



Improvement in desalination performance of thin film nanocomposite nanofiltration membrane using amine-functionalized multiwalled carbon nanotube



Hamed Zarrabi^a, Mohammad Ehsan Yekavalangi^a, Vahid Vatanpour^{a,*}, Abbas Shockravi^a, Mahdie Safarpour^b

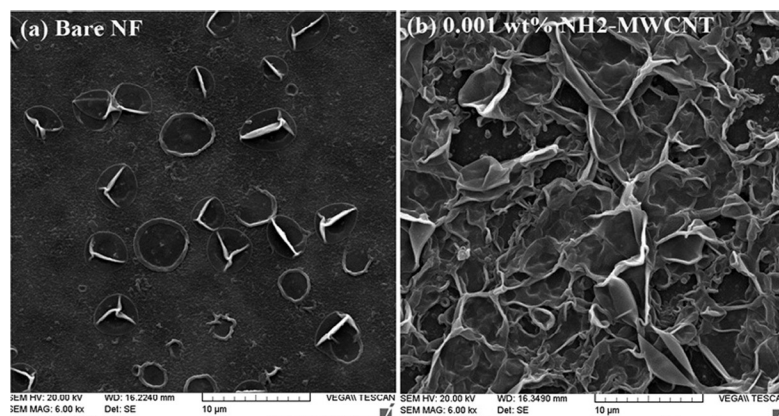
^a Faculty of Chemistry, Kharazmi University, 15719-14911 Tehran, Iran

^b Research Laboratory of Advanced Water and Wastewater Treatment Processes, Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

HIGHLIGHTS

- Polyamide NF membrane blended with NH₂ functionalized MWCNT was prepared.
- Analyses showed higher hydrophilicity and smoother surface for modified membranes.
- NF membrane modified with 0.005 wt% NH₂-MWCNT showed best separation performance.
- Membranes containing NH₂-MWCNT in the polyamide layer improved fouling resistance.

GRAPHICAL ABSTRACT



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ABSTRACT

A modified thin film composite nanofiltration (TFC/NF) membrane was prepared by interfacial polymerization between piperazine and trimesoyl chloride monomers and NH₂ functionalized multiwalled carbon nanotube (NH₂-MWCNT) as a hydrophilic modifier. The surface morphology and hydrophilicity of the prepared NF membranes were studied by scanning electron microscopy (SEM) and water contact angle measurements, respectively. These analyses showed the higher hydrophilicity and the smoother surface of the modified membranes. Also, the separation performance of the membranes was investigated using 2000 mg/L of Na₂SO₄ and NaCl solutions tested by cross-flow filtration system. The NF membrane modified with 0.005 wt% NH₂-MWCNT presented the best separation performance, including 36.71 and 95.72% rejection of Na₂SO₄ and NaCl salts, respectively. The fouling resistance of the membranes was also studied using bovine serum albumin (BSA) protein as a model fouling agent, based on the water flux decline during the filtration process. Results showed that the membranes containing NH₂-MWCNT in the polyamide layer have improved fouling resistance compared to the unmodified NF.

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1. Introduction

Millions of people worldwide have no access to safe drinking water [1]. Access to clean water remains exigent issue, while over 70% of

* Corresponding author.

E-mail addresses: vahidvatanpour@khu.ac.ir, vahidvatanpour@yahoo.com (V. Vatanpour).

earth's surface is water [2]. The conventional way to clean up brackish water, desalinate seawater and remove harmful ions from contaminated water is to utilize NF/RO membranes [1].

The most common method for constructing polyamide NF/RO membranes is interfacial polymerization (IP). This technique is based on polycondensation reaction between two monomers, one is two-functional amine and another is tri-functional acid chloride. The aqueous amine solution, at first saturate the support and after contacting with organic phase containing acid chloride monomer, an ultrathin layer is quickly formed at the interface of two phases and remains attached to the support. The reaction take place at the organic side of the interface owing to poor solubility of acid chloride in water and well solubility of amine in organic solvents [3,4]. This method leads to forming a thin polyamide selective layer on the surface of porous polysulfone support. To achieving proper IP, a combination of properties such as well controlled nano-scale thickness, low rate of defects as a result of self-sealing mechanism, control of cross-linking and hydrophilicity equilibrium via appropriate choice of monomers are involved [3,5]. Also, choosing proper additives and using nanomaterials with hydrophilic properties may increase hydrophilicity or rejection of NF/RO membranes [6].

Incorporating nanoparticles in the polyamide layer during membrane preparation is an economical method because only a little amount of the nanoparticles is used. The nanomaterials have unique properties such as huge surface area and a large numbers of functional groups. The incorporation of nanomaterials during preparation of the polyamide membranes has resulted in enhance in water flux of active layer. The hydrophilic nanomaterials could improve polyamide film formation by enlarging the wet zone on the top of support layer, increasing the monomers diffusion rate to the interface; controlling reaction pH as a buffer agent and capturing by products [7,8]. In addition, nanoparticles could enhance membranes hydrophilicity and fouling resistance. Obviously, embedding of nanofillers could improve both permeability and antifouling properties of the mixed matrix membranes [9–12].

Some hydrophilic nanoparticles were applied for modification of the polyamide thin film nanocomposite (TFN) membranes such as TiO₂ [10], Zeolite [11], Ag [12], Al₂O₃ [13], zirconium phosphate [14], graphene oxide [15], and carbon nanotube [16]. The specific functionalities of these nanomaterials have initiated new degrees of freedom in the thin film composite (TFC) membrane design that merges the necessary properties of conventional membrane polymers with the benefits of the nanofillers. Among them, the carbon-based nanoparticles due to same nature with organic monomers could uniformly disperse in the prepolymerization solutions.

Carbon nanotubes (CNTs) derivatives have been shown to improve performance of the nanocomposite membranes [17,18]. The physical and chemical properties of carbon nanotubes are crucially important to the TFN membrane performance. The antifouling properties of the membranes having CNTs have been related to the functional hydrophilic groups [19] and also, biocidal properties of the CNTs since they can break the cell membranes of microorganisms and interrupt the metabolic pathways, next death and/or inactivation of microorganisms could take place [16,20]. However, effective functionalization along with hydrophilicity and controlled surfaces charges, leads to enhance in permeation flux and salt rejection in thin film composite membranes [21]. The amino-functionalized CNTs might interact well with PA of TFC membrane when they are introduced during IP, due to the combined action of electrostatic attraction and hydrogen bonding. Additionally, the large specific surface area of aminated MWCNTs provides adsorption sites and diffusion channels for water, resulting in significant improvement in water production. With regards to membrane fouling, it is believed that the presence of such amine functionalized groups could considerably mitigate fouling of the TFN membrane in a long run.

In this report, amine functionalized multiwalled carbon nanotube (MWCNT-NH₂) was applied in polyamide layer of NF membrane for desalinate water. Various amounts of piperazine (PIP) monomer, camphor

sulfonic acid and triethylamine additives and constant amount of trimesoyl chloride (1,3,5-tricarboxyl chloride) were used to achieve the optimized polyamide layer formulation. The effect of different concentrations of MWCNT-NH₂ on flux, rejection of monovalent and divalent salt and antifouling of NF membranes was studied.

2. Experimental

2.1. Materials and reagents

MWCNTs were purchased from Plasmachem GmbH Company, Germany. The MWCNTs have diameter of 5–20 nm and the length of 1–10 μm were used to prepare MWCNT-NH₂. Polysulfone (PSf Ultrason S6010 with M_w = 58,000 g/mol, BASF, Germany) and *N*-methyl-2-pyrrolidone (NMP, Merck Co., Germany) were used to fabricate asymmetric porous support of NF membrane on polyester non-woven fabric. PIP and TMC monomers were obtained from Sigma-Aldrich, USA. Triethylamine (TEA) and (+)10-camphor sulfonic acid (CSA) (all purchased from Merck Co., Germany) were used as additives of interfacial polymerization process. Industrial grade *n*-hexane (mixture of isomers), as the organic phase of interfacial polymerization, was supplied by Mahshahr Petrochemical Co., Iran and was dried using molecular sieve prior to use. NaCl, Na₂SO₄, H₂SO₄, HNO₃, SOCl₂ and *N,N*-dimethylformamide (DMF) all were from Merck Co., (Germany) and bovine serum albumin (BSA, M_w = 67,000 g/mol) was obtained from Sigma-Aldrich Co.

2.2. Preparation of NH₂-functionalized MWCNTs

At first, the oxidized MWCNTs were prepared by oxidizing of raw MWCNTs. The MWCNTs (8.55 g) were dispersed in a flask containing a mixture of concentrated H₂SO₄/HNO₃ (3/1, v/v). The mixture was refluxed and heated at 90 °C for 8 h to oxidize MWCNTs [17,22]. For obtaining the acyl chloride MWCNTs, 0.3 g of the prepared MWCNT-COOH was suspended in 75 mL of SOCl₂ and 5 mL DMF; and sonicated for 1 h and then heated at 70 °C for 24 h to convert the surface-bound carboxyl groups to acyl chloride groups. The precipitate was then heated in oven at 80 °C to remove excess thionyl chloride. After preparation of MWCNT-COCl, it was storage in vacuum oven at 20 °C until use.

To prepare NH₂-functionalized MWCNTs, as-synthesized purified acyl chloride MWCNTs were functionalized by aromatic diamine. In this method, 0.3 g of MWCNTs-COCl material was dispersed in 80 mL of dichloro methane (CH₂Cl₂) as solvent containing 5 g aromatic diamine of 4,4'-diamino diphenyl methane (DDM). After that, the resulted mixture was sonicated for 15 min and next refluxed for 24 h at 90 °C. NH₂-functionalized MWCNTs were prepared through amide linkage. The resulting suspension was vacuum filtered by a 0.45 μm PTFE membrane, next it was washed with acetone and dried at 90 °C for 24 h [23,24].

2.3. Preparation of NH₂-MWCNT/NF membranes

For preparation of asymmetric porous support, casting solution of 19 wt% PSf in 81 wt% NMP was used. After complete dissolution of the polymer, the solution was casted on non-woven fabric using an automatic film applicator and followed by standard process of non-solvent induced phase inversion. The resulted film directly immersed in distilled water (coagulation bath 25 °C) for 24 h and then dried until using.

Polyamide thin films were formed on top of the PSf supports using different concentrations of monomers and additives. Table 1 represents the amount of reagents used for achieving the optimized PA formulation. In a typical interfacial polymerization process, the PSf supports were immersed in distilled water around 30 min prior to use; then they were removed from the water and allowed to contact with an aqueous solution containing 1 wt% PIP, 3 wt% CSA, 3 wt% TEA and 0.1 wt% sodium dodecyl sulfate (SDS) for 10 min. The SDS was used as a surfactant to best wetting of the support with MPD aqueous solution.

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