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Synthesis and characterization of reverse osmosis membranes modified with BaTiO₃ nanoparticles to improve performance

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Abstract

This paper deals with the synthesis and the characterization of reverse osmosis membranes reached by barium titanium oxide nanoparticles. A composite membrane containing BaTiO₃ nanoparticles (NPs) was prepared by the in situ interfacial polymerization (IP) process on porous polysulfone supports. Aqueous m-phenyl diamine (MPD) and organic trimesoyl chloride (TMC)-NPs mixture solutions were used in the IP process. BaTiO₃ NPs with a size between 100–200 nm were used as the fillers to fabricate nanocomposite membranes at concentrations ranging from 0.001% to 0.01% wt%. The membranes were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscope (AFM) and contact angle technique. Their performances were evaluated based on the water permeability and salt rejection. Results indicated that the BaTiO₃ nanoparticles are well dispersed in polyamide (PA) layer and improved membrane performance under optimal concentrations. By changing the content of filler (by introducing different concentration of BaTiO₃ nanoparticles inside the Reverse Osmosis Membrane (0.001% to 0.01% wt%), hydrophilicity and roughness of the composite membranes were increased. Notably, the permeate water flux increased from 26 to 42 L/m²h at BaTiO₃ concentration of 0.009% with the maintaining of sodium chloride (NaCl) high salt rejection of 98%. These results were obtained with initial NaCl concentration of 2000 ppm and under pressure of 225 psi. For the hydrophilicity, the contact angle was decreased from 73° to 24°.

Keywords: *nano-BaTiO₃, reverse osmosis (RO) membrane modified, nanocomposite.*



1 Introduction

In recent, the shortage of fresh water has become a crucial challenge throughout the world because of pollution caused by huge number of industries and deficiencies in water management. In addition, the rapid population growth is also one of the major cause for the fresh water shortage as the needs of agriculture and energy consumption are increasing day by day (Chaibi [1]). Therefore, seawater and brackish water desalination have been emerged as one of the most suitable and alternate source of fresh water, which can fulfil the demand of water for drinking, irrigation and industrial development (Elimelech and Phillip [2]). Among various desalination technologies, the membrane-based reverse osmosis (RO) process is dominating the global desalination market, due to its simple design and excellent scale-up capability (Penate and Garcia-Rodriguez [3]). In the RO desalination process, high performance semi-permeable membranes play a crucial role to determine the quality of water and also affect the overall energy consumption (Shannon *et al.* [4]). Therefore, high efficiency RO membranes with improved productivity along with good salt rejection ability are highly desired. In early 1980s polyamide (PA) thin film composite (TFC) membranes were developed and till now it is most widely used desalination membranes due to its good stability over a wide range of pH and high intrinsic water permeability (Larson *et al.* [5]).

A new class of reverse osmosis nanocomposite membranes has been developed with improved water permeability just by incorporating different types of nanoparticles within polyamide films (Jeong *et al.* [6]). This concept of doping nanoparticles into the PA film, enables the new generation for the development of novel potential RO membranes. Different types of nanomaterials have been investigated for such applications including silica, zeolite, mesoporous carbon, carbon nanotubes, pure metal and nanometal oxides (Lind *et al.* [7]; Jadav and Singh [8]; Kim and Deng [9]; Kim *et al.* [10]; Zhao *et al.* [11]). The unique functionalities of these materials have introduced new degrees of freedom in the RO membrane design, which combines the essential properties of conventional membrane polymers with the advantages of nanomaterials. Among various nanoparticles, BaTiO₃ nanoparticles are now the most frequently used nano-fillers in RO membranes that lead to enhance permeability of polyamide active layers.

Notably, the nanostructure of polyamide active layers is believed to have two distinct layers namely, a nodular polyamide (dense phase) on the support side and a more open structure of loose polyamide on the surface side. A lot of research has suggested that the dense phase of polyamide, apparently acts as the true separation barrier (Freger [12]; Pacheco *et al.* [13]; Freger [14]).

In this study, BaTiO₃ nanoparticles have been purchased from Sigma Aldrich. The structural framework, particle diameter and elemental composition of BaTiO₃ nanoparticles were characterized by using different techniques (scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD)). The RO nanocomposite membranes were prepared by adding BaTiO₃ nanoparticles in m-phenyl diamine (MPD) and organic trimesoyl

chloride (TMC) via interfacial polymerization (IP) process. The novelty of this paper is in incorporation of BaTiO₃ particles in membranes in view to significantly enhance the performance of filtration technology in terms of permeation, rejection. The eventual membrane structure was also studied in this work.

2 Experimental

2.1 Materials

Various chemicals and reagents which were used in this study were of high purity.

2.2 Preparation of the nanocomposite membranes

A commercial polysulfone (PS-20, Sepro) product named PS-20 was immersed in an aqueous solution of 2 wt% 1,3-phenylenediamine (MPD, >99%, Sigma-Aldrich) for 2 min. Then the excess MPD aqueous solution was removed by pressing under a rubber roller. The material was again immersed in 0.1wt% 1,3,5-benzenetricarbonyl trichloride (TMC, >98%, Sigma-Aldrich) TMC/n-hexane (99%, Sigma-Aldrich) solution for 1 min, then rinsed with 0.2 wt% Na₂CO₃, (>99%, Scharlau) washed with DI water and finally stored in a refrigerator at about 4°C in DI water until use. The nanocomposite membranes were made by dispersing 0.001-0.01 g of commercial BaTiO₃ (Aldrich, >99%) in the TMC/hexane solution by ultrasonication for 1h at room temperature.

2.3 Characterization and instrumentation

The surface morphology and microstructure of the as-synthesized nanocomposite membrane was examined by means of scanning electron microscope (SEM, FEI Nova-Nano SEM-600). Atomic force microscopy was used to analyze the surface morphology and roughness of the prepared membranes. The AFM device was nano surf scanning probe-optical microscope (Bruker). Contact angle analysis was performed using a Ramé-Hart Model 250. The performance of the prepared membranes was analyzed through a cross-flow system (CF042SS316 Cell). The valid membrane area in this system was 42 cm². The Feed water temperature was 25°C with pH adjusted between 6–7, 2000 ppm feed NaCl and 1 gallons per minute (gpm) feed flow rate (AL-Hobaib *et al.* [15]).

3 Results and discussion

3.1 Characterization of BaTiO₃ nanoparticles

3.1.1 XRD analysis

The BaTiO₃ nanoparticles were characterized by XRD, SEM and EDX. Figure 1 shows typical XRD spectra of the powder after thermal treatment. The appearance of seven pronounced diffraction peaks shows characteristic of



BaTiO₃. The average grain size can be calculated using the Debye–Sherrer equation (Cullity [16]). After a correction for the instrumental broadening, the obtained average value of the crystallites is 130 nm.

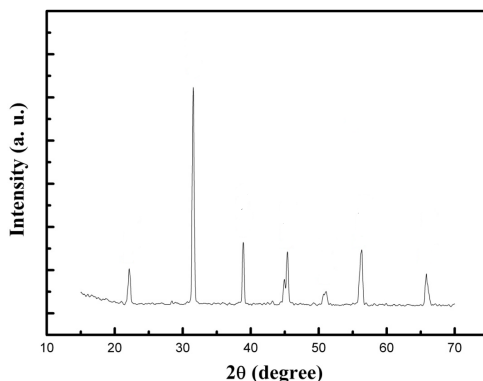


Figure 1: XRD patterns of nanoparticles BaTiO₃.

3.1.2 SEM analysis

Figure 2 shows the surface morphology and EDX analysis of BaTiO₃ nanoparticles. An estimate of size of the grains indicates that they are in the form of crystallites with dimensions between 120 nm and 170 nm. The EDX analysis during the SEM observation confirms that the presence of Ba and Ti, in good agreement with XRD results.

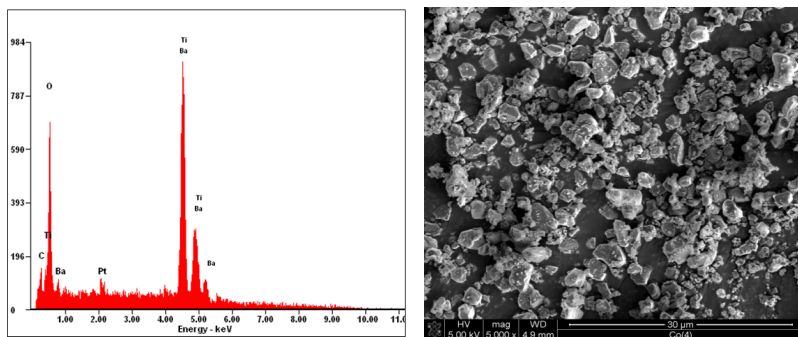


Figure 2: SEM and EDX images of nanoparticles BaTiO₃.

3.2 Characterizations of modified membrane with BaTiO₃ nanoparticles

3.2.1 SEM analysis

Figure 3(a) shows EDX spectra and SEM image of the TFC-reference membrane (without BaTiO₃ nanoparticles). The impregnation of BaTiO₃ does not have a great effect on the overall morphology of TFC in the tested weight range, but

partial aggregation of BaTiO_3 was observed in samples (Figure 3(b)). The difference between the images indicates clearly the presence of BaTiO_3 particles. This was further confirmed by EDX quantitative and AFM analyses.

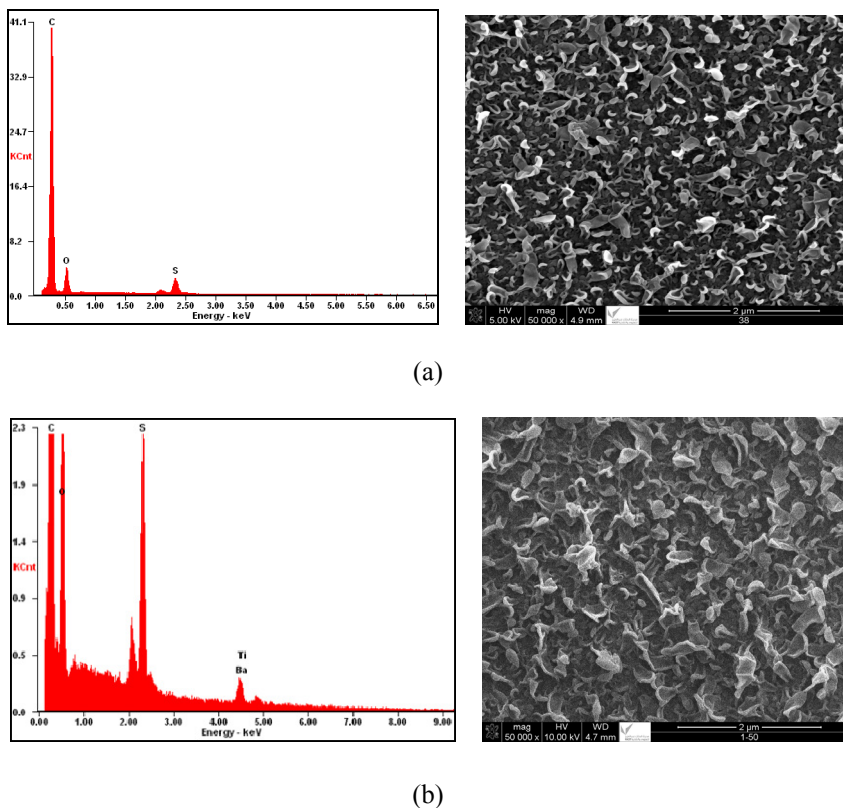


Figure 3: SEM images and EDX of membranes. (a) EDX and SEM of TFC reference; (b) EDX and SEM of modified membrane (0.009 wt%).

3.2.2 Atomic Force Microscope (AFM) analysis

AFM was used to further analyze the morphology of membrane surface. AFM measurements of membranes containing different contents of BaTiO_3 nanoparticles are shown in Figure 4. It can be observed that the roughness (R_a) values increased with increasing barium titanate content in the membranes.

3.2.3 Contact angle measurements

Figure 5 shows measurements of the contact angle for the various weights of BaTiO_3 . The embedding BaTiO_3 into TFC membrane can drop contact angle significantly from 73° to about 24° , then, did not change significantly, in spite of the increasing content of BaTiO_3 .

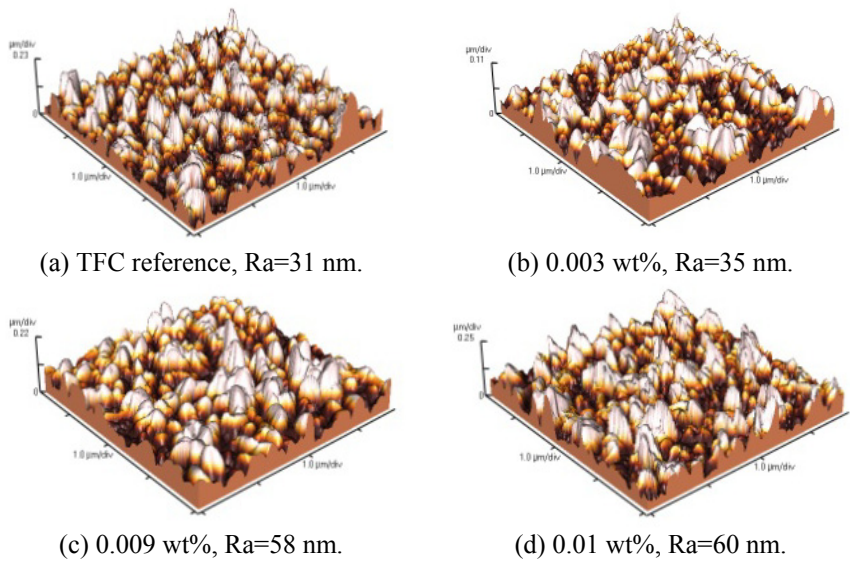


Figure 4: AFM images of TFC reference membrane and modified membranes.

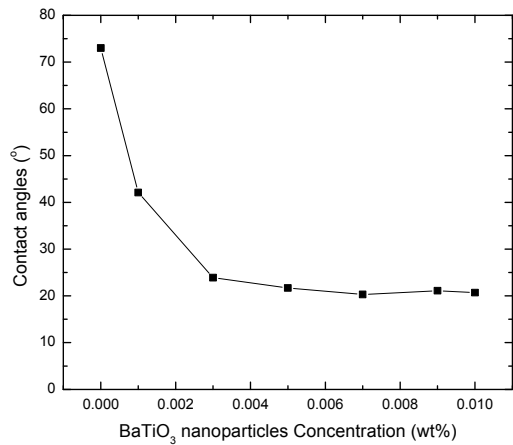


Figure 5: Contact angles of membranes containing different amounts of BaTiO₃ nanoparticles.

3.2.4 Flux and salt rejection

Figure 6 presents the water fluxes and the salt rejection of all the prepared membranes. As the weight of added BaTiO₃ is increased, the water flux of the membrane increases to a peak value and then begins to decrease. The BaTiO₃/TFC hybrid membrane exhibits the highest water flux (42 L/m²h) when the concentration of added BaTiO₃ is 0.009 g. This flux represents an improvement of 165% over that of the TFC membrane. The salt rejection ratios

of all the prepared membranes were unchanged. When the weight of added nano-BaTiO₃ exceeds 0.009 g, the water flux begins to decrease. This phenomenon is the synergetic result of decreased porosity and aggregation of nano-BaTiO₃.

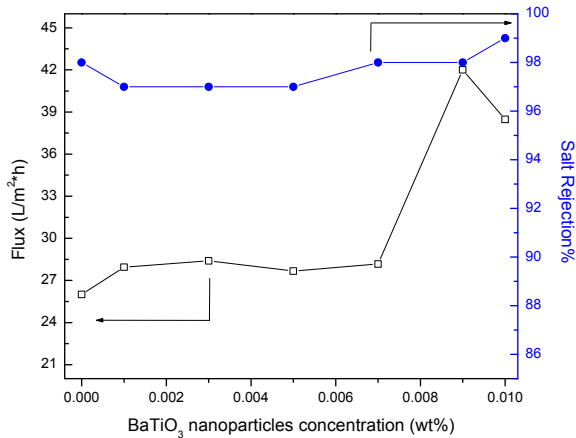


Figure 6: Water permeate fluxes and salt rejections of modified membranes.

3.2.5 Concentration of MPD

Modified membranes were prepared by varying the concentration of MPD and TMC and keeping the mass of added BaTiO₃ at 0.009 g. The influence of MPD and TMC concentrations on permeate flux and salt passage is presented in Figure 7 and Figure 8, respectively. The molar ratio of amine groups on the MPD to the acid chloride groups on the TMC, based on the concentrations of MPD and TMC used in the polymerization process is reported in these figures as well. All membranes exhibited salt passage values of less than 5%, but permeate flux varied significantly.

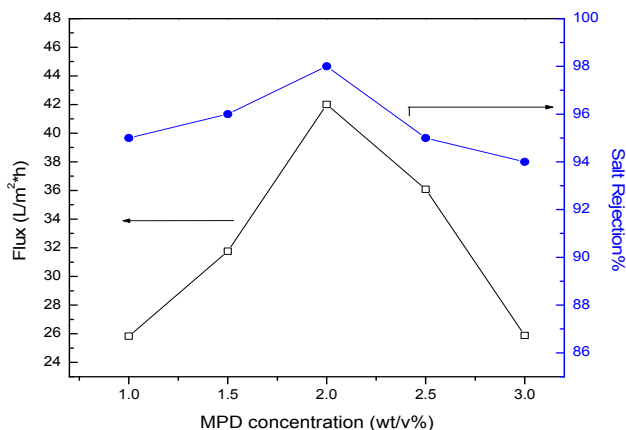


Figure 7: Modified membranes performance on varying concentration of MPD (TMC, 0.1%).

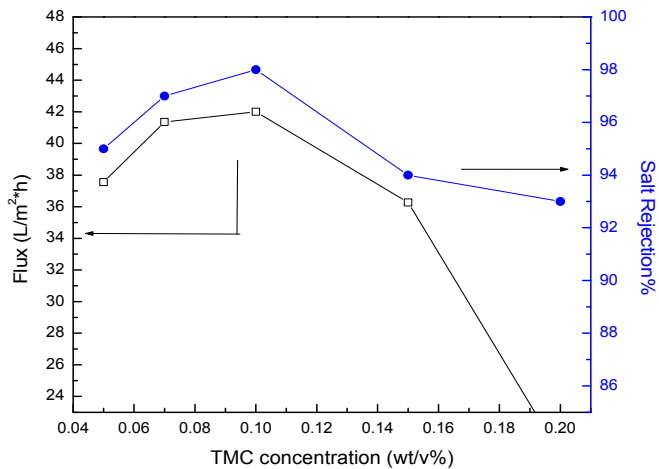


Figure 8: Modified membranes performance on varying concentration of TMC (MPD, 2%).

3.3 Summary

There are many literature reports regarding the performance of interfacially polymerized of commercial polyamide TFC membranes and aromatic polyamide TFC desalination membranes based on MPD and TMC (Jeong *et al.* [6]; Singh and Aswal [17]; Jadav and Singh [8]; Kwak *et al.* [18]; Lee *et al.* [19]; Ning *et al.* [20]; Saleh and Gupta [21]). The transport properties of the membranes prepared in this study were comparable to those of the membranes reported in Table 1.

Table 1: Summary of membrane characteristics from previous studies.

Nanoparticles type	Salt Rejection (%)	Flux (L/m²h)	Ref.
BaTiO ₃ nanoparticles	98.0	42.00	This work
Zeolite nanoparticles	93.0	40.20	[6]
Silica nanoparticles	91.0	27.20	[17]
Silica nanoparticles	71.7	40.80	[8]
TiO ₂ nanoparticles	96.6	24.50	[18]
TiO ₂ nanoparticles	95.0	9.10	[19]
Zeolite nanoparticles	90.5	43.70	[20]
Al ₂ O ₃ nanoparticles	88.0	5.00	[21]



4 Conclusion

The BaTiO₃ powders were embedded, with different weights, into polyamide membrane via interfacial polymerization process. The powders strongly affect the properties of the membrane. SEM and EDX confirm the formation of polyamide membrane embedded with BaTiO₃ nanoparticles. The contact angle of the membrane decreases from 73° to 24° when the weight of NPs is increased. The thin film nanocomposite (TFNC) hybrid membrane exhibits the highest water flux (42 L/m²h) when the weight of added BaTiO₃ is 0.009 g; in addition, the salt rejection is not obviously changed.

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