Control of irreversible fouling by application of dynamic membranes

M.T. Pessoa de Amorim*, Ilia Rosa Afonso Ramos

Department of Textile Engineering, University of Minho, Campus de Azurém, 4800-058 Guimarães, Portugal
Tel. +351 (25) 351-0286; Fax: +351 (25) 3510293; email: mtamorim@det.uminho.pt

Abstract

The use of dynamic membranes formed *in situ* by deposition of a colloidal suspension on a porous support as a pre-treatment of membranes is an attractive method to reducing irreversible membrane fouling. A polyethersulfone, PVDF, membrane with a neutral load, hydrophilic character and a cut-off of 30,000 Dalton was studied after treatment with hydrophilic polymers, such as polyetylenoglycol and polyvinyl alcohol. The selectivity and permeability of the membrane without treatment and of the dynamic membranes formed with hydrophilic polymers were measured with a solution of a reactive dye, Black Remazol B, at different pH values. Simultaneously, fouling of the membrane was controlled. It was observed that for identical conditions permeate flux is higher with membranes treated with solutions of hydrophilic polymer and irreversible fouling decreased with the treatment of the membranes.

Keywords: Fouling; Dynamic membranes; PEG; PVA; Reactive dye

1. Introduction

The use of ultrafiltration (UF) in wastewater cleaning, namely in the textile industry, has been the object of numerous studies. It has been found that this method is economical and highly effective for these kinds of wastewaters [1–3].

UF is a technique characterised by low energy consumption and the separation of dye and other pollutants found in textile wastewaters can be achieved without chemical additives.

Three aspects are very important for the selection of a membrane for a specific separation: material, pore size and shape. The chemical, thermal and mechanical resistance are determined by the material, as is the susceptibility to fouling. Membrane pores determine — to a large extent — which molecules pass through the membranes and which are retained. The cleaning efficiency

*Corresponding author.

and irreversible fouling are related to membrane shape, membrane material and pre-treatment of the membrane.

The use of polymers to form dynamic membranes has been investigated in the reduction of susceptibility to irreversible membrane fouling in the treatment of different wastewaters, specifically to textile effluents [4–7]. The aim of the study was to verify the possibility of using dynamic membranes, formed by UF of some solutes on the reduction of susceptibility to irreversible membrane fouling.

2. Material and methods

Fully hydrolysed poly(vinyl alcohol) (PVA) and two polyethylene glycols (PEG) with a molecular weight of 3,400 and 8,000 g mol^{-1} were used to treat a commercially available asymmetric polyethersulfone UF membrane, PM 30, with 30 kDa molecular weight cut-off. The UF separations were studied with an azo dye, Reactive Black 5, CI 20505, with a molecular weight of the 991.8 g mol^{-1}, used without further purification. The appropriate pH values were obtained by adding acetic acid or sodium hydroxide.

An Amicon Millipore stirred cell (model 8100) was used. The effective surface of the membrane amounted to 4.16 cm^2. All filtration experiments were conducted at a stirring rate of 1400 rpm, and a system temperature of 22°C. Volume flux and dye retention were determined after steady conditions of flow were achieved.

Dye concentration in aqueous solutions was determined spectrophotometrically at appropriate wavelength, using a Unican UV/VIS 2 apparatus. The dye rejection is defined as $R_{dye} = (1 - C_p/C_b)$ where C_p is the concentration of dye in the permeation and C_b is the concentration of dye in the bulk solution.

The dynamic membrane was formed by filtration of 5 ml of an aqueous solution containing 1 g.L^{-1} of the polymer. All experiments were conducted at a constant transmembrane pressure of 3.5 bars. During membrane formation, the permeation rate was measured. Deposition of polymer on the membrane was quantified by determining the total solids contents through weight difference of permeate evaporated at 103°C.

In order to study the effect of polymer film on membrane filtration, experiments with hydrolysed dye solutions of Reactive Black 5 at three different pH values — 5.0, 5.9 and 9.0 — were performed.

3. Results and discussion

At the beginning of the experiments, a standard run was carried out by filtering distilled water at different operating pressures. The membrane permeability with the dye solution without the use of the dynamic membrane was also measured for comparison proposes. The results relative to UF permeate fluxes with the PM30 membrane are shown in Fig. 1 for water and the dye solution.

The hydrodynamic resistance for the membrane was calculated from the initial water permeation according the equation

$$J_v = \frac{\Delta P}{\eta R_m}$$

where ΔP is the gradient of hydrostatic pressures across the membrane, η is the fluid viscosity and
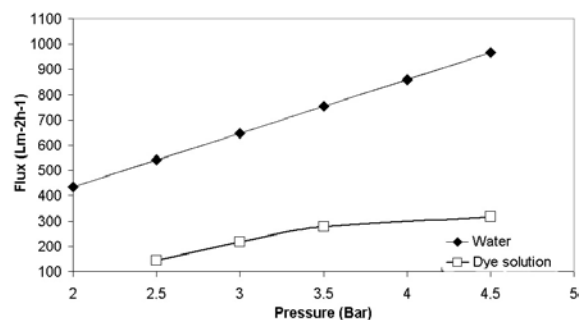

Fig. 1. Flux vs. pressure for the water and dye solution.

R_m the hydrodynamic resistance of the membrane. In terms of permeability, the equation can be expressed as $J_v = L_p \Delta P$ where L_p is the hydraulic permeability coefficient [8].

The viscosity of the water was calculated according to the equation presented by White [9]. The hydrodynamic resistance obtained for the membrane was $1.743 \pm 0.015 \times 10^{12}\,\mathrm{m}^{-1}$. The value of the hydrodynamic resistance achieved was in the range of UF membranes [6].

The drop in the flux value for the dye solution can be attributed to an adsorption of the dye onto the membrane, which was indicated by the presence of colour on the membrane after filtration and pore blockage, as observed in other studies [2]. The polymer was retained by the porous support and the flux, after a steady condition of flow was achieved, and dye rejection of the original and treated membranes is shown in Tables 1 and 2.

Figs. 2a–c show the dye retention from feed solutions at pH 5.0, 5.9 and 9.0 while Fig. 2d exhibits the permeate flows of the same feeds of

the membrane treated with PEG and PVA. From Figs. 2a–c, it is seen that the retention of dye increase with increasing of the feed pH and the separation capabilities of dynamic membranes are increasing as the molecular weight of the polymer is increased. No distinct trend can be observed in the permeate flux of a dynamic membrane; the pH at which the dye solution is feed as shown in Fig. 2d. After each test the membrane was then rinsed with distilled water for 15 min, after which a new run with dyes solution was initiated. From the results it seems that the deposition of the polymer resulted in the formation of a secondary membrane which controlled the permeate flux and rejection of the filtration process.

During UF, the overall resistance to flow can be represented as a combination of two types of resistance: one time-dependent, which increases with time, irreversible fouling; and another resistance that remains constant, membrane resistance. According Tansel et al. [10], the decrease of the flow along the time originated by irreversible fouling of the membrane can be related with the initial flow in agreement with the equation

$$\frac{J_{(t)}}{J_{(o)}} = \frac{\left(R_m + R_f\right)_{t=0}}{\left(R_m + R_f\right)_{t=t}}$$

in which R_f is the irreversible fouling.

Fig. 3 shows the variation of the irreversible resistance with respect to running time with the

Table 1
Polymer retained by the membrane

	Polymer (%)	SD
PEG (3,400 g.mol^{-1})	33.00	2.65
PEG (8,000 g.mol^{-1})	52.33	2.52
PVA (31,000–50,000 g.mol^{-1})	88.00	2.00

Table 2
Flux and dye rejection values with membrane PM 30

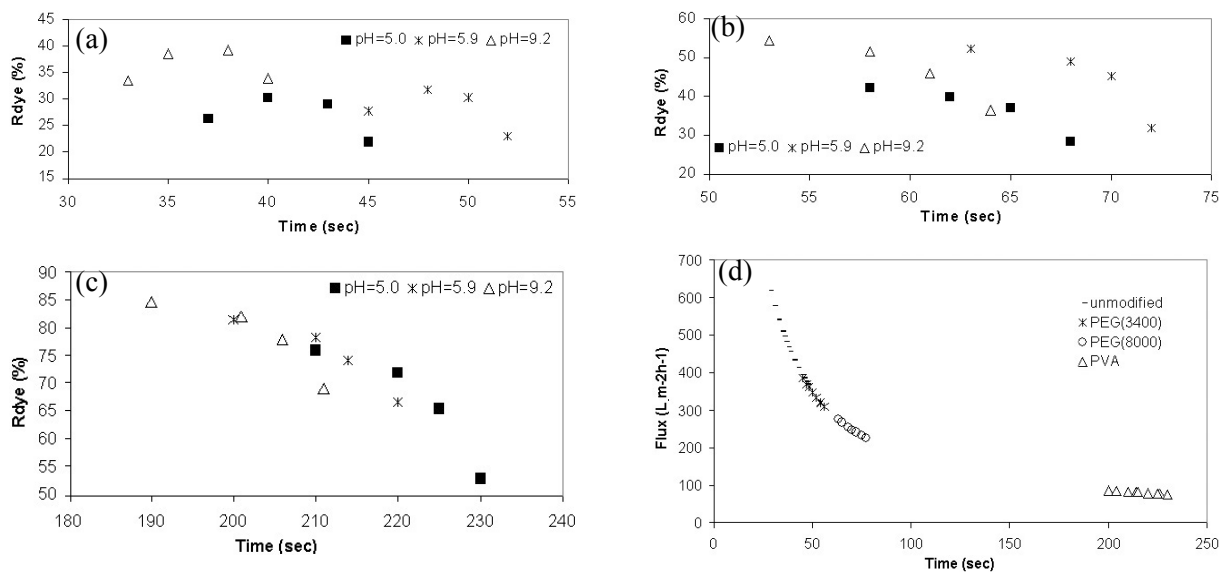|	Flux, L.m^{-2} h^{-1}			R_{dye}, %		
pH	5.0	5.9	9.0	5.0	5.9	9.0
Unmodified membrane	460	405	525	22	23	27
PEG (3400 g.mol^{-1})	395	375	440	28	30	39
PEG (8000 g.mol^{-1})	260	243	280	37	45	46
PVA	76	82	84	65	75	77

Fig. 2. Rejection vs. time. (a) PEG 3400, (b) PEG 8000, (c) PVA and (d) flux vs. time.
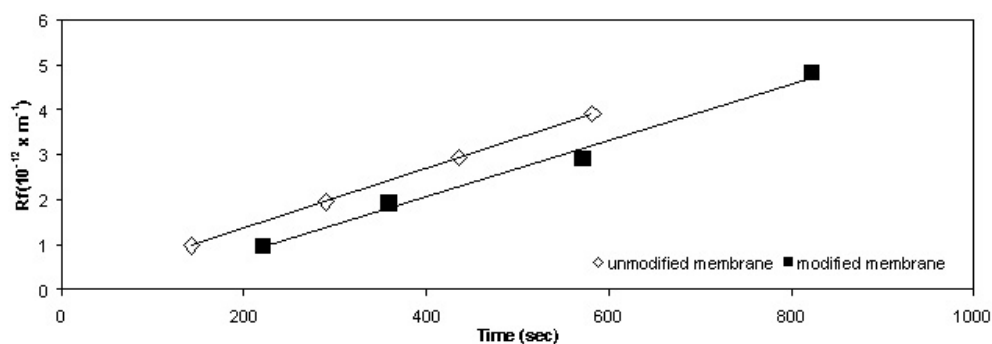

Fig. 3. Variation of irreversible resistance vs. running time.

Table 3
Data from linear correlation for the experiment

	Slope	SD	Intercept	SD
Unmodified	6.7×10^{-3}	3.2×10^{-6}	0.04	1.2×10^{-3}
Modified	6.2×10^{-3}	4.0×10^{-4}	−0.43	0.239

unmodified and modified membrane. The figure suggests a linear increase in R_f with time and a decrease of the resistance due to fouling for membranes treated with polymers. In Table 3 the values obtained for experimental data treatment are given.

The possibility of regeneration of the membrane was studied by inverse washing of the cell with distilled water with intensive mixing and in the absence of pressure. The hydraulic permeability of the PM 30 was almost completely restored. The results in Fig. 3 show that the

membrane treatment with a polymer decreases the irreversible fouling when dye solutions are filtered. When the treatment of the PM 30 membrane is not performed, the low-molecular-weight molecules in the feed can enter into the porous space of the membrane studied and plug it.

4. Conclusions

From the results it seems that the deposition of the polymer resulted in the formation of a secondary membrane which controlled the permeate flux and rejection of the filtration process. During UF, the overall resistance to flow can be represented as a combination of two types of resistance: one time-dependent which increases with time (Fig. 3), irreversible fouling, and another resistance which remains constant, membrane resistance.

The results show that the membrane treatment contributes to decreasing irreversible fouling when dye solutions are filtered and represents a promising method to be used in wastewater treatment by the textile industry.

References

[1] C.A. Buckley, Water Sci. Technol., 25 (1992) 10.

[2] B. Van der Bruggen and C. Vandecasteele, Environ. Sci. Technol., 35(17) (2001) 3535–3540.

[3] I. Koyuncu, M.F. Sevimli, I. Ozturk and A.F. Aydin, Water Sci. Technol., 43 (2001) 233–241.

[4] N. Li, Z.Z. Liu and X. Shuguang, J. Membr. Sci., 169 (2000) 17–28.

[5] R.B. Townsend, The Technical Support for the Application of Dynamic Membrane Plants for the Treatment of Industrial Effluents, 1994.

[6] M.H. Al-Malack and G.K. Anderson, Sep. Sci. Technol., 33 (1998) 2491–2511.

[7] M. Altman, R. Semiat and D. Hasson, Desalination, 125 (1999) 65–75.

[8] M. Mulder, Basic Principles of Membrane Technology, 2nd ed., Kluwer Academic, Netherlands, 1996.

[9] F.M. With, Fluid Mechanics, McGraw Hill International Editions, 1988.

[10] B. Tansel, W.Y. BAO and I.N. Tansel, Desalination, 129 (2000) 7–14.