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Surface modification of polyethersulfone ultrafiltration (PES-UF) membrane using myoglobin as modifying agent

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ABSTRACT

Surface modification is one of the practical approaches in fouling mitigation strategy. This study investigated the usage of myoglobin as surface-modifying molecule coated on polyethersulfone ultrafiltration membrane. The pH and concentration of myoglobin solution were used as the modification parameters. Characterization of the surface-modified polyethersulfone (PES) membrane was performed using Fourier transform infrared spectroscopy, contact angle, surface charged measurements, and scanning electron microscopy. The membrane performance toward permeability of lysozyme (model protein) was evaluated at the different stirring speed and feed concentrations. The results show that the water contact angles changed up to 47.13% and hydraulic results are markedly increased by 55.9%, indicating that the hydrophilicity of the surface-modified PES membrane has been improved due to the surface pretreatment. The rejection of lysozyme via surface-modified membrane also indicates significant enhancement (up to 21.43%). The results of flux behavior study also proved that surface modification resulted in decrease of flux decline occurrence.

Keywords: Fouling; Surface modification; Myoglobin; Lysozyme

1. Introduction

Over the recent decades, pressure-driven membrane process has been the choice for concentrating and purifying protein molecule from the cells or broths. Ultrafiltration (UF) is often viewed as a process depends solely on size-based separation and these membranes are mostly fabricated from polymeric materials, and polyethersulfone (PES) had been the foremost choice owing to its superior selectivity, stability, and good thermal and mechanical strength. Due to these properties, PES seems to be ideally meets with the desirable UF membrane characteristics which should be of high selectivity and flux. Unfortunately, despite of these advantages, the hydrophobicity of PES still remains to be the prime constraint for the wide utilization of this polymer as the opted fabrication material for protein application, since the adsorption of proteins is widely acknowledged to occur severely on the hydrophobic surfaces compared to the hydrophilic ones [1]. This protein adsorption is irreversible in nature and cannot be easily removed by washing with buffer solutions or water. As the operating time increases, the gel layer will be formed and gradually, this layer will reaches its solubility limits. This consequently will lead to a serious membrane fouling and a rapid declination of permeate flux. Later it will contribute to a reduction in permeability and

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results in a loss of productivity over time. Since membrane replacement due to fouling required a large operating cost, many types of economically relevant membrane modification techniques have been introduced. Since materials interact with the environment through interfaces, it is believed that both the kind and the strength of such interactions are largely depending on the surface properties of the materials [2]. As a result, interest has been vastly concentrated to change the hydrophobic surface characteristics of hydrophobic membrane to hydrophilic. Coating is one of the surface modification methods, which can change the surface characteristic of the membrane without impairing their transport properties [3]. Moreover, coating can be performed in the existing membrane installations and this does not require a high manufacturing cost [1]. Most importantly, the type of coating also can be tailored to the specific application of interest. Coating comprises the adsorption of suitable water soluble polymers or surfactants from solution onto the hydrophobic membrane surface. The process could be done via a physical adsorption method by casting the hydrophilic components on the outer layer of the membrane or by simply immersing the membrane in the hydrophilic polymer solutions. Former researchers have modified the hydrophobic membranes by coating the hydrophilic polymers on different base membranes, for instance, chitosan/poly (acryolnitrile), carboxylmethyl chitosan/poly(ethersulfone), chitosan/polystyrene, and polyvinyl alcohol/polypropylene [3]. More recently, natural and synthetic peptides have been emerged as a new class of antifouling material. It was reported that hydrophilic neutral peptides showed comparable protein adsorption resistivity to PEG-based self-assembled monolayers. Lin et al. [4] have also claimed that one strategy to modify the hydrophobic polymeric membrane surface is to coat the membrane with hydrophilic polymers, proteins, or peptides. They have modified the PES membrane with a peptide sequence based from fibronectin to improve the adipose-derived stem cell adhesion and the findings were very impressive [4]. In this work, polyethersulfone ultrafiltration (PES-UF) has been modified by a simple dip coating, utilizing myoglobin as the coating material. Myoglobin was chosen as it is a type of protein derived from natural source; so that it was expected to be nontoxic and biocompatible, as well as hydrophilic protein.

2. Materials and method

2.1. Materials

The materials used in this research are of analytical grade. The membranes were fabricated from ternary casting solution consisting of PES as polymer, N-methyl-2-pyrolydone (NMP) (supplied by Merck) as a solvent, and water (H_2O) as a nonsolvent with composition of PES/NMPwater: 15/85 w/w ratio. Series of proteins, lysozyme (14 kDa), bovine serum albumin, with MW of 68 kDa, trypsin (23 kDa), pepsin (35 kDa), and ovalbumin (45 kDa), were used in the determination of molecular weight cut-off (MWCO). Myoglobin was used as the surface modifier agent, which was purchased from Sigma Aldrich.

2.2. Membrane preparation and modification

Native PES membranes were prepared by dry–wet phase inversion method. The membranes were then posttreated with two stages of coagulant bath, water and methanol, to ensure an excess solvent was totally removed as well as strengthen the molecules structure built in the membrane. The membrane surfaces were then modified by dipping myoglobin solution at different pH values (5.0, 7.0, 9.0, and 11.0) and concentrations (30, 50, and 70 mg/L). Myoglobin (protein) was selected as the coating agent as the membrane surfaces functionalized with amine groups will be more resistant to protein accumulation, thus preventing the fouling [5]. The membranes were then rinsed using phosphate buffer and pressed softly using tissue for few minutes to allow the removal of excessive myoglobin solution from the membrane surface. Finally, the membranes were air dried.

2.2.1. Membrane characterization

Membranes were characterized by means of surface chemistry, hydrophilicity, electrical potentiality, and MWCO. For all characterizations, the native (unmodified) membrane was used as the control. Myoglobin deposition analysis was carried out using protein assay method. The membranes were cut into pieces and 1% w/w of sodium dodecyl sulphate (SDS) solution was prepared. By using pipette, the small cut membranes were inserted into the conical flask and placed in the mechanical shaker for one hour. After the shaking process has been completed, the suspension was filtered. The concentration of protein in the SDS solution, which was regarded as the amount of deposited myoglobin, was measured by using UV–vis spectrophotometer and calculated by using the following equation:

$$C_y = W_g/A,$$

where C_y is the amount of coated myoglobin (g/cm^2), W_g is the weight (g) of protein, and A is the

membrane effective area (cm^2). The chemical characteristics were examined by using attenuated total reflection and Fourier transform infrared spectroscopy (FTIR). The hydrophilicity of membranes was quantified using contact angle measurement. Contact angle is a convenient way to assess the hydrophilicity/hydrophobicity degree of membranes surface and provides information about the interaction energy among the surface and the liquid. The low value of contact angle reflects that the membrane is hydrophilic, while the high angle is likely to appoint the hydrophobicity attributes of the membrane. In this study, sessile drop method was applied and average values of three points on the membrane surface were measured by using a face contact angle meter. Then, the electrokineticity of the membranes was determined using the electro-kinetic analyzer and a flat-plate measuring cell. Zeta potentials were calculated from the measured streaming potentials using the Fairbrother–Mastin (F-M) equation. The determination of membrane charge is important, since it has been significantly reported that the surface charge of a synthetic membrane has a noteworthy influence on its separation mechanism. The cross-section and surface morphology of membranes were visualized using scanning electron microscopy (SEM).

2.2.2. Membrane performance test

After the characterization, membranes were then examined in terms of its permeability and ability toward protein separation. Membrane permeability was determined by allowing the pure water to pass through the compacted membrane. The information of pure water permeability (PWP) is important to explain the morphological attributes of the membrane. It is a fundamental quantity with respect to the membrane and could reflect the porosity of the membrane. The PWP can be expressed as P_m ($L/m^2\,h\,bar$) and can be obtained by plotting the graph of flux vs. pressure (Hagen Poisseuille equation),

$$J_v = P_m \Delta P,$$

where ΔP is the applied pressure and J_v is the water flux. A constant value of the PWP, i.e. the linear dependence of the pure water flux, J_v on pressure, points to the unchangeable membrane porosity. If the water flux dependence on pressure deviates from linearity, the PWP of a membrane is not constant and it indicates the changes in the membrane's porous structure. Thus, by measuring a dependence of the membrane's PWP on pressure, a state of the membrane's active layer porosity can be characterized. Then, membranes were subjected to flux behavior analysis. This step is important to evaluate the fouling tendency of the selected membrane and consequently, further verify the effectiveness of the membrane to be utilized in lysozyme separation. Permeate was collected for every five minutes. Then, volume permeated was measured and fluxes were calculated. Lysozyme concentrations in both feed and permeate were measured by using UV–vis spectrophotometer at a wavelength of 280 nm. The steps were repeated until consecutive flux was obtained and the graphs of flux vs. time were then plotted. All fluxes were calculated using a simple mathematical equation (Table 1) developed by Capar et al. [6]. J_{cwi} is the initial permeate flux, J_{ww} is the steady state flux, J_{cwf} is the flux of the pure water through the fouled membrane, and J_{cwc} is the water flux of the water-cleaned membrane. Through the obtained results of flux declination trends, the degree of concentration polarization and nonspecific protein clogging onto the membrane surface could be evaluated. Thus, the fouling level of the membrane could be estimated. Finally for lysozyme separation study, only membrane with the best characteristics and with the excellent fouling property was utilized. UF experiment was performed using dead end cell with processing volume of 300 mL and effective permeation area of 14.6 cm^2. Nitrogen gas was used to pressurize the system and to maintain the transmembrane pressure (TMP). Fresh membrane discs were used for each run. Ten milliliter of sample was collected from the pure water flux permeation. Feed (lysozyme) pressure was controlled in a range of 1–5 bars by using compressed nitrogen. Influence of the rheological properties such as stirring speed and feed concentrations on lysozyme productivity and selectivity was also assessed. The speeds were screened in the range of 300, 600, 900, 1,200, and 1,500 rpm, whereas the feed concentrations were studied in the arrays of 300, 500, and 700 mg/L, respec-

Table 1
Various equations of Flux decline fraction Capar et al. [6]

Formula	Type of flux decline (FD)
$(J_{cwi} - J_{ww})/J_{cwi}$	Total flux decline
$(J_{cwf} - J_{ww})/J_{cwf}$	Concentration polarization
$(J_{cwi} - J_{cwf})/J_{cwi}$	Fouling (irreversible+reversible)
$(J_{cwc} - J_{cwf})/J_{cwc}$	FD due to reversible fouling
$(J_{cwi} - J_{cwc})/J_{cwi}$	FD due to irreversible fouling

J_{cwi} = initial flux; J_{ww} flux at steady state; J_{cwf} = flux of fouled membrane; and J_{cwc} = flux of water-cleaned membrane.

tively. In this step, the suitable speed and feed for the lysozyme separation were selected.

3. Results and discussion

3.1. Characteristics of surface-modified membrane

PES membranes have superior mechanical strength and excellent thermal and pH stabilities. However, their hydrophobic nature makes them susceptible to protein fouling. In this study, we have improvised membrane hydrophilicity through deposition of myoglobin as surface-modifying molecules. Effect of pH and concentration of myoglobin that deposited onto membrane surface were observed in the aspects of membrane characteristics and the flux decline occurrence.

3.1.1. Effect of myoglobin pH

Surface-modified PES membranes with myoglobin were carried out at four different pH values, i.e. 5, 7, 9, and 11 (coded as MPH5, PMH7, MPH9, and MPH11, respectively) and native membranes as a control. The results clearly show that the membrane characteristics depend on the pH of the solution. The results are also consistent with the fact that highest improvement of membrane hydrophilicity and amount of myoglobin deposition takes place near the isoelectric point (pI) of that protein (pI of myoglobin is 7). Table 2 shows the amount of myoglobin deposit with respect to pH. MPH5 and MPH7 show the highest amount of myoglobin deposition as compared to MPH9 and MPH11. Since the pI of myoglobin is 7.0, it will be positively charged at lower pH values. It would therefore promote strong adsorption of protein onto the surface. This would result in lower myoglobin deposition of negatively charged, i.e. MPH9 and MPH11 (pH above pI) due to larger degree of repulsion amid myoglobin and PES membrane. The improvement by means of hydrophilicity and less fouling is expected to be maximum at pH 7 (its PI). Fig. 1(a) shows the FTIR results for all surface-modified membranes with respect to pH variation. As expected, all membranes displayed a typical spectra of PES membrane, i.e. aromatic bands at 1,578 and 1,485 cm^{-1} from the benzene ring [7]. The peak in the area around 1,240 cm^{-1} was attributed to the ether groups, while the other one at 1,040 cm^{-1} belongs to the SO_3^- compound from the sulfonic group of PES [8]. The significant difference in surface-modified membranes as compared to native membrane was the peaks appearance in the range of 3,700–2,500 cm^{-1} region, attribute to the existence of O–H and N–H stretching frequencies [9]. This hydroxyl (OH) and amide (NH) bonds might be attributed to the presence of proteins (myoglobin) on the membrane outer surface. The small peaks around 2,900–2,800 cm^{-1} and 1,730–1,720 cm^{-1}, which indicated the presence of stretching H-bond and carbonyl groups from AA, respectively, appeared for both MPH7 and MPH5, but it is almost invisible for MPH9 and MPH11. The presence of myoglobin on the membranes surfaces is additionally supported by assignments of bands around 1,650 cm^{-1}, which is the characteristic of amide I (C–O). All of these observations signified that myoglobin is successfully coated onto the membrane surface.

Surface-modified membranes were further characterized for surface hydrophilicity, surface charge, and MWCO. A summary of all the determined characteristics is given in Table 2. Hydrophilicity or wettability of the membranes was evaluated by contact angle measurement. Results for contact angle indicate that lower values of contact angle are obtained for all the

Table 2
Effect of myoglobin pH and concentration on membrane characteristics

Membranes ID	Myoglobin deposition (g/cm^3)	Permeability coefficient ($L/m^2\,h\,bar$)	Contact angle (°)	Z_p (mol/m^3)	MWCO (kDa)
At various pH					
NATIVE	0	9.92	85.0	−12.38	39
MPH5	26.53	17.66	16.23	6.673	23
MPH7	26.71	20.11	58.0	0.000	20
MPH9	17.3	12.63	63.3	−5.750	30
MPH11	11.69	9.92	65.5	−6.150	36
At various myoglobin concentration					
MPH7-30	16.8	16.83	60.0	−0.005	27
MPH7-50	17.7	17.66	58	0.0000	20
MPH7-70	8.6	8.60	66.0	−0.0014	34

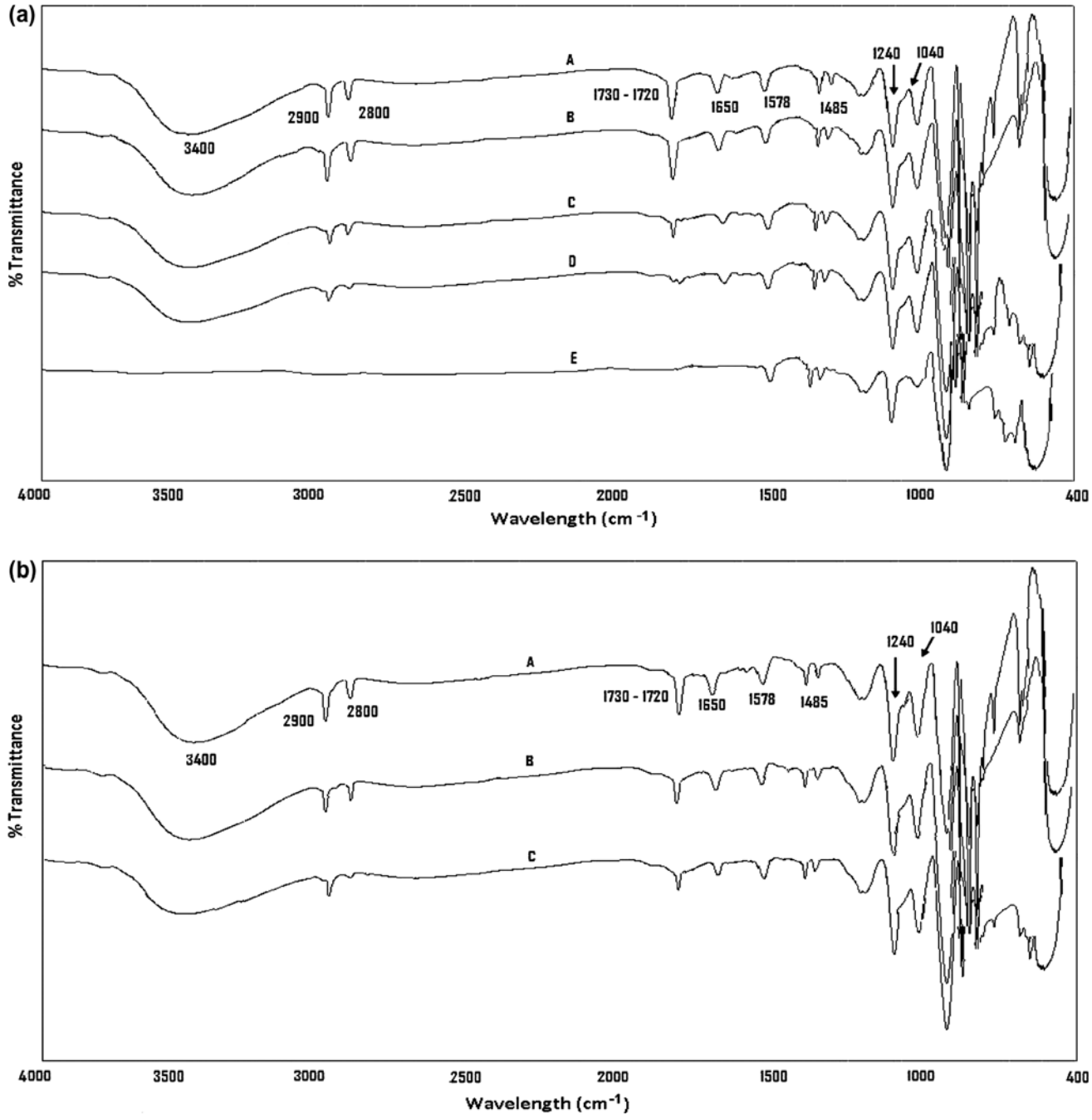

Fig. 1. FTIR spectra of (a) various pH, [A (MPH7) B (MPH5) C (MPH9) D (MPH11) & E (Native)] and (b) various myolobin concentration [A (MPH7-50) B (MPH7-30) C (MPH7-70)].

myoglobin coated membranes compared to that of native membrane. This finding verified that the surface wettability of the surface-modified membrane has been increased due to the surface pretreatment. The optimum contact angle value of 58.0 was obtained for MPH7 membrane. At pH 7.0, myoglobin is uncharged (pH = pI) and proteins are strongly hydrophobic at their PI. Thus, the adsorption of myoglobin on membranes is postulated due to the hydrophobic interaction [10]. These results implied that there was a substantial increase of surface hydrophilicity for myoglobin-coated membranes due to surface modification. With the improvement in hydrophilic properties, the membrane will be more prone to fouling, since it is

generally accepted that the hydrophilic membrane is the fouling rebellious membrane. In the aspect of surface charge, the adsorption of myoglobin on the surface of PES membrane causing the streaming potential measured across the membrane to change from a profile characteristic of the native membrane to a profile characteristic of the adsorbed myoglobin. Myoglobin is a type of protein and it is a well-known fact that, proteins will exhibit a different charge based on the pH of the environmental solution. When the pH is above its pI, proteins will possess a negative charge. On the other hand, if the pH is lowered far below the pI, the protein will lose its negative charge and contains only positive charge [11]. At certain value when pH = pI, the positive and negative charges on the protein will be equal and protein will experience a zero net charge. Since the pI of myoglobin is 7.0, the membrane will be positively charged at the pH < 7.0 and negatively charged at the pH > 7.0. From Table 2, it was clearly shown that membranes dipped in myoglobin solution of pH 5 possess a positive charge, became neutral charge when coated at pH 7.0, and negatively charged for myoglobin solution having pH 9.0 and 11.0. Subsequently, the MWCO of myoglobin-coated membrane was relatively lower than native membrane. This might be attributed by partial pore blocking caused by the adsorption of myoglobin onto the membrane surface, consequently, resulting in smaller MWCO. The smallest MWCO is achieved for MPH7, which is 20 kDa, due to the highest myoglobin adsorption to the membrane surface.

The characterization was further proceeded to structural classification using SEM. Fig. 2(a)–(e) displays the morphological micrographs of cross-sectional image of native, MPH7, MPH5, MPH9, and MPH11, respectively. The myoglobin-coated membranes exhibited morphology of asymmetric structure consisting of a dense skin layer, a porous sublayer, and fully developed macrovoids at the bottom. The skin typically accounts for 1–2% of the entire thickness of the film and the pore size increasing gradually from skin layer to the bottom. The significant difference between the unmodified (Fig. 2(a)) and modified membranes (Fig. 2(b)–(e)) is the presence of dense sponges-like structure pitted between the two stratums of finger like and thick skin layer. This spongy

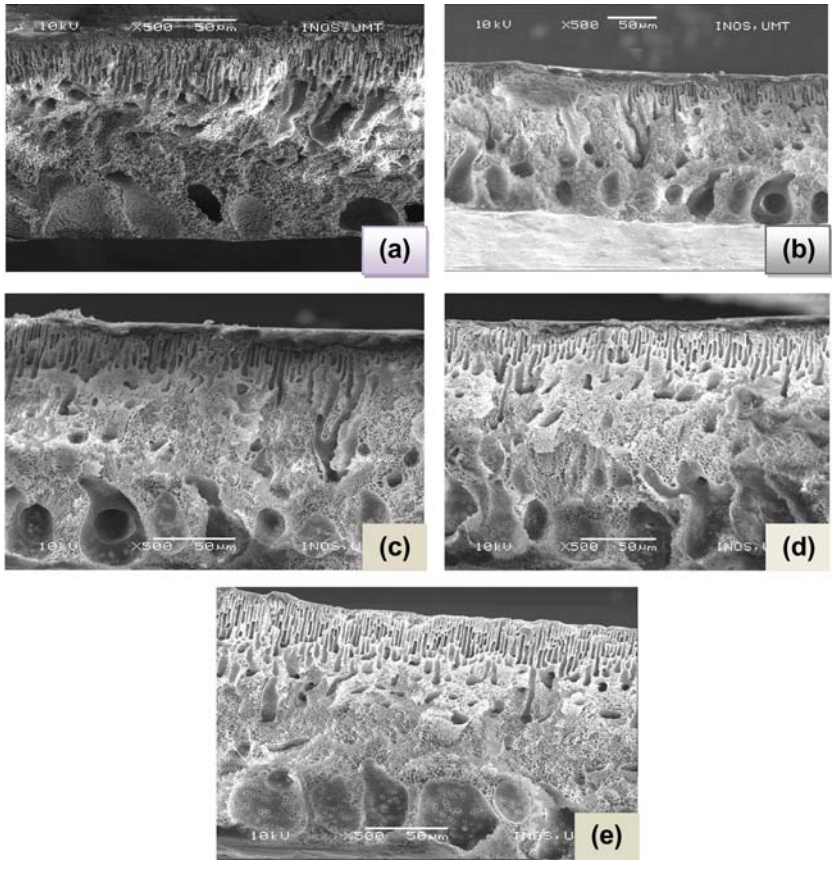

Fig. 2. SEM (500×) cross sectional image of membranes: (a) native, (b) MPH7, (c) MPH5, d) MPH9, and (e) MPH11.

layer probably explained the lower water permeability coefficient for this membrane since it promotes the resistance to water flow, thus resulting in lower permeability characteristics [12]. In contrast, myoglobin-coated membranes (Fig. 2(b)–(e)) exhibit less spongy constitution, with more porous finger-like and tear drop-like structures. These types of structures promote higher water permeability ability and were confirmed with PWP coefficients and myoglobin deposition obtained from modified membranes at various pH values (Table 2). The PWF for all membranes lies within the theoretical flux of UF commercial membrane for protein application (±10–50 $L/m^2 h$) and also demonstrates a very good approximation with the Hagen–Poiseuille equation. The maximum PWP (20.11 $L/m^2 h$) was obtained for the membrane deposited with the myoglobin solution having the pH value of 7.0 (MPH7 membrane). This finding agrees to the formerly obtained myoglobin deposition level, which is highest for this membrane. When the deposition of myoglobin is higher, the water resemblance area will be larger, consequently leads to the decrease in contact angle. Hence MPH7 membrane had showed the highest degree of hydrophilicity, leading to a lower resistance to water flow. MPH7 membrane was then further tested for myoglobin concentration effects.

3.1.2. Effect of myoglobin concentration

The interactions of solution and solid membrane phase are also dependent on the solute concentration, thus its separation performance is significantly affected by concentration polarization and membrane fouling. It is also observed that the pH effect is more pronounced at lower ionic strength [13]. The manipulation of both effects (pH and solution concentration) certainly provides maximum rejection of the desired solute. In this step, the pH of myoglobin was fixed to pH 7.0 and myoglobin solutions were studied at three different concentrations such as 30, 50, and 70 mg/L (coded as MPH7-30, MPH7-50, and MPH7-70, respectively).

Fig. 1(b) shows the FTIR spectra of myoglobin-coated membranes. The typical infrared regions for PES are: aromatic bands at 1,578 and 1,485 cm^{-1} from the benzene ring, 1,240 cm^{-1} from ether groups, and 1,040 cm^{-1} from PES sulfonic groups. Apparently, the bands at 3,700–2,500 cm^{-1} (O–H and N–H), 2,900–2,800 cm^{-1} (H-bonds), and 1,730–1,720 cm^{-1} (spectra for AA from carbonyl groups), all which denotes the peaks of (proteins) myoglobin, are highly intensified in MPH7-50 membrane. It was proved that the highest adsorption of myoglobin occur on MPH7-50 membrane. The results for membrane characterization including contact angle, membrane surface charge, and MWCO are given in Table 2. The results of contact angle measurement showed that the native membrane (base) had a contact angle of 85˚. The modified membrane using the myoglobin concentrations of 30, 50, and 70 mg/L gave the contact angles of 60˚, 58˚, and 66˚, respectively. The increased amount of myoglobin deposit was responsible for the increased hydrophilicity of the modified membranes. It could also be observed that the deposited myoglobin onto membrane surface seems to be saturated at concentration of 30 mg/L, as the contact angle values were not much as different as compared to membranes coated with 50 and 70 mg/L. In the aspect of MWCO, quite significant differences were shown by MPH7-30, MPH7-50, and MPH7-70 i.e. 27, 20, and 34 kDa, respectively. MPH7-50 showed the lowest MWCO which is in line with contact angle values. MWCO for MPH7-70 was close to unmodified membrane. It is postulated that, the membrane surfaces were completely coated after treatment with 50 mg/L myoglobin. Any increase of myoglobin concentration beyond 50 mg/L will cause the myoglobin to be leached instead of accumulating on the membranes surface. In this case, myoglobin is no longer residues on the membranes surface, thus changing its character to the unmodified membrane. The obtained zeta potential is the lowest for MPH7-70 (−0.0014). This increase of coating solution concentration will lower the surface charged, as more myoglobin is adsorbed to cover the surface. Fig. 3(a)–(c) shows the cross-sectional image of the membranes pretreated with myoglobin of different concentrations (MPH7-30, MPH7-50, and MPH7-70). The obtained photographs confirmed that, all membranes are asymmetric across the thickness, have a dense skin layer, and highly porous sublayer, which increase progressively in porosity from the skin to the interior of the membrane [14]. It was shown that MPH7-50 (Fig. 3(b)) posses the smallest microvoids as compared to others. The morphological observations were congruent to the PWP values of modified membrane, whereby the highest P_m is obtained for MPH7-50 membrane (17.66 $L/m^2 h bar$).

3.2. Permeate flux behavior analysis

Fouling has been identified as a major drawback in UF process. It is a complex phenomenon as a result of the interactions between the membrane structural properties and solute(s) in the feed stream. There are three major factors that contribute to fouling i.e. membrane properties (such as hydrophilicity, surface topology, and membrane charges), solution properties

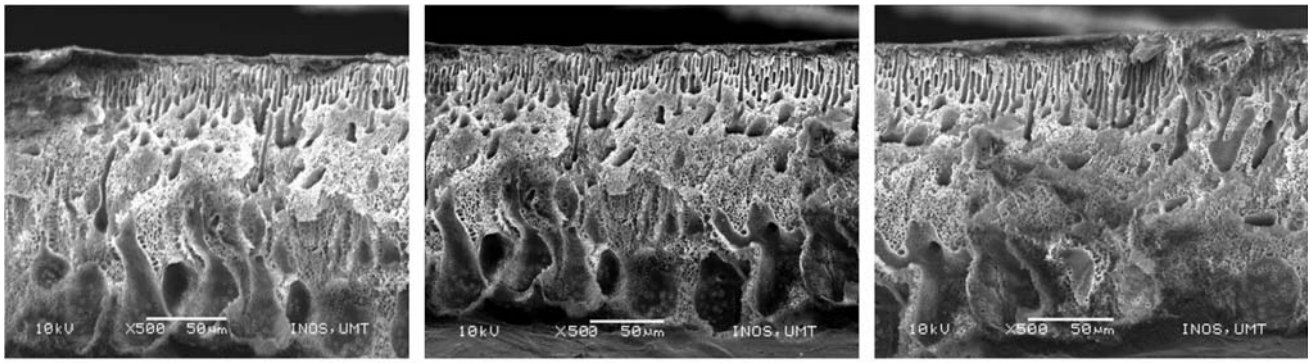

Fig. 3. SEM (1000×) cross sectional image of membranes: (a) MPH7-30, (b) MPH7-50, and (c) MPH7-70.

(such as solute charges, functional group, and ionic strength), and operating parameters (such as stirring speed, pressure, and feed concentration). Major effects of fouling are the reduction of process flux and selectivity. The initial decline in permeate flux is mainly due to the build-up of osmotic pressure of the solution, whereas the gradual decline may be considered as a combined effect of build-up of deposited layer on the membrane surface and deposition of solute particles in the membrane pores. Finally, the permeate flux attains a steady state value which is limited by the external hydrodynamic conditions such as stirring speed or cross-flow velocity. In this study, the effects of pH, feed concentration, and stirring speed on the flux decline were observed. The permeate fluxes were measured through four parameters: (1) initial clean water flux (J_{cwi}), the first flux determined with clean membrane; (2) wastewater flux (J_{ww}), the flux stabilized with respect to time during wastewater filtration; (3) clean water flux of the fouled membrane (J_{cwf}), the clean water flux measured with the fouled membrane; and (4) the clean water flux of the cleaned membrane [6]. The extents of concentration polarization and fouling were calculated via flux decline analysis as given in Table 1. In this work, we have used lysozyme as our protein model.

Fig. 4 shows lysozyme flux profile of modified membrane with different pHs and feed concentrations. Generally, flux declines gradually over a period of time and then attains a steady state value. This confirms that flux decline is mainly caused by the gradual growth of the deposited layer on the membrane surface over the period of operation. In lysozyme filtration (MWCO = 14.7 kDa), it takes about 20–30 min for stirred cell to attain the steady state value. The feed flux declines were about 20% of the initial flux, for the feed concentration of 300 and 500 mg/L, and slightly higher reduction (about 34%), for feed concentration of 700 mg/L. It means that higher feed concentration led to a higher overall resistance, hence a greater percentage of flux loss. This statement was further confirmed with the calculated flux analysis as given in Table 3. The MPH7 exhibited the highest flux and least flux decline, followed by MPH5, MPH9, and MPH11. It could be postulated that the fouling resistance of MPH7 is high due to the highest hydrophilicity and smallest pore size (Table 2). If the pores are much smaller than particles to be separated, the particles will not get trapped in the pores, but instead will suspend on the surface under the shear forces (or turbulence) generated by flow. Fouling resistivity of this membrane was further assessed using flux recovery ratio (FRR). FRR was calculated by denominating the initial pure water flux (before protein filtration), J_1 by J_2. Results (Table 4) show that, the FRR for MPH7-50 is high whereby the ratio of J_2/J_1 close to unity. This signifies the ability of water to clean the membrane, thus pertaining that the hydrophilic structure of the membrane caused the weaker association of lysozyme residual with water [15]. Thus, it is concluded that, membrane MPH7-50 is effective toward fouling minimization in protein separation. Therefore, it will be applied in the succeeding part of this research, which is a protein separation study.

3.3. Protein separation study

In this study, the impact of stirring speed on the performance of lysozyme permeability was examined at five different rates of stirrer rotation; 300, 600, 900, 1,200, and 1,500 rpm. The effects of three different feed concentrations (300, 500, and 700 mg/L) were also observed upon separation performance.

3.3.1. Effect of stirring speed

Fig. 5(a) and (b) shows the flux and rejection profile for different TMP at various operating speed. The

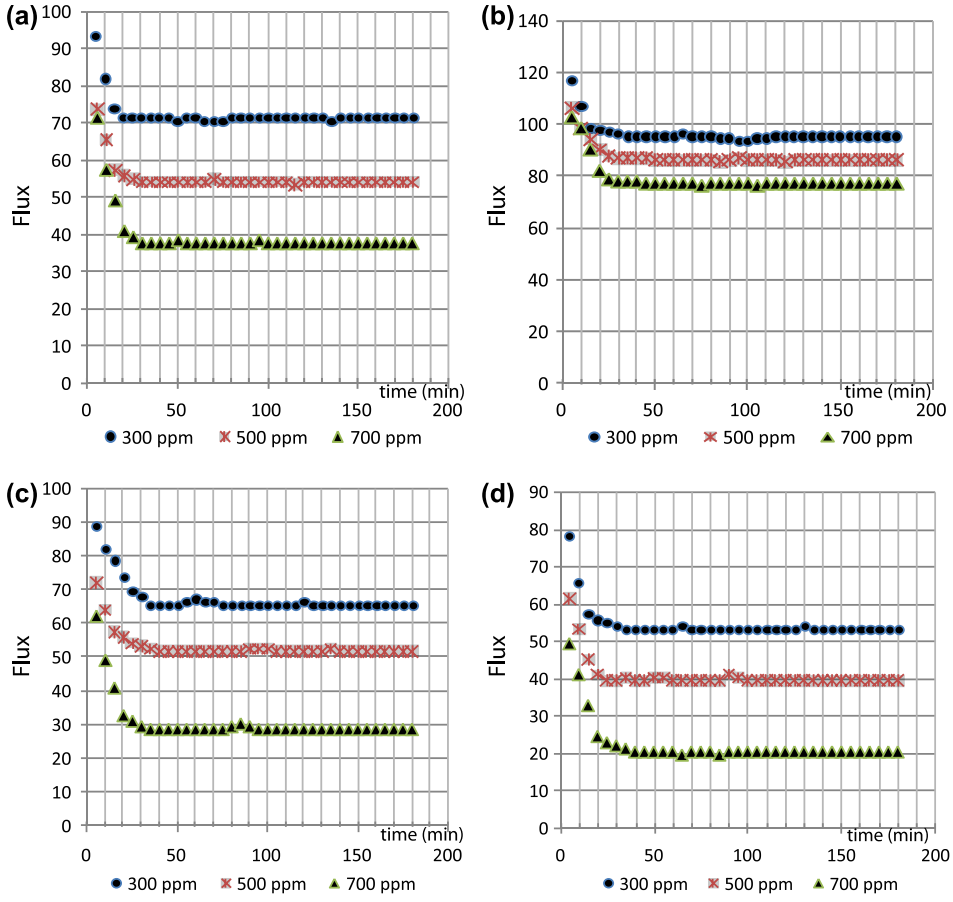

Fig. 4. Flux profile as a function of time for myoglobin-coated membranes at various pH and feed concentration: (a) MPH-5, (b) MPH-7, (c) MPH-9, and (d) MPH-11.

Table 3
Effect of feed concentration membrane flux decline for MPH7, MPH5, MPH9 and MPH11

Flux decline parameter	Feed concentration (mg/L)											
	MPH5			MPH7			MPH9			MPH11		
	300	500	700	300	500	700	300	500	700	300	500	700
Total FD	23.67	26.66	47.13	18.31	19.23	21.67	25.93	28.41	53.95	31.58	35.99	58.33
FD due to CP	1.15	1.49	6.11	0.85	0.94	1.05	1.25	1.56	7.88	3.00	4.01	10.69
Flux due to R	20.00	22.09	36.37	17.73	17.83	19.50	21.36	22.9	41.54	25.55	27.53	44.01
Flux due to IR	3.70	4.45	11.49	0.70	0.77	1.66	4.63	5.68	14.49	5.26	7.99	16.67

Notes: FD = flux decline; CP = concentration polarization; R = reversible; and IR = Irreversible.

Table 4
Effect of feed concentration on the FRR of MPH7-50 membrane

Membrane ID	Feed concentration (mg/L)	FRR (%)
MPH7-50	300	99.39
	500	99.33
	700	99.23

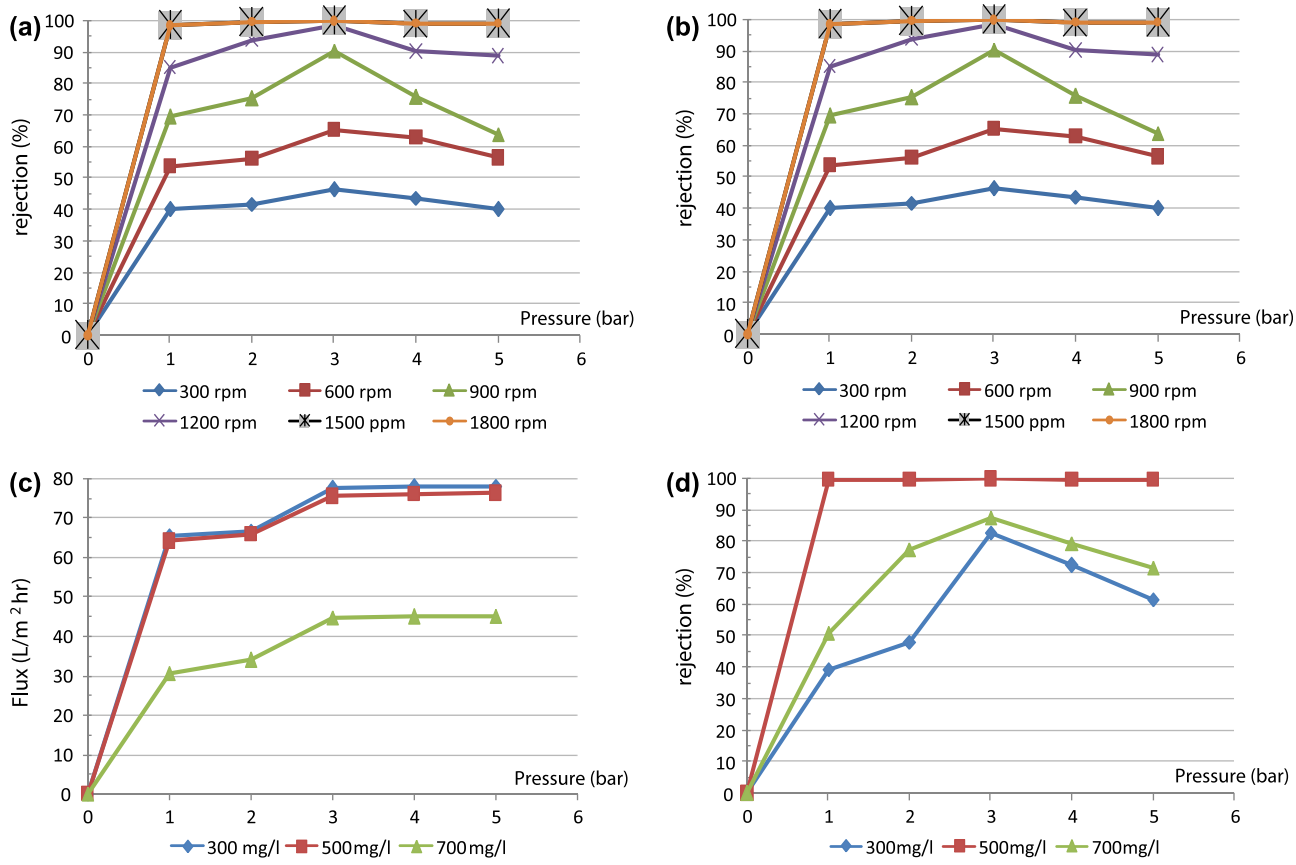

Fig. 5. Effect of stirring speed and feed concentration on MPH7-50 membrane flux and rejection profile at various pressure: (a) flux profile at various stirring speed, (b) rejection profile at various stirring speed, (c) flux profile at various feed concentration, and (d) rejection profile at various feed concentration.

obtained results show that at all stirring speed level of lysozyme permeability and rejection increases at the applied pressure of 1–3 bars. The higher pressure caused the fluxes to leveled-off and the rejections were declined. Thus, it is concluded that 3 bar is the limiting pressure for lysozyme isolation using MPH7-50. It was clear that higher TMP will increase the solution flux and subsequently increased the rejection of protein in the feed. However, after a certain point, cake layers will be developed on the membrane surface, causing the flux to be declined. Thus, increase in TMP will only lead to a higher compaction of this layer [16]. The greatest rejection and flux was attained for 1,500 rpm speed which is 99% and 80 L/m^{2}h, respectively (Fig. 6(a)). At this point, agitation and mixing of the fluid near the membrane surface will "sweeps" away the accumulated solutes, therefore limit the concentration development at the vicinity of the membrane which could help in minimizing the negative effect of concentration polarization.

3.3.2. Effect of feed concentration

Feed concentration which influences viscosity and density of the solution has a considerable influence on the degrees of solutes flux and selectivity [17]. The flux and rejection profile for 300, 500, and 700 mg/L feed concentrations at pressure of 1–5 bars are shown in Fig. 5(c) and (d), respectively. It is shown that the membrane performances were in the order of 300 > 500 > 700 mg/L. This sort of series had been presumed since a low feed concentration will evidently provide a high permeation rate. Significant decline in flux and rejection was noticed at the case of 700 mg/L feed concentration. It seems that there is an optimized feed concentration, whereby a good trade-off between flux and rejection was obtained at 500 mg/L (Fig. 6 (b)). This is due to the fact that, although the smaller feed concentration (300 mg/L) offers a higher level of flux, the decrease in the total protein concentration in the feed leads to the low rejection of the protein.

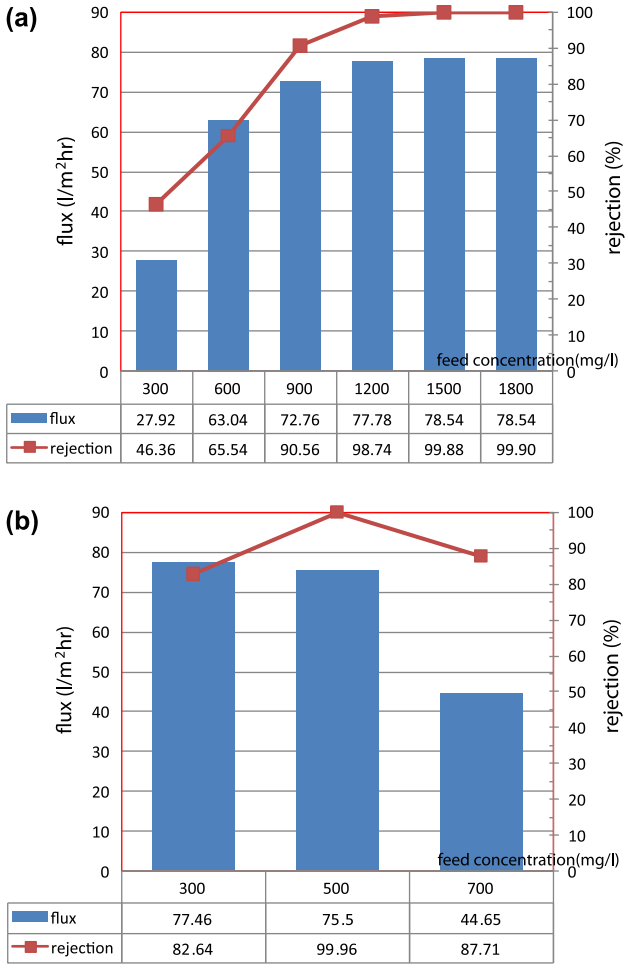

Fig. 6. Flux and rejection profile of feed concentration aMPH7-50 for operating pressure of 3 bar at various (a) stirring speed and (b) myogobin concentration.

4. Conclusion

In this research, hydrophilicity and performance of protein rejection of PES-UF membranes have been successfully improved by coating myoglobin, which acts as surface-modifying molecule. Myoglobin solution of pH 7.0 with the concentration of 50 mg/L has been selected as the modification parameters. Study on various stirring speed and feed concentration reveals these rheological conditions are deemed to play a vital role in the degree of protein rejection by UF membrane. The proper adjustments of both these parameters will lead to flux maximization and subsequently, protein separation will be enhanced.

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References

[1] C. Ba, D.A. Ladner, J. Economy, Using polyelectrolyte coatings to improve fouling resistance of a positively charged nanofiltration membrane, J. Membr. Sci. 347 (2010) 250–259.
[2] M. Tirrell, E. Kokkoli, M. Biesalski, The role of surface science in bio-engineered materials, J. Surf. Sci. 500 (2002) 61–83.
[3] S. Boributh, A. Chanachai, R. Jiraratanon, Modification of PVDF membrane by chitosan solution for reducing protein fouling, J. Membr. Sci. 342 (2009) 97–104.
[4] Y.C. Lin, C.A. Brayfield, J.C. Gerlach, J.P. Rubin, K.G. Marra, Peptide modification of polyethersulfone surfaces to improve adipose-derived stem cell adhesion, Acta Biomater. 5 (2009) 1416–1424.
[5] E.S. Hatakeyama, C.J. Gabriel, J.L. Lohr, J.E. Bara, R.D. Noble, B.D. Freeman, D.L. Gin, New protein resistant coating for water filtration membranes based on quaternary ammonium and phosphonium polymers, J. Membr. Sci. 330 (2009) 104–116.
[6] G. Capar, U. Yetis, L. Yilmaz, The most effective pre treatment to nanofiltration for the recovery of print dyeing wastewater, Desalination 212 (2007) 103–113.
[7] H. Susanto, M. Ulbricht, Characteristics, performance and stability of polyethersulfone ultrafiltration membranes prepared by phase separation method using different macromolecular additives, J. Membr. Sci. 327 (2009) 125–135.
[8] H. Yu, Y. Cao, G. Kang, J. Liu, M. Li, Q. Yuan, Enhancing antifouling property of polysulfone ultrafiltration membrane by grafting zwitterionic copolymer via UV-initiated polymerization, J. Membr. Sci. 342 (2009) 6–13.
[9] H. Susanto, S. Franzka, M. Ulbricht, Dextran fouling of polyethersulfone ultrafiltration membranes—causes, extent and consequences, J. Membr. Sci. 296 (2007) 147–155.
[10] L.H. Huisman, P. Pradonas, A. Hernandez, The effect of protein–protein and protein–membrane interactions on membrane fouling in ultrafiltration, J. Membr. Sci. 179 (2000) 79–90.
[11] M. Van der Veen, Spreading of proteins and its effect on adsorption and desorption kinetics, Colloids Surf. B: Biointerf. 54 (2006) 136–142.
[12] K. Boussu, B. Van der Bruggen, A. Volodin, C.V. Haesendock, J.A. Delcour, P. Van der Meeren, C. Vandecasteele, Characterization of nanofiltration membranes with self made polyethersulfone membrane, Desalination 191 (2006) 245–253.
[13] R. Ghosh, Z. Cui, Fractionation of BSA and lysozyme using ultrafiltration: Effect of pH and membrane pre-treatment, J. Membr. Sci. 139 (1998) 17–28.
[14] I. Pinnau, B.D. Freeman, Membrane formation and modification, ACS Symposium Series, vol. 744, American Chemical Society, Washington, DC, 1999, pp. 1–20.
[15] G. Rice, A. Barber, A. O'Connor, G. Stevens, S. Kentish, Fouling of NF membranes by dairy ultrafiltration permeates, J. Membr. Sci. 330 (2009) 117–126.
[16] J. Wang, J. Liu, J. Lu, Z. Cui, Isolation and purification of superoxide dismutase from garlic using two-stage ultrafiltration, J. Membr. Sci. 352 (2010) 231–238.
[17] S. Bhattacharjee, S. Ghosh, S. Datta, C. Bhattacharjee, Studies on ultrafiltration of casein whey using a rotating disk module: Effects of ph and membrane disk rotation, Desalination 195 (2006) 95–108.