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Effect of microwave treatment on morphological and separation characteristics of polysulfone hemodialysis hollow fiber membranes

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Abstract

Polysulfone is a widely used polymer for hemodialysis membranes. Improving polysulfone membrane hemocompatibility and removing toxins are highly desirable for the quality of life of the dialysis patient. The main objective of this work is the investigation of a novel dual post treatment approach comprising the effect of microwave treatment on hydrogen peroxide-treated polysulfone hollow fiber (PS HF) membranes. Microwave treatment of fibers impregnated with magnesium chloride was adopted. The morphology, structure, and surface properties of the membranes were comprehensively characterized using scanning electron microscopy, Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, contact angle and zeta potential measurements. The mechanical properties of the treated fibers were also investigated. The performance of the studied membranes was evaluated in terms of pure water permeability and sieving coefficients of urea and creatinine. Results indicated that membrane mechanical properties and hydrophilicity could be enhanced using microwave treatment while maintaining a stable chemical structure. The hollow fiber membrane mean pore size decreased by (4.5-66%) for both microwave and combined treatments, while no significant change was observed on membrane average porosity. After fibers were subjected to MW treatment (3-7% $MgCl_2$), there was a slight variation in the urea and creatinine sieving coefficients and a considerable alteration in permeability. Microwave post-treatment in wet conditions could be applied as a useful technique for tuning hemodialysis PS HF membranes.

Keywords: hemodialysis; polysulfone; hollow fiber membrane; microwave; post-treatment

1. Introduction

Dialysis membranes are essential for the livelihood of patients with kidney failure. Nearly three million people worldwide receive dialysis to sustain their lives, and this number is expected to exceed five million by 2030 [1,2]. In Egypt, approximately 54,000 patients underwent dialysis in 2022 [3]. Polysulfone (PS) is one of the most widely used polymers in the fabrication of hemodialysis membranes as it has improved mechanical and thermal stability, strength, ease of processability, and resistance to chemical attack [4]. Despite these advantages, PS membranes are susceptible to fouling and blood interaction during the dialysis process due to poor hydrophilicity and hemocompatibility [5-7]

The current trend to improve dialysis performance is to increase hemodialysis (HD) membrane toxins removal, reduce its protein binding ability, and improve hemocompatibility [8-10]. Membrane hemocompatibility is associated with decreased protein adsorption, complement activation, and surface-induced coagulation which depends on membrane functionality and surface properties. HD membranes should have a reduced membrane surface charge, hydrophilic surface, and low roughness [8,11]. HD membrane hemocompatibility can be improved via bulk modification by functionalization of the polymer substrate, blending with polymers, the inclusion of organic and inorganic additives during the spinning process, physical surface treatment, and chemical surface functionalization [12], [13]. Membrane physical treatment methods such as heat treatment, plasma treatment, and microwave (MW) treatment could affect the membrane surface morphology and separation performance and could be achieved more easily without membrane degradation or change in its chemical structure [14-16].

Microwave treatment is a simple, low-cost method that can be easily implemented on an industrial scale. Few studies were conducted on the effect of microwave treatment on hollow fiber membranes. The effect of microwave irradiation on PES/DMF/LiBr membranes was studied and compared with the thermal annealing method in a water bath [16]. The results of

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the study indicated that the microwave post-treatment method improved the membrane performance in a short period, where membrane flux was 23% higher with a slight increase in rejection from 92% to 95% for polyethylene glycol, molecular weight 6000 Da (PEG 6K), and the membrane contact angle was lower compared to thermally annealed membranes. Another study indicated that MW post-treatment of PES HF membrane could be used to tune the surface morphology and mechanical properties in NaCl solution, where a NaCl concentration of 2% reduced the surface roughness by 19.2% and showed the highest break stress compared to untreated fibers [17]. The combination of loading nano-silica and MW treatment was found to be effective in manipulating the properties of PVDF membrane [18].

The present work presents a novel dual post treatment approach comprising microwave post-treatment under wet conditions following H_2O_2 treatment of polysulfone dialysis hollow fiber membrane. Post-treated fibers were evaluated in terms of surface morphology, roughness, contact angle, pure water permeability, and sieving coefficients of urea and creatinine.

2. Experimental

2.1. Materials

Spun polysulfone hollow fiber (PS HF) membranes used in this study were impregnated with magnesium chloride ($MgCl_2.6H_2O_2$, 99%, M.W. 203.3) as a source of a divalent ion during microwave treatment. The $MgCl_2$ was purchased from Sisco Research Laboratories Pvt. Ltd, India. For evaluation of the sieving coefficients, urea and creatinine were purchased from El-Nasr Pharmaceutical Chemicals Co. and Alpha Chemicals Co., Egypt respectively. Potassium chloride (>99% Sigma Aldrich), sodium hydroxide (>98% Sigma Aldrich), and HCl (37%) were used in the zeta potential analysis.

2.2. Methods

Microwave treatment was carried out in a household microwave oven (900-watt, DAEWOO Electron KOR-1A 6A, Korea) equipped with a temperature controller. Different concentrations of $MgCl_2$ solutions ranging between 0% and 7% were prepared using distilled water (conductivity =10μS). PS membranes samples were soaked in the prepared solutions and then treated in a microwave oven at 55°C for 10 minutes. Both the conductivity and pH of the treatment solutions were measured before and after microwave treatment. The samples were classified into two groups based on the membranes used. PS Hollow fiber membrane was used in Group I and hydrogen peroxide (H_2O_2) treated PS Hollow fiber membrane was used in Group II. Hollow fiber membranes denoted A and AH are control samples for Group I and Group II respectively. Table 1 shows the coding of the treated samples.

2.3. Membrane characterization

2.3.1. NMR Spectroscopy

A JEOL ECA NMR spectrometer was used to measure the NMR spectra of the membrane samples where dimethyl sulfoxide (DMSO) was used as the solvent.

2.3.2. FTIR Spectroscopy

The surface functional groups of all HF membrane samples were determined using a Fourier transform infrared (FTIR) analyzer. FTIR analysis was carried out using (FT/IR-6100 from A Jasco, Japan detector) infrared spectrophotometer with the transmittance mode with a scanning range of 400 cm^{-1} to 4000 cm^{-1}.

Table 1: Sample coding and treatment conditions in the current study

Sample code	Group	Membrane	Treatment solution
Amw	Group I	PS Hollow fiber	Distilled water
Amw1%			1% $MgCl_2$
Amw3%			3% $MgCl_2$
Amw5%			5% $MgCl_2$
Amw7%			7% $MgCl_2$
AHmw	Group II	Hydrogen peroxide-treated PS Hollow fiber	Distilled water
AHmw1%			1% $MgCl_2$
AHmw3%			3% $MgCl_2$
AHmw5%			5% $MgCl_2$
AHmw7%			7% $MgCl_2$

2.3.3. Scanning electron microscopy (SEM)

The cross-section and surface morphology of raw and MW treated fibers were observed using (SEM JEOL SEM 6000 Neoscope desktop) bench-top scanning electron microscope. Hollow fiber membranes were washed using RO water and air

dried. A sharp razor was used to cut the membrane samples before being sputter-coated with gold for 30 seconds prior to SEM imaging. Energy dispersive X-ray analysis (EDX) was also used for elemental analysis on the membrane surface.

2.3.4. Roughness

The PS HF membrane surface roughness was analyzed using a TT-AFM workshop (resolution =1.5 μm), where Gwidyyon software was used for analyzing roughness variables. The outer membrane surface (5 μm × 5 μm) was scanned using vibrating mode. An average of five measurements were undertaken for each sample.

2.3.5. Water contact angle (CA)

The hydrophilicity/hydrophobicity of the HF membranes was measured using a contact angle instrument (OCA 15EC). A drop of distilled water was placed on the outer surface of the dried membrane at room temperature. CA was measured at five different locations for each sample from which the mean CA and standard deviation were estimated.

2.3.6. Mechanical properties

The mechanical properties including tensile stress, tensile strain, and Young's modulus of PS HF membranes were studied using a benchtop Tinius Olsen H5kS universal tensile testing machine (with a 5N load cell) for a fiber length of 10 cm. Horizon software package was used to estimate the aforementioned mechanical properties.

2.3.7. Average Porosity (ε)

The average porosity of the HF was measured using the gravimetric method. HF samples were cut into about 2 cm lengths and then dried for 1 hour. Dried samples (about 2g) were soaked in kerosene for 1 day, then removed and weighed. Average Porosity was calculated according to the following formula [19]

$$\boldsymbol{\varepsilon}(\%) = \frac{\frac{w_{W1}-w_o}{D_{kerosene}}}{\frac{w_1-w_o}{D_{kerosene}}+\frac{w_o}{D_{polymer}}} * \mathbf{100} \qquad 1$$

Where ε is the membrane porosity (%), w_1 is the weight of the wet membrane (g), w_o is the weight of the dry membrane (g), $D_{kerosene}$ is the kerosene density (0.82 g/cm^3), $D_{polymer}$ is the polysulfone density (1.24 g/cm^3).

2.3.8. Mean pore size

The mean pore size of the studied PS HF membranes was measured using a Belsorp Max device (MicrotracBel. Corp., Japan) using liquid nitrogen via the Brunauer-Emmett-Teller (BET) method surface analyzer where its theory explains the physical adsorption of gas molecules onto a solid membrane surface [20,21].

2.3.9. Zeta potential

The surface charge of the PS membranes was obtained using a SurPASS electrokinetic analyzer (Anton-Paar GmbH, Austria). Before measurements, hollow fiber membranes were sectioned using a razor and then mounted on the sample holder using double-sided glue and completely covered with fibers. The channel height was 110 ± 5 μm. Liquid KCl (10 mM) was used as the electrolyte solution. The pH value of the solution was adjusted using an automatic titrator to a range of (3- 9). The zeta potential was calculated from the obtained streaming potential using Helmholtz-Smoluchowski equation [22]

$$\boldsymbol{\zeta} = \frac{\boldsymbol{\eta K_B}}{\boldsymbol{\varepsilon_0 \varepsilon_r}}\left(\frac{\boldsymbol{dE_z}}{\boldsymbol{\Delta p}}\right) \qquad 2$$

2.4. Membrane performance evaluation

The performance of the hollow fiber membrane was evaluated in terms of pure water permeability and sieving coefficients for urea and creatinine. For this purpose, lab-scale glass modules were assembled using a bundle of 20 fibers with an effective length of 20 cm. All experiments were performed by the inside-out flow configuration using HYFLUX MES-S-5000 membrane evaluation system.

2.4.1. Pure water permeability

Pure RO water was allowed to pass through the membrane at a constant feed pressure of 1 bar until reaching a constant flow rate. Pure water permeability was determined from

$$\boldsymbol{L_p} = \frac{\boldsymbol{V}}{\boldsymbol{A.\Delta P.t}} \qquad 3$$

Where L_p is the pure water permeability (L.m^{-2}.hr^{-1}.bar^{-1}), V is the permeate volume (L), A is the effective membrane area (m^2), Δp is the trans-membrane pressure (bar), and Δ t is the permeate collection time (h).

2.4.2. Sieving coefficients (SC)

Membrane separation performance was evaluated using urea (MW 62 Da) and creatinine (MW 113.12 Da) to represent small toxins in the blood. All experiments were performed under constant trans-membrane pressure (0.5 bar) and at room temperature. Test solutions of urea 1000 ppm and creatinine 100 ppm in a saline solution (0.9% NaCl) were prepared separately. Permeate samples were collected 30 minutes after start-up to ensure stability and then collected after 1 and 2 hours, respectively. Urea and creatinine concentrations were analyzed using UV spectrophotometry. The sieving coefficient was calculated from

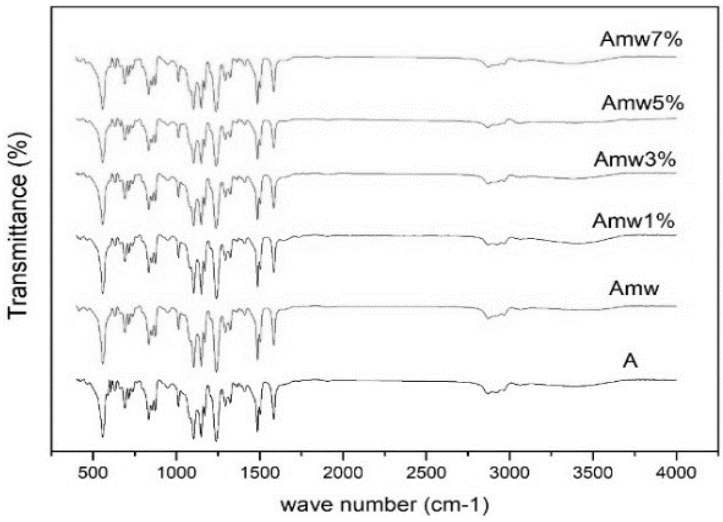
$$\boldsymbol{SC} = \frac{\boldsymbol{C_1}}{\boldsymbol{C_0}} \qquad 4$$

Where SC is the sieving coefficient, C_0 and C_1 are the concentrations of feed and permeate respectively.

3. Results and Discussion

3.1. Structural analysis

Membrane structure was analyzed using FTIR, NMR, and EDX. The effect of microwave irradiation on PS HF membrane under wet conditions was studied using FTIR spectroscopy in the range of (4000-400 cm $^{-1}$) as shown in Figure 1. All membranes showed the main characteristic peaks of polysulfone at 1148.81 cm $^{-1}$ representing O-S-O stretching, 1238.19 cm $^{-1}$ for C-O-C stretching, and at 1583.73 cm $^{-1}$ C=C on the benzene ring [23,24]. The transmittance band at around 2,980-2,800 cm $^{-1}$ represents the C-H group in PEG [25]. FTIR Transmission analysis revealed the stability of PS polymer main functional groups. Structural stability of PS membranes was observed from NMR results as shown in Figure 2, as there is no change in the main characteristic bonds of PS.



A

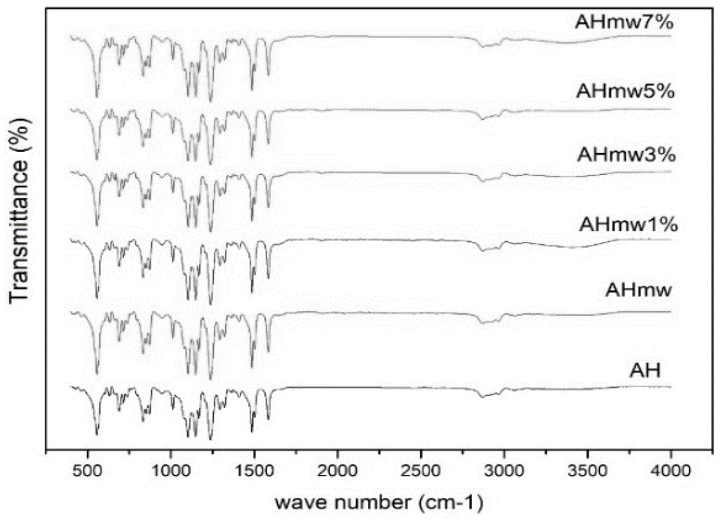


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Figure 1: FTIR analysis of raw and microwave-treated samples, (A) Group I, (B) Group II

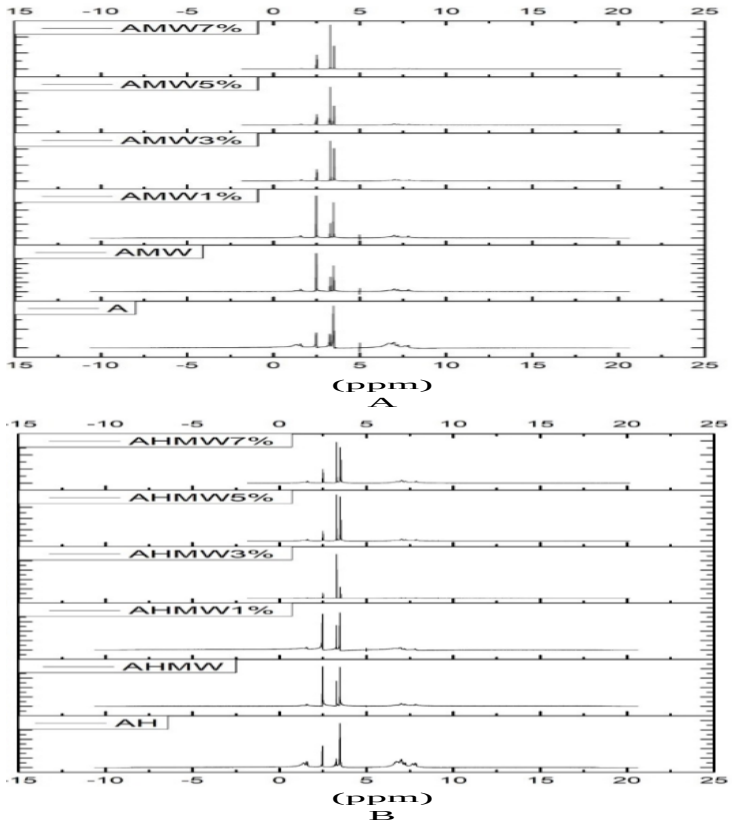

Figure 2 : NMR analysis of raw and microwave-treated samples, (A) Group I, (B) Group II

EDX analysis of raw and post-treated PS membrane samples are shown in Table 2. It is seen that the main elements (C, O, S) ratio was almost constant. Mg and Cl were detected on the membrane surface for salt-treated samples, after washing with distilled water several times.

Table 2: EDX analysis mass % values of studied PS HF membranes

Group	Sample	C	O	S	Mg	Cl
Group I	A	64.44	29.37	6.19	0.00	0.00
	Amw	66.65	26.69	6.66	0.00	0.00
	Amw1%	64.05	24.45	8.01	1.62	1.86
	Amw3%	66.47	27.91	5.06	0.56	0.22
	Amw5%	70.17	23.78	5.62	0.13	0.32
	Amw7%	68.40	25.80	5.19	0.39	0.21
Group II	AH	67.05	27.22	5.73	0.00	0.00
	AHmw	67.21	26.70	6.09	0.00	0.00
	AHmw1%	63.95	25.06	7.82	1.54	1.64
	AHmw3%	60.25	29.18	4.63	2.48	3.46
	AHmw5%	59.77	25.76	3.48	4.21	6.79
	AHmw7%	56.61	31.14	3.20	3.46	5.58

3.2. Membrane morphology

Cross-sectional and surface SEM images of PS HF microwave-treated samples (Group I) and microwave-treated samples after H_2O_2 treatment (Group II) are shown in Figures 3 and 4 respectively. Samples showed a double-layer finger-like structure with inner and outer sponge layers. Cross-section images indicate that membrane morphology remained stable after being subjected to microwave treatment. Also, no cracks were observed on the membrane surface indicating that the selected treatment conditions maintained the membrane morphology. A previous study also showed no cracks in the PES HF

membrane after microwave treatment at 90 °C for 10 minutes in 1% NaCl solution concentration [16]. The membrane cross-section indicates morphological stability although the measured dimensions show slight variations in both the inner and outer diameters, which could be associated with spinning conditions.

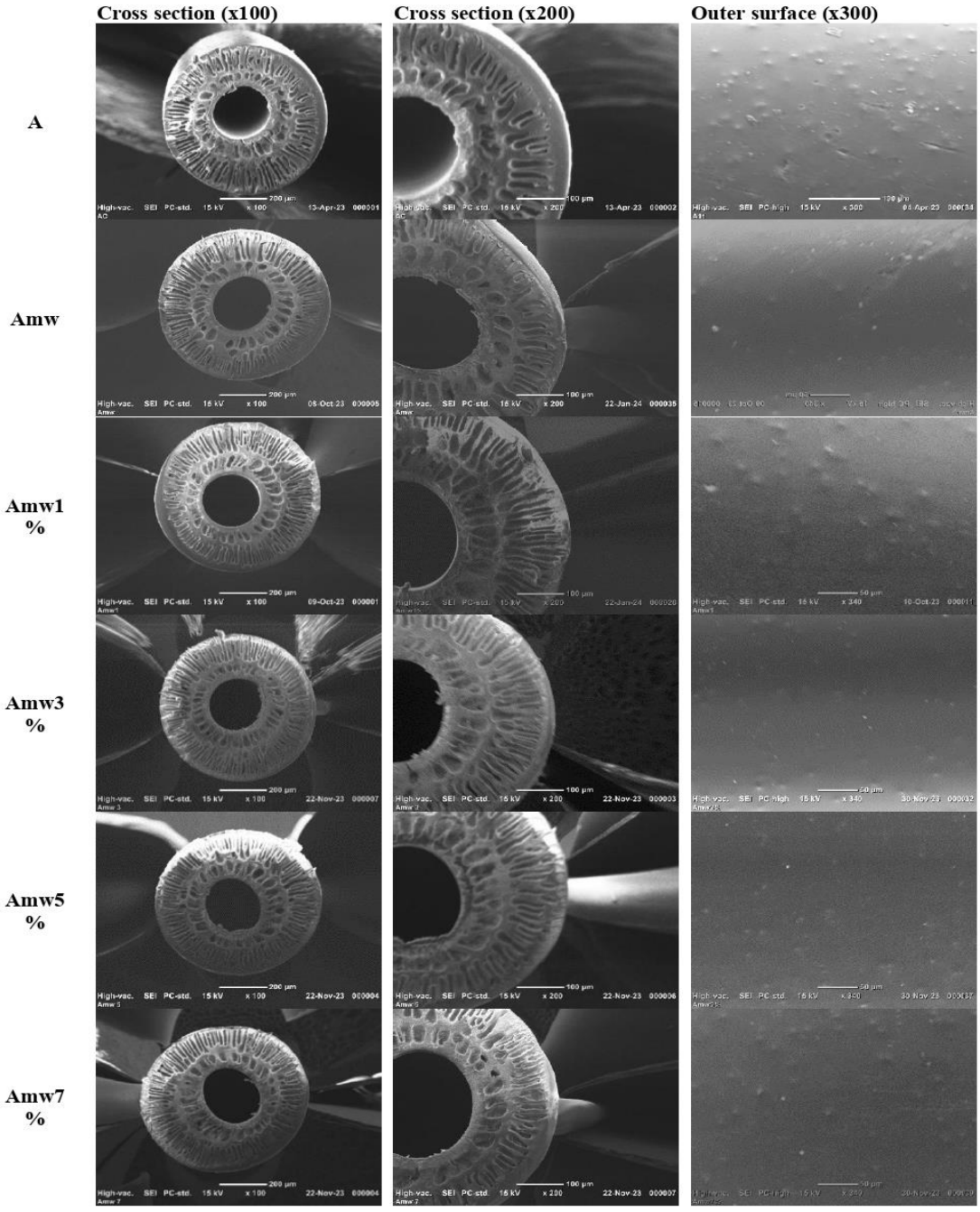

Figure 3: SEM images of raw and microwave-treated PS HF samples (Group I)

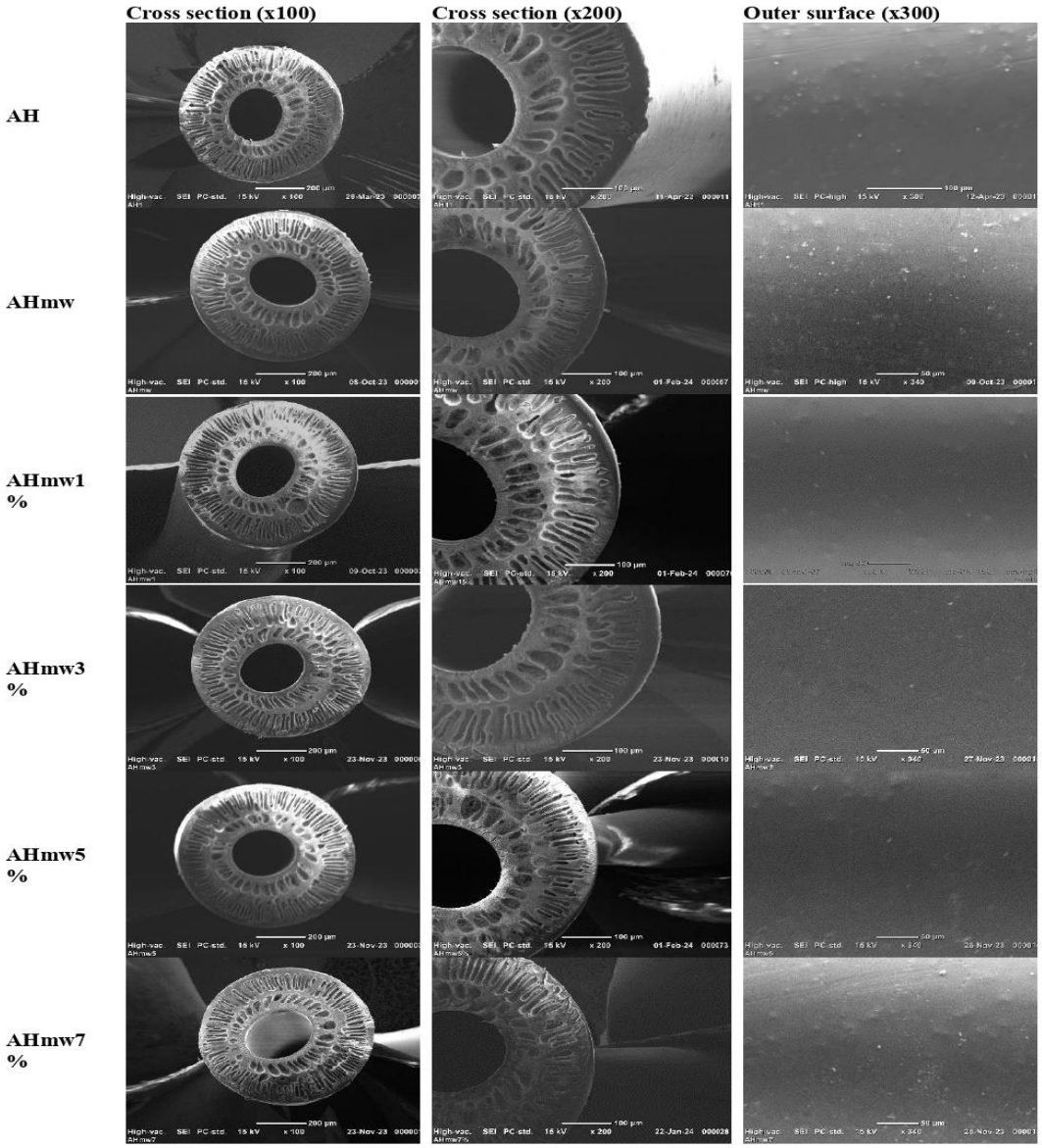

Figure 4: SEM images of H_2O_2 and microwave-treated samples after H_2O_2 treatment (Group II)

3.3. Roughness

Surface roughness is an important parameter affecting membrane hemocompatibility, where reduced values are more favourable. Increased surface roughness could lead to hemolysis or rupture of red blood cells and enhanced platelet adhesion [25,26]. The effect of microwave post-treatment on the roughness of tested samples is presented as 3D images at an area of (5×5 μm) in Figure 5, and the Ra and Rms roughness values are presented in Figure 6. It is observed that Ra roughness values varied between (5-17 nm) and (7-16) for Groups I and II respectively. Rather similar Figures have been detected for Rms. The membrane roughness increased after exposure to microwave treatment for all samples in Group I, having a more significant increase for samples Amw3%, Amw5%, and Amw7%. Also, for the H_2O_2-treated membrane, roughness increased for all treated samples except samples treated in distilled water which showed a decreased value of roughness by 39%. Both samples Amw5% and AHmw5% have the highest roughness values for studied fibers with Ra values of 16.14 and 15.85 nm respectively. A previous study showed increased values in PES HF membrane roughness after microwave treatment in NaCl solution except for a concentration of 2%, where roughness decreased by about 20% [17]. Westphalen et al. measured the surface roughness of commercially available CTA and PAES HD membranes, where the Ra values were (5.4,7.5) and (10.5,15.9) for inner and outer surfaces respectively, in an area of 2×2 μm [28]. Thus, the results obtained in the present study are in agreement with the reported roughness for commercial membranes.

As far as surface roughness is concerned, high values were observed for 3% and 5% $MgCl_2$ MW treated samples. These results do not reflect internal lumen side roughness. It is expected that mass transfer on the dialysate side is important in case of hypocalcemia.

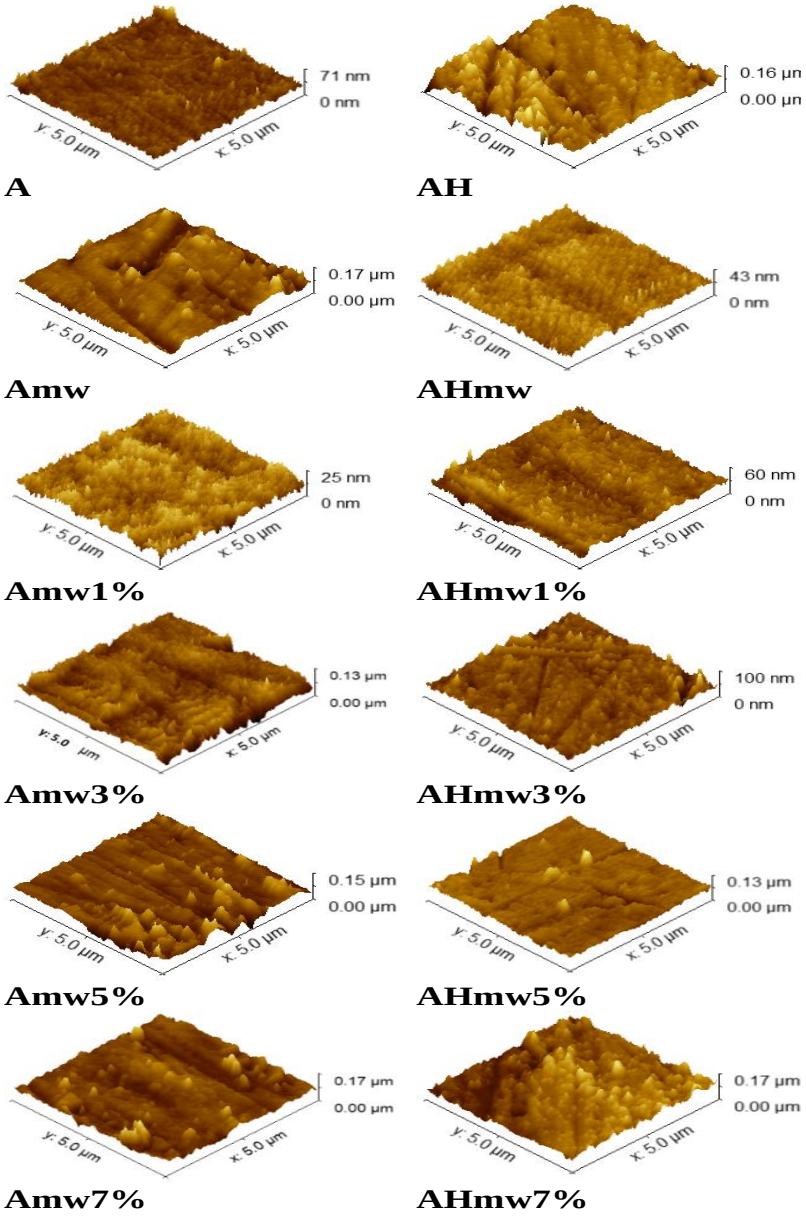

Figure 5: AFM images of PS HF membranes for Group I and Group II

3.4. Contact angle

Adsorption of plasma proteins during HD leads to secondary membrane formation, which may affect uremic toxins removal and hemo-compatibility of the dialyzer [7]. Lower contact angle means also higher surface availability for better mass transfer. Hydrophilicity improves the HD membrane antifouling property and consequently its hemo-compatibility through less protein adsorption and lower complement activation [29]. Also, hydrophilicity is also associated with efficient removal of small and medium molecules. These findings were approved by a clinical study on 70 patents using three commercially available dialyzers (FX CorAL 600, Polyflux 170H, and SureFlux 17UX). The FX CorAL 600, has a more robust hydrophilicity which efficiently removes small and medium toxins during online HD and showed the best hemocompatibility among the studied dialyzers [30].

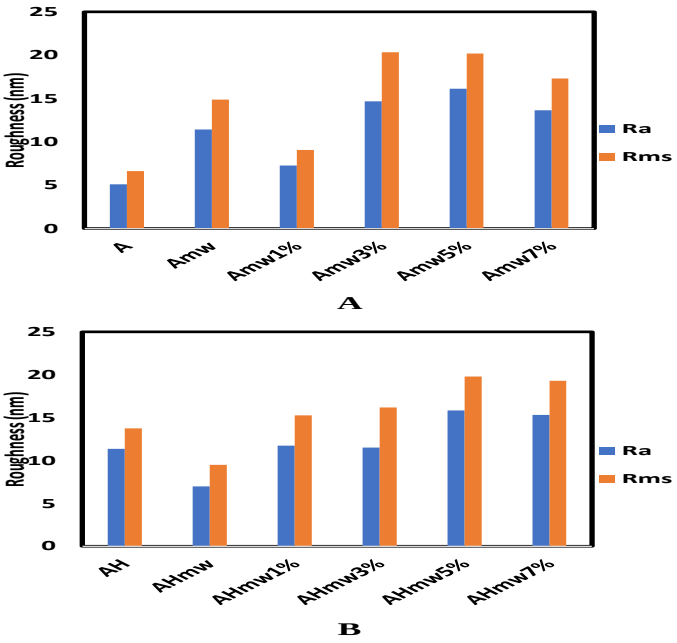

Figure 6: PS HF membrane roughness for raw and microwave-treated samples, A: Group I, B: Group II

Figure 7 shows the effect of microwave treatment on the PS membrane, where the error bar represents the standard deviation. In Group I, the membrane contact angle decreased for all samples except for the Amw1% where the contact angle increased by 6%. A more significant increase in membrane hydrophilicity was observed for the treated fibers and a less significant increase was observed for MW treated samples in distilled water only. Conversely, the membrane's contact angle increased for all Group II treated samples except sample AHmw7% which had the lowest contact angle with a decreased percentage of 18%. These findings indicate that PS membrane hydrophilicity could be altered using microwave post-treatment. On the other hand, another study revealed that MW post-treatment decreased membrane hydrophilicity for all studied PVDF membranes [18]. The effect of microwave irradiation and thermal annealing on PES/DMF/LiBr membranes were also studied and it was found that the membrane contact angle was lower compared to thermally annealed membranes [16]. Despite the minor differences in contact angle results, the effect of microwave showed slightly better improvement nearly in all cases. However, at higher salt concentrations 3% and 5% in Group I results have been improved (with a decline in contact angle by 15.4%-14.7%) as compared to 1%. In conclusion, MW improved wettability at salt concentrations 3% and 5% in Group I. This impacts better mass transfer for toxins and salts, better ultrafiltration rate and lower protein adsorption due to lower complement activation.

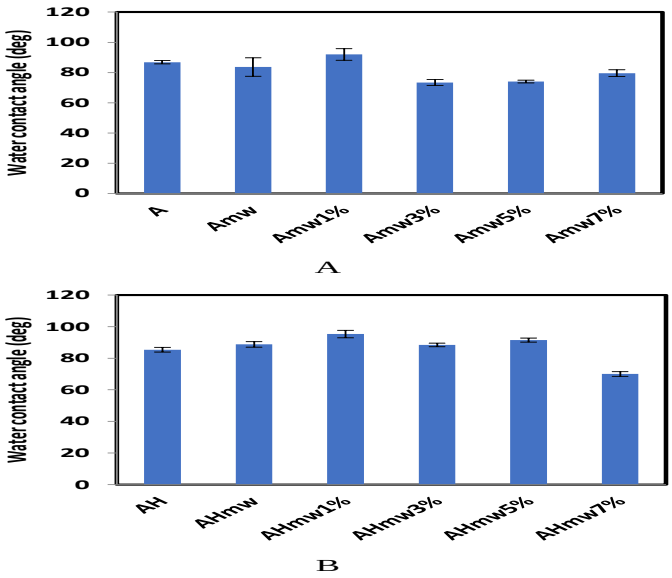

Figure 7: Effect of microwave treatment on PS HF membrane contact angle, A: Group I, B: Group II

3.5. Mechanical properties

Hemodialysis membrane should have high mechanical stability to prevent membrane damage during fiber assembly and to withstand blood pressure during dialysis period. As indicated in Table 4, the mechanical properties of the membranes were investigated in terms of break stress, break strain, and Young's modulus. The results indicate that using microwave treatment could enhance the mechanical properties of the raw PS HF membrane for Group I. The break stress increased from 3.89 to 4.18 MPa for the microwave-treated sample in distilled water (Amw). Treatment using 3% $MgCl_2$ salt resulted in the highest break stress (4.52 MPa), with a 16.2% increase compared to the raw sample. The break strain of the fiber also increased after microwave treatment using either distilled water or $MgCl_2$ salt solution bath, and the highest break strain was observed for the Amw7% with an increase of 56% compared to the raw sample. Young's Modulus increased after microwave treatment for all salt concentrations except 7% $MgCl_2$ which showed a slight decrease.

On the other hand, a decrease in break strain was observed for Group II compared to the control sample (H_2O_2 treated sample). Also, break stress decreased in all Group II samples except AHmw1%. The highest break strain was observed for the AHmw7% with a value of 27.7%, while the AHmw3% showed the

highest break stress in this group with a value of 4.34 MPa, which is interestingly of similar trend as Group I.

A previous study of PES membrane treated with MW in NaCL solution (1–4 wt%) showed that both break stress and break strain values decreased for all samples except at 2% NaCl salt concentration where it increased by 8.8% and 17% respectively [17]. Through other work on PVDF membrane, it was shown that both break stress and strain decreased after exposure to MW treatment in aqueous NaCl solution [18].

3.6. Average Porosity (Ɛ) and Mean Pore size (BET analysis)

Membrane ultrafiltration rates and clearance depend on both pore size and porosity [31]. The average total porosity results for the raw and post-treated PS HF membrane samples are shown in Table 4. Generally, no significant changes in average porosity were observed. Referring to Group I, a slight decrease in the average porosity was observed for all samples. On the other hand, in Group II, a slight decrease in porosity was observed for AHmw and AHmw1%, and a slight increase in membrane porosity was observed for samples impregnated with $MgCl_2$ at concentrations of 3, 5 and 7%. AHmw7% had the highest porosity.

Table 3: Mechanical properties of microwave-treated HF membrane compared with raw samples

Group	Sample	Break stress MPa	SD	break strain%	SD	Modulus MPa	SD
Group I	A	3.89	0.073	20.7	2.19	118	2.3
	Amw	4.18	0.023	28.4	1.71	127	7.6
	Amw1%	4.08	0.082	23.6	1.00	128	3.7
	Amw3%	4.52	0.113	28.3	2.66	121	7.7
	Amw5%	4.4	0.909	23.9	2.64	123	4.1
	Amw7%	4.11	0.084	32.3	3.37	114	2.9
Group II	AH	4.24	0.085	26.7	2.78	124	5.4
	AHmw	4.08	0.082	25.7	2.47	122	2.8
	AHmw1%	4.06	0.174	26.3	6.03	121	4.4
	AHmw3%	4.34	0.073	23.5	1.62	123	2.7
	AHmw5%	4.11	0.085	26	2.72	116	3.8
	AHmw7%	3.76	0.107	27.7	3.09	103	6

***SD standard deviation.**

Table 4: Average porosity of PS HF membranes

Group I		Group II	
Code	Porosity %	Code	Porosity %
A	80	AH	80
Amw	79.2	AHmw	79.3
Amw1%	78.9	AHmw1%	79.7
Amw3%	79.3	AHmw3%	81.4
Amw5%	79.3	AHmw5%	81.3
Amw7%	79.4	AHmw7%	82.2

Table 5 shows the mean pore size of raw and treated PS membranes evaluated from BET analysis. Results indicate that microwave treatment resulted in a decline in pore size compared to control samples, in both groups, A and AH, respectively. Referring to Group I, a slight decrease in pore size was observed for fibers treated using MW in distilled water, while a more significant decrease was observed (up to 35.5%) when adding $MgCl_2$ salt into the treatment solutions. More significant changes were observed in Group II, where the decrease percentage in pore size exceeded 65% for AHmw3% and AHmw7%. Similar results were observed in a previous study, where pore size tends to decrease from 10nm to 7.1 nm after MW treatment for PVDF membrane in 2% NaCl solution [18].

So, it may be concluded that the selected treatments only affected the size of the surface pores, while almost no effect was noticed on the average porosity. It is worth mention that the membrane is operating in in-out configuration mode, so the controlling mechanism depends on the inner void structure. Results of porosity measurements tend to indicate significant impact on surface pore size as obtained by BET measurements, while results of average porosity indicate overall minimal impacts which confirm the role of internal pore structure as a governing parameter in membranes operating by in-out flow mode.

Table 5: Mean pore size of PS HF membranes

Group I		Group II	
Sample code	Pore size (nm)	Sample code	Pore size (nm)
A	9.72	AH	12.53
Amw	9.28	AHmw	6.77
Amw1%	7.88	AHmw1%	6.96
Amw3%	6.49	AHmw3%	4.25
Amw5%	7.05	AHmw5%	7.37
Amw7%	6.27	AHmw7%	4.75

3.7. Zeta potential

Membrane functional groups dissociate in the presence of aqueous solution generating charge. The charge of the membrane surface affects membrane biocompatibility as it significantly affects protein adsorption and complement activation. Zeta potential profile, which is considered an indicator of membrane surface charge, was estimated for Group I fibers at a pH of 7.4 to mimic the pH of human blood as shown in Figure 8. It is seen that the zeta potential profile differs after post-treatment with different $MgCl_2$ concentrations. All membranes were observed to have negatively charged surfaces over the studied pH range. At a pH of 7.4Samples A, Amw, Amw1%, Amw3%, Amw5%, and Amw7% had zeta potential values of -10.36, -8.77, -13.05, -10.28, -6.31 and -14.24 mV respectively. Sample Amw5% had the lowest negative charge.

A study estimated the zeta potential of eight commercially available HD membranes at pH 7.4 and the results showed that the membranes had the following zeta potential values for the different dialyzers used: FX CorDiax (−5.56 mV), SUREFLUX (−6.28 mV), FX CorAL (−2.38 mV), ELISIO (−7.12 mV), Polyflux (−7.15 mV), Xevonta (−7.30 mV), and THERANOVA (−9.39 mV). The FDX dialyzer had the most negative charge of −25.74 mV [32]. Also, this study concluded that a membrane with a near-neutral zeta potential showed reduced complement activation and the highest biocompatibility. Another study revealed that a higher membrane negativity resulted in a higher potential to activate blood coagulation [33].

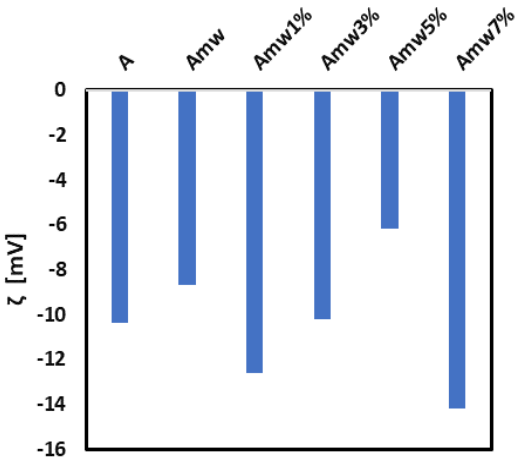

Figure 8: Zeta potential of studied PS membranes at pH 7.4

3.8. Performance evaluation

3.8.1. Pure water permeability

The effect of microwave treatment on the permeability of PS HF microwave post-treated membranes was studied at a trans-membrane pressure of 0.5 bar and is presented in Figure 9. Results revealed that microwave treatment at 55°C for 10 minutes in $MgCl_2$ solution or in distilled water could significantly alter the membrane ultrafiltration coefficient. Interestingly, the same trend was observed in both groups, where the permeability values tend to decrease when treated in distilled water or at a salt concentration of 1%. The permeability values tend to increase with increasing salt concentration from 3 to 7%. The lowest and the higher permeabilities were observed to be at a salt concentration of 1%, and 7%, respectively in both groups. The effect of microwave enhancement on flux is manifested at 7% Group I & II due to the effect of higher salt concentration during MW utilization. It is interesting to notice that higher salt concentration is needed to improve utilization of MW energy. Hemodialysis membrane flux is one of the most important determining parameters in the dialysis process. Commercially available hemodialysis membranes are classified according to membrane flux into three main categories low, high flux, and protein leak membranes. Recent studies indicate that high flux membranes are the most adequate membranes for dialysis with the lowest mortality rate [34, 35].

3.8.2. Sieving coefficient

The sieving coefficient (SC) indicates the possibility of passage of various toxins through a particular dialysis membrane. SC of small toxins including urea and creatinine was studied for PS HF membranes after one and two hours of operation as presented in Table 6. Urea sieving coefficient values equal to or exceeding 0.95 were found for most of the studied membranes except for Amw1%, AHmw and AHmw1% which had the least SC values of 0.61, 0.86 and 0.68 after 1 hour of operation. This is consistent with the membrane permeation results. Also, creatinine SC values approached unity for all studied samples again except for Amw1%, AHmw and AHmw1%. After 2 hours of treatment, some SC values barely exceeded one, which could be explained as a result of concentration polarization [36, 37]. High values of SCs for urea and creatinine are important parameters indicating the ability to use such membranes in hemodialysis application. It may be concluded that selecting proper treatment conditions could alter membrane flux while maintaining acceptable SC values. This result is consistent with a previous study which revealed that microwave post-treatment could increase PES-LiBr membrane flux by 23% with a slight increase in membrane rejection [16].

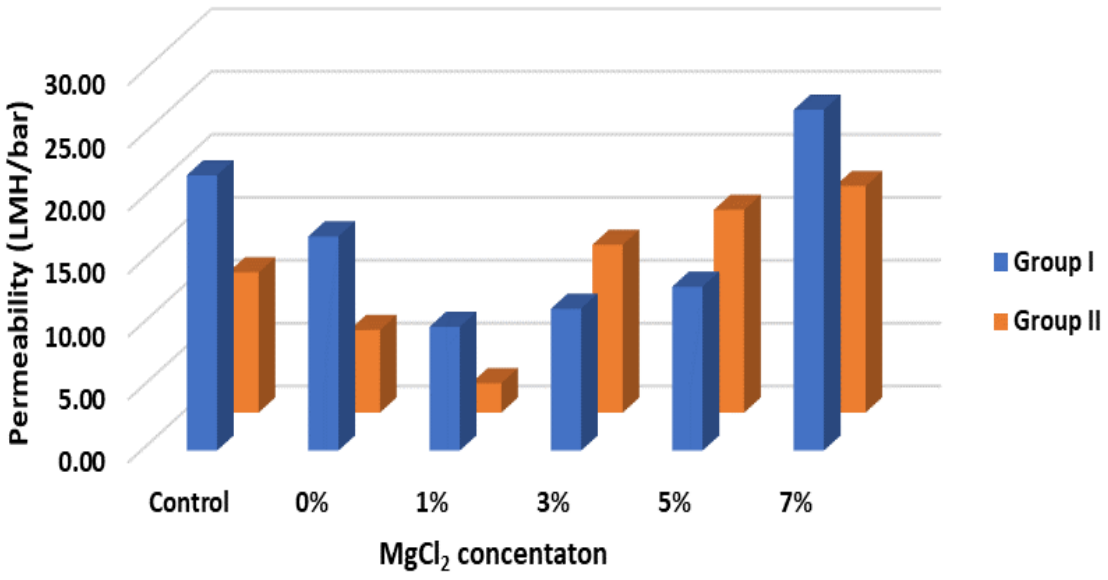

Figure 9: Pure water permeability of studied PS membranes

Table 6: Urea and creatinine sieving coefficient of raw and treated PS HF membrane

Sample		Sieving coefficient*			
		Urea		Creatinine	
		1st hr.	2nd hr.	1st hr.	2nd hr.
A	Group I	0.99	1.01	0.98	1
Amw		0.95	0.97	0.93	0.95
Amw1%		0.61	0.95	0.91	0.95
Amw3%		0.98	0.99	0.983	1
Amw5%		0.95	0.97	1	1.03
Amw7%		0.96	0.99	0.98	1.01
AH	Group II	0.96	0.98	0.97	1.01
AHmw		0.86	0.92	0.76	0.91
AHmw1%		0.68	0.95	0.75	0.95
AHmw3%		1	1.02	0.95	0.996
AHmw5%		0.977	1.011	0.975	0.986
AHmw7%		0.968	1.011	0.956	1.004

* All sieving coefficient experiments were performed at TMP=0.5 bar.

In view of the above-mentioned analysis, the best conditions should be associated with increased hydrophilicity, lower contact angle, improved external surface roughness and higher salt concentration 5 to 7% at stated microwave treatment conditions.

4. Conclusions

Microwave post treatment has the potential to induce changes in HD HF membrane properties and separation performance. Structural stability of PS membranes was observed via both NMR and FTIR analysis. Membrane mechanical strength and hydrophilicity could be significantly enhanced using MW treatment. A significant change was also observed in the membrane zeta potential. It was observed that roughness (Ra) of H_2O_2 MW treated sample in distilled water was decreased by 39% compared to the control sample. Microwave treated samples showed Ra roughness between (7-17 nm) and (7-16) for Groups I and II respectively. The obtained results agree with the reported roughness for commercial membranes. MW treatment could alter membrane flux within ranges of (9.8 to 27.1) and (2.3- 18) $L.m^{-2}.hr^{-1}.bar^{-1}$ for raw and H_2O_2 treated PS membranes respectively with slight changes in sieving coefficient. Microwave treatment could be considered a low-cost effective method for tuning HD HF membrane characteristics and performance without affecting membrane structure and stability.

3. Conflicts of interest

There are no conflicts to declare.

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