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Ultrafiltration of oily water under different conditions, considering critical and limiting flux

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ABSTRACT

It is over a decade since the concept of critical flux was introduced. From that time intensive research has been done to find the functionality and dependency of critical flux for different feeds and membranes. The studies focussed on critical flux in the field of oily water filtration are scarce, however, there are numerous membrane units which have been applied to treat wastewater contaminated with oil. It might be due to the fact that in this kind of filtration the oil drops form a gel layer on the surface of the membranes and this gel layer formation is not the case with feeds where the concept of critical flux has been studied (suspended solids forming a cake layer). In membrane filtration of oily water, knowledge on the existence of critical flux and the influence of different parameters on it may enhance a better operation of the membrane units.

In order to find the critical flux, a set of experiments was carried out in constant pressure mode using varying pressures from 0.5 to 4 bars. A cycling pressure approach (increasing and decreasing pressure) was applied to find the possible critical flux in a system consisting of emulsified oil and salts. It was found that a weak form of critical flux in some cases might exist close to the lowest pressure. No strong form of critical flux was observed from comparison between pure water and permeate flux since the permeate flux differed significantly from the initial pure water flux even at the lowest pressure.

The existence of a limiting flux and its dependency on operating conditions was proven in some cases. The limiting flux was established under different operating conditions, including oil concentration, pH, temperature, salts and flow velocity. The results showed that this flux was significantly influenced by variations in flow velocity and temperature.

Keywords: Critical flux; Limiting flux; Oil emulsion; Salts; Ultrafiltration

1. Introduction

Today membrane processes are more often considered as alternatives to conventional processes. It is because of their unique advantages like higher performance, smaller foot print, and lower cost which make them reliable competitors to other processes. However, drawbacks such as concentration polarisation and fouling prevent an increased application of membranes. Concentration polarisation is a natural consequence of filtration while fouling happens when pressure exceeds the limiting value. These two phenomena are inevitable, but could be managed to have less effect on the performance of membrane filtration.

Fouling and concentration polarisation were the subjects of many investigations in the last decades. Several

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methods have been suggested to retard their influences. These methods may be classified into two main groups. The first one consists of the methods which concern the modification of membranes by using grafting, blending, or plasma treatment, while the second group includes the methods which are dealing with the operating conditions of the filtration process. Adjusting the operating conditions by operating at lower pressure, pre treatment of feed, and increasing flow velocity and shear rate are all considered as some examples for different approaches to keep the permeate flux stable. In this group, another approach, which recently got more attention in the literature and in industry is operating the membrane units under subcritical flux conditions. The concept of critical flux was introduced for the first time in 1995 by Field et al. [1]. Since then, it was extensively studied in different systems, and new definitions were introduced.

The critical flux is known as a key parameter when controlling membrane performance, it distinguishes between two distinct zones, one without fouling while the other one is accompanied with fouling and flux decline [2]. The boarder between these two zones is very narrow and, therefore, the critical flux should be determined accurately. This can be done by comparing the permeate flux with the pure water flux at the same pressure [3] or by cycling the pressure (in constant pressure mode) [2] or the flux (in constant flux mode) [4]. Recently, Espinasse et al. [2] improved the previous techniques to determine the critical flux more accurately. They conducted their study for a suspension of PVC latex in water at various ionic strength and different hydrodynamic conditions in constant pressure mode.

The critical flux concept differs from the limiting flux; the first one is the maximum flux where there is no deposited layer on the surface and operation is without any fouling, while the limiting flux is the maximum flux independent of pressure increase in an operation where the fouling saturates the filtration capacity of the membrane [1]. It was pointed out that the limiting flux happens when the critical flux is reached at all points of the membrane surface [2, 5]. This relationship between the critical and limiting flux was studied by Bacchin [6]. He observed that for a suspension of latex the critical flux was 2/3 of the limiting flux. Since achieving the limiting flux in the experiments is easier, the obtained correlation may be applied in determining the critical flux.

Reviewing the papers and research trends reveals that the majority of work about critical flux has been dedicated to suspensions, colloidal systems [1, 2] and proteins [7], while the available information for other kinds of systems, like emulsions, is limited [1, 8].

This paper presents the results of assessment of the critical flux in a rather complex system consisting of oil emulsion and salts. This kind of mixture may be faced in the filtration of brackish or sea water contaminated with hydrocarbons. The mixture is more complex than what was studied before by other researchers. In a system containing oil, there are some additional phenomena such as oil coalescence or even phase inversion on the surface of the membrane, therefore, the behaviour of flux is different with normal colloidal and suspension systems. Thus, the simulation and extension of previous results for example from latex systems to oil systems may lead to a wrong answer. Moreover, the mechanism of back diffusion, which is the main mechanism in controlling the formation of a concentration polarisation layer, is different. The size of the oil droplets in our study varied between 1–3 μm while in the work carried out by Espinasse et al. [2] the size of the latex particles was about 20 nm. The different size distribution of drops or particles between these two systems (oil and latex) and their physical nature (oil is deformable while latex is rigid) implies that there should not be any similarity between them.

A theoretical prediction of the critical and limiting flux is still impossible as the theory of interaction between oil, salt and the surface of a membrane is not developed and the surface interaction can significantly vary from one system to another [1]. Therefore, the critical flux needs to be determined experimentally. The results can be useful as a guide in the proper operation of filtration units.

Since different factors affect the value of the critical and limiting flux, in order to consider all factors and to get a clear conclusion the design of experiments method (DOE) was applied. The results of the applied method and their analysis by analysis of variance (ANOVA) are presented in the following sections.

2. Materials and methods

2.1. Materials

The experiments were carried out in a laboratory scale UF apparatus as shown in Fig. 1.

The membrane used in the experiments was a regenerated cellulose membrane C-100F with a cut-off equal to 100 kg/mol and an effective surface area of 44 cm^2, provided by Microdyn-Nadir GmbH, Germany.

The prepared emulsions were based on a cutting oil (saBesto cut + cool, Würth) which is composed of mineral oil (70 wt %), surfactants, biocides and corrosion inhibitors. Other chemicals used in the experiments were: NaOH (10 wt %), HCl (37 wt %), calcium chloride-2-hydrate (Riedel- de Haën) and sodium chloride (Merck). The water used in the experiments was distilled water having a conductivity of about 1.0 μS/cm measured at a temperature of 24 °C. The emulsions were prepared by adding the oil to distilled water. The salts were added in the next step and then pH was adjusted by adding HCl or NaOH.

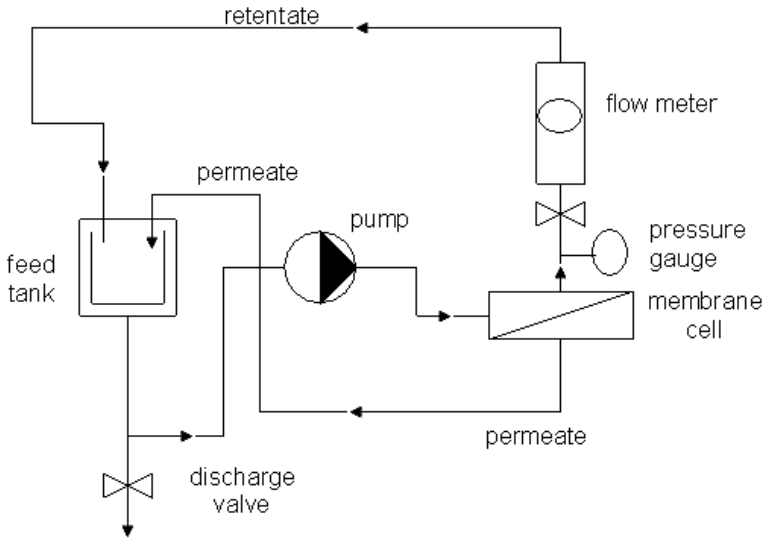

Fig. 1. A schematic diagram of the UF experimental apparatus.

2.2. Methods

2.2.1. Filtration – critical flux experiments

The method which was used to obtain the critical flux was based on the proposed method by Metsämuuronen et al. and Espinasse et al. [2, 7]. According to this method the pressure is increased and decreased in equal steps. The critical flux is defined as the lowest flux that creates an irreversible deposition on the surface. Fig. 2 II shows a scheme of the pressure variation. With this procedure reversible fouling (or concentration polarisation) is distinguished from irreversible fouling.

In total, eight different pressures from 0.5 to 4 bar were assessed. The effect of flux hysteresis was studied by reducing the final pressure (4 bar) to the lower pressures in four steps (3.5, 2, 1, 0.5 bar).

It is known that the critical flux depends on the back transport from the membrane surface and on membrane-solute interactions. It is reported that flow velocity, temperature and solute concentration are affecting the back transport while pH, solute concentration and electrolyte concentration and charge may contribute due to the solute-membrane interactions.

In order to study the effect of different factors on the permeate flux, a set of experiments were carried out. In this experimental set, six factors including pH, oil concentration, temperature, flow velocity, and salt concentration ($CaCl_2$ and NaCl) were varied at three levels (from low to high). Each trial was done at various pressures ranging from 0.5 to 4 bar. The combination of the factors and levels was done by using the Taguchi method which is a type of design of experiments (DOE) method. The factors, the corresponding levels and the combination of them are presented in Table 1.

To evaluate the tendency of the membrane to foul and determine reversible and irreversible fouling, water flux was measured before and after filtration. All the pure water flux measurements were done at the same temperature and pressure before and after filtration.

3. Results and discussion

There are two different forms of critical flux: the strong and the weak form [9]. The type of critical flux is determined by comparing the permeate flux linear curve with the pure water flux. If the permeate flux linear curve equates the water flux the deviation point is called the strong form of the obtained critical flux, but if the constant linear flux-pressure curve deviates from the beginning from the pure water flux the deviation point shows the weak form of critical flux [1, 9]. Figure 2 shows the comparison between water and permeate flux at the lowest pressure for trial 1. As can be seen there is a significant difference between the pure water and the permeate flux. These differences depend on the operating conditions. It was observed that with increasing the pH, oil concentration, $CaCl_2$, and the temperature of the feed the differences between pure water and permeate flux reduced. However, it still deviated from the water flux line (the results are not presented here).

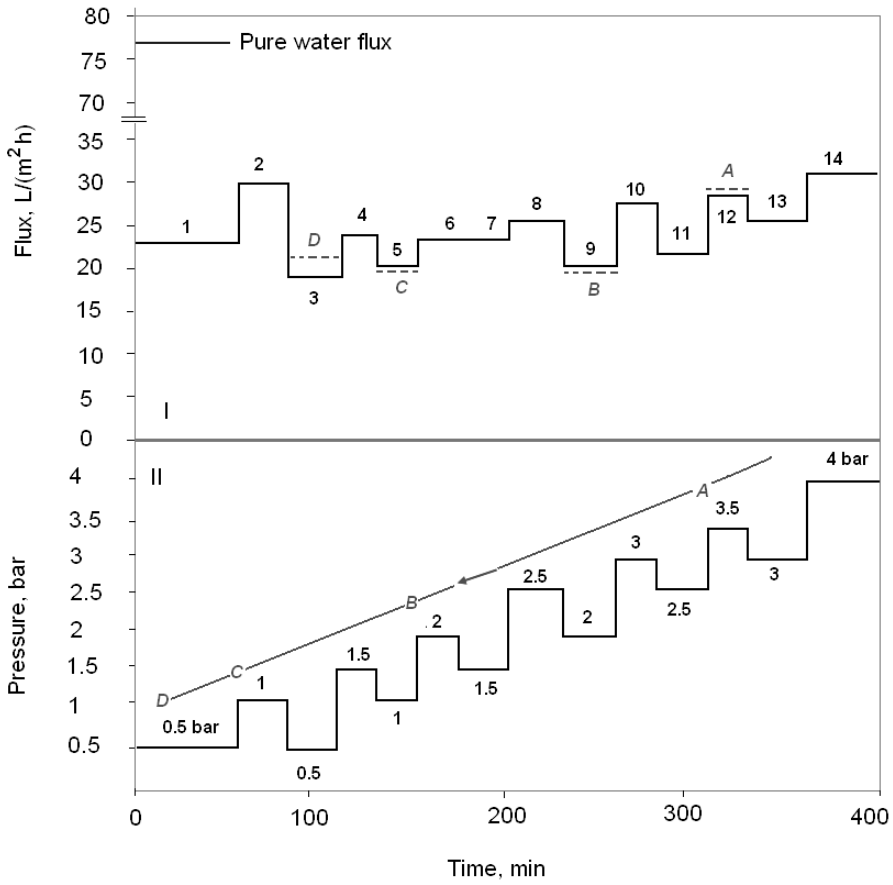

Fig. 2. Comparison between permeate fluxes at upward and downward pressures, and at the descending stage when the pressure was reduced in four steps (dash lines show the flux in the descending step). Operating conditions: pH 5, oil concentration 0.5 v/v %, temperature 25°C, $CaCl_2$ 0.01 mol/L, NaCl 0.001 mol/L, step filtration time 20 min.

The results of the comparison between permeate flux (up and down) at the first pressure (0.5 bar) for all the trials are presented in Table 2. It is clear that almost in all of the trials there are some differences between the permeate flux going upwards and downwards with pressure. The difference varies between trials. This may be due to the complexity of the system which increases the propensity of the membrane to foul at some conditions. Having a look at Table 2 shows that trials (2 or 8) with higher temperature and flow velocity have smaller differences in permeate flux (up and down). In some other cases (trial 17) the fouling happens rapidly and even at very low pressures. Therefore, the permeate flux-pressure gradient is lower than the pure water flux, but this gradient is not linear, therefore, even the weak form of the critical flux cannot be seen. The results are in agreement with what is obtained by Bacchin et al. [9] for complex systems. Lowering pressure below 0.5 bar was not possible with the used equipment.

The existence of a critical flux in our system was also examined by the pressure-stepping method. As can be seen in Fig. 2 when pressure increased one step from 0.5 to 1 bar flux increased (moved from point 1 to 2 in Fig. 2I) but when pressure decreased again to 0.5 bar the flux was lower than in the formal step (point 3 and 1 in Fig. 2I). A reasonable explanation is fouling, because if it were concentration polarisation then by decreasing the pressure, the concentration polarisation should reduce and the flux should be the same as in the previous step [10, 11].

Another parameter which shows that fouling occurs during filtration is the flux recovery parameter. The parameter is defined as the difference between the flux values at the same pressure during the ascending and descending steps. The dash lines in Fig. 2 show the pressures and the corresponding fluxes during the

Table 1
Experimental set and factor levels for the designed experiments.

Trials/ Factors	A*	B	C	D	E	F
1	5	0.5	25	2.6	0.01	0.001
2	5	1.5	35	2.9	0.05	0.01
3	5	3	45	3.3	0.1	0.05
4	7	0.5	25	2.9	0.05	0.05
5	7	1.5	35	3.3	0.1	0.001
6	7	3	45	2.6	0.01	0.01
7	11	0.5	35	3.3	0.1	0.01
8	11	1.5	45	2.6	0.01	0.05
9	11	3	25	2.9	0.05	0.001
10	5	0.5	45	2.9	0.05	0.01
11	5	1.5	25	3.3	0.1	0.05
12	5	3	35	2.6	0.01	0.001
13	7	0.5	35	2.6	0.01	0.05
14	7	1.5	45	2.9	0.05	0.001
15	7	3	25	3.3	0.1	0.01
16	11	0.5	45	3.3	0.1	0.001
17	11	1.5	25	2.6	0.01	0.001
18	11	3	35	2.9	0.05	0.05

*A: pH, B: Oil concentration (v/v %), C: Temperature (°C), D: Flow velocity (m/s), E: $CaCl_2$ (mol/L), F: NaCl (mol/L).

Table 2
Comparison of permeate fluxes (upwards and downwards) for different trials at 0.5 bar.

Trials/flux	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Permeate flux, up (L/(m^2 h))	21	39	111	43	79	34	21	61	55	126	21	46	92	30	35	66	68	16
Permeate flux, down (L/(m^2 h))	17	39	97	38	83	25	16	64	35	127	16	43	91	28	27	67	31	12
Difference between up and down flux	4	0	14	5	-4	9	5	3	20	1	5	3	1	2	8	-1	37	4

descending step for Trial 1. The results for the rest of the trials are presented in Table 3. The flux recovery varied but in general it was below 50%. In some cases a very low recovery (about 1% to 3%) was observed.

The weak form of the critical flux was not obtained in each trial in the assessed pressure range, but a limiting flux was observed. The pressure at which it occurred and the observed limiting flux values for the trials are given in Table 4. It is clear that the value of the limiting flux and the corresponding pressure vary with the operating conditions and emulsion contents.

Further analysis was done on the available data in Table 4 by using ANOVA to determine the factors which have most influence on the limiting flux [11]. The results of this analysis are presented in Fig. 3. This figure shows that the order of the most important factors is; flow velocity, temperature, oil concentration and pH. In the previous work temperature contributed the most on the permeate flux while flow velocity and pH had less effect. The obtained results are different from what was previously reported for similar conditions but with a lower amount of salts [11]. This shows the importance of the amount of salts.

4. Conclusions

A system consisting of emulsified oil and salts is rather complex and has a high propensity to foul the membrane. This is the main reason to the lack of a critical flux in some conditions. The weak form of critical flux was presumed to be close to the lowest pressure when temperature and flow velocity were adjusted to their highest levels.

The constant pressure mode of filtration did not show reliable results since a steady flux was not reached

Table 3
Calculated flux recovery between fluxes in ascending and descending steps during ultrafiltration.

Pressure/ Trials	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
3.5	-2	6	4	5	12	2	0	1	0	3	-1	1	7	2	2	9	7
2	-3	12	39	13	27	4	6	2	2	59	-4	3	29	4	3	28	20
1	3	13	46	8	21	6	13	-2	27	32	-1	0	18	3	6	16	39
0.5	0	10	26	10	7	8	16	-1	25	31	3	-2	25	4	10	16	52

Table 4
Comparison between the limiting fluxes for different trials.

Trials	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Pressure (bar)	2.5	3.5	3.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.0	2.5	2.0	2.5	2.0	2.0	2.0
Flux ($L/(m^2h)$)	20	50	140	43	125	22	14	75	30	200	18	60	140	60	40	90	90	7

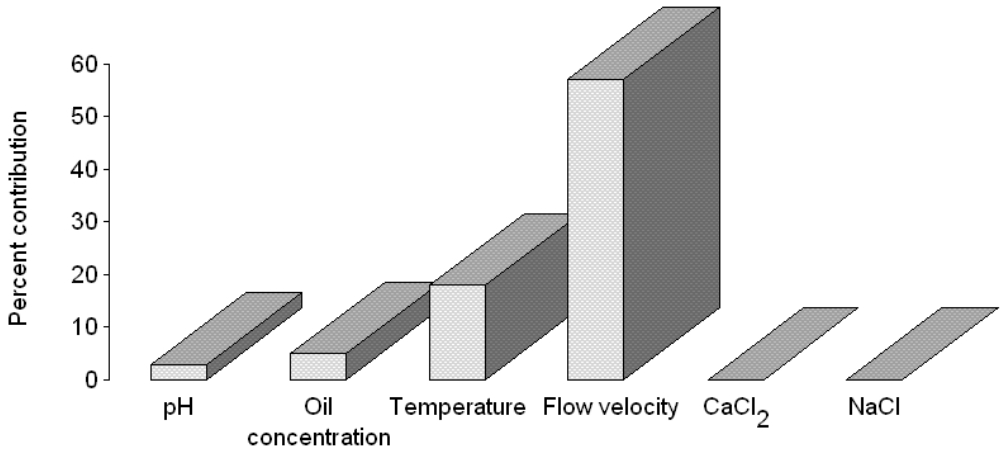

Fig. 3. The contribution of different factors on the limiting flux values.

within the filtration time (20 and 90 min). Therefore, it was suggested that another mode of filtration (constant flux) would be assessed for the determination of the critical flux, and pressures below 0.5 bar should be used also.

The operating conditions have a significant influence on the permeate fluxes. The conditions also affect the limiting flux. It was observed that cycling the pressure caused hysteresis effects. The hysteresis was also a function of the operating conditions.

The limiting flux was affected by the operating conditions, but to varying amount. The biggest impact on flux was observed for the flow velocity and temperature. Other parameters like oil concentration and pH had less effect.

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