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Improving anti-fouling properties of alumina tubular microfiltration membranes through the use of hydrophilic silica nanoparticles for oil/water separation

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ABSTRACT

In this study, hydrophilic silica nanoparticles (Si NPs) were used to modify α-alumina tubular membranes to improve their performance in terms of flux, oil rejection, and anti-fouling properties. Our work focuses on enhancing membrane performance, particularly for difficult applications such as produced water treatment. The prepared membranes were applied for oil-in-water emulsion treatment. After coating hydrophilic Si NPs, the oil contact angle improved from 133.8° to 171.4°. To prevent Si NPs from leaching off the surface of α-alumina tubular membranes, polyvinyl alcohol was used to coat the membranes as a pre-treatment step before Si NP modification. After coating the membrane with Si NPs, the roughness of the membrane surface decreased, likely leading to less fouling. After coating Si NPs, Total Organic Carbon rejection increased from 93.1% for pristine α-alumina tubular membranes to 97.7% for silica-modified membranes because of hydrophilic improvements of the modified membranes. The Si NP coating improved the anti-fouling property of membranes with the flux recovery ratio increasing from 71.3% for pristine α-alumina tubular membranes to 85.9% for silica-modified membranes. Scanning Electron Microscopy, Energy- dispersive X-ray spectroscopy, oil contact angle, and Atomic Force Microscopy characterization tests were done. The tests showed successful Si NPs impregnation and altered wettability.

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Oil/Water emulsion; membrane filtration; dip coating; hydrophilicity; silica modification

Introduction

Wastewater is a major environmental concern. Several industries release wastewater, often containing organic species, into the environment, including metallurgy, transportation, food processing, and oil and gas extraction and refining, which has a detrimental effect on the environment.[1,2] “Produced water,” is the water that is produced concomitantly with oil and gas extraction, and is a major source of wastewater which can cause significant environmental damage.[3–5] There is a critical need for efficient purification processes for oil- water separation to treat produced water.[6] Various technologies have been investigated for purifying this type of wastewater including flocculation, membrane filtration, flotation, absorption, ultrasonic separation, coagulation, heating, ozonation, and electric fields.[7–12]

Membrane technology is an increasingly viable option for treating wastewater that contains organic species. Membrane based separation processes have been investigated for the removal of oil from wastewater historically and have gained appreciable momentum.[13–16] The main advantage that membrane separation provides over other technologies is efficient separation performance while maintaining relative simplicity of operation.[17] Among the various modes available for membrane separation, microfiltration (MF) and ultrafiltration (UF) are the most efficient for oil/water separation.[18,19] Different types of materials have been studied for MF and UF including polymer composites, metal meshes, filter paper, manganese oxide nanowires, textiles, silicon, and plastics.[20–27] Recently, many reports have emerged in the literature wherein separation has been carried out using the MF mode using polymer and ceramic membranes that showed promising results.[28–30] Membranes made out of ceramic materials such as alumina, zirconia, titania, and silica have attracted far more attention than other materials because of their biological, thermal, chemical, and mechanical resistance.[31–33] Membranes made out of materials like paper, textile, and polymers are cheaper than ceramic membranes but corrode far more easily. Among ceramic membranes alumina membranes are chemically inert and thus can be employed in a varied pH range.[17] Muller et al.[34] employed α-alumina membranes with a

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pore size of 0.8 to separate oil-in- water (O/W) emulsions, with oil droplet size and concentration of 4 μm and 250 ppm, respectively. They reported stable permeability and a rejection rate of 30 L m^{-2} h^{-1} bar^{-1} and 30%.[35] Hua et al. studied the performance of α-alumina membranes with a 50-nm pore size for oily wastewater treatment with a 500 ppm oil concentration. The results showed stable permeability and rejection rate of 63.9 L m^{-2} h^{-1} bar^{-1} and 98.1%, respectively.[36]

Grafting and coating are two commonly used methods for modifying membranes to improve their fouling properties and enhance the efficiency of operation.[37] Zhang et al. grafted a zwitterionic monolayer onto α- alumina ceramic membranes to enhance the anti- fouling property of the membranes and increased the flux concerning O/W emulsions.[38] Membranes have been coated with both hydrophilic and hydrophobic coatings in literature.[39] The main disadvantage of hydrophobic coatings is the rapid increase in membrane fouling, which stops the filtration process and increases operational costs. To overcome these issues, hydrophilic coatings can be used which impart a higher efficiency in the anti-fouling tendency.[40,41] Chang et al. improved the hydrophilicity of a commercial Al_2O_3 membrane by coating it with a nano-sized Al_2O_3 coating.[40] The authors reported a water flux enhancement of the modified membrane by 20% compared with the pristine one.

This current work describes the effects of modifying α-alumina membranes with different loadings of hydrophilic fumed silica particles to improve the hydrophilicity of the membranes and increase their performance characteristics. A pretreatment step was conducted using PVA to ensure uniform coating of Si NPs on the membranes and also to reduce the subsequent leaching of the nanoparticles from the membranes. Tests were conducted using pure deionized water and (O/W) emulsions to evaluate the resistance to fouling and rejection of the oil phase.

Experimental

Materials

In this study, α-alumina tubular membranes (70-mm length, 11-mm outer diameter, 8-mm inner diameter, 0.2-μm pore size) were purchased from Ceramco, USA. Hydrophilic silica nanoparticles (16 nm, A200, AEROSIL) were provided by Evonik, Germany. Polyvinyl alcohol (PVA, 80% hydrolyzed, average molecular weight 9000–10000 grams/mole) was purchased from Sigma-Aldrich. All uncertainties in the figures (error bars) represents the standard deviations in the data obtained.

Membrane preparation

Initially, α-alumina tubular membranes were washed with deionized water to remove dust and pollutants and then dried in an oven at 60°C overnight. A coating solution was prepared by dispersing the hydrophilic silica nanoparticles (Si NPs) into deionized water and stirring for 2 h to form a homogeneous Si NPs solution at weight percentages of 0.25%, 0.5%, 1%, and 3% as summarized. The membranes modified with 0.25%, 0.5%, 1%, and 3% Si NPs were named as M0.25, M0.5, M1 and M3 respectively, while the unmodified membrane was named M0. Before coating the Si NPs on the surface of the α-alumina tubular membrane, a pre-treatment process was conducted using PVA solution. For the pre-treatment process, the α-alumina tubular membrane was immersed in 10 wt.% PVA solution[42] and then dried in the oven at 60°C overnight (Fig. 1a,b). The pre-treatment process was repeated four times to ensure most of the void and vacant sites of the pristine α-alumina tubular membrane were filled with PVA. The pre-treated membranes were then immersed in Si NPs solution at various weight percentages of 0.25%, 0.5%, 1%, and 3%. The process of immersing in Si NP solution was repeated four times for each of the modified membranes and then was dried for a day. The fabricated membranes were then calcinated at 550°C for 3 hours to remove PVA (PVA melting point is 200°C) and form mesoporous Silica coated membranes (Fig. 1e).

Membrane test

Microfiltration experiments were conducted at room temperature in a cross-flow filtration system using a tubular membrane module with a membrane surface area of 16.2 cm^2. The setup consisted of a 37.8-L feed tank equipped with a pump (Stenner Peristaltic Metering Pump USA) to pump the feed solution to the membrane module. A needle valve was installed in the output of the membrane module to pressurize the system. A bypass line with a pressure gauge was used to set the pressure at a given value, and a flowmeter was used to adjust the feed flow rate on the retentate side. The permeate flow across the membrane was continuously collected and weighed by a digital balance. The retentate flow from the output of the membrane module was recycled to the feed tank. A schematic of the cross- flow filtration system is shown in Fig. 2. The

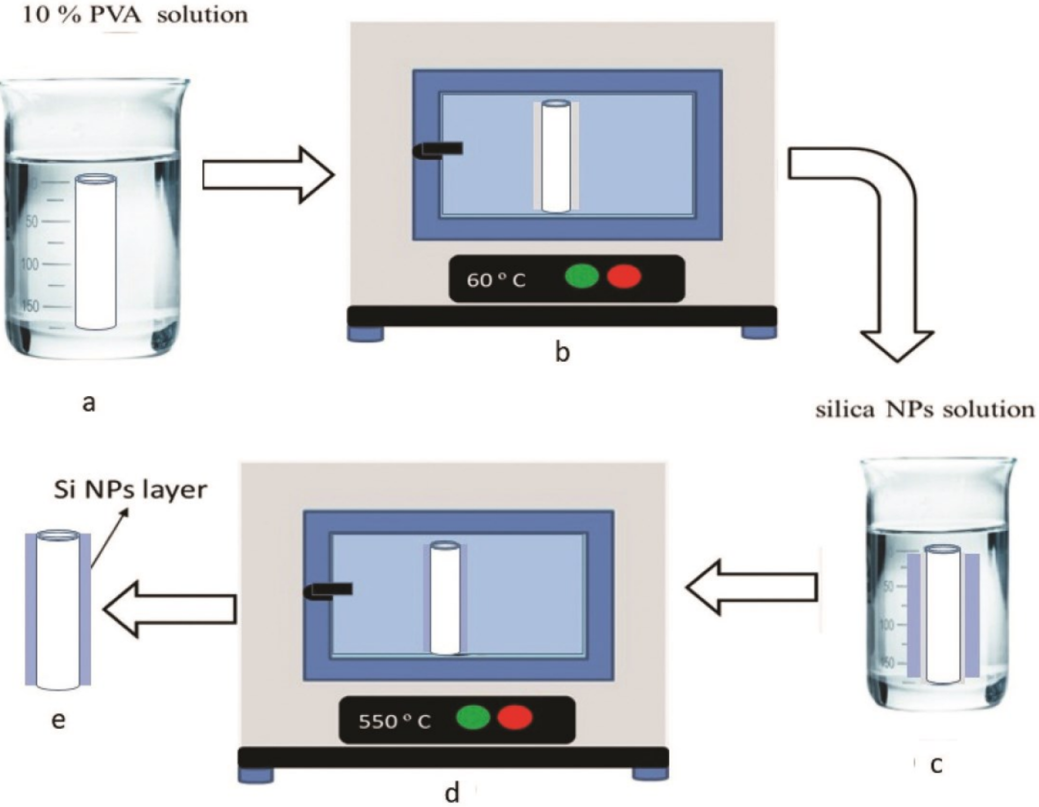

Figure 1. Schematic of the preparation process of the Si NPs coating on α-alumina tubular microfiltration membranes.

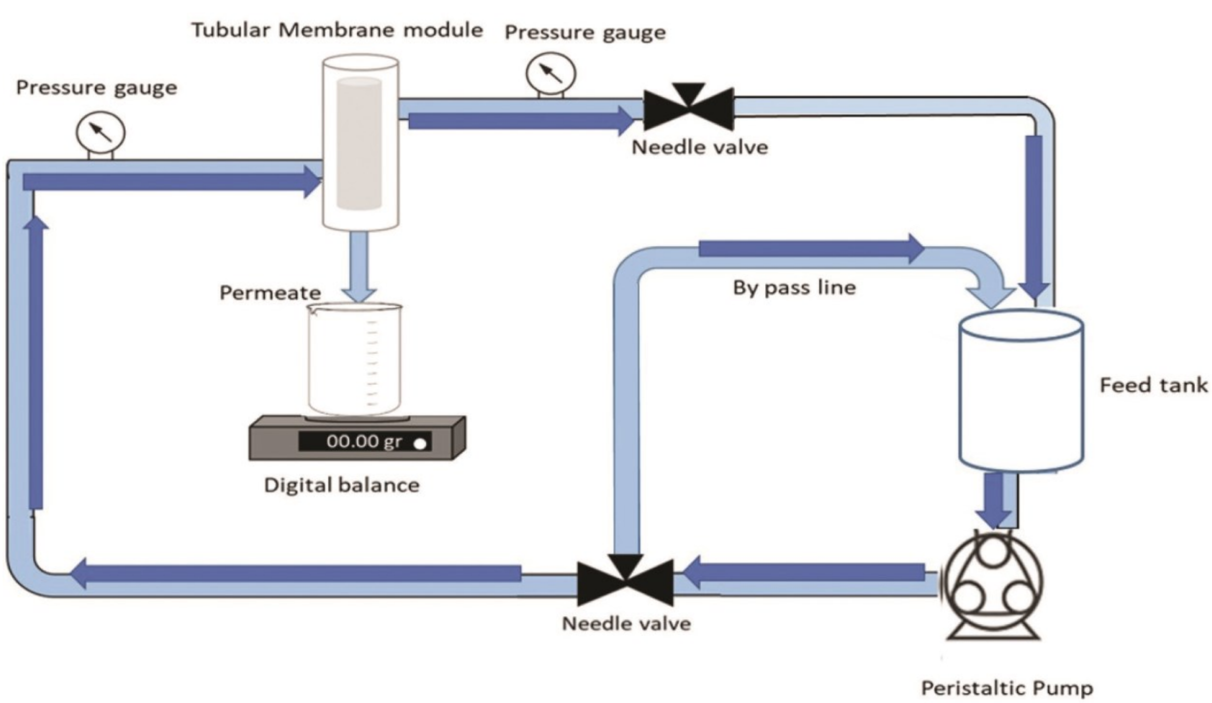

Figure 2. Schematic of microfiltration cross-flow experimental set-up.

performance of the unmodified (the pristine α-alumina) and modified membranes was evaluated with pure water and O/W emulsion filtration, which are significant measures of membrane performance. The oil rejection was obtained as follows:

$$R(\%) = \left(1 - \frac{TOC_P}{TOC_F}\right) \times 100 \tag{1}$$

where R is oil rejection (%), and TOC_F and TOC_P are the total organic carbon concentration (Oil concentration) on the feed and the permeate side, respectively. The permeation flux was obtained using the following equation:

$$J = \frac{V}{A \times t} \tag{2}$$

where J, permeation flux (L m^{-2} h^{-1}), V (L) is the volume of water that passes through the membranes as permeate, A (m[2] is the effective membrane surface area, and t (h) is the permeation time.

Anti-fouling property of the membranes

Anti-fouling is another significant property to evaluate the performance of a membrane. After the installation of a membrane in the membrane module, pure water was run through the membrane for 1 hr to calculate the pure water flux ($J_{w,1}$). The pure water was then replaced with an O/W emulsion in the feed tank, and the membrane was tested for 1.5 hrs to obtain flux (J_p). During the O/W emulsion operation process, layers of oil were formed on the surface of the membrane which resulted in fouling. The cake layers were removed from the surface of the membranes by deionized water washing for 10 min. The feed tank was then loaded with clean water, and the regenerated membranes were tested again to obtain a second water flux ($J_{w,2}$). The flux recovery ratio (FRR) was calculated as follows:

$$FRR = \left(\frac{J_{w,2}}{J_{w,1}}\right) \times 100 \tag{3}$$

Characterization

An FEI Quanta 600F field emission scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDS) system was employed to observe the membrane surface morphology and elemental composition of the membranes. The membrane samples were coated with a 4–5 nm thick gold layer to prevent any charges. The oil contact angle (OCA) of the membrane surface was measured by a contact angle goniometer (Core Laboratories IFT-10) at room temperature. OCA was measured at three different spots of the membrane surface. The average OCA of the α-alumina tubular and the prepared membranes were reported. To measure the TOC, Hach Method 10,173 (15 to 150 mg/L C) was used with a DR 5000™ UV-Vis spectrophotometer (HACH Company, USA). Surface topology and membrane roughness before and after Si NPs coating were analyzed using AFM and MFP-3D Infinity Asylum Research (Santa Barbara, CA, USA), respectively. A 5 µm × 5 µm area of each sample was fixed using a holder of double- sided tape. Three different spots on the surface of the membrane were tested, and the average values of roughness were reported.

Emulsion analysis

O/W emulsions were prepared using cyclohexane as the oil phase, and 18.2-MΏ-cm resistivity DI water was used as the continuous phase. A surfactant, Sodium Dodecyl Sulphate (SDS), was used to make the emulsions. SDS is a water-soluble surfactant having an HLB value of 40. An Ultra-Turrax digital homogenizer operating at 15,000 RPM was used to emulsify samples. The homogenizer was run for 10 min after the last drop of cyclohexane was added to the water. SDS was added to the continuous phase before the cyclohexane and homogenized at 3000 RPM for 5 min to mix the surfactant. The oil phase concentration was 1000 ppm, and the weight percentage of the surfactant was 0.13%. The optical analysis was carried out using an Olympus B×53 cross- polarized optical microscope. The microscope is equipped with a high-speed camera to analyze the droplet size of the emulsion accurately. Image J was used to analyze the images obtained from the microscope. Details of the methods for determining the emulsion droplet size distribution may be found elsewhere.[43] Fig. 3 shows the droplet size distribution of the emulsions used for the membrane tests. The mean droplet size (diameter) was found to be 3.07 ± 1.75 µm. Emulsions were prepared within 1 hour of the experiments.

Results and discussion

Membrane characterization

Fig 4 shows the SEM cross-sections of M0 (pristine membrane) and M3 (modified membrane). The higher magnification images in panels a and b show that M0 has a rough structure. However, applying a 3% solution of Si NPs (M3) resulted in a ~ 29-µm thin coating of Si on the surface of the α-alumina tubular membrane, which made the surface smoother (Fig. 4 M3-c and d).

images of the α-alumina tubular membrane M0 (a-b) and modified membranes M0.25–3 (c-j) with Si NPs are given in Fig. 5. The Si NPs were coated on the surface and gradually covered the pore channels of the α-alumina tubular membrane (Fig. 5c-j). Increasing the Si NPs coating solution concentration from 1% to 3%

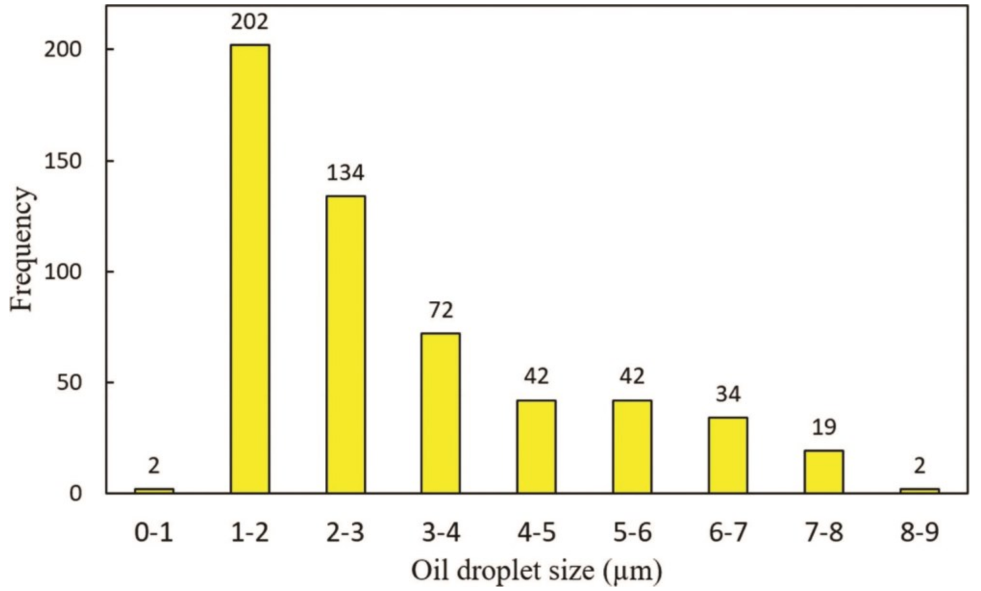

Figure 3. The oil droplet size distribution (diameter) of the O/W emulsion.

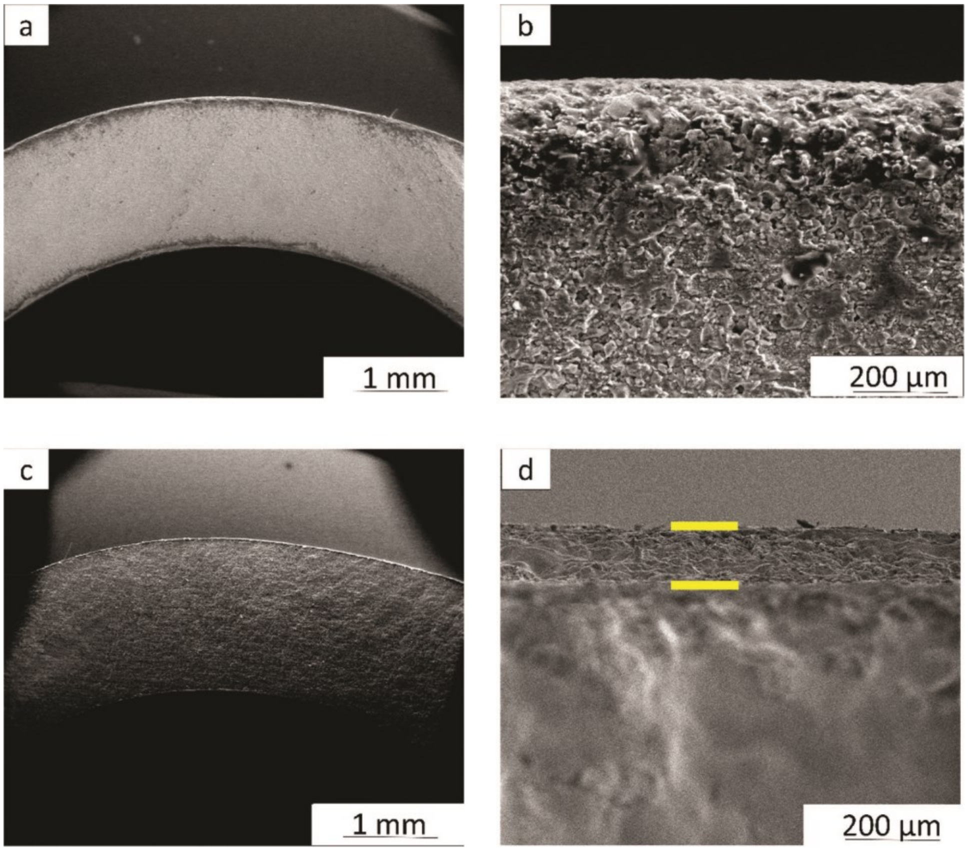

Figure 4. The cross-section SEM images of (a-b) M0 and (c-d) M3.

The two yellow lines represent the thickness of the silica coating as visible during SEM investigations. The surface covered the surface and most of the pore channels of the membrane (Fig. 5i-j). In this case, the pores of the

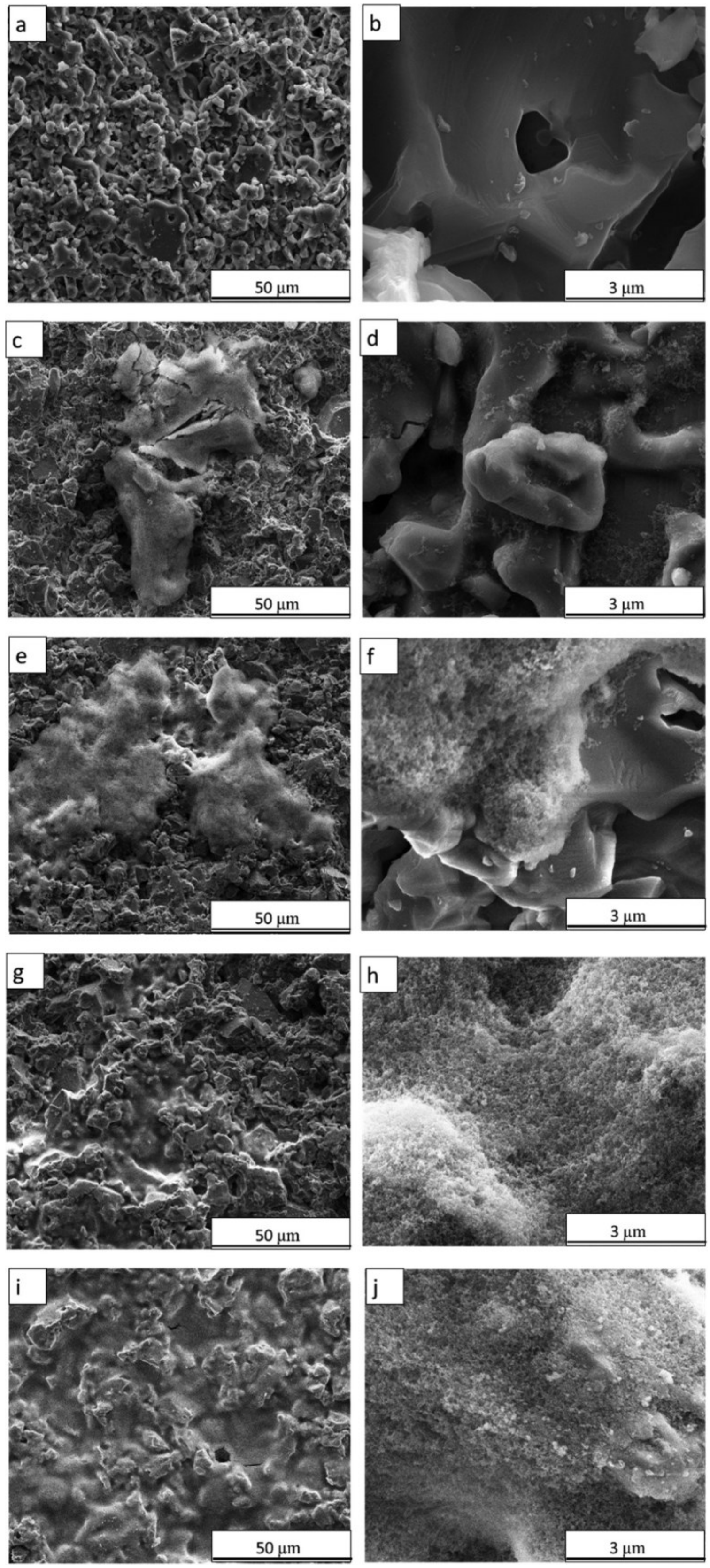

Figure 5. The surface SEM images of (a-b) M0, (c-d) M0.25, (e-f) M0.5, (g-h) M1, and (i-j) M3.

membrane were partially blocked. The SEM images showed that by coating 0.5%, an optimal concentration of coating was achieved since the pores of the membrane were not blocked, and also the coverage was not incomplete.

Surface roughness plays an important role in membrane fouling phenomena.[44,45] The membrane becomes more vulnerable to fouling with the enhancement of membrane roughness because the rougher surface has a higher affinity for particles to deposit.[44]

After coating the membrane surface with Si NPs, AFM analysis was performed to study the changes in surface roughness. AFM images (scan size of 20 µm × 20 µm) of the uncoated and coated membranes are shown in Fig. 6, and the values of the surface roughness parameters of the membranes including the average roughness (S_a), root mean square height (S_q), and the height difference between the highest peak and the lowest valley (S_t) are presented in Table 1. As indicated in Fig. 6a, the M0 membrane with "hill-and-valley" morphology had a rougher surface than the modified membranes. Fig 6a-e confirmed that the surface of the modified membranes became smoother after coating Si NPs. Diminished surface roughness of fabricated membranes leads to lower fouling due to smoothening of the surface reducing the affinity for fouling. More specifically, Sa, Sq, and St are 708 ± 40 nm, 877 ± 21 nm, and 6142 ± 451 nm for M0, respectively, while the corresponding roughness values decreased to 498 ± 161 nm, 623 ± 200 nm, and 4123 ± 1169 nm for M3.

Si NPs leaching

To investigate the amount of Si NPs coating on the surface of the α-alumina membrane, EDS was performed on the M3 membrane. To study the effect of the pre-treatment process using PVA, EDS was measured for M3 fabricating without and with the PVA pre- treatment process. Three spots that were one cm apart on the surface of M3 were selected to measure EDS as shown in Fig. 7. The membrane was marked on the inner side to identify the area of the spots. The SEM ruler was used to capture the same spots to get reliable data (Fig. 7). The EDS results for the amount of Si NPs coating are summarized in Table 2. According to the EDS result, the pre-treatment process using PVA improved Si NPs coating on the surface of the α- alumina membrane. The amount of Si NPs coated on α- alumina membrane spots 1, 2, and 3 increased from 4.28%, 86%, and 3.99% for the M3 membrane without the pre-treatment process to 34.22%, 26.98%, and 44.63% for M3 membrane with the pre-treatment process, respectively. The coated Si NPs can be attributed to the sticky property of PVA, which helped to enhance Si NPs coating.

Using PVA to conduct the pre-treatment process not only improved Si NPs coating but also decreased Si NPs leaching from the surface of the modified membranes. The Si NPs leaching from the surface of M3 fabricating without and with PVA pre-treatment are summarized in Table 3. Using PVA before coating Si NPs helped stabilize Si NPs on the surface of the α-alumina tubular membrane. Even after 12 hours of O/W emulsion operation, a very small amount of Si NPs leached from the surface of M3 fabricating with PVA than without the PVA pre-treatment process. Silica leaching from spots 1, 2, and 3 on the surface of M3 increased from 0, 38.7%, and 9.4% for M3 fabricating with PVA to 21.7%, 76.7%, and 75% for M3 fabricating without PVA after 12 hrs of O/W emulsion filtration.

Wettability study

The wettability of the unmodified membrane (M0) was evaluated by measured the oil contact angle (OCA). The α-alumina tubular membranes were modified by coating them with super hydrophilic Si NPs. According to some studies, α-alumina tubular membranes (M0) are inherently hydrophilic.[41,46,47] To study the effect of Si NPs coating on the wettability of membranes, underwater OCA, which is an indicator of hydrophilicity, was measured using cyclohexane (2 µL). As shown in Fig. 8, coating Si NPs increased the OCA significantly, which means the Si NPs endowed hydrophilic properties to the membranes. For instance, OCA increased from 140° for M0 to 171° for the M3 membrane. Increasing hydrophilicity by coating Si NPs improved the anti-fouling properties of the modified membranes because oil components have a lower tendency to stick on the surface of modified membranes.[44,48]

TOC rejection and flux

Fig 9 represents the water permeability of the pristine and modified membranes as a function of time. Hydrophilicity and membrane pore size had a significant impact on water permeability. As shown in Fig 9, for all the membranes, the water permeability decreased during the O/W separation because oil components were immediately deposited on the surface of the membrane, leading to the formation of a fouling layer. Then, the water permeability rapidly decreased within the 1st hour of O/W separation.[49] The water permeability reduced more slowly as the filtration operation continued because the oil layer became more dynamically stable.[49,50] In this study, steady water permeability was obtained after the formation of the stable fouling layer during the third hour of O/W filtration operation (Fig 9). The initial and stable permeability increased by 39% for M0 and 35% for M1, respectively (Table 4). The water permeability enhancement can be assigned to the hydrophilic improvement of M1 by coating Si NPs. After increasing Si NPs coating from 1% to 3%, the corresponding values decreased by 39% because the pore channels of the

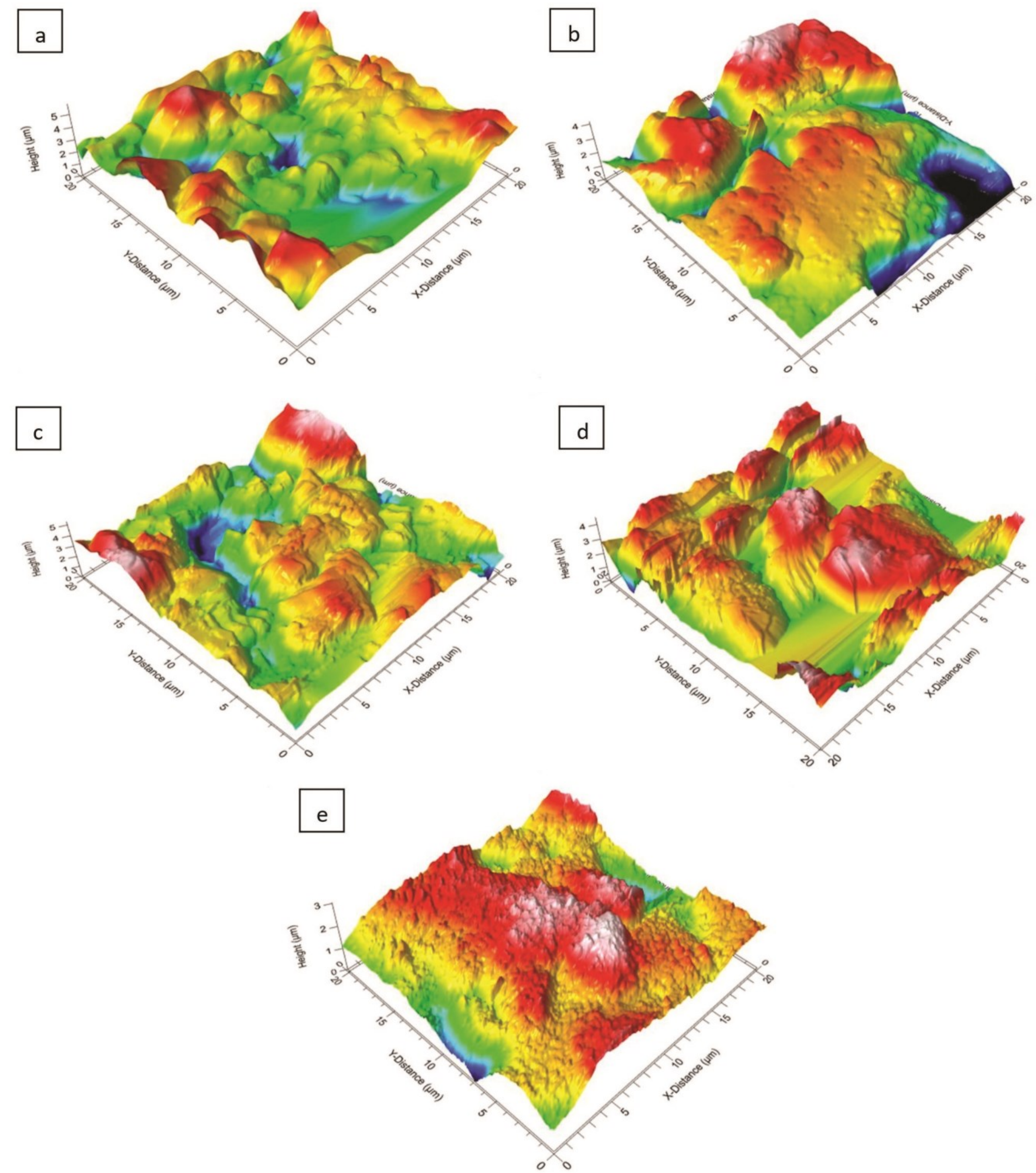

Figure 6. AFM images of M0 (a), M0.25 (b), M0.5 (c), M1 (d), and M3 (e).

modified membranes became blocked (Fig 5e-j). The water permeability for the M3

Table 1. The surface roughness parameters of the membranes.

	Roughness Parameters		
Membrane name	S_a (nm)	Sq (nm)	S_t (nm)
M0	708 ± 40	877 ± 21	6142 ± 451
M0.25	662 ± 33	825 ± 46	5678 ± 775
M0.5	593 ± 99	751 ± 121	5110 ± 1128
M1	505 ± 128	627 ± 160	4608 ± 1320
M3	498 ± 161	623 ± 200	4123 ± 1169

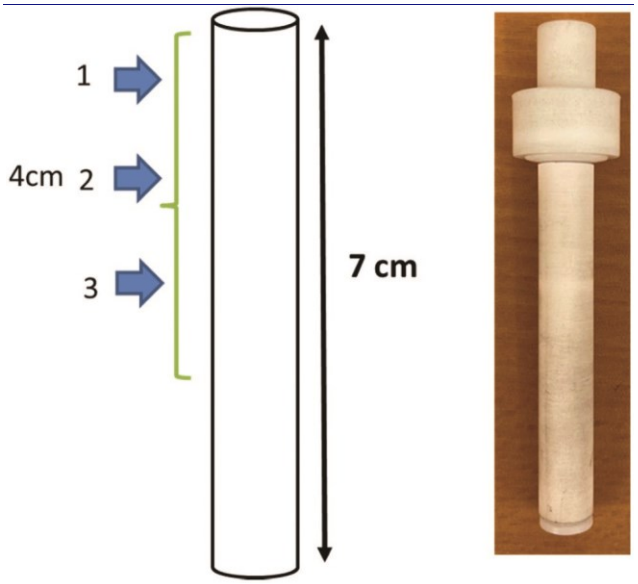

Figure 7. Locations on membrane surface analyzed by EDS for active surface area.

membrane that was fabricated without PVA pre-treatment decreased significantly compared with other membranes attributed to Si NPs leaching from the membrane surface (Fig 9 and Table).

Fig 10 shows the performance of membranes in terms of organic component removal for the first three hours of O/W operation filtration. The modified membranes showed better performance than the unmodified membrane (M0). TOC rejection increased from 93.1% ± 0.4 for M0 to 97.7% ± 0.25 for M3 because of the hydrophilic improvement of the modified membranes (Fig. 8). In addition, by coating Si NPs on the membrane surface, the pore size of membranes decreased (Fig. 5). The TOC rejection increased from the 1st hour to the 3rd hour of O/W filtration operation for almost all the tested membranes, most likely because pure water extraction from O/W emulsion increased oil concentration in the feed tank. Consequently, the membrane pore channels were mostly covered and blocked, which resulted in oily particles being added to the fouling layer over the membrane surface.[50,51] Thus, increasing the oil concentration decreased penetration through the membrane, which caused higher TOC rejection.[49,50]

Anti-fouling properties of the membranes

The anti-fouling properties of the unmodified and modified membranes depend upon the hydrophilic properties of the membranes. Therefore, we studied the fouling resistance of the membranes by treating an O/W emulsion. Fig 11 shows the FRR (flux recovery ratio) of the unmodified (M0) and modified membranes. As exhibited, in all O/W treatment operations, the average values of the FRR increased from 71.3% for M0 to 85.9% for M1, which can be attributed to the hydrophilic improvements of modified membranes after coating with super hydrophilic Si NPs (Fig. 8). However, by coating more Si NPs, the average values of the FRR decreased from 85.9% for M1 to 67.7% for M3, which is attributed to Si NPs accumulation on the membrane surface and pore blockage. Another possible explanation for increasing FRR can be roughness reduction after coating Si NPs resulting in a lesser number ofr valleys and alleys for oil components to stick on the membrane surfaces.

Table 2. Effects of the pretreatment process on the elemental composition and amount of Si NPs coating on the M3 membrane.

Spot	Element	Membrane composition without PVA pre-treatment	Membrane composition with PVA pre-treatment
1	Al	95.72	65.78
	Si	4.28	34.22
2	Al	93.14	73.02
	Si	6.86	26.98
3	Al	96.01	55.37

Si	3.99	44.63

Table 3. Si NPs leaching from the surface of M3 fabricating with and without PVA after 12 hr operation of O/W emulsion filtration.

spots	Silica leaching from M3 fabricating with PVA after 12 hr operation of O/W emulsion filtration(%)	Silica leaching from M3 fabricating without PVA after 12 hr operation of O/W emulsion filtration(%)
1	<1	21.7
2	38.7	76.7
3	9.4	75

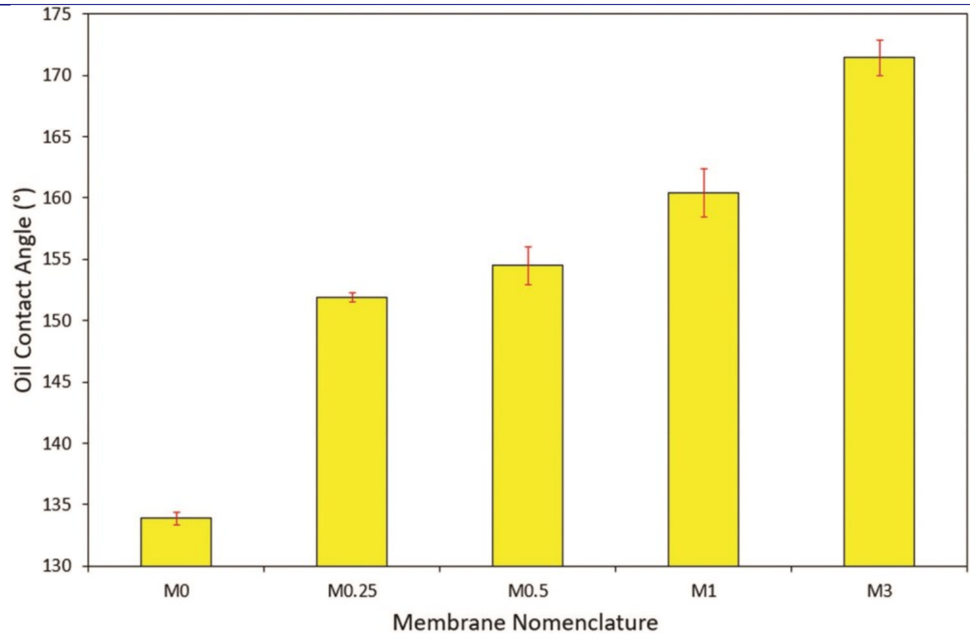

Figure 8. Underwater oil contact angles of cyclohexane on the unmodified and modified membrane by coating Si NPs.

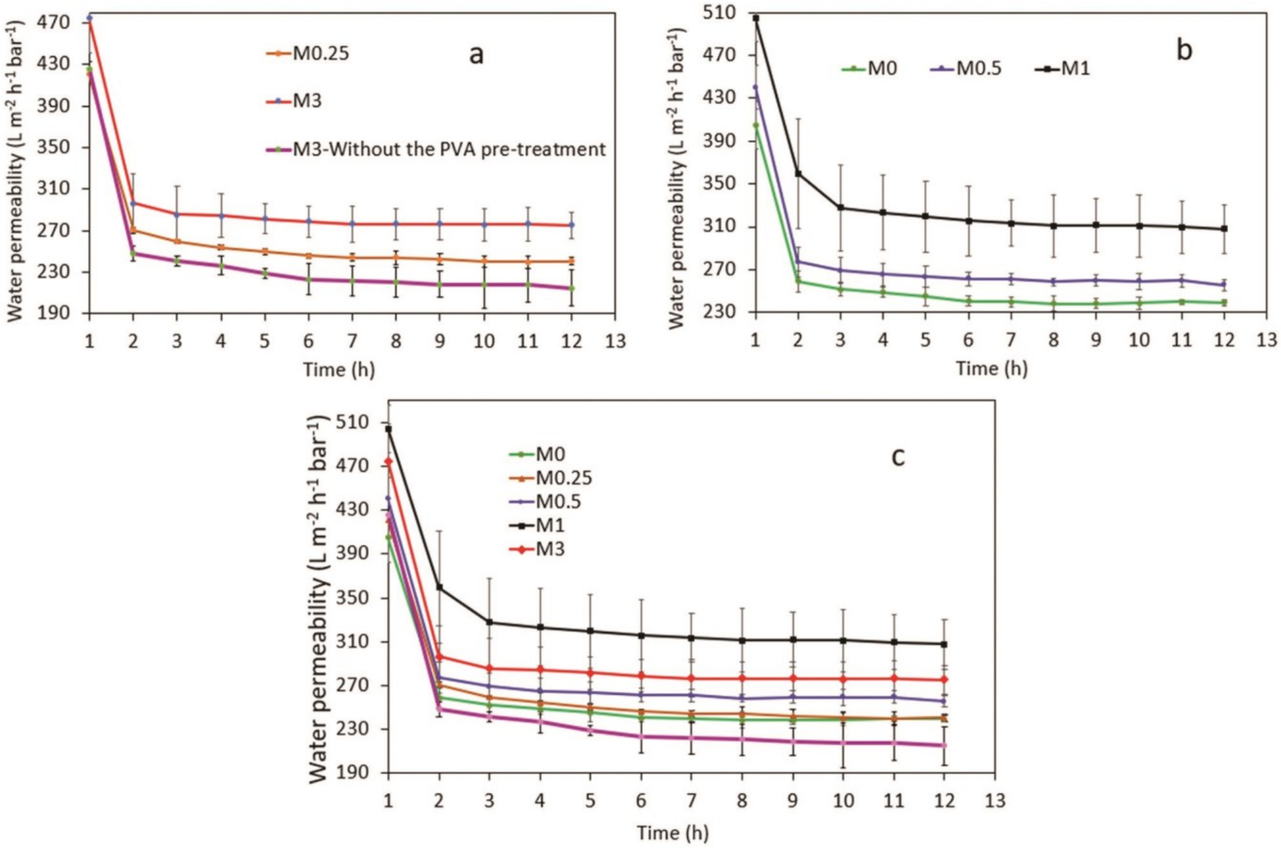

Figure 9. Water permeability for various membranes vs. time,(a) M0, M0.5 and M1 (b) M0.25, M3 and M3 without PVA treatment, and (c) all the membranes combined.

Table 4. Initial and stable permeability of the α-alumina and modified membranes.

Membranes	Initial permeability (L m^{-2} h^{-1} bar^{-1})	Stable permeability (L m^{-2} h^{-1} bar^{-1})
M0	406 ± 8.5	246 ± 2.2
M0.25	420 ± 3.0	244 ± 4.1
M0.5	450 ± 11.9	264 ± 4.0
M1	482 ± 3.4	312 ± 8.5
M3	459 ± 4.0	279 ± 5.9
M3 without the PVA pre-treatment	417 ± 1.7	229 ± 2.4

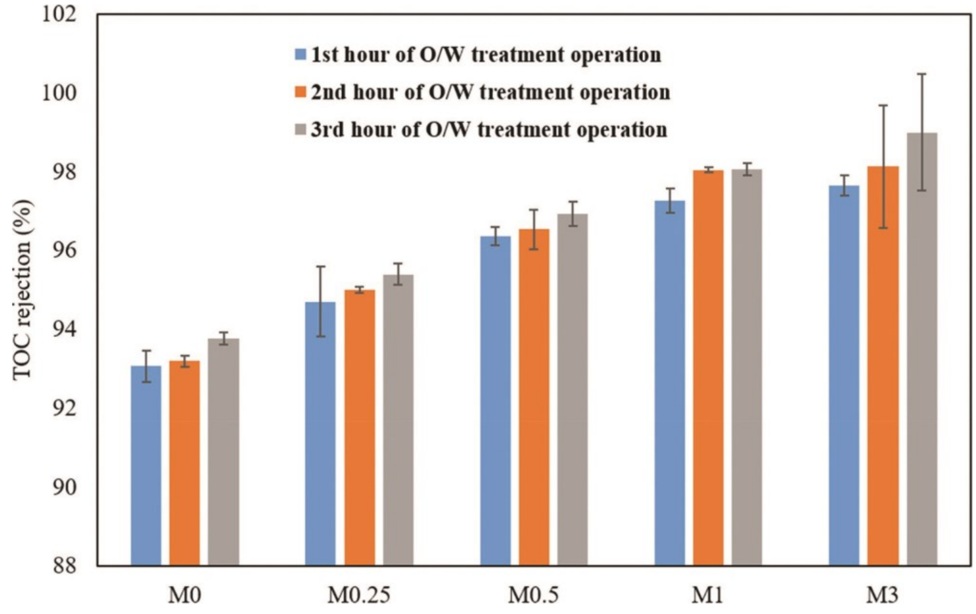

Figure 10. TOC rejection of various membranes for the first three hours of O/W treatment filtration.

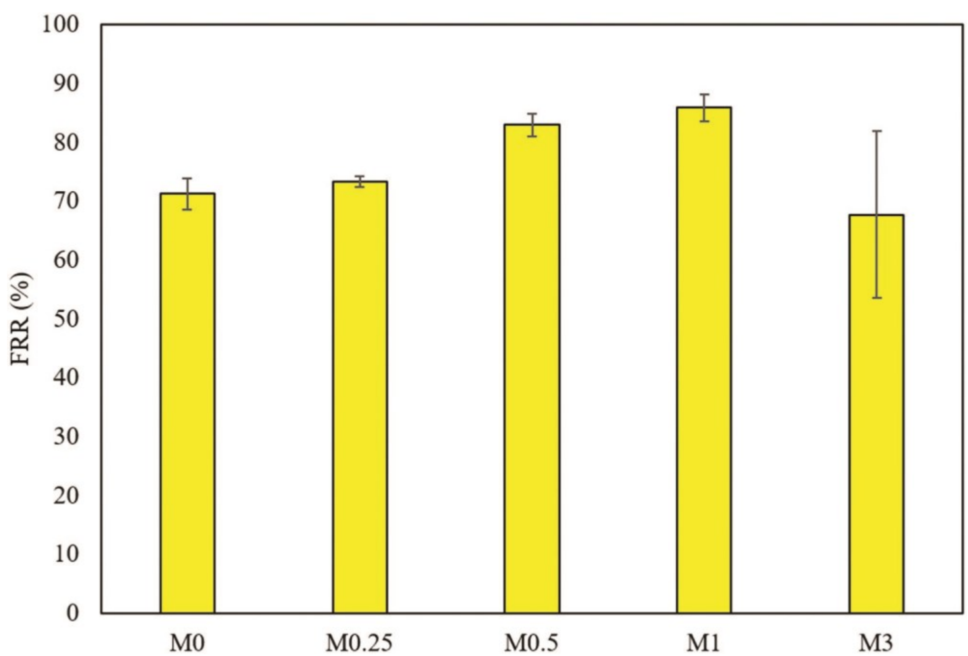

Figure 11. Flux recovery ratios (FRR) of the unmodified and modified membranes.

Table 5. Performance comparison of ceramic MF membranes for treating oil-in-water emulsion in the literature.

Materials	configuration	Pore size (µm)	Oil concentration (ppm)	TMP (bar)	Droplet size (µm)	Permeability ($Lm^{-2}h^{-1}bar^{-1}$)	R(%)	Refs
Mullite	Hollow fiber	0.7	500	0.15	1	880	97	[49]
Modified Al_2O_3	Tubular	0.14	1000	1.6	1.79	505	98.5	[40]
Fly ash/Al_2O_3	Cylindrical	0.1	200	0.5	0.06–10	165	99.2	[29]
Mullite monolith	Tubular	0.4	1000	1	1.09	35	93.8	[52]
Kaolin-Quartz	Flat	1.06	100	2.07	0.99	96	87	[53]
Mullite monolith	Tubular	0.45	1000	2.07	2	48.6	97.6	[50]
Silicon Carbide	Circular disk	0.4	500	0.5	1	324	98.52	[54]
α-Al_2O_3	Tubular	0.2	1000	0.35	1–9	311.5	96.5	This study

Comparison of membranes in the literature

Table 5 compares various membranes for filtering oil-in-water emulsions in terms of the membrane material and configuration, oil concentration, filtration operation condition, flux, and oil rejection. To develop a more energy- efficient membrane, we performed our experiments at lower pressure. Our membrane performed well in terms of water flux and oil rejection, especially when compared to literature data for other ceramic membranes (Table 5). O/W emulsions were filtered at the lowest flow to find a potential membrane for industry application, flux, and oil rejection in this study were relatively high compared with most of the other studies.

Conclusion

Si NPs were coated on α-alumina tubular membrane supports using dip-coating that improved membrane hydrophilicity and reduced the roughness of the modified membranes. Our work shows that the PVA technique that we employed led to a more homogeneous distribution of silica NPs on the membrane surface. The membranes that were modified with 1 wt.% silica NP solution exhibited improved water flux compared to unmodified membranes. This result, supported by contact angle data, illustrates the ability of silica to hydrophilize the membrane surface. In terms of fouling, the decreased roughness of the treated membrane led to a reduction in fouling based on the flux recovery ratio (FRR). The initial and stable permeability increased from 406.2 ± 8.5 and 245.7 ± 2.2 L m^{-2} h^{-1} bar^{-1} for the unmodified membrane (M0) to 482.4 ± 3.4 and 311.5 ± 8.5 L m^{-2} h^{-1} bar^{-1} for the M1 membrane, thereby illustrating the ability of the membrane to process more fluid than an unmodified membrane due to the enhancement in hydrophilicity and anti-fouling properties.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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Statement of novelty

The membrane development technique combines a novel pre-treatment method (using Polyvinyl alcohol) and a silica grafting technique to produce stable fumed silica coatings on membranes. After incorporating the hydrophilic Si NPs, the oil contact angle (OCA) improved from 133.8° to 171.4°. In addition, the surface roughness and associated containment traps on the membrane surface decreased, likely leading to less fouling. Total Organic Carbon (TOC) rejection increased from 93.1% for pristine α-alumina tubular membranes to 97.7% for silica-modified membranes because of hydrophilic improvements of the modified membranes. The Si NP coating improved the anti-fouling properties of membranes as evidenced by the flux recovery ratio increasing from 71.3% for pristine α-alumina tubular membranes to 85.9% for silica-modified membranes. To the best of our knowledge, there are no literature sources reporting the separation of oil and water using α-alumina membranes modified with fumed silica in a continuous cross-flow process.

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