

Investigating the Effect of Various Oxidizing Agents on the Surface Functionalization of Microporous Polypropylene Membranes

Milad Fonouni, Reza Yegani, Akram Tavakkoli, and Sanaz Mollazadeh

Abstract—Wet chemical functionalization is an easy and efficient method, which connects the polar functional groups to the surface of polymeric membranes. In this work, KClO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 were dissolved in sulfuric acid and used to functionalize microporous polypropylene (PP) membranes, fabricated via thermally induced phase separation (TIPS) method. The optimum concentration of oxidizing agents and sulfuric acid as well as the membrane immersion time in oxidizing solutions were determined. The percentage of re-construction phenomenon was about 3.1%, 24% and 34.7% for PP membrane treated by KClO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 , respectively. The results showed that the absorbance intensities of $-\text{OH}$ and $\text{C}=\text{O}$ peaks as well as the variety of functional groups in the samples treated by KClO_3 are remarkably higher than that of the samples treated by $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 . BSA filtration experiments revealed that the total fouling ratio (TFR) and irreversible fouling ratio (IFR) decreased from 75% and 63.6% for pristine membrane to 50.3%, 53.4%, 55.6% and 27.6%, 27.6%, 27.3% for modified membranes by KClO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 , respectively. The flux recovery (FR) of treated membranes was about twice higher than that of the nascent membrane. The results indicated that incorporation of hydrophilic functional groups on the surface of PP membranes improves the fouling resistance behavior.

Keywords: functionalization, KClO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , microporous polypropylene (PP) membrane, wet chemical oxidation

I. INTRODUCTION

Application of polymeric membranes in microfiltration (MF) and ultrafiltration (UF) processes have attracted great attention [1]. Polyolefin based polymeric membranes such as polypropylene (PP) and polyethylene (PE) exhibit exceptional abilities including excellent resistance to various acidic and alkaline solutions, cost-effectiveness, high stiffness, good tensile strength, and inertness toward acids, alkalis and wide range of chemical solvents [2,3]. However, they suffer from poor functionality, which restricts their application in many industries. Their intrinsic hydrophobic nature results in easy fouling during protein purification and recovery as well as membrane bioreactors. Therefore, the membrane surface need to be modified to

obtain a better performance and higher resistance against fouling phenomena [4]. Due to this dilemma, surface modification of polymers has long been considered as a major objective in variety of research topics. Surface modification has recently attracted great attention since it provides more potential and easier procedure than other methods *e.g.* polymer blending [5]. It is generally accepted that an increase in membrane hydrophilicity offers better fouling resistance because protein and many other foulants are naturally hydrophobic compounds [4]. Among the various surface modification techniques, the dry method includes activation of polymer surface with air [6], oxygen [7], argon [8] and ammonia [9] plasma; UV/ozone [10, 11]; and corona discharge [12]. Although dry methods look promising in the laboratory scale, their industrial applications and scale up seem to be more challenging due to the limitation of areas that can be covered by UV and plasma devices and require expensive and intricate equipment. The wet method involves either deposition of a suitable layer over the membrane surface through physical adsorption of charged amphiphilic molecules, copolymer layer, layer-by-layer (LBL) self-assembly or through chemical modification using self-assembled monolayers (SAM), UV grafting or direct treatment with reactive chemicals like piranha solution [13]. In wet chemical oxidation methods, conventional acids such as nitric acid, sulfuric acid and phosphoric acid, alone or in combination with hydrogen peroxide, sodium hypochlorite, permanganate, potassium chromate, potassium dichromate and transition metal nitrates are used [14]. Due to the presence of tertiary carbons and unsaturated sites in PP matrix, oxidation potential is greatly enhanced, leading to the formation of oxygen-containing groups, which greatly affect the surface polarity and the adhesion properties of the polymer [15,16]. Tehrani and Shoushtari [15] studied the effect of chemical oxidation treatment on dyeability and improvement of tonality of PP fibers using a mixture of potassium chlorate and sulfuric acid. FTIR spectroscopy confirmed the presence of polar groups such as $-\text{OH}$. However, in comparison with untreated fibers, a rapid decline in tenacity and tensile strain of oxidized samples were observed. They suggested that dissolving of oxidizing agents in sulfuric acid is more efficient than other acids and has a less negative impact on the membrane physical properties. Debashis *et al.* [13] studied the hydrophilicity and stability of chemically modified PDMS surface using piranha and KOH solutions. Their findings demonstrated a maximum reduction in contact angle from 110 to 27 degree after the surface treatment.

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J. C. Eriksson *et al.* [17] has explored that dissolution of KMnO_4 in H_2SO_4 can efficiently oxidize the PE surfaces. They also examined the oxidizing performances of other oxidizing agents such as KClO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ on different polymers such as polystyrene. According to their study, the main chemical groups formed on the treated PE surface using $\text{KMnO}_4/\text{H}_2\text{SO}_4$ solution were sulfo, hydroxyl, carboxyl, carbonyl and ester groups. However, they did not investigate the physical properties of the treated surface. In the most wet chemical treatment methods, researchers mainly focused on the variety of created functional groups without paying attention to the microporous structure of the membrane. For the membrane related studies, it is very important to functionalize the surface without inflicting any serious damage on the membrane microscopic structure and mechanical strength. Therefore, in this work the impacts of various oxidizing agents such as potassium chlorate, potassium permanganate and potassium dichromate, solved in sulfuric acid, on the surface functionality, surface hydrophilicity and anti-fouling properties of PP microporous membranes were investigated. A set of analyses including Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), static contact angle measurement, ATR-FTIR analysis, pure water flux and mechanical strength measurement was carried out to characterize the membranes. Furthermore, anti-fouling behavior of the treated and nascent membranes was investigated through dynamic filtration of BSA protein solution.

II. MATERIALS AND METHODS

Isotactic polypropylene (iPP) with commercial grade (EPD60R, MFI= 0.35 g/10 min) was purchased from Arak Petrochemical Co. Analytical grade of potassium chlorate (KClO_3), potassium permanganate (KMnO_4) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) were purchased from Merck, used as oxidizing agents. Reagent grade of sulfuric acid was purchased from Merck, used as solvent for oxidizing agents. Mineral oil (MO) as diluent, acetone as extracting agent and Irganox 1010 as heat stabilizer were purchased from Acros Organics, Merck and Ciba Co., respectively. Bovine serum albumin (BSA, $M_n = 67$ kDa), purchased from Sigma-Aldrich, was used as organic foulant to evaluate the membrane anti-fouling performance. Buffer solution was prepared using HPLC grade water (less than 18 $M\Omega$) obtained from Razi Serum Co. All chemicals were used as received without any further purification unless otherwise described.

A. Fabrication of Flat Sheet Microporous Polypropylene (PP) Membrane

Flat sheet PP membranes were prepared via thermally induced phase separation (TIPS) method using in-house manufactured sealed batch mixer setup. 29 wt% PP, 70 wt% MO and 1 wt% of heat stabilizer were fed to a glass vessel. The sealed glass vessel was kept in the silicone oil bath at 170°C and blended for 2 h. The solution was allowed to degas for 30 minutes and then the

homogenized dope solution was poured on pre-heated glass plates and spread out using a casting knife and immediately immersed into water bath with an adjusted temperature to induce phase separation. The thickness of all cast membranes was fixed at 500 μm . The obtained samples were detached from the glass and immersed in acetone for 24 h to extract the diluent. Membranes were dried in a vacuum oven at room temperature for 24 h. Differential scanning calorimetry (DSC-Shimadzu 60) analysis confirmed that no mineral oil was remained in the fabricated membranes (data not shown). The amount of initial materials and fabrication procedure were selected according to the optimum values reported in our previous published articles [18,19].

B. Membrane Surface Modification and Characterization

Oxidizing solutions were prepared by dissolving measured amounts of oxidizing agents and sulfuric acid at ambient conditions. Membrane surface modification was carried out by immersing the PP membranes in the oxidizing solutions. In this regard, PP membranes were soaked in oxidizing solutions for a specific time intervals and subsequently were immersed in DI water to stop the oxidation reaction. Treated membranes were dried in vacuum oven at room temperature for 24 h. A set of characterization tests consisting of SEM, ATR-FTIR analysis, static contact angle measurement, AFM analysis, mechanical strength measurement, and pure water permeation was carried out. Dynamic protein fouling experiments were also performed to investigate the fouling specifications of chemically modified membranes.

C. Static Contact Angle Measurement and AFM Analysis

The hydrophilic/hydrophobic properties of the treated membranes were examined by the static contact angle measurement. The static contact angle of a drop of water on the membrane surface was measured by contact angle goniometer (PGX, Thwing-Albert Instrument Co.). In order to minimize the inaccuracy of measurement, at least 5 contact angles on different points of the samples were averaged to get a reliable result. Atomic force microscopy (AFM) examinations for surface roughness analysis were carried out using Nanosurf Mobile-Smicroscope. The tapping mode was used to map the membrane morphology at room conditions. Samples were prepared by cutting the membranes longitudinally in very narrow ribbons of less than 5 mm wide and 5 mm long.

D. Tensile Strength

The tensile strength of the fabricated membranes was determined by using a tensile testing machine (STM-5, Santam, Iran) at an extension rate of 50 mm min^{-1} . The samples were cut into pieces 8.0 cm in length and 1.5 cm in width. The effective length was 5 cm and two 1.5 cm edges of the samples were stuck in the machine. The thickness of each sample was measured by a micrometer. Three trials were conducted for each sample and the mean values were reported.

E. Attenuated Total Reflectance Spectra- Fourier Transform Infrared Spectroscopy (ATR-FTIR)

In order to investigate the chemical structure and the type of functional groups created on the membrane surface, ATR-FTIR analyses were carried out by infrared spectroscopy apparatus (BRUKER-TENSOR 27).

F. Scanning Electron Microscopy (SEM)

The microscopic morphology of the fabricated membranes was characterized by Scanning Electron Microscope (SEM) (MV2300CAM SCAN) with an accelerating voltage of 15 kV. Cross-section samples were prepared by fracturing the membranes in liquid nitrogen. All samples were coated with gold by sputtering before observation to make them conductive.

G. Pure Water Flux

Pure water flux (PWF) of membranes was determined using an in-house fabricated dead-end filtration system in which the membrane area is 5 cm². A flat sheet membrane module was connected to the bottom side of a cylindrical vessel with a volume of 1.5 L. The contents of the vessel were gently mixed using a magnetic stirrer during all filtration tests. In order to minimize the compaction effects, the pre-wetted membranes were compacted for 30 min at 2.5 bar. Then the pressure was reduced to 2 bar and after reaching steady state, water flux was calculated through the following equation:

$$J = M / (t.A) \quad (1)$$

where J is the pure water flux, M is the collected mass of water (kg), A is the membrane area (m²) and t is the time (h). All permeation analyses were repeated at least 3 times and the average values were reported.

H. Filtration Experiments and Fouling Analyses

In order to evaluate the fouling behavior of treated membrane, BSA protein filtration experiments were carried out in a dead-end filtration setup with an effective membrane area of 5 cm². A method similar to one reported by Jafarzadeh and Yegani, [20, 21] and Yang *et al.* [22] was used and the obtained results were compared with the results obtained from pristine membrane. The protein solution was prepared by dissolving 1.0 g of BSA powder in 1 L of standard phosphate buffer saline (PBS) solution. The amount of total fouling ratio (TFR), reversible fouling ratio (RFR), irreversible fouling ratio (IFR) and flux recovery (FR) was calculated using the following equations:

$$TFR = \left(\frac{J_0 - J_1}{J_0} \right) \times 100 \quad (2)$$

$$RFR = \left(\frac{J_2 - J_1}{J_0} \right) \times 100 \quad (3)$$

$$IFR = \left(\frac{J_0 - J_2}{J_0} \right) \times 100 \quad (4)$$

$$FR = \left(\frac{J_2}{J_0} \right) \times 100 \quad (5)$$

where J_0 , J_1 , J_2 respectively are the pure water flux through a clean membrane, the pure water flux of the

fouled membrane and the pure water flux of the membrane after cleaning and removing the cake layer with sponge over the membrane surface. In all experiments, the filtration analyses were conducted under the constant trans-membrane pressure (2.0 bar), constant room temperature (20°C) and constant stirring speed (400 rpm) of the reservoir. All permeation analyses were repeated at least 3 times and the average values were reported.

III. RESULTS AND DISCUSSION

A. Selecting the Appropriate Conditions for Surface Treatment of the Membranes

The optimized concentration of sulfuric acid, the type and concentration of oxidizing agent and the immersion time are key parameters for better control of the rate of oxidation reaction and the efficacy of the surface modification. A higher acid concentration, a stronger oxidizing agent and a longer immersion time correspond with a higher potential for membrane to be destroyed. In the case of lower acid concentration and a weak oxidizing agent, however, either the reaction time will be increased or the degree of functionalization would not be satisfactory. In this regard, a set of experiments was carried out to determine the appropriate concentrations of sulfuric acid and oxidizing agents, and the suitable immersion time. Among several oxidizing agents, KClO₃, KMnO₄ and K₂Cr₂O₇ were selected as the most conventional oxidizing agents [17]. Experiments were carried out in three different sets: set A, B and C, which correspond with KClO₃, K₂Cr₂O₇ and KMnO₄ oxidizing solutions, respectively. Three different concentrations of sulfuric acid consisting 98 wt%, 80 wt% and 60 wt% ; nominated as “strong”, “moderate” and “weak” acidic solutions respectively were prepared, while the concentration of oxidizing agents were kept constant. The PP membrane samples were immersed in prepared solutions for different time intervals, e.g. 30, 60, 90, 120 and 180 min and subsequently were soaked in DI water for 30 min to stop the oxidation reaction. The comparison between the efficacy of various oxidizing agents was performed at constant weight percent of each oxidizing agent in various acidic solutions. The oxidizing circumstances were labeled as a:b:c where a, b and c represent the weight percent of the oxidizing agent, the weight percent of acid solution and the immersion time (min), respectively. In sets A and B of the experiments, measured amount of KClO₃ and K₂Cr₂O₇ were dissolved in “strong”, “moderate” and “weak” sulfuric acid solutions. According to the literatures, the weight percent of oxidizing agents in all solutions was kept constant at 1 wt% [23]. KMnO₄ is a strong oxidizing agent and should be carefully handled when preparing the oxidizing solution, since it has been listed as the most dangerous reagent. Its immiscibility in concentrated sulfuric acid (>80 wt.%) has been reported [17, 24], therefore, in set C of the experiments, measured amount of KMnO₄ was dissolved in three different concentrations of sulfuric acid including 70 wt%, 60 wt% and 50 wt%, respectively. The results of

contact angle and mechanical strength measurements for set A are shown in Fig. 1(a) and Fig. 1(b) respectively. As can be seen in Fig. 1(a) as acid concentration increased, contact angle decreased for all samples. It is observed that the decrease in contact angle was more pronounced, when the “strong” sulfuric acid was used. However, Fig. 1(b) shows that the mechanical strength of treated membranes with “strong” sulfuric acid was severely decreased to lower than the threshold value of mechanical tensile required for MF and UF operations [25]. On the other hand, for the membranes treated with “weak” sulfuric acid, the decrease in contact angle was negligible. Therefore, sulfuric acid with “moderate” concentration, 80 wt%, was selected as an appropriate acid concentration for the rest of the experiments. In order to select the appropriate concentration of oxidizing agent, three different concentrations of 1, 2 and 3 wt% $KClO_3$ in “moderate” sulfuric acid were prepared.

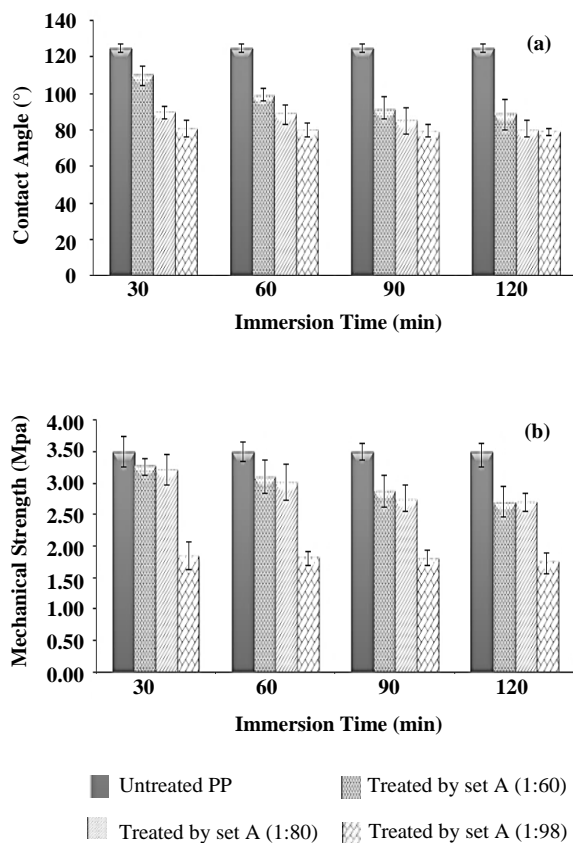


Fig. 1. The effect of concentration of sulfuric acid containing 1 wt% of $KClO_3$, and various immersion times on: a) static contact angle, and b) mechanical strength of PP microporous membrane. (Set A of treatment oxidizing solutions).

The results for contact angle and mechanical strength are shown in Fig. 2(a) and Fig. 2(b), respectively. Fig. 2(a) shows that the rate of decrease in contact angle was quite high in the initial immersion time intervals; less than 30 min. However, when immersion time increased to 120 min, the contact angle began to level off. Any further increase in immersion time, e.g. 150 and 180 min, increased the contact angle. Fig. 2(b) depicts that with increasing the

concentration of oxidizing agent (higher than 1 wt%), mechanical strength again decreased to the values lower than the threshold mechanical tensile. It is likely due to the breakage of the interconnected microporous structure of the membrane network. It is observed that when immersion time increased to more than 120 min, mechanical strength increased as well. It is mainly due to the re-construction phenomenon, which usually occurs for polyolefins immersed in oxidizing solutions for longer time intervals [3]. Similar experiments were carried out for sets B and C. The obtained results are summarized in Tables I and II. The selection strategy to determine the optimized compositions of oxidizing solutions was based on the fact that treated membranes should expose a reasonable degree of hydrophilicity, contact angle (as lower as possible) and mechanical strength. Therefore the optimum values for sets A, B and C were selected as (1:80:120), (1:80:60) and (1:60:60), respectively, which hereafter, will be mentioned as the optimized oxidation circumstances.

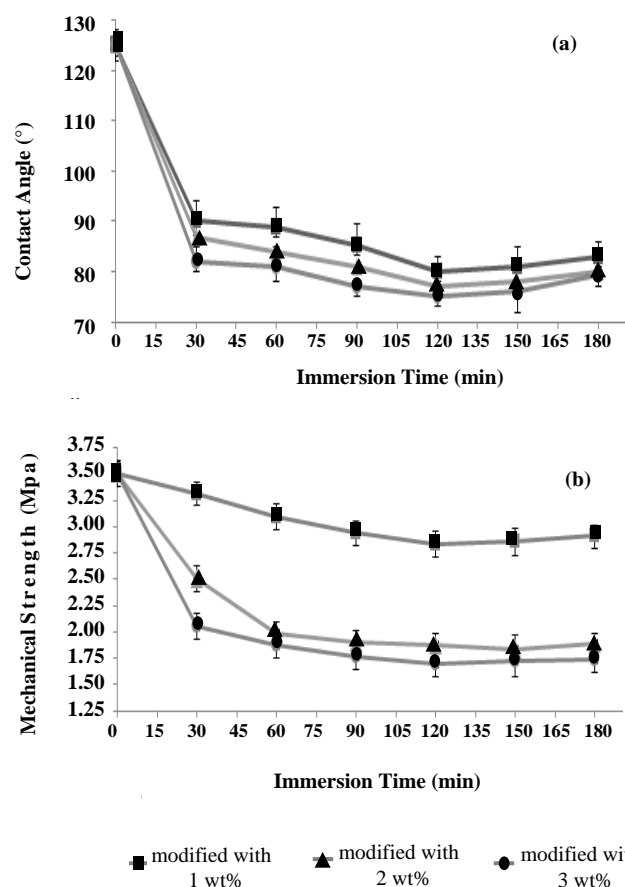


Fig. 2. The effect of the concentration of $KClO_3$ oxidizing agent in 80 wt% sulfuric acid in various immersion times on: a) static contact angle, and b) mechanical strength of PP microporous membrane. (Set A of treatment oxidizing solution).

B. Cross Section and Surface Morphology

Cross section SEM images with different magnifications and surface SEM micrographs of PP membranes treated by optimized oxidation circumstances in different magnifications are shown in Figs. 3, 4 and 5, respectively. Comparing the treated PP membranes with pristine one,

confirms that almost no significant changes were made on the shape, structure and morphology of the cross section and surface of the membranes. The obtained results are consistent with our proposed selection strategy in which the creation of serious effects on the microporous structure of membranes was prevented. An interesting aspect of the oxidized polymer surfaces is worth mentioning here. The oxidized surfaces are usually higher in energy than the original pristine surface and may experience a phenomenon called surface re-construction, which was noted early by Baszkin *et al.* [26] and Andrade *et al.* [27], and has been well studied by Gagnon and McCarthy [28], and Holmes-Farley *et al.* [29]. This phenomenon includes diffusion of the polar oxygen functionalities away from the surface toward to the bulk.

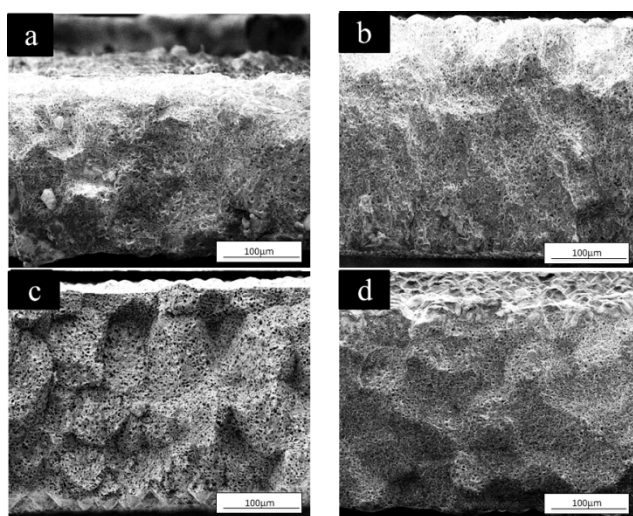


Fig. 3. The cross-sectional SEM micrographs of PP membranes at low magnification. a) Pristine PP membrane, b) treated by optimized set A (1 wt% KClO₃ : 80 wt% H₂SO₄ : 120 min immersion time), c) treated by optimized set B (1 wt% K₂Cr₂O₇ : 80 wt% H₂SO₄ : 60 min immersion time), d) treated by optimized set C (1 wt% KMnO₄ : 60 wt% H₂SO₄ : 60min immersion time).

TABLE I

THE EFFECT OF THE CONCENTRATION OF SULFURIC ACID CONTAINING 1 WT% OF K₂Cr₂O₇ (SET B) AND KMnO₄ (SET C) AT VARIOUS IMMERSION TIMES ON STATIC CONTACT ANGLE (CA) AND MECHANICAL STRENGTH (MS) OF TREATED PP MICROPOROUS MEMBRANE

Experiment Set		Immersion time			
Characterization	Set B	30 min	60 min	90 min	120 min
CA	(1:98:t)	*	*	*	*
M.S		*	*	*	*
CA	(1:80:t)	91.2	84.5	81	80.1
M.S		3.32	2.84	1.92	1.85
CA	(1:60:t)	110.2	98.8	91.2	89
M.S		3.27	3.1	2.88	2.6
Characterization	Set C	30 min	60 min	90 min	120 min
CA	(1:70:t)	92	81.8	80.9	79
M.S		2	1.9	1.83	1.77
CA	(1:60:t)	93.3	83.7	81	80
M.S		3.1	2.8	1.95	1.82
CA	(1:50:t)	105	100	97.1	93
M.S		3.34	3.14	2.98	2.78

*Brown precipitate was formed on the membrane surface

TABLE II

OBTAINED RESULTS FOR THE EFFECT OF K₂Cr₂O₇ (SET B) AND KMnO₄ (SET C) OXIDIZING AGENT CONCENTRATIONS IN 80 AND 60 WT% OF SULFURIC ACID IN VARIOUS IMMERSION TIME ON THE STATIC CONTACT ANGLE (CA) AND MECHANICAL STRENGTH (M.S) OF TREATED PP MICROPOROUS MEMBRANE.

Experiment Set		Immersion time					
characterization	Set B	30 min	60 min	90 min	120 min	150 min	180 min
CA	(1:80:t)	91.2	84.5	81	80.1	80.7	81.2
M.S		3.32	2.84	1.92	1.85	1.88	1.91
CA	(2:80:t)	82.66	81.4	80	78.9	79.2	80.2
M.S		1.89	1.79	1.7	1.64	1.77	1.81
CA	(3:80:t)	80.1	79.1	78.2	76	78.3	78.9
M.S		1.65	1.6	1.51	1.48	1.5	1.59
characterization	Set C	30 min	60 min	90 min	120 min	150 min	180 min
CA	(1:60:t)	93.3	83.7	81	80	80.4	80.9
M.S		3.1	2.8	1.95	1.82	1.88	1.9
CA	(2:60:t)	91.7	81.2	80	79	79.5	80.2
M.S		1.9	1.86	1.79	1.75	1.8	1.9
CA	(3:60:t)	90	90.2	79	78	78.2	79.2
M.S		1.85	1.78	1.7	1.69	1.74	1.79

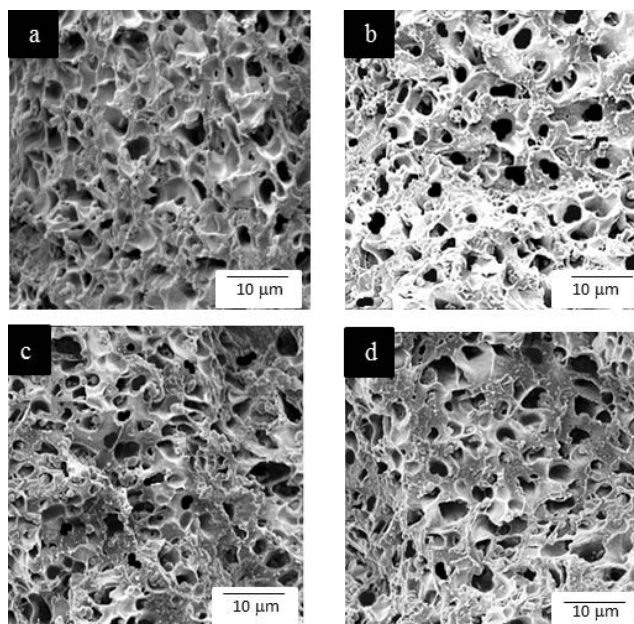


Fig. 4. The cross-sectional SEM micrographs of PP membranes at high magnification. a) Pristine PP membrane, b) treated with optimized set A (1 wt% KClO₃ : 80 wt% H₂SO₄ : 120 min immersion time), c) treated with optimized set B (1 wt% K₂Cr₂O₇ : 80 wt% H₂SO₄ : 60 min immersion time), d) treated with optimized set C (1 wt% KMnO₄ : 60 wt% H₂SO₄ : 60 min immersion time).

Fig. 6 shows the changes in contact angle with elapsed time intervals for treated PP membranes with optimal oxidizing solutions; sets A, B and C. The minimum initial contact angles, obtained immediately after treatment with KClO₃, K₂Cr₂O₇ and KMnO₄ were 80, 84.5 and 83.7, respectively, and subsequently increased and saturated to about 82.5, 105 and 115, respectively, after about 15 days of preservation. In the case of membrane treated by KClO₃, the re-construction trend shows that the increase in contact angel was almost leveled off after 15 days. For other oxidizing agents; however, the contact angle was still increasing after 15 days. Increase in contact angle was in good agreement with other reports [11,30,31] indicating that there was a slow hydrophobic recovery of the

chemically treated surface due to the migration of untreated low molecular weight (LMW) species, from the bulk to the surface, or due to the re-construction of the hydrophilic functional groups away from the surface [13]. Thus the recovery percentage of the measured contact angels for the treated PP membranes was estimated to be about 3.1%, 24.0% and 37.4% for KClO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 oxidizing agents, respectively. The findings also concluded that KClO_3 seemed to have very good performance and stability for extended periods with a contact angel saturation value lower than other oxidizing agents.

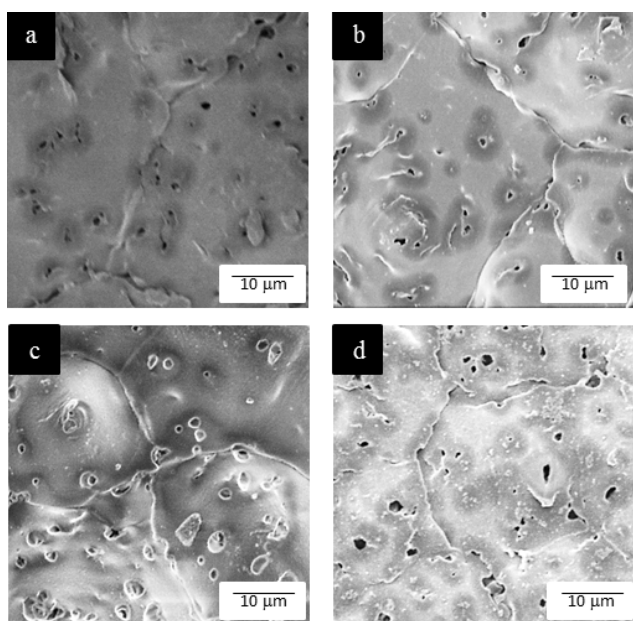


Fig. 5. The surface SEM micrographs of PP membranes. a) Pristine PP membrane, b) treated with optimized set A (1 wt% KClO_3 : 80 wt% H_2SO_4 : 120 min immersion time), c) treated with optimized set B (1 wt% $\text{K}_2\text{Cr}_2\text{O}_7$: 80 wt% H_2SO_4 : 60 min immersion time), d) treated with optimized set C (1 wt% KMnO_4 : 60 wt% H_2SO_4 : 60 min immersion time).

TABLE III

LIST OF ATR-FTIR PEAKS OBTAINED FOR THE VARIOUS FUNCTIONAL GROUPS PRESENT ON THE PP MICROPOROUS MEMBRANE IN FIG. 6 AND FIG. 7.

IR region (cm^{-1})	Functional group
3050-3700	O-H stretching vibration
2700-2950	C-H stretching vibration
1610-1820	C=O stretching vibration
1384-1475	(CH_2 and CH_3) flexural vibration
1166	C-O stretching vibration of carboxylic
1045	C-O stretching vibration of alcohol
850-910	S-O stretching vibration

C. ATR -FTIR Analysis

FTIR spectroscopy was used to describe the existence of various functional groups and the quantity of chemical changes on the PP membrane surface after treatment using optimum condition and oxidizing solutions. Fig. 7 indicates the ATR-FTIR spectra of the pristine and treated PP membranes. The existence of functional groups of different chemical bonds at PP surface corresponding to

different peaks was analyzed to choose the best oxidation circumstance among the sets A, B and C. The spectra with respect to wave numbers are listed in Table III with remarks showing conditions for functionalized PP membrane.

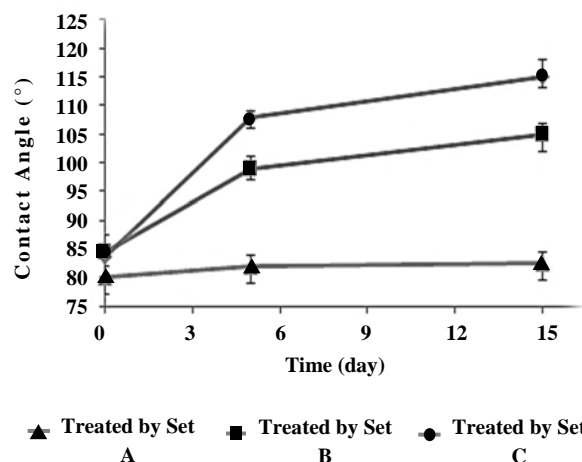


Fig. 6. Re-construction effect of PP microporous membranes treated with optimized oxidation circumstances of: a) set A, b) set B, c) set C.

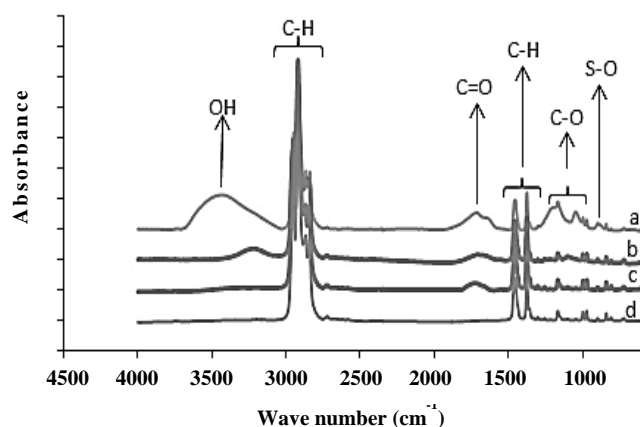


Fig. 7. ATR-FTIR spectra of: a) PP microporous membrane treated with set A, b) PP microporous membrane treated with set B, c) PP microporous membrane treated with set C, and d) pristine PP microporous membrane.

The peaks in the range of 2700-2950 and 1384-1475 cm^{-1} , appeared in all samples, correspond to the C-H bond stretching vibration and flexural vibrations of CH_2 and CH_3 groups of the C-H bond in PP, respectively. The peaks in the range of 3050-3700 cm^{-1} correspond to the O-H bond stretching vibration and the peaks in the range of 1610-1820 cm^{-1} correspond to the C=O bond stretching vibration. Obtained results show that the absorbance intensities of O-H and C=O peaks in the samples treated by set A (KClO_3) are remarkably higher than those in the samples treated by set B ($\text{K}_2\text{Cr}_2\text{O}_7$) and set C (KMnO_4). The peaks in the range of 1166 and 1045 cm^{-1} correspond to C-O bond stretching vibration of carboxylic acid and alcohol functional groups, respectively. Similar to the O-H and C=O functional groups, the absorbance intensity of C-O peaks in the samples treated by set A (KClO_3), are extremely higher than that in the samples treated by other

oxidizing agents. Finally the peaks in the range of 850-910 cm^{-1} correspond to the S-O bond stretching vibration [32]. The results confirm the variety of the functional groups created on the PP membrane surface using KClO_3 oxidizing agent. It was supposed that the higher absorbance intensity as well as the variety of functional groups might enhance the benefit of other following post treatment processes, therefore, the spectra of the samples in set A of experiments was taken after different immersion times of 60, 90, 120, 180, 240 min, which are shown in Fig. 8. The gradual increase of all functional groups intensities with treatment time signifies the hydrophilic characteristics of the PP surface modified with KClO_3 . In comparison with other functional groups, the increase in the absorbance of O-H group is more pronounced, suggesting that KClO_3 would be a promising oxidizing agent for those surfaces reacting with silane coupling agents. The silane capability of increasing surface wettability resulting in chemical bridge formation with OH covered substrates is previously reported [33]. It is due to the fact that the silanol groups formed by hydrolyzation of silane alkoxy groups with inorganic materials, adhere and bond to the hydroxyl groups on the surface of the materials [34].

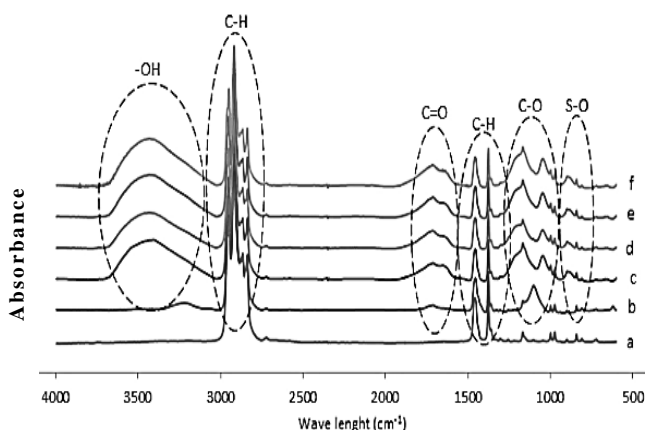


Fig. 8. ATR-FTIR spectra of: a) pristine PP microporous membrane, b-f): PP microporous membrane treated with set A (1:80:t) in various immersion times of 60, 90, 120, 180 and 240 min.

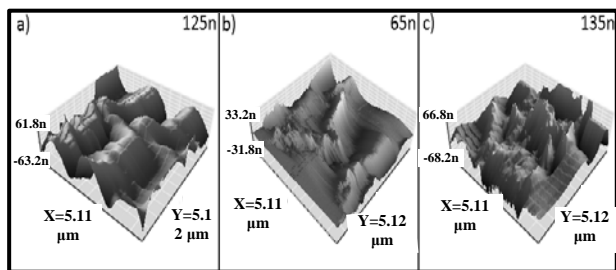


Fig. 9. Effect of immersion time on pure water flux of PP microporous membranes treated with set A, set B and set C, at fixed concentration of oxidizing agent and sulfuric acid.

D. Effect of Surface Modification on Pure Water Flux

Prepared membranes were treated with optimized composition of oxidizing agents denoted by sets A, B and C in different time intervals and then pure water flux (PWF) tests were carried out to identify the impact of

surface modification on the membrane performance. The obtained results are shown in Fig. 9.

The pure water flux (PWF) of pristine PP membrane is about $28 \text{ L m}^{-2} \text{ h}^{-1}$, which corresponds with the data shown by zero immersion time. The results showed that PP membranes treated by all oxidizing agents always kept higher PWF. It can be seen from Fig. The maximum PWF for the PP membranes treated by set A was obtained when the membrane was immersed for 120 min, while the maximum PWF values for treated membranes by sets B and C were achieved when the membranes were immersed for 60 min. To our surprise, the PWF results for all sets were consistent with the optimized oxidation circumstances, which were obtained in the section, entitled as “selecting the appropriate conditions for surface treatment of the membranes”. In fact, for permeation process, the pore size and surface hydrophilicity are key parameters which influence the water flux [35]. Since our SEM micrographs (Figs. 4 and 5) showed no discernible changes in the pore size and pore structure of the treated membranes, only surface hydrophilicity affect the improvement in PWF. An interesting point was observed for the PP membranes treated by set B as it showed the maximum PWF in comparison with other sets. In order to clarify this point, AFM images were taken for optimized oxidizing circumstances.

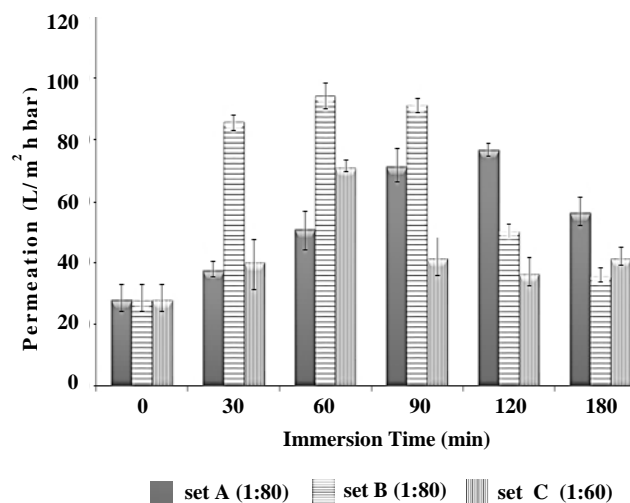


Fig. 10. AFM images of PP microporous membranes treated with a) set A, b) set B and c) set C.

The results, depicted in Fig. 10, revealed that the surface roughness of the samples treated by set B, is lower than that of the samples treated by sets A and C. Similar to our previous findings [20,21] the degree of roughness amplifies the wettability of the surface toward its intrinsic properties. For a hydrophilized surface in which contact angle is lower than 90° , roughening will decrease the contact angle resulting in higher PWF.

E. Protein Filtration and Fouling Analyses

Dynamic BSA protein filtration tests were carried out to investigate the surface properties and anti-fouling performance of the chemically treated membranes. In order

to omit the effect of electrostatic repulsion on antifouling properties, which might occur during chemical treatment processes, the pH of protein solutions was kept at 4.8 using an acidic buffer, since the isoelectric point (IEP) of BSA is 4.8.

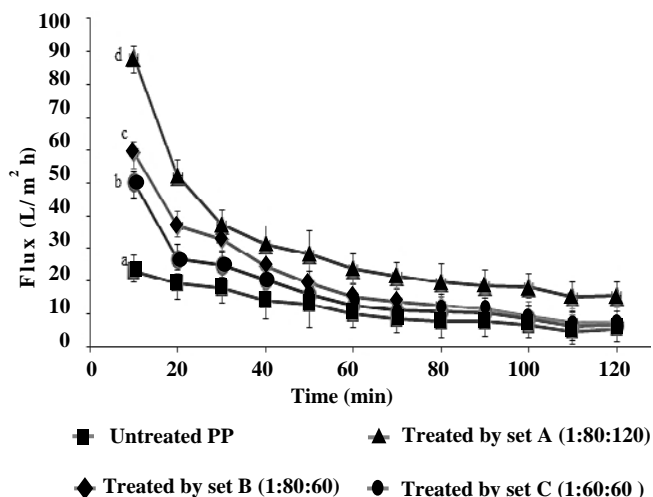


Fig. 11. Flux-time behavior of: a) pristine PP microporous membrane, b-d) PP microporous membranes treated with set C, set B and set A.

TABLE IV
ANALYSES OF FOULING PROPERTIES OF PRISTINE AND TREATED PP MICROPOROUS MEMBRANE BY OPTIMIZED OXIDIZING SOLUTION CIRCUMSTANCES OF SETS A, B AND C.

Samples	J_0 ($L \cdot m^{-2} \cdot h^{-1}$)	J_1 ($L \cdot m^{-2} \cdot h^{-1}$)	J_2 ($L \cdot m^{-2} \cdot h^{-1}$)	RFR(%) ^(a)	IFR(%) ^(b)	TFR(%) ^(c)	FR(%) ^(d)
Untreated PP	28	7	10.2	11.4	63.6	75	36.4
Treated by Set A (1:80:120)	76.8	38.2	55.6	22.7	27.6	50.3	72.4
Treated by Set B (1:80:60)	94.42	44	68.4	25.8	27.6	53.4	72.4
Treated by Set C (1:60:60)	72.92	32.4	53	28.3	27.3	55.6	72.7

- a) Reversible Fouling Ratio (RFR)
- b) Irreversible Fouling Ratio (IFR)
- c) Total Fouling Ratio (TFR)
- d) Flux Recovery (FR)

Fig. 11 compares the results of the flux decline behavior of treated and pristine membranes. The obtained results showed that the permeation flux of BSA protein solution for pristine membrane decreased rapidly at the beginning of filtration. However, the situation for treated membranes was different, in which the decrease in permeation fluxes were considerably delayed. This may be attributed to the adsorption and subsequently deposition of BSA onto the surface of the pristine membrane via strong hydrophobic interaction between protein and hydrophobic surface of the PP membrane. Existence of polar functional groups on the surfaces of treated membranes imposes the hydrophilic property and resists against protein fouling in the absence of electrostatic interactions. Additional information about

membranes fouling including, total fouling ratio (TFR), reversible fouling ratio (RFR), irreversible fouling ratio (IFR) and flux recovery (FR) are summarized in Table IV. It can be seen that the pristine PP membrane showed the highest TFR, confirming that this membrane was easily fouled by BSA molecules. Hydrophilic properties of treated membranes decreased the TFR from 75% for the pristine PP membrane to 50.3%, 53.4% and 55.6% for the treated membranes by set A, set B and set C, respectively. Moreover, IFR of the membranes decreased from 63.6% for pristine PP membrane to 27.6%, 27.6% and 27.3% for treated membranes by set A, set B and set C, respectively. This indicates that incorporation of hydrophilic functional groups on the surface of PP membranes not only increased the fouling resistance, but also decreased the irreversible fouling ratio. A similar trend was obtained for the FR values, in which treated membranes showed enhanced flux recovery in comparison with pristine membrane.

IV. CONCLUSION

Polymeric membranes suffer from poor functionality which restricts their application in many industries. Their intrinsic hydrophobic nature also causes them to be easily fouled in protein filtration and purification processes. Surface functionalization is an efficient method to introduce polar groups on the surface of polymeric membranes. Three strong and well identified oxidizing agents including $KClO_3$, $K_2Cr_2O_7$ and $KMnO_4$ were dissolved in sulfuric acid to prepare oxidizing solutions. The optimum concentration of oxidizing agent, sulfuric acid and membrane immersion time were determined. The obtained results concluded that the samples treated with $KClO_3$ seemed to exhibit better performance and stability for extended periods. In addition they showed a contact angle saturation value lower than the samples treated with $K_2Cr_2O_7$ and $KMnO_4$. ATR-FTIR results showed that the absorbance intensity of O-H, C=O and C-O peaks in the samples treated by $KClO_3$, were remarkably higher than that of the samples treated by $K_2Cr_2O_7$ and $KMnO_4$. BSA filtration experiments showed that the total fouling ratio (TFR) was remarkably decreased for the membranes treated by oxidizing solutions. Moreover, the portion of irreversible fouling ratio decreased in treated membranes while the portion of reversible fouling ratio and flux recovery increased. This indicates that incorporation of hydrophilic functional groups on the surface of PP membranes not only increases the fouling resistance, but also decreases the irreversible fouling ratio.

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