Fouling resistant membrane tailored by polyethylene glycol in oxidative environment for desalination

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Abstract. Surface modification is very efficient and scalable approach to achieve improved membrane performance. We treated Reverse Osmosis Thin Film Composite (TFC RO) membrane with various concentrations of Polyethylene Glycol (PEG), a hydrophilic polymer after activation with sodium hypochlorite. This treatment resulted in an increment of the water flux by 43% and the salt rejection by 2.36% for the 3000 mg/l PEG-treated membrane. Further, these PEG-treated membranes were exposed to a mixture of 3000 mg/l PEG and 1000 mg/l sodium hypochlorite for 1 hour. Further modification of this membrane by PEG and sodium hypochlorite mixture increased the water permeance up to 133% when compared with the virgin TFC RO membrane. We characterized the treated membranes to understand the changes in wettability by contact angle analysis, changes in surface morphology and roughness by scanning electron microscope (SEM) and atomic force microscope (AFM) analysis.

Keywords: antifouling; desalination; membrane; thin film composite; sustainability

1. Introduction

Reverse Osmosis (RO) membrane technology has found wide acceptance for desalination and water reuse applications (Greenlee *et al*. 2009 and Li and Wang (2010)). Contemporary Reverse Osmosis membrane comprises of an aromatic polyamide dense barrier layer, formed over a microporous support of Polysulfone (Tang *et al*. 2007). This membrane has found wide commercial acceptance owing to its performance in terms of salt rejection and water-flux with affordability in terms of price. However, there are some issues relating the usage of the TFC RO membrane like biofouling and water-flux decline and quick replacement of membrane in high fouling environment (Subramani *et al*. 2010 and Creber *et al*. 2010).

Polyethylene glycol has an antifouling ability, large exclusion volume, hydrophilicity, flexible long chains and unique co-ordination with surrounding water molecules in an aqueous medium; which makes it a good candidate for imparting hydrophilicity (Kang *et al*. 2007). In recent years, the surface alteration of membranes by the immobilization of PEG chains was reported in ultrafiltration and RO membrane (Freger *et al*. 2002, Chinpa *et al*. 2010, Sagle *et al*. 2009, and Kang *et al*. 2011). Ray *et al*. 2017 reported that the aromatic polyamide membrane modified by Polytheylene glycol has lower mineral scaling with calcium carbonate and calcium sulfate in presence of humic acid. Gholami *et al*. 2018 reported that Polyethylene glycol diacrylate coating over polyamide membrane could improve

chlorine resistance of the membrane. Commercial Reverse osmosis membrane coated with Hydroxyethyl methacrylate demonstrated the lower biofouling. Bucs *et al*. 2017 have presented role of amphiphilic copolymers in biofouling control. It has been reported that Polyol functionalized Reverse Osmosis membranes have better transport properties and boron removal performance by Di Vincenzo *et al*. 2017.

Oxidation of polyamide in a controlled manner can enhance the trans-membrane water flux reported by Raval *et al*. 2010. Authors have reported surface alteration on the commercial TFC-RO membrane by oxidation with sodium hypochlorite aided by Glycerol to improve the performance of the TFC-RO membrane (Raval *et al*. 2018)

Surface alteration harnessing the controlled oxidation is scalable and effective approach to modify the membrane surface. The present paper demonstrates the novel method to bind PEG on polyamide layer without a grafting monomer and thus presents one of the most effective and straightforward approaches to enhance the performance of the membrane towards ultra-low energy membrane process development. Ultra-low energy membrane process and the membrane with better anti-fouling performance are the needs of an hour for sustainable membrane process development particularly for water reuse applications.

2. Experimental

2.1 Materials

TFC RO membrane from Hydranautics, USA, Polyethylene Glycol- 600 (PEG) was purchased from TCI Chemical (India) Pvt. Ltd., sodium hypochlorite (laboratory

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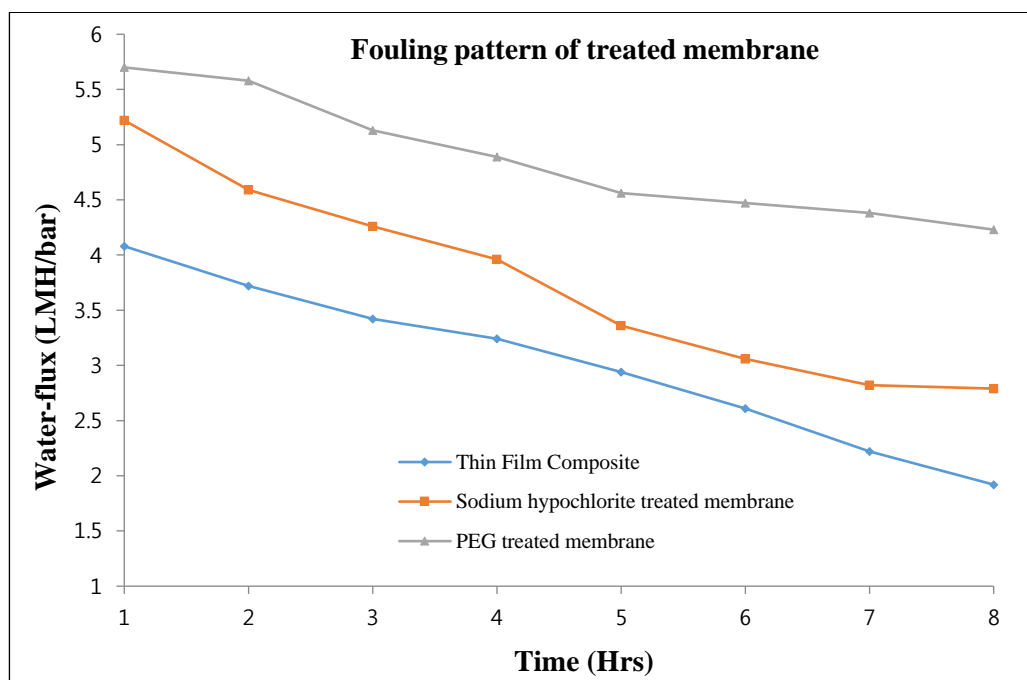E-mail: hirenraval@csmcri.res.in

Fig. 1 Colloidal silica fouling in the cross-flow membrane testing at 600 psig pressure

reagent grade, 4%–6% available chlorine w/v from RFCL Limited, India), Potassium Iodide (Sigma Aldrich), Starch (Sigma Aldrich), Sodium thiosulfate (Sigma Aldrich).

2.2 Method

Polyamide TFC RO membrane was cut into a strip of 11 cm X 22 cm. This strip was cleaned with deionized water, stuck on the glass plate, treated with the sodium hypochlorite solution of 1000 mg/l for 60 minutes, further 1000 – 10,000 mg/l Polyethylene glycol (PEG) solutions for 60 minutes each, and cured at 80^OC for 10 minutes. The membrane was cut in two pieces and one of them; was subjected to the mixture of 1000 mg/l sodium hypochlorite and 3000 mg/l PEG solution for 60 minutes and the other was washed with DI water and stored in DI water. All modified membranes were tested for salt rejection and water flux performance and characterized to understand the change in performance. The characterization of membrane was done to understand the surface morphological changes on the membrane.

2.3 Membrane performance

The membrane coupons were tested for salt rejection and water flux in the standard cross-flow testing kit at 250-psi pressure in the brackish water of 2000 mg/l sodium chloride after pressurizing the membrane samples for 1 hour and taking average of 4 membrane samples. We evaluated the membrane fouling by 5000 mg/L colloidal silica solution at higher pressure of 600 psig under cross-flow membrane testing kit for 8 hours to evaluate its performance after colloidal silica fouling. Also, we evaluated the fouling of Thin Film Composite RO (TFC RO) membrand and surface modified TFC RO membrane by dipping them in 5000 mg/L colloidal silica solution for 5 days in static mode.
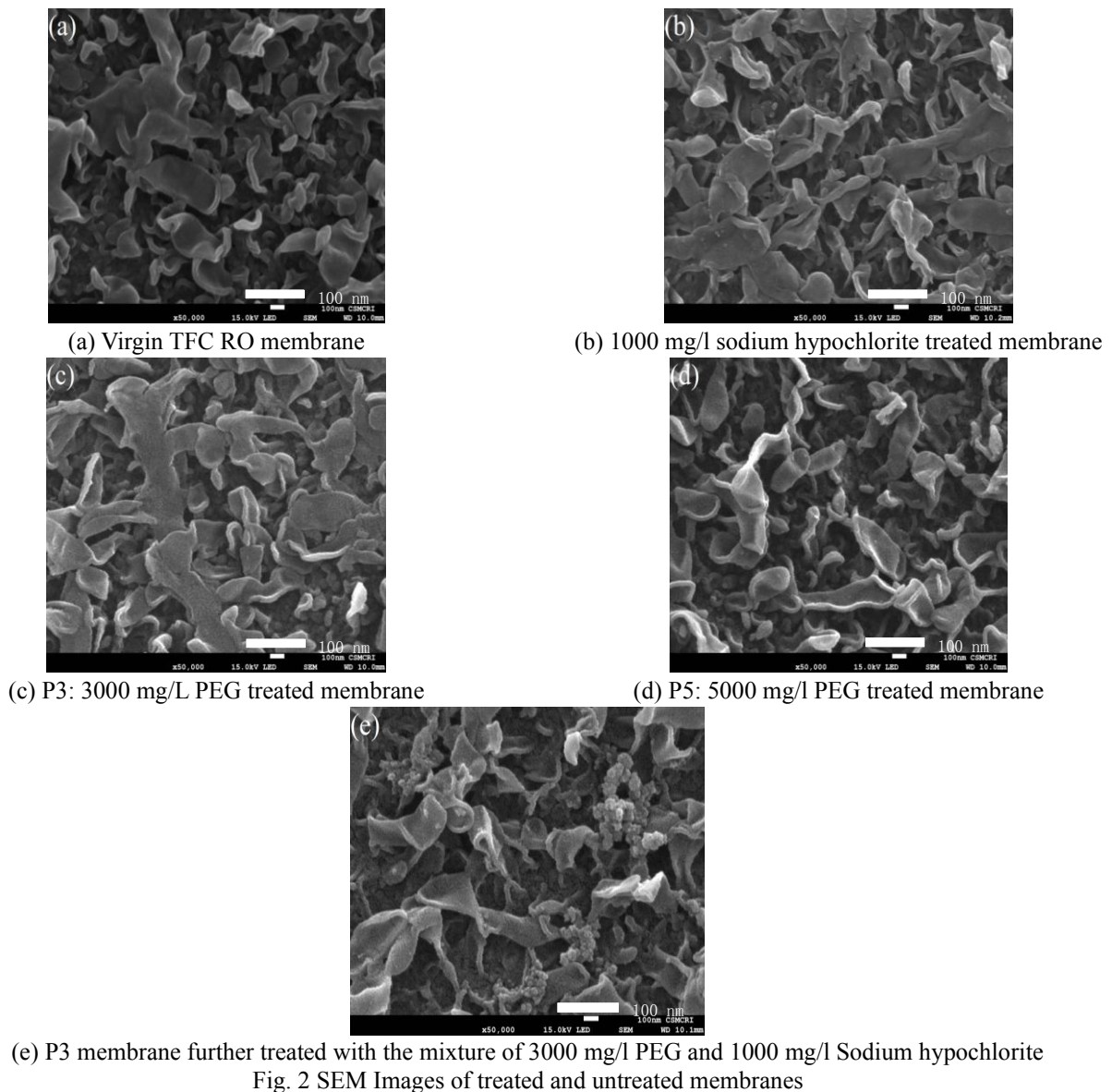
Table 1 Performance of different treated membranes

Code*	PEG concentration (mg/l)	Average water flux (LMH/Bar)	Average salt rejection (%)
T*	0	1.31	95.2
H*	0	1.70	92.78
P1*	1000	1.73	96.99
P2*	2000	1.80	97.42
P3*	3000	1.85	97.45
P4*	4000	2.02	97.07
P5*	5000	2.17	95.56
PH1*	1000	2.64	94.79
PH2*	2000	2.71	95.11
PH3*	3000	3.06	95.85
PH4*	4000	2.91	95.45
PH5*	5000	2.42	93.44

[* T: virgin TFC RO membrane, H: TFC RO membrane exposed to 1000 mg/l sodium hypochlorite, P1, P2, P3, P4, P5: TFC RO membrane treated with 1000 mg/l sodium hypochlorite and 1000, 2000, 3000, 4000, 5000 mg/L PEG solution for the 60 min each, respectively, PH1, PH2, PH3, PH4 and PH5 indicates the membrane P1, P2, P3, P4 and P5 treated with the mixture of 3000 mg/l PEG and 1000 mg/l sodium hypochlorite solution.]

2.4 Membrane characterization

The hydrophilicity/wettability of modified membranes in comparison with Thin Film Composite Reverse Osmosis membrane were evaluated by contact angle analysis. The contact angles of membranes were measured by Drop Shape analyser by Kruss Optronic Germany and the average value has been reported. Scanning electron micrographs were taken to understand the top surface morphology by Field

(a) Virgin TFC RO membrane

(b) 1000 mg/l sodium hypochlorite treated membrane

(c) P3: 3000 mg/L PEG treated membrane

(d) P5: 5000 mg/l PEG treated membrane

(e) P3 membrane further treated with the mixture of 3000 mg/l PEG and 1000 mg/l Sodium hypochlorite

Fig. 2 SEM Images of treated and untreated membranes

emission Scanning electron microscope Jeol Japan. Surface roughness features were evaluated by Atomic force microscopy by NTEGRA Aura, NT-MDT Instruments, Russia.

3. Results and discussions

3.1 Salt rejection and water flux performance of membranes

Table 1 shows the salt rejection and water flux data. There was an increasing trend in salt rejection of membrane with the rise in PEG concentration from 1000 mg/l to 3000 mg/l, and the highest salt rejection was achieved at 97.45% with 3000 mg/L PEG treatment with about 41% increase in water flux as compared to virgin RO membrane. Further increasing PEG concentration, the salt rejection declined slightly, however; the water-flux increased. This indicatesthe hydrophilicity imparted by PEG adhesion to membrane surface. When the membrane was further treated
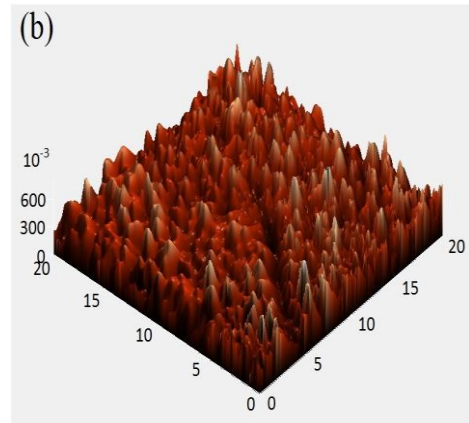
by 3000 mg/L PEG and 1000 mg/L sodioum hypochlorite, the water flux increased by 133% of its original value in case of PH3, while maintained its salt rejection performance. Sodium hypochlorite solution oxidized PEG and formed unstable peroxide which binds to polyamide membrane while oxidizing it in the controlled manner. This resulted in increased water-flux but decline in salt rejection was masked due to presence of Polyethylene glycol.

3.2 Fouling and Water-flux decline

The water-flux declined of TFC RO membrane due to static fouling with colloidal silica solution is 50.94% whereas, the water-flux decline due to fouling is only 24.27% in case of the membrane modified with 3000 mg/L Polyethylene glycol (P3). Fig. 1 shows the fouling and water-flux decline on account of colloidal fouling when fouled in cross-flow membrane testing kit; which shows that % water flux decline is significantly less in case of treated membrane.
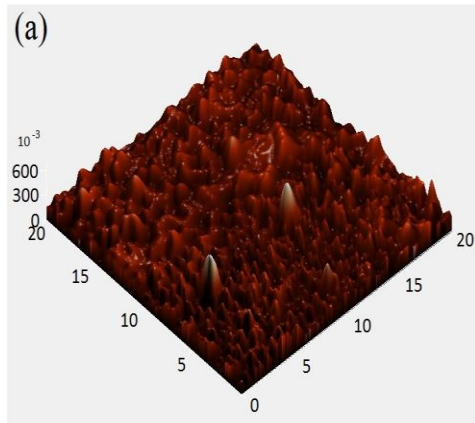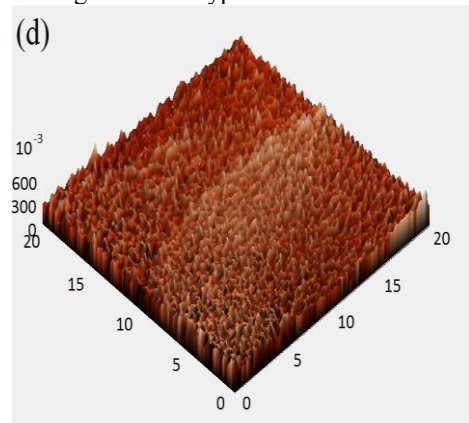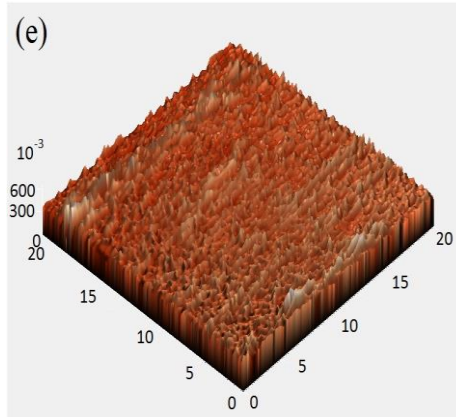
(a) Virgin TFC RO membrane
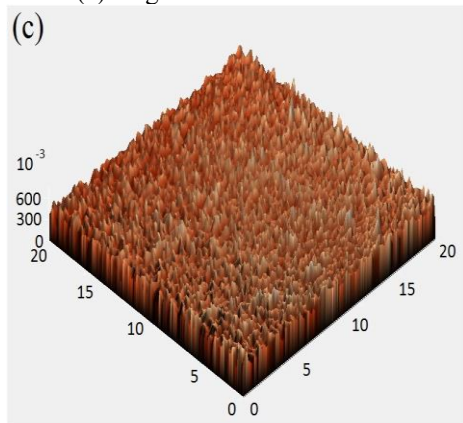
(b) 1000 mg/l sodium hypochlorite treated membrane

(c) P3: 3000 mg/L PEG treated membrane

(d) P5: 5000 mg/l PEG treated membrane

(e) P3 membrane further treated with the mixture solution of 3000 mg/l PEG and 1000 mg/l Sodium hypochlorite

Fig. 3 AFM Images of treated and untreated membranes

3.3 Contact angle analysis

The hydrophilicity and wettability of membrane is an important parameter to evaluate the surface modification for improving the water-flux. The contact angle of virgin TFC RO membrane was 51.25º; which declined to 43.58º on sodium hypochlorite treatment. The lowest contact angle of 26.48º was observed for the membrane treated with 3000 mg/L polyethylene glycol. This decreasing trend in the contact angle shows the increasing of hydrophlicity/wettability of the membrane and explains increased water flux of modified membrane as compare the commercial TFC-RO membrane.

3.4 Field emission Scanning electron micrographs (SEM)

We can observe that the virgin TFC-RO membrane has typical ridge and valley structure, which was modified with the treatment as shown in Fig. 2. Presence of small globules in Fig. 2(e) indicates the structural modification and change in morphology with the treatment.

3.5 Atomic force microscope images (AFM)

Fig. 3 (a) to (e) shows significant difference in membrane surface features with the treatment. The surface

morphology of membrane changes is visible. The average roughness of the membrane increased from 50.9 nm to 139 nm from (a) to (e) with the treatment and surface area ratio also increased steadily with the treatment. Water transport rate through membrane increased because of increase in roughness; which explains the increase in water-flux. The increment in specific surface area because of the increase in roughness translates to more surface becoming available for water transport; which contributes towards increase in water-flux.

4. Conclusion

It was concluded that the commercial TFC-RO membrane performance altered by the treatment: 1000 mg/l sodium hypochlorite solution for 1 hour followed by dipping in 3000 mg/L PEG solution for a period of 1 hour with curing at 80°C for the 10 min showed 41% increase in water-flux and a modest increase in salt rejection. Also, when 3000 mg/L PEG-treated membrane, further subjected to another 1-hour dipping in the mixture solution of the 3000 mg/l PEG, and 1000 mg/l sodium hypochlorite showed 133% increase in water-flux as compared with the virgin TFC RO membrane. SEM images showed the changes in surface morphology of the modified membrane. The contact angle of such modified membrane declined from 51.25° to 26.48°, which demonstrated increased hydrophilicity. The water-flux decline of TFC RO membrane due to fouling with colloidal silica solution at 600 psig was 50.94% whereas, the same due to fouling is only 24.27% in case of the membrane modified with Polyethylene glycol. The treated membrane had increased roughness and surface area ratio and thus higher area for water transport. Thus, membrane performance in terms of water-flux was significantly improved and fouling due to colloidal silica declined. It demonstrates that the future work can be done in this area for developing the ultra-low energy membrane process with lower fouling.

Acknowledgment

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