Thin Film Nanocomposite Membrane Impregnated with Clay Nanoparticles for Water Desalination
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Abstract: Fabrication high performance reverse osmosis (RO) membrane at low cost is necessary in desalination industry. In this paper, we report the use of clay nanoparticles (NPs) to improve RO thin film composite (TFC) membrane. Different concentrations of NPs were embedded into polyamide (PA) active layer of TFC membrane through interfacial polymerization (IP). Results indicated that the membrane impregnated with clay NPs exhibited higher water flux and fouling resistant than the pristine one, and maintained good salt rejection.

Keywords: Thin film nanocomposite (TFN); Reverse Osmosis (RO); polyamide (PA); nanoparticles (NPs)

INTRODUCTION
Nowadays, massive interest in the use of membrane technology for water desalination has emerged [1]. Thin-film composite (TFC) membrane, which is fabricated by interfacial polymerization (IP) between m-Phenylenediamine (MPD) and trimesoyl chloride (TMC) on polysulfone (PSU) support, is considered as the most widely used desalination membrane [2]. However great efforts have been exerted to enhance TFC membrane properties, fabricating a membrane with high performance and low cost is a big challenge [3]. On 2007, Hoek and his coworkers [4] developed a new approach to enhance TFC membrane performance by embedding Zeolite NPs into polyamide (PA) active layer through interfacial polymerization (IP). Result indicated that the membrane impregnated with zeolite NPs showed higher water flux as compared to unmodified membrane. This is because zeolite NPs are hydrophilic, and their presence in membrane PA layer increased water adsorption, thus, improved water flux. Since then, researches have been conducted to enhance membrane performance by incorporating NPs into membrane matrix [5-13].

Clay NPs have been used in water treatment because they are eco-friendly and cheap [14]. Monticelli and his coworkers [15] successfully improved ultrafiltration membrane performance by dispersion of clay NPs into membrane structure. In addition, an enhancement in the composite film mechanical properties was noticed. Another study by Khranovskyy [16] showed that the addition of clay NPs in casting solution of UF membrane improved membrane surface wettability. The objective of this paper is to study the effect of clay NPs incorporation into PA thin film layer of membrane. The hydrophilic nature and cheap price of clay were utilized with the purpose of fabricating high performance RO-TFN membrane.

MATERIALS
Commercial polysulfone (PSU, 0.03) sheet were purchased from MicroVantage™ WGPS Series. M-Phenylenediamine (MPD) and trimesoyl chloride (TMC) were obtained from Sigma Aldrich. Clay nanoparticles (NPs-70 nm) were purchased from Sigma Aldrich.

Polysulfone Layer Preparation
Commercial PSU sheet was used as a support layer. The fabrication process is graphically illustrated in scheme 1. First, m- MPD solution, which prepared by dissolving 15 wt.% MPD in DI water, was poured on PSU sheet for 3 minutes. Excess solution on MPD-PSU sheet was removed by squeegee roller. Next, TMC solution, which was prepared by dissolving 0.13 wt % TMC in hexane, was poured on MPD-PSU sheets for 3 minute. The reaction between MPD and TMC resulted in the formation of PA thin film layer. Then, the membrane was washed with DI water and kept in room temperature for at least 12 hours before test. Clays NPs were dispersed in TMC solution at different concentrations.
Scheme 1. Clay TFN membrane fabrication

TFN membrane Characterization

Contact angle measurement was used to estimate membrane surface hydrophilicity. A contact angle video system was used for this measurement. The contact angle of each sample was measured six times, and the average value was reported.

A high pressure-cross flow RO system was used to determine membrane performance figure 1. The membrane was comprised in dead end cell under 270 Psi for 10 hours (2000 ppm NaCl at 25 °C). The water flux was determined by equation

\[ J_w = \frac{\Delta V}{A \tau} \]

Where \( J_w \) is permeation flux (L/m²h), \( A \) is membrane area (cm²), and \( \tau \) is filtration time (h).

Salt rejection was determined by eq. 2:

\[ R \% = (1 - C_p/C_f) \times 100 \]  

where R is salt rejection, \( C_p \) is permeation conductivity and \( C_f \) is feed conductivity.

RESULT AND DISCUSSION

Figure 2 presents water contact angel measurement of the membranes at different concentrations of NPs. It was observed that the contact angle decreased from 60 to 38 by increasing NPs concentration from 0 to 0.10 wt. %, indicating the enhanced wettability of membrane impregnated with clay NPs.
Fig-2: Contact angle measurement

Water flux of membrane at different NPs concentrations is presented in figure 3. As it can be seen, the water flux increased with higher loading of NPs. Because the hydrophilicity of membrane surface was increased upon addition of NPs, a water layer was chemically adsorbed on membrane surface. When this layer came in contact with the water, it might adsorb more water layers by Van Der Waals forces, and consequently improved water flux [17].

Fig-3: Water Flux of Clay TFN at different NPs concentrations

Figure 4 presents salt rejection of TFN membrane at different concentrations of NPs. The salt rejection decreased from 99 to 97.2 % by increasing NPs concentration from 0 to 0.1%. This is because the NPs might affect the IP reaction between MPD and TMC during IP reaction, causing PA layer defect [18]. Salty water could have penetrated the membrane through these defects; therefore, membrane rejection efficiency was declined.
The fouling resistance of clay TFN membrane was determined by using humic acid as an organic foulant in feed solution (30 mg/l), and the results are presented in figure 5. Membrane fouling resistance was improved upon addition of clay NPs. This was caused by the higher hydrophilicity of modified membrane which reduced the attachment of organic foulants on membrane surface [19].

Figure 6 shows the normalized flux of TFC and 0.1% Clay TFN before and after rinsing with DI water. As it can be seen, the modified membrane could recover 98% of its initial water flux after rinsing process while TFC recovered only 80%, indicating the good efficiency of the modified membrane in flux recovery.

CONCLUSION

Clay NPs successfully incorporated into PA active layer of TFC membrane. When compared to membrane without clay, significant enhancement in membrane wettability was achieved. The permeability was increased from 30 to 47 L/m² h and salt rejection was above 97 %. Also, the fouling resistance of modified membrane was higher. This study presents a novel/cheap approach to modify the traditional TFC membrane.

REFERENCES


