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Anti-fouling behaviors of surface functionalized high density polyethylene membrane in microfiltration of bovine serum albumin protein

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ABSTRACT

An essential characteristic for high performance inherently hydrophobic membranes such as microporous high density polyethylene (HDPE) membranes is to have a hydrophilic surface. In this project, wet chemical functionalization as a facile and effective method was developed to give a hydrophilic property to HDPE membranes using polar functional groups. $KClO_3$, $K_2Cr_2O_7$ and $KMnO_4$ were selected as oxidizing agents. The optimum concentrations and treatment time intervals were determined for each oxidizing agent. Water contact angle and pure water flux measurements were conducted to evaluate the surface hydrophilicity and membrane performance, respectively. The results showed that among different oxidizing agents, 1wt% $K_2Cr_2O_7$ solution with 60 min immersion time had the highest impact on the pure water flux. The percentage of re-construction phenomenon was about 4.70%, 21.94% and 32.6% for the HDPE membranes treated by $KClO_3$, $K_2Cr_2O_7$ and $KMnO_4$, respectively. In addition, the attenuated total reflectance spectra-Fourier transform infrared spectroscopy (ATR-FTIR) results confirmed the presence of hydroxyl groups (O–H peak appeared at 3418.78 cm^{-1}) in the membrane modified by $KClO_3$. Bovine serum albumin (BSA) filtration experiments revealed that the total fouling ratio (TFR) and irreversible fouling ratio (IFR) decreased from 88.10% and 42.60% for pristine membrane to 65%, 68% and 72% and 26.60%, 29.30% and 35% for the modified membranes treated by $KClO_3$, $K_2Cr_2O_7$ and $KMnO_4$, respectively. The results indicated that incorporation of hydrophilic functional groups on the surface of HDPE membranes improved the fouling resistance behavior. **Polyolefins J (2017) 4: 13-26**

Keywords: Microporous high density polyethylene (HDPE) membrane; wet chemical oxidation; functionalization; $KClO_3$; K_2Cr_2O7; $KMnO_4$.

INTRODUCTION

Polymer surface functionalization has become the topic of many researches in the field of materials science over the past decade. Such surface functionalization and modification play major roles in the outcome of processes ranging from degradation of polymers to fabrication of high performance biocompatible anti-fouling polymeric membranes. Interfacial chemistry at the polymer-liquid interface creates significant technological problems like adhesion, wettability, biocompatibility and gas permeability [1]. Previous researches on polymeric membrane separation technology highlighted unique and remarkable properties such as low capital and operating cost, relatively small footprint, lack of additives and ease of operation, demonstrating that the utilization of membranes in separation processes is a breakthrough in engineering and environmental processes [2-4]. It is important to know that the membrane used in a membrane process largely contributes to the

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final product quality or, in other words, the ''heart'' of a membrane process is the membrane itself. Therefore, a proper membrane is required for an effective separation process [5]. Current researches on membranes mainly focus on polymeric membranes due to their better control of the pore forming mechanism, higher flexibility and smaller spaces required for installation when compared to inorganic membranes [2]. Unfortunately, polymers, as initial materials for membrane fabrication, often do not possess the suitable surface properties needed for specific membrane separation applications (e.g. hydrophobic membrane in waste water treatment). In fact, some membrane polymers such as high density polyethylene (HDPE) and polypropylene (PP), that are mechanically strong and chemically stable, usually show inert surfaces properties from both chemically and biologically point of view. In the same manner, polymers with active surfaces usually do not possess excellent mechanical properties, critical for their successful application with a long lifespan. Due to this dilemma, surface functionalization of membrane polymers has been greatly studied as a new technology for polymeric membranes, especially used in the fields of biotechnology, bioengineering, and recently in wastewater treatment [6-8]. In general, there are two methods to prepare HDPE microporous membranes including thermally induced phase separation (TIPS) and melt-spinning and cold-stretching (MSCS) methods. Compared to those formed by the MSCS method, HDPE membrane prepared by the TIPS process shows well-controlled porosity, diversified pore structure and excellent mechanical property [9-13]. As a commodity of membrane material, HDPE imposes an excellent mechanical strength, thermal and physicochemical stability, hydrophobicity and low price [14-16]; untreated non-polar HDPE surfaces, however, have adverse problems in adhesion, coating, painting, coloring, packaging, etc. [17]. Applications of polymeric membranes in wastewater treatments e.g. application of polyolefin membranes in membrane bioreactor have also faced to many critical obstacles such as undesirable protein adsorption and cell adhesion on the membrane surface, due to the poor biocompatibility of polyolefin based membrane. Protein-induced membrane fouling is caused by protein adhesion on the membrane surface and protein deposition in the membrane pores. Membrane fouling during filtration can result in a significant loss of performance in selectivity and permeation flux, and thus may imply a limitation on the membrane application [18]. It is generally accepted that an increase in the membrane hydrophilicity offers a better fouling resistance because protein and many other foulants are hydrophobic in nature [19]. Commonly, there are several strategies to provide conventional hydrophobic membranes with hydrophilic properties, including surface coating [20, 21], surface modification by grafting hydrophilic monomers [22-24] and blending with hydrophilic polymers [25-27]. Among these modification methods, surface coating and grafting are suitable for the hydrophilic modification of the HDPE membrane fabricated via the TIPS method. However, both of those proposed methods suffer from some drawbacks. Firstly, the coated surface layers on the membrane surface are subjected to removal during operation or by aggressive cleaning procedures [20]. Secondly, the surface grafting may induce some changes in the membrane pore size distribution and result in reduced permeability. Moreover, both the methods are relatively complex two-step hydrophilic membrane forming processes [21, 28]. Wet chemical oxidation method seems to be promising due to its one-put one-step nature, in which conventional acids such as nitric acid, sulfuric acid, and phosphoric acid, alone or in combination with hydrogen peroxide, sodium hypochlorite, permanganate, chromate/dichromate of potassium and transition metal nitrates are used [18]. Gagnon and McCarthy [29] described a procedure designed to force the diffusion of polar organic functional groups from the bulk to the surface of polymers by taking advantage of interactions between polymer functional groups and a polar condensed phase in contact with the polymer. They used $KClO_3$ and sulfuric acid to chemically modify the polyethylene (PE) film. Their results revealed that it was possible to rationally control the polarity of polymer surfaces by controlling the number of polar functional groups created on the surface or away from the surface. Eriksson et al. [30] explored the chemical constitution of 20 $KMnO_4$/H_2SO_4 oxidized PE surfaces. Comparisons were made with $KClO_3/H_2SO_4$ and $K_2Cr_2O_7/H_2SO_4$ as oxidizing agents. According to their obtained results, the main chemical groups formed on the PE surface, treated by $KMnO_4/H_2SO_4$, were sulfo, hydroxyl, carboxyl, carbonyl and ester. However, they did not investigate the physical properties of the treated surface. Catoire et al. [31] studied the formation of carbonyl groups on the surface of the low-density polyethylene (LDPE)

by chemical oxidation. The treated surfaces were analyzed by scanning electron microscopy (SEM), attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy and Ca^{2+} adsorption tests. Their results showed that the M_n (II) ions were adsorbed on the polar sites produced by oxidation of PE. Wang et al. [32] investigated the surface treatment of linear low density polyethylene (LLDPE) and LDPE blends using nitric, sulfuric and chromic acids. Their results indicated that the most polar groups were incorporated into the samples treated by chromic acid. These findings were confirmed by SEM and surface roughness tests. In most wet chemical treatment methods, researchers mainly focused on the polymer surface without paying attention to the microporous structure of the membrane. In developing membrane-related researches, it is very important to functionalize the surface without inflicting any serious damage on the membrane mechanical strength and microscopic structure. Due to the microporous structure of HDPE membrane fabricated via the TIPS method, it is expected that the oxidizing solution can penetrate into the microporous structure during the wet chemical functionalization method. Therefore, in addition to the surface of the membrane, the inner parts and bulk of the membrane are also affected.

In the current work, which aimed to enhance the hydrophilicity of HDPE membranes, various oxidizing agents such as $KClO_3$, $K_2Cr_2O_7$, $KMnO_4$, dissolved in sulfuric acid, were used. A wide rang of analyses including static contact angle, scanning electron microscopy (SEM), atomic force microscopy (AFM), ATR-FTIR analysis, pure water permeation flux and mechanical strength were employed to investigate the structure and performance of modified HDPE membranes. In order to clarify the fouling mitigation of the treated membranes, BSA protein filtration experiments using dynamic filtration of BSA protein solution in a dead-end filtration setup were also carried out.

EXPERIMENTAL

Material

A commercial HDPE polymer (MFI = 0.35 g/10 min) was supplied by Tabriz Petrochemical Company (TPC). Analytical grade of potassium chlorate ($KClO_3$), potassium permanganate ($KMnO_4$) and potassium dichromate ($K_2Cr_2O_7$) were purchased from Merck and used as oxidizing agents. Reagent grade of sulfuric acid was purchased from Merck and 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 model foulant to evaluate the membrane performance. Buffer solution was prepared using HPLC grade water (less than 18 MΩ) obtained from Razi Serum Co. Phosphate buffer saline (PBS, pH = 7.4) was prepared by adding a certain amount of buffer salts to deionized water. All chemicals were used as received without any further purification unless otherwise described.

Fabrication of flat sheet microporous high density polyethylene (HDPE) membrane

Flat sheet HDPE membranes were prepared via thermally induced phase separation using an in-house manufactured sealed batch mixer setup. 19 wt% HDPE, 80 wt% MO and 1 wt% of the heat stabilizer were fed to a glass vessel. The sealed glass vessel was kept in a silicone oil bath at 160°C and blended for 2h. The solution was allowed to degas for 30 min and then a homogenized dope solution was poured on pre-heated glass plates and spread out using a casting knife and immediately immersed into the water bath with a fixed temperature to induce phase separation. The thickness of all cast membranes was fixed at 500 µm. The obtained sample was detached from the glass and immersed in acetone for 24 h to extract the diluent. The 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 remained in the fabricated membrane (data not shown).

Membrane surface modification and characterization

Oxidizing solutions were prepared by dissolving measured amounts of the oxidizing agents in measured amounts of sulfuric acid at ambient conditions. Membrane surface modification was carried out by immersing the HDPE membranes in the oxidizing solutions. In this regard, the HDPE membranes were soaked in the oxidizing solutions for a specific time interval and subsequently were immersed in DI water to stop the oxidation reaction. The treated membranes were dried in a vacuum oven at room temperature for 24 h. A set

of characterization tests consisting SEM micrograph, ATR-FTIR analysis, static contact angle measurement and AFM analysis, mechanical strength measurement and pure water permeation were carried out. Dynamic protein fouling experiments were also performed to investigate fouling specifications of the chemically modified membranes.

Membrane characterization

Static contact angle measurement and AFM analysis

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

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. The samples were cut into 3 cm × 0.5 cm in length and width, respectively. The effective length was 5 cm and two 1.5 cm edges 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.

Attenuated total reflectance – 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 an infrared spectroscopy apparatus (BRUKER-TENSOR 27).

Scanning electron microscopy (SEM)

The microscopic morphology of the fabricated membranes was characterized by a scanning electron microscope (MV2300CAM SCAN) with an accelerating voltage of 15kV. Cross-section samples were prepared by fracturing the membranes in liquid nitrogen. All samples were coated with gold by sputtering to make them electrically conductive.

Pure water permeation

The pure water flux of membranes with 5 cm^2 area was determined using an in-house fabricated dead-end filtration system. To minimize compaction effects, the pre-wetted membranes were compacted for 30 min at 2.0 bar. Then the pressure was reduced to 1.4 bar and after reaching steady state, the 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 (m^2) and t is the time (h).

Filtration experiments and fouling analyses

In order to evaluate the fouling behavior of the treated membrane, BSA protein filtration experiments were carried out in a dead-end filtration setup with an effective membrane area of 5 cm^2. A similar method was reported by Jafarzadeh et al. [33, 34] and Zhi et al. [35]. The results obtained here were compared with the results obtained from the pristine membrane. The protein solution was prepared by dissolving 1.0 g of BSA powder in 1 L of a standard phosphate buffer saline (PBS) solution. The amounts of total fouling ratio (TFR), reversible fouling ratio (RFR), irreversible fouling ratio (IFR) and flux recovery (FR) were calculated by the following equations:

$$TFR = (J_0\text{-}J_1J_0) \times 100 \quad (2)$$

$$RFR = (J_2\text{-}J_1J_0) \times 100 \quad (3)$$

$$IFR = (J_0\text{-}J_2J_0) \times 100 \quad (4)$$

$$FR = (J_2J_0) \times 100 \quad (5)$$

where J_0, J_1, J_2 are the pure water flux through a clean membrane, the pure water flux of fouled membrane and the pure water flux of membrane after cleaning and removing the cake layer with sponge over the membrane surface, respectively. In all experiments, the filtration analyses were conducted in a reservoir under a constant trans-membrane pressure (1.4 bar),

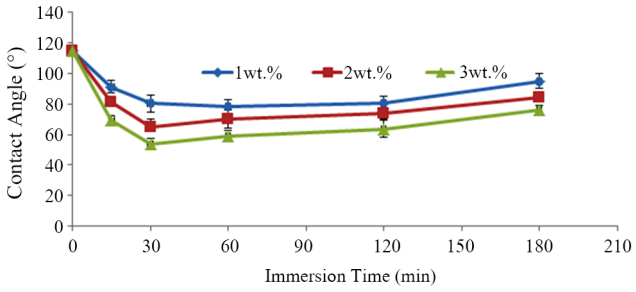
constant room temperature (20°C) and constant stirring speed (400 rpm).

RESULTS AND DISCUSSION

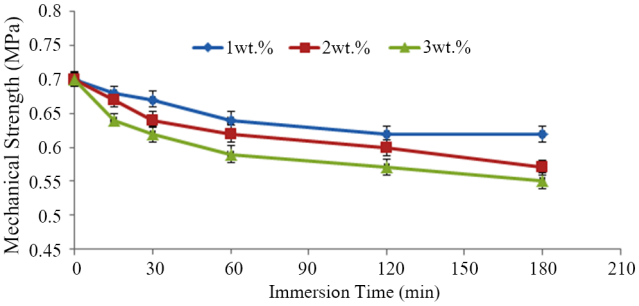
Selecting the appropriate concentrations of oxidizing agents and immersion time for each oxidizing agent

The optimized concentration of sulfuric acid, the type and concentration of oxidizing agent and immersion time are key parameters in controlling the rate of oxidation reaction and the effectiveness of the surface modification. A higher acid concentration, stronger oxidizing agent and longer immersion time are corresponded to a higher potential for the membrane to be destroyed. In the case of lower acid concentration and weak oxidizing agent, however increasing the reaction time as well as the degree of functionalization would not be satisfactory. In this regard, a set of experiments was carried out to determine the appropriate concentrations of oxidizing agents and immersion time. Among several oxidizing agents, $KClO_3$, $KMnO_4$ and $K_2Cr_2O_7$ were selected as the most conventional oxidizing agents [30]. Experiments were carried out in three different sets entitled as Set A, Set B and Set C corresponding to $KClO_3$, $K_2Cr_2O_7$ and $KMnO_4$ oxidizing solutions, respectively. Three different concentrations of oxidizing agents consisting 1,2 and 3 wt%, respectively, were dissolved in sulfuric acid, while the concentrations of sulfuric acid were kept constant at 80 wt%. HDPE membrane samples were immersed in the prepared solutions for different time intervals, e.g. 15, 30, 60, 120 and 180 min, and subsequently were soaked into DI water for 30 min to stop the oxidation reaction. The oxidizing solutions 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 immersion time (min), respectively. In Sets A and B of experiments, 1 wt %, 2 wt% and 3 wt% of $KClO_3$ and $K_2Cr_2O_7$ were dissolved in sulfuric acid. According to the literatures, the weight percent of sulfuric acid in all solutions was kept constant at 80 wt % [32, 36]. $KMnO_4$ is a strong oxidizing agent and should be carefully handled during the preparation of oxidizing solution since it has been listed as the most dangerous reagent. Its immiscibility in concentrated sulfuric acid (>80 wt%) has been already reported [30, 37], therefore, in a Set C of the experiments, 1 , 2 and 3 wt% of $KMnO_4$ were dissolved in 65 wt% of sulfuric acid, respectively. In order to select the appropriate concentration of oxidizing agent, three different concentrations of $KClO_3$ e.g. 1, 2 and 3wt % in 80 wt % of sulfuric acid were also prepared. The results obtained for contact angle and mechanical strength for Set A are shown in Figure 1-a and Figure 1-b, respectively. It can be observed that in Figure 1-a the rate of decreasing contact angle is quite high at the initial immersion time intervals (<30 min); however, any further increase in immersion time, e.g. 150 and 180 min, increases the contact angle.

Figure 1-b shows that with increasing the concentration of oxidizing agent (>1wt%), the mechanical strength decreases. It may be due to the breakage of interconnected microporous structure of membrane network. Similar experiments were carried out for Set B and Set C. The obtained results are summarized in Table 1. The selection strategy to determine the optimized compositions of oxidizing solutions was based on the fact that the 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 (1:80:30), (1:80:60) and (1:65:30), respectively.



(a)



(b)

Figure 1. Effect of $KClO_3$ oxidizing agent concentrations in 80 wt.% sulfuric acid in various immersion times on the (a) static contact angle and (b) mechanical strength of HDPE microporous membrane (Set A of treatment oxidizing solution)

Table 1. Obtained results for the effect of $K_2Cr_2O_7$ (Set B) and $KMnO_4$ (Set C) oxidizing agent concentrations in 80 and 65wt.% of sulfuric acid, respectively at various immersion times on static contact angle (CA) and mechanical strength (M.S) of the treated HDPE microporous membrane.

Experiment Set		Immersion time				
Characterization	Set B	15 min	30 min	60 min	120 min	180 min
CA	(1:80:t)	108	92	80.2	70	73.5
M.S		0.67	0.66	0.63	0.61	0.6
CA	(2:80:t)	99	84	71.3	64.9	69.3
M.S		0.65	0.62	0.58	0.56	0.53
CA	(3:80:t)	85	71	65	59	63.5
M.S		0.61	0.56	0.54	0.53	0.51
Characterization	Set C	15 min	30 min	60 min	120 min	180 min
CA	(1:65:t)	97.4	84	76.1	72.5	70.1
M.S		0.69	0.68	0.67	0.65	0.63
CA	(2:65:t)	84.5	73.1	66.8	63.8	60.31
M.S		0.67	0.66	0.64	0.62	0.58
CA	(3:65:t)	70.4	65.4	59.2	55.3	53.2
M.S		0.66	0.64	0.61	0.58	0.54

ATR -FTIR analysis

FTIR spectra are used to describe the existence of various functional groups and the degree of chemical changes on the HDPE membrane surface after treatment using optimum conditions of oxidizing solutions. Figure 2 indicates the ATR-FTIR spectra of the pristine and treated HDPE membranes using various oxidizing agents. The existence of various functional groups of different chemical bonds at the HDPE surface corresponding to different peaks, was analyzed to select the best oxidation condition among Sets A, B and C. The spectra in wavenumbers are listed in Table 2 with remarks showing conditions for the functionalized HDPE membrane. The peaks in the range of 2700-2950 cm^{-1}, 1384-1475 cm^{-1} and 710-750 cm^{-1}, appeared in all samples, correspond to the C-H bond stretching vibration, flexural vibrations of the C-H bond and C-H long-chain band in HDPE, 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. The obtained results show that the absorbance intensities of -OH peak in the samples treated by the Set A ($KClO_3$) are remarkably higher than those in the samples treated by Set B ($K_2Cr_2O_7$) and Set C ($KMnO_4$), respectively. The peaks in the range of 1166 and 1045 cm^{-1} correspond to the C-O bond stretching vibration of carboxylic acid and alcohol functional groups, respectively. Similar to the –OH and C=O functional groups, the absorbance

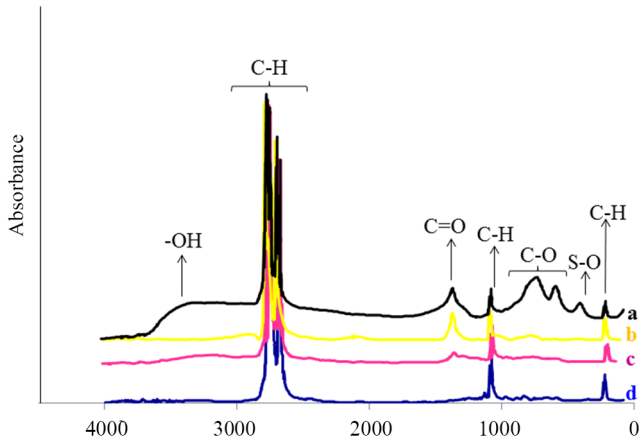


Figure 2. ATR-FTIR spectra of (a) HDPE microporous membrane treated by Set A, (b) HDPE microporous membrane treated by Set B, (c) HDPE microporous membrane treated by Set C and (d) pristine HDPE microporous membrane

Table 2. List of ATR-FTIR peaks of the various functional groups present on the HDPE microporous membrane obtained from Figure 2.

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	(C-H) flexural vibration
1166	C-O stretching vibration of carboxylic
1045	C-O stretching vibration of alcohol
850-910	S-O stretching vibration
710-750	(C-H) long-chain band

intensities of C-O peaks in the samples treated by Set A ($KClO_3$) are extremely higher than those 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 [38]. The results confirm the variety of the functional groups created on the HDPE membrane surface by 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 for other following post treatment processes, but as can be seen in Figure 2, the intensity of C=O absorbance in Set B is more pronounced. The presence of oxidized functional groups, particularly the carboxylic acid moieties, significantly modifies the surface properties of the functionalized membranes. The generally accepted mechanism for polymer surface modification is the formation of functional groups, such as C–O and C=O hydrophilic groups [39, 40], on the surface. The carboxylic acid groups are also useful as the starting point for further chemical elaboration[16]. Therefore, the spectra for the Set B of experiments were measured for different immersion times including 15, 30, 60, 120 and 180 min, as shown in Figure 3. The gradual increase of the intensities of the functional groups with treatment time signifies the hydrophilic characteristics of the HDPE surface modified with $K_2Cr_2O_7$. In comparison with other functional groups, the intensity of the absorbance of C=O functional group is more pronounced for the samples treated by Set B.

In order to explain the reason for the increase in the intensity of the C=O peak, we may refer to the following explanations. A dichromate salt and aqueous sulfuric acid are used to prepare in situ chromic acid, which is the most powerful and commonly available oxidizing agent. A primary alcohol is first oxidized to an aldehyde (via a chromate ester intermediate). Under acidic conditions, the aldehyde oxygen acts as a base and abstracts a proton, the carbonyl carbon is attacked by water (whose oxygen acts as a nucleophile) and simultaneously the carbonyl π-bond breaks and then finally the resulting molecule is deprotonated by another water molecule, yielding a diol. The diol is then subjected to further oxidation by the remaining chromic acid, which occurs by the same mechanism as the initial oxidation of an aldehyde. The ultimate result is a carboxylic acid [41]. Figure 4 compares the oxidation states of primary, secondary and tertiary alcohols with those obtained by oxidation or reduction. The symbol [O] indicates an unspecified oxidizing agent. It should be noted that oxidation of a primary or secondary alcohol forms a carbonyl group by the removal of two hydrogen atoms; one from the carbonyl carbon and another from the hydroxyl group. A tertiary alcohol cannot easily oxidize because there is no hydrogen atom available on the carbonyl carbon [41].

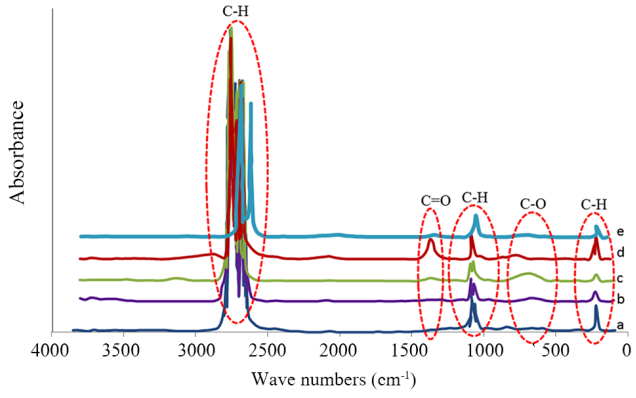


Figure 3. ATR-FTIR spectra of the (a) pristine HDPE microporous membrane, (b-e) HDPE microporous membrane treated by Set B (1:80: t) in various immersion times including; 15, 30, 60, 120 and 180 min, respectively.

Cross-section and surface morphology

The morphology of the cross-section and the surface of the membrane was observed with scanning electron microscopy (SEM). Cross-section and surface SEM micrographs of the HDPE membranes treated under the optimized oxidation circumstances are

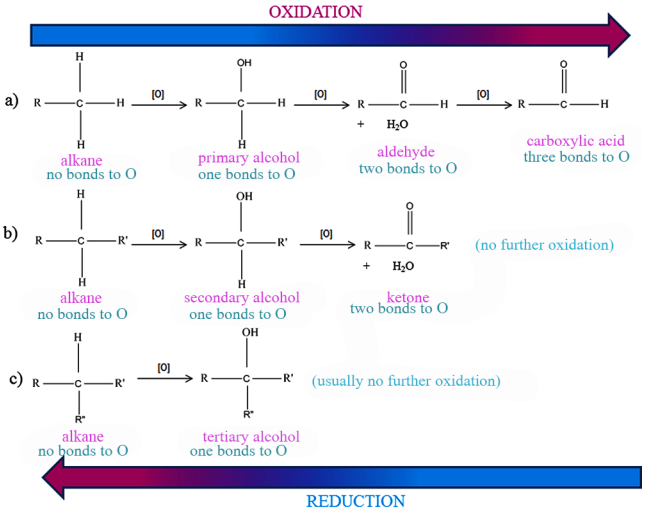


Figure 4. Oxidation states of alcohols. (a) Oxidation of a primary alcohol leads to an aldehyde, and further oxidation leads to an acid. (b) Secondary alcohols are oxidized to ketones. (c) Tertiary alcohols cannot be oxidized without breaking carbon–carbon bonds.

shown in Figures. 5 and 6, respectively. Comparing the treated and pristine HDPE membranes revealed that for all oxidizing sets, significant changes were made on the shape, structure and morphology of the membranes. The obtained results disclosed that in Set B, the change in pore size was the least among the other sets. An interesting aspect of the oxidized polymer surfaces is that the oxidized surfaces are usually higher in energy than the original pristine surface and may experience a phenomenon called surface re-construction, which was first studied by Baszkin et al. [42, 43] and then by Gagnon et al. [29] and Whitesides and Holmes-Farley [44]. This is the diffusion of the polar oxygen functionalities away from the surface toward the bulk. Figure 7 shows the changes in the contact angle with elapsed time intervals for the HDPE membranes treated with the optimal oxidizing solutions; Sets A, B and C. The minimum initial contact angles, obtained immediately after the treatment, were 80.27°, 80.2° and 84° for the samples treated by

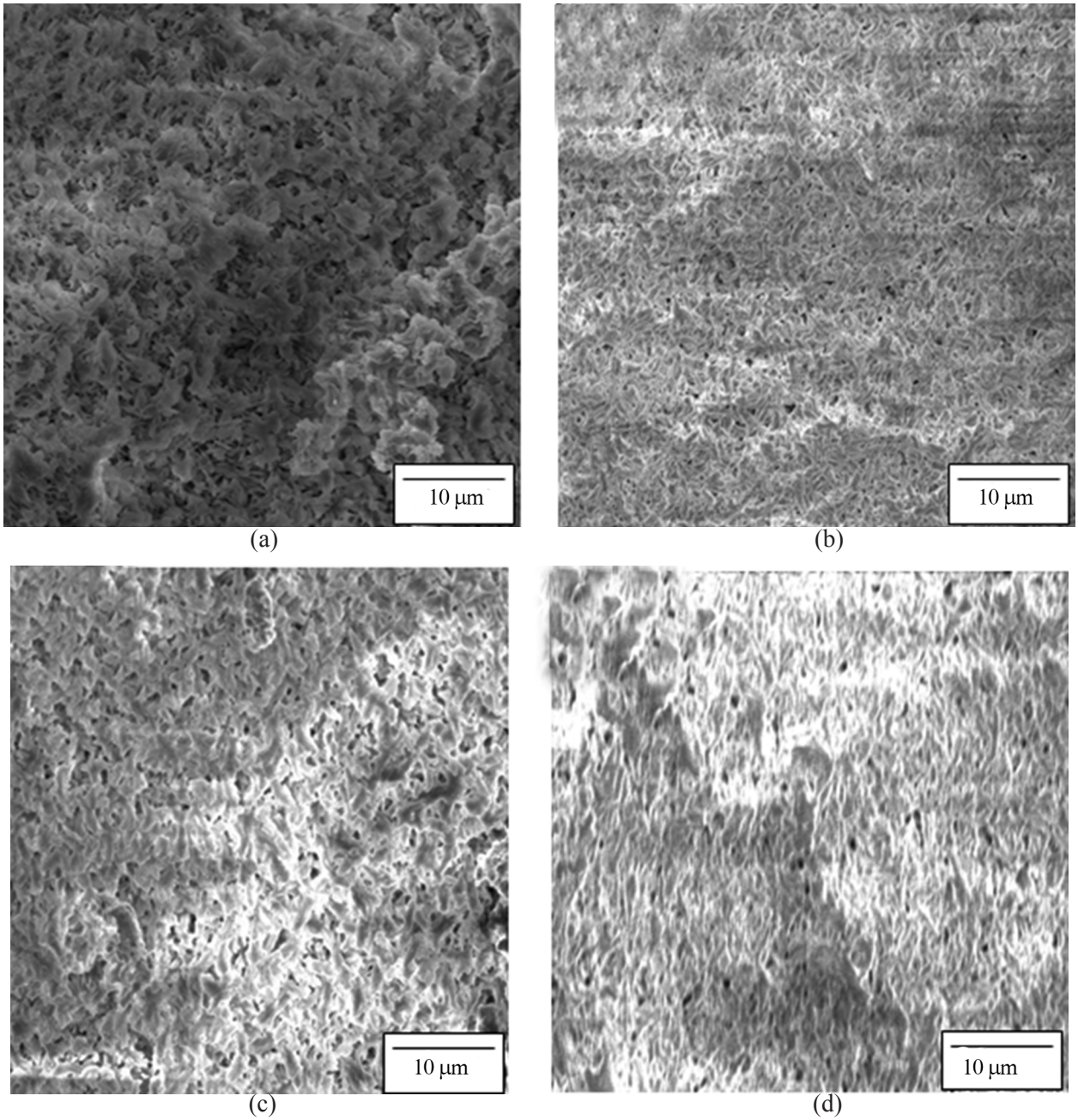


Figure 5. Cross-sectional SEM micrographs of HDPE membranes (a) Pristine HDPE membrane, (b) treated by optimized Set A ($KClO_3$wt.%: H_2SO_4wt.%: Immersion time (min)) (1:80:30), (c) treated by optimized Set B ($K_2Cr_2O_7$ wt.%: H_2SO_4wt.%: Immersion time (min)) (1:80:60), (d) treated by optimized Set C ($KMnO_4$wt.%: H_2SO_4wt.%: Immersion time (min)) (1:65:30).

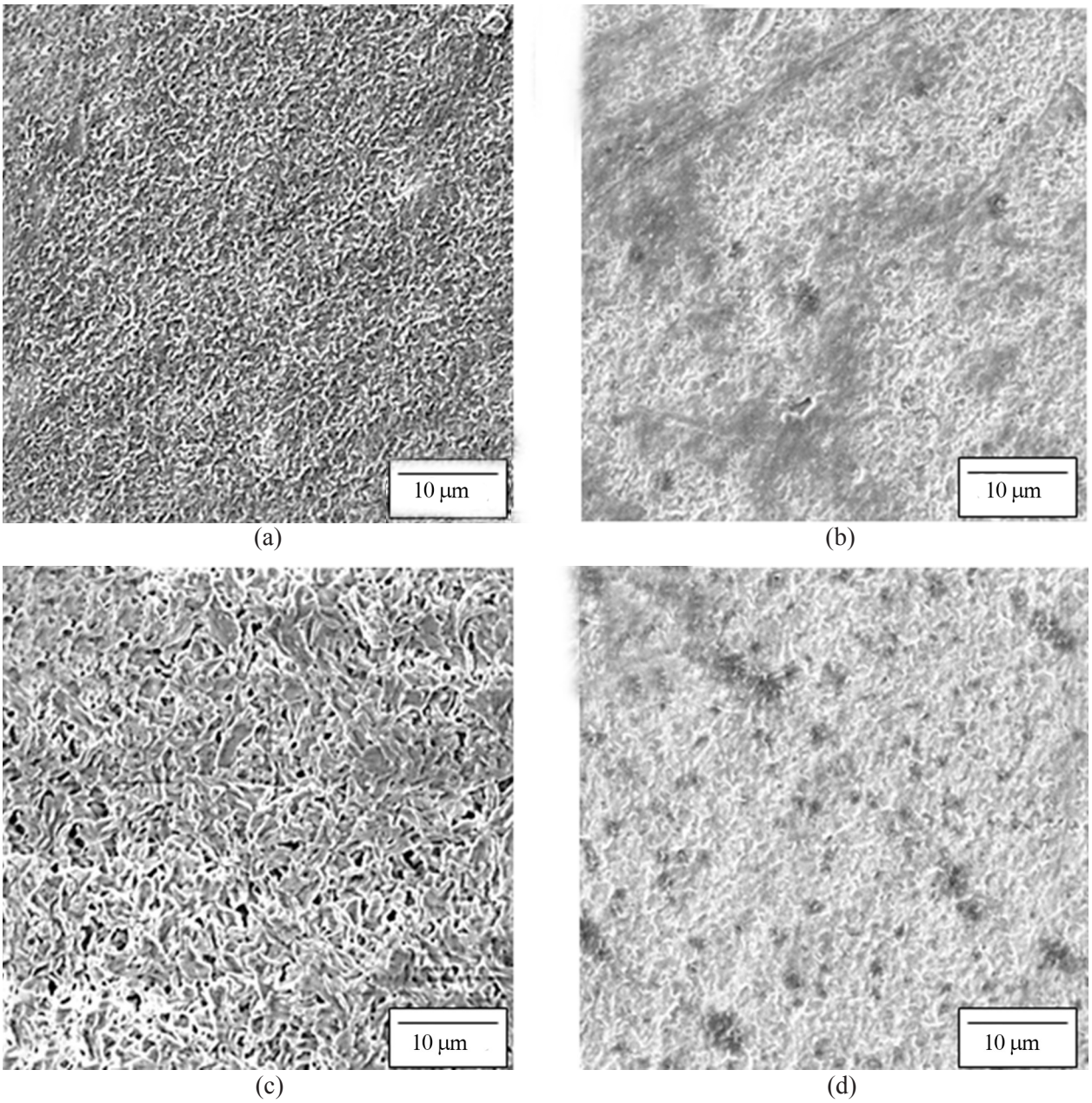


Figure 6. Surface SEM micrographs of HDPE membranes (a) Pristine HDPE membrane, (b) treated by optimized Set A ($KClO_3$wt.%: H_2SO_4wt.%: Immersion time (min)) (1:80:30), (c) treated by optimized Set B ($K_2Cr_2O_7$ wt.%: H_2SO_4wt.%: Immersion time (min)) (1:80:60), (d) treated by optimized Set C ($KMnO_4$wt.%: H_2SO_4wt.%: Immersion time (min)) (1:65:30).

$KClO_3$, $K_2Cr_2O_7$ and $KMnO_4$, respectively, which subsequently increased and saturated to about 84°, 97.79° and 111.38°, respectively after about 30 days of preservation. The increase in the contact angles are in good agreement with other reports[45-47], indicating that there is a slow hydrophobic recovery for the chemically treated surface due to the migration of untreated low molecular weight (LMW) species from the bulk to the surface, or due to reconstruction of the hydrophilic functional groups away from the surface [48]. Thus the recovery percentages of the measured contact angles for the treated HDPE membranes is estimated to be about 4.71%, 21.94% and 32.6% for $KClO_3$, $K_2Cr_2O_7$ and $KMnO_4$, respectively. Comparing the obtained results revealed that the re-construction of treated membrane by Set B took place much faster. It was reported that chromic acid-oxidized polyethylene rapidly became hydrophobic when it was heated in air [29]. In any application of a modified polymeric membrane, a critical cause of concern is stability of the functional groups created on the surface. Based on our results, $KClO_3$ seems to have a better performance

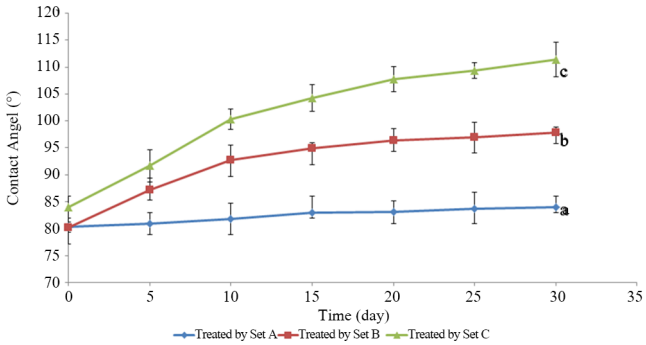


Figure 7. Re-construction effect of HDPE microporous membrane treated by optimized oxidation circumstances of (a) Set A, (b) Set B and (c) Set C.

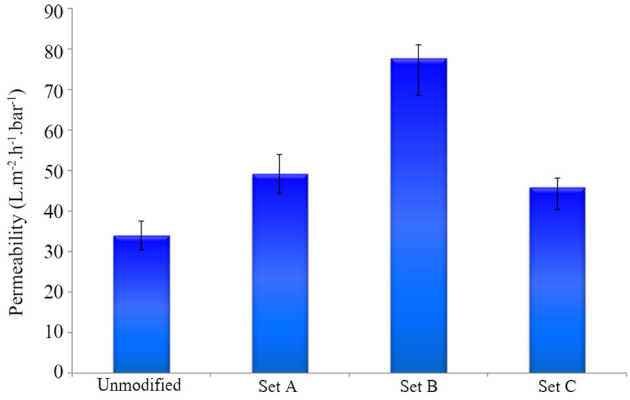


Figure 8. Comparison of pure water flux of HDPE microporous membranes treated by the optimized circumstance for Set A, Set B and Set C.

and stability for extended periods of time with a comparatively lower contact angle saturation value than other oxidizing gents.

Effect of surface modification on pure water flux

Pure water flux (PWF) tests were carried out for the membranes treated with the optimized oxidizing agents of Sets A, B and C and the obtained results are shown in Figure 8. The pure water flux (PWF) of pristine HDPE membrane was about 34 $L.m^{-2}.h^{-1}$. The obtained results showed that the HDPE membranes treated by all oxidizing agents kept higher PWF. The maximum PWFs for the HDPE membranes treated by Set A, Set B and Set C were 49.3, 78.40 and 45.00 $L.m^{-2}.h^{-1}$, respectively. Great difference in the PWFs can be attributed to the fact that in the water permeation test, the pore size and surface hydrophilicity are the key parameters influenced by the water flux [49]. Since the SEM micrographs (Figure 5) showed discernible changes in the pore size and pore structure of the membranes treated with Set B, therefore, not only surface hydrophilicity but also pore size and pore structure improved the PWF. An interesting point was that the HDPE membranes treated by Set B showed the maximum PWF in comparison with other Sets A and C. In order to clarify this point, AFM images were taken for the optimized oxidizing circumstances. The results, shown in Figure 9, indicate that the surface roughness of the sample treated by Set B, is lower than that of those treated by Sets A and C. Similar to our previous findings [33, 34] degree of roughness amplified the wettability of the surface toward its intrinsic properties. For a hydrophilized surface in which the contact angle is lower than 90°, roughening will decrease the contact angle resulting in higher PWF.

Protein filtration and fouling analyses

Dynamic BSA protein filtration tests were carried out to investigate the surface properties and anti-fouling performances of the chemically treated membranes. In order to omit the effect of electrostatic repulsion on the antifouling properties, which might occur during chemical treatment processes, the pH of protein solution was kept at 4.8 using an acidic buffer, since the isoelectric point (IEP) of BSA is 4.8.

Figure 10 shows the results of flux decline behavior of treated and pristine membranes. The obtained results show that the permeation flux of BSA protein solu-

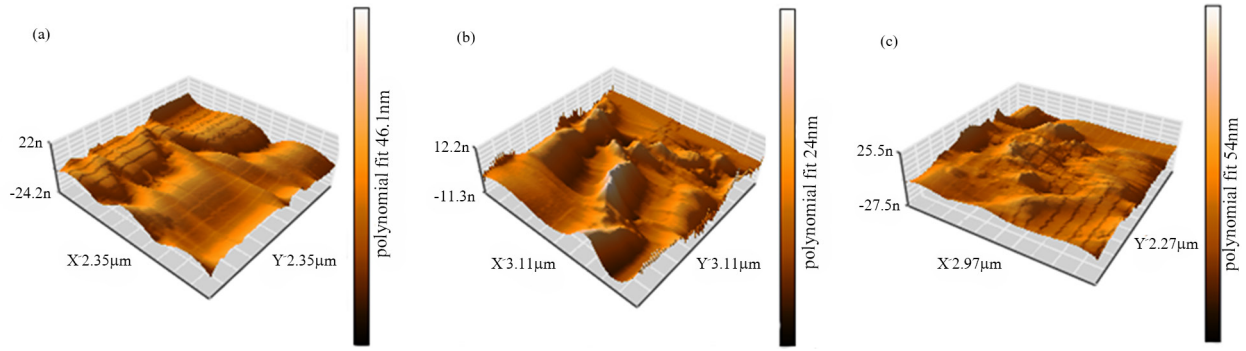


Figure 9. AFM images of the HDPE microporous membranes treated by (a) Set A, (b) Set B and (c) Set C.

Table 3. Analyses of fouling properties of pristine and treated HDPE microporous membrane by optimized oxidizing solution circumstances of Set A, Set B and Set C.

Samples	J_0 (L.m^{-2}.h^{-1})	J_1 (L.m^{-2}.h^{-1})	J_2 (L.m^{-2}.h^{-1})	RFR(%)[a]	IFR(%)[b]	TFR(%)[c]	FR(%)[d]
Untreated HDPE	34	4.04	19.51	45.50	42.60	88.10	57.40
Treated by Set A (1:80:120)	49.30	17.25	36.18	38.40	26.60	65.00	73.40
Treated by Set B (1:80:60)	78.4	25.08	55.42	38.70	29.30	68.00	70.70
Treated by Set C (1:60:60)	45.00	12.60	29.25	37.00	35.00	72.00	65.00

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

tion for pristine membrane decreases rapidly at the beginning of filtration. The conditions for the treated membranes, however, are different in which decrease in the permeation fluxes is considerably delayed. This may be attributed to the adsorption and subsequently deposition of BSA onto the surface of pristine membrane via the strong hydrophobic interactions between the protein and hydrophobic surface of HDPE membrane. Existence of polar functional groups on the surfaces of treated membrane 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 3. It can be seen that pristine HDPE membrane shows the highest TFR, confirming that this membrane is easily fouled by BSA molecules. Hydrophilic properties of treated membranes decreased the TFR values from 88.10% for pristine HDPE membrane to 65%, 68% and 72% for the membranes treated by Set A, Set B and Set C, respectively. Moreover, IFR of membranes decreased from 42.60% for pristine HDPE membrane to 26.60%, 29.30% and 35% for treated membranes by Set A, Set B and Set C, respectively. This indicated that incorporation of hydrophilic functional groups on the surface of HDPE 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 the treated membranes showed enhanced flux recovery in comparison with pristine membrane.

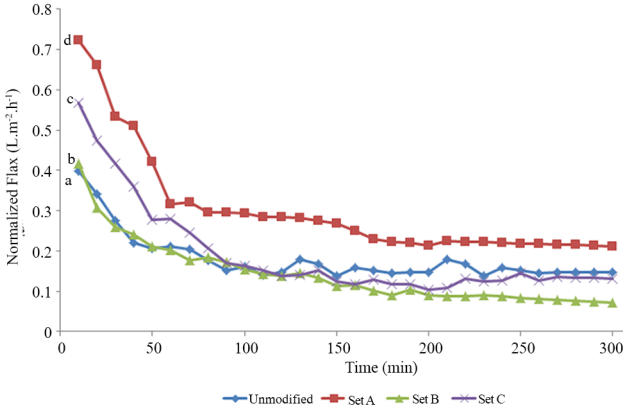


Figure 10. Normalized flux-time behavior of (a) pristine HDPE microporous membrane, (b-d) HDPE microporous membranes treated by Set C, Set B and Set A, respectively.

CONCLUSION

Polymeric membranes usually 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 and easy way to introduce polar groups on the surface of polymeric membrane. 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 each oxidizing agent and membrane immersion time were determined. The obtained results concluded that $KClO_3$ had better performance and stability for extended periods of time with a comparatively lower contact angel saturation values than the $K_2Cr_2O_7$ and $KMnO_4$, respectively. However $K_2Cr_2O_7$ showed higher PWF.

The ATR-FTIR results showed that the absorbance intensities of –OH and C-O peaks in the samples treated by $KClO_3$ are remarkably higher than those in the samples treated by $K_2Cr_2O_7$ and $KMnO_4$, respectively. However, absorbance intensities of C=O peak in the samples treated by $K_2Cr_2O_7$ are higher than those in other oxidizing agents. BSA filtration experiments showed that the total fouling ratio (TFR) was remarkably decreased for the membranes treated by oxidizing

solutions. Moreover, the portions of irreversible fouling ratios decreased for treated membranes, while the portions of reversible fouling ratios and flux recoveries increased. This indicated that incorporation of hydrophilic functional groups on the surface of HDPE membranes not only increased the fouling resistance, but also decreased the irreversible fouling ratio.

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