Preparation and characterization of a low-pressure efficient polyamide multi-layer membrane for water treatment and dye removal

Yaghoub Mansourpanah*, Maryam Samimi
Membrane Research Laboratory, Lorestan University, Khorramabad 68137-17133, Iran

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A B S T R A C T
Recently, fabrication of membranes with low energy consumption has gained much attention of research. The aim of the current work was to design a new low-pressure and efficient multi-poly (piperazine-amide) thin layer which each layer formed alternatively upon a polyester nonwoven backing without using a polymeric support (unlike usual thin film membranes which use an ultrafiltration support). A desired rejection toward CuSO4 and Congo red dye was obtained about 80 and 97%, respectively. Estimated pore size of the membranes (using molecular weight cut off test) showed the values from 150 to 325 Da.

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Introduction

In recent decades, membrane processes have gained much attention as efficient separation technologies [1,2]. Membrane separation processes have many industrial applications and their ability for separation depends on the properties of the membrane such as hydraulic permeability, fouling result, thickness, pore size, membrane material, surface charge and variables like filtration time, system pressure, feed concentration and ambient temperature.

Desalination technologies are used to desalinate sea water and brackish waters and are often considered as energy-intensive processes [3]. One of the major desalination technologies currently in use is based on membrane separation. Energy consumption, especially in RO plants, is a major concern in membrane processes and can reach to as high as about 50% of the permeate cost in high pressure driven membrane processes [4]. In driven-pressure membranes the water in the feed (rejection side) is forced into the permeate side through the membrane by applying a pressure difference across the membrane. In this situation, high feeding pressure is required to overcome the osmotic pressure on the feed side. Operating pressures required for the purification of brackish water are lower than those of seawater due to their lower osmotic pressure caused by lower feed water salinity.

Specific energy consumption (SEC) describes the energy needed to produce a cubic meter of permeate. Accordingly, the SEC is given by Eq. (1):

$$SEC = \frac{\Delta P}{\eta_f Y_f}$$  \hspace{1cm} (1)

where $\Delta P$ is transmembrane pressure, $\eta_f$ is pump efficiency and $Y_f$ is total water recovery which is a measure of process productivity and can be expressed as Eq. (2):

$$Y_f = \frac{Q_p}{Q_f}$$  \hspace{1cm} (2)

where $Q_p$ and $Q_f$ are permeate and feed flow rates, respectively [5]. Nowadays, considerable researches have focused on minimizing the SEC of water desalination [5].

Most commercial and laboratory scale NF membranes have a thin film composite structure with a selective layer above the porous substrate (mostly UF membranes). Among different thin layer membrane fabrication methods, interfacial polymerization technique is the most commonly used method [6–9]. This technique is based on a poly condensation between an amine functional group (PIP) and an acid chloride functional group (TMC) [10,11]. In recent decades, many studies have concentrated on creating the desired alterations on the thin layers to improve their structure and performance. Adding different appropriate additives into the thin layer matrix during the polymerization process and changing thin layer preparation conditions are the most popular techniques [12–15].
Wastewaters contaminated with metals such as Cd, Cr, Cu, Ni, As, Pb, and Zn are the most hazardous among chemical wastewaters. Treatment of metal-contaminated wastewater prior to its discharge to the environment is necessary because of their serious health concerns. Heavy metals can be absorbed by organs due to their easy solubility in the environments [16]. Copper is one of the heavy metals which cause some diseases such as Wilson disease and insomnia as well as liver damage [17]. Recently membrane technology has shown high potential for the treatment of heavy metal-containing effluents [18].

In the current work, a novel multilayer poly (piperazine-amide) thin layer was prepared on a nonwoven backing only (without applying a UF polymeric support) using piperazine (PIP) and trimesoyl chloride (TMC) by in situ interfacial polymerization technique. The UF support is commonly used in the preparation of commercial thin film membranes and increases the mechanical properties and performance of the thin film composite membranes [19]. The main goal of this study was to eliminate the support to achieve low energy consumption by applying low transmembrane pressure. For this purpose, a few poly (piperazine-amide) thin layers were separately formed on a nonwoven backing which resulted in the formation of an appropriate barrier to reject copper ions and desalting of water in which the formed thin layers showed higher flux than traditional thin film membranes. As a result, the operating pressure was greatly reduced which in turn decreased the required energy level. Finally, morphology and other characterizations of the prepared multi-thin layers were investigated using FE-SEM, AFM, ATR-IR, swelling ratio, molecular weight cut off, water contact angle test and a membrane set-up.

**Experimental**

**Materials**

1,3,5-Benzeneetricarboxyltrichloride (TMC, 98%), n-hexane, piperazine (PIP) and triethylamine (TEA, 99.5%) were obtained from Merck. Na₂SO₄ and CuSO₄ salts (Merck) were utilized for the investigation of ion rejections. Methanol, ethanol, CaO, acetic acid, ammonium acetate, sodium periodate and acetyl acetone were purchased from Merck. Ribose, sucrose and raffinose were purchased from Sigma-Aldrich and were applied for the evaluation of the MWCO of the membranes. Bovine Serum Albumin powder [some properties are as follows: assay >96%, mol wt. 66 kDa, solubility >40 mg/mL in H₂O] was used for the evaluation of antifouling properties and Congo red and Safranin were applied for studying the dye rejection ability of the membranes which were obtained from Sigma-Aldrich. Deionized water (DI) was used throughout the study.

**Preparation of multi-layer thin film membranes**

Poly (piperazine-amide) thin film membranes were prepared by interfacial polymerization process on a polyester nonwoven backing. A flat sheet of nonwoven backing was placed between two Teflon frames 0.7 cm high with inner cavity of 7.5 cm × 20 cm and the membranes were prepared as follows:

An aqueous solution containing PIP (0.15 wt%) and TEA (0.4 wt %) was poured on the top of the backing and was allowed to wet the surface in ambient temperature. After a while, the surface was rolled by a soft rubber roller to eliminate any tiny bubble which may have been formed. After 5 min, the excess aqueous amine solution was removed. Then, the organic TMC solutions (two certain concentrations) were poured into the Teflon frames and were left for 5 min when the conventional interfacial polymerization reaction occurred. After 5 min, the excess organic solution was removed from the frames and the membrane was heated in an oven at 70 °C giving a mono layer of poly (piperazine-amide) on top of the nonwoven backing. To fabricate the second and third poly (piperazine-amide) thin layers on top of the first layer, the above polymerization approach was repeated.

To improve and investigate the performance and efficiency of the membranes, the third poly (piperazine-amide) layer was prepared with two different concentrations of TMC (0.1 and 0.15 wt %) in the organic solution. Table 1 shows the compositions of the obtained poly (piperazine-amide) thin layer membranes.

**Characterization of the membranes**

**ATR-FTIR**

Chemical alterations of poly (piperazine-amide) thin layer membranes were monitored using an Equinox 55 Bruker FT-IR spectrometer (Germany) with an attenuated total reflection (ATR) attachment. Totally 32 scans were taken during IR study for each sample and the resolution of the spectrometer was 4 cm⁻¹.

**Scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDX)**

SEM apparatus was employed to obtain images of membrane surfaces and cross sections. Samples of the membranes were frozen in liquid nitrogen and were then fractured. After sputtering with gold they were observed by a field emission scanning electron microscope (FE-SEM–MIRA3 LMU, TESCAN, Czech) coupled with an energy dispersive X-ray spectroscopy (EDX) at 15 kV. The nonwoven backing could not be broken in liquid nitrogen. Accordingly, viewing the cross-section of these thin layer membranes was not possible.

**Atomic force microscopy (AFM)**

Atomic force microscopy (AFM, non-contact mode) was utilized to analyze surface morphology, smoothness and roughness of the membranes. The used AFM apparatus was a Dual Scope™ scanning probe–optical microscope (DME model C-21, Denmark). Small pieces of the prepared membranes (1 cm²) were cut and glued on a glass substrate. The membrane surfaces were analyzed in a scan size of 5 μm × 5 μm. Pore size of the membranes and roughness parameters were measured by SPM–DME software.

**Dynamic water contact angle**

A liquid contact angle measuring equipment (G10, KRUSS, Germany) was used to evaluate the hydrophilicity of poly (piperazine-amide) multilayer membranes. Distilled water was used as probe liquid in all experiments. To minimize experimental error, the contact angles between DI water and each sample surface were measured at seven random locations and their average values were reported. Droplets (2 μL) with the rate of 1 μL/s were inserted into the membrane surface and a side view image was taken after 10 s [20].

**Swelling degree**

In order to evaluate the degree of multi-layer swelling, which indicates the undesirable interaction between the membrane and the liquid permeate, the membrane samples were kept in distilled water at room temperature for 24 h, then the samples were dried in an oven at 70 °C and the membrane mass was measured.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Organic phase TMC (wt%)</th>
<th>Organic phase PIP (wt%)</th>
<th>Organic phase TEA (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono-layer (M)</td>
<td>0.1</td>
<td>0.15</td>
<td>0.4</td>
</tr>
<tr>
<td>Bi-layer (B)</td>
<td>0.1</td>
<td>0.15</td>
<td>0.4</td>
</tr>
<tr>
<td>Triple-layer (Tₐ₁)</td>
<td>0.1</td>
<td>0.15</td>
<td>0.4</td>
</tr>
<tr>
<td>Triple-layer (Tₐ₁₅)</td>
<td>0.15</td>
<td>0.15</td>
<td>0.4</td>
</tr>
</tbody>
</table>