

New composite membrane for water softening

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Received 26 June 2000; accepted 10 July 2000

Abstract

A novel route to the preparation of nanofiltration membranes has been proposed. The method consists of the photografting of polymer on to the surface of porous membranes. The method was tested with polysulfone ultrafiltration membranes and poly(acrylic acid) in water solution. It has been shown that the surface modification is stabilised by crosslinking with N,N'-methylene bis acrylamide and that the grafting does not require any photoinitiator and any purification of the reactants. Moreover, by the proper choice of the wavelengths, the UV irradiation does not induce any significant copolymerisation of the reactants inside the aqueous solution. The irradiation conditions, the monomer concentration and the permeability of the support membrane were examined. The water softening properties of the novel membranes were measured in dead-end mode and at a 95% recovery. A large range of performances has been obtained which demonstrates the feasibility of the UV irradiation as an environmentally friendly and versatile (flexible) technology to prepare nanofiltration membranes.

Keywords: Nanofiltration; Softening; UV photografting; Surface modification; Membrane preparation

1. Introduction

Conventional softening technologies are being replaced by nanofiltration as the membrane operation does not add by-products to finished water or by-product disposal cost. Specifications for an ideal softening membrane include low cost, high fluxes, high rejection of

bivalent ions, low rejection of monovalent ion and high rejection of small organic molecule (pesticides, NOM), no or little pre- or post-treatment, low fouling, chemical and biological resistance. For domestic needs, the ability to operate at very low pressures — typically 400 kPa, with a high recovery — typically 95%, is an important requirement. As for reverse osmosis, the usual approach to nanofiltration membranes involves thin-film composite technology generally based on interfacial polymeri-

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sation. This technology needs the use of solvents and reactants leading to waste disposal costs.

In this paper, we report about another route to the formation of nanofiltration membrane by modification of ultrafiltration membranes with grafted polymer. This was accomplished by UV irradiation.

Modification of membranes by photografting has already been described by several authors with different objectives such as fouling reduction [1,2], biomolecule immobilization [3] or providing switchable permeability [4]. In our knowledge, photografting as a route to elaborate nanofiltration by modification of porous membranes has not yet been suggested.

As one objective was to develop an environmentally friendly technology, an ultrafiltration polysulfone membrane was chosen since this polymer is intrinsically photoactive and that no photoinitiators are required [5]. Acrylic acid has been selected as a well studied model for photopolymerisable monomer, poly(acrylic acid) is bound to surface membrane with covalent bond in order to increase life time of surface modification; it could also be expected that a negatively charged modified membrane will provide repulsive interaction with anions and improve the rejection of salts [6,7]. Since the pKa of poly(acrylic acid) is about 4.8, the pH will strongly influence the salts rejection; moreover the pH-dependent swelling of the polymer [4] could also influence the permeability of the nanofiltration membrane.

This work presents the first results obtained on the graft parameters (wavelengths, monomer concentration, irradiation time) on the membrane performance.

2. Materials and method

The membrane used is a flat sheet polysulfone membrane. It has been obtained by phase inversion (collodion was kindly provided by

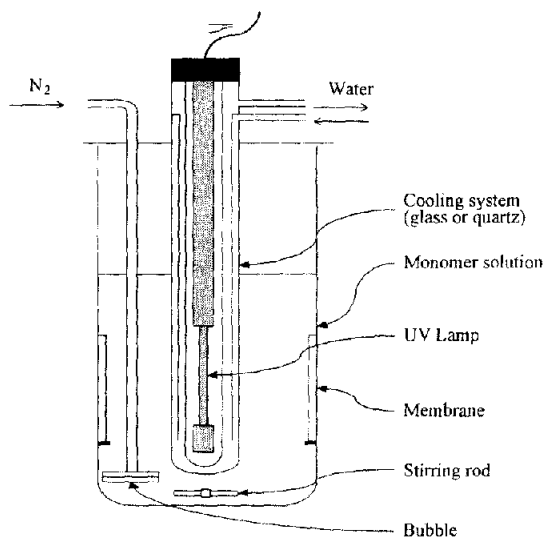


Fig. 1. Photoreactor schema.

Polymem SA, Fourquevaux, France). Preparation of this ultrafiltration membrane is reproducible and flux obtained was $400 \text{ l.h}^{-1}.\text{m}^{-2}$ ($\pm 10\%$) at 400 kPa. Acrylic acid (C_{AA}), N, N'-methylene bis acrylamide (Cr), 1-methyl 2-pyrrolidinone products were purchased from Aldrich and used as received. Acrylic acid concentration is given in mass percentage; N, N'-methylene bis acrylamide (crosslinker) concentration (Cr) is calculated in molar percentage referring to acrylic acid mole number. Water used for nanofiltration experiences was either reverse osmosis water for synthetic solutions, or directly tap water.

The photoreactor (Fig. 1) is composed by a cylindrical chamber in which membrane has been introduced. A UV lamp is placed in the centre of reactor. It is a polychromatic lamp, model UV Hanau Heraeus TQ 150 (Hg medium pressure). The cooling system can be in glass (Duran 50) or in quartz, so that wavelengths received by the membrane can be controlled (glass $\lambda > 300 \text{ nm}$, quartz $\lambda > 220 \text{ nm}$). Different

light intensities are received by the membrane when the cooling system is made in glass (470 mW/cm²) or in quartz (248 mW/cm²).

Experimental method was as follows: as-casted membrane was washed with reverse osmosis water, introduced in the reactor, then laid on the wall (skin exposed to UV light). Solutions of acrylic acid and crosslinker, in adequate concentration, were bubbled with nitrogen. The UV lamp was dipped in the reactor when its permanent regime had been established ($t = 60$ s). The membrane was irradiated during a given time. Then it was put out of the reactor and washed with reverse osmosis water. Membranes were kept in aqueous formaldehyde solution (1% weight).

Water flux was measured at 400 kPa using reverse osmosis water with an unstirred cell (Amicon 8050) having a 50 ml volume and 13.2 cm² active membrane area. The rejection of ions was measured for a volumic reduction factor, VRF, equal to 15 (94% recovery). Values were obtained, either for a synthetic solution of calcium chloride at 50 mg.l⁻¹ in calcium ion, or with tap water (calcium concentration between 20 and 50 mg.l⁻¹).

Calcium concentrations in initial feed C_0 and in total permeate C_p were measured by a sequential plasma torch ICP (Jobin Yvon JY 24). The mean rejection of calcium was then given by Eq. (1):

$$\bar{R} = 1 - \frac{C_p}{C_0} \quad (1)$$

Solutions for UV spectrophotometry were prepared in 1-methyl 2-pyrrolidinone for polysulfone and reverse osmosis water for monomers. They were analyzed using a UV spectrophotometer Anthelie (Secoman).

3. Results and discussion

First works carried out in the laboratory have shown that the photografting technology can be

used to elaborate nanofiltration membrane from an ultrafiltration membrane. Ageing tests (7 d in reverse osmosis water at 60°C) have shown that surface modification obtained was not stable. An addition of a low quantity of crosslinker has then been proved efficient to stabilise the modification in this ageing test (Table 1). The uncrosslinking surface modification is not stable: as indicated by the flux and calcium rejection values which are the same, than for the initial ultrafiltration membrane. In opposite, crosslinking surface modification is permanent: flux and calcium rejection are maintained after the ageing test.

3.1. Acrylic acid concentration of grafting solution influence onto membrane properties

Flux and rejection values vs. acrylic acid concentration are represented in Fig. 2. This study has been done with a quartz reactor and a 0.1% crosslinker concentration.

At constant irradiation time, we can observe a flux decrease and a rejection increase with an acrylic acid concentration increase. However, in these conditions the flux and rejection values are still relatively low.

Flux and rejection tend respectively to a constant value when acrylic acid concentration increases. From Fig. 2 we can say that the grafting is no more efficient when acrylic acid concentration is higher than 5%: flux and calcium rejection tends to a constant value. This efficiency decrease could be explained by UV absorption. With an increase of acrylic acid concentration, UV absorption by the solution increases (Beer-Lambert law) and light intensity received by membrane decreases. Therefore, the number of radicals created on the membrane surface decreases.

Consequently to this important absorption, UV irradiation will also induce copolymerization of acid acrylic and crosslinker in solution. We have observed that solution viscosity increases

Table 1

Crosslinker effect on ageing test (7 d in reverse osmosis water at 60°C); Grafting parameters: $C_{AA} = 2.5\%$, $[Cr] = 0.5\%$

Irradiation time, min	Without crosslinker		With crosslinker					
	Calcium rejection, %		Flux (400 kPa), $l.h^{-1}.m^{-2}$ at 25°C		Calcium rejection, %		Flux (400 kPa), $l.h^{-1}.m^{-2}$ at 25°C	
	Before	After 7 d	Before	After 7 d	Before	After 7 d	Before	After 7 d
2	14	0	55.6	360	7	7	6.8	6.8
3	39	0	4.4	380	18	17	3.6	3.6
5	51	0	2.8	368	57	57	1.6	1.6

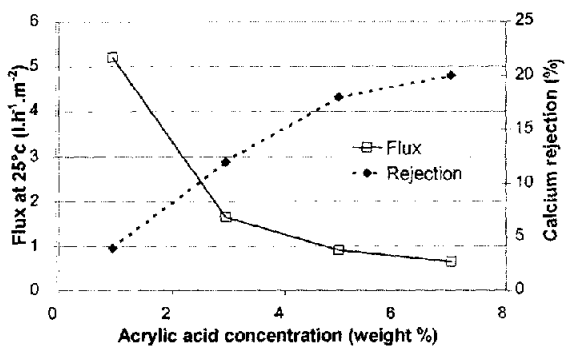


Fig. 2. Acrylic acid concentration influence on membrane properties; Quartz reactor $[Cr] = 0.1\%$, $t_{irr} = 5$ min; Pressure = 400 kPa, $[Ca^{2+}] = 50 mg.l^{-1}$.

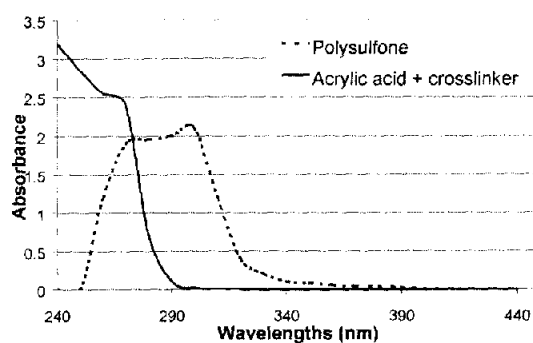


Fig. 3. Polysulfone and monomers solutions UV spectra.

up to gel formation and a layer is deposited on the reactor walls and on the UV lamp. This solution copolymerisation is a drawback for an industrial scale-up for several reasons. First, this solution copolymerisation consumes monomers, which are not used for grafting, and produces by-products. Secondly, the deposited layer on the wall of the UV lamp would cause a progressive decrease of the light intensity inducing a variation in product quality.

From this point, there are two problems to solve. How to improve fluxes and calcium rejection and reduce solution copolymerisation? First, we can adjust grafting parameters as such as irradiation time, wavelength, light intensity or

crosslinker concentration. Secondly, we can choose different polysulfone membranes with varying pore size, porosity or permeability. In this paper, first data on the influence of irradiation time, wavelength and support membranes are presented. Nevertheless, the first point to study is how to limit solution copolymerisation.

3.2. Wavelengths and irradiation time influence onto membrane properties

Trials conducted with a wavelength irradiation above 300 nm (by using a glass cooling system) show a lower copolymerisation

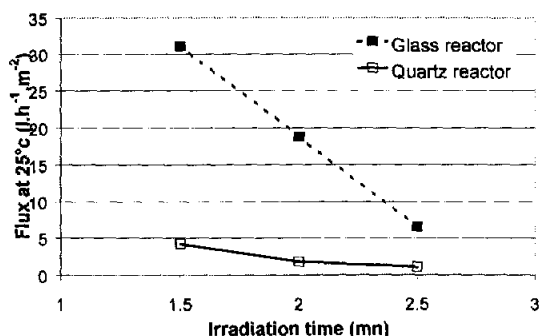


Fig. 4. Wavelengths and irradiation time effects on flux values; $C_{AA} = 2.5\%$, $[Cr] = 0.5\%$; Pressure = 400 kPa, $[Ca^{2+}] = 50 \text{ mg.l}^{-1}$.

(limpid solution, no deposit and no viscosity increase). This is explained by examining the absorption spectra of monomers and polysulfone solutions. For wavelengths above 300 nm, Fig. 3 shows that photosensibilisation of polysulfone is still possible without photoinitiator (i.e: polysulfone absorbs UV light). In the same conditions, monomers solution does not absorb and then the copolymerisation of acrylic acid and crosslinker is certainly negligible.

Ageing tests equally show that nanofiltration membranes in these conditions are able to resist to ageing test for 7 d at 60°C.

Figs. 4 and 5 show the influence of wavelengths range and irradiation time on flux and rejection. These figures show that an increase in irradiation time gives lower fluxes and higher calcium rejection.

These results also indicate that, for an irradiation with a glass reactor, a significant improvement of performance is possible in comparison with an irradiation with a quartz reactor: flux values are 6 times higher while rejection values remain the same. Wavelengths used are consequently a very important parameter since experiments with $\lambda > 300 \text{ nm}$ rather than $\lambda > 220 \text{ nm}$ can limit copolymer

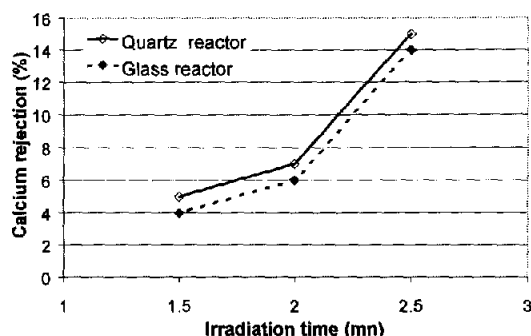


Fig. 5. Wavelengths and irradiation time effects on calcium rejection values; $C_{AA} = 2.5\%$, $[Cr] = 0.5\%$; Pressure = 400 kPa, $[Ca^{2+}] = 50 \text{ mg/l}$.

formation in solution and increase the flux at constant rejection value.

Explanation of this phenomenon is not easy. On the one hand, light intensity received by membrane surface is not the same for a glass and a quartz reactor, this can probably induce a difference in the number of radicals created onto the polysulfone surface and in depth into the skin layer grafting. On the other hand, the grafted layer composition obtained with glass reactor is different from the grafted layer formed using quartz reactor. In the latter, the grafted copolymer chains are physically associated with copolymers formed in solution.

3.3. Membrane support influence

Another idea to improve the flux of the modified membrane is to use a porous support of the membrane having a higher initial water flux. In adjusting the parameters of the inverse phase process, different ultrafiltration membranes can be prepared with a water flux in the range 400 to 2400 $\text{l.h}^{-1}.\text{m}^{-2}$ (at 400 kPa). After irradiation with the quartz reactor, the results given in Fig. 6 show that when the support membrane permeability increases, the flux for the modified

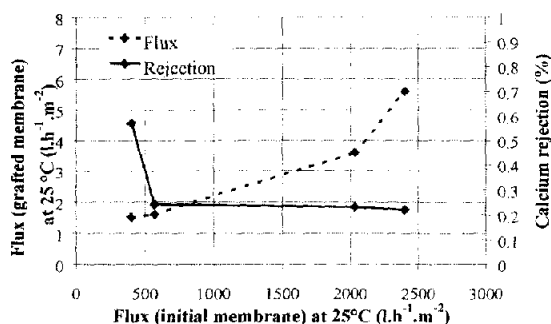


Fig. 6. Ultrafiltration membrane porosity effect on flux and rejection values; Quartz reactor, $[Cr] = 0.5\%$, $t_{ir} = 5$ min; Pressure = 400 kPa, $[Ca^{2+}] = 50$ mg/l.

membrane increases and rejection does not drop significantly. This unexpected important observation would deserve analyses, more particularly ultrafiltration membrane needs to be characterised in terms of pore size, porosity.

3.4. Tap water softening

In order to prove the efficiency of the modified membranes for tap water softening, few tests were performed. The results in Table 2 show that calcium rejection is higher (and flux lower) with tap water than with synthetic solution. This difference can be attributed to several parameters. In particular, tap water contains bivalent anions (as SO_4^{2-}) and repulsion is more important for these bivalent ions than for chloride ions, and calcium rejection increase can be expected. Another effect is the pH, which has an influence on poly(acrylic acid) properties ($pK_a = 4.8$). So, with a synthetic solution ($pH = 5.5$), few carboxylic groups are still protonated, inducing a decrease of the charge density. For tap water ($pH = 7.5$), all acid groups are ionised (COO^- form) and the membrane has a maximum charge density. This charge density

Table 2

Calcium rejection and flux vs. water type ($C_{AA} = 2.5\%$, $[Cr] = 0.5\%$, glass reactor)

Irradiation time, min	Calcium rejection, %		Flux (400 kPa), $l.h^{-1}.m^{-2}$ at 25°C	
	Synthetic solution	Tap water	Synthetic solution	Tap water
1.5	1	24	32	24
2	5	35	18	12
2.5	7	68	6	4

difference combined to grafted copolymer chains swelling might also be an explanation for the performance obtained with tap water. The higher rejection would also induce a stronger concentration polarisation effect and would also explain the lower flux.

4. Conclusions

A novel route to the preparation of nanofiltration membrane has been demonstrated. The method consists in photografting a polymer on the surface of porous membranes. The method was tested with polysulfone ultrafiltration membranes and poly(acrylic acid) in water solution. It has been shown that the surface modification is stabilised by crosslinking with N, N'-methylene bis acrylamide and that the grafting does not require any photoinitiator and any purification of the reactants. The water softening properties of the novel membranes were measured in dead end mode and at a 95% recovery. A large range of performances has been obtained which demonstrated the feasibility of the UV irradiation as an environmentally friendly and versatile technology to prepare nanofiltration membranes.

Several ways to improve the membrane performance have been discussed. Flux was im-

proved by a factor 6 by choosing a wavelength range above 300 nm without any significant drop in calcium rejection; moreover in this irradiation condition, no significant copolymerisation inside the monomers solution occurred. Flux was also improved by a factor 3 by using a more permeable support membrane without any significant change in calcium rejection. Irradiation time and monomers concentration could be optimised in order to adopt the membrane performance to a defined application.

This preliminary study will be continued to clarify multiple points that have been raised during this work. To achieve the objective it is necessary to determine ultrafiltration membrane characteristics grafting yield and the grafted layer structure (inside the membrane and on the surface).

The influence of grafting parameters (light intensity, wavelengths, irradiation time and monomer concentration) on membrane characteristics and properties will be also further examined.

Acknowledgements

Financial support for this work was provided by the Région Midi Pyrénées and by the Centre National de la Recherche Scientifique (Programme ECODEV-PROSETIA). The authors want to thank Miss Sandrine Desclaux for her excellent technical assistance.

References

- [1] M. Nyström and P. Jarvinen, *J. Membr. Sci.*, 60 (1991) 275.
- [2] Y.M. Lee, S.Y. Ihm, J.K. Shim, J.H. Kim, C.S. Cho, Y.K. Sung, *Polymer*, 36 (1995) 81.
- [3] M. Ulbricht and M. Riedel, *Biomaterials*, 19 (1998) 1229.
- [4] M. Ulbricht, *React. and Funct. Poly.*, 31 (1996) 165.
- [5] H. Yamagishi, J.V. Crivello and G. Belfort, *J. Membr. Sci.*, 105 (1995) 237.
- [6] W.R. Bowen and H. Muktar, *J. Membr. Sci.*, 122 (1996) 263.
- [7] C. Combe, C. Guizard, P. Aimar and V. Sanchez, *J. Membr. Sci.*, 129 (1997) 147.