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Performance and antifouling properties of PVDF/PVP and PSf membranes in MBR: A comparative study

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Abstract. In this study, the performance and antifouling properties of polysulfone (PSf) and polyvinylidene fluoride/polyvinylpyrrolidone (PVDF/PVP) membranes in a membrane bioreactor (MBR) were investigated. The membranes were prepared via phase inversion method, and then characterized by a set of analyses including contact angle, porosity and water flux and applied in a lab-scale MBR system. Soluble microbial product (SMP), extracellular polymeric substance (EPS), FTIR, gel permission chromatography (GPC) and particle size distribution (PSD) analyses were also carried out for MBR system. The results showed that the MBR with PSf membrane had higher hydrophobic organic compounds which resulted in formation of larger flocs in MBR. However, in this MBR had high compressibility coefficient of cake layer was higher (n=0.91) compared to MBR with PVDF/PVP membrane (n=0.8); hence, the fouling was more profound. GPC analysis revealed that compounds with molecular weight lower than 2 kDa are more formed on PSf membrane more than PVDF/PVP membrane. The results of FTIR analysis confirmed the presence of polysaccharide and protein compounds on the cake layer of both membranes which was in good agreement with EPS analysis. In addition, the results showed that their concentration was higher for the cake on PSf membrane.

Keywords: PVDF/PVP; PSf; Cake layer specification; MBR

1. Introduction

In MBR technology has been utilized for wastewater treatment since 1969. In current years, the application of membrane bioreactor (MBR) instead of the conventional activated sludge process (CASP) is becoming more common (Drews, 2010). MBR have many advantages over the CASP such as high removal efficiency and the flexibility of operations (Hazrati *et al.* 2016; Kertesz, 2014; Tobino *et al.* 2016). However, the major obstacle for MBRs is membrane fouling and operational optimization of MBRs is affected by antifouling properties of membranes (Behboudi *et al.* 2018b; Hazrati *et al.* 2018; Meng *et al.* 2017; Nam *et al.* 2015; Zhou *et al.* 2010). Parameters like the sludge and membrane specifications and operational conditions can also play a major role in membrane fouling (Mirzavandi *et al.* 2019). Although EPS is the vital membrane foulant, floc adhesion and cake formation can be considered as a next stage of membrane fouling in MBRs. Four forces applied on single floc nearby the membrane in the sludge suspension include: 1-the permeate drag force, 2-the inertial lift force, 3-the net gravity force (gravity force minus buoyant force), 4-the shear force and Brownian diffusion force. The motion of floc depends on the predominant forces on it in MBRs (Qu *et al.* 2018; Teng *et al.* 2019).

Physical and chemical properties of the membrane play a crucial role in membrane surface fouling in the MBRs (Alsalhy *et al.* 2018; Lee and Young, 2012; Marbelia *et al.* 2016). Key physical properties of the membrane such as pore size distribution, roughness and porosity have different impacts on fouling rate (Drews, 2010). On the other hand, chemical factors such as membrane structure, antifouling properties, hydrophobicity and antibacterial activities contribute in membrane fouling (Behboudi *et al.* 2018a). Moreover, fouling depends on attraction forces between intra-atomic and hence the materials of membrane. Studies have shown that polymeric membranes such as polyethylene, polypropylene, PVDF and PSf can be used in MBR systems. PSf is hydrophilic but polyethylene, polypropylene and PVDF are hydrophobic. Therefore, they need surface modification to become hydrophilic.

The presence of different compounds in MBR system such as soluble organic compounds, soluble microbial products (SMP) and extracellular polymeric substances (EPS) with both hydrophilic and hydrophobic properties can also play a significant role in performance of membranes (Campo *et al.* 2017; Lin *et al.* 2014; Martín-Pascual *et al.* 2016; Zhang *et al.* 2016). Previous work have shown that the membrane fouling is affected by some factors such as hydraulic retention time (HRT), sludge retention time (SRT), and biomass characteristics such as floc size, morphology, EPS, SMP, and viscosity (Krzeminski *et al.* 2017; Zeng *et al.* 2018; Zhang *et al.* 2017). Even it can be said that membrane properties such as hydrophobicity, pore size and porosity can affect sludge properties; but it can be claimed that so far, no study has been conducted in this field. Therefore, in this study, two

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membranes were made out of neat PSf and PVDF/PVP and their performance was studied in MBR system.

2. Materials and methods

2.1 Materials

Polysulfone (Ultrason 6010) was purchased from BASF and commercial Polyvinylidene fluoride (PVDF) polymer (MW = 534,000 g/mol) was purchased from Sigma–Aldrich. Polyvinylpyrrolidone (PVP, MW = 40,000 g/mol) as pore former was purchased from Sigma–Aldrich. N-N-dimethylformamide (DMF, anhydrous, 99.9%) was purchased Shandong Hualu-Hengsheng Chemical Co., Ltd.

2.2 Preparation of membranes

PSf membrane was prepared via non-solvent induced phase separation method. PSf (17 wt.%) was dissolved in DMF in a sealed vessel by stirring at room temperature (25 °C) for 24 h and then the solution was left to degas overnight before its using. To begin casting the membrane, the non-woven polyester fabric was attached to a clean glass plate and then wet with solvent and any excess solvent was removed using an air knife. The homogeneous solution was cast over the non-woven fabric with thickness of 250μm, and then submerged in tap water bath at room temperature. The phase separation was occurred and microporous structure was formed.

The PVDF/PVP membrane was prepared via non-solvent induced phase separation method. Initially, the mixture of PVDF (14 wt. %) and PVP (1 wt. %) were dissolved in DMF and stirred for 24 h at room temperature to obtain homogenies solution. After degassing process, dope solution was cast on the non-woven fabric with thickness of 250μm which was attached to a clean glass plate and then submerged in DI water bath at room temperature for 48 h. The bath was refreshed two times to remove all the residual solvent. Finally, prepared membrane was dried at room temperature for further use.

2.3 Characterization of membranes

2.3.1 Contact angle, porosity and mean pore radius

The contact angle between membrane surface and water droplet was measured using sessile drop method. Membrane porosity was determined by water wetting method (wet and dry methods). In this method, membranes were cut into known dimension and their weights were measured precisely in dry condition. Then the membranes were floated in water until their pores were filled with water. After their withdrawal from water, they were dried by a cotton pad and they were reweighed. Mass porosity of the membrane can be calculated by equation (1) (Behboudi *et al.* 2018a):

$$\varepsilon(\%) = \frac{(w_2 - w_1)/\rho_2}{w_1/\rho_1 + (w_2 - w_1)/\rho_2} \times 100 \quad (1)$$

In ε which shows mean volume porosity of the membrane, w_2 is the weight of wet sample (gr), w_1 denotes the dry sample weight, ρ_2 is the density of wetting liquid and ρ_1 is membrane density.

To determine mean surficial pores of the membrane, the method based on pure water permeability was used. In this method, first the volume of the pure passed water was measured. Then using Guerout-Elford-Ferry (GEF) equation (2), the mean radius of the pores can be calculated (Behboudi *et al.* 2016):

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon)8\eta LQ}{\varepsilon A \Delta P}} \quad (2)$$

In this equation, r_m (mm) is the mean radius of the pores, η (Pa.s) is the pure water viscosity, L (m) shows the membrane thickness, Q (m^3/s) is the volume of the water passed from the membrane, ε denotes the mean volume porosity of the membrane, A (m^2) is the membrane area and ΔP (MPa) is the applied pressure on the membrane.

2.3.2 Pure water flux

Membrane water flux was measured by a dead-end system. The membrane was placed inside the module and the tank was filled with distilled water. The membrane was placed under 0.1 bar and after reaching to stable condition, the amount of passed water was measured. This flux is called J_0. Three trials were performed per each sample and the average values were reported as the permeability of each type of flat sheet membrane.

2.3.4 Investigation of membranes resistance against fouling

After the filtration in the MBR system, the membrane module was removed from the bioreactor and again submerged in water bath to record the water flux after fouling (J_1). Finally, the formed cake layer on the membrane surface was gently removed and the membrane was washed with DI water. The pure water flux after removal of cake layer (J_2) was measured. The membrane fouling properties and flux behavior can be obtained by J_0, J_1 and J_2 parameters.

Having values of J_0, J_1, J_2 and J_3, we can obtain valuable information on membrane fouling and their resistance against this phenomenon. Total fouling, reversible, irreversible and recovery flux can be obtained by following equations relative to pure water flux from clean membrane module (Behboudi *et al.* 2017):

$$\text{Total fouling rate (TFR)} = \frac{J_0 - J_1}{J_0} \quad (3)$$

$$\text{Reversible fouling rate (RFR)} = \frac{J_2 - J_1}{J_0} \quad (4)$$

$$\text{Irreversible fouling rate (IFR)} = \frac{J_0 - J_2}{J_0} \quad (5)$$

$$\text{Recovery flux (RF)} = \frac{J_2}{J_0} \quad (6)$$

As there is a direct relationship between fouling mechanism and reduction of flux, resistance in serial model is the simplest method which use Darcy law (equation 7) to

predict the passing flux (Chang and Kim, 2005):

$$J_p = \frac{1}{A} \times \frac{dV_p}{dt} = \frac{\Delta P}{\eta\left(R_m + R_c + R_p + R'\right)} \quad , \left[\frac{L}{m^2.h}\right] \tag{7}$$

Where, ΔP is the pressure difference on two sides of the membrane [Pa], A represents the membrane useful surface [m^2], V_p is the volume of passing flow [L], t denotes the operation time [h], η is the dynamic viscosity of the fluid [Pa.s], R_m is the intrinsic resistance of the membrane, R_c shows the cake resistance, R_p indicates reversible blockage resistance and R' shows the irreversible pore blockage resistance [1/m]. Each resistance can be calculated by equations of 8 to 12:

$$R_m = \frac{TMP}{(\eta * J_0)} \tag{8}$$

$$R_T = \frac{TMP}{(\eta * J_1)} \tag{9}$$

$$R' = \frac{TMP}{(\eta * J_3)} - R_m \tag{10}$$

$$R_c = R_T - \frac{TMP}{(\eta * J_2)} \tag{11}$$

$$R_p = R_T - (R_c + R_m + R') \tag{12}$$

2.4 MBR set up

The dimensions of the membrane bioreactor for this setup were of 30×10×12 cm (Fig 1). The effective volume in the reactor was 2L. The aerobic sludge used in the MBR basin was supplied from the activated sludge of the Tabriz Petrochemical Company then adapted with synthetic feed for one month. The synthetic wastewater used in this research was formulated to simulate petrochemical industrial wastewater in terms of chemical oxygen demand (COD).

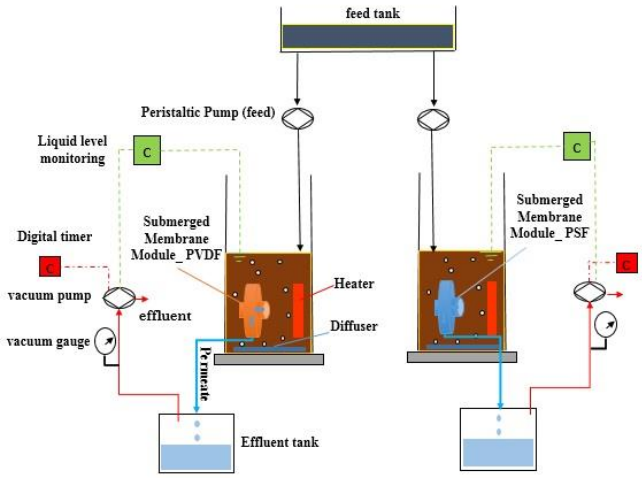


Fig. 1 A lab scale MBR

2.5 Analytical methods for MBR

2.5.1 Analysis of Fourier transform infrared spectrometer (FTIR)

FTIR analysis was used to characterize the major functional groups of organic matters in cake layer that formed on membrane surface (Wang *et al.* 2009). The cake layer that removed from the membrane surface was dissolved in 500 mL pure water. After that, about 50 mL of the solution were centrifuged for 10 min at 9000 rpm. The foulants pellet were placed in incubator for 48 h at 55˚c. The dry foulants used for FTIR analysis.

2.5.2 GPC analysis

This test was carried out on membrane cake after dissolving in 500 ml distilled water. The samples were centrifuged for 10 min at the rate of 9000 rpm. Then the remaining EPS was extracted by thermal methods. The obtained solution was then centrifuged by the same method and the supernatants were sent for GPC tests after passing through 0.45 μm filter.

2.5.3 SMP and EPS analysis

SMP and EPS concentrations were measured according to Chang's method (Chang and Lee, 1998). Protein fraction (SMPp and EPSp) was measured by Bradford's method (Zhang *et al.* 1999); while the corresponding polysaccharide fraction (SMPc and EPSc) was measured by phenol–sulfuric acid method (DuBois *et al.* 1956).

Relative hydrophobicity of the SMP and EPS was measured according to Rosengerg's method (Rosengerg *et al.* 1980). 50 ml sludge sample was sufficiently mixed with 50 ml n-hexane in a separating funnel for 0.5 hour. After that, a 0.5 hour settling was conducted to allow complete separation of the two phases of aqueous and organic. Then SMP and EPS values were measured for aqueous phase. The relative hydrophobicity is expressed as the ratio of the separated aqueous phase concentration to the initial concentration of the sample.

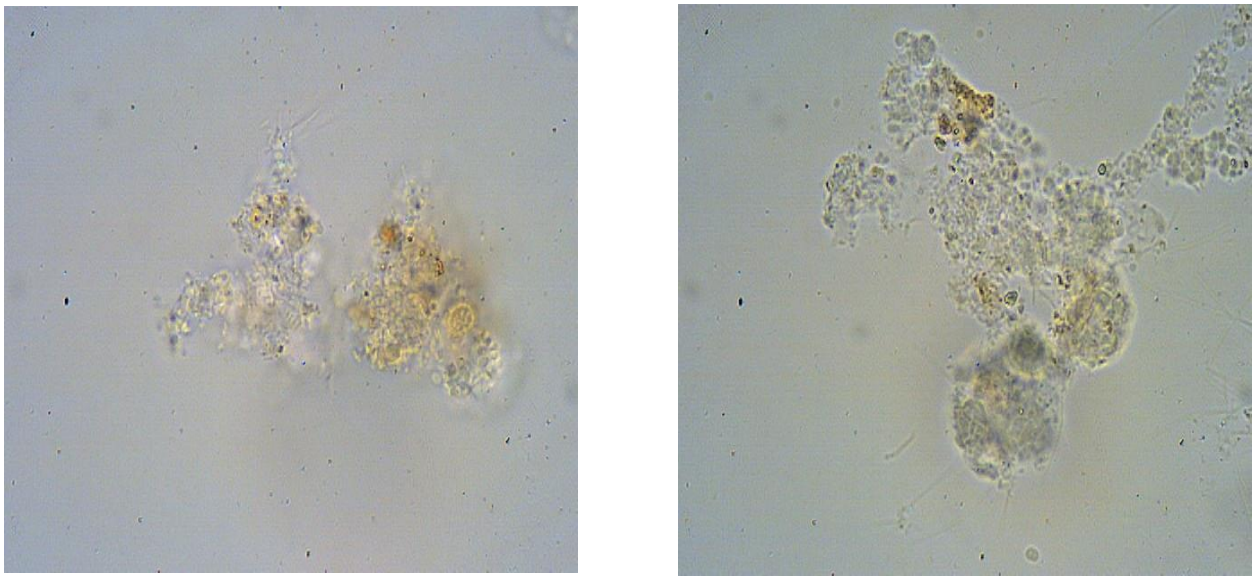
2.5.4 Microscope observation

The sludge flocs were examined by light microscopy and the images were captured on a Yu JIE, XSP21-01T microscope attached with a PC-based charge-coupled device.

3. Results and discussion

3.1 Characteristics of the membranes

Table 1 summerizes the characteristics of prepared membranes. It can be seen that pure water flux of PVDF/PVP membrane is higher than that of PSf one. This can be attributed to other characteristics of the membrane such as mean pore radius and the porosity. Mean pore radius of PVDF/PVP membrane is about two times of PSf membrane which can facilitate water permeation through the former one. It should be noted that even though the contact angle of PVDF/PVP membrane is higher than that of PSf membrane, the hydrophilicity of it increased due to



(a) for first reactor **(b)** for second reactor

Fig. 2 Microscopic observation of sludge

Table 1 Mean pore radius, pure water flux, porosity, and contact angle of prepared membranes

Membrane	Mean pore radius (μm)	Pure water flux (LMH)	Porosity (%)	Contact angle (º)
PSf	0.968 ± 0.141	65.38 ± 1.23	67 ± 2	60.3 ± 2.1
PVDF/PVP	2.081 ± 0.103	73.08 ± 1.87	73 ± 1	71.9 ± 1.4

the presence of PVP. It was shown that the contact angle of neat PVDF/PVP membrane is about 90º (Lü *et al.* 2016) and as shown, it decreased to about 72º (Table 1). There is an oxygen atom double-bonded to a carbon atom in the PVP chains. Therefore, the interaction between water molecules and membrane matrix can be increased which improves the hydrophilicity. The presence of PVP can also help water permeation throughout PVDF/PVP membrane.

3.2 SMP and EPS concentrations

SMP and EPS concentration of sludge as well as the hydrophobicity and hydrophilicity value are provided in Table 2. Results showed that hydrophilic SMP concentration was decreased in the second reactor resulting in decline of total SMP. This decrease could be due to several reasons: they can be destroyed during synthesis by biomass or enter the membrane pores (Jiang *et al.* 2010). As the pores inside in the membrane of the second reactor is more hydrophilic, some hydrophilic compounds of SMP entered the pores giving rise to their blockage. But in the first reactor, total and hydrophobic and hydrophilic SMP were not changed significantly. Therefore, it can be said that organic compounds did not enter the pores; hence the fouling of this reactor is lower compared to second reactor. In some studies, it has been expressed that one of the major factors of membrane fouling is higher content of SMP especially its hydrophilic component (Yuniarto *et al.* 2013).

Table 2 SMP and EPS concentrations of sludge and their hydrophobicity and hydrophilicity values

MBR	SMP (1 days)			SMP (End of operation)		
	Total	hydrophilic	hydrophobic	Total	hydrophilic	hydrophobic
First reactor (PVDF/PVP)	59 ± 5	37 ± 1	22 ± 4	62 ± 4	38 ± 2	24 ± 2
Second reactor (PSf)	58 ± 4	35 ± 3	23 ± 1	45 ± 4	21 ± 3	24 ± 1
MBR	EPS (1 days)			EPS (End of operation)		
	Total	hydrophilic	hydrophobic	Total	hydrophilic	hydrophobic
First reactor (PVDF/PVP)	147 ± 8	95 ± 6	52 ± 2	126±9	91 ± 8	35 ± 1
Second reactor (PSf)	147 ± 7	93 ± 5	54 ± 2	100±7	42 ± 3	58 ± 4

Moreover, EPS concentration results showed that hydrophobicity of EPS was decreased in the first reactor while the hydrophobic component of EPS of the sludge was higher in the second reactor in end of operation. One of the reasons for formation of larger flocs in MBR is higher hydrophobicity of EPS (Arabi and Nakhla, 2008). Therefore, it is anticipated the sludge inside the second reactor forms larger flocs in comparison with the first one. Results of particle size distribution can prove this prediction. These results indicate that flocs formation does not require higher EPS; but the surface properties are also important. It was also expressed that higher filament bacteria can be a reason for increased hydrophobicity of EPS (Meng *et al.* 2006). Microscopic observations however, showed no filament bacteria in the bioreactors (See Fig. 2).

3.3 Particle size distribution

Generally, increase of sludge particle size will reduce their penetration into membrane pores and enhance their chance to be transmitted from membrane surface to the bulk phase (Jin *et al.* 2013). Due to high reverse speed, larger

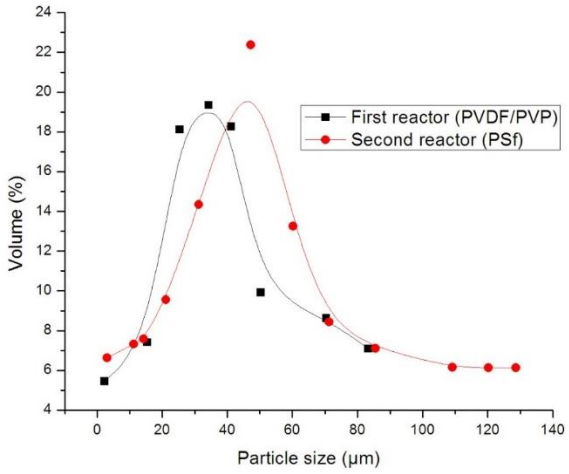


Fig. 3 Particle size distribution in both MBR

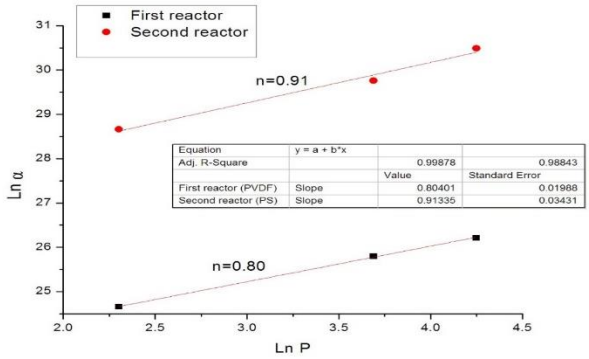


Fig. 4 Compressibility coefficient in both MBR

flocs have smaller contribution in membrane fouling (Meng and Yang 2007). Fig. 3 shows the particle size distribution for both bioreactors at the end of operation. As it can be seen, mean of sludge particle size was 35 and 45 micrometer for first and second reactor, respectively. As the EPS compounds of the second reactor are more hydrophobic (PSf membrane is more hydrophilic; so hydrophobic compounds were accumulated in MBR), biomass bulks were attached to each other giving rise to increase of flocs size. Regarding larger sludge particle size in second reactor, it was anticipated to have cake layer with lower compressibility (see Fig. 4); however the cake layer in the first reactor had lower compressibility coefficient; hence, the membrane fouling was lower (n=0.91 for the second reactor and n=0.80 for the first one). The reason could be presence of hydrophilic compounds entering the pores of second reactor which had lower porosity which gave rise to a compressible cake layer.

3.4 Variation of permeate flux

In this study, both MBRs were working under constant pressure of 0.1 bar in which flux reduction indicated membrane fouling. Fig. 5 shows flux reduction for both membranes until the end of operation. As it was shown, for

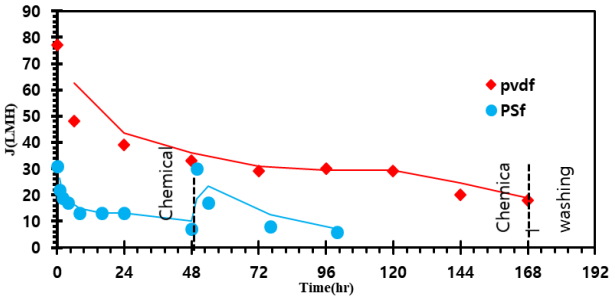


Fig. 5 Permeate flux for both MBR

Table 3 The results of fouling resistance distribution and fouling rate

Resistance	$R_m * 10^{-11}$ (m^{-1})	$R_p * 10^{-11}$ (m^{-1})	$R_c * 10^{-11}$ (m^{-1})	$R' * 10^{-11}$ (m^{-1})	$R_t * 10^{-11}$ (m^{-1})
First reactor (PVDF/PVP)	1.897	1.001	4.506	0.105	7.509
Second reactor (PSf)	2.120	2.253	40.551	0.133	45.056
Fouling rate		RFR (%)	IFR (%)	TFR (%)	RF (%)
First reactor (PVDF/PVP)		69	5	75	95
Second reactor (PSf)		89	6	95	94

PVDF/PVP membrane, initial flux was more than PSf membrane; moreover, flux reduction occurred earlier in PSf membrane. The reason for this results, it is that sludge properties were important which will be discussed in pervious sections. Furthermore, although hydrophilicity of PS is higher, but PVDF/PVP membrane porosity was more than PSf. In general, flux reduction can be due to three main reasons: resistance of membrane, membrane pores fouling and formation of more cake layer. To estimate the fouling mechanism, each of the resistances was separately calculated (Table 3). Results showed that the membrane resistance was higher in the second reactor; also, pores and cake layer resistances of this reactor were more than the first one. These results indicated that membrane type such as its hydrophilicity for alone can't reduce membrane fouling in biological systems. Other factors such as sludge properties should be also investigated simultaneously. Moreover, results in Table 3 revealed that total (TFR), reversible (RFR) and irreversible fouling rate (IFR) of PVDF/PVP membrane were far better (smaller) than PSf membrane. Also recovery flux percentage (RF) for PVDF/PVP membrane was higher than PSf membrane.

3.5 FTIR analysis

FTIR analysis was performed on both reactors as depicted in Table 4. The most important peaks were related to wavenumber of 2944 reflecting O-H functional groups and 1061 showing C=O bind. These peaks were assigned to polysaccharide compounds (Jin *et al.* 2010, 2013). On the other hand, comparison of cake layers indicated that polysaccharides of the second reactor are lower compared to first one. In addition to these two peaks, two other peaks emerged at wavenumbers of 1651 and 1555 indicating C-N

Table 4 The results of FTIR for cake layers in both reactors

Wavelength	Functional group	Absorbance (%)	
		First reactor (PVDF/PVP)	Second reactor (PSf)
1061	C=O	65	78
1555	(C-N) Amid (II)	58	83
1651	(C-N) Amid (I)	69	95
2944	O-H	51	78

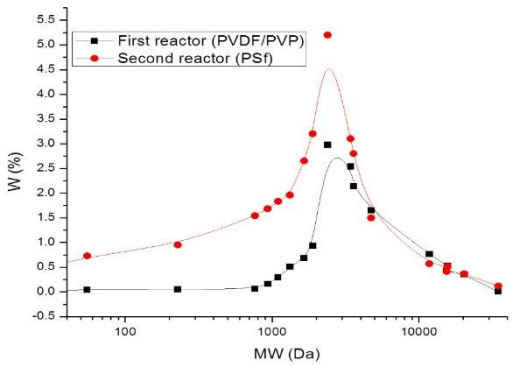


Fig. 6 Molecular weight distribution for both MBR

functional group of first and second type amides (Shariati *et al.* 2011). Therefore, protein compounds also existed in the cake in addition to polysaccharides. Also, regarding their adsorption level, similar to polysaccharides, protein content of the second reactor was significantly reduced. EPS results also showed that polysaccharide and protein contents of the cake in the first reactor were lower than the second one. In this content, FTIR test is a reliable test for checking these items.

3.6 GPC analysis

Organic compounds with low molecular weight play a prominent role in membrane fouling (Hazrati *et al.* 2018). Therefore, GPC analysis was conducted to determine the molecular weight of organic compounds to investigate the effect of membrane type on improvement of cake properties. The results are provided in Figure 6. As it is clear, second reactor has more organic compounds with molecular weight below 2 kDa; therefore, it can be said that these compounds play important role in fouling of PSf membranes. The reason for accumulation of these compounds could be presence of hydrophilic organic compounds. It must be noted that compounds with higher molecular weight did not change significantly probably due to the fact that compounds with molecular weight over 4 kDa are mainly eliminated by biological method (Ji *et al.* 2010).

4. Conclusion

In this study, two membranes were synthesized from PVDF/PVP and PSf and studied in terms of MBR membrane fouling. Results are as follows:

1) Both membranes had proper flux in the pure water due to improvement of their hydrophilicity and porosity; but in MBR system, PSf membrane showed intense flux reduction.

2) In contrary to our expectation, PVDF/PVP membrane not only reduced cake layer but also decreased the pore fouling relatively.

3) GPC analysis showed that organic compounds with molecular weights below 2 kDa have higher accumulation on PSf membrane; therefore, they can be one of the reasons of flux reduction in this membrane.

4) FTIR analysis of the cake showed that EPS of the cake is mainly composed of polysaccharides and proteins.

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