

Postsynthesis Modification of a Cellulose Acetate Ultrafiltration Membrane for Applications in Water and Wastewater Treatment

A. Morão,^a I. C. Escobar,^b M. T. Pessoa de Amorim,^c A. Lopes,^a and I. C. Gonçalves^a

^a Department of Chemistry, University of Beira Interior, 6201-001 Covilhã, Portugal

^b Department of Chemical and Environmental Engineering, University of Toledo, Toledo, OH 43606; Isabel.Escobar@utoledo.edu (for correspondence)

^c Department of Textile Engineering, University of Minho, 4800-058 Guimarães, Portugal

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A technique for postsynthesis modification of a cellulose acetate ultrafiltration membrane with possible application in water and wastewater treatment is studied. The technique used an oxidizing agent (persulfate) to develop free radicals on the membrane surface, and that was expected to promote grafting of hydrophilic macromolecules (polyethylene glycol). A chain-transfer agent (2-mercaptoethanol) was tested to control the grafting process, avoiding the formation of long chains that usually lead to high permeability losses in other graft techniques. The modifications aimed at the decrease of the fouling susceptibility of the membrane studied. The possibility of an increase in rejection was also investigated. The membrane was characterized before and after modification, by attenuated total reflectance–Fourier transform–infrared spectroscopy, scanning electron microscopy, atomic force microscopy, and in terms of the rejection of neutral reference solutes. The information given by the different techniques of characterization provided strong evidences of the occurrence of modification, although permeation of (real) foulants was the decisive test. To obtain information about the fouling tendency of the nonmodified and modified membranes, two different kinds of foulants were used: a humic acid (usually found in surface waters) and textile auxiliaries (representing one of

the most important industries in Portugal). The results showed an increase in the rejections of the humic acid, and significant improvements in the performance of the membrane with respect to fouling tendency in the case of the textile auxiliaries. © 2005 American Institute of Chemical Engineers Environ Prog, 24: 367–380, 2005

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1. INTRODUCTION

In membrane processes, two contributions to flux decline are generally recognized [1]. The first is fouling [the irreversible (adhesive) macromolecular adsorption], which refers to specific intermolecular interactions between macrosolutes present in the feedwater and the membrane that occur even in the absence of filtration. The second is concentration polarization, which is an increase in the concentration of rejected solutes or particulate matter near the membrane surface. This concentration increase leads to a reduction in flow across the membrane. This effect occurs in addition to the fouling observed in a nonflowing system and is reversible upon cessation of filtration.

Although concentration polarization is undesirable, it is sometimes possible to control because it is reversible. Cross-flow filtration and backwashing are two common ways to reduce the effects of concentration polarization [2, 3]. The materials on the membrane

surface, which cannot be removed by cross-flow operation, backflushing, or backpulsing, result in permanent flux decline and lead to irreversible adhesive adsorption or membrane fouling. Many researchers [4–11] agree that organic matter is considered a major contributor to abiotic membrane fouling in water separation applications. Membrane replacement resulting from fouling is the single largest operating cost when membranes are used in water separation applications [12, 13], and is thus the greatest hindrance to the widespread use of membranes.

Coulombic solute–membrane interactions lead to the easier adsorption of proteins and other colloidal substances on the surface [14–21]. Thus, the use of hydrophilic membranes would be expected to decrease fouling. However, commercially available purely hydrophilic (known as low-fouling or nonfouling) membranes have been recently shown to undergo faster permeate flux declines and require more frequent chemical cleanings than regular hydrophobic membranes [22].

Hydrophilic membranes have a superior fouling resistance [23–25], but are not resistant to chemicals [26]. Hydrophilic membranes foul in the presence of non-ionic surfactants [26, 27] as a result of hydroxyl and/or carboxyl membrane functional groups adsorbing non-ionic surfactants by hydrogen bonding or acid–base interactions [28].

The work presented here focuses on the development of an *in situ* technique to graft a hydrophilic monomer onto the hydrophobic surface of a membrane. This modification will lead to increased hydrophilicity, which is expected to decrease fouling tendency while enhancing the permeability and selectivity properties of the modified membrane.

2. THEORETICAL BACKGROUND

An intensive area of research is membrane modification to produce fouling-resistant membranes through postsynthesis modifications, which include the modification of existing membranes. Considerable work has been done to modify membrane surfaces to reduce hydrophobicity and improve fouling resistance, given that organic matter and microorganisms adsorb to membrane surfaces mostly because of hydrophobic interactions [14]. Increasing hydrophilicity leads to the formation of hydrophilic channels that increase rates of water permeation [29]. Modification methods that have been investigated include ion-beam irradiation [30], plasma treatment or grafting [31, 32], UV-induced grafting [33], chemical sulfone enrichment [34], chemical dehydrofluorination by alkaline solution [35], coating temperature-sensitive polymeric brushes [36], grafting with pH- and ionic strength-sensitive polymeric brushes [37, 38], γ -irradiation-induced grafting [39], physical adsorption of water soluble polymers [26], formation of Langmuir–Blodgett films [40], thermal grafting of a hydrophilic polymeric surface coating [41], and photografting with UV irradiation [42].

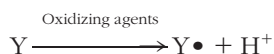
An ideal membrane would combine the high chemical resistance of hydrophobic membranes that makes them more stable and resilient, with the excellent fouling resistance of hydrophilic membranes. This can be

achieved only through modifications of hydrophobic membranes to be rendered more hydrophilic [27].

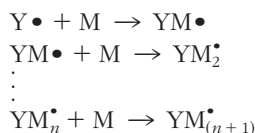
A problem often associated with grafting modifications is a loss in permeability of the membrane because grafted polymers produce high-density and long-length chains that block membrane pores; however, these are essential to make the membranes more hydrophilic [43]. Further, most membrane surface modifications use graft polymerization, which involves the use of UV irradiation in deaerated environments for radical development. A problem with this technique is that, although it is effective in radical formation, it would be too expensive and not feasible for *in situ* modifications. Graft polymerization could be particularly attractive if modifications were possible *in situ* [44].

Of specific interest here is the grafting of hydrophilic monomers to hydrophobic membrane surfaces. Among the most promising low-adsorbing materials that can be grafted to membranes are poly(ethylene glycol) (PEG) and poly(ethylene oxide) (PEO) because these substances have flexible chains that reduce adsorption [45].

Oxidizing agents have previously been shown to initiate grafting of acrylic monomers to polyamide fibers [46–48] arising from the removal of hydrogen to form radicals [49, 50]. If the polymeric structure is represented by Y, in the presence of oxidizing agents, a dehydrogenation of groups on the surface of the membrane occurs to develop a radical (Y•) with the release of hydrogen ions:



In the presence of monomers, represented by M, a chain propagation reaction may occur to form macroradicals on the membrane surface:



Previous studies have observed significant losses of membrane permeability [33, 43–45, 51–57] after monomer grafting because of long chain length produced [37, 43, 58–60]. Grafting high-density and long-length chain polymers, however, is essential to impart the surface hydrophilicity [43]. Chain-transfer agents (represented by Z) may be used to control the degree of polymerization during free-radical polymerization. Chain-transfer agents can simultaneously terminate growing polymer chains and generate new radicals, resulting in a higher chain density with a lower length [43, 61]:



Thus, a chain-transfer agent minimizes chain length and maximizes density through the development of new radicals instead of propagation of a single chain

Table 1. Modification of the membranes.*

Test	Reactant			Observed
	PS	PEG	2-ME	
Part I				
1		10(a)	5	(a) PS & PEG, 2-ME
2	10	2.5	5	
3	10	5	5	
4	10	10	5	
5	10	5	2.5	
6	10	5	1	
7	10	10	0	
8	10(b)	10 + 10(b)	2.5	(b) PEG, PEG & PS, 2-ME
Part II				
9	10	5	2.5	$T = 12^\circ \text{C}$
10	10	5	1	$T = 12^\circ \text{C}$
11	10(c)	5	2.5	(c) PS (1.5%) & MBS (metabisulfite) (1.2%)
12	10	5	2.5	
13	10	5	2.5	
14	10	5(d)	2.5(d)	(d) PS + PEG + 2-ME

*Conditions used: contact times (in minutes); PS (sodium persulfate, 1.5%); PEG [poly(ethylene glycol), 200–10%]; 2-ME (2-mercaptoethanol, 0.5%). Symbols: simultaneous addition (&); sequential addition (,); sequential addition in the same beaker (+).

length, a necessary condition for imparting the desired surface hydrophilicity.

When considering cellulose acetate, given that this was the material of the membrane selected to be studied, modifications through other possible mechanisms must also be considered. In fact, the oxidation of the cellulose and its derivatives, such as cellulose acetate, occurs similarly to the oxidation of the simplest sugars [62, 63]. The primary OH groups may be oxidized to aldehyde and carboxyl groups, and secondary OH groups to ketone groups, with rupture of the ring yielding two aldehyde groups, and these may be converted to carboxyls. Under these conditions it is possible to attach a poly alcohol, such as PEG to the membrane surface, when it comes together with the carboxylic groups of cellulose acetate (CA), as they undergo condensation to form an ester. In that case, a free OH remains at the end of the chain on the surface of the membrane.

3. EXPERIMENTAL

3.1. Modification of the Membrane

A CA ultrafiltration (UF) membrane from GE Osmonics was used in all the tests performed in this study. The oxidizing agent studied to treat membranes was sodium persulfate (1.5%). The macromolecular monomer used for modification was poly(ethylene glycol) 200 (PEG 200) in 10% solutions. Finally, 2-mercaptoethanol (0.5%) a moderate reducing agent, was used to control the grafting process. 2-Mercaptoethanol may also act as a chain-transfer agent (CTA) because it is known that thiols have high rates of chain transfer [58, 61]. All the reagents used were of analytical grade.

Before the modifications the virgin membranes were

kept in distilled water for 24 h, in the dark. The membranes were then compacted, passing distilled water at high pressure, until a steady flux was obtained. Stirred cells were used for this purpose. Two sets of experiments were performed. In the first set of experiments (Part I) a pressure of approximately 5 bar was applied, which is roughly the maximum pressure supported by the stirred cell used (a 10 mL cell from Amicon/Millipore, model 8010, made of polysulfone material). In Part II of the experiments, a 300 mL stainless steel stirred cell from Sterlitech was used, and membranes were compacted at 8 bar. The time needed to achieve a steady flux decreases considerably, from 6–8 to 1–2 h.

The modifications were performed by immersion of the precompact membranes in solutions containing the reactants, for a certain period of time, with gentle stirring. The same reactants and the same concentrations were always used, but the contacting times in the different solutions were varied (see Table 1). Also, the order of application of the reactants was always the same—first persulfate, then PEG 200, and finally 2-mercaptoethanol—with the exception of tests 1, 8, 11, and 14. Temperature was near 25° C in all tests, except tests 9 and 10, performed at 12° C.

After modification, the membranes were kept (in the dark) in distilled water for at least 24 h before being used. Water was changed twice during this period of time.

3.2. Identification of the Occurrence of Modifications

The occurrence of modifications in the surface of the membranes was investigated by microscopy through atomic force microscopy (AFM) using a Nanoscope IIIa scanning probe microscope, and scanning electron mi-

croscopy (SEM) using a JOEL 6100 SEM, and by attenuated total reflectance–Fourier transform-infrared spectroscopy (ATR–FTIR). FTIR spectra were recorded in a Nicolet-Avatar 360 FTIR spectrometer, performing 64 scans per sample, using 8 cm^{-1} resolution. Zinc selenide was the ATR crystal material used in this work.

The occurrence of modifications inside the pores was also investigated, by determination of the rejections of neutral solutes in the membranes, before and after modification. Rejection of a solute R_{obs} is defined as

$$R_{obs} = 1 - \frac{C_p}{C_b} \quad (1)$$

where C_p is the concentration of the solute in the permeate and C_b is the concentration in the feed (bulk solution). The observed rejection R_{obs} should be distinguished from the intrinsic rejection R_m :

$$R_m = 1 - \frac{C_p}{C_m} \quad (2)$$

that relates the concentration in the permeate and at the membrane surface (C_m). The two rejections are related by the mass transfer coefficient (k_s) in the film adjacent to the membrane's active surface by the following relationship [64, 65]:

$$R_{obs} = \frac{1}{1 + \left(\frac{1}{R_m} - 1\right) e^{J_v/k_s}} \quad (3)$$

where J_v is the volumetric flow rate of the permeate. The term J_v/k_s is usually referred to as the Péclet number in the boundary layer. Assuming for the membrane a porous structure consisting of cylindrical pores, Deen [66] showed that the intrinsic rejection of a neutral solute is fundamentally a function of the pore radius (r_p), solute radius (r_s), flux, and other structural parameters of the membrane, and always increases with the flux, until maximum values is reached, denoted R_∞ . According to Deen [66] R_∞ is dependent on only r_p and r_s , and thus it can be easily verified using Eq. 3 that when R_m reaches R_∞ , R_{obs} has to decrease as the flux increases. Thus, the change in the intrinsic rejection of a neutral solute may be adopted as the criterion to identify the occurrence of modifications inside the pores. Alternatively, if intrinsic rejections are not available, the observed rejection may also be used, if determined at constant hydrodynamic conditions (that is, constant k_s) and constant flux. Dextran T70 (from Amersham) was used as the reference solute because this solute shows intermediate rejections on this membrane. Generally, dextrans are also well known to have very low adsorption to membranes.

The procedure used to determine the rejections in the 10 mL stirred cell was as follows. In each test, after compaction of the membrane (and modification, when it was the case) the cell, filled with a solution of dextran

(1.0 g/L), was pressurized at a previously determined pressure, to obtain a flux of $80\text{ L h}^{-1}\text{ m}^{-2}$. A 4 mL aliquot was collected and sent to waste, and also the solution inside the cell. The cell was refilled with the solution, and again a 4 mL aliquot was collected, of which 2 mL was used as a sample to be analyzed. The flux was always checked for the 3rd and 4th mL collected. The stirring speed was always the same in all experiments, but not determined. Concentrations (in the permeate and initial solution) were determined by total organic carbon (TOC) analysis using a Tekmar Dohrmann, Phoenix 8000 UV-Persulfate TOC analyzer.

For the 300 mL stirred cell, the procedure was slightly different. In this case, the cell was filled with the solution, and 10 mL was first collected to determine the flux, at a certain pressure, and then another 10 mL to a small cup for determination of concentration. The stirring speed in these tests was at 900 rpm. Concentrations in the permeate and initial solution were determined using a differential refractive index detector (Shodex RI-71), by direct injection of the samples, using distilled water in the reference compartment. The detector was previously calibrated (with standard solutions of dextran T70) against distilled water.

3.3. Fouling Tests

After characterization of nonmodified and modified membranes, permeation of (real) foulants was the decisive test. Two types of fouling agents were tested:

1. A humic acid, in the presence of CaCl_2 , to simulate the possible application of modified membranes in the treatment of surface waters, and also because humic acid is a molecule of considerably high hydrophobicity, and thus its rejection might respond to changes in the hydrophilicity of the membrane.
2. Typical textile auxiliaries found in an industrial effluent (which is one of the most important industries in the region of Beira Interior, Portugal). The concentrations of the textile auxiliaries used correspond to average values found in a yarn manufacture/weaving/finishing mill of the wool sector (thus to simulate the effluent) and are shown in Table 2. Dyes were excluded from this study because of their excessive tendency to adsorb on membranes and also because the case being studied was not of a dye house.

3.3.1. Fouling by Humic Acid

Four tests were performed with a 5 ppm solution of humic acid (sodium salt, technical grade 50–60% from Acros Organics, Geel, Belgium), also containing CaCl_2 0.001 M (calcium enhances the adsorption of the organic compound). Two tests were performed with the nonmodified membrane (tests A and B), and two with the modified membrane (tests C and D). In test “C” calcium chloride was not initially added, but only after 30 min of permeation.

These experiments were performed in the 10 mL stirred cell (see section 3.1), applying a pressure of 4.8 bar, always using the same stirring speed. The cell was filled with the solution, and a 10 mL aliquot of permeate was collected each time (in fact, the total capacity of these cells is 12 mL). Then, the cell was refilled and the

Table 2. Yarn manufacture, weaving, finishing (scouring) auxiliary products tested: results of COD determinations.

Product—Function	Concentration used (g/L)	COD (mgO ₂ /L)
Yarn manufacture		
Ziturool—Spinning lubricant	0.5	1259
Marsax—Sizing agent	0.5	311
Hispassil—Sizing agent	0.3	3
PR-575—Anti-static	0.3	388
Weaving		
Duron Warp Wax—Sizing agent	0.5	229
Finishing (Scouring)		
Aminex Mel—Softener	0.13	52
Foryl-LN—Detergent	0.13	277
Hispogal-HS—Antiwrinkle	0.24	155
Total (COD)		2674

filtration proceeded by repeating this procedure for 7 h of effective filtration. The permeate flux and the rejections were determined along the time of the tests. Rejections were determined by TOC analysis (using the analyzer mentioned in section 3.2).

The analysis of the structure of the humic acid deposits on the membranes was performed from SEM images obtained after the experiments with nonmodified and modified membranes.

3.3.2. Fouling by Textile Auxiliaries

The study with textile auxiliaries was carried out in the 300 mL stirred cell, mentioned in section 3.1. The experimental procedure used in this case was completely different because no solid residues were deposited on the membranes. Thus, more severe conditions had to be used to obtain significant fouling.

First, the membranes were fouled by permeation of the solution being tested at 8 bar, using 900 rpm of stirring speed; after collecting 50 mL of permeate that volume was sent back to the cell, and this was repeated seven times (350 mL collected). Under these conditions an approximately steady flux was obtained. After this procedure, fluxes were determined at the same stirring speed (900 rpm) for various pressures (1 to 8 bar) and rejections at 60 and 120 L h⁻¹ m⁻², with the same solution, the composition of which remained approximately unchanged because the permeate was always sent back to the cell (apart from a total of only 6 mL that was removed for analysis to determine the rejections; this volume corresponds to 2% of the total volume of the feed solution). The rejections were calculated from chemical oxygen demand (COD) essays, according to the standard procedure [67]. Finally, the solution was removed and a permeability test performed (with distilled water) with the membranes fouled. This allows the determination of a resistance attributed to fouling, according to the so-called model of the resistances in series [68]. For a clean membrane, the method is based on the following relationship:

$$J_w = \frac{\Delta P}{\eta_0 R_b} \quad (4)$$

where J_w is the volumetric water flux, R_b is the hydraulic resistance of the membrane, and η_0 is the viscosity of the permeate. However, for a fouled membrane, an additional resistance R_f will be present, when passing (clean) water through the membrane:

$$J_w = \frac{\Delta P}{\eta_0 (R_b + R_f)} \quad (5)$$

Thus, the values of R_f can be determined, under specific (and similar) conditions for all the solutes in nonmodified and modified membranes, if R_b is previously determined (when the membrane is clean), and this enables a comparison of the tendency of each solute to foul the membranes.

4. RESULTS AND DISCUSSION

4.1. Analysis of the Occurrence of Modifications

As explained in section 3.2, characterization of the membranes before and after the chemical treatments was performed to obtain information about possible changes in pore size and/or modifications on the surface of the membranes tested. The investigation of occurrence of modifications in pores was done by determination of rejections of neutral solutes. The results are as follows.

In Part I of the experiments (see Table 1) the rejections of dextran T70 were determined in conditions of constant flux, in a 10 mL stirred cell (see Figure 1). To compare the rejections of nonmodified and modified membranes extreme care was taken during these tests to ensure that constant fluxes were obtained, and exactly the same volume of permeate was collected to be analyzed (see section 3.2), given that rejections strongly depend on the imposed flux for this solute and this membrane.

As can be observed in Figure 1, the rejections apparently increase with the modifications. In fact, although the conditions used in all the tests (1–8) were different (see Table 1), there is a clear tendency toward an increase in the rejections after modification, when these are compared with the average rejection of the

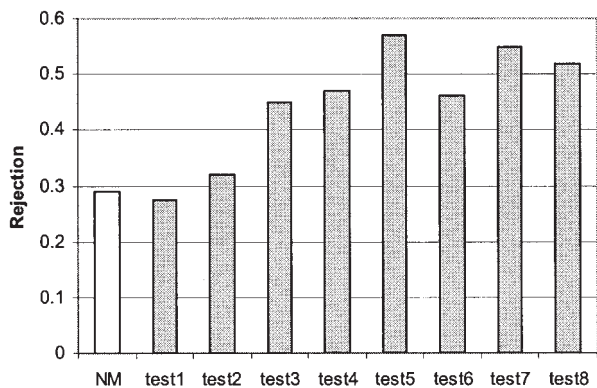


Figure 1. Rejection of dextran T70 in nonmodified and modified membranes, determined at constant flux ($80 \text{ L h}^{-1} \text{ m}^{-2}$). NM-non-modified (average). Tests performed in a 10 mL stirred cell from Amicon/Millipore. See conditions of modifications in Table 1 (Part I).

nonmodified membranes. The rejections of nonmodified membranes varied between 21 and 33%. The more significant results were obtained in test 5, where nearly a 100% increase in rejection was obtained. Because of this result, conditions of the modifications used in the fouling tests were those of test 5. As will be seen below, both ATR-FTIR and AFM analysis confirm the occurrence of modification under these conditions of treatment. Another important result is that the hydraulic permeability (L_p) of the membrane is much less affected by the modifications (Figure 2). In fact, the average value of the L_p/L_{p0} obtained in all tests shown in Figure 2 is 0.99, with the experimental values between 0.89 and 1.09. However, a considerable degree of variability was found between the values of permeability of the various samples, which varies between 75 and $122 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$ ($95 \text{ L h}^{-1} \text{ m}^{-2} \text{ bar}^{-1}$ on average). This variability could be ascribed, in principle, to a possibly low homogeneity of the membrane itself. In fact, the membrane used in these tests was an industrial sheet, whereas the experimental sample size membrane used was small ($4.18 \times 10^{-4} \text{ m}^2$). This low

homogeneity is particularly obvious when comparing the hydraulic permeabilities of the samples tested (see Figure 2), even after compaction (that is, after the water fluxes had been stabilized; see section 3.1). Thus, it is possible that some variability may exist between the samples, for instance, in terms of membrane thickness. Differences of pore radius would be, in principle, less likely to occur, given that the pore radius (such as the chemical properties of the membrane) is a microscopic property of the polymer itself (and thus should not be reflected at the scale of the areas used in the tests).

The variability in hydraulic permeability might affect rejections (Figure 3), and to obtain a clear understanding of the phenomena involved, a more detailed analysis had to be performed. This was attempted in Part II of the experiments. In these tests, the rejections were determined as a function of the flux (see Figure 4) before and after modification. It is obvious from the plots that rejections strongly decrease with flux, for this solute and membrane, which has several important implications.

First, observed rejections decrease with flux only when the intrinsic rejection is approaching or reaches its maximum value R_{∞} , which depends only on the ratio r_s/r_p (see section 3.2). Thus, the determination of intrinsic rejections under these conditions is straightforward. To obtain the intrinsic rejections, a plot of $\ln[(1 - R_{obs})/R_{obs}]$ vs. J_v was done in each case and the values of R_m and the mass transfer coefficient in the polarization layer (k_s) were obtained from the intercept and the slope, respectively, according to the relationship

$$\ln\left(\frac{1 - R_{obs}}{R_{obs}}\right) = \ln\left(\frac{1 - R_m}{R_m}\right) + \frac{J_v}{k_s} \quad (6)$$

that can be readily derived from Eq. 3. The obtained values of R_m (and k_s) are indicated in Table 3. As can be seen, intrinsic rejections are very high for this solute, and thus it is easy to understand that they cannot change significantly with the modifications.

Second, if intrinsic rejections do not change with the modification, but observed rejections do increase (as can be seen in Figures 1 and 3), this implies that the modification may have some effect in lowering the

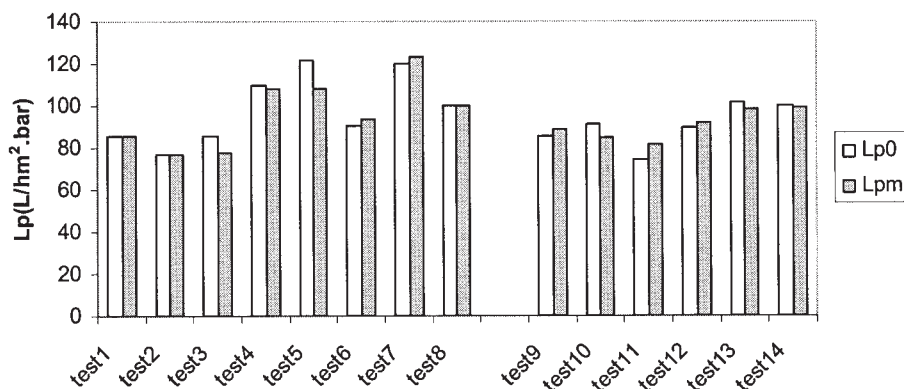


Figure 2. Hydraulic permeabilities (L_p) of the membrane samples used in modification tests. L_{p0} , before modification; L_{pm} , after modification.

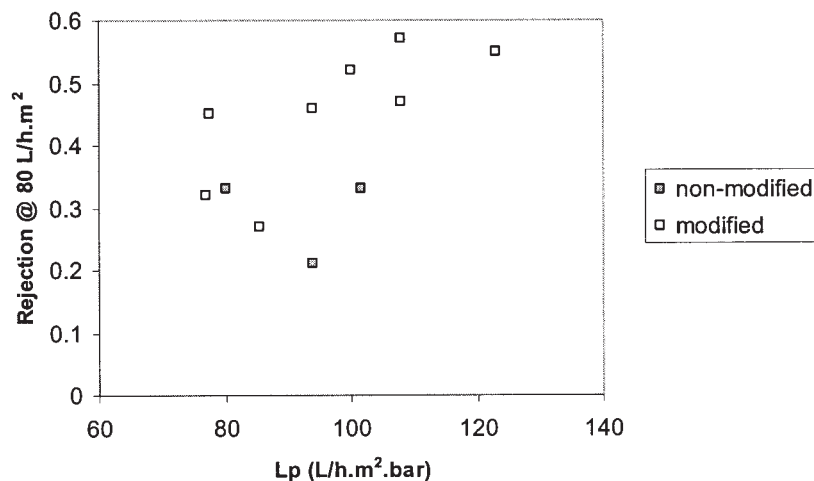


Figure 3. Analysis of the possible effect of the hydraulic permeability (L_p) on the rejections of dextran T70 in nonmodified and modified membranes.

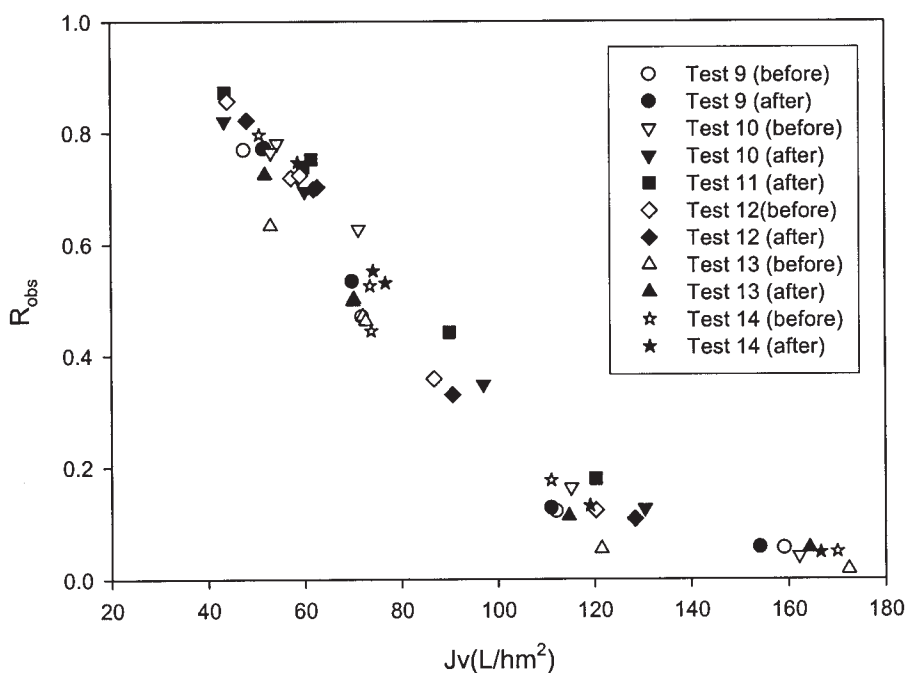


Figure 4. Rejection of dextran T70 before and after modification of the membranes, determined as a function of the flux. Tests performed in a 300 mL stirred cell from Sterlitech (pressures between 1 and 8 bar). See conditions of modifications in Table 1 (Part II).

solute concentration near the membrane (by decreasing it), although pore size is not affected. This also agrees with the fact that hydraulic permeabilities are not affected by the modifications. More work has to be performed, however, to obtain a better understanding of the processes involved.

The ATR-FTIR spectra of the modified and non-modified membranes, for modification conditions of test 5 (see Table 1), are presented in Figure 5. The spectra have the baseline corrected to enable a better comparison. A simple qualitative analysis of FTIR spectra showed an increase in 1738 cm^{-1} absorption, re-

lated to the carbonyl groups, and in the intensity of the OH stretching ($\sim 3410\text{ cm}^{-1}$) absorption, of the treated samples [69]. The former might be related to the occurrence oxidation of the (cellulose acetate) membrane, and the latter with the grafting of the PEG chains. However, the most remarkable difference in the spectra is that of a band at 1593 cm^{-1} that disappears with modification. The disappearance of this band is certainly more difficult to interpret.

The AFM images provide important information that also suggests the occurrence of modification (see Figure 6). In fact, the AFM images reveal the existence of

Table 3. Determination of the intrinsic rejection (R_m) and mass transfer coefficient (k) of dextran T70 in nonmodified and modified membranes.

Test	R_m		k_s (m/s)	
	Nonmodified	Modified	Nonmodified	Modified
9	93.2%	95.9%	7.64×10^{-6}	6.79×10^{-6}
10	96.8%	96.3%	6.70×10^{-6}	6.97×10^{-6}
11		97.8%		6.23×10^{-6}
12	97.9%	97.6%	5.66×10^{-6}	6.03×10^{-6}
13	93.9%	91.9%	6.71×10^{-6}	8.14×10^{-6}
14	93.5%	95.6%	8.00×10^{-6}	7.30×10^{-6}

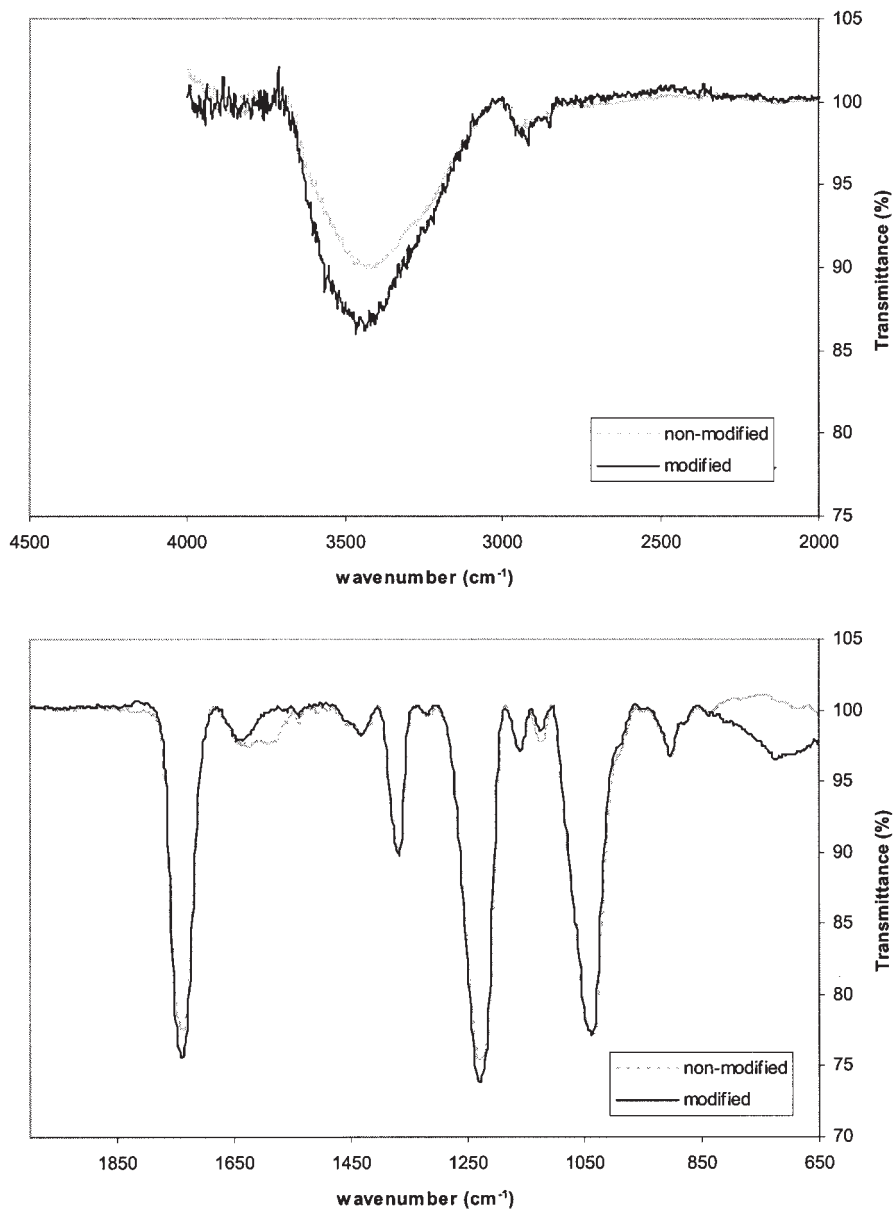


Figure 5. ATR-FTIR spectra of nonmodified and modified membranes. Modification was performed in conditions of test 5 (see Table 1). Dotted line: nonmodified membrane; solid line: modified membrane.

very “high” peaks in the surface of the modified membrane that are absent in the nonmodified membrane. The appearance of peaks is reflected in a strong increase of

the average rugosity with the modification, from 7.956 to 15.776 nm, and this might be related to the grafting of polymer chains in the surface of the membrane.

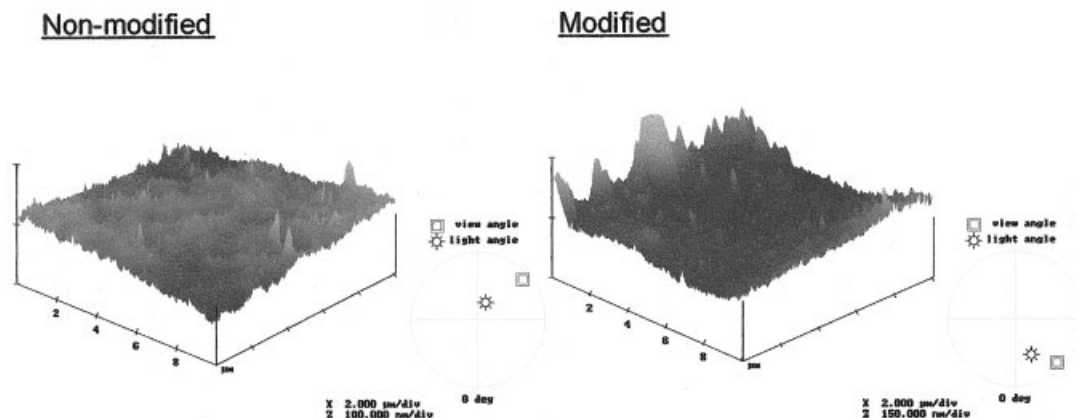


Figure 6. Atomic force microscopy (AFM) images of nonmodified and modified clean membranes.

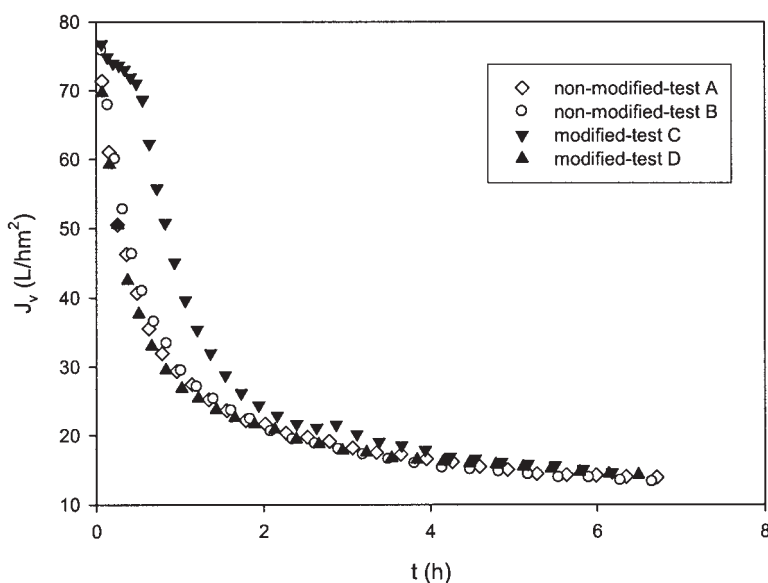


Figure 7. Fouling tests with humic acid for nonmodified and modified membranes. Permeate flux (J_v) along the time (t) of the experiments. Tests performed in a 10 mL stirred cell from Amicon/Millipore.

4.2. Fouling Tests

4.2.1. Humic Acid

The results obtained in the fouling tests performed with humic acid are shown in Figures 7–9. The fluxes and rejections were monitored throughout the experiments. It is important to note here that care was taken in choosing membranes of approximately the same values of L_p (the values were between 76 and 78 L h⁻¹ m⁻² bar⁻¹) in the tests performed, to avoid the possibility of differences in L_p affecting rejections and fouling. Figure 7 shows the flux decrease as a function of time of the experiments. First it is interesting to note the effect of the addition of CaCl₂ on the occurrence of fouling. This effect may be explained by the formation of Ca²⁺-mediated bonds between functional groups (with negative charge) in the cellulose acetate membrane and the humic acid (that was used in the form of a negative ion). With respect to the effect of modification, the most relevant fact is that, again, fluxes do not seem to be affected by the modification; however,

the rejections of humic acid do increase with modification (see Figure 8). The fact that fluxes are not affected by the modification may be explained by the possible increase in the hydrophilicity of the membrane that is expected to occur (given the highly hydrophilic nature of PEG chains).

SEM images were taken of the deposits of humic acid over the nonmodified and modified membranes, to investigate possible effects of the change in the hydrophilicity of the membrane on the structure of the deposits (Figure 9). The surface was observed in different zones and perspectives: that is, in the central zone of the deposits (where the deposited layers were uniform), the zone near the cut (in this region the deposited cake looks cracked), and also a cross-sectional image. No significant differences were found in the structure of the deposits, and this may be a result of the excessive accumulation of the product on the surface of the membrane.

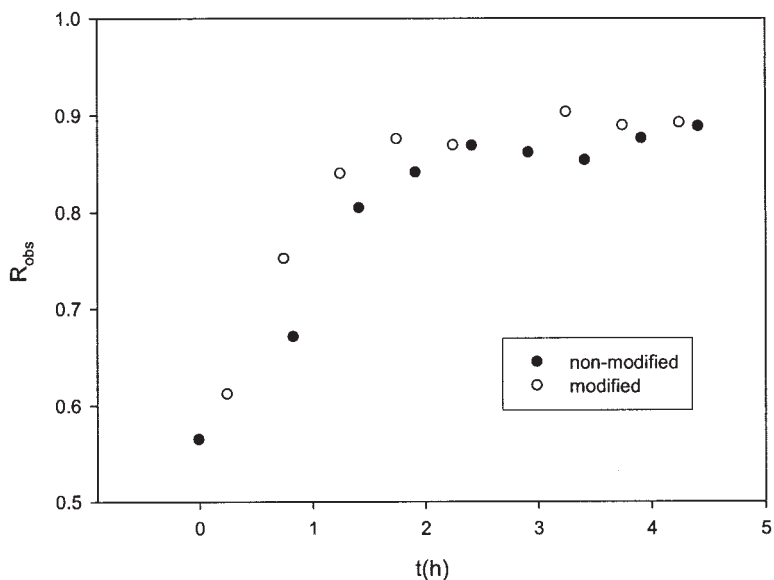


Figure 8. Fouling tests with humic acid for nonmodified and modified membranes. Rejection of humic acid along the time (t) of the experiments. Tests performed in a 10 mL stirred cell from Amicon/Millipore.

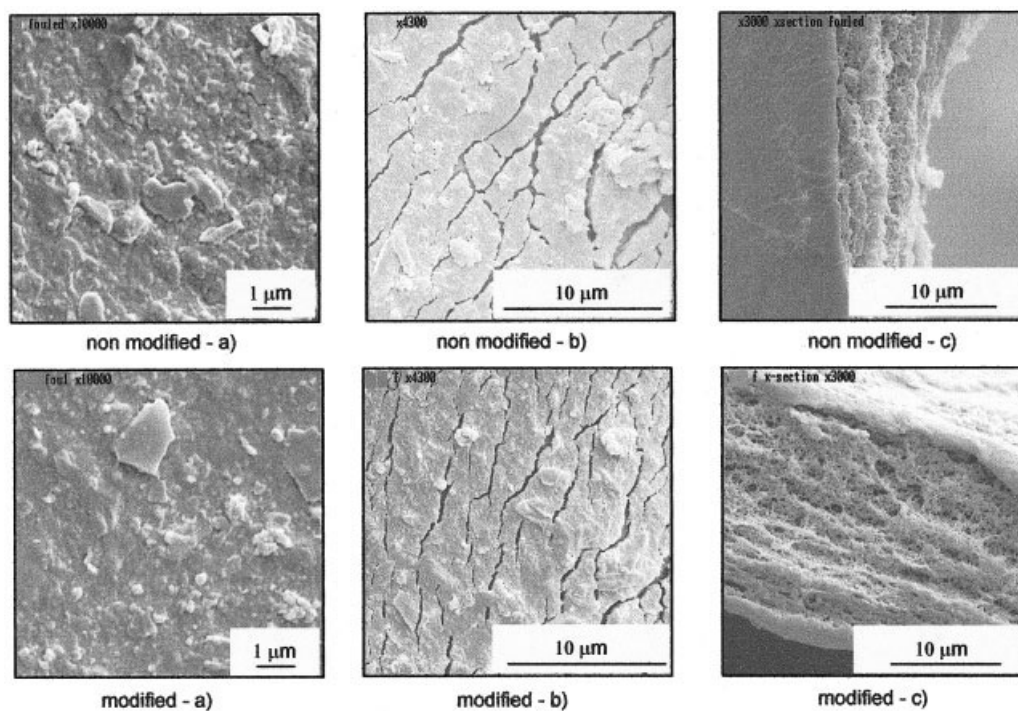


Figure 9. SEM images of the membranes fouled with humic acid deposits: (a) central zone; (b) near the cut; (c) cross section.

4.2.2. Textile Auxiliaries

As explained in section 3.3.2 the membranes (non-modified and modified) were fouled with the various products, under application of a considerably high pressure (8 bar), to achieve significant fouling. After the fluxes were stabilized (and at 350 mL were filtered, as explained in section 3.3.2), determination of flux vs. pressure was carried out (Figure 10) to obtain information about concentration polarization, which should be

distinguished from fouling. In fact, under the conditions of the tests performed

$$J_v = \frac{\Delta p - \Delta \pi}{\eta_0(R_b + R_f)} \quad (7)$$

where $\Delta \pi$ is the osmotic pressure difference between the permeate and the solution adjacent to the mem-

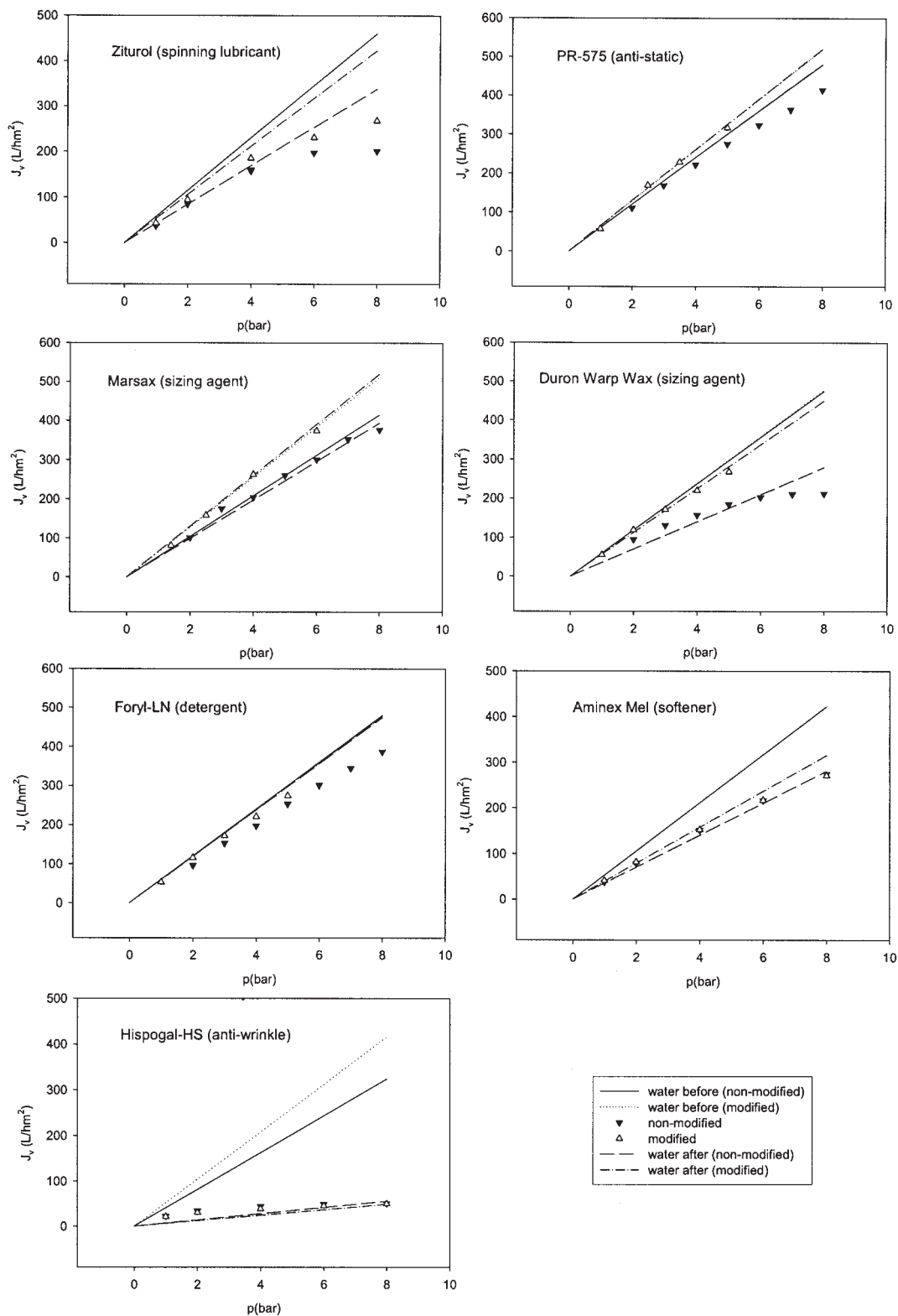


Figure 10. Permeation of textile auxiliaries in nonmodified and modified membranes. Flux (J_v) vs. pressure (p). Tests performed in a 300 mL stirred cell from Sterlitech.

brane in the feed side, according to the model of the osmotic pressure [68] and assuming that the membrane is already fouled. Thus, comparing the obtained values of J_v vs. Δp for the solution studied, with J_w vs. Δp using

pure water (at the end of the experiments) it becomes possible to distinguish concentration polarization from fouling, assuming that R_f remains constant (Figure 10). As can be seen, the various products behave differently

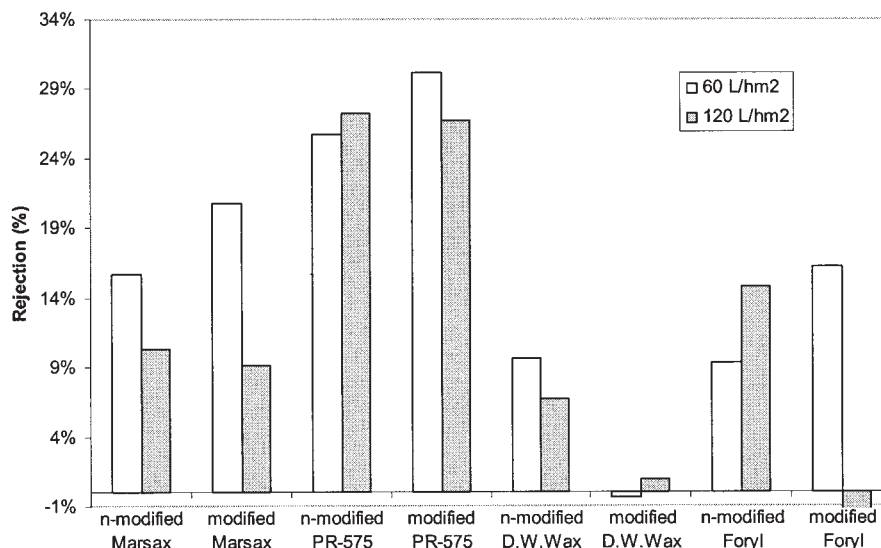


Figure 11. Rejections of the textile auxiliaries in nonmodified and modified membranes. A comparison is made at two different imposed permeate fluxes (60 and 120 L h⁻¹ m⁻²). Tests performed in a 300 mL stirred cell from Sterlitech.

with respect to their propensity to foul the membranes and to generate an osmotic pressure difference.

The surfactants (the detergent Foryl-LN; the anti-static agent PR-575) generate a significant osmotic pressure gradient, but do not cause fouling of the membranes. The decrease in fluxes resulting from concentration polarization was slightly lower for the modified membranes, in both cases.

On the opposite side are the antiwrinkle (Hispogal-HS) and the softener (Aminex Mel). With respect to these products, the flux decreases essentially because of fouling, and no significant effects derived from concentration polarization are found. For these two products fouling was very significant, especially for Hispogal-HS, and in this case, it is difficult to analyze the effect of the modification, explained by the fact that the interaction between this product and the membrane is very high. For Aminex Mel, it is possible to see a positive effect of the modification that decreases fouling.

For the spinning lubricant (Zituro) both concentration polarization and fouling affect the fluxes, and again it was found that fouling is significantly more pronounced in the nonmodified membrane. Concentration polarization seems not to be affected by the modification. For the sizing agents (Duron Warp Wax and Marsax) fouling is (again) more pronounced for the nonmodified membrane, especially for Duron Warp Wax.

Thus from these results it may be concluded that modification of the membranes may have an important effect in decreasing fouling, which could be eventually related to an increase in the hydrophilicity of the membranes. The way it affects concentration polarization is less obvious to interpret.

The effect of modification on rejections is also an important aspect studied. Rejections of the products (COD rejections) at two different values of flux (60 and

120 L h⁻¹ m⁻²) are compared in Figure 11. The spinning lubricant (Zituro), the softener (Aminex Mel), and the antiwrinkle agent (Hispogal-HS) are not included in this graph, given that the rejections found for these products are nearly 100%, in all the range of pressures tested (1–8 bar). The results are not completely elucidative, but it is interesting to note that rejections are always found to increase with the modification at the lowest flux (60 L h⁻¹ m⁻²), with the only exception of Duron Warp Wax, and decrease, in all cases, at the highest flux (120 L h⁻¹ m⁻²). This result—which is very difficult to interpret with our present knowledge—is certainly a topic of interest for further study.

The resistances arising from fouling calculated in each case, from Eqs. 4 and 5 (see section 3.3.2) are shown in Table 4. Thus, it is possible to divide the products in three main classes: those with low fouling characteristics (PR-575, Foryl-LN, and Marsax), those with intermediate tendencies to foul the membranes (Duron Warp Wax, Zituro, and Aminex Mel), and Hispogal-HS, which is a very strong foulant. A clearly positive effect of the modification is found for interme-

Table 4. Resistance attributed to fouling (R_f) in tests performed with the textile auxiliaries in nonmodified and modified membranes.

Product	$R_f/10^{12}$ (m ⁻¹)	
	Nonmodified	Modified
Marsax	0.5	~0
PR-575	~0	~0
Foryl-LN	0.1	~0
Duron Warp Wax	3.7	0.3
Zituro	2.4	1.7
Aminex Mel	2.5	1.8
Hispogal-HS	15.0	22.7

diate (and low) foulants, but in the case of Hispogal-HS the calculated value of R_f was higher for the modified membrane. This result indicates that modifications may also have negative effects with certain types of compounds, and in this case it appears that the possible increase in hydrophilicity increased even more the interaction between the membrane and the product, which is remarkably high. Thus, the membrane lost almost all its permeability. This may be an effect similar to that observed by Alexander *et al.* [22], as referred to in the introduction.

5. CONCLUSIONS

Chemical modification of a commercial ultrafiltration cellulose acetate membrane was achieved, using a simple experimental procedure, that might be used to perform *in situ* modifications. An oxidant agent, a highly hydrophilic macromolecule, and a chain-transfer agent were used to modify the membrane. Care was taken in not using too aggressive oxidation conditions, to preserve the mechanical and chemical properties of the original nonmodified membrane. Chemical modification of the surface was apparently obtained, as suggested from ATR-FTIR analysis. In fact, an increase in the carbonyl absorption band appears, repeatedly, in spectra of modified membranes, and an increase in the band corresponding to OH groups may indicate that grafting of the PEG molecules was in fact achieved.

One of the most important consequences of the modification was a strong increase in the rugosity of the membrane, observed by AFM analysis, and possibly contributed to an enhancement of mass transfer in the boundary layer. In fact some evidences of such an enhancement were indirectly concluded from the observed rejections of a neutral solute (dextran T70), which apparently increased at constant flux, and this could not be ascribed to an increase of the intrinsic rejections because these were found to be very high in this membrane (~96–97%).

In terms of the possible application of modified membranes in water treatment, the fouling of non-modified and modified membranes with a humic acid was studied. It was found that the modifications may have some effect in increasing the rejections of the organic compound. Despite the increase in rejections, the fluxes seemed to have been unaffected by the modification, and this may be attributable to an increase in the hydrophilicity of the membrane, which enhanced water transport.

With respect to the possible application of modified membranes to treat industrial wastewaters, a study of fouling with textile auxiliaries was also performed. These products represent one of the most important industries in Portugal. Modifications were found to decrease the fouling tendency of all the products tested, except one, an antiwrinkle agent. This product had a remarkably high affinity for the membrane, and the modification seemed to increase that affinity even more, thus increasing fouling.

NOTATION

C_b = concentration in bulk solution, mol/m³
 C_m = concentration at membrane surface, mol/m³

C_p = concentration in permeate, mol/m³
 J_v = permeate flux, m/s or L h⁻¹ m⁻²
 J_w = water flux, m/s or L h⁻¹ m⁻²
 k_s = mass transfer coefficient in the boundary layer, m/s
 L_p = hydraulic permeability, m s⁻¹ Pa⁻¹ or L h⁻¹ m⁻² bar⁻¹
 r_p = pore radius, m
 r_s = solute radius, m
 R_f = resistance attributed to fouling, m⁻¹
 R_h = hydraulic resistance, m⁻¹
 R_m = intrinsic rejection
 R_{obs} = observed rejection
 R_∞ = intrinsic rejection at infinite flux
 η_0 = viscosity of permeate, Pa·s
 $\Delta\pi$ = osmotic pressure difference, Pa or bar
 Δp = transmembrane pressure, Pa or bar

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