). Textile wastewaters have complex characteristics due to the usage of several kinds of dyes and auxiliary chemicals, which are often toxic (Capar et al., 2006). Furthermore, textile effluents are subjected to significant variations due to the changing properties of the textile products; they are heavily colored and exhibit high temperatures.
Although conventional physical-chemical and biological treatments are able to achieve legislative requirements for discharge to the environment, they might not be considered efficient enough to allow water reuse in the production process. However, membrane technologies such as Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO) have proven to be very effective in the treatment of textile effluents (Chakraborty et al., 2003) and, additionally, they have proven to save operation costs and water consumption by water recycling. Nevertheless, membrane separation processes have the drawback of flux decline, mainly due to membrane fouling, which leads to a decrease in the overall process productivity (Mattaraj et al., 2011). Flux decline can be almost entirely attributed to the

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formation of a polarized and/or cake layer on the membrane surface as well as blocking of membrane pores. Textile effluents can cause membrane fouling especially if they are used directly as influent to NF or RO membranes. In order to avoid fouling and membrane deterioration it is necessary to carry out an appropriate pretreatment prior to NF or RO processes by means of several technologies which include membrane processes such as microfiltration and ultrafiltration (Fersi and Dhahbi, 2008).
On the other hand, permeate flux and selectivity are affected by operating conditions and therefore it is important to determine the effects of different parameters (transmembrane pressure, cross-flow velocity, temperature, feed concentration, etc) on membrane performance (Moresi and Sebastiani, 2009).
In the present work the use of an UF ceramic membrane for the removal of Reactive Black 5 (RB5), a hazardous azo reactive dye widely used in textile industry, was studied. The aim of the work was to assess the impact of feed characteristics (temperature and dye concentration) and operating pressure on the evolution of permeate flux and dye rejection.

2. Experimental

2.1 Materials

For the preparation of the feed solution an azo reactive dye, C.I. Reactive Black 5 (Sigma-Aldrich), with a molecular weight of 991.82 g/mol, was used. An INSIDE CéRAM® (Tami Industries) multichannel tubular ceramic membrane was used to filter the aqueous RB5 solutions. This membrane was 250 mm long and had an external diameter of 10 mm. It consisted of seven channels, each one with a hydraulic diameter of 2 mm. The active layer (ZrO_2-TiO_2) was deposited on the internal side of a titanium support. The membrane effective filtration area was 132 cm^2 and the molecular weight cut-off was 150 kDa. The experimental value of deionized water permeability at 25 ºC was 145.4 $L\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1}$.

2.2 Cross-flow UF experiments

In order to study the effect of feed characteristics and operating pressure on the membrane performance, a series of total recycle runs were carried at different feed concentrations (50, 100 and 500 mg/L) and temperatures (25, 30, 35 and 40 ºC) and at different TMP (1, 2, 3 and 4 bar). All runs were performed at a constant cross-flow velocity of 3 m/s.
The runs were carried in a temperature- and pressure-controlled UF plant described elsewhere (Alventosa-deLara et al., 2012). Permeate flux and rejection coefficient were monitored throughout the UF experiments, which were long enough to reach the pseudo-steady state conditions (8 h). After each run the membrane was subjected to a cleaning procedure which allowed initial permeability recoveries higher than 90 %.
Permeate flux was gravimetrically measured and the concentration of RB5 on feed and permeate streams was spectrophotometrically determined (λ=592 nm). To evaluate the filtration efficiency in removing the dye, the rejection coefficient (R) was calculated as:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \cdot 100 \quad (1)$$

where C_p and C_f are the concentration of dye in the permeate and feed respectively. Membrane performance was also evaluated by means of the average permeate flux (Jp_{av}), and the cumulative flux decline (SFD). Jp_{av} indicates the volume of permeate obtained per unit of time and membrane area and was calculated as follows:

$$Jp_{av} = \frac{1}{t_N} \cdot \int_0^t Jp(t) \cdot dt \quad (2)$$

where t is the time of operation, t_N is the time corresponding to the last value of permeate flux considered and Jp(t) is the permeate flux evolution along time. In order to obtain the Jp evolution, the experimental data were interpolated using Mathcad® and a regression model was obtained by means of linear least square fitting. SFD, which characterizes the flux decline throughout the experiment, was calculated according to Eq. 3:

$$SFD = \sum_{i=1}^{N} \frac{Jp(0) - Jp(i)}{Jp(0)} \tag{3}$$

where N is the point corresponding to the end of the experiment, Jp(0) is the initial permeate flux and Jp(i) is the permeate flux at different operating times.

3. Results and discussion

3.1 Effect of TMP

Figure 1 shows the evolution of permeate flux and dye rejection with time at four different transmembrane pressures, a temperature of 25 ºC and feed dye concentration of 100 mg/L. As observed, at any TMP the variation of Jp can be divided into two stages, a sharp initial decay followed by a pseudo-steady stage. At the early period of filtration, the flux reduces very quickly probably due to the rapid membrane blocking caused by the adsorption of dye particles onto the membrane surface and into the pores. The reduction rate in Jp becomes slower after approximately 30 minutes. The accumulation of particles during the run and the concentration polarization phenomenon may lead to the formation of a cake layer onto the membrane surface. When the solute flux driven toward the membrane by convection is compensated by the back transport of the solute away from the membrane a constant cake layer thickness is reached, which is followed by a nearly constant permeate flux.

Increasing in TMP leads to higher permeate flux due to higher driving force and thus, the average permeate flux obtained is greater as pressure increases, as it can be seen from Table 1. However, the fast reduction of permeate flux at the beginning of the process is more severe as TMP increases. This fact can be numerically confirmed by the calculated values of cumulative flux decline (SFD), shown in Table 1.This parameter summarizes the information on the evolution of permeate flux with time throughout the experiment. The greater the SFD is, the faster and more noticeable the flux decline is, thus indicating that membrane fouling is more severe. The substantial increase in SFD with TMP could be explained because the convection of particles toward the membrane surface is enhanced under higher pressure, which leads to a greater deposition of dye particles onto the membrane surface and into the pores.

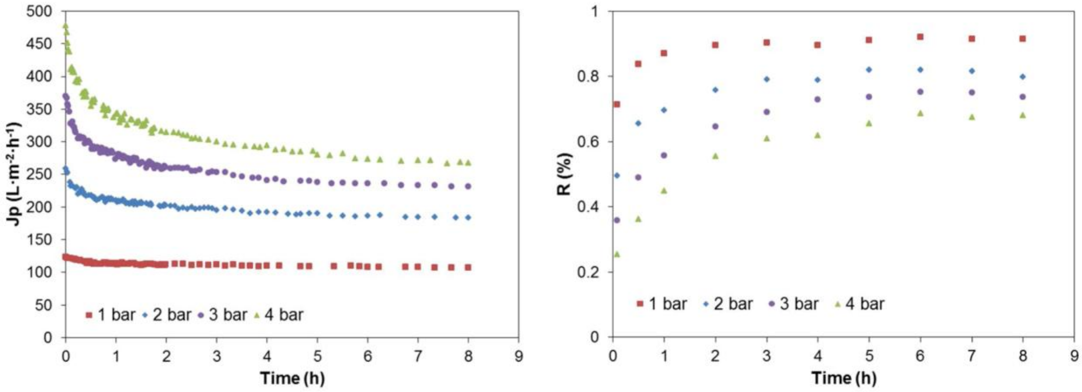

Figure 1: Effect of TMP on permeate flux (Jp) and dye rejection (R).

Table 1: Influence of TMP on Jp_{av} and SFD.

TMP (bar)	Jp_{av} ($L \cdot m^{-2} \cdot h^{-1}$)	SFD
1	110.52	48.23
2	195.85	115.03
3	252.55	153.02
4	301.41	176.44

On the other hand the curves representing the evolution of dye rejection show that R increased with time under any TMP tested. This phenomenon could be explained by the greater accumulation of dye particles as operating time extended. The cake layer formed by the rejected molecules may operate as an additional resistance to permeate, preventing the passage of dye particles. The rejection coefficient decreased by increasing TMP, reaching steady-state values which ranged between 68 % and 91 %. This is probably due to the passage of more dye molecules through the membrane under increased TMP, which ultimately resulted in an increase in permeate concentration.
Similar results regarding the effect of TMP on membrane performance were obtained by Das et al. (2009) and Martí-Calatayud et al. (2010).

3.2 Effect of Feed Concentration

The results obtained in the experiments performed at three different feed dye concentrations, a temperature of 25 ºC and a TMP of 3 bar are illustrated in Figure 2. The evolution of Jp and R follow the same trend as in the previous case: Jp decreases and R increases with operating time. It is observed that permeate flux increases with dilution of the feed. As stated by Das et al. (2009), as dye concentration increases, availability of dye molecules to be deposited on the membrane surface increases, providing more hindrance to the passage molecules and resulting in lower permeate flux. Since membrane fouling is more severe, a more pronounced flux decline is observed at higher dye concentration, especially during the initial moments of the run.
These observations are in agreement with the obtained values of Jp_{av} and SFD, presented in Table 2. As expected, the average permeate flux obtained is lower and SFD is greater as feed dye concentration increases, due to the enhanced fouling of the membrane.
Regarding dye rejection, the steady-state value reached at the run with dye concentration of 50 mg/L (92 %) is higher than the rejection obtained at higher dye concentrations (around 75 %). The increase in dye concentration increases the possibility of particles accumulating onto the membrane surface and passing through the pores, which results in lower dye removal efficiency.

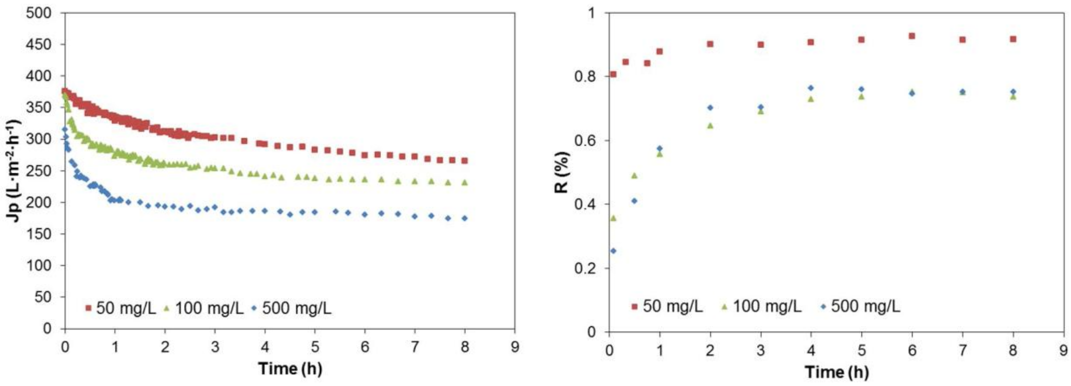

Figure 2: Effect of feed concentration on permeate flux (Jp) and dye rejection (R).

Table 2: Influence of concentration on Jp_{av} and SFD.

C (mg/L)	Jp_{av} ($L·m^{-2}·h^{-1}$)	SFD
50	298.41	95.97
100	252.55	153.02
500	192.14	184.44

3.3 Effect of Feed Temperature

The impact of feed temperature on membrane performance is illustrated in Figure 3, which presents the results of the experiments performed at four different temperatures, a dye concentration of 100 mg/L and a TMP of 3 bar. It is evident from the figure that an increase in feed temperature leads to higher permeate flux. This fact may be attributed to the decrease in feed viscosity and the increase of

diffusivity. As a consequence of lower viscosity the transport of solvent through the membrane intensifies, yielding a higher permeate flux.
Table 3 shows the calculated values of Jp_{av} and SFD at different feed temperatures. As previously stated, the volume of permeate obtained per unit of time and membrane area is higher as temperature increases. Moreover, SFD is lower at higher temperatures, which indicates that membrane fouling is less severe under these conditions.
As it can be seen from Figure 3, an increase in feed temperature slightly improves the effluent quality since dye rejection increases. By increasing temperature from 25 ºC to 30 ºC the value of steady state rejection coefficient increases from 74 % to 80 %. Due to the decrease in viscosity, the transport of solvent through the membrane increases, leading to a lower permeate dye concentration, which results in a higher rejection coefficient. Beyond 30 ºC, however, the effect temperature is very slight.
The improvement of membrane performance with increasing temperature was also observed by Xu et al. (2010) in the treatment of seawater with ceramic membranes.

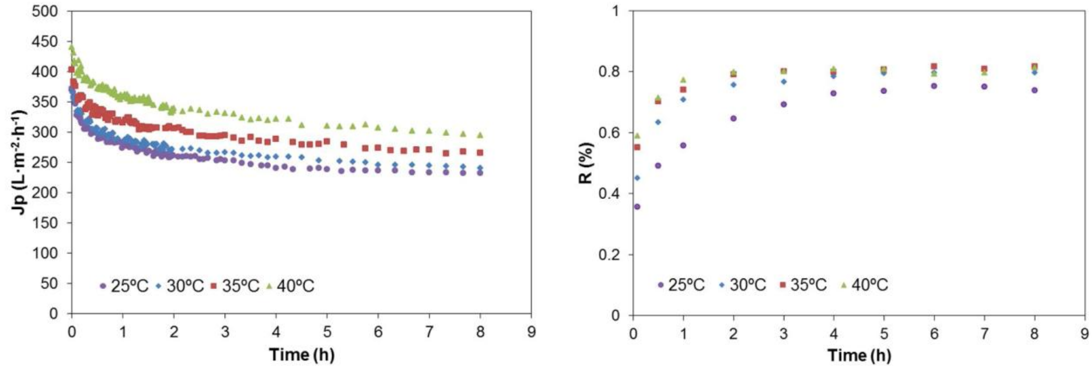

Figure 3: Effect of feed temperature on permeate flux (Jp) and dye rejection (R).

Table 3: Influence of feed temperature on Jp_{av} and SFD.

T (ºC)	Jp_{av} ($L\cdot m^{-2}\cdot h^{-1}$)	SFD
25	252.55	153.02
30	264.94	134.96
35	291.52	126.23
40	327.07	118.19

4. Conclusions

Membrane fouling and, as a consequence, membrane performance are highly influenced by operating conditions and feed characteristics. In this study a tubular UF ceramic membrane was used to assess the effect of feed characteristics (concentration and temperature) and operating pressure during the treatment of aqueous solutions of an azo reactive dye, Reactive Black 5. Permeate flux and dye rejection were monitored throughout the experiments and the curves of Jp and R versus time were obtained. Additionally, parameters such as average permeate flux and cumulative flux decline were used to evaluate the membrane performance under different operating conditions.
The obtained results indicated that average permeate flux was higher at higher operating pressure. However, an increase in TMP also led to a more pronounced flux decline and to a decrease in dye rejection. Regarding the effect of feed dye concentration, it was observed that higher concentration entailed lower permeate flux and more noticeable flux decline. Moreover, when dye concentration was increased, the loss in removal efficiency was significant. On the other hand, an increase in feed temperature led to higher permeate flux and slightly improved the permeate quality.

Finally, the relatively high dye rejections obtained are an indicator of the suitability of UF technology for the removal of RB5 from aqueous solutions. In this way, the subsequent treatments with other membrane technologies, such as Nanofiltration or Reverse Osmosis, might be more easily performed, with the aim of reusing the effluents in the production process.

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References

Alventosa-deLara E., Barredo-Damas S., Alcaina-Miranda M.I., Iborra-Clar M.I., 2012, Ultrafiltration technology with a ceramic membrane for reactive dye removal: Optimization of membrane performance, Journal of Hazardous Materials 209-210, 492- 500.

Capar G., Yetis U., Yilmaz L., 2006, Reclamation of printing effluents of a carpet manufacturing industry by membrane processes, Journal of Membrane Science 277, 120-128.

Chakraborty S., Purkait M.K., DasGupta S., De S., Basu J.K., 2003, Nanofiltration of textile plant effluent for color removal and reduction in COD, Separation and Purification Technology 31, 141-151.

Das R., Bhattacherjee C., Ghosh S., 2009, Effects of operating parameters and nature of fouling behavior in ultrafiltration of sesame protein hydrolysate, Desalination 237, 268- 276.

Fersi C., Dhahbi M., 2008, Treatment of textile plant effluent by ultrafiltration and/or nanofiltration for water reuse, Desalination 222, 263- 271.

Khouni I., Marrot B., Moulin P., Amar R.B., 2011, Decolourization of the reconstituted textile effluent by different process treatments: Enzymatic catalysis, coagulation/flocculation and nanofiltration processes, Desalination 268, 27- 37.

Martí-Calatayud M.-C., Vincent-Vela M.-C., Álvarez-Blanco S., Lora-García J., Bergantiños-Rodríguez E., 2010, Analysis and optimization of the influence of operating conditions in the ultrafiltration of macromolecules using a response surface methodological approach, Chemical Engineering Journal 156, 337- 346.

Mattaraj S., Jarusutthirak C., Charoensuk C., Jiraratananon R., 2011, A combined pore blockage, osmotic pressure, and cake filtration model for crossflow nanofiltration of natural organic matter and inorganic salts, Desalination 274, 182-191.

Moresi M., Sebastiani I., 2009, Ultrafiltration of food biopolymers: a dimensionless approach to the generalized darcy model parameters, Chemical Engineering Transactions, 17, 867-872 DOI: 10.3303/CET0917145.

Xu J., Chang C.-Y., Gao C., 2010, Performance of a ceramic ultrafiltration membrane system in pretreatment to seawater desalination, Separation and Purification Technology 75, 165-173.