WASTEWATER TREATMENT USING A MODIFIED CELLULOSE ACETATE MEMBRANE

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The main objective of this work has been to study the performance of membranes developed for treating purified wastewater. Polymeric membranes have been developed from solutions containing cellulose acetate (AC) and polysulfone (PSF), using N,N-dimethylformamide (DMF) as solvent and polyethylene glycol (PEG) as additive. The phase inversion method was chosen as a technique for producing the membrane films. The incorporation of PEG allowed us to study the effect of the additive on the morphological structure, and to predict the performance of the membranes formed. Examining the flux, permeability and selectivity of the membranes allowed studying the efficiency and performance of each membrane. The application results achieved in wastewater treatment at Chenoua/TIPAZA station were very satisfactory and in accordance with the standards required by WHO. The optimal performance, in terms of permeability and selectivity, was obtained for the MC membrane with the composition: PSF/PEG/AC of 25/12/63.

Keywords: cellulose acetate (AC), polysulfone (PSF), polyethylene glycol (PEG), nanofiltration, effluent treatment

INTRODUCTION

The use of membrane technology has been booming in recent years in various industrial and socio-economic sectors, namely, agri-food, water treatment, the dairy, as well as the pharmaceutical and healthcare industries. The evolution of regulations, as well as consideration of new substances found in water, has contributed, in part, to the development and use of membranes. This development permitted to diversify the membrane systems proposed and, in parallel, to improve their conditions of use and operation.[1]

The membrane process is a mechanical process that allows separating the various constituents of a mixture by passing it through a porous interface (paper filter, ceramic, membrane, *etc*.). To cope with the problem of water scarcity, this process has been proven practical, usable on a large scale and less expensive, being considered as an alternative and sustainable solution to produce water of good quality. It has a triple advantage vis-à-vis competitive conventional technologies (distillation, separation, extraction and others). Indeed, it is particularly energy-efficient, does not require any addition of chemical compounds, which can lead to downstream treatment, is faster, more efficient and easily adaptable.[2]

This technology is based on advanced membrane filtration. It separates water from soluble substances, such as oils, organic substances (soaps), suspended solids and metals (particulate or ionic). It is based on the application of a pressure difference that allows the transfer of the solvent through a membrane whose pore size ensures the retention of solutes. It involves a number of operations, classified according to a decreasing pore size, as follows: microfiltration, ultrafiltration, nanofiltration and reverse osmosis. The appropriate material for preparing these membranes, as well as the appropriate synthesis method, plays a crucial role in its efficiency and performance. The raw material of the membrane may be organic (polymers) or inorganic in nature, and the majority of commercialized polymer membranes are produced via a phase separation process.[3,4]

Our work consists in developing membranes for the treatment of different effluents and evaluating their filtration efficiency. This part is devoted to the synthesis of cellulose acetate (AC) and polysulfone (PSF) based polymer membranes, using N,N-dimethylformamide (DMF) as solvent and polyethylene glycol (PEG) as additive. The phase inversion method has been chosen as a technique for producing the membrane films. The prepared membranes were characterized by the molecule weight cut-off (MWCO) method. Filtration tests were performed to study membrane performance in terms of flux, permeability, and selectivity. Samples of treated wastewater from the Cheneoua Treatment and Purification Plant (STEP) (Tipaza, Algeria) were used in our membrane applications.

EXPERIMENTAL

Fabrication of membranes by phase inversion

The considered method of preparation of the polymer membranes is the phase separation induced by a non-solvent (water) NIPS (Fig. 1). The principle of this process is based on the penetration of a non-solvent into a polymer solution, which results in the separation between the polymer-rich phase and the discontinuous phase poor in polymer. The polymer-rich phase represents the matrix of the membrane and the polymer-poor phase lies at the origin of the pores.

The solutions were prepared by mixing polysulfone (PSf) with cellulose acetate (AC), in different amounts, in DMF solvent at 90 °C and in the presence of PEG 400 as additive. The polymer solution with a total polymer concentration of 17.5 wt% was mechanically stirred at 500 rpm to get a homogenous solution. The homogeneous solution obtained was then allowed to rest (without stirring) for one hour to remove air bubbles. An appropriate amount of the collodion solution was homogeneously spread manually on a glass plate, using a 150 µm thick film applicator. After 30 seconds evaporation, the films were immersed into a coagulation bath at 4 °C. Thermal annealing was performed for all the membranes in an oven at 90 °C for 15 minutes,[5-7] with the exception of the MC' membrane. After that, all the membranes were stored in distilled water. The casting solution became turbid and the mixture was not homogeneous at 30% polysulfone concentration, which allowed concluding that the compatibility of the mixture was obtained for the formulations with PSf in amounts lower or equal to 25%.

Table 1
Composition of PSF/PEG/AC mixtures

Denotation	PSf	PEG	AC	Solution observation
MPSf	100	0	0	Homogenous
MA	15	10	75	Homogenous
MB	30	10	60	Heterogenous
MC/MC’	25	12	63	Homogenous
MD	40	20	40	Heterogenous
ME	5	5	90	Homogenous
MF	10	15	75	Homogenous
MG	0	10	90	Homogenous
MH	10	0	90	Homogenous
Mac	0	0	100	Homogenous

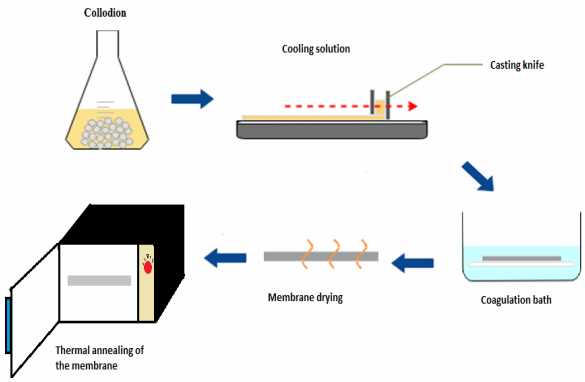

Figure 1: Preparation of membranes *via* the phase inversion method with thermal annealing

Figure 2: Diaphragm filtration system test bench photo[5]

Filtration experiments were carried out using the pilot system shown in Figure 2, designed and built in the laboratory by the DDESM (Distillation and Desalination of Sea Water and Brackish Water) team from the Solar Equipment Development Unit, Renewable Energies Development Center.

The solutions were prepared from neutral or ionic solutes with different concentrations. They were filtered at pressures ranging from 2 to 25 bar, at room temperature. For the determination of the filtration flux, the density of the solutions was assumed slightly different from that of the pure water because of the low concentration of solutes.

A comparison of the initial water permeability value with that obtained after filtration of the solutes makes it possible to detect the occurrence of membrane clogging. In general, no clogging was observed after a simple washing with water.

In specific cases of filtration, such as purified wastewater, washing procedures were applied, which will be detailed in the relevant Results and Discussion sections. The concentrations of the permeate were determined either by a conductivity meter (in the case of a simple salt solution), or by a spectrometer.

Equation (1) determines the flux of pure water known as pure water permeability (PWF) and that of the solutions to be treated:

$$Jp = \frac{V}{\Delta t.S} \quad (1)$$

where Jp is the pure water permeation flux ($Lm^{-2}\ h^{-1}$), V is the volume of permeate in (L), S is the effective membrane surface area (m^2) and Δt is the time (h).

The rejection rate of a species (noted T_R) is defined as the percentage of species retained by the membrane. In the case of complex mixtures, an individual release rate was defined for each type of solute.[5] The rejection rate was calculated using Equation (2) shown below:

$$T_R = 1 - \frac{C_P}{C_f} x100 \quad (2)$$

where C_P and C_f represent concentrations in the permeation and feed solutions, respectively (wt%).

RESULTS AND DISCUSSION

Molecular weight cutoff (MWCO) of membranes

Figure 3 illustrates the release of solutes through the PSf/AC membrane as a function of their molecular weights. The MWCO of the membranes was determined by interpolation of the values obtained for a 90% rejection rate, and is listed in Table 2. It is observed that the separation of the solute increases with the increase of the molecular weight of the solute, rejection being detected at about 83% of PEG 400 for the MC membrane. It varies between 85% and 88%, respectively, for the MA and MG membranes. It exceeds 91% for all the membranes for a PEG 600 feed and records total removal for the pure acetate MAc membrane. The other membranes show a rejection rate close to 100% for a 1000 Da PEG solution, with the exception of the MA and MC membranes, which recorded rejection rates of 97% and 95%, respectively.

According to these results and according to the literature, it was concluded that the pores of the membrane are of nanometer size, which is in the range of NF membranes.[8-9] It is clearly demonstrated that the membranes that contain PSf have a higher MWCO, compared to the membrane without PSf, and that PSf/AC membranes that contain PEG as an additive have a higher MWCO compared to those without additive.

Performance of membranes

The permeation plot of pure water *versus* time indicates that the pure water flux (PWF) of the PSF/AC/PEG hybrid membranes is greater than that of the membrane from pure acetate MAc, which is about 5.6 L/m^2h at 10 bar. The incorporation of 10% of PSf by weight into the mixture did not improve the flux, which remained close to that of the MAc membrane. On the other hand, the addition of 10% PEG slightly increased the flux to 8.5 L/m^2h for the MG membrane. The increase is more apparent for the MA membrane for a flux of 33 L/m^2h, while the best flux was obtained for the MC membrane. It was 7.5 times higher than that of the MAc membrane, which consists of 12% by weight of PEG and 25% of PSf. Among others, an increase in PSf in the solution of the polymer blend of 5 to 25% by weight of the total polymer increases the flux from 13.5 to 45.6 L/m^2h at 10 bar.

The highest flux is obtained for the membrane containing the highest percentage of PSf in the mixture. This may be due to its partial compatibility, causing greater free energy in the mixture. This leads to a larger segmental space in the polymer chain between cellulose acetate and polysulfone.[10]

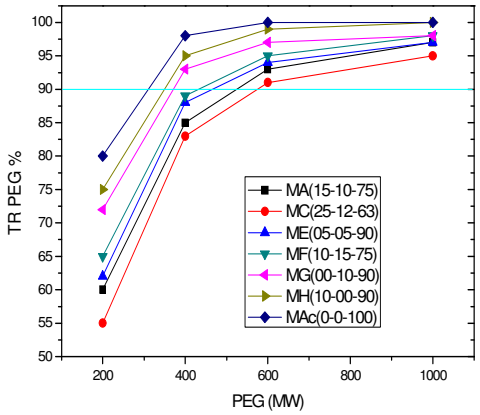

Figure 3: Rejection *vs* molecular weight of PEG for all membranes

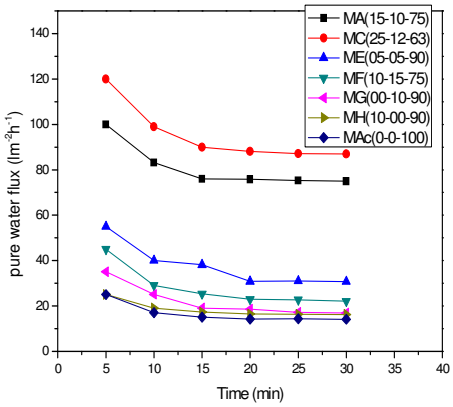

Figure 4: Evolution of pure water flux (PWF) as a function of time at 20 bar

Table 2
Values of different parameters for MC and MC' membranes

Membrane	MCWO (Da)	µp (nm)	PWF (L/m^{2}h at 20 bar)	Lp (L/m^{2}h bar)	Contact angle (°)
MC	579.12	0.45	87.2	4.003	60±1
MC'	35000	7.16	6553.19	302.12	61±2

The same flux behavior is observed for all the membranes at a pressure of 20 bar (Fig. 4). The flux increases from 14.3 L/m^{2}h for the pure MAc acetate membrane to 87.2 L/m^{2}h for the MC membrane; which is 6 times higher. The PWF of the membranes increases by incorporating the PEG within the mixture, which is due to the decrease in the hydraulic strength of the mixture, causing the thinning of the upper layer of the skin and higher porosity. It should also be noted that improving the hydrophilic membrane will also facilitate the diffusion of water through the membrane.

This confirms previous research, which has concluded that the addition of PEG improves PWF, and implies better hydraulic permeability and thus low hydraulic resistance of the membrane. It was found that, whatever the water to be treated,[6] the most abundant flux is recorded for the membrane having a PEG level that varies between 5-12%. In this interval, we notice that when the rate of PEG increases the flux increases, while beyond this value, *i.e.* for a rate higher than 12% PEG, the flux decreases. This correlates with the previous results and confirms that the membrane exhibiting porous surface morphology confers better flux. For this purpose, the MC membrane is considered to be the most efficient membrane for a PEG level of 12% and the highest PEG/PSf ratio.

Study of the thermal annealing effect

In order to better illustrate the effect of thermal annealing on the performance of the membrane, it is useful to make a quantitative comparison *via* Table 2, which regroups the values of different parameters of the two membranes MC and MC' with the same composition of the PSF/PEG/AC mixture: 25/12/63, and which differs by thermal annealing. The membrane labeled MC is the membrane that has undergone thermal annealing at 90 °C for 10 min.

In this comparison, a clear difference could be observed for the parameters studied. It was found that the pore size and its distribution decreased sharply after the treatment, and a significant change in MWCO occurred after the treatment, *i.e.* from 35 KDa for the MC' membrane to 579.12 Da for the MC membrane. The same has been observed for pore distribution (µp): the pore size is almost 16 times smaller for the MC membrane (0.45 nm), compared to that of the MC' membrane (7.16 nm). Regarding the pure water flux and permeability, it is obvious that the MC' membrane reaches very high values for these parameters (Lp), and it can be classified as a UF membrane. These values are about 6553.6 L/m^{2}h and 302.12 L/m^{2}h at 20 bar, while with thermal annealing they dropped to 87 L/m^{2}h and 4 L/m^{2}h bar at 20 bar. These results clearly indicate that thermal annealing induces compression of the polymer

chain and decreases the free volume.[11-13] Therefore, the thermal annealing process is an efficient method for adapting the pore size of the ultrafiltration membrane (MWCO) to a nanofiltration membrane (MWCO between 200 and 1500 Da and a pore size between 0.1 and 2.0 nm).

In summary, these results prove that thermal annealing is a powerful tool for regulating the state of polymeric aggregates and the pore structure of membranes. The pore sizes obtained are adapted to the range of dense membranes, reverse osmosis membranes, nanofiltration membranes. This treatment is a simple and effective strategy for converting an ultrafiltration membrane to a nanofiltration membrane, based on hydrophilic copolymers and additive polymers.

Flux study of treated wastewater

In this part, purified wastewater from the Cheneoua/Tipaza station was used for the treatment. It was characterized by conductivity equal to 1819 µS/cm, cloudy appearance (turbidity = 18 NTU) and basic pH (equal to 8.5 at a temperature of 15.7 °C). Figure 5 shows the evolution of treated wastewater flux as a function of time. The results show that the permeate flux remains almost constant with the filtration time for all the membranes. The best flux is observed for the MC membrane, which reaches 75.70 L/m^{2}h, followed by the MA membrane with 65.94 L/m^2.h. On the other hand, a lower value of the flux density is observed for the MAc membrane, of about 13.3 L/m^{2}h. Indeed, this confirms that the flux increases with increasing PEG content and PSF/PEG ratio in the mixture for the treatment of wastewater. The results of purified wastewater streams vary in the following order: MC > MA > ME > MF > MG > MH > MAc.

Flux weight loss is defined as the decrease in solution flux relative to pure water flux (PWF). This loss is observed for all the membranes. The greatest estimated loss, of 14.74%, corresponds to the MC membrane containing 25% PSf; while it is 13.33% for the MA membrane, which has contains 15% PSf. This loss decreases for the MF, ME and MG membranes, varying from 7 to 9%. In fact, it can be noted that the higher the content of PSf in the membrane, the greater is the weight loss. This is explained by the fact that the pores of the latter are wider, thus leading to clogging and a decrease in flux. Meanwhile, the MAc membrane is characterized by the lowest weight loss, of the order of 3.45%. Indeed, cellulose acetate membranes tend to have a very low flux and good resistance to fouling. The pH change as a function of time is shown in Figure 6. The obtained values are constant for all the membranes. The pH is between 7.39 and 8.07. These values meet the standards required by WHO (World Health Organization) and FAO (Food and Agriculture Organization) (Table 3), which establish the lower and upper limits as 6.5 and 8.5, respectively.

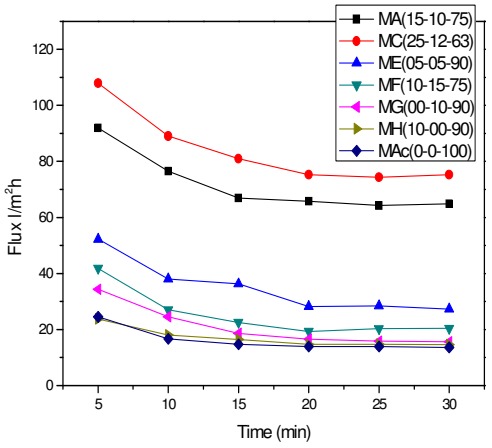

Figure 5: Flux of treated wastewater as a function of time for all the membranes

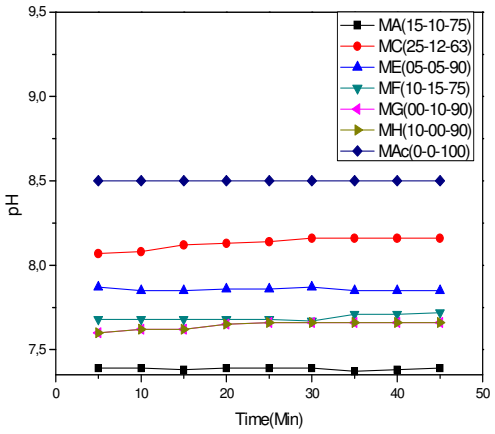

Figure 6: pH variation as a function of filtration time

Table 3
FAO, WHO and Algerian standards[2]

FAO standards			
Parameters	No problem	Low and moderate	Severe problems
Conductivity (µS/cm)	<750	750-2000	>3000
Parameters	WHO standards		Limit values of release in a receiving environment (Algerian standards)
NO_2^- (mg/L)	1		-
NO_3^- (mg/L)	50		-
SM (mg/L)	<20		35
pH	6.5-8.5		6.5-8.5
BOD (mg/L)	<30		33
COD (mg/L)	<90		120
NH_4^+ (mg/L)	<0.5		-
Iron (mg/L)	-		3
Dissolved oxygen (mg/L)	> 5very good 3-5 good 2-3 average 1-2 bad/<1very bad		-

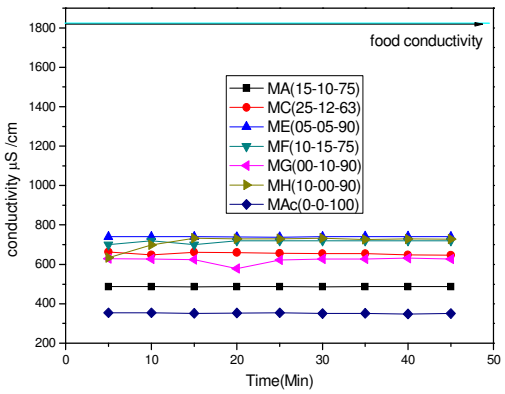

Figure 7: Conductivity variation as a function of filtration time

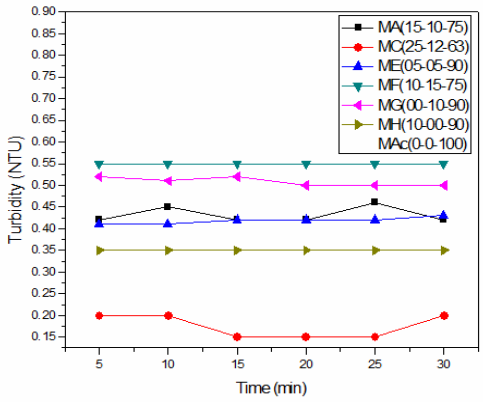

Figure 8: Turbidity variation as a function of filtration time

As shown in Figure 7, conductivity shows almost constant values over time for all the membranes. It decreases considerably compared to the initial value (treated wastewater) of 1819 µS/cm. The conductivity of the MAc membrane is equal to 351 µS/cm, that of the MA membrane has a conductivity of 485 µS/cm, and the other membranes have conductivities between 600-800 µS/cm. This confirms that the latter retains the least undissolved solid matter. The conductivity values obtained after the treatment are satisfactory and are consistent with WHO standards.

The evolution of the discharge of purified wastewater turbidity as a function of filtration time is presented in Figure 8. Experimental results reveal very high retention of turbidity, compared to that of the initial solution, which is equal to 18 NTU. It falls to very low values, giving rise to retention rates ranging from 96.94 to 98.88% for all the membranes. The membranes can eliminate almost all the particles from suspensions. Moreover, the clarity of the water obtained after the filtration is very significant.

Retention rate for treated wastewater

The filtration system makes it possible to analyze the water treated using the different membranes at a working pressure of 20 bars and for an operating time of 45 minutes. The filtration tests allowed examining the retention of different materials that existed in the water samples. Table 3 groups the physico-chemical parameters used to

analyze water quality at the inlet and the outlet of the permeate. The obtained results indicate good quality of the permeate water, the concentrations of the physico-chemical parameters being in agreement with both Algerian standards and those for international discharges (OMS), as presented in Table 3.

Overall, a decrease in all the parameters was observed for all the membranes, leading to a satisfactory rejection rate (Fig. 9). It can be concluded that the membranes are effective for the treatment of wastewater. COD removal reached a maximum of 90% for the MAc membrane and a minimum of 67% for the MC membrane. As between 10-51% nitrite is eliminated, its release is the lowest. Nitrate removal varies between 50-65%, and its initial concentration does not exceed the threshold required by WHO. It should also be noted that the amount of dissolved oxygen increased after the filtration, the values obtained being classified as of good quality, according to WHO standards.

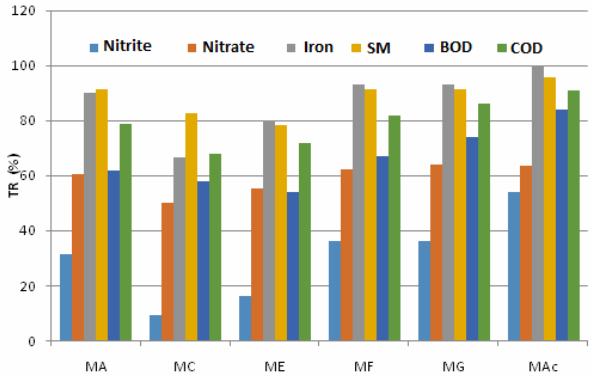

Figure 9: Retention rate (TR) of various compounds from purified wastewater for all the membranes

Concerning the ammonium concentration, the spectrometer used cannot detect values lower than 0.47 mg/L. This value also remains satisfactory to the standards recommended by WHO, it corresponds to a minimum retention estimated at 71.15%. Several studies have been devoted to the elimination of COD, turbidity and conductivity parameters, and it has been remarked that only NF membranes can achieve it simultaneously for all of them.[13] According to the results, it can be concluded that our membranes are effective, taking into account the simultaneous removal of COD, turbidity and conductivity. This supports the hypothesis that our membranes belong to the NF class.

CONCLUSION

To concluded, the thermal annealing permitted to obtain nanoscale pores for all the membranes. It has been shown that this technique allows controlling pore size. Thus, NF membranes have been obtained with MWCO of the order of 300-600 Da. The MC and MA membranes have lower release rates, but they meet the requirements of WHO and FAO. Indeed, taking into account flux and permeability parameters, they can be classified as the best membranes in terms of performance and efficiency. The obtained results for the treatment of wastewater indicate that the optimal performance in terms of permeability and selectivity was achieved for the MC membrane, with the composition PSF/PEG/AC of 25/12/63.

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