Titanium dioxide nanoribbons/multi-walled carbon nanotube nanocomposite blended polyethersulfone membrane for brackish water desalination

Mohamed Shabana,⁎, Abdallah M. Ashraf,⁎,⁎, Heba AbdAllahc, H.M. Abd El-Salamb

a Nanophotonics and Applications Lab, Physics Department, Faculty of Science, Beni-Suef University, Beni-Suef 62514, Egypt
b Department of Chemistry, Faculty of Science, Beni-Suef University, Beni-Suef 62514, Egypt
c Chemical Engineering and Pilot Plant Department, Engineering Research Division, National Research Centre, 33 El-Bohouth St. (Former El-Tahrir St.), Dokki, Giza, PO Box 12622, Egypt

ARTICLE INFO

Keywords:
Nanoribbons
Multi-walled carbon nanotubes
Polyethersulfone membrane
Low-pressure reverse osmosis
Brackish water desalination

ABSTRACT

A series of titanium dioxide nanoribbons (TNRs)/multi-walled carbon nanotubes (MWCNTs)/polyethersulfone (PES) blend membranes with different proportions of TNRs/MWCNTs were synthesized via phase inversion method. The nanocomposite (TNRs/MWCNTs) prepared by hydrothermal method followed by chemical vapor deposition (CVD). Energy dispersive X-ray (EDX) analyses and X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) used for characterizing the nanocomposite. The characterization revealed that the nanocomposite consists of a single phase of TiO2-B and multi-walled carbon nanotubes. The mass ratio of TNRs/MWCNTs is 1:1. The morphology of TiO2-B is a nanoribbons structure with porous pits on its surface. Multi-walled carbon nanotubes (MWCNTs) grow on these nanoribbons and form a network structure-like. The influence of nanocomposite incorporation on the morphology, porosity, contact angle, mechanical properties, and performance of the prepared membranes was investigated as a function of pure water flux and salt rejection %. The hydrophilicity is increased by increasing the nanocomposite content whereas the contact angle and porosity decreased. The SEM images showed that the spongy-like structure of bare-PES is changed by incorporation of TNRs/MWCNTs to a macro-void structure. The nanocomposite reinforces and enhances the mechanical properties of the synthesized membranes. The tensile strength increased from 45.7 to 96.6 kg/cm² by blending 0.5 wt% TNRs/MWCNTs. Also, the incorporation of TNRs/MWCNTs increases the ac electrical properties of the membrane regarding the conductivity (σ), dielectric constant (ε) and...
1. Introduction

Nanofiltration (NF) and low-pressure reverse osmosis (LPRO) membranes are very promising techniques used in water treatment and desalination [1, 2]. NF and LPRO membranes are appropriate for desalination of brackish water. NF membrane offers high flux with low operating pressure, but it may have low salt rejection than LPRO membrane [3, 4]. Both of them are effective for removing organic compounds from water when the membrane can make electrostatic repulsion with the ionized functional group of organic compounds. Also, sieving mechanisms due to the pore size effect can strongly affect the membrane rejection [5, 6]. However, the membrane performance can change with time which may be caused by polarization, adsorptive, gel layer formation, and fouling. This change can affect the transportation across the membrane [7]. Membrane fouling count on surface porosity, pore size and hydrophobicity [8]. The surface of the membrane is essential for its performance [9].

Polymeric membranes are widely used due to their simplicity, flexibility, toughness, and low-cost fabrication. Nevertheless, they have a limited mechanical, chemical, and thermal resistance as well as a poor anti-fouling ability. The poor anti-fouling ability was ascribed to their limited mechanical, chemical, and thermal resistance [9]. The addition of an inorganic nanomaterial such as carbon nanotubes (CNTs) [12, 13], graphene oxide [14], titanium dioxide nanotubes [15], or zeolite [16] can be considered as a modifier to improve selectivity, strength, anti-fouling, and permeability properties of the polymeric membranes. CNTs have unique mechanical, thermal, and electrical properties. The low thermal expansion coefficient, high aspect ratio, and high in axis strength of CNTs can reinforce the membrane [17, 18]. In another hand, TiO2 nanomaterials are low-cost and nontoxic structures with high chemical stability, photocatalytic and antifouling activities [19]. Among these TiO2 nanostructures, TiO2-B nanoribbons (TNRs) possess high surface area to volume ratio and nanoporous nature due to the formation of the nano pits on their surfaces [20]. Hence, TNRs and CNTs are considered as perfect modifiers for the polymeric membrane due to their structure, hydrophilicity and high surface area.

Polyethersulfone (PES) membranes are widely used in RO membrane for water desalination and biomedical fields. PES membrane has a good thermal, mechanical, and oxidative properties with high glass temperature. However, the hydrophobicity of PES membrane which acts as a barrier in the separation processes can be considered as a disadvantage property [11]. Phase inversion method is the most popular technique for membrane preparation due to its simplicity, low-cost and massive product. Also, this method is more convenient than other methods for blending the polymer matrices with different nanostructures to improve their performance [21]. Shaban et al. reported that the addition of Titanium nanotubes to PES increase membrane porosity and enhance the performance of membrane [19]. Celik et al. conclude that the blending of PES with CNTs enhances the fouling resistance for membrane [22]. Zinadini et al. stated that the addition of graphene oxide nanoparticles to PES leads to the formation of a lateral pore in the membrane morphology. [14]. Also, Vatanpour et al. reported that the coated CNTs with TiO2 nanoparticles improve the antifouling properties of PES [23]. Based on literature survey and the amazing properties of TNRs and CNTs, it is highly expected that blending of PES with optimized TNRs/MWCNTs nanocomposite can lead to a new category of blending membranes with improved properties. However, TNRs/MWCNTs/PES membranes not previously investigated and the effect of the ribbons structure with nanotubes on the performance of membranes not studied yet.

In this work, we investigated the enhancement of PES membrane properties and performance through the incorporation of nanoporous structure from TNRs/MWCNTs nanocomposite. The effects of TNRs/MWCNTs ratio on the morphology, total porosity, contact angle, mechanical properties, ac electrical properties, water flux, and salt rejection % were investigated. The filtration performance of membranes was tested by using LPRO system for high salinity brackish water desalination.

2. Experimental

2.1. Materials

Polyethersulfone (PES ultrason E6020P, MW = 58,000 g/mol) was supplied by BASF Company, Germany. DMF, N,N-dimethylformamide (CAS No. 68-12-2) was purchased from Sigma-Aldrich, Germany. TiO2 powder (CAS No. 13463-67-7), Fe(NO3)3·9H2O (CAS No. 7782-61-8), Co(NO3)2·6H2O (CAS No. 10026-22-9) and Al(NO3)3·9H2O (CAS No.7784-27-2) were obtained from Loba Chemie, India. 36.6% HCl was supplied by scharlau, Spain. 98% H2SO4, and 69% HNO3 were bought from SDFCLI, India. Commercial C6H4 gas, 32% NH2OH and NaOH were delivered from ADWIC, Egypt.

2.2. Methods

2.2.1. Fabrication of TNRs/MWCNTs composite

The alkaline hydrothermal method was used for producing TNRs. 4 g of TiO2 powder was added to 400 ml of 10 M NaOH and stirred for 30 min. The resultant solution was poured into a 1 L autoclave. Then, the autoclave was placed in an oven for 24 h at 170 °C. After that, the product was filtrated and washed with 0.1 M HCl and distilled water. Finally, the produced white powder was dried at 80 °C for 4 h and calcined at 450 °C for 2 h [24].

A certain amount from the prepared TiO2 nanoribbons was added to Fe(NO3)3·9H2O, Co(NO3)2·6H2O and Al(NO3)3·9H2O with mass ratios 10 TiO2:20 Fe:20 Co:50 Al2O3 in 100 ml distilled water under stirring. Ammonia solution was added drop by drop until pH value become 8. Then, the complete precipitation happened. The solution was aged for 2 h at room temperature, then it filtrated and washed with distilled water. The product was dried at 80 °C for 4 h and then calcined at 450 °C for 4 h to remove excess of nitrate [25].

A certain amount of the functionalized titanium nanoribbons was used as a catalyst for the growth of CNTs by tubular chemical vapor deposition (CVD) technique. C6H6 was used as a carbon source, and N2 was used as a carrier gas. The ratio of C6H6 to N2 was 1:10 v/v. The growth of CNTs was carried out for 50 min at 700 °C [26]. The as-