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Cross-flow ultrafiltration of stable oil-in-water emulsion using polysulfone membranes

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ABSTRACT

This paper focuses on the treatment of oily wastewater coming out from the post-treatment unit of petroleum industries using cross-flow mode of ultrafiltration. Four types of polysulfone (PSf) membranes which had been synthesized using different combinations of additives and solvents were used and their performances were evaluated by treating with laboratory made oil-in-water (o/w) emulsion and later the selected membranes were tested for their applicability to the industrial oily water also known as 'produced water'. Experiments were carried out mainly to study the influence of cross-flow rate on membrane performance. The study showed that with increase in cross-flow rate, the flux increases significantly; but the oil rejection (%) shows a decreasing trend. Also change in morphological properties of membranes due to addition of different molecular weight PVP and PEG are found to have a significant impact on the permeate flow rate and hence subsequent oil removal. The oil retentions of all the four membranes were over 90% and oil concentration in the permeate was below 10 mg L^{-1} with the synthetic oily water, which met the requirement for discharge. However, the rejection was found to be below 80% for all the membranes with the 'produced water' although the flux was reasonably high. This suggests that the membranes need further modifications to improve their properties such as average pore size and pore size distribution in order to tackle the difficulty of lower oil separation due to penetration of the smaller oil droplets along with the permeate.

1. Introduction

Crude oils are complex mixtures of a large number of hydrocarbons which vary in their toxicity to aquatic and terrestrial life. 'Produced water', which is the water co-produced during oil and gas manufacturing, contains dispersed oils and suspended particles. These 'produced waters' constitute the single largest waste stream from oil and gas exploration and production activities. Environmental regulations require that maximum total oil and grease concentrations in discharge waters be 10–15 mg L^{-1} [1]. Major pollutant in wastewater generating from oil field is oil which may range between 100 and 1000 mg L^{-1} or higher depending on the efficiency of demulsification and nature of crude oil.

All the traditional methods are mostly not efficient enough for treating stable o/w emulsions (size $\leq$20 μm) especially when the oil droplets are finely dispersed and the concentration is very low. Because the emulsion droplets, which are of micron and submicron size, require a very long residence time to rise onto the top for enabling gravity separation and even addition of chemicals cannot break the emulsions effectively. Reports say that these techniques can reduce oil concentration to hardly 1% by volume of the total wastewater and cannot efficiently remove oil droplets below 10 μm size [2,3]. The water phase obtained from such treatment is generally required to be further purified to meet the accepted effluent standard for discharge into the river.

The use of membrane technology offers a potential solution to the problem of micron sized oily wastewater. The porous membrane matrix can promote coalescence of micron and submicron oil droplets into larger ones that can be easily separated by gravity [4]. Some of the most promising methods based on membrane separation processes are dehydration of oil emulsion by pervaporation [5], or by reverse osmosis (RO) [6], flocculation followed by microfiltration (MF) [7], MF [8], membrane distillation (MD) [9] and ultrafiltration (UF) [10].

A number of researchers have reported their works on membrane UF/MF process for oily water treatment. Ohya et al. [8] studied the effect of the average pore size in porous glass tube membranes on the performance of the cross-flow MF of o/w emulsion and found that filtration mechanism varied with membrane pore diameter. The oil rejection was found to decrease from 94% to 80% as the membrane pore size increased from 0.27 to 1.47μm. Effectiveness of a polyvinyl alcohol (PVA) membrane selected for UF of synthetic oily water was evaluated in a study carried

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Nomenclature

CF	Compaction factor
CFV	Cross-flow velocity
CFR	Cross-flow rate
DMAc	Dimethyl acetamide
EWC	Equilibrium water content
FD	Flux declination
MD	Membrane distillation
MF	Microfiltration
NF	Nanofiltration
NMP	N-methyl pyrrolidone
PEG	Poly(ethylene glycol)
PF	Permeate flux
PSf	Polysulfone
PTFE	Polytetrafluroethylene
PVDF	Polyvinylidene difluoride
PVP	Polyvinylpyrrolidone
PWF	Pure water flux
RO	Reverse osmosis
SP	Separation parameter
TDS	Total dissolved solids
TMP	Transmembrane pressure
UF	Ultrafiltration

Notations

A	Effective membrane area (m^2)
C_f	Concentration in the feed ($mg\,L^{-1}$)
C_p	Concentration in the permeate ($mg\,L^{-1}$)
C_{ss}	Concentration in the permeate at steady state ($mg\,L^{-1}$)
J_p	Permeate flux ($L\,m^{-2}\,h^{-1}$)
J_w	Pure water flux ($L\,m^{-2}\,h^{-1}$)
N_t	Porosity
Q_p	Volume of the permeate (L)
Q_t	Volumetric flow rate of permeate ($m^3\,s^{-1}$)
Q_w	Volume of water permeated (L)
r_{av}	Average pore size
R	Rejection (%)
R_m	Membrane hydraulic resistance (m^{-1})
W_p	Weight of the permeate (kg)

out by Wu et al. [11] using a pilot-scale continuous cross-flow membrane filtration system. Within the range of experiments, the PVA UF membrane had a superior permeate flux (more than 200 $L\,m^{-2}\,h^{-1}$) and a relatively high oil retention (93%). Hua et al. [12] carried out cross-flow MF processes with oily wastewater (oil concentration ≈500 ppm) using a ceramic (α-Al_2O_3) membrane with 50 nm pore size. The TOC removal efficiencies higher than 92% were achieved under all experimental conditions. Treatment of oily wastewater produced from post-treatment unit of refinery processes using flocculation and MF with zirconia membrane was studied by Zhong et al. [7]. The results of MF tests showed that the tendency of membrane fouling decreased and the permeate flux and permeate quality increased with flocculation as pre-treatment. Lobo et al. [13] studied the effect of cross flow velocity (CFV) and pH on UF of model metalworking o/w emulsion using Carbosep tubular ceramic membranes with two different cut offs (50 and 300 kDa) in a TMP range of 0.05–0.4 MPa and concluded that both permeate flux and COD retention decreased drastically at low pH values. Li et al. [14] in their study used a tubular UF module equipped with PVDF membranes modified by inorganic nano-sized alumina particles to purify oily wastewater from an oil field. They found that the addition of nanosized alumina particles improved membrane antifouling performance. Gorouhi et al. [15] conducted the MF operation to separate oil from oily wastewater using polypropylene (PP) membrane with 0.2 μm pore size manufactured by MEMBRANA in cross-flow mode. It was found that increasing temperature, TMP and flow rate increases both permeate flux and water content in permeate. Scott et al. [16] investigated the behaviour of the cross-flow MF of "stable" dispersions of an immiscible organic solvent (tridecanol) in water with mean droplet size of 1 μm, using commercial MF membranes composed of either PSf, nylon, polytetrafluroethylene (PTFE) (all having mean pore size of 0.2 μm) or a mixed cellulose acetate/nitrate (having mean pore size of 0.2, 0.45 and 1.2 μm). The membrane pore size which achieved rejections of greater than 90% was 0.2 μm when the TMP was at 0.8 bar and the CFV was held between 3 and 4 $m\,s^{-1}$. Xu et al. [17] studied the performance of the asymmetric hollow fiber membranes prepared from wet-spun 25 wt% solids of 20:5:75 (wt ratio) polyetherimide (PEI)/poly(ethylene glycol) (PEG) 600/dimethyl acetamide (DMAc) and 19:1:5:75 PEI/polybenzimidazole (PBI)/PEG 600/DMAc solutions for oil–surfactant–water separation. PEI is hydrophobic while PBI and PEG are hydrophilic and have been employed as additives to the membranes. For the oil–surfactant–water emulsion (1600 ppm surfactant and 2500 ppm oil), experimental results illustrated that the rejection rates for surfactant, TOC and oil obtained were 51.4–79.1%, 83.1–92.7% and more than 99%, respectively. Hao et al. [18] prepared crosslinked poly(ethylene oxide) fouling resistant membranes and employed in oil/water cross-flow filtration experiments. Results showed that the coated membranes had water flux values 400% higher than that of an uncoated PSf membrane after 24 h of operation, and the coated membranes had higher organic rejection (≈98.5%) than the uncoated membranes. Li et al. [19] developed a hydrophilic hollow fiber UF membrane fabricated from a new dope containing cellulose/monohydrate N-methylmorpholine-N-oxide (NMMO·H_2O)/PEG 400 with a mass ratio of 8/88/4 using the immersion precipitation technique for oil–water separation.

From the above review, though it appears that many studies related to oily wastewater have been carried out, but most of the reported investigations mainly have focused on treating oily water having oil concentration equal to or higher than 1000 $mg\,L^{-1}$. Oily water with oil droplets of size higher than 50 μm is in unstable state and as such separation is comparatively simpler. But oil droplets of less than 20 μm size are considered to be highly stable and so is very difficult to separate particularly when oil concentration is in lower range. Therefore, analysis of water collected from the effluent treatment plants of most of the industries reveals that the oil content is still quite high above the allowable discharge standard of 10 $mg\,L^{-1}$. To the best of our knowledge, a very limited experimental studies on such treated water having oil droplets below 5 μm size with PSf membrane have been carried out so far.

This paper reports the application of synthesized PSf membranes for oily wastewater separation. Four different systems (PSf/NMP/PVP, PSf/NMP/PEG, PSf/DMAc/PVP and PSf/DMAc/PEG) of membranes were synthesized and characterized accordingly, which are reported in our previous publications [20,21]. Here, the results of the application of the four PSf membranes of different compositions in separating oil from synthetic oily water as well as industrial oily water at different conditions have been elaborated. Cross-flow UF mode of operation is considered for this study. The objective of the study was mainly to observe the effect of cross-flow rates (CFRs) on the steady state permeate flux (PF) and rejection of oil (%R) at two different transmembrane pressures (TMPs) with a feed of constant concentration and pH. Finally the study aims to identify the most suitable membrane based on a parameter called 'selection parameter'.

Table 1
Composition of the different membranes; PSf: 12 wt%.

Membrane systems	Membranes	Solvents (wt%)		Additive (wt%)	
		NMP	DMAc	PVP	PEG
PSf/NMP/PVP24000	M_1	83	–	5	–
PSf/DMAc/PVP360000	M_6	–	83	5	–
PSf/NMP/PEG20000	M_9	83	–	–	5
PSf/DMAc/PEG20000	M_{12}	–	83	–	5

2. Experimental

2.1. Membranes

2.1.1. Raw materials

PSf (average molecular weight 30,000 Da) supplied by Sigma–Aldrich Co., USA, was used as the main polymer in the membrane casting solution. Reagent grade NMP (99.5% purity) and DMAc (99% purity) supplied by Central Drug House (CDH) Ltd., India were used as solvents without further purification. Reagent grade PVP and PEG were used as additives separately into the casting solution in order to get membranes with varying morphological and permeation properties. Deionized water from Millipore system (Millipore, France) was used as the main non-solvent in the coagulation bath in preparing the membranes.

2.1.2. Membrane preparation and characterization

Flat sheet PSf membranes were prepared by immersion precipitation (i.e. phase inversion) method. Measured amount of polymer (PSf) along with PVP and PEG was dissolved in the two solvents viz. NMP and DMAc, separately at room temperature (≈25 °C) and relative humidity (≈72%) to make the casting solution. The polymer (PSf) concentration was kept constant at 12%, keeping the solvent and additive concentration at 88%. Altogether twelve membranes were obtained considering all the combinations which were designated as M_1, M_2, ... M_{11}, M_{12}. Details of which can be found in our previous publication [22]. Based on the batch study of synthetic oily water with all the membranes [22], M_1, M_6, M_9 and M_{12} membranes are selected to carry out the cross-flow UF study. Table 1 represents the compositions of these four membranes.

The prepared membranes were characterized by morphological analysis and permeation experiments. The morphology of the membranes was investigated by microscopic observations (SEM analysis) and the liquid displacement tests. SEM analysis provided the images of membrane cross-section and top surface. The average pore size (r_{av}) and porosity (N_t) along with cumulative pore size distribution for each membrane were obtained from the liquid displacement tests. The properties of the membranes were measured in terms of pure water flux (J_w), equilibrium water content (EWC), hydraulic resistance (R_m) and compaction factor (CF). The details including the method of membrane preparation and characterization techniques are reported elsewhere [20,21]. All the values of these properties are shown in Table 2.

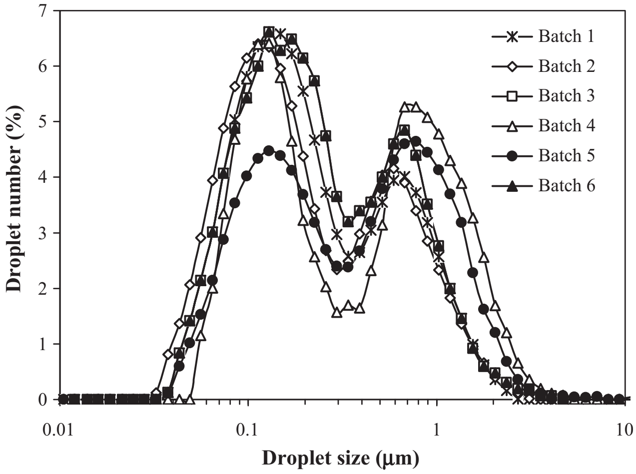

Fig. 1. Size distributions of oil droplets in synthetic oily water prepared in different batches; oil concentration: 100 mg L^{-1}.

2.2. Oil-in-water emulsion

2.2.1. Synthetic oily water

In o/w emulsions, oil is dispersed as liquid droplets through the water which is the continuous phase. These oil droplets generally have a tendency to coalesce to form bigger drops. The smaller the droplets, the greater is the surface tension which means greater the force will be needed to merge among themselves; so such emulsion is said to be stable in comparison to an emulsion containing larger oil droplets. As this study was associated with the UF of stable o/w emulsion, so it was attempted to prepare samples of oily water containing smaller sized oil droplets (<10 μm). Crude oil supplied by Guwahati Refinery, Indian Oil Corporation Limited (IOCL), India was used without any treatment to prepare the emulsion. The details of the preparation and characterization of o/w emulsion are given in our previous publications [22]. The emulsion was stable with respect to coalescence and homogeneous nature of the solution (i.e. absence of oil layer on the top of the solution) for at least two weeks. During this period of two weeks, the droplet size distribution, absorbance and pH of the feed with regular time interval were found to be almost the same. Fresh feed was prepared after an interval of two weeks to keep the consistency of feed properties. Fig. 1 shows the size distributions of oil droplets in the feed prepared in some batches before conduction of the UF experiments. From the figure, it is observed that the distributions were almost similar with minor variations. It is also seen that the size range of the emulsion droplets in the feed is within 0.03–5 μm with an average size of 0.39 μm. The properties of the feed with 100 mg L^{-1} oil content in normal conditions are shown in Table 3.

2.2.2. Industrial oily water (produced water)

Industrial oily wastewater also known as 'produced water' was collected from Oil India Limited (OIL), Duliajan, Assam, India. It is a premier Indian national oil company and is mainly engaged in exploration and production of crude oil and natural gas. It is known that crude oil is found trapped in porous rocks beneath domes of

Table 2
Properties of membranes used for cross flow experiments.

Membranes	r_{av} (nm)	$N_t \times 10^{-9}$ (cm^{-2})	PWF (L m^{-2} h^{-1}) at 103.4 kPa	EWC (%)	CF
M_1	3.62	2.6	219.7	46.8	1.76
M_6	3.21	10.5	45.8	70.0	1.12
M_9	3.42	2.1	1605.1	78.8	1.27
M_{12}	3.39	2.2	308.7	76.4	3.8

Table 3
Properties of oily water (both synthetic and industrial) used for cross flow experiments.

Type of oily water	pH	Density ($kg\,m^{-3}$)	Oil content ($mg\,L^{-1}$)	Emulsion droplet size distribution (μm)
Synthetic	6.12	995	100	0.03–5.0
Produced water[a]	8.73	1001	366	0.02–0.2

[a] TDS: 4160 $mg\,L^{-1}$.

impermeable rock. Since oil is lighter than water, it floats on water and becomes caught between the water below it and the impermeable surface above it. So when crude oil is extracted, it generally comes out of the well along with a significant amount of water and, often, small amount of natural gas. Conventional separation methods are employed to separate water and gas from the crude oil prior to sending to the refineries. This water which still contains considerable amount of small droplets of oil in the form of o/w emulsion is known as the ‘produced water’.

The ‘produced water’ so collected was not suitable for direct application to UF as it contained considerable amount of free floating oil on the top and solid particles at the bottom which are likely to clog the membrane pores as well as obstruct the flow through the pipings used in the experiment. So, preliminary treatments were carried out with the sample. At first, the solid particles were removed by gravity settling. Then the water was made free from the floating oil (formed by the coalescence of the bigger oil droplets) by skimming followed by normal filtering using a common porous filter paper. The resulting oily water (i.e. the filtrate) which was almost free from solid particles and free oil, but still appeared turbid, was considered for carrying out further studies. Before UF experiments, the pretreated ‘produced water’ was characterized in terms of oil content, average size of the oil droplets, pH, density and total dissolved solids (TDS). The distribution of the size of the oil droplets and the remaining solid particles in the ‘produced water’ obtained by the laser particle size analyzer are shown in Fig. 2. It is seen that the size ranges from about 0.02 to 0.2 μm with an average size of 0.1 μm. The pH and TDS of the water were obtained using the digital portable water/soil kit (Model: VSI – 06D1, VSI Electronic Pvt. Ltd., Chandigarh, India). The properties of the ‘industrial water’ in normal conditions are shown in Table 3.

2.3. Cross-flow ultrafiltration experiment

The dead-end mode is usually used mainly for laboratory experiments; while in contrast to that, cross-flow mode has been actually applied in continuous operations for the separation of solutes in industry. The schematic of the cross-flow experimental setup is shown in Fig. 3. The setup consists of a feed tank, a peristaltic pump (Model PP20, Miclins India), a permeate tank and the cross-flow cell. The cell is a rectangular shaped stainless steel chamber with a cross-sectional area of $144 \times 10^{-4}\,m^2$. The membrane sheet was placed inside the cell supported on a thin net type steel plate fitted with the help of a rubber gasket. The effective area of the membrane sheet was $6 \times 10^{-4}\,m^2$. The cell is equipped with one pressure gauge at the middle which gives the trans-membrane pressure (TMP) i.e. the pressure across the membrane. The feed solution was circulated by the peristaltic pump from the feed tank through the cell. The permeate side was open to the atmosphere and the TMP was controlled by adjusting the valve manually on the retentate side. The circulating flow rate was obtained from the reading displayed by the pump; the permeate was collected in a beaker on the electronic balance and the permeate flux was obtained by measuring the time to collect a certain weight of fluid. The retentate was recy-

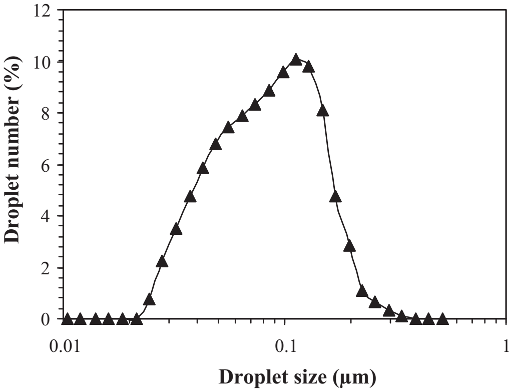

Fig. 2. Size distribution of oil droplets in “produced water”.

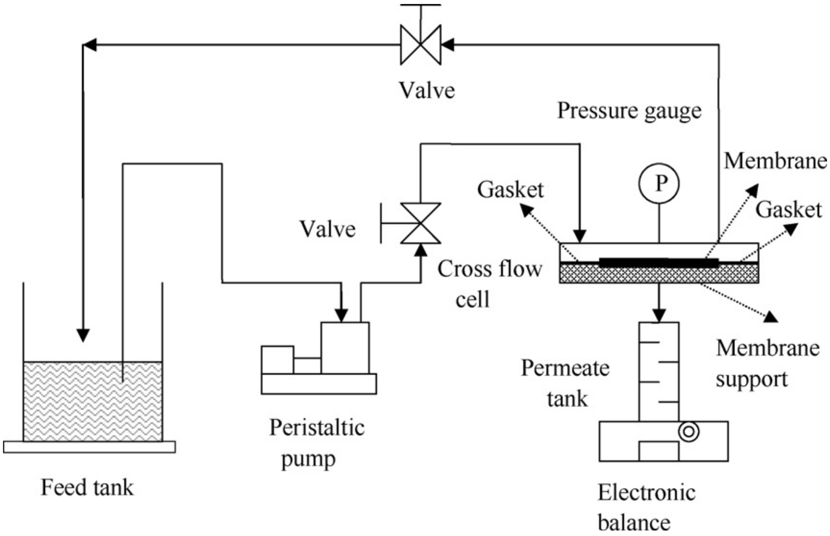

Fig. 3. Schematic of the cross-flow experimental setup.

Table 4
The summary of the operating conditions for synthetic oily water.

Membrane type	Oil concentration in feed (mg L^{-1})	TMP (kPa)	Feed pH	CFR × 10^6 ($m^3\ s^{-1}$)
M_1, M_6, M_9, M_{12}	100	103.4, 172.4	6.12	2.4, 3.1, 4.0

cled continuously to the feed tank while the permeate sampled for analysis was returned to the feed tank for maintaining a consistent feed concentration.

2.4. Procedure

2.4.1. Synthetic oily water

The cross-flow UF was carried out with the four selected membranes mainly to observe the effect of cross-flow rates (CFRs) on the steady state flux and rejection at two different TMPs. The initial oil concentration in the feed was kept at 100 mg L^{-1} and the pH was at its original value which was 6.12. The two TMP values chosen were 103.4 kPa (15 Psig) and 172.4 kPa (25 Psig) and three CFR values, i.e. $2.4 \times 10^{-6}\ m^3\ s^{-1}$, $3.1 \times 10^{-6}\ m^3\ s^{-1}$ and $4.0 \times 10^{-6}\ m^3\ s^{-1}$ were considered to see the differences in membrane performance. The duration of each experiment was about 1 h. Experiments were conducted at ambient laboratory conditions, i.e. at a temperature of 25 °C (approximately) with an initial feed volume of 500 mL. Since the permeate volume and its oil content were much smaller compared to the feed volume and its oil content, the feed concentration was assumed to be constant during each experiment.

After each run, the feed tank and the setup, including the membrane was washed thoroughly for 30 min. by recirculation of distilled water. Further, membrane cleaning was accomplished by following the procedure as mentioned in elsewhere [22]. All new experiments were performed with the cleaned membranes. The summary of the operating conditions is presented in Table 4.

Permeate fluxes (PFs) J_p were estimated as a function of time under the specified operating conditions using the following equations:

$$J_p = \frac{Q_p}{A \Delta t} \tag{1}$$

and

$$Q_p = \frac{W_p}{\rho_p} \tag{2}$$

where Q_p is the volume of the permeate (L), W_p is the mass of permeate (kg) measured gravimetrically with a digital electronic balance, ρ_p is the density of permeate (kg L^{-1}), A is the effective membrane area (m^2) and Δt is the sampling time (h).

The compositions of the retentate and permeate varied with filtration time, particularly at the early stage of the process; so the

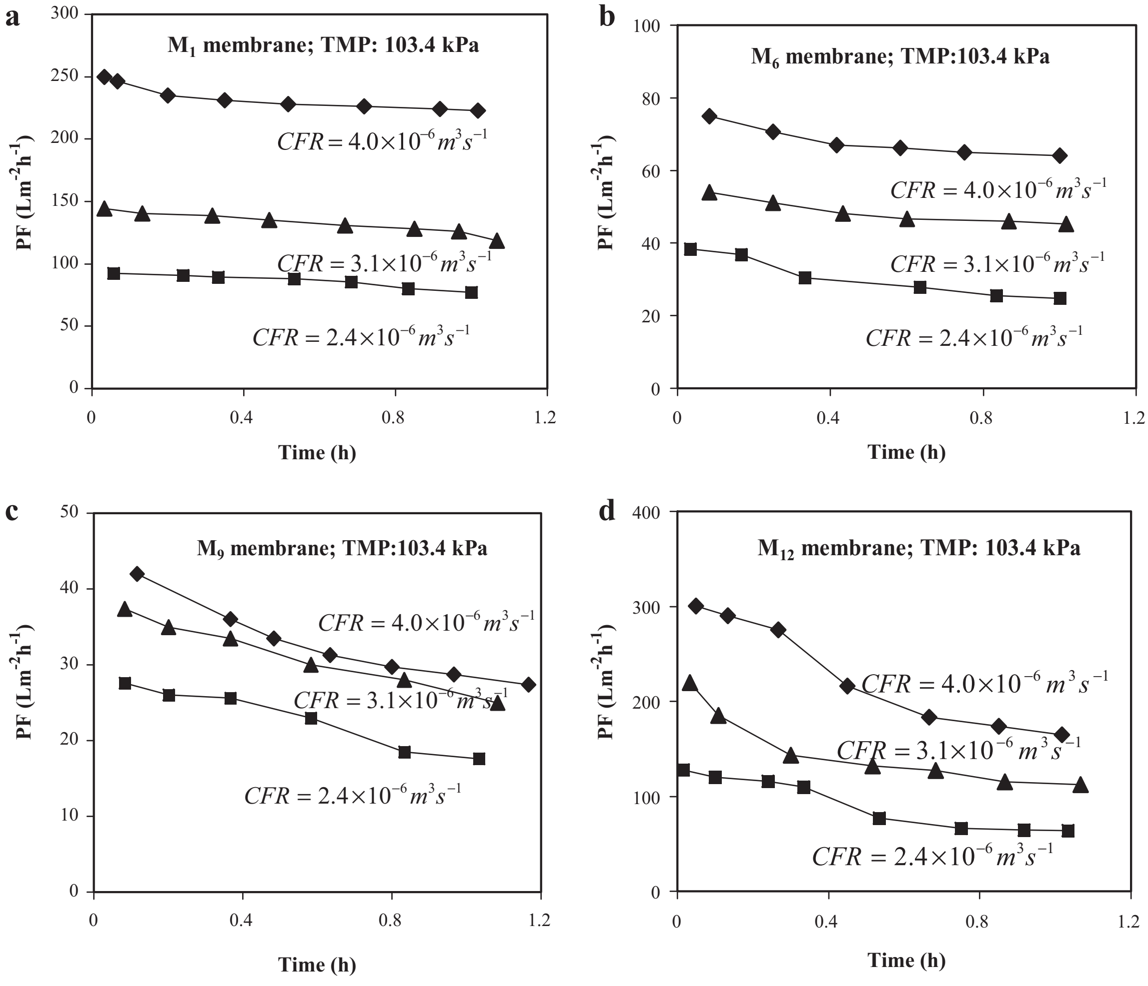

Fig. 4. Variation of permeate flux (*PF*) with time for M_1, M_6, M_9 and M_{12} membranes at different CFRs; TMP: 103.4 kPa; oil concentration: 100 mg L^{-1}.

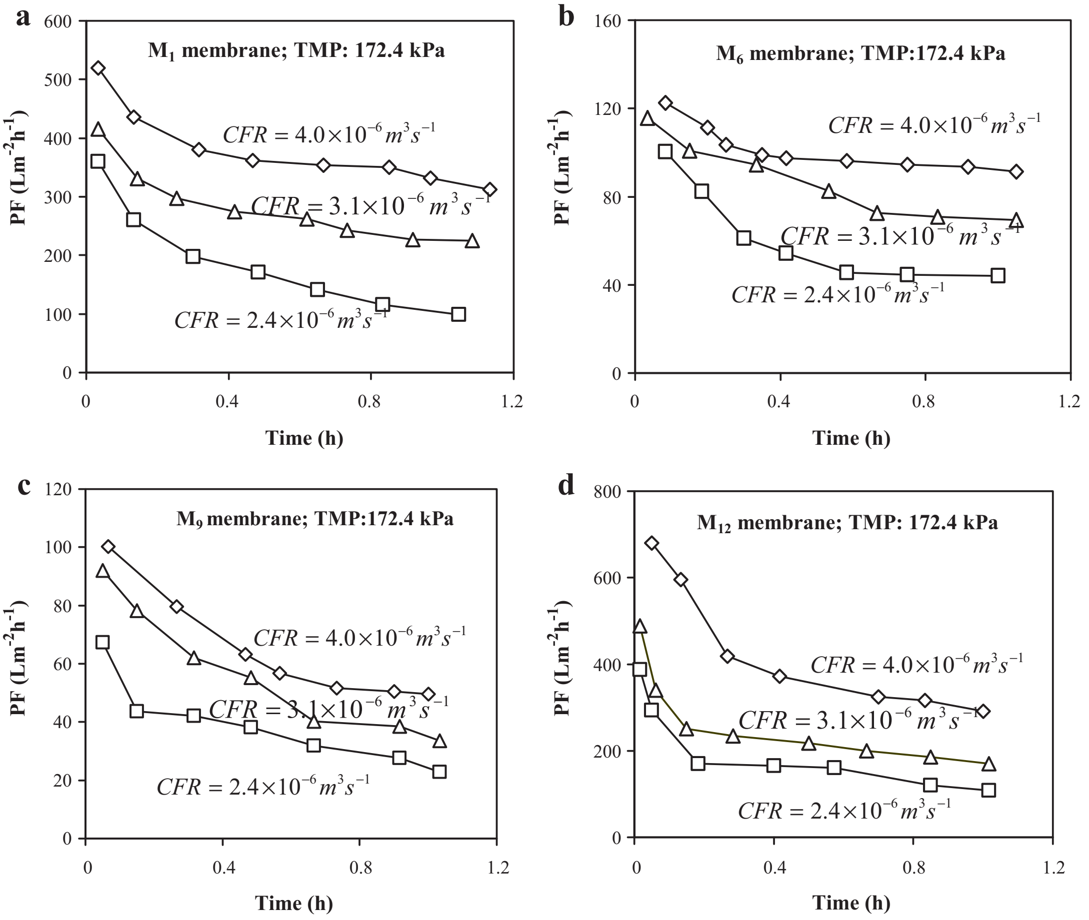

Fig. 5. Variation of permeate flux (*PF*) with time for M_1, M_6, M_9 and M_{12} membranes at different CFRs; TMP: 172.4 kPa; oil concentration: 100 mg L^{-1}.

rejection of oil (R) was calculated after 1 h when the flux reached almost the steady state, using the following equation:

$$R(\%) = \left[1 - \frac{C_{ss}}{C_f}\right] \times 100 \tag{3}$$

where C_{ss} and C_f are the concentrations of oil in permeate at steady state (after 1 h) and in feed (mg L^{-1}), respectively. In this study, the oil concentrations in the permeate and in the feed were determined using a UV–vis spectrophotometer (Perkin-Elmer, Lamda-35). The maximum absorbance was obtained at a wavelength of around 235 nm for all concentrations of oil. The flux declination, i.e. *FD* after a certain time, *t*, was calculated using the following equation:

$$FD_t\,(\%) = \left(1 - \frac{J_{pt}}{J_{pi}}\right) \times 100 \tag{4}$$

where J_{pi} is the initial permeate flux (L m^{-2} h^{-1}) and J_{pt} is the permeate flux at time, *t* (L m^{-2} h^{-1}). The declination of flux (*FD*) with time is an indication of membrane fouling. The membrane fouling is likely to be a combination of initial pore blocking by smaller oil droplets in the emulsion and deposition of oil layer on the surface which modifies the effective pore size distribution of membranes. Thus, after each UF experimental run, the membranes were cleaned with Labonene, which is a laboratory detergent solution. To check the effect of membrane cleaning, the pure water permeability of each membrane was verified before and after cleaning the membrane.

A parameter called 'selection parameter' (*SP*) in L m^{-2} h^{-1} was defined to relate all the criteria (i.e. *PF*, *R* and *FD*) for comparison of performance of each membrane as follows:

$$SP = \frac{PF \times R}{FD} \tag{5}$$

So higher *SP* value for a membrane indicates higher flux or/and higher rejection with a lower range of fouling.

2.4.2. Industrial oily water (produced water)

Experiments with produced water were conducted in cross-flow mode at the optimum TMP (obtained from the batch study) [22] and at a CFR of 3.1×10^{-6} (m^3 s^{-1}) using the same cross-flow setup. The *PF* and *R* were found out as mentioned in the preceding section. Finally, the cross-flow results of synthetic oily water were compared with those of industrial oily water.

3. Results and discussion

Operating conditions such as transmembrane pressure (TMP) and cross flow rate (CFR) have significant effects on membrane performance. In this section, mainly the effects of different CFR on membrane performance are reported and discussed with respect to *PF*, *R* (%) and flux declination (*FD*) for two values of TMP. The findings obtained for the four types of membranes (M_1, M_6, M_9 and M_{12}) under the same conditions are discussed highlighting the effect of CFR. Feed properties like oil concentration and pH are some of the important factors that usually affect the membrane morphological properties and hence the performance. These effects are considered in the batch study and have been elaborated in our previous paper [22].

Table 5
PF values of M_1, M_6, M_9 and M_{12} membranes at different conditions.

Cross flow rates (CFRs) × 10^6 ($m^3\ s^{-1}$)	Permeate flux after 1 h ($L\,m^{-2}\,h^{-1}$)							
	103.4 kPa				172.4 kPa			
	M_1	M_6	M_9	M_{12}	M_1	M_6	M_9	M_{12}
2.4	77.0	24.8	17.6	64.0	99.0	44.0	22.8	108.0
3.1	126.1	45.3	25.0	112.2	226.0	69.4	49.6	170.0
4.0	223.0	64.0	28.7	165.0	332.0	91.0	33.5	291.0

3.1. *Synthetic oily water*

3.1.1. *Effect of cross-flow rate (CFR)*

Figs. 4 and 5 show the variation of permeate flux with time for the four selected membranes at the two TMP values, i.e. 103.4 kPa and 172.4 kPa, respectively. From the figures, it is seen that the permeate flux decreases with time and approaches a steady state after a certain duration of time for all the membranes. The oil rejected by the membrane accumulates near the membrane surface and the concentration gradient causes the flux to decline. The flux declines at a higher rate in the initial period which is more obvious for higher TMP, i.e. 172.4 kPa (Fig. 5) for all the membranes. However, M_9 and M_{12} membranes show significant flux declination even at TMP of 103.4 kPa indicating their higher fouling tendency compared to the other two (i.e. M_1 and M_6). The figures also depict the fact that the CFR has a significant impact on the flux values irrespective of the membrane types. For example, at TMP of 103.4 kPa, for M_1 membrane the flux increases from 77.0 to 223.0 $L\,m^{-2}\,h^{-1}$ when the CFR is raised from 2.4×10^{-6} to $4.0 \times 10^{-6}\ m^3\ s^{-1}$; while at TMP of 172.4 kPa, the flux rises from 99.0 to 332.0 $L\,m^{-2}\,h^{-1}$. Similar observations are noted with all the membranes irrespective of the TMP. The accumulation of oil near the membrane surface gives rise to concentration polarization which can be mitigated at higher cross-flow velocities as turbulence increases near the membrane surface.

The increase in flux with increase in CFR is due to the fact that at high CFR, the extent of accumulation of rejected oil on the membrane surface is decreased reducing the total resistance. Therefore, higher flux is obtained at higher CFR for all the membranes. Table 5 reports the different values of *PF* calculated after 1 h at the two values of TMP considered in this study. It is seen that out of all the four membranes, the highest flux is obtained for M_1 membrane, i.e. 332 $L\,m^{-2}\,h^{-1}$ for a CFR of $4.0 \times 10^{-6}\ m^3\ s^{-1}$ and at a TMP of 172.4 kPa. The lowest flux is seen with M_9 membrane with a value of 17.6 $L\,m^{-2}\,h^{-1}$ at a CFR of $2.4 \times 10^{-6}\ m^3\ s^{-1}$ and a TMP of 103.4 kPa.

The effect of TMP can also be understood from Figs. 4 and 5 and Table 5 which reveal that higher *PF* is obtained at higher TMP irrespective of the CFR and the types of membranes used. Similar kind of results were also obtained with the dead end mode of operation [20].

Table 6 shows the *FD* values calculated after 1 h of UF operation using Eq. (4) for the four membranes at all the three CFRs and the two TMPs. From the table, it is seen that high CFR reduces the %*FD* which supports the trend of increase of *PF* at higher value of CFR. For example, for M_1 membrane the *FD* value decreases from 16.6% to 10.8% at a TMP of 103.4 kPa and from 61.9% to 36.2% at 172.4 kPa when CFR is raised from 2.4×10^{-6} to $4.0 \times 10^{-6}\ m^3\ s^{-1}$. These values of *FD* also reveal the effect of TMP on the extent of membrane fouling. The table also shows an increasing trend of %*FD* at higher TMP (172.4 kPa) compared to lower TMP (103.4 kPa) for all the membranes which is consistent with the batch UF study.

The rejection of oil from the synthesized oily water is calculated as %*R* using Eq. (3) and is reported in Fig. 6(a) and (b). From the figures it is understood that the trends of *R* (%) with increase in TMP in cross-flow UF are similar to those obtained in the batch UF study; that is, *R* (%) decreases at higher values of TMP for all the CFR values considered. This is because of the fact that as the TMP increases, the applied pressure overcomes the capillary pressure that prevents the oil from entering the membrane pores leading to penetration of some oil droplets. The increase in CFR also has an adverse effect on oil rejection as seen from Fig. 6. This is possibly due to the fact that high CFR leads to breaking of oil droplets into finer droplets which can cause penetration of some amount of oil through the pores resulting in less %*R*. Thus, despite getting a high *PF* value with high CFR, a very high CFR should not be recommended to avoid oil penetration through the membrane pores. The rejection is seen to be higher at 103.4 kPa for all the values of CFR compared to those at 172.4 kPa irrespective of the membrane types. Table 7 reports the %*R* values corresponding to all the four membranes obtained at the three CFRs and the two TMPs. It is seen that highest separation is obtained at a TMP of 103.4 kPa and a CFR of $2.4 \times 10^{-6}\ m^3\ s^{-1}$ for all the membranes.

3.1.2. *Effect of membrane type*

Analyzing Tables 5 and 6, the effect of membrane material and composition on *PF* and *FD* (%) can also be understood. M_9 membrane shows the least *PF* while M_1 and M_{12} membranes experience reasonably high flux for all the conditions. The difference in *PF* for different membranes may be attributed to the variation of their morphological structure due to the addition of different molecular weight additives viz. PVP and PEG in the individual membrane system (Table 1). Porosity (N_t), hydrophilicity (EWC) and the morphology of the membrane sublayer (CF) play an important role in determining the *PF* (Table 2).

On the other hand, analyzing the *FD* (%) from Table 6, it is seen that M_{12} membrane experiences the maximum *FD* indicating its highest tendency of fouling which is in agreement with that found in the batch study [22]. Considering the TMP value at 103.4 kPa and a CFR value of $3.1 \times 10^{-6}\ m^3\ s^{-1}$, the flux decline analysis up to 1 h of operation shows that M_1 membrane exhibits the least flux dec-

Table 6
Values of *FD* (%) for different membranes at different operating conditions after 1 h of operation.

Cross flow rate (CFR) × 10^6 ($m^3\ s^{-1}$)	Flux declination (%)							
	103.4 kPa				172.4 kPa			
	M_1	M_6	M_9	M_{12}	M_1	M_6	M_9	M_{12}
2.4	16.6	18.4	36.2	50.0	61.9	56.2	66.1	72.1
3.1	12.5	16.1	33.1	49.0	45.7	39.9	63.6	65.1
4.0	10.8	14.6	31.7	45.1	36.2	25.6	49.0	57.2

Table 7
Values of %*R* for different membranes at different operating conditions after 1 h of operation.

Cross flow rates (CFR) × 10^6 ($m^3\ s^{-1}$)	*R* (%)							
	103.4 kPa				172.4 kPa			
	M_1	M_6	M_9	M_{12}	M_1	M_6	M_9	M_{12}
2.4	95.2	95.8	96.8	90.1	92.0	93.7	94.0	86.3
3.1	94.4	95.2	96.6	87.8	91.5	93.0	93.6	85.7
4.0	93.2	95.1	95.2	87.1	90.2	92.4	93.4	85.1

lination (i.e. 12.5%) which is followed by M_6 membrane while M_{12} membrane is found to have the maximum *FD* (49.0%). This may be attributed to the difference in pore size distribution between the membranes. Also, the role of different degree of hydrophilicity of the membranes cannot be ruled out. Because, higher the hydrophilicity, more will be the swelling of membrane due to absorption of water which will alter the membrane structure to some extent. However, at 172.4 kPa and same CFR value, M_6 membrane displays the least *FD* (i.e. 39.9%) which is followed by M_1 membrane. This may be due to the difference in degree of pore blocking by oil droplets at higher TMP. During the course of ultrafiltration, large oil droplets tend to settle on the membrane surface acting as a barrier to permeate flow; while the small droplets try to pass through the membrane pores causing pore blocking.

Again, the %*R* is found to be above 90% (i.e. oil content in the permeate is less than 10 mg L^{-1}) at both the values of TMP for all the membranes except M_{12} membrane (Fig. 6, Table 7), the highest %*R* being obtained with M_9 membrane under all operating conditions. These results may be evidently attributed to the different structure (both top surface and sub-layer) of the membranes formed from different combination of solvent and additives. Generally, membrane with bigger pore size combined with a looser structure (evaluated from CF, Table 2) results in poor separation performance. Table 7 shows the applicability of the three membranes, i.e. M_1, M_6 and M_9 for separation of oil. Table 8 demonstrates comparison of performances of all the four membranes in terms of *SP* calculated by Eq. (5) at a TMP of 103.4 kPa and a CFR of 3.1 × 10^{-6} $m^3\ s^{-1}$. From the values, it may be clearly seen that M_1 membrane performs the best which is followed by M_6 membrane. Thus, M_1 membrane may be recommended out of the four membranes for industrial application.

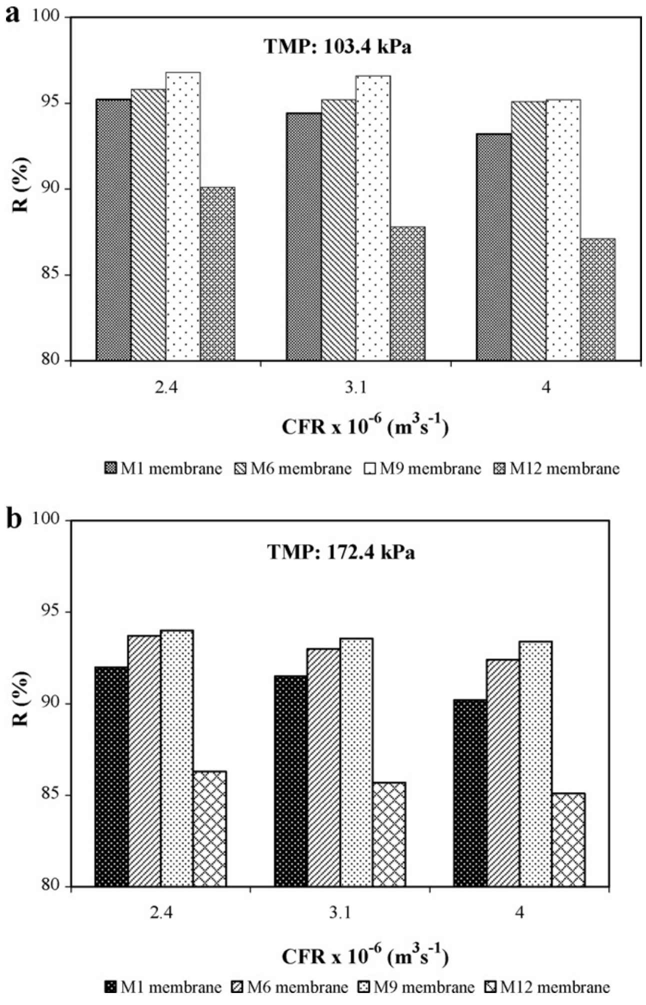

Fig. 6. Effect of CFR on rejection of oil (%*R*) at (a) 103.4 kPa and (b) 172.4 kPa.

Table 8
Comparison of the performance of different membranes after 1 h at a TMP of 103.4 kPa and a CFR of 3.1 × 10^{-6} $m^3\ s^{-1}$.

Membranes	*PF* ($L\ m^{-2}\ h^{-1}$)	*R* (%)	*FD* (%)	*SP* ($L\ m^{-2}\ h^{-1}$)
M_1	126.1	94.4	12.5	952.3
M_6	45.3	95.2	16.1	267.9
M_9	25.0	96.6	33.1	72.9
M_{12}	112.2	87.8	49.0	201.0

3.2. Industrial oily water

The cross-flow study with synthetic oily water shows that the performance of M_1 membrane was the best which was followed by the M_6 membrane; so these two membranes were considered for the cross-flow study with industrial oily water to see their applicability. The membranes were tested to separate oil from the ‘produced water’ obtained from OIL, Assam. The feed after the pretreatment steps (discussed in Section 2.2) was subjected to cross flow UF operation. The permeate obtained from each experiment was analyzed in terms of oil content.

Fig. 7 shows the behaviour of permeate flux with time at the selected operating conditions for M_1 and M_6 membranes. M_1 membrane is seen to exhibit the highest flux (128 $L\ m^{-2}\ h^{-1}$), with a greater degree of flux declination (43.1%) while for M_6 membrane, the flux is 70 $L\ m^{-2}\ h^{-1}$ with flux declination of (31.6%). However, the rejection of oil is found to be quite less compared to that with synthetic oily water which is 77.5% with M_1 membrane and 78.8% with M_6 membrane.

Table 9 illustrates a comparison between the performance of the membranes with synthetic and real oily water (produced water) in

Table 9
Comparison of the performance of different membranes for synthetic and produced water.

Membranes	Cross-flow UF	
	Synthetic water *SP* ($L\ m^{-2}\ h^{-1}$)	Produced water *SP* ($L\ m^{-2}\ h^{-1}$)
M_1	952.3	230.2
M_6	267.9	174.6
M_9	72.9	–
M_{12}	201.0	–

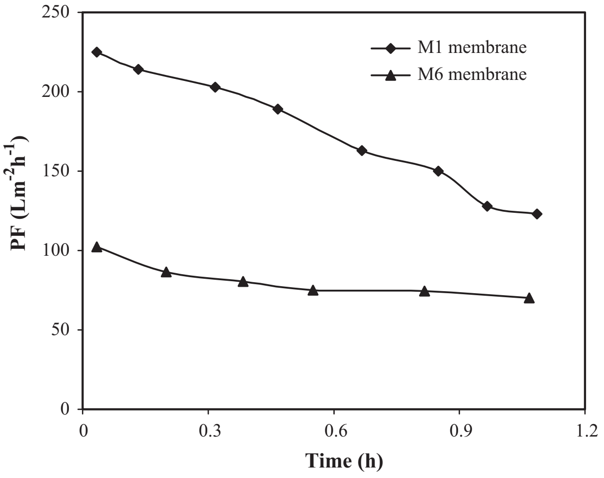

Fig. 7. Variation of permeation flux with time for M_1 and M_6 membranes with produced water as the feed.

cross-flow mode of UF. The difference in the performance for all the membranes with real oily water from those obtained with synthetic oily water is possibly due to the difference in properties between the two feeds which are mainly the difference in oil droplet size distribution and the pH values. The prospect of high soluble oil content in produced water compared to synthetic oily water may also be an another possible explanation behind this difference. However, it is observed that the M_1 membrane displays higher value of *SP* compared to M_6 membrane irrespective of the type of feed (i.e. synthetic or real oily water) and the type of operation mode (i.e. batch or cross-flow) of UF.

The results obtained from both the batch and cross-flow UF of the produced water show that the prepared membranes are successful in bringing down the oil content in the permeate from 366 mg L^{-1} to approximately 50 mg L^{-1} which is still higher than the acceptable discharge limit of 10 mg L^{-1}. But with the synthetic oily water, the permeate quality was up to the mark. The reason for the membranes not being able to do so with produced water may be explained from the difference in size distribution of oil particle for the produced water (Fig. 2) and the synthetic oily water (Fig. 1).

In order to improve oil separation, the membranes can be modified to improve their properties such as pore size and pore size distribution, hydrophilicity, etc. through the application of different techniques such as changing the composition of membrane casting solution, membrane surface coating, etc. In addition, to tackle the difficulty of lower oil separation due to penetration of the smaller oil droplets along with the permeate, cascading effect of different membrane units, e.g. UF followed by NF or RO should be explored to get a realistic membrane separation unit.

4. Conclusion

In this work, the separation of oil from synthetic oil-in-water emulsion with modified PSf membranes using cross-flow mode of ultrafiltration has been shown. The effects of CFR and membrane types on permeate flux, oil rejection and flux declination have been investigated in detail. Finally, the cross-flow UF was carried out at a TMP of 103.4 kPa and a CFR of 3.1×10^{-6} m^3 s^{-1} with the produced water. The findings of this study may be summarized as follows:

1. At constant TMP, with increase in CFR, the permeate flux increases; this is due to the removal of the accumulated oil from the membrane surface reducing the total resistance to permeate flow. However, the percent oil rejection (%*R*) shows a marginal decreasing trend because of fragmentation of the droplets at higher CFR leading to oil penetration along with the permeate.
2. At constant CFR, increase in TMP increases the permeate flux; this is due to the increase in driving force across the membrane. However, rejection of oil (%*R*) is found to decrease as high TMP is likely to force the small sized oil droplets to pass through the pores of the membrane.
3. Higher TMP makes the flux decline faster at all CFR by introducing greater number of oil droplets into the membrane pores causing pore plugging at a faster rate while higher CFR has just the reverse effect by reducing the effect of concentration polarization.
4. All the membranes except M_{12} membrane are found to produce permeate of acceptable quality (i.e. oil content less than 10 mg L^{-1}).
5. M_1 membrane is found to give the highest value of *SP* (952.3 L m^{-2} h^{-1}) while M_9 membrane shows a minimum value of *SP* (72.9 L m^{-2} h^{-1}) at a TMP of 103.4 kPa and a CFR of 3.1×10^{-6} m^3 s^{-1}. Thus, M_1 membrane may be recommended for treating oily water at normal condition.
6. The results of the applicability of the membranes in separating oil from “produced water” by cross-flow UF shows that the oil content in the permeate has not met the discharge standard of 10 mg L^{-1}. This suggests that the UF operational unit should be followed by an another operational unit, e.g. nanofiltration or reverse osmosis in order to meet the discharge standard of 10 mg L^{-1}.

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