Influence of Nanoparticles in Membrane Properties

DANIELA L. BURUIANA[1], CATALINA ITICESCU[1], GEANINA L. TIRON[1], STEFAN PINTILIE[1], CRISTIAN SILVIU SIMIONESCU[1], MIRCEA BARNAURE[2], STEFAN BALTA[1]*

[1]Dunărea de Jos University of Galati, 47 Domeneasca Str., 800008, Galati, Romania
[2]Technical University of Civil Engineering Bucharest, 122-124 Lacul Tei Blvd., 020396, Bucharest, Romania

Membrane processes are a way to remove unwanted elements from wastewater stream. The permeability is an important parameter to filter wastewater and membrane fouling is of great interest in membrane filtration because reduce wastewater flow through the membrane. In order to improve the filtration process, many studies have investigated the use of nanoparticles added in the polymeric membranes and how much influence the permeation properties of membranes. A variety of nanoparticles have been used to modify polymer membranes, such as Al_2O_3, SiO_2, TiO_2, ZrO_2, Fe_3O_4, Ag. Nanoparticles are used to improve the properties of membranes like hydrophilicity, permeability and fouling resistance. This paper shows the influence of the TiO_2 nanoparticles with a concentration of 0.125 wt.%, on the permeation properties and dyes rejection of the PES and PSf membranes and makes a comparison with the results obtained by other authors.

Keywords: TiO_2 nanoparticles, PES, PSf, membranes

The interface between two phases that act as a selective barrier represents the membrane [1]. Commercial membranes are obtained mainly from organic polymer [2]. Polymeric membranes are famous because it's easy to control the necessary properties, in general is not an expensive material and due to the uniform porosity is possible to make a selective transfer of chemical species [1]. Nowadays, the most used polymers are polysulfone (PSf), polyethersulfone (PES) and polyvinylidene fluoride (PVDF). These polymers show a high degree of utilization because provides high tolerance to *p*H, chlorine and high temperatures and are stable from the mechanical point of view [3]. It also presents some disadvantages such as low hydrophilicity, low fouling resistance and low water permeability [3]. In the case of a hydrophobic membrane, fouling is severe due to the interaction between the membrane material and the dissolved microbial cells [2]. Membrane fouling can be defined as a pollutant deposition on the membrane surface or the absorption of pollutants in the membrane pores. Membrane fouling phenomenon is reversible with additional operating costs and at the same time irreversible because of the alteration of membrane properties [4]. The effect of membrane fouling is the reducing of water flux in time and increasing the level of energy needed. Thin film composite (TFC) membrane, have a thin active layer on a porous support and are widely applied in wastewater treatment, industrial water production and water softening [6]. Thin film composite membranes have the advantage that the active layer and the substrate can be improved separately to achieve higher performance [7]. Changing the top layer of the membrane offers new properties in addition to the existing ones [8]. Researchers have shown that if control the particle distribution in the polymer matrix the permeation properties of the membrane can be improved [9, 10]. Polysulfone is a polymer with good chemical and thermal stability, strength and flexibility and good film forming [11]. Due to these properties, low costs and their applicability in large areas, polysulfone membranes are used in processes especially for wastewater treatment, protein separation and drug purification [12]. Analyzing polymeric materials used to obtain membranes for ultrafiltration and nanofiltration processes, polyethersulfone (PES) is used for membrane manufacturing because it shows good physical and chemical properties [13, 14].

Experimental part

Materials

Polyethersulfone (PES) and polysulfone (PSf) supplied by Solvay (Belgium) was employed as the base polymers. 1-methyl-2-pyrrolidone (NMP, 99.5%) was used as the polymer solvent. The support layer (Viledon FO2471) used for the membrane manufacturing was obtained from Freudenberg (Weinheim, Germany). TiO_2 nanoparticles were purchased from Sigma-Aldrich (St. Louis, MO). Six different dyes were used to explore the size interaction in the interface solute-membrane pore. Organic compounds purchased from Acros Organics (Belgium) were selected in order to cover a large range of molecular mass. The selected dyes were methyl red (269.21 Da), neutral red (288.77 Da), methylene blue (319.85 Da), Sudan black (456.54 Da), Victoria blue (506.10 Da), Congo red (696.67 Da).

Preparation of membrane

Neat PSf and PES membranes and blended with TiO_2 nanoparticles were prepared using phase inversion induced by immersion precipitation. The TiO_2 blended membranes were prepared by dispersing 0.125 wt.% nanoparticles in the corresponding volume of NMP for three hours by mechanical stirring at 200 rpm and room temperature. After formation of a homogenous solution, polymer was added and dispersed by mechanical stirring at 200 rpm for 24 h. The films were cast with 250μm thickness using a filmograph (K4340 Automatic Film Applicator, Elcometer). The prepared films were immersed in a non-solvent bath (distilled water at 20°C) for precipitation.

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* *email: stefan.balta@ugal.r; Tel: 0741529968*

Filtration experiments

The prepared membranes were characterized for water flux and pure water permeability using dead end filtration experiments. The pure water flux was determined from a compaction experiment at a transmembrane pressure of 10 bars and a constant temperature of 25°C in dead-end mode with a Sterlitech HP4750 Stirred Cell. A nitrogen cylinder coupled with the pressure regulator was connected to the top of vessel to pressurize the cell. The active membrane area was 14.6 cm^2.

Membrane characterization

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

Results and discussions

Adding 0.125 wt.% TiO_2 nanoparticles in the PES and PSf membranes, the permeability and pure water flux increase. This effect of nanoparticles on the permeation properties is due to the increase of the porosity and of the affinity of nanoparticles to water.

The pure water permeability (PWP) was determined by measuring the pure water flux (Jw) at different transmembrane pressures (ΔP) from 2 to 14 bar; the slope of the linear regression of the water flux as a function of transmembrane pressure was determined as the permeability. The PWP was calculated by the following equation:

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

TiO_2 nanoparticles were added in the polymeric solution because the TiO_2 nanoparticles attached on the surface membranes can have a risk to the environment. Such negative effect can be avoided by adding nanoparticles in the membranes structure by various methods, such as self-assembly [15, 16] entrapment and chemical binding [17]. Considering all these three methods, entrapment and chemical binding can achieve higher performance. Using the entrapment method it is seen an improvement in the resistance of nanoparticles connection [18]. A higher concentration of TiO_2 nanoparticles in thin film decreases considerably the selection capacity of TFC membranes [19]. Through the chemical binding method, membranes have a strong bond of nanoparticles, but show the disadvantage that it can only apply to certain types of TFC membranes and it changes the structure of the membranes surface [18]. The results obtained by others authors on the use of TiO_2 nanoparticles on the PES membranes is shown in figure 1.

Analyzing the results of Guiping Wua et.al., in his study on the composition PES membranes having 15 wt.% concentration and TiO_2 nanoparticles with a concentration of 0.7 wt.% obtained a water flow of 365 (L/m^2h), (fig. 1).1 TiO_2 / PES-1. The results of the sample TiO_2 / PES-2 were obtained by Jesu' s Maria Arsuaga et.al., using PES 20 wt.% and 0.4 wt.% TiO_2 getting a water flow of about 200 (L/m^2 h). In the sample TiO_2 / PES-3, Kim Jeonghwan et.al. has used 27 wt.% PES and 0.125 wt.% TiO_2 getting a water flow of about 200 (L / m^2h).

Adding 0.125 wt.% TiO_2 nanoparticles in PES membrane structure, stability and pure water flux increase, this effect is shown in figure 2.

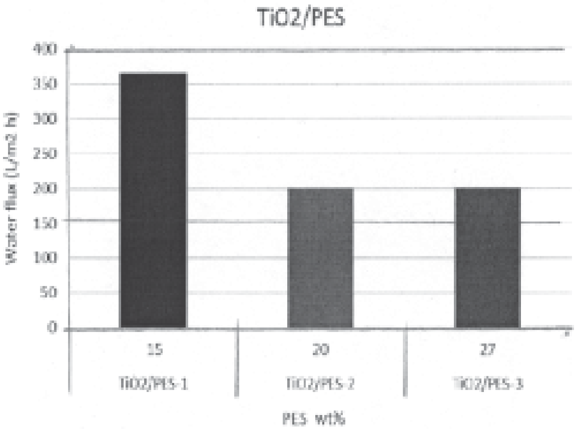

Fig. 1. The use of TiO_2 nanoparticles in diferent wt.% of PES membranes

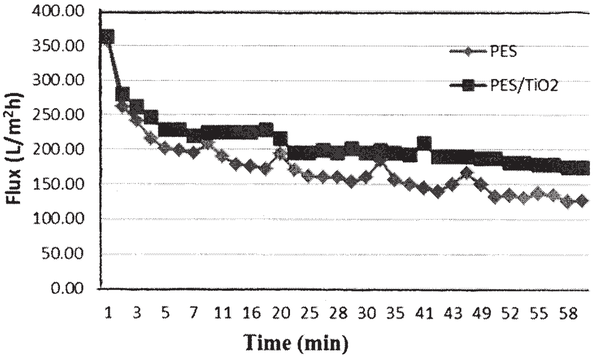

Fig. 2. The influence of the TiO_2 nanoparticles on the pure water flux of PES membranes

For the rejection experiments, different commercial dyes with increasing molecular mass were used, figure 3.

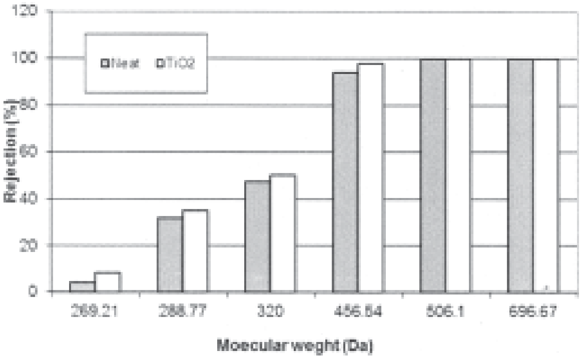

Fig. 3. The influence of the TiO_2 nanoparticles on rejection potential

Analyzing the results shown in figure 3 it can be concluded that at higher molar mass of dyes the membrane rejection increases for both type of membranes. Adding TiO_2 nanoparticles in the membranes structure, the rejection potential increase.

Flux stability increase for the PES membranes blended with TiO_2 nanoparticles, due to the decrease of the compactation of membrane at the pressure of 10 bars. In the same time the water flux increase because of the affinity of nanoparticles to water.

The results of current studies on PSf membranes blended with TiO_2 nanoparticles is shown in figure 4.

Bae Tae-Hyun's et.al. tested polymeric membranes with 15 wt.% PSf and 0.3 wt.% TiO_2 and obtained 230 (L/m^2h) water flow (sample TiO_2 / PSf-1). The results of the sample TiO_2 / PSf-2 were obtained by D. Emadzadeh et.al., using PSf 17.33 wt.% and 1 wt.% TiO_2 getting a water flow of 855.2 (L/m^2h). In the sample TiO_2 / PSf-3, Yanan Yang et.al.

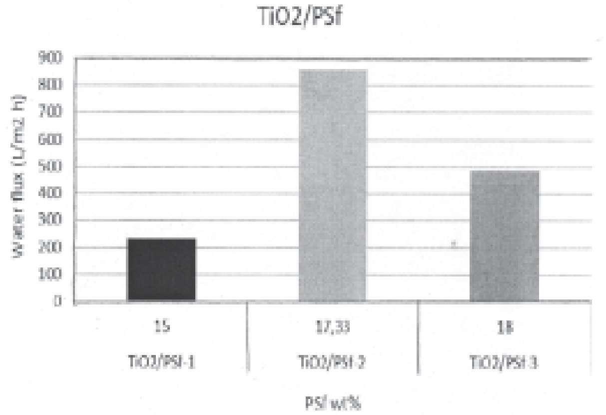

Fig. 4. The use of TiO_2 nanoparticles in diferent wt.% of PSF membranes

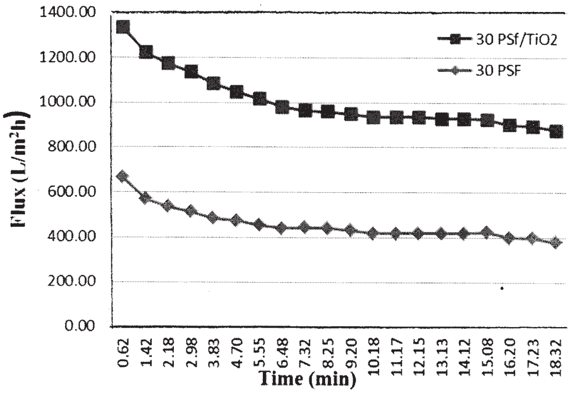

Fig. 5. The influence of the TiO_2 nanoparticles on the pure water flux of PSf membranes

has used 18 wt.% PSf and 2 wt.% TiO_2 getting a water flow of 488 (L/m^2 h).

For PSf membranes blended with TiO_2 nanoparticles the pure water flux have an important improvement comparing with the results obtained for neat membranes. This effect can be observed in figure 5.

Adding TiO_2 nanoparticles in the PSf membranes, the porosity increase and this lead with a better permeability and water flux, and the top layer decrease this having the same effect on the permeation properties. The evolution of pure water flux in time is similar for the blended membranes with neat membranes.

The influence of the addition of TiO_2 nanoparticles to the PSf membrane morphology is shown in figure 6. Cross-sectional observations of synthesized membranes were performed with scanning electron microscopy (SEM). The composite membranes with TiO_2 nanoparticles showed that the top layer became thinner than that of the neat PSf membrane.

Figure 6 shows that the number of macrovoids increase for the membranes blended with TiO_2 and the sponge-like structure is more pronounced.

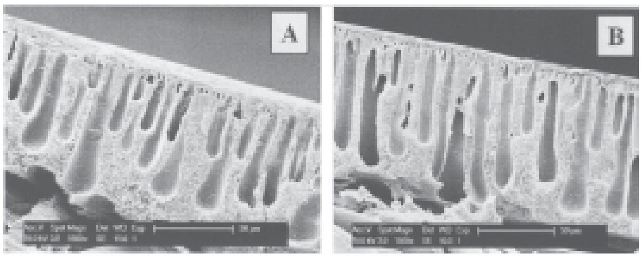

Fig. 6. Cross-sectional SEM images of: A) PSf (without TiO_2) and B) PSf/TiO_2 (0.125 wt.% of TiO_2)

Conclusions

The use of nanoparticles in polymeric membranes has an important influence on the improving the water permeation, retention potential and fouling resistance. This influence is due to the structure modification of the membranes, nanoparticles improving the porosity and decreasing the pore size. Are many methods to use nanoparticles in membrane synthesis, but because of the environmental issue the most used are that who entrap nanoparticles in the membrane structure. The deposition of nanoparticles on the membranes surface, have is a cheaper method because is necessary less amount of nanoparticles but the stability in time can be a problem to the environment. Rejection potential increase for the membranes blended with TiO_2 nanoparticles due to the decreasing of the pore size.

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