Effects of TiO₂ NTs% on Polyethersulfone/TiO₂ NTs Membranes

Mohamed Shaban^{1*}, Hany Hamdy¹, Heba AbdAllah², Lamiaa Said^{1,3} and Ahmed Abdel khalek³

1. Nanophotonics and Applications Lab, Department of Physics, Faculty of Science, Beni-Suef University, Beni-Suef 62514, Egypt

2. Engineering Research Division, Chemical Engineering & Pilot Plant Department, National Research Center, Dokki 12311, Egypt

3. Department of Chemistry, Faculty of Science, Beni-Suef University, Beni-Suef 62514, Egypt

Abstract: In this work, PES (polyethersulfone)/TiO₂ nanotubes membranes were fabricated by a simple and cheap method. The TiO₂NTs (titanium dioxide nanotubes) are prepared by the hydrothermal method, the tubes had a narrow size distribution with an average inner diameter of 3-5 nm and outer diameter of 10-13 nm. TiO₂NTs blended PES membranes are prepared by phase inversion method with different nanotubes percentage (0.18%-0.85%). The morphology of PES membrane was obviously affected by the addition of TiO₂NTs. The prepared membranes were applied on a vacuum desalination system and the desalination results showed that the salt rejection % and permeate flux of the membrane are enhanced through the addition of TiO₂NTs. The membrane with higher (0.85%) TiO₂NTs content resulted in a decrease of salt rejection % because of the defective membrane structure.

Key words: Blend membranes, hydrothermal method, phase inversion method, polyethersulfone, titanium dioxide nanotubes.

Nomenclature

C_f :	Concentration at feed bulk (mg/L)
C_p :	Concentration at permeate (mg/L)
J :	the permeate flux (kg/m ² h)

1. Introduction

Membrane processes like MF (microfiltration), UF (ultrafiltration), NF (nanofiltration), and RO (reverse osmosis) are used individually or integrated with other traditional techniques in many industries to recover rare metals, toxic chemicals, polymer binders, etc. [1]. Also, membrane processes are considered as one of the most required techniques in water treatment applications. The membrane filtration process may be designed to operate using the positive pressure or negative pressure (i.e., vacuum pressure) as a driving force. The pressure that is used to drive water through membrane is called TMP (transmembrane pressure). PES (polyethersulfone) is widely used in many

industries due to its thermal stability, mechanical strength, and chemical inertness. Improvement of hydrophilicity and blood compatibility on polyethersulfone membrane occurred by blending sulfonated polyethersulfone to use as biomaterials [2]. Also polyethersulfone membrane's properties could be enhanced by using nanomaterials to use in water desalination [3-8]. Nano metal oxides have been mainly used for salt rejection% enhancement and fouling mitigation. At the other hand, TiO₂ (Titanium dioxide) has been the focus of numerous investigations in recent years because of non toxicity, low cost, heavy metal adsorbent, corrosion resistance, photocatalytic effect (that can decompose organic chemicals and kill bacteria), and self cleaning (anti fouling) effect [9].

Here, an efficient method is proposed to prepare PES/TiO₂ nanotubes composite membranes by phase inversion method. In addition, the membrane characteristics were evaluated in terms of flux and salt rejection for different percentages of TiO₂ nanotubes.

Corresponding author: Mohamed Shaban, Ph.D., Ass. Professor, research fields: Experimental Physics, Nanophotonics and Applications. E-mail: mssfadel@yahoo.com; mssfadel@aucegypt.edu.

2. Experimental Details

The TiO₂NTs (titanium dioxide nanotubes) were prepared by hydrothermal method [8]. In this method, 3 gm of TiO₂ powder were added to 10M NaOH, and the mixture was stirred for 30 min at ambient temperature. Afterwards, it was heated at 150 °C in a Teflon-lined autoclave. A treatment time of at least 24 h was considered to be sufficient for the dissolution of the starting TiO₂ powder [10]. The white product was filtered and washed with 1N HCl and DI Water. Then the sample was dried in an oven at 80 °C for 4 h and post-treated at 500 °C for 3 h.

The membranes are fabricated by phase inversion method using different percentage of TiO₂NTs (0.18%, 0.35%, 0.53% and 0.85%). TiO₂NTs was dissolved in solution of 0.5% SDS (sodium dodecyl sulphate) and the solution was stirred for 3 h. The blend membrane was prepared using 20% PES dissolved in NMP (N-methyl pyrrolidone). The mixture was stirred for 6 h at room temperature and left in refrigerator for 24 h to remove air bubbles. The membrane was obtained using casting knife on glass plate. The prepared blend membrane on glass plate was dipped in DI water for washing and storage until use.

The TiO₂ raw material and the prepared TiO₂NTs characterization were carried out using field emission scanning electron microscope (LEO 55 FE-SEM), transmission electron microscope (JEOL JEM-2100 TEM), and XRD (X-ray diffraction). In addition, the prepared membranes were characterized by FTIR (Fourier transform infrared spectroscopy).

3. Results and Discussion

Fig. 1(a) shows XRD pattern of raw TiO₂ nanopowder. This pattern shows a pure anatase phase of TiO₂ with crystal size ranged from 120 nm to 130 nm. Fig. 1(b) shows top-view FE-SEM image of TiO₂ raw material. It showed that the TiO₂ raw material has a particulate shape with average size of 126 nm. This size agrees well with the value that obtained from XRD pattern.

The morphology of the prepared TiO₂NTs by the hydrothermal method was characterized by (c) FE-SEM and (d) HR-TEM images as shown in Fig. 1. The prepared nanotubes are open ended nanotubes of narrow size distribution with an average inner diameter of 3-5 nm and outer diameter of 10-13 nm. The length of TiO₂NTs is observed to be greater than 300 nm. It is observed from TEM image that the TiO₂NTs are single wall nanotubes.

Fig. 2(a) illustrates XRD pattern of the as-prepared TiO₂ nanotubes after the hydrothermal treatment. It indicated that the crystal phase of TiO₂ nanotubes changed from anatase to a mixed phase of Ti₉O₁₇ and H₂Ti₄O₉·H₂O. By the post-treating of TiO₂ nanotubes at 500 °C for 3 h, only the anatase phase of TiO₂ is existed as shown in Fig. 2(b).

The FTIR spectra of the pure PES membrane and PES/TiO₂ Nanotubes blend membrane are shown in Fig. 2(c). The band at 810 cm⁻¹ represent the substitution of the aromatic ring of (C-H), whereas the band at 1 – 168 cm⁻¹ indicates a sulfonated anion bound to an aromatic ring. It was recognized that the asymmetric stretching vibration of TiO₂ nanotubes groups appears around 574 cm⁻¹ and 1,712 cm⁻¹. The sharp absorption peak at 571.8 cm⁻¹ was ascribed to Ti-O bond. In addition, the band around 893 cm⁻¹ represents the stretching vibration of short Ti-O bonds involving non-bridging oxygen coordinated with sodium ions from sodium dodecylsulfate ions.

Fig. 1 (a) XRD pattern, (b) FE-SEM image of the raw TiO₂ powder, (c) FE-SEM and (d)HR-TEM of TiO₂NTs.

Fig. 2 XRD patterns of (a): as-prepared TiO₂NTs (1: Ti₉O₁₇, 2: H₂Ti₄O₉·H₂O) and (b): TiO₂NTs post -treated at 500 °C for 3 h; (c) FTIR spectra of pure PES membrane and PES/ TiO₂ Nanotubes (0.85%) blend membrane.

Moreover, the peak observed at 1,598.7 cm⁻¹ for PES/TiO₂ membrane was found to be shifted from the band given in the literature at 1,674 cm⁻¹ [3, 11]. This shift can be ascribed to interactions of TiO₂ with the sulfone group and ether bond in polyethersulfone structure. Finally, the difference in peak intensities and broadening of the peaks between pure PES and PES/TiO₂ membranes may be ascribed to the dimensional confinement possessed by adding the TO₂

nanotubes.

Fig. 3 shows SEM images of (a) top surface, (c) bottom surface of pure PES membrane, (b) top surface, and (d) bottom surface of the PES/TiO₂NTs membrane. As shown in Fig. 3 (a and c), the prepared membrane without TiO₂NTs is asymmetric membrane with top and bottom porous surfaces. Whereas, the prepared PES/TiO₂NTs membrane is asymmetric membrane with the dense top surface, as illustrated in Fig.3 (b), and porous bottom surface, as illustrated in Fig.3 (d). The white dots on the bottom and top surfaces (Fig. 3 (b, d) may be ascribed to the addition of sodium dodecylsulfate which is antifouling addition. Also, the dense top surface means this membrane is suitable for desalination process. Thus, the produced membrane can be classified as antifouling RO-NF membrane.

Fig. 4 illustrates the relationship between TiO₂NTs percentage in the prepared membrane and salt rejection % (%R), which was calculated by $\%R = ((C_f - C_p)/C_f) \times 100$. Where C_p is the concentration at permeate (mg/L) and C_f is the concentration at feed bulk (mg/L). Fig. 4 indicated that the increasing of TiO₂NTs percentage can lead to increase in salt rejection % as the pore size decrease to the nano-scale.

Fig. 3 Top view SEM images of (a, c) top and bottom surface of pure PES membrane, respectively. (b, d) top and bottom surface of PES/TiO₂NTs membrane, respectively.

Fig. 4 Effect of TNTs % on (a) salt rejection % and (b) Permeate Flux.

In addition, the salt rejection % has reached to 98% when 0.85% TiO₂NTs is used in the preparation of blend membrane.

In addition, the permeate flux (J) are studied at the same different TiO₂NTs percentages as shown in Fig.4. The permeate flux increases when increasing the TNTs percentage. This may be attributed to the increase of the membrane porosity as the ratio of the nanotubes increased. At 0.85% TiO₂NTs percentage, the permeate flux was found to be 5.45 Kg·m⁻²·h⁻¹.

4. Conclusions

The asymmetric PES/TiO₂NTs mixed matrix membranes are fabricated by phase inversion method, where hydrothermal synthesis of TiO₂NTs was performed and the sample post-treated at 500 °C for 3 h. The TiO₂NTs sample had uniform tubular shape with open-ended. A large amount of the tubes had a narrow size distribution with an average inner diameter of 3-5 nm and outer diameter of 10-13 nm. The structure of the membrane was obviously affected by addition of TiO₂NTs. The prepared membranes were applied on desalination system (vacuum membrane distillation system). Salt rejection % and permeate flux of the membrane were enhanced through adding TiO₂NTs. Higher (0.85%) TiO₂NTs content resulted in a decrease of salt rejection % because of the defective membrane structure.

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