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High flux and fouling resistant reverse osmosis membrane modified with plasma treated natural zeolite

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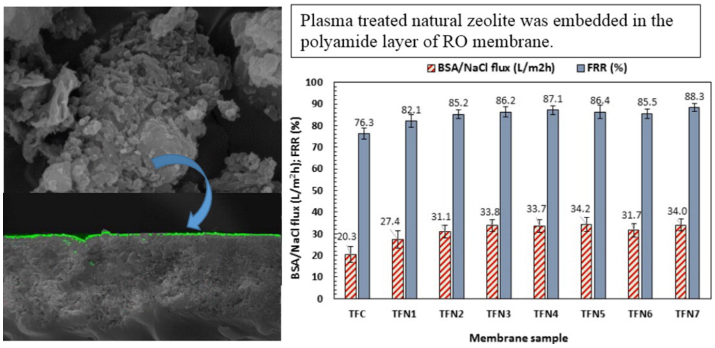
HIGHLIGHTS

- Natural clinoptilolite was treated using glow discharge plasma technique.
- Plasma treated clinoptilolite was embedded in the polyamide layer of TFC-RO membrane.
- Hydrophilicity, permeability and fouling resistance of the modified RO membranes improved.

GRAPHICAL ABSTRACT



Plasma treated natural zeolite was embedded in the polyamide layer of RO membrane.

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ABSTRACT

Polyamide reverse osmosis (RO) membrane was fabricated by interfacial polymerization of *m*-phenylenediamine and trimesoyl chloride and modified with natural clinoptilolite as a hydrophilic zeolite material embedded in the polyamide layer. The effect of glow discharge plasma treatment with different plasma gas pressures was investigated on the physical and chemical properties of the natural clinoptilolite and the resulted modified membranes. Scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) spectroscopy of the untreated and treated clinoptilolite confirmed the variation of its surface properties and formation of new Si—OH—Al bonds during the plasma treatment. The embedding of hydrophilic clinoptilolite in the polyamide layer decreased the roughness of membrane surface. Also, the water contact angle of the membranes showed the improved hydrophilicity of the modified membranes which was confirmed with the results of permeation tests. The membrane modified with 0.01 wt.% clinoptilolite treated under 1.0 Torr oxygen as the plasma gas showed the highest water flux improvement (39%) and fouling recovery ratio (88%) compared to the unmodified membrane.

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1. Introduction

Global water crisis and clean water shortage is one of the most important concerns of humanity today. Membrane separation, as a green and effective technology to regenerate clean water, is the most widely used desalination technology. Reverse osmosis (RO) has developed as the predominant membrane-based desalination technology of seawater or brackish water because it is simple to design, energy-efficient and it has excellent scale-up capability [1]. In the RO process, the produced water quality and total energy consumption depend strongly on the performance of the used semi-permeable membranes. Therefore, high efficiency RO membranes with improved productivity besides good salt rejection and fouling resistance are seriously needed [2].

Thin-film composite (TFC) membranes are currently the main RO membranes used for desalination. A typical TFC membrane contains an ultra-thin polyamide selective layer along with a porous polysulfone (PSf) support cast on a non-woven fabric layer [3]. In the common TFC membrane, the top selective layer is fabricated in-situ by interfacial polymerization of *m*-phenylenediamine (MPD) and trimesoyl chloride (TMC) as aromatic polyamine and polyacyl halide monomers [4]. The characteristics of the polyamide layer and the bottom porous substrate of the TFC membrane can be individually modified to obtain the desired membrane performance; i.e., the ultra-thin layer can be optimized for the preferred combination of water flux and salt rejection, while the porous support can be designed for suitable pore size, good mechanical properties as well as minimum resistance to permeate flow [5].

Although there are many developments in RO technology, fouling is still considered as the main challenge for the wide application of the RO desalination technique [6]. The fouling leads to the flux decline of the RO membrane and increase the operating costs. Two main mechanisms are considered in the membrane fouling phenomenon: fouling and blocking of the membrane pores and fouling of the membrane surface which occurs due to accumulation of several impurities such as suspended inorganic or organic materials. Recently, several strategies have been investigated to increase the fouling resistance of the RO membranes such as addition of co-solvent during the interfacial polymerization [7], incorporation of hydrophilic additives or substitution of more hydrophilic monomers [8,9] and surface modification using different techniques [10–12]. In this regard, organic-inorganic nanocomposite membranes have attracted great attention. Many researchers have reported that thin film nanocomposite RO (TFN-RO) membranes may improve the membrane performance such as permeability, selectivity, durability and chlorine resistance compared with that of a bare polyamide membrane [6,13–20]. Furthermore, the polymer networks can positively affected by the physical (mechanical, magnetic, optical, conducting, catalytic) and biomedical (antimicrobial, anticancer) properties of the embedded inorganic nanoparticles [3]. Incorporating of inorganic nanoparticles can increase the permeability of the polyamide membrane by providing a direct path for water transport or modifying the membrane network structure, thereby enhancing the water flux. Several TFN-RO membranes with improved desalination performance have been reported by addition of inorganic porous materials (e.g., pure metal, metal oxide, carbon nanotubes and zeolite nanoparticles) in the literature [6,13–20].

Zeolite nanomaterials are now the most commonly used inorganic material for embedding into the polyamide layer of RO membranes. Incorporation of zeolite materials into polyamide layer of the TFC membrane can improve the water flux without large loss of salt rejection under high pressure during RO process. The permeability improvement may be related to the well-defined sub-nanometer pores in the zeolite nanomaterials which can provide favorable flow channel for water molecules while exclude the solutes such as hydrated sodium ions to pass through. The related salt rejection mechanism is regarded as “size exclusion” because the pores inside zeolite are between the diameters of hydrated salt ions and water molecules [3]. Therefore, the zeolite containing TFN-RO membranes can overcome the well-known “trade-off” restriction of RO membranes in which the salt rejection will perpetually decrease with increased permeability.

Table 1
The codes of prepared RO membranes.

Membrane code	Clinoptilolite concentration in the MPD solution (wt.%)	Pressure of plasma gas used to treatment of clinoptilolite (Torr)
TFC	0.000	–
TFN1	0.010	–
TFN2	0.005	0.1
TFN3	0.010	0.1
TFN4	0.005	0.5
TFN5	0.010	0.5
TFN6	0.005	1.0
TFN7	0.010	1.0

Dong et al. [20] have studied TFN-RO membranes incorporated with NaY zeolite nanoparticles dispersed in the dense nodular polyamide layer. Their results showed that under the optimum conditions and using 0.15 wt.% zeolite, the water flux increased from 23.3 to 43.7 gal/ft^2/day while providing a high salt rejection of 98.8% for 16,000 ppm NaCl solution. In another earlier study, Fathizadeh et al. [19] modified the polyamide TFN membrane by nano-NaX zeolite and showed the improvement of physical, chemical and surface characteristics and performance of the modified TFN membranes. They observed the highest water flux and the lowest salt rejection under TMC and MPD concentration of 0.15% and 3% w/v, respectively, and 0.2% w/v nano-NaX zeolite. Kim et al. [21] used aminated template free zeolite nanoparticle (aTMA) for fabrication of nanocomposite RO membrane to improve chlorination resistance and membrane performance. The salt rejection and water flux of the RO membranes containing aTMA were 98.8% and 37.8 L/m^2 h, respectively.

The synthesis of zeolites usually requires highly complicated equipment and toxic metal-organic precursors. Therefore, the modification and application of natural zeolite materials can be a promising strategy to benefit their desirable properties. Plasma consists of electrons, neutral species and negative and positive ions, which is called the fourth state of matter. Plasma using techniques are low cost, simple and environmentally-friendly, which are utilized to modify the functional characteristics of various materials for different applications [22,23]. Recently, non-thermal plasma techniques including dielectric-barrier discharge, radio frequency discharge, silent discharge, glow discharge have attracted considerable attention for surface treatment of different materials [24]. For example, the plasma modification has enhanced the activity and surface structure of natural zeolite [25]. The surface of kaolin has been modified using the cold plasma approach to increase the removal efficiency of methylene blue from aqueous solution [26]. CO_2, N_2 and Ar plasmas have been used for the surface treatment of sepiolite to improve the adsorption of malachite green from polluted water [27]. In addition, natural pyrite has been treated applying oxygen and nitrogen glow discharge plasmas to enhance its catalytic

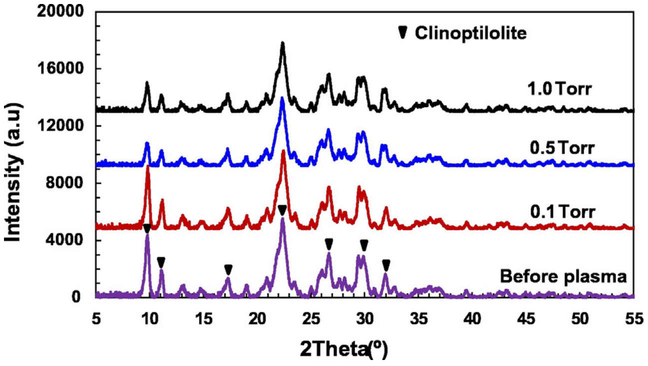

Fig. 1. XRD patterns of the clinoptilolite samples before and after plasma treatment.