

## Effective factors in the treatment of kerosene–water emulsion by using UF membranes

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### ABSTRACT

The effects of different parameters including membrane type (regenerated cellulose and polysulphone), transmembrane pressure (TMP), the content of oil in the feed, the flow velocity of the feed and pH on the ultrafiltration of an emulsion of kerosene in water were studied.

It was found that the important factors affecting ultrafiltration were, in order, membrane type, pressure and oil concentration. The greatest flux at the optimum conditions here of 3 bar, an oil content of 3% (v/v) and with membrane type C30F was predicted as 108 L/(m<sup>2</sup> h) that was within the range of the confidence limit of the measured value of 106 L/(m<sup>2</sup> h). The normalised FTIR results of the virgin cellulosic membranes C30F and C100F showed more abundant OH groups. The bigger number of OH groups implies a greater hydrophilicity. The larger observed flux in the C30F is related to a higher number of pores as well (surface porosity) compared with the C100F membrane.

In the “polarised regime” from 3 bar upwards, flux was independent of pressure for all membranes and was assumed to be determined by the back diffusion transport. Despite the fact that both the PS100H and C100F membranes had the same cut-off (100 kg/mol), the hydrophilic C100F showed a superior permeate flux. The strongest drop of flux with time due to oil fouling was observed for the C100F although it was hydrophilic. In the case of the PS100H, both FTIR and SEM showed that cake layer formation was not the cause of fouling. Meanwhile the SEM and FTIR results of fouled C100F provided evidence of adsorptive and gel formation fouling.

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### 1. Introduction

In most industry such as petroleum production, petrochemical, metal, food and cosmetics usually a wastewater containing an emulsion of oil in water is produced. The emulsion consists of water (up to 90%), oil (mineral, animal, vegetable and synthetic) and surfactant [1,2]. It was reported that more than 2000 million tons of wastewater is produced by oil refineries only in the European Union countries [3]. Because of its toxic nature and the significant effects of this wastewater on the surrounding environment (soil, water) it needs to be treated before it is released to the environment. There are several methods such as dissolved air flotation (DAF) [4,5], adsorption [6], biological treatment [7,8], sedimentation in a centrifugal field [9] and in hydrocyclones [10], and membrane filtration [11–13] which can be used for the treatment of different

kinds of oily wastewater. Since the upper limit of permissible oil in the effluent is steadily reduced by governing bodies, industries have to improve the treatment plants to meet the new limits. In some cases, it is really difficult or even impossible to meet the new limits using conventional methods. This problem will be particularly serious if the industrial facilities are close to urban areas, as is the case in the Tehran refinery. In this refinery the wastewater after the treatment plant has been discharged for a long time to evaporative ponds. A long residence time caused pollutants to penetrate to the aquifer which supplies water for people around the refinery. Therefore, additional unit operations should be adopted in a post-treatment to meet the proper requirements.

Membrane-based systems have successfully been applied or considered as possible candidates for post-treating this kind of liquid wastes in industrial plants. Easy operation, lower cost in some cases [14] and capability of reducing contaminants to below the limits are the main advantages of these systems. However, drawbacks like fouling and polarisation and decline of flux with time has caused that the process has not been accepted by all industries.

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**Table 1**  
Technical data on the membranes used in this study

	Membrane name		
	PS100H	C30F	C100F
Membrane material	Hydrophilised polysulphone	Regenerated cellulose	Regenerated cellulose
Cut-off (kg/mol)	100	30	100
Pure water flux (L/(m <sup>2</sup> h))	300–600	300–600	200–400
pH range	1–14	1–11	1–11
Maximum temperature (°C)	95	55	55

Reviewing the publications reveals, however, different aspects such as the effect of membrane type and operating conditions on the performance of the treatment [14–18], the effect of modification of membrane to retard fouling [1,19–21], an integrated process to increase the quality of the permeate [11,22] process modeling by empirical and theoretical models [23–25] and cleaning [26] have been extensively studied, but because of the complexity of the membrane process still rather much research is needed.

The complexity of the system implies a complementary study of all different issues of filtration to mitigate fouling and concentration polarisation. Based on our knowledge and literature review we found that there are only a few reports [27,28] which considered all effective factors in the filtration simultaneously and in a systematic way, i.e. by using an experimental design approach. This lack of information and also our interest to check out the performance of available membranes on the market for treatment of tap water to remove oil and other hazardous components at a range of conditions were our motivation for this work.

To simulate the polluted water a model solution of oil in water was used. The oil phase was kerosene which was used as the results of previous analysis showed that pollutant components can be modeled by mixing kerosene with water.

The aim of our work was to consider the effect of important operating conditions like oil concentration, pH and the membrane type on the filterability of three different commercial UF membranes and determining the optimum conditions for the given sets of values to get the best flux. The results of this study may be used as a guideline to operate the UF systems at the best conditions.

The results of filtration and the analyses which were carried out by using analysis of variance (ANOVA) will be presented and discussed in this study.

## 2. Materials and methods

### 2.1. Membranes

Two regenerated cellulose ultrafiltration membranes with a cut-off of 100 and 30 kg/mol and one hydrophilised polysulphone membrane with a cut-off of 100 kg/mol were used in this study (Microdyn-Nadir GmbH, Germany). All membranes were rectangular flat sheet with a size of 2 cm × 23 cm or 0.0046 m<sup>2</sup>, installed in a polycarbonate module (made at LUT, Finland). The technical data of the membrane is shown in Table 1.

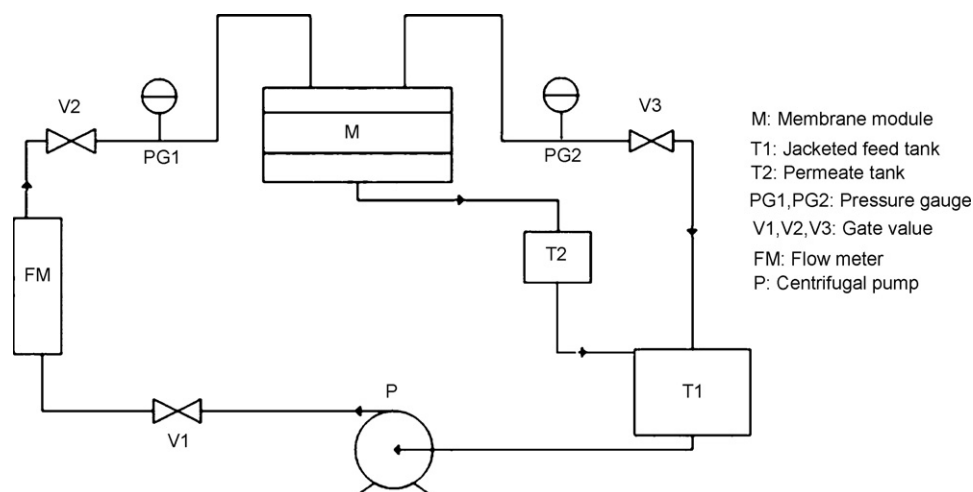
### 2.2. Preparation of emulsions

Emulsions were prepared from distilled water and kerosene using Tween 80 as the emulsifier. The volume percents of oil in water were 3, 5 and 7% (v/v). Tween 80 was added to the mixture of distilled water and kerosene and the whole system was mixed with a mixer (IKA-WERKE, Germany) for 15 min at about 1000 rpm. To make Tween 80 act as an emulsifier its concentration was adjusted to 0.002 wt.% which is above its Critical Micelle Concentration (CMC) which is reported to be about 0.0013 wt.% [29].

The size of oil emulsion droplets in the feed and permeate was measured by a laser diffraction particle size analyser, model LS 13320 manufactured by Beckman Coulter Co.

### 2.3. Experiments

Fig. 1 shows a schematic diagram of the experimental set-up used in this study. The feed was pumped to the module by using a centrifuge pump. Flow was regulated using valves V1 and V2 while the pressure on the membrane was adjusted by valve V3.



**Fig. 1.** Schematic diagram of the experimental equipment.

**Table 2**  
Summary of factors and levels, obtained results (permeate flux) and S/N ratio in each trial

Trial number	Pressure (bar)	pH	Feed velocity (m/s)	Feed oil content (% v/v)	Membrane type	Flux 1 (L/(m <sup>2</sup> h))	Flux 2 (L/(m <sup>2</sup> h))	S/N
1	2.5	11	0.4	3	PS100H	70	69	37
2	2.5	8	1.0	5	C30F	97	96	40
3	2.5	4.5	0.8	7	C100F	69	70	37
4	3	11	0.4	5	C30F	96	95	40
5	3	8	1.0	7	C100F	75	76	38
6	3	4.5	0.8	3	PS100H	74	75	37
7	2	11	1.0	3	C100F	70	69	37
8	2	8	0.8	5	PS100H	57	58	35
9	2	4.5	0.4	7	C30F	76	76	38
10	2.5	11	0.8	7	C30F	79	78	38
11	2.5	8	0.4	3	C100F	74	73	37
12	2.5	4.5	1.0	5	PS100H	65	64	36
13	3	11	1.0	7	PS100H	72	73	37
14	3	8	0.8	3	C30F	108	109	41
15	3	4.5	0.4	5	C100F	78	77	38
16	2	11	0.8	5	C100F	67	68	37
17	2	8	0.4	7	PS100H	46	45	33
18	2	4.5	1.0	3	C30F	92	91	39

The feed stream splits in two streams, one, the concentrate which contains non-passing components is returned to the feed tank. The other one, the permeate, contains components passing through the membrane and it is measured by a balance. The permeate after measurement was returned to the feed tank in order to have a feed with constant concentration.

Temperature was kept constant, about 30 °C, during the experiment by circulating water around the jacketed feed tank.

An experimental design method (Taguchi) was used to design the experiments. The Taguchi method is a useful method for systematic study of different effective factors and it has been applied for many years [28]. The advantages, like prediction of the results with less numbers of experiments and determination of the optimum conditions based upon the obtained results, have made the method very popular in industry as well as in science.

In this study five different factors including pH, transmembrane pressure (TMP), oil content of the feed, membrane type and feed velocity were chosen as controllable factors and permeate flux as the response factor. They were adjusted at three levels (low, medium and high). The choice of the factors and their levels was based on a literature survey. All factors and their levels were combined to 18 trials. Permeate flux was measured after a certain time (60 min) in each trial. This time was chosen to reduce the error caused by the initial rapid drop of flux.

The pH values used were 4.5 (acidic condition), 8 (near to neutral condition) and 11 (alkaline condition). The oil concentrations were 3, 5 and 7% (v/v) which are close to the oil content in the oily wastewater (usually between 3 and 5%, v/v). The feed velocities were adjusted to 0.4, 0.8 and 1 m/s.

A summary of factors and their levels in the proposed experimental plan and the results of the experiments are presented in Table 2.

**Table 3**  
S/N ratio for levels of each factor and S/N differences between these levels where permeate flux has been optimised

Factors	L1 <sup>a</sup>	L2	L3	L2 – L1	L3 – L2
1 Pressure	37.5	38.4	36.4	0.9	-1.9
2 pH	37.5	37.3	37.5	-0.2	0.2
3 Flow velocity	37.1	37.8	37.4	0.7	-0.3
4 Oil concentration	38.1	37.5	36.7	-0.6	-0.8
5 Membrane type	36.0	39.1	37.1	3.1	-1.9

<sup>a</sup> L1: level 1; L2: level 2; L3: level 3; L2 – L1: difference between levels 1 and 2; L3 – L2: differences between levels 2 and 3.

### 3. Results and discussion

#### 3.1. Taguchi results

A parameter which is defined for comparing the trials and the influence of a factor in the Taguchi method is the ratio of the desired factor to the noise created during the experiment, S/N.

Since a higher flux is desirable in this experiment “the bigger the better” criterion was chosen for the S/N ratio. The following equation shows how this ratio can be calculated for a data set:

$$S/N = -10 \log_{10} \left[ \frac{1}{[(Y_1)^2 + (Y_2)^2 + \dots + (Y_N)^2]/N} \right] \quad (1)$$

where  $Y_1$  and  $Y_2$  are the first and second response factors (Flux 1 and Flux 2 for each trial in Table 2), and  $N$  is the number of observations (here 2 since each trial was repeated).

The average value of S/N for different trials is presented in Table 2. It may be seen that the largest value of S/N is for trial No. 14 where the pH is 8, the membrane is the C30F and the pressure is about 3 bar.

This ratio (S/N) for a factor may be calculated by averaging the S/N at different levels. For example the S/N for the second factor, pH at high level, is equal to the average value of S/N for each trial where pH is at the first level, i.e. trials 1, 4, 7 and 10, 13, 16. The S/N for the second and third level is calculated similarly.

In Table 3, the S/N for each level of factor and the differences between levels are presented. A negative sign shows that the effect is decreasing and vice versa. In optimum conditions a positive and bigger value of S/N is desired. Therefore, the levels which gives the biggest positive S/N ratio determines the optimum conditions for the considered factor. Comparing the S/N for different factors shows that the most significant variation is observed for membrane type while for the rest of the factors the variation is not very clear.

The quantitative analysis of the influences and the relative importance of the controllable factors may be provided via ANOVA. Table 4 shows the results of this analysis. The last column in this table shows the percent contribution of each factor which is the most important value achieved. It is defined as the portion of total observed variance in the experiment of each significant factor. A greater value means more contribution to the final results. In comparison with other factors, pressure and membrane type appear to have the biggest contribution to the results.

The second most important parameter in Table 4 is the  $F$ -ratio, which is defined as the ratio of variance due to the effect of a factor

**Table 4**

Results of analysis of variance (ANOVA) for each factor

	Factors	DOF <sup>a</sup>	Sum of squares	Variance	F-Ratio	Pure sum	Percent
1	Pressure	2	11.3	5.68	18.4	10.7	21.3
2	pH	2	0.18	0.09	0.29	0.00	0.00
3	Flow velocity	2	1.52	0.76	2.47	0.91	1.79
4	Oil concentration	2	5.42	2.71	8.78	4.81	9.53
5	Membrane type	2	29.8	14.9	48.2	29.1	57.8
6	Error/others	7	2.16	0.31	–	–	9.54
7	Total	17	50.4	–	–	–	100.0

<sup>a</sup> Degree of freedom.

to the variance due to the inherent error of the system. Therefore, an  $F$  value less than 1 means that the effect of that factor is not important in comparison with the error term. In Table 4, the  $F$ -ratio for pH is less than 1 and thus the effect may be regarded as insignificant and can be neglected. This was not the case in the former study where a high pH was one of the most important factors [27]. The  $F$ -ratio may also be used to rank the factors according to their significance. Based on these discussions, Table 4 shows that the important factors in order are membrane type, pressure, oil concentration and flow velocity.

In Table 4, the row which is marked as error/others refers to the errors which are caused by uncontrollable factors (noise), which are not included in the experiment and experimental error. In general, the value should be below 50%, otherwise the results would not be reliable. Here, the calculated error is about 10% which is much less than the limit. It means that almost all effective factors have been considered and the error of the experiment is not significant.

ANOVA may be used to estimate the process performance at optimum conditions. In the estimation only the significant factors are taken into account. The results of estimated performance are listed in Table 5. The permeate flux at these conditions is given by this analysis as 108 L/(m<sup>2</sup> h). Since the optimum conditions are not belonging to any of the trials in Table 2, a confirmation experiment was done to verify the predicted result. If the average results of the experiment are within the confidence limit then the prediction is acceptable. The value of the flux at optimum conditions was mea-

sured as 106 L/(m<sup>2</sup> h) and it may be seen that it is within the range of the confidence limit.

### 3.2. Discussion

The five factors studied in this research may be classified as structural and non-structural. The type of membrane that features the hydrophilicity and pore size distribution is classified as a structural factor. It has a direct influence on the water permeation of the membrane. Transmembrane pressure, feed oil content, pH and feed velocity are classified as non-structural factors. The effect of each individual factor on membrane performance will be discussed in more detail in the following sections.

#### 3.2.1. Effect of membrane type

The hydrophilicity and the pore size distribution are the two major features of the structural factor named as membrane type in this study. The former is influenced by the “chemical structure” of the membrane material and it is normally related to the number of hydrophilic groups (like OH groups) in the chemical structure of the membrane. This is while the latter is related to the “physical structure” of the membrane. In general a membrane with a greater pore size and a stronger hydrophilicity shows a higher permeate flux (water-based solution).

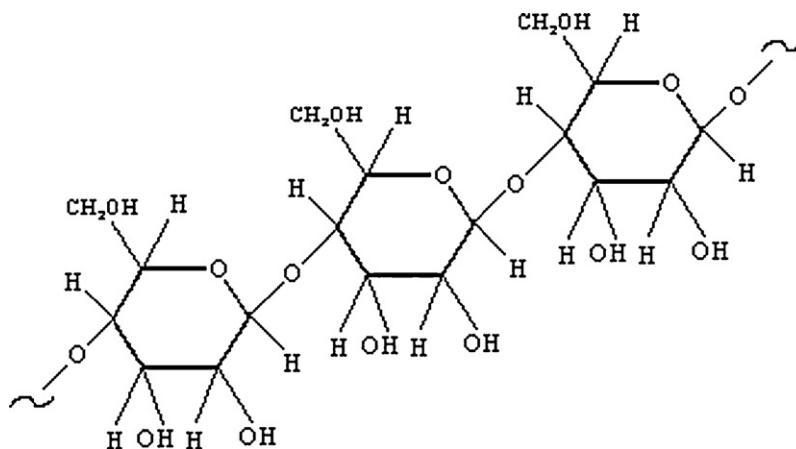
The high number of OH groups (Fig. 2) in regenerated cellulose membranes apparently makes these membranes very hydrophilic.

Fig. 3 shows the chemical structure of polysulphone. There are no OH groups in polysulphone. Thus it is expected that the water permeation (flux) is lower than in a regenerated cellulose membrane with the same pore size while in Table 1 the water flux is higher. This probably is attributed to the size distribution of membrane pores which apparently is wider for PS100H including very large pores.

**Table 5**

Estimated performance at optimum conditions

	Factors	Level description	Level	Contribution
1	Pressure	3 bar	3	0.96
2	Oil concentration	3% (v/v)	1	0.64
3	Membrane type	C30F	2	1.69

**Fig. 2.** Chemical structure of regenerated cellulose.

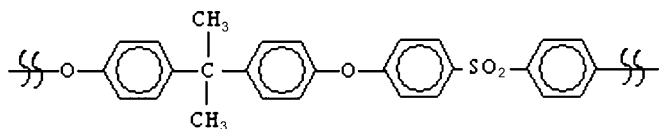


Fig. 3. Chemical structure of polysulphone.

Comparisons between the water permeate fluxes of the C30F and the C100F membranes (Table 1, initial water flux reported by manufacture) show that although these membranes are made from a similar material, there is a significant difference in their function. This can be attributed to a higher number of hydrophilic groups in the C30F structure or to a higher number of pores (pore density) in the C30F membrane. Its physical structure also differs from that of the C100F [30].

Fig. 4 shows normalised FTIR results of virgin C30F and C100F membranes. The characteristic peaks of the OH group are highlighted. The wave number of the OH group is about  $3300\text{ cm}^{-1}$  [30]. As can be seen the peak height of the C30F is higher than for the C100F. The two extra peaks ( $1743$  and  $1236\text{ cm}^{-1}$ ) in the C30F spectrum are related to ( $\text{C}=\text{O}$ ) and ( $\text{C}-\text{O}$ ) bonds which have probably come from the solvent and/or from the hydrolysis process [30].

The membrane hydrophilicity also affects the oily water permeation. The hydrophilicity of the membrane induces preferably water adsorption on the surface and hence the surface becomes less fouled by oil.

It can be seen from Table 3 that when the membrane was made from polysulphone and not from regenerated cellulose, a change occurred in the S/N ratio. This can be explained by the fact that cellulose is much more hydrophilic than polysulphone and, therefore, it is less affected by oil.

The S/N ratio is not better with the C30F membrane than with the C100F membrane. This may be because of the pore size distribution. It was reported by the membrane manufacturer that the C100F has a greater molar mass cut-off, while in this study it showed a weaker flux.

### 3.2.2. Effect of TMP

Fig. 5a shows the variation of permeate flux versus TMP. In general, permeate flux increases with increasing TMP but it does

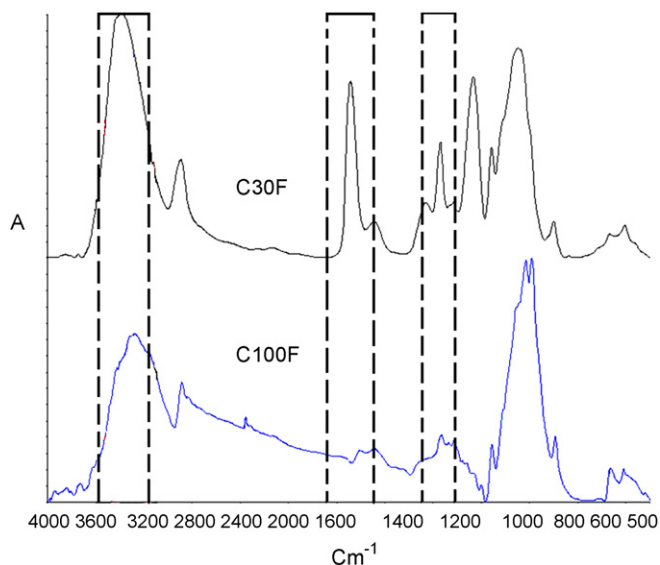


Fig. 4. Comparison between number of OH groups ( $3300\text{ cm}^{-1}$ ) in virgin C30F and C100F membranes.

not change monotonously and often becomes independent of pressure.

A further increase in pressure will again temporarily increase the convective transport to the membrane surface while the back diffusion is fixed. Thus the pressure just affects the polarised layer thickness and makes it more thick or compact, i.e. an increase in the resistance of the polarised layer compensates for the effect of increase in pressure. Therefore, in the “polarised regime”, flux is independent of pressure and is solely determined by the back-diffusive transport. It is indicated in Fig. 5a that the permeate flux becomes almost constant at 3 bar for each membrane.

### 3.2.3. Effect of feed oil content

Fig. 5b shows the variation of permeate flux versus oil content. It can be seen that the permeate flux always decreases with oil content.

With increasing the oil contents on the feed side the thickness of the polarised layer on the membrane surface increases more readily. The flux decline rate depends on the membrane. The rate is higher for the C30F membrane. This membrane is very hydrophilic but because of the higher number of pores and consequently higher flux, the pore blockage possibility may be greater.

Comparison of PS100H and C100F membrane performance reveals the effect of hydrophilicity on the permeate flux. According to the manufacturer, these membranes have the same cut-off ( $100\text{ kg/mol}$ ), however, the hydrophilic membrane shows a higher flux in the filtration of oil in water emulsions.

### 3.2.4. Effect of feed velocity

Fig. 5c shows the variation of permeate flux versus feed flow velocity. As can be seen, an increase in flow velocity does not increase the flux as much as the oil concentration or pressure. The Reynolds number is almost the same in the velocity range of this study. The maximum value for the Reynolds number is about 3000 at  $1\text{ m/s}$  feed velocity (maximum velocity in these trials). This means that increasing the flow velocity is not sufficient to change the flow regime from laminar to turbulent. The small improvement in flux can be attributed to mitigation of concentration polarisation by increasing the back diffusion transport. Furthermore, the hydraulic diameter of the flow channel is very small (about  $2\text{ mm}$ ), which causes a strong shear tension in the channel that prevents fouling to increase.

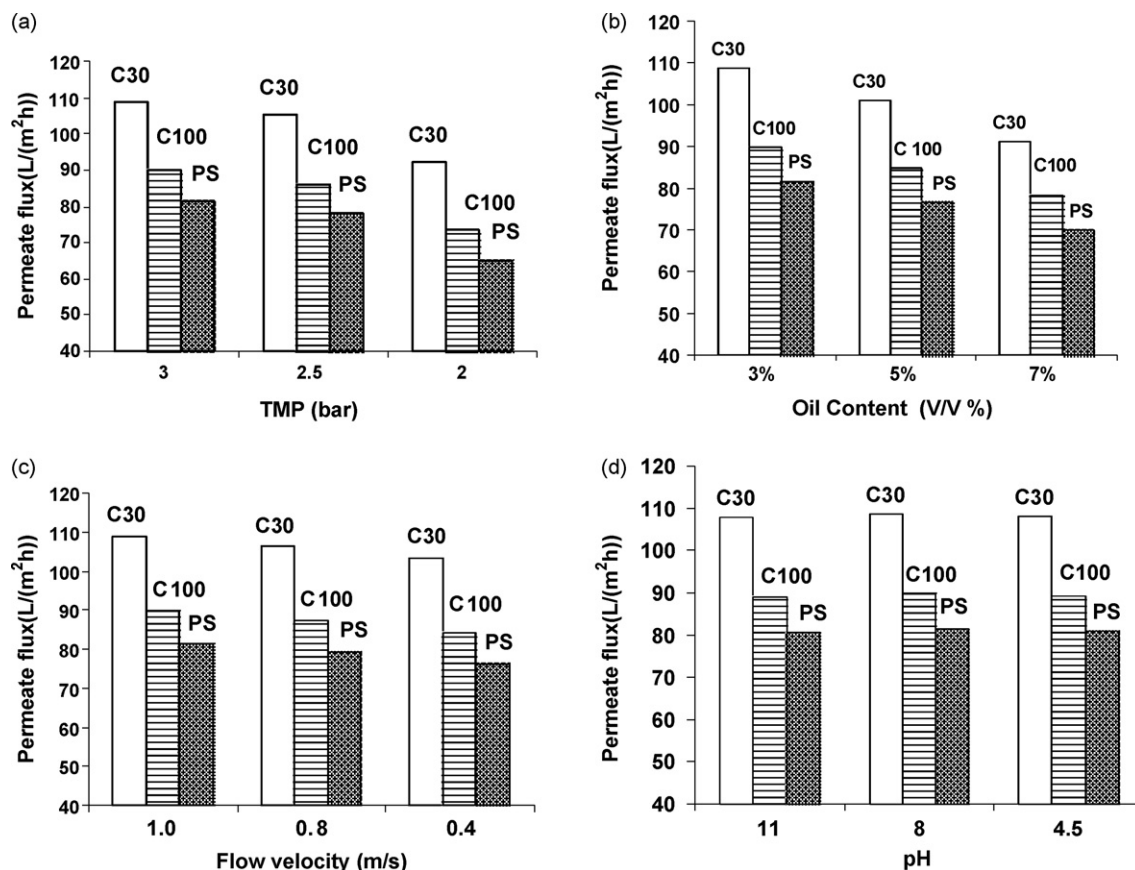
### 3.2.5. Effect of pH

The variation of permeate flux versus pH is shown in Fig. 5d. No significant changes can be detected which is in accordance with the conclusion based on ANOVA. This is reasonable because the active layers of these membranes are made up of materials that can exist in different ionisation states depending on pH. It seems that pH affects the membrane surface charge and, consequently, the solute adsorption mechanisms.

There are several mechanisms of surfactant adsorption onto solid substrates from aqueous solution. Adsorption of emulsifier or other charged particles and droplets on the membrane surface can increase the rate of polarised layer formation and decreases the water permeate flux.

In this study, distilled water is supplied from an RO set-up and is almost deionised. On the other hand, the emulsifier is a nonionic surfactant [29]. Then there should not be any charged particle or droplet in the aqueous solution. So, the membrane surface charge variation in the result of pH variation cannot change the permeate flux [14].

The other possibility is that the oil droplet surface is affected by pH. The emulsifier (Tween 80) is a nonionic surfactant which adsorbs on the droplet surface by Van der Waals interaction [31].



**Fig. 5.** Variation of permeate flux versus pressure, oil concentration, flow velocity, and pH for the used membranes. In each figure the rest of the operating conditions were fixed at optimum conditions—(a) pH 4.5, flow velocity: 1 m/s, oil concentration: 3% (v/v); (b) pH 4.5, flow velocity: 1 m/s, TMP: 3 bar; (c) pH 4.5, TMP: 3 bar, oil concentration: 3% (v/v); (d) flow velocity: 1 m/s, TMP: 3 bar, oil concentration: 3% (v/v).

This interaction can be changed by pH to affect the stability of the emulsion. In an unstable emulsion, the oil droplets can attach to each other and make bigger droplets. It was observed that the pH had no influence on the emulsion stability.

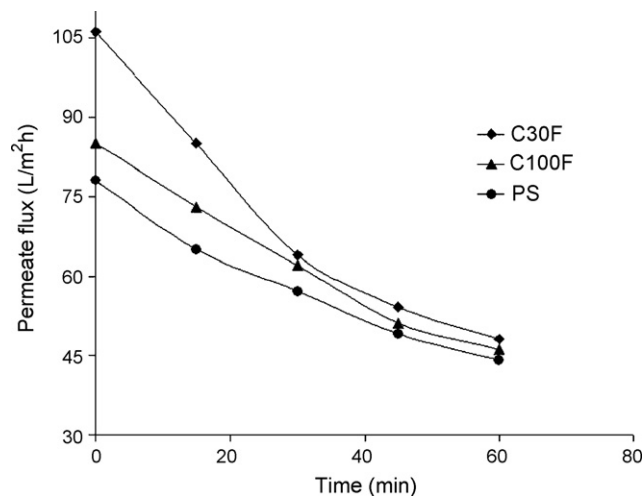
### 3.3. Fouling

The variation of permeate flux versus time, which indicates fouling, is shown in Fig. 6. The permeate fluxes in Fig. 6 are measured at the optimum conditions shown in Table 5. In general, flux declines with time but the rate of this decline is not the same for all of the membranes. The biggest drop was observed for the C30F. Even though the membrane was hydrophilic it was fouled by oil. This phenomenon may be related to critical flux. C30F has a critical flux achieved at about 0.8 bar [30] but the permeate fluxes in Fig. 6 are measured at optimum conditions (3 bar) that are above the critical pressure and then an increase in pressure in this region results in increasing fouling. In particular conditions, fouling may lead to gel layer formation (Fig. 7 for C100F membrane) but this is not what was observed for the PS100H membrane (Fig. 8).

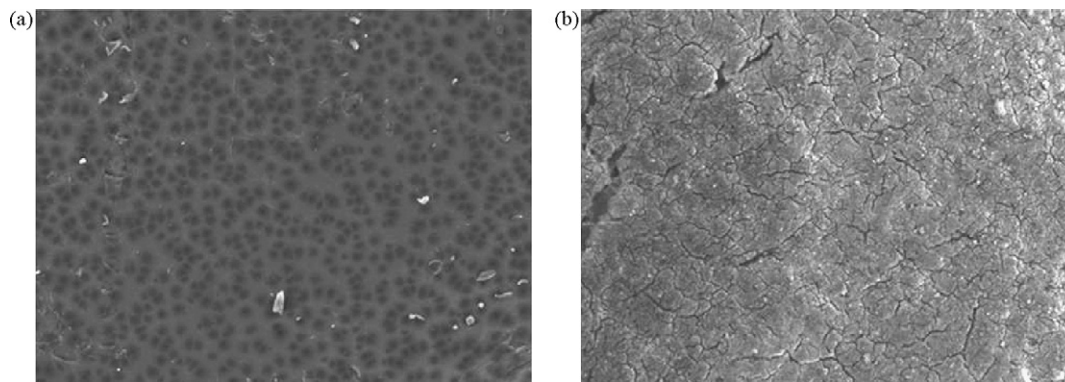
C100F and PS100H follow the same manner in fouling (Fig. 6), but the type of fouling is different. Fig. 7 shows that the fouling of the C100F membrane was similar with cake layer formation (pores which can be seen in Fig. 7a are covered with a layer and cannot be seen in Fig. 7b). The new peak in the FTIR spectrum of the C100F membrane (Fig. 9) may also be considered as an evidence for fouling. The composition of this layer based on an FTIR library database is “aromatic group”.

Since FTIR is a surface sensitive method, therefore, if something is adsorbed on the surface it could be detected using this method. The lack of new peaks means that fouling in PS100H was probably due to pore blockage (Fig. 10).

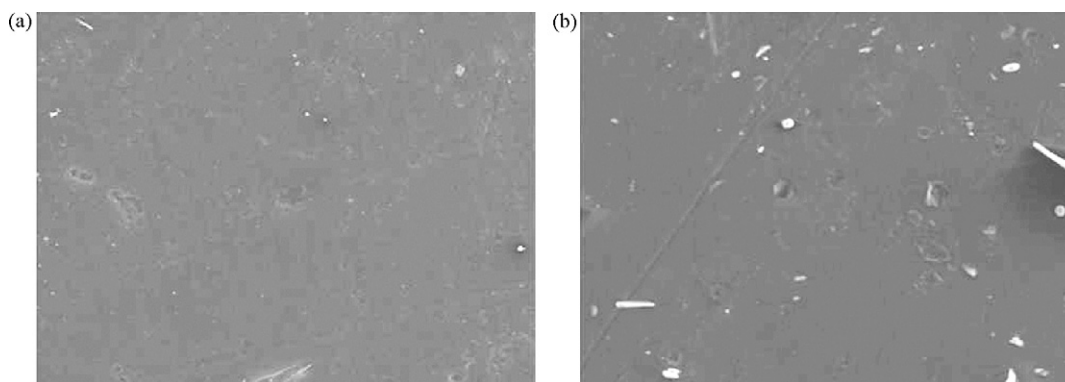
The review of the total, fouling and concentration polarisation resistances of the C30F, C100F and PS100H membranes which are listed in Table 6 indicates that although the cellulose membranes have higher polarisation and fouling resistance than the polysul-



**Fig. 6.** Variation of permeate flux versus time (in 1 h) for the used membranes.



**Fig. 7.** SEM photos that show the virgin and the fouled surface of the C100F membrane: (a) virgin surface and (b) fouled surface (magnification of 700 $\times$ ).



**Fig. 8.** SEM photos that show the virgin and the fouled surface of the PS100H membrane: (a) virgin surface and (b) fouled surface (magnification of 700 $\times$ ).

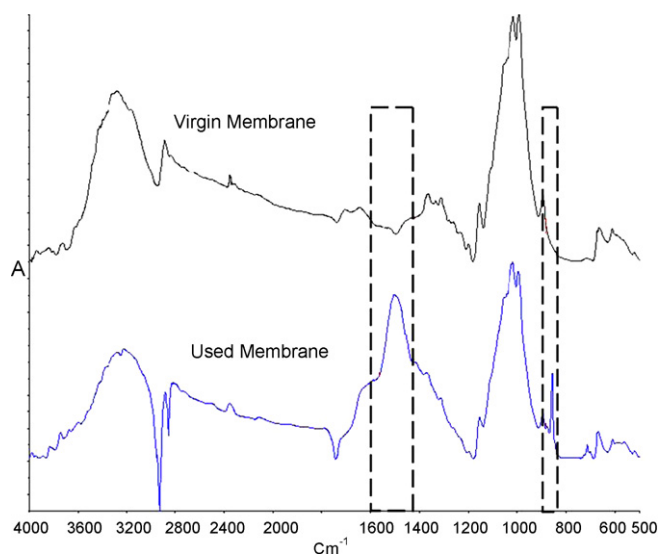
phone membrane, the total resistances of these membranes are smaller. The higher flux which can be observed for the cellulose membranes may also be explained by the resistance model.

The membrane resistance in Table 6 was measured at the start of the optimum trial shown in Table 5. The total resistance was measured at the end of this trial. After this, membrane cleaning was performed and then the total fouling and membrane resistances were measured and then the fouling resistance was calculated.

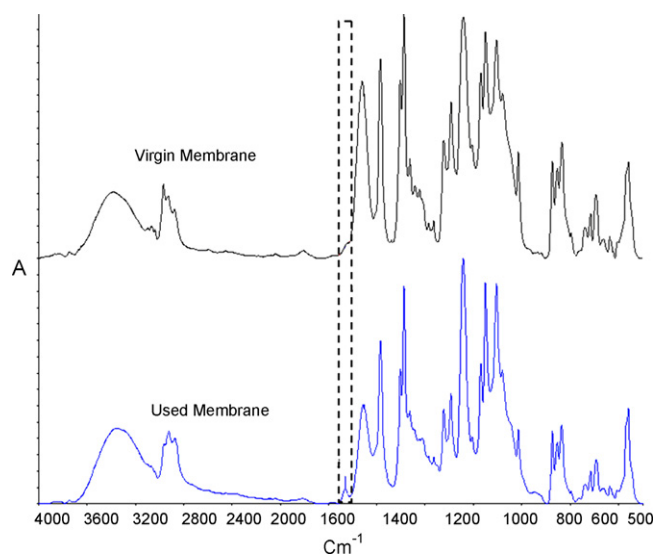
After calculation of the total, the membrane and the fouling resistances, the concentration polarisation resistance was calculated.

#### 4. Retention

The amounts of oil in the permeate and feed samples were analysed by a total organic carbon, TOC meter. The value of TOC in the permeate of all the tested membranes was below 50 ppm which



**Fig. 9.** FTIR result comparing the virgin and used C100F membrane and indicating the fouling.



**Fig. 10.** FTIR result comparing the virgin and used PS100H membrane and indicating the fouling.

**Table 6**

Membrane, fouling, concentration polarisation and total resistances for the studied membranes

	Membrane type		
	PS100H	C100F	C30F
Membrane resistance ( $m^{-1}$ )	$15.02 \times 10^{12}$	$11.84 \times 10^{12}$	$7.48 \times 10^{12}$
Fouling resistance ( $m^{-1}$ )	$1.38 \times 10^{12}$	$1.83 \times 10^{12}$	$2.43 \times 10^{12}$
Concentration polarisation resistance ( $m^{-1}$ )	$9.8 \times 10^{12}$	$10.74 \times 10^{12}$	$11.34 \times 10^{12}$
Total resistance ( $m^{-1}$ )	$26.2 \times 10^{12}$	$24.41 \times 10^{12}$	$21.25 \times 10^{12}$

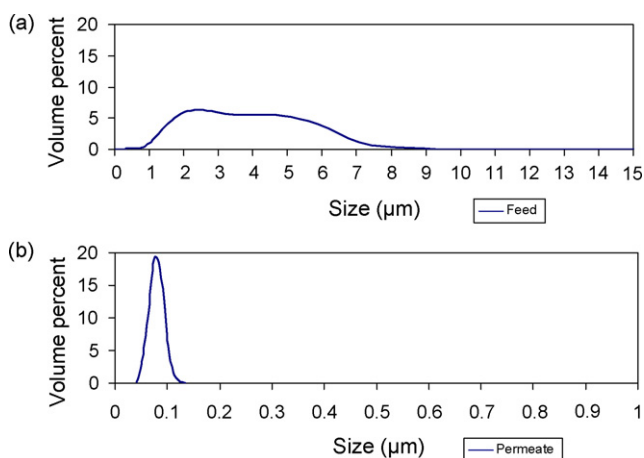


Fig. 11. Size distribution of emulsion droplets for feed (a) and permeate (b).

compared with an initial value of 3500 ppm in the feed solution shows above 98% retention.

The size of emulsion droplets in feed and permeate which were measured by a laser diffraction particle size analyser is presented in Fig. 11. The decrease of the mean emulsion size droplet from 4  $\mu m$  in the feed (Fig. 11a) to less than 0.1  $\mu m$  in the permeate (Fig. 11b) can also be considered as an evidence for high retention of oil by the membranes.

## 5. Conclusions

The effect of membrane type, pressure, feed oil content, pH and feed velocity on ultrafiltration of oil in water emulsions was studied. The experimental study was designed and analysed by the Taguchi statistical method. The results from the experiments were further examined based on the chemical and physical structures of the membrane as revealed by FTIR and SEM.

The calculated error/others of about 10% in Table 4 verified that almost all effective factors had been considered and the error of the experiment was not significant. The Taguchi analysis showed that the most important factor affecting filtration was the membrane type itself.

Also, based on the quantitative analysis, ANOVA, pressure and membrane type appeared to contribute the most to the results. An *F*-ratio less than 1 showed that the pH effect could be regarded as insignificant and the important factors in order were membrane type, pressure, oil concentration and flow velocity.

ANOVA was used to estimate the greatest flux at the optimum conditions of 3 bar, an oil content of 3% (v/v) and the membrane type, being C30F. The calculated flux, 108 L/(m<sup>2</sup> h), was within the range of the confidence limit of the measured value, 106 L/(m<sup>2</sup> h).

The highest flux of the cellulosic C30F membrane compared with the C100F membrane was attributed to a higher number of

hydrophilic groups in the C30F structure and/or a higher number of pores in the C30F membrane. The normalised FTIR results of the virgin C30F and the C100F membranes illustrated that the characteristic peaks of the OH group in the C30F was stronger than that in the C100F membrane.

In the “polarised regime” from 3 bar upwards, flux was independent of pressure for all membranes and was assumed to be determined by the back-diffusive transport. Despite the fact that both the PS100H and the C100F membranes had the same cut-off (100 kg/mol), the hydrophilic C100F showed a superior permeate flux. The strongest drop of flux with time due to oil fouling was observed for the C100F membrane although it was hydrophilic. In the case of the PS100H, both FTIR and SEM showed that the cake layer formation was not the cause of the fouling like with the C100F membrane but probably due to pore blocking because of its hydrophobic nature.

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