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Fabrication and water desalination performance of piperazine–polyamide nanocomposite nanofiltration membranes embedded with raw and oxidized MWCNTs

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ABSTRACT

Multiwalled carbon nanotubes (MWCNTs) were exposed to acid solution containing HNO_3 and H_2SO_4 to synthesis of oxidized MWCNTs and used for preparation of piperazine-based polyamide thin film nanocomposite nanofiltration membrane. Both raw and oxidized MWCNTs were applied in the fabrication of the membranes with four different concentrations of 0.001, 0.002, 0.005, and 0.01 wt. % in the piperazine solution. Salt rejection, permeation, and antifouling properties of unfilled, raw and oxidized MWCNTs embedded membranes were investigated. Water flux for 0.005 wt. % oxidized MWCNTs significantly increased due to this fact that membrane hydrophilicity improved as a result of functionalization of MWCNTs. Contact angle measurements confirmed the improvement of hydrophilicity by adding oxidized MWCNTs to the membranes. Surface SEM and AFM images illustrated that the MWCNTs made surface of the membranes smoother and macro-voids enlargement leads to water flux enhancement. The antifouling properties were investigated using bovine serum albumin (BSA)/salt solution. The results showed that the membranes with a smoother surface had a better resistance against the fouling. The salt rejection performance exhibited that by embedding of the raw MWCNTs and oxidized MWCNTs, improvement in rejecting of Na_2SO_4 salt can be observed. It could conclude that the addition of both raw and oxidized MWCNTs could improve the desalination performance of the piperazine–polyamide NF membranes.

1. Introduction

For the last two decades, membrane processes have become one of the most important approaches to enhance water and wastewater treatment in commercial scales. This mostly comes from the high stability, great efficiency and low energy requirement of the membrane processes [1,2]. Based on this technology, separation and concentration have technically become possible due to their efficiency. Among all the membrane processes such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), and so on, the NF membranes have shown significant features in energy consumption and ease of operation. The NF membranes separation characteristics are between RO and UF. The NF membranes have the advantage of retaining low molecular weight organics, divalent ions and relatively large monovalent ions from water solution due to the separation mechanisms, in which this retention is higher than UF membrane and lesser than RO membranes [3].

Most of NF membranes are thin film composite (TFC) membranes prepared by interfacial polymerization (IP) technique [4]. The TFC nanofiltration membrane usually consists of three components: a polyester non-woven fabric base, an asymmetric porous support (usually polysulfone UF membrane) casted onto the base, and an ultra-thin selective skin layer (piperazine-amide) formed by the IP in-situ on the surface of the support [4,5]. Each layer is fit to specific requirements for maximum performance. The selective skin layer of TFC membrane is principally responsible for permeability and selectivity [6]. A great number of TFC membranes have been successfully developed to give two key parameters to NF membranes, high permeation flux and moderate solute rejection for evaluating their performance.

Nowadays, usage of nanocomposite membranes is increasingly growing, where a nanofiller material will disperse in a polymer matrix [7]. Mixed matrix/nanocomposite membranes have shown satisfactory characteristics in sorption capacity, reaction, and sepa-

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ration [8-10]. Carbon nanotubes (CNTs), as an excellent choice for fabricating mixed matrix membranes, have been found extremely helpful to achieve maximum flux and solute rejection with reduced operating pressure in order to solve the problems which address this issue [11,12]. Wu et al. prepared MWCNTs/polyester thin film nanocomposite (TFN) membranes by IP of triethanolamine (TEOA) and trimesoyl chloride (TMC) on a polysulfone supporting membrane. They found that water permeability would go up if the carboxylated MWCNTs concentration in aqueous phase increases up to 0.5 mg/mL. Additionally, the resulted membrane showed a fine long-term stability [13]. Majeed et al. have used three concentrations of hydroxyl functionalized MWCNTs in polyacrylonitrile (PAN), 0.5, 1 and 2 wt. % whose results showed an increase in water flux by 63% at 0.5 wt. % loading compared to the neat PAN membranes. Furthermore, comparing the MWCNTs embedded membranes with the neat ones in case of resistance against compaction have exhibited that loading of 2 wt. % MWCNTs caused to 36% improvement as well as an increase over 97% in tensile strength of the membranes [14]. Shah and Murthy reported synthesizing a functionalized MWCNT/PSf composite membrane by the phase inversion method using DMF as solvent, in which the amount of composite membranes had a crucial role in morphology, and permeation properties of the membranes. Rejection of heavy metal showed a great result with increasing the amount of MWNTs and the interesting results were seen at a pressure of 0.49 MPa [15]. Stretz and co-workers investigated the fabrication of ultrafiltration membranes applying polysulfone/nano-TiO_2/multiwalled carbon nanotube with variable ratios of TiO_2/MWCNTs to watch effects on membrane pore size, fouling, permeation, and rejection of humid acid (HA). They reached the conclusion that an equivalent mixture of both NPs provided the possibility to make properties of a single membrane better under both types of fouling conditions [16]. In a study, through self-polymerization of mussel-inspired dopamine (DA), Cheng et al. successfully coated a layer on the polyethylene glycol (PEG) based NF membrane. After being coated with mussel-inspired polydopamine, the hydrophilic PEG based membranes showed an increase in the salt rejection. Their results exhibited that in spite of increase in feed concentration up to 800 ppm, the rejections to all of antibiotics remained high [17]. Xu et al. fabricated a novel nanocomposite organic solvent nanofiltration (OSN) membrane by one-step deposition of mussel-inspired octaammonium polyhedral oligomeric silsesquioxane onto supports. The prepared membrane showed remarkable performance for dyes removal which may encourage the design of advanced nanocomposite membranes for environmental application [18].

The functionalized MWCNTs have been used for preparation of polyamide TFC membranes for reverse osmosis and forward osmosis purpose [19-21]. For polyamide nanofiltration performance, to our knowledge, only amine-functionalized MWCNTs have been applied [22].

Since MWCNTs show a significant improvement in mechanical, chemical, and thermal in membrane properties as well as permeation, rejection, and antifouling properties, the amount of MWCNTs to reach this goal is important. To address this issue, investigation in oxidized and non-oxidized MWCNTs is an appropriate field that seems a lot of work can be done. To our knowledge, the raw and oxidized MWCNTs are not used in preparation of piperazine-amide nanofiltration membranes. In this study, the performance of unfilled NF membrane, raw MWCNTs and functionalized MWCNTs embedded membranes in polyamide layer was investigated. To emphasize the impact of concentration on different aspects of the membranes, all of these membranes were synthesized with different concentrations of MWCNTs varying between 0.001 to 0.01 wt. % and the resulted membranes were tested by permeation, salt rejection and BSA fouling experiments.

2. Materials and methods

2.1. Materials

The pristine MWCNTs (length 10–30 μm, diameter 20–30 nm and inner diameter 5–10 nm, purity 95%) were manufactured from US Research Nanomaterials, Inc. Polysulfone (PSf), used for preparation of the supports, was obtained from BASF Company (Germany). Piperazine (PIP, 99.5%), trimesoyl chloride (TMC, 99%), solvent of *N*-methyl-2-pyrroldiinone (NMP, 99%), sulfuric acid (98%), nitric acid (65%) and n-hexane (99%) were purchased from Merck chemical Company. Hollytex 3329 non-woven fabric was used as a polyester support for preparation of PSf layer.

2.2. Functionalization of MWCNTs

To functionalize pristine MWCNTs, they were mixed with an acid mixture of a 3:1 mixture of concentrated HNO_3 and H_2SO_4, following 30 min sonication and after that, they were refluxed for 16 h at 90 °C. This step is supposed to purify the synthesized raw MWCNTs from metal catalysts and graphite and other impurities and inserting hydrophilic functional groups on the CNTs surface. Then, the solution was diluted with distilled water to reach neutral solution with a pH 5–6. This was followed by filtering the MWCNTs using PVDF ultrafiltration membranes and put those in an oven for 24 h at 80 °C in order to dry those [22].

2.3. Membrane fabrication

The UF support membranes were fabricated by the non-solvent induced phase inversion technique, which is a widely used method for the fabrication of polymeric membranes. Polyester non-woven fabric is used for membrane strength. To prepare the membranes, first dried polysulfone granules were dissolved in NMP solvent with concentration of 19 wt. %. Then with a constant speed (400 rpm) and temperature fixed at 50 °C, the solution was mixed on a stirrer. Eventually the prepared solution was put in a dark place to reduce the bubbles dissolved in it. Afterward the solution was casted on the surface of non-woven fabrics using Doctor Blade to make uniform films with thickness of 175 µm. Next, immediately, they were immersed in water bath (25 °C) to consolidate and form supports.

Table 1 presented the characteristics of the prepared wet PSf support. More characterization of the used support was presented in previous work [24].

To convert these support membranes to NF membranes, first they were immersed in a piperazine aqueous solution bath (2 wt. %) for 10 min, followed by immersing these membranes in another bath which contained TMC solution (0.4 wt. %) in n-hexane for 2 min. After that the membranes were washed with n-hexane and put in an oven for 10 min in 70 °C to form a dense polyamide layer. The process of synthesizing was over and the membranes were kept in distilled water.

To fabricate nanocomposite membranes, the PIP solutions were mixed with the MWCNTs and sonicated for 30 min, and then the supports were immersed in these solutions. The rest was similar to previous procedure.

2.4. Characterization of membrane

Scanning of the surface and cross-sectional morphology of the membranes was conducted using scanning electron microscope (SEM) with a VEGA (TESCAN, Czech Republic) one. In order to prevent the sample charging, the dried samples were sputtered by a very thin layer of gold in an electro-plating device. After sputtering with gold, they were viewed with the microscope at 20 kV.

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