INFLUENCE OF POLYMER CONCENTRATION ON THE PERMEATION PROPERTIES OF NANOFILTRATION MEMBRANES

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Abstract: Driving force membrane processes seem to be most useful for water treatment. Membranes are very effective in removing a wide variety of water contaminants. Therefore, the use of these processes in water purification to replace or to improve conventional treatment has increased. An inherent problem of membranes is fouling, the accumulation of materials (foulants) near, on, or within the membrane that causes a reduction in the amount of product water over time. As a result of fouling, capital and operating costs of membrane systems are higher, making them less attractive. A membrane is an interphase between two adjacent phases acting as a selective barrier, regulating the transport of substances between the two compartments. The main advantages of membrane technology as compared with other unit operations in (bio) chemical engineering are related to this unique separation principle, i.e. the transport selectivity of the membrane. Separations with membranes do not require additives, and they can be performed isothermally at low temperatues and - compared to other thermal separation processes - at low energy consumption. Nanofiltration (NF) separate or remove small molecules or ions from a solvent (most often water) by means of pressure – driven filtration through a dense polymeric membrane. Combination of selectivity with a high permeability to water and mechanical strength sufficient to withstand high pressures is achieved by using thin film composite membranes comprising a dense film of 10-200 nm (active layer) supported by a thick asymmetric porous film. In this paper is describing the manufacturing processes of Polyethersulfone membranes (PES). A Polyethersulfone membranes was made with different concentration of polymer in N-Methyl-pyrrolidone (NMP) solvents. The influences of the polymer concentration on the membranes permeation properties were studied. After the preparations all membranes were studied for a comparison with cross flow and dead-end equipments to see the flux and permeability of pure water. The permeation results and the SEM photography show the influence of the polymer concentration, increasing concentration permeation properties are decreasing.

Keywords: membrane, nanofiltration, PES

1. Introduction

Nanofiltration (NF) is widely applied in the treatment of waste water and in the production of drinking water [1,2] because provide a feasible process allowing a high retention of multivalent ions as well as organic molecules. However, one of the main drawbacks of the nanofiltration performance is the fouling phenomenon, usually attributed to adsorption of organic substances on the membrane surface. Membrane fouling lead in diminished the membrane performance, serious deficient production, and excessive operating costs [6,7]. Because of the fouling, the dyes rejection [8-10] and the permeation properties [11-13] of the membranes decrease due to a higher hidrophobicity of the membrane surface. Membrane fouling depends by the membrane characteristics [14-17] and by the filtration mode (cross-flow or dead-end filtration) [18].

In order to increase the effectiveness of nanofiltration membranes, some properties such as hydrophilicity and fouling resistant should be improved. The membranes were synthesized at four different polymer concentrations 25, 27, 30 and 32 wt.% by the phase inversion method. This method means that after dissolution of the polymer in a solvent, the polymer solution has to be cast to a thin film with different thickness on a support layer. In our case the thickness of the polymer layer was 250 µm. The support layer, with the thin polymer film on it, is then immersed in a non-solvent bath, deionized water. Due to the diffusion of the non-solvent in the polymer film, the polymer solution becomes thermodynamically unstable, resulting in two phases: a polymer-poor phase (the

pores of the membrane) and a polymer-rich phase (the matrix).To make a good comparison of membrane characteristics some properties like hydrophobicity, permeability and morphology were studied.

2. Experimental

2.1. Materials

The solvent used was 1-Methyl-2-pyrrolidone and he support layer (type Viledon FO2471) used for the membrane manufacturing was obtained from Freudenberg (Weinheim, Germany). The polymer, Polyethersulfone type Radel, was supplied by Solvay (Belgium) and was used as the base polymer. To determine the membranes flux and the permeability was used distillated water.

2.2. Membrane preparation

NET polymeric membranes were manufactured at four different concentration of polymer (25, 27, 30 and 32 wt.%) in NMP, using the phase inversion induced by immersion precipitation method.
Preliminary experiments made by others researchers showed that the membrane with 30 and 32wt.% of PES are the most suitable concentrations to obtain NF membranes.

The casting solution was obtaining adding polymer in the solvent solution and mixed at 40^0C on the mechanical stirring at 200 rpm for 24 hours. On a polyester support a thin film of the polymer solution with a thickness of 250 μm was cast with a filmograph (K4340 Automatic Film Applicator, Elcometer). Membrane was immersed in distillate water for precipitation and after 15 minutes was washed to remove the excess of solvent. For every type of membrane, four different solutions were made and from every solution three membranes was manufactured and tested to obtain the true values of the membranes properties.

2.3. Filtration experiment

To study the performance of the membranes, permeability and flux, were used a dead-end (Fig. 1a.) and cross flow filtration (Fig. 1b.) installations.

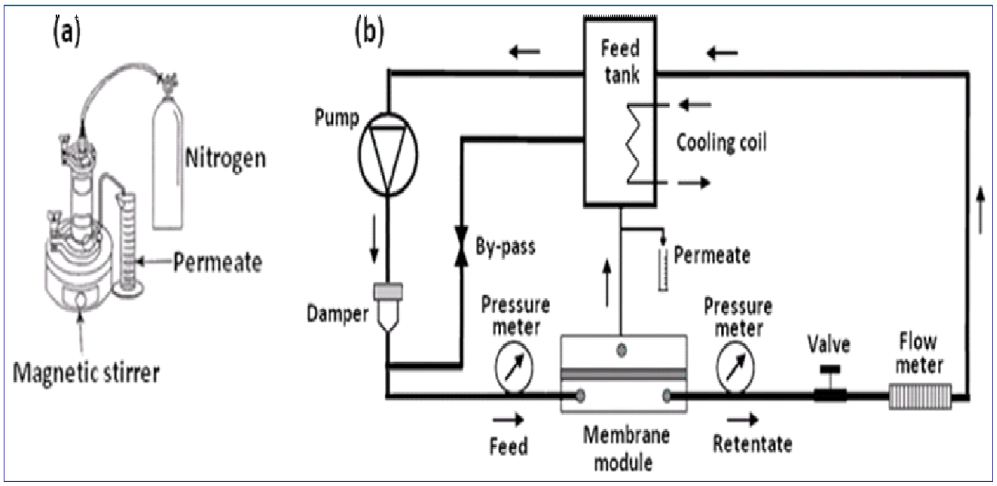

Figure 1. *Filtration equipment: a) dead-end and b) cross flow*

The pure water flux experiments were carried out with a commercial cross flow unit on laboratory scale. The permeability of the prepared membranes were studied using two dead end modules Sterlitech HP4750 at the room temperature and desirable pressure. The pressure was realized with a nitrogen cylinder and a pressure regulator, connected to the dead-end cell. The solution volume used for every experiment was 250 ml and the permeate was collected in a graduate cylinder. The pure water flux was determined at 10 bar pressure and the time was measured at every 5 ml of permeate.

To determine the pure water permeability (*PWP*) was measured the water flux (J_w) at six different pressure (ΔP) from 5 to 20 bar. The *PWP* was calculated by the following equation:

$$PWP = \frac{J_w}{\Delta P} \qquad 1)$$

To determine the pure water flux and membranes behavior for a long time all the membranes was tested in a cross flow installation. All experiments were realized at 24 ^{o}C and the applied pressure was 8 bar. The membranes

surface area was 0.0059m^2 and the time for every experiment was 24 hours.

2.4. Characterization of the membrane surface and morphology

To study the hydrophilicity/hydrophobicity of the membranes was used a Drop Shape Analysis System DSA 10 Mk2 (fig. 2b.). On the cleaned and dry membrane surface was placed a distillate water droplet of 2 µl and the contact angle between the membrane surface and the droplet was calculated (fig. 2a). The final value o the contact angle for every type of membranes was the average of 21 measurements, seven determinations for three different membranes.

Figure 2. *Contact angle measurements: (a) the principle and (b) the setup*

Scanning electron microscopy (SEM) measurements were performed for characterization of the surface and cross-section of the membranes. For the cross-section analysis the samples was prepared by fracturing the membranes in liquid nitrogen and sputtered with gold. The images were made with a Philips XL30 FEG and Phylips FEI, QUANTA 200 instruments. . Surface SEM images were made with a Phylips FEI, QUANTA 200 instrument with an accelerating voltage of 20 KeV

3. Results

3.1. Pure water flux and permeability

For the determination of pure water flux the filtration experiments were carried out with a commercial nanofiltration unit on laboratory scale. In all experiments the applied pressure was 8 bar and the temperature was 24^{0}C. To minimize concentration polarization a feed velocity of 4.0 m/s was used. The membrane surface area was 0.0059m^2. The evolution of flux was followed in time during 24 h. For analysis and comparison the values after 24 h of filtration were used.

Figure 3 shows that the permeation flux of PES membranes. The polymer concentration has an important influence on the pure water flux. When the polymer concentration decrease the pure water flux increase. The best membranes in term of water flux are at 25 wt% of PES.

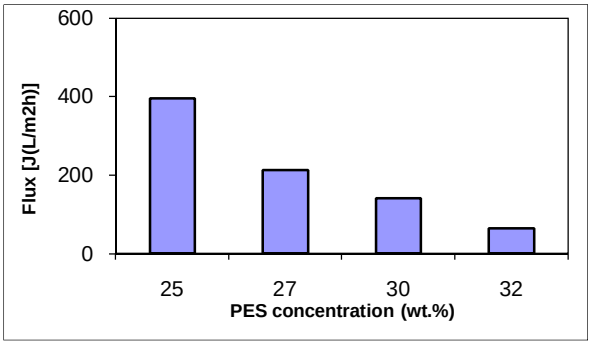

Figure 3. *Pure water flux at different concentration of PES*

Membranes with 25% of PES have a good permeability but because of the weaker mechanical resistance have an important instability of flux in time (figure 4). Hence, the increase of polymeric material enhances the membrane mechanical resistance.

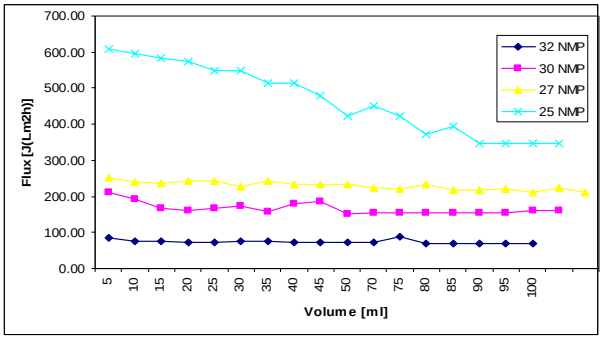

Figura 4. *Pure water flux for different PES concentration*

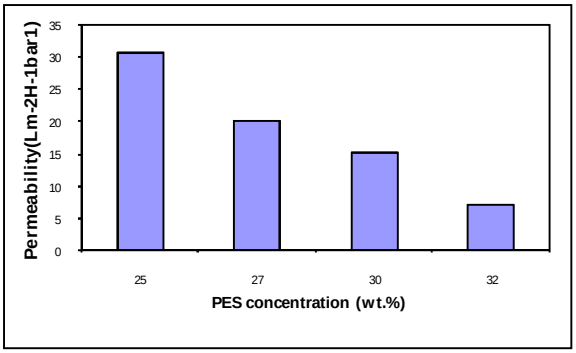

Figure 5. *Permeability at different PES concentration.*

Increasing the concentration of PES the membranes pore size decrease and in consequence permeability decrease. Figure 5 confirm the same influence of the polymer concentration on the permeability like in the case of pure water flux.

Membrane at 25 wt.% of PES have the higher permeability but because of them instability in time are not the ideal membranes to be selected for future experiments. Membranes a 27wt.% of PES appear to be the best membranes for nanofiltration experiment.

3.2. Contact angle

Contact angle determination is a well-known method to study the membrane surface hydrophobicity, since a hydrophilic membrane surface gives rise to a low contact angle [16].

Figure 6 shows the measured contact angles for neat PES membranes for four different polymer concentrations, indicating that membrane hydrophilicity increases as decreases the polymer concentration. The effect of polymer concentration on membrane hydrophilicity should be explained in terms of pore size and porosity considering.

Results are in concordance with permeation properties. Membrane with 25 wt.% of PES have the most hydrophilic surface.

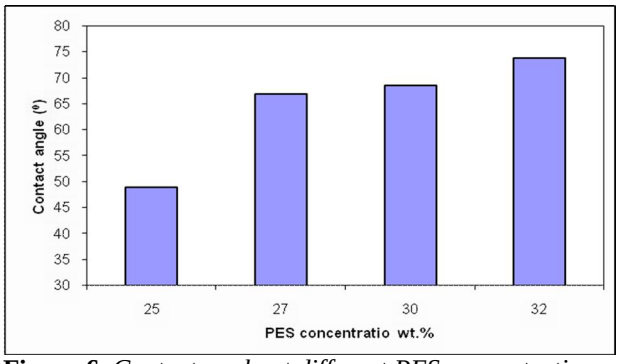

Figure 6. *Contact angle at different PES concentration*

3.3. Membrane morphology characterization

The permeation properties of neat membranes can be better explained by the Scanning Electronic Microscopy (SEM) analyses. Figure 7 presents SEM images of the cross-sections of 25, 27, 30 and 32 wt.% PES. From the SEM images is observed that polymer concentration has a clear effect on the membrane structure, which can be described in terms of membrane pore size and porosity variations

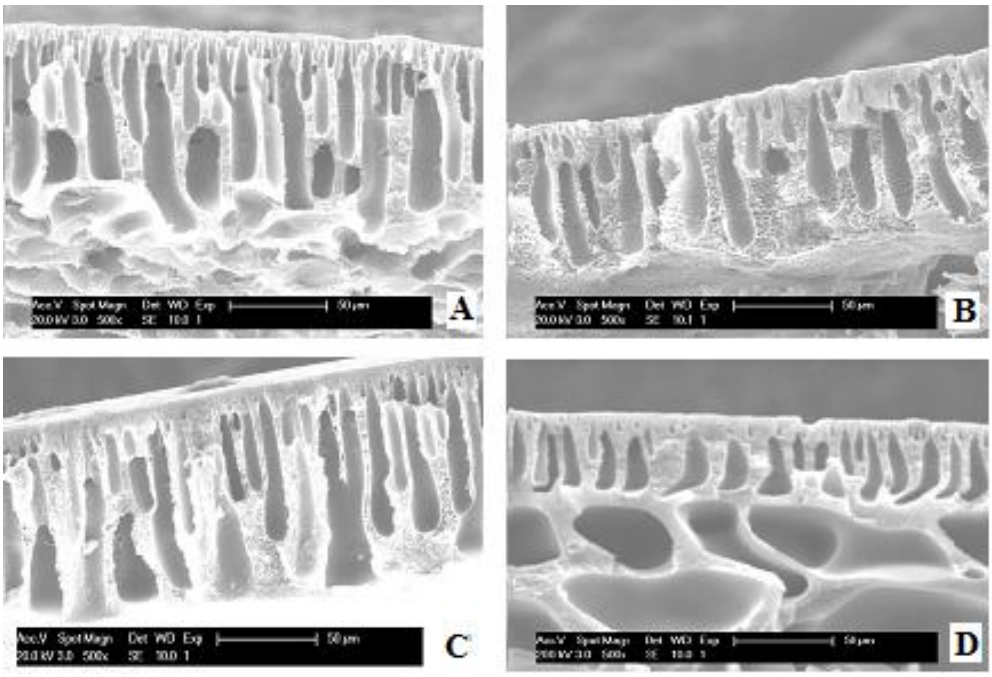

Figure 7. *Cross section SEM photography of membranes at different PES concentration: a) 25%PES, b)27%PES, c)30%PES, d)32PES*

Membranes with 25% of PES (figure 7 a) have macrovoids in the structure who lead to a better permeability but, how was observed at the pure water flux, with an instability of flux in time. The pore size and geometry change as the polymer concentration increase, figure 7 a,b,c,d for 25, 27, 30 and respectively 32 wt.% of PES, in the same time suppress the macrovoid and increase the thickness of the top layer [17]. For 30 and 32 wt.% of PES the permeability and pure water flux is smaller because the bottom with the top layer are not connected by macrovoids and a sponge structure is formed. For membrane with 27 wt.% of PES the bottom is connected with the top layer, porosity is uniform distributed and the pores structure are like fingers.

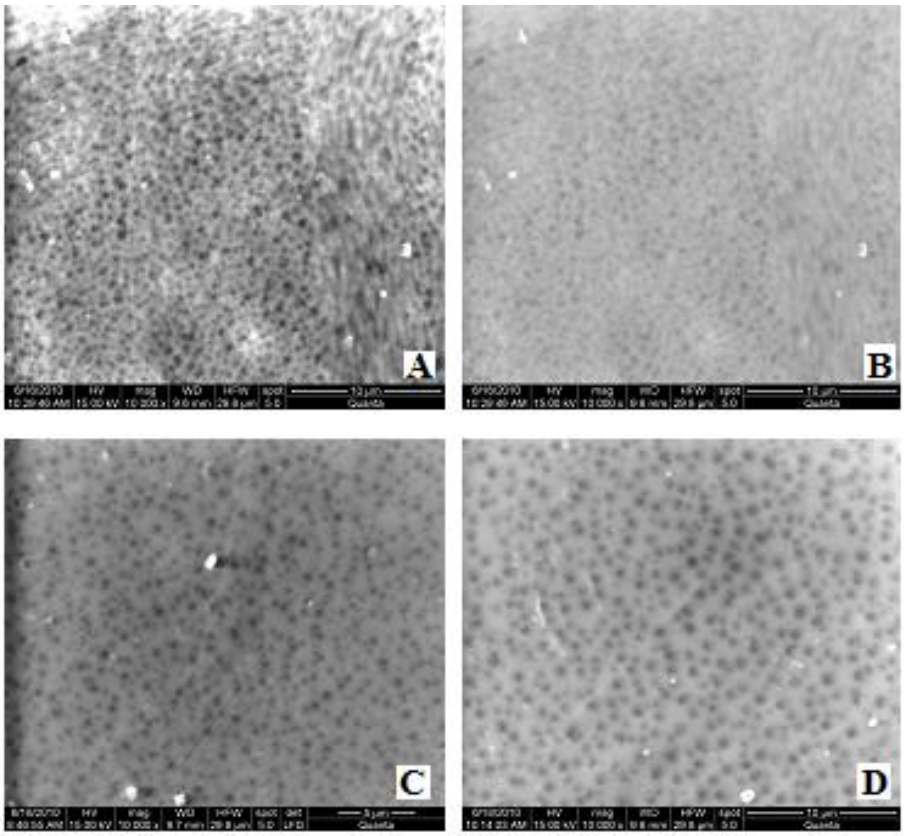

Figure 8. *Surface SEM photography at different concentration of PES: a) 25, b) 27, c) 30 and d) 32wt.%.*

Figure 8 show surface SEM photography of membranes at different concentration of PES. By increasing the concentration of PES it was observed that the porosity of the membranes decreases. Membranes with 25 wt.% of PES are the most porous in comparison with membranes at higher concentration.

4. Conclusions

A systematic study of influence of polymer concentration was carried out, testing a large number of membrane samples.

The polymer concentrations have a high influence on the membranes properties and have a negative effect on the water permeation and hydrophobicity. The results from permeation experiment and from analysis of membrane morphology show the negative influence of polymer concentration. At 25 wt.% of PES, membranes have a good permeability but flux show instability in time. Because of this behaviour for industrial application membrane with higher concentration of PES need to be selected.

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