

ORIGINAL RESEARCH PAPER

## Investigation of Dip-Coating Parameters Effect on The Performance of Alumina-Polydimethylsiloxane Nanofiltration Membranes for Desalination

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### ABSTRACT

The objective of this work is to investigate the effect of dip-coating parameters on the performance of Alumina-PDMS hybrid nanofiltration membranes for water desalination. Ceramic supports used in this work were prepared with a 340 nm average pore size and 34% total porosity. The aim is to determine optimum conditions of dipping time, PDMS concentration, and withdrawal speed in order to achieve high rejection and flux values. Dip-coating parameters were considered as dipping time (60 - 120 s), withdrawal speed (5 - 15 mm/s) and PDMS concentration (10 - 20 wt. %). Hybrid membranes were characterized using FE-SEM and FTIR analysis techniques. Pure water flux and salt rejection were also measured to evaluate the rejection performance. Alumina-PDMS hybrid nanofiltration membranes fabricated with dipping time = 120 s, withdrawal speed = 15 mm/s and 10 wt. % PDMS exhibited the best performance giving 30.5% rejection for NaCl and 53.8% for Na<sub>2</sub>SO<sub>4</sub>.

**Keywords:** Alumina; Dip-Coating; Hybrid Membranes; Nanofiltration; PDMS

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## INTRODUCTION

Membrane separation processes have found several applications in various industrial processes. Nanofiltration with a low energy consumption can be a good alternative for separation purposes as a pressure driven membrane-based process intermediate between reverse osmosis (RO) and ultrafiltration (UF), rejecting very small moieties due to relatively high charge and pores smaller than 2 nm [1].

Inorganic-organic hybrid nanofiltration membranes can have advantages such as selectivity, high flux as well as chemical and thermal resistance with mechanical stabilities under pressures up to 20 bar. Much focus is devoted to the development of new classes of membranes for improving filtration

performance under solvent resistant conditions, i.e. improving chemical and mechanical stability, reducing swelling effects of polymeric membranes and enhancement of solvent affinity [2]. Hybrid membranes can be prepared using ceramic substrates and polymeric top layers through sol-gel dip-coating [3, 4], spray coating [5], self-assembly [6], grafting [7] and spin coating [8]. Among these, dip-coating as a simple and inexpensive technique is considered as one of the most desirable alternatives. Dip-coating provides opportunities to explore the impact of coating parameters such as polymer concentration and dipping time during the fabrication procedure to obtain a membrane with the desired pore diameter and flux-rejection combination [9].

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Various polymers are used as the top layer of hybrid ceramic-polymer membranes. PDMS with a unique set of characteristics including high free volume, backbone flexibility, thermal and chemical stability, hydrophobicity and solubility in non-polar solvents [10], is among polymers used as the thin selective layer in different membrane processes like pervaporation [11] and thin film composite (TFC) nanofiltration [2, 12]. PDMS membranes are mostly prepared on polymeric supports such as polyethersulfone (PES) [13], polyethylene (PE) [14], polysulfone (PS) [15], cellulose acetate (CA) [16], poly(vinylidene fluoride) [17], polyetherimide (PEI) [18], polyacrylonitrile (PAN) [19] and polyamide (PA) [20], although ceramic supports are also utilized. For example, Hong et al. carried out pervaporation of IPA and water using PDMS/ceramic composite membranes prepared via dip-coating. The variation of selectivity and flux at various feed compositions and operating temperatures was explained through plasticization by IPA and capillary condensation of water [21]. Song & Hong fabricated cellulose acetate-ceramic membranes by dip-coating and rotation drying technique using a ceramic support with a 100 nm surface average pore size and CA concentration of 20% tested for dehydration of ethanol and isopropanol [8]. Xiangli et al. prepared a PDMS/ceramic composite membrane for pervaporation. The results showed that polymer concentration was the most significant variable influencing permeation and selectivity. Maximum flux of  $19.5 \text{ kg m}^{-2} \text{ h}^{-1}$  was obtained under following preparation conditions: polymer concentration = 7.4wt%, crosslink agent concentration = 10wt.% and dip-coating time = 60 s [22]. Kim et al. coated PDMS on a polysulfone (PSF) support for propylene recovery from off-gas stream. They prepared a novel organic-inorganic composite membrane by adding silica nanoparticles to the PDMS solution and the results showed enhanced separation factor and propylene permeance enhancement from 5.2 to 7.3 and 31 to 36 GPU, respectively (1 GPU equals  $10^{-6} \text{ cm}^3/\text{cm}^2 \text{ s cmHg}$ ) [23].

Polysiloxane-based polymers like PDMS have often been used as polymeric SRNF [2, 10]. Pinheiro et al. designed a new fabrication method for grafting PDMS on a supported  $\gamma$ -alumina membrane (pore size = 5 nm) using polysiloxane mono(2,3 epoxy) polyether terminated polydimethylsiloxane (PDMS) [2]. Tanardi et al. described grafting of mesoporous alumina membranes with hydride terminated polydimethylsiloxane with vinyltriethoxysilane

linking agent to create a dense network structure grafted inside the ceramic pores. Grafting reactions were successfully carried out and approved by permeability-rejection tests. Coupling agents were found to create network structures with a higher density grafted in the  $\gamma$ -alumina pores [24]. Nandi et al. prepared CA-ceramic composite membranes using the dip-coating technique. Ceramic supports were prepared from kaolin with an average pore size of 560 nm and total porosity of 33%. Dip-coating parameters were the concentration of CA solution (2-8 wt.%) in acetone and dipping time (30-150 s) [9].

In this study, hybrid nanofiltration membrane preparation using dip-coating is performed for investigation of dip-coating parameters. Low-cost ceramic supports were prepared using  $\alpha$ -alumina powder as the raw material [25]. According to previous studies, alumina-PDMS hybrid membranes are used for pervaporation [21, 26] and SRNF [2]. However, this study is devoted to desalination for investigating the dip-coating parameters (dipping time, withdrawal speed) and PDMS concentration in n-heptane in order to optimize the membrane performance regarding flux and rejection of inorganic salts.

## EXPERIMENTAL

### Materials and Methods

$\alpha$ -Alumina ( $\text{Al}_2\text{O}_3$ ), Polyvinyl alcohol (PVA), n-heptane, Tetraethyl orthosilicate (TEOS) and dibutyltin dilaurate were purchased from Merck Co. and used as received. Hydroxy terminated polydimethylsiloxane (PDMS) was obtained from Sigma-Aldrich ( $M_w = 18000 \text{ g mol}^{-1}$ ) and a kinematic viscosity of 750 cSt. Sepahan Irman Tech dip-coater (Iran) was also used for film application.

### Characterization

Surface and cross-section morphologies of the composite membranes were characterized by SEM and FE-SEM. Samples were dried under vacuum at 25 °C for 40 min and coated with gold before SEM imaging. The chemical composition of the top layer of the modified support or the  $\text{Al}_2\text{O}_3$ /PDMS composite NF membrane was characterized using ATR-FTIR technique.

### Support Preparation

The substrate is prepared through dry casting technique (Fig. 1). A proper amount of alumina powder is mixed with a 7 wt% PVA solution. The suspension is pressed in a template, then sintered at 1250 °C for 2 h [3].

### Preparation of composite membrane

PDMS/ceramic composite membranes were prepared by the conventional dip-coating method. PDMS was dissolved in n-heptane and then the crosslinking agent (TEOS) and 0.2 wt% catalyst dibutyltin dilaurate were added to the polymer solution. The polymer mixture was stirred at room temperature for 30 min and degassed under vacuum. The outer surface of the ceramic support was polished with 600 mesh sandpaper and washed several times with deionized water under ultra-sonication and dried in open air at room temperature. Nomenclature of various composite membranes fabricated with varying PDMS concentration in n-heptane (10 – 20 wt. %), dipping time (60 – 120 s) and withdrawal speed (5 – 15 mm/s) are presented in Table 1.

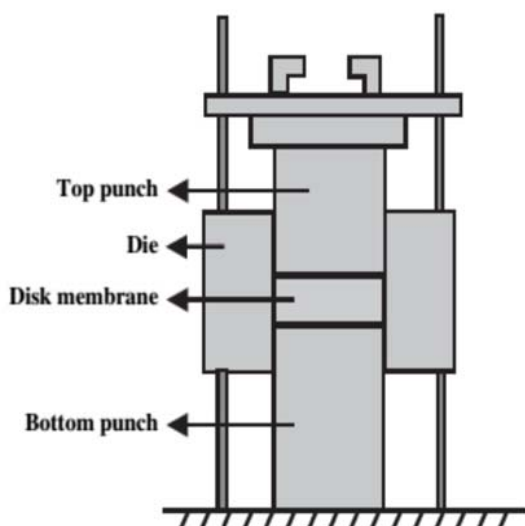


Fig. 1: Schematic of Dry pressing process.

### Flux and rejection experiments

Rejection performance tests were conducted with a cross-flow membrane module at 20 °C. The schematic diagram of the apparatus is shown in Fig. 2.

At steady state, the weight of permeate collected in the flask was measured to obtain the total flux, (J):

$$J = \frac{V}{A \times t} \quad (1)$$

Where V is the total mass permeated during the experiment time interval t and A is the effective membrane area.

Feed and permeate salt concentrations were measured using electric conductivity meter (Ecomet conductivity meter C65) in order to calculate the salt rejection according to:

$$\alpha = \frac{C_s - C_d}{C_s} \times 100\% \quad (2)$$

Where,  $C_s$  and  $C_d$  denote the salt concentrations of feed and permeate.

## RESULTS AND DISCUSSION

### Membrane morphology

Fig. 3 shows the FE-SEM image of the alumina substrate, showing a dense and uniform structure preventing crack formation at high operating pressures.

FE-SEM micrograph of the hybrid alumina-

Table 1: Nomenclature of different fabricated PDMS/ceramic composite membranes.

Sample	Dipping Time (s)	PDMS conc. (wt%)	Withdrawal speed (mm/s)
M1	60	10	15
M2	120	10	15
M3	120	20	15
M4	120	20	5

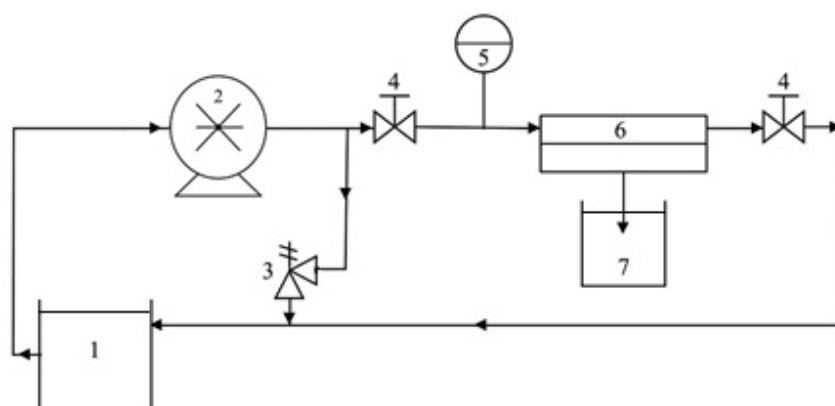


Fig. 2: Schematic diagram of membrane modal apparatus for membrane performance tests: (1) feed tank, (2) pump, (3) Pressure valve, (4) valves, (5) Pressure gauge, (6) membrane module, (7) permeate flask.

PDMS membrane (M2) substrate structure is given in Fig. 4 which confirms PDMS coating on the substrate surface.

#### ATR-FTIR ANALYSIS

The modified support and hybrid NF membranes (M2) were characterized using ATR-FTIR (Fig. 5). The peaks at  $2968\text{ cm}^{-1}$  and  $2924\text{ cm}^{-1}$  are ascribed to C–H asymmetric stretching and symmetric

stretching of methyl ( $\text{CH}_3$ -) groups of PDMS. The strong peak at  $1245\text{ cm}^{-1}$  is caused by symmetric C–H bending and peaks at  $871\text{ cm}^{-1}$  and  $791\text{ cm}^{-1}$  are caused by Si–C vibration and  $\text{CH}_3$  rocking from the  $\text{SiCH}_3$  group. The two peaks at  $1095$  and  $1017\text{ cm}^{-1}$  are ascribed to the Si–O–Si bond. These peaks at  $791$ ,  $1017$ ,  $1095$ ,  $1245\text{ cm}^{-1}$  and  $2968\text{ cm}^{-1}$  confirm the presence of polydimethylsiloxane groups on the  $\alpha\text{-Al}_2\text{O}_3$ /PDMS membrane [4, 27].

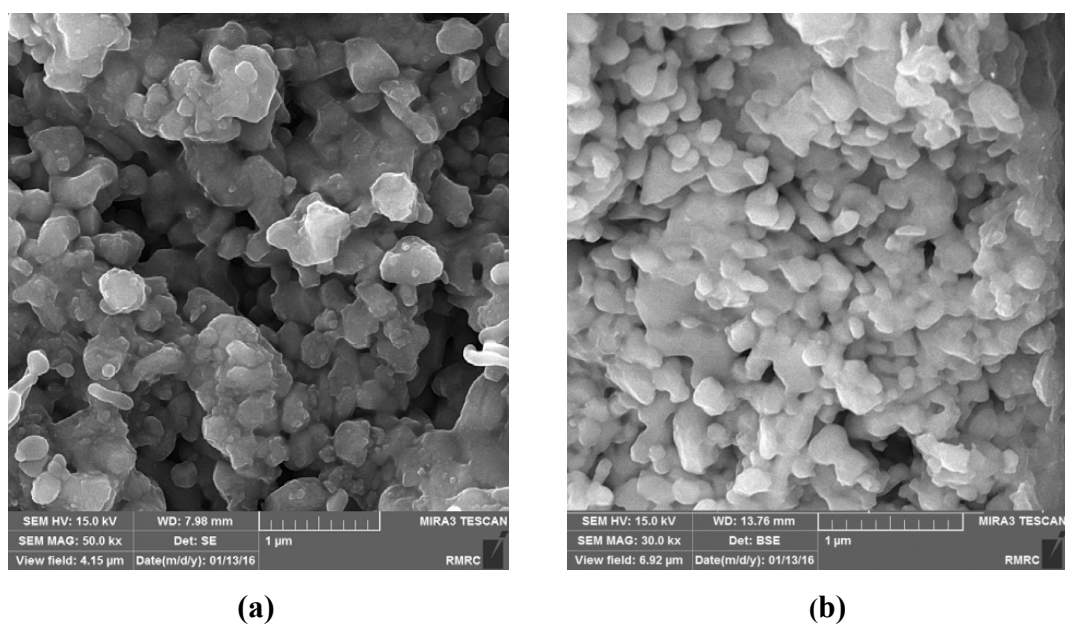


Fig. 3: FE-SEM images of alumina support membrane: (a) top surface image, (b) cross-section image.

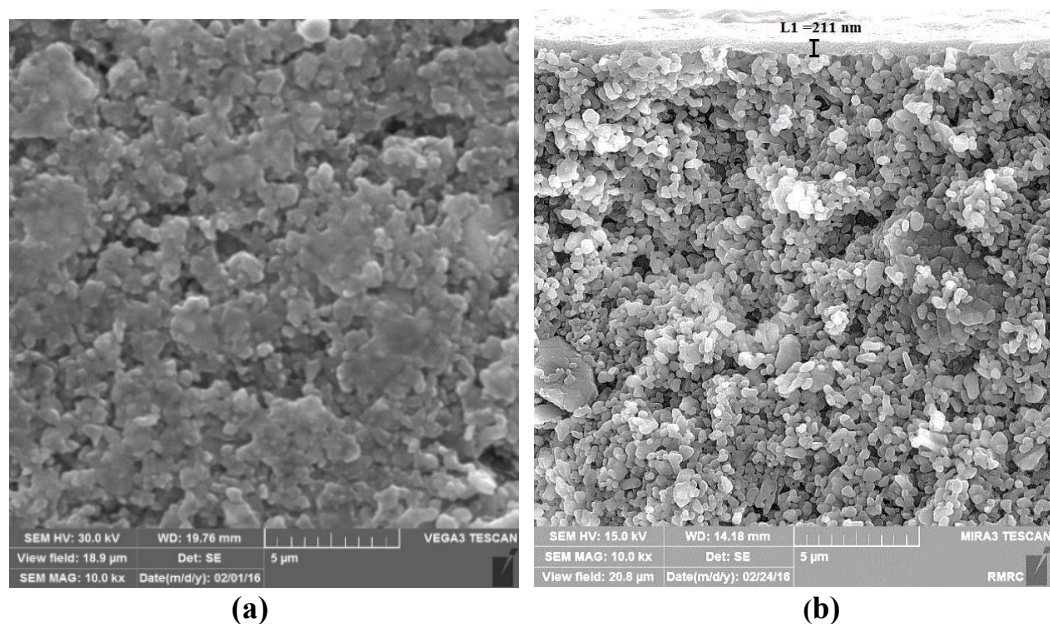


Fig. 4: FE-SEM image of Alumina/PDMS hybrid nanofiltration membrane (M2). (a) Top view, (b) Cross-section view.



### Effect of dip-coating parameters

Dip time and withdrawal speed are investigated as well as polymer concentration. The variations of parameters are given in Table 2 with their relative rejection characteristics. High dip time and low polymer concentration are needed to obtain high salt rejection. At 120 s dip time and 10 wt. % polymer concentration and 15 mm/s withdrawal speed the highest rejection is obtained as 30.5% for NaCl and 53.8% for  $\text{Na}_2\text{SO}_4$ .

### Pure water fluxes

Fig. 6 shows that pure water fluxes of the membrane support and hybrid NF membrane vary with the operating pressure. Pure water flux is  $81 \text{ L m}^{-2} \text{ h}^{-1}$  for

the membrane support at 0.6 MPa operating pressure which is in agreement with Gestel's data for inorganic composite membranes [28]. Fig. 6 shows the effect of pressure on pure water flux of hybrid nanofiltration membranes with different dip-coating parameters. Pure water flux for both support and Hybrid NF membrane exhibits a linear relationship with pressure and pure water flux is enhanced by increasing the operating pressure [29].

### Feed concentration

Salt concentration can influence the rejection performance of hybrid membranes [1]. Fig. 7 shows the effect of feed concentration on the rejection for single salt NaCl and  $\text{Na}_2\text{SO}_4$  solutions. All filtration

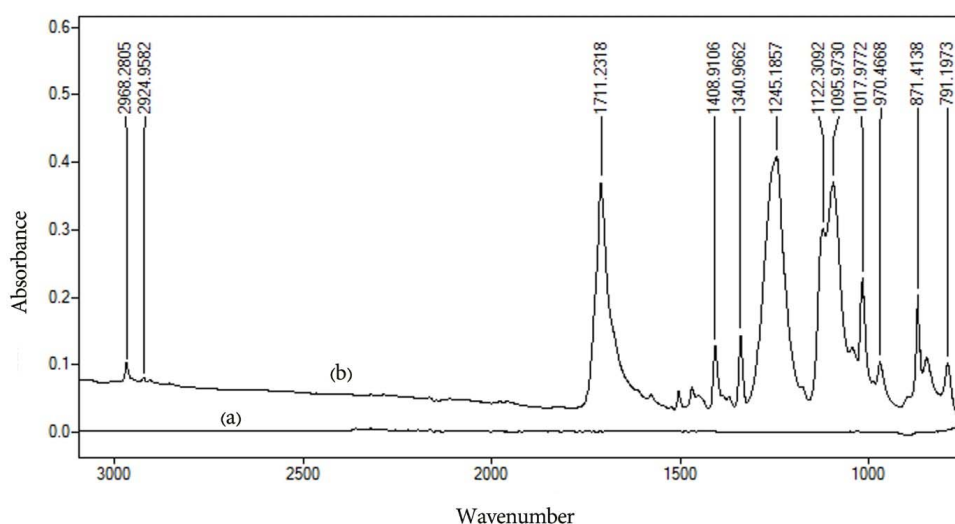


Fig. 5: ATR-FTIR absorbance spectra of (a) alumina substrate, (b) Alumina/PDMS hybrid nanofiltration membrane (M2).

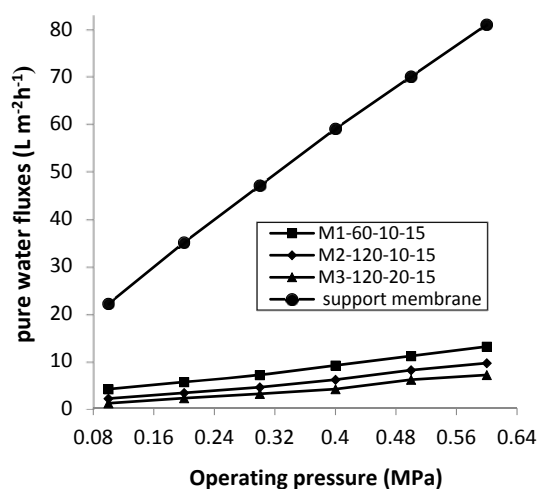


Fig. 6: Effect of operating pressure on pure water flux.

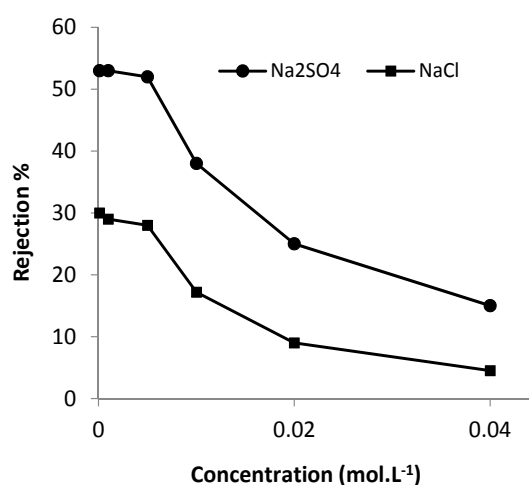


Fig. 7: Effect of feed concentration on the rejection performance.

measurements were conducted at 0.5 MPa based on M2-120-10-15 dip-coating parameters. In 0.0001–0.04 mol L<sup>-1</sup> concentration range, alumina-PDMS membrane exhibited higher retention rates toward di-valent cations compared to the mono-valent cation. Decreased rejection with salt concentration can be explained by the decreased thickness of the electric double layer with increased salt concentration (i.e. higher ionic strength) and hence lower rejection rates [30, 31].

#### Membrane performance for salt rejection

Figs. 8, 9 and 10 show the effect of operating parameters on the salt rejection of the composite NF membranes for NaCl and Na<sub>2</sub>SO<sub>4</sub> solutions. All filtration measurements were conducted at feed concentration = 0.001 mol L<sup>-1</sup>.

Fig. 8 shows the rejection of Na<sub>2</sub>SO<sub>4</sub> and NaCl increased from 45.8 to 53.8 and 23.7 to 30.5 while dipping time was increased from 60 (M1-60-10-15) to 120 s (M2-120-10-15). This salt rejection

Table 2: Dip-coating parameters and rejection of membranes at 0.6 MPa operating pressure.

Number	Dipping time (s)	Polymer concentration (wt%)	Withdrawal speed (mm/s)	Rejection Na <sub>2</sub> SO <sub>4</sub> (%)	Rejection NaCl (%)
M1	60	10	15	49.1	27.2
M2	120	10	15	53.8	30.5
M3	120	20	15	46.1	22.1
M4	120	20	5	50.1	27

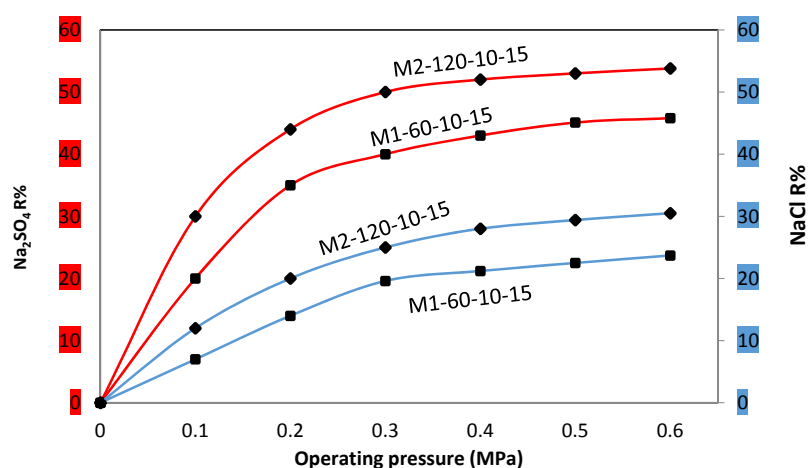


Fig. 8: Effect of operating pressure (MPa) and dip-coating parameter on the Rejection%.

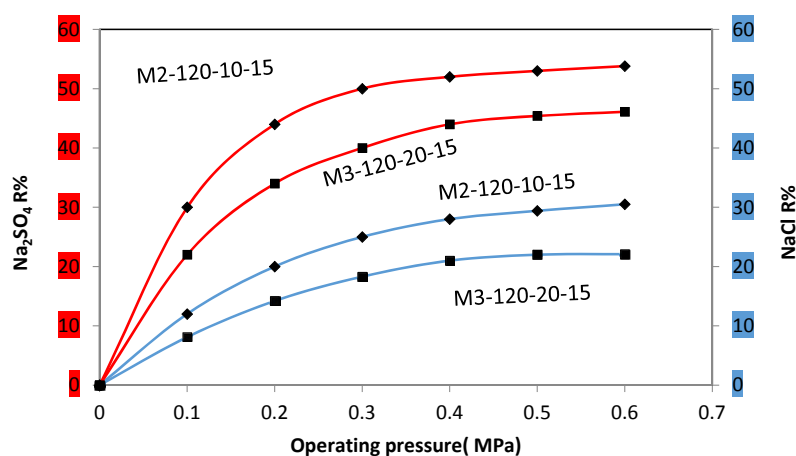


Fig. 9: Effect of operating pressure (MPa) and dip-coating parameter on the Rejection%.

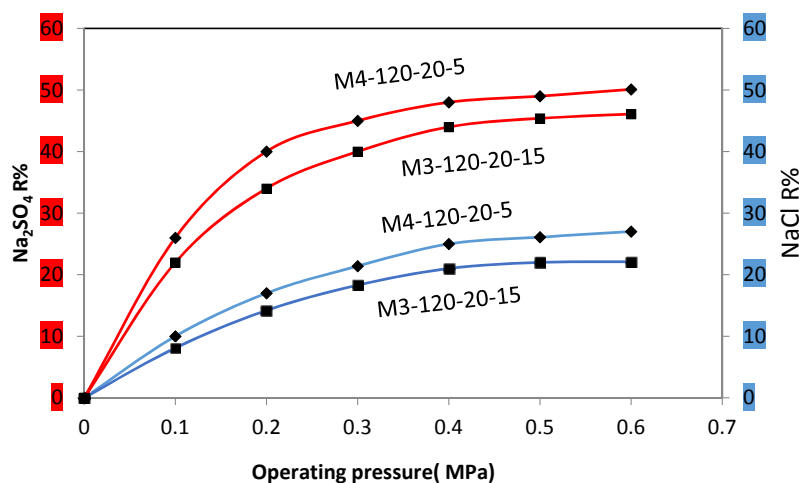


Fig. 10: Effect of operating pressure (MPa) and dip-coating parameter on the Rejection%.

enhancement can be due to the increased polymer coating on the ceramic membrane resulting in smaller porosity and pore sizes in the hybrid membrane. So, due to sieving mechanism, salt rejection is increased [9].

Fig. 9 shows the rejection of  $\text{Na}_2\text{SO}_4$  and NaCl increasing from 46.1 to 53.8 and 22.1 to 30.5 when the polymer concentration was reduced from 20 wt.% (M3-120-20-15) to 10 wt.% (M2-120-10-15). So, increasing the polymer solution concentration results in the reduction of salt rejection.

According to Fig. 10, rejection of  $\text{Na}_2\text{SO}_4$  and NaCl are enhanced from 46.1 to 50.1 and 22.1 to 27.0 when the withdrawal speed was reduced from 15 mm/s (M3-120-20-15) to 5 mm/s (M4-120-20-5). So, reducing the withdrawal speed can increase the salt rejection.

## CONCLUSIONS

In this study,  $\alpha$ -alumina-PDMS hybrid nanofiltration membranes are fabricated using the dip-coating technique for investigation of dip-coating parameters. Low-cost ceramic supports were prepared using  $\alpha$ -alumina powder as raw material for water desalination. Effect of Dip-coating parameters, PDMS concentration in n-heptane (10 wt. % to 20 wt. %), dipping time (60 to 120 s) and withdrawal speed (5 mm/s to 15 mm/s) on the prepared membranes were studied. The results of FE-SEM and ATR-FTIR analyses indicate the coating of PDMS on the support. The analysis shows that dip-coating parameters of (M2-120-10-15) membrane have better performance compared to other membranes. For the Hybrid

NF membrane, rejection of 30.5% for NaCl and rejection of 53.8% for  $\text{Na}_2\text{SO}_4$  are obtained.

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## CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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