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Use of ultrafiltration membranes in the treatment of refinery wastewaters

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ABSTRACT

Conventional treatments of refinery wastewaters no longer meet today's international standards because of the high concentrations, low efficiency or high costs. Membrane processes such as ultrafiltration have been accepted as a versatile separation process for refinery wastewater treatment in recent years. This study focuses on optimizing the operating parameters of ultrafiltration for treating these effluents. It was the aim of this investigation to determine the suitability of four different membranes with different pore sizes for the ultrafiltration of Arabic Aramco crude oil diluted in tap water. The Carbon-Zircon 500 Å tubular membrane was selected among the tested membranes after it proved to be a total barrier for the oil at any feed concentration and gave the highest permeation flux, which is optimized at about 200 l/h.m^2 with optimal operating parameters. The influence of operating parameters on the flux decline and the deposit specific cake resistance were studied. Results showed that increased feed concentration severely decreased the permeate flux, but transmembrane pressure and shear stress had relatively little effect on the flux decline. The specific cake resistance depends strongly on the pressure and the concentration and is independent of the temperature and cross-flow velocity due to shearing forces. The oil rejection depends on the membrane characteristics and the type of emulsion. The main parameter affecting the process is temperature, as this determines the droplet size distribution which strongly influences the permeation flux. Filtration models were used to characterize the type of fouling that occurs. Results showed that there is an absence of irreversible fouling and the main limiting process is the mass accumulation on the membrane surface.

Keywords: Ultrafiltration; Refinery wastewaters; Barrier membranes; Fouling

1. Introduction

Conventional treatments of refinery wastewaters no longer meet the international standards because of the high concentrations, low efficiency and high costs. These effluents, which can contain a complex composition (oil, fatty acids, emulsifiers, corrosion inhibitors, bactericides and other chemicals) [1,2], cannot be discharged into the natural environment or drained to the sewage system without prior treatment, which creates major ecological and pollution control problems throughout the world and

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can plug injection wells as well. The traditional methods for emulsion separation can be classified as chemical, mechanical, thermal and biological. However, these processes are not efficient enough and have several disadvantages [1]. Recently, ultrafiltration (UF) has become accepted as a suitable method of emulsion waste treatment and it is presently regarded as a well-established unit process [3], considered to be a fully acceptable solution from the viewpoint of environment protection [4]. UF of oil emulsions has been used to clean different effluents containing oily bilge water, cutting oils or soluble oils [5], hydrocarbon emulsions [6,7], oil-in-water emulsions used usually for metalworking fluids [2] containing engine oil, surfactants and deionized water [2]. The advantage of this process is the high quality of the permeate and low operating costs [1,2].

Nevertheless, the development of membrane processes for industrial wastewater treatment is hampered by the relatively low permeation flux performance due to concentration polarization and fouling. Although there have been several studies on the membrane separation of oil/solvents in water emulsions, there is a lack of understanding of the basic phenomena that determine flux performances and oil rejection in these systems to an extent that could impede engineering developments [4–6,8].

The permeation flux is also affected by the raw materials of the membranes and the cut-off molecular size, as well as by operational conditions such as driving pressure, velocity and physical proprieties of the feed. Besides, the existence of transition zones between porous media of drastically different granular size introduces major discrepancies between the predicted and the measured hydraulic resistance. The less permeable membranes are the ones most sensitive to this boundary layer resistance [9]. The lower is the cut-off of the membrane the lower is the permeate flux under the same pressure [9].

Several authors found that the permeate obtained from the UF process contains some traces of oil; less then 5 ppm [1,2,5,11] and between 5 and 78 ppm [2,3,7]. Some of them used a supplementary second stage of treatment (membrane distillation, reverse osmosis, photocatalytic) to obtain an oil-free permeate. Gryta et al. [1], using UF tubular membranes made from PVDF (type FP 100, PCI Membrane System) to treat bilge water collected from Szczecin harbour in Poland, found a permeate oil concentration of 4.9 mg/dm^3, TOC 8.6 mg C/dm^3 and TDS 3700 mg/dm^3. In order to obtain permeate free of oil, they used membrane distillation as a supplementary second stage to treat UF permeate. This hybrid process results in a complete removal of oil and a very high reduction of the TOC (99.5%; 1.8 mg C/dm^3) and TDS (99.9%; 1.4 mg/dm^3). Karakulski et al. [11] found permeate with residual oil during UF of oily wastewater. They obtained permeate free of oil by combining UF with reverse osmosis. On the other hand, several authors found permeate free of oil while filtering different oily emulsions of wastewater using different UF membranes and whatever the feed concentrations [4,6,12].

In this paper we study the separation of refinery wastewaters containing emulsions of Arabic Aramco crude oil diluted in tap water using the UF process. We tested four different organic and inorganic membranes with cut-off ranges between 10^5 and 3×10^5 Daltons. The first step towards the design of an efficient and economical treatment is the selection of an appropriate membrane. From an operational point of view, inorganic membranes are more suitable than organic ones [9]. Therefore, a tubular Carbosep membrane was selected for this study after it proved to be a total barrier for the oil and gave the highest filtrate flux. Irreversible and reversible models have been employed to help analyze the flux decline for different operating parameters.

2. Material and methods

2.1. Experimental unit

The emulsion was filtered in a UF apparatus equipped with tubular membranes. The membrane length is 23.5 cm and internal diameter of 0.6 cm. The retentate and the permeate were re-circulated to keep the concentration and the volume constant in the feed tank; the UF system used is represented schematically in Fig. 1. A diaphragm valve was used to control the pressure in the system. The effective membrane area is 44.3 cm^2. To operate the homogenous of the feed solution the unstable emulsion was continuously stirred and thermoregulated in a 20 L storage tank. When the droplets are still deposited on the tank walls or on the surface, the emulsion was recirculated in the tank by a centrifugal pump at high shear

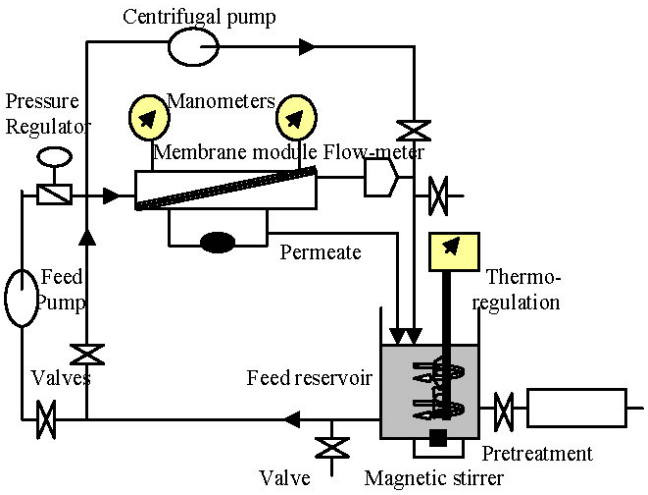

Fig. 1. Experimental unit.

rates to have a stabilized condition, with respect to coalescence, from the beginning of the experiments (Fig. 1).

2.2. Feed preparations

The emulsion was made with Arabic Aramco crude oil added at various concentrations to tap water. The oil density was 800 kg/m^3. The concentration of the solution was made by measuring the weigh of the water and oil.

2.3. Measurements and analysis

Filtration flux: Filtration flow-rate and flux were determined by measuring the time required to collect a given filtrate volume.

Size distribution: Droplet size distribution was quantified using a Malvern Mastersizer/E laser granulometer which gave a distribution by droplet numbers.

Analyses: The collected permeate was analyzed by extraction and infrared absorptiometry, OCMA-220 Horiba, and confirmed by HPLC.

2.4. Membrane cleaning

Between the experiments, the membranes were regenerated by the following procedure:

- Tap water was run through the membrane at low pressure for 30 min to remove the deposited droplets
- 30 min static washing with a 3% sodium hydroxide solution
- Tap water static washing
- 30 min static washing with a 3% in volume nitric acid solution
- Tap water static washing

This procedure almost re-established the original water flux of the membrane, which means that no appreciable permanent fouling of the membrane by the emulsions took place, even at high concentrations.

3. Results and discussion

3.1. Membrane: selection and rejection

The membrane must be carefully selected depending on the type of oily wastes to be processed. Several authors demonstrate that the best module in oily waste UF is a tubular module, because of its resistance to particle fouling, membrane-exchange comfort, and the ability to apply a high linear velocity of the oily emulsion over the membrane surface [4]. For these reasons a tubular module has been used in this study.

Four types of tubular membranes were tested. The nature and the porosity of these membranes are presented in Table 1.

Table 1
Tested membranes

Nature of membrane	Ref.	Pore size (Å)	Manufacturer
Alumine	A	250	SCT
Alumine zircon	AZ	500	SCT
Carbon zircon	CZ	500	Tech-Sep
Carbon carbon	CC	2000	Carbone-Lorraine

Table 2
Droplet size and standard deviations

Temperature (°C)	20	25	30	35
Mean diameter (μm)	65	10	4	2
Standard deviation (μm)	68	32	6	2
Diameter of the smallest droplets (μm)	0.8	0.5	0.4	0.4

At low concentration, no oil was detected in the permeate during the whole filtration run for all tested membranes, oil is therefore fully rejected. The largest pore size of the membranes used as given by the manufacturer is 0.2 μm, is considerably smaller than the smallest droplet in the feed solution which is in the range of 0.4 to 0.8 μm (Tables 1 and 2). This could also be due to high surface tension of the oil droplets that induces forces towards the membrane surface. However, for high concentration and high pressure (C >2 g/l and ΔP >4 bars), a severe flux decline was observed and the permeate contained about 50 ppm of oil for all the membranes except for the CZ membrane where an absolutely limpid permeate was obtained without any traces of oil until the membrane became fully blocked (Fig. 2). This could be explained by the fact that under high driving pressure the fine droplets are deformed and forced to pass through the membrane pores. But, with this assumption, a membrane should be more selective than the other membranes due to its smallest average pore size. Oil droplets were rejected by CZ membrane only due to its hydrophilic characteristics contrary to the other three membranes which were hydrophobic. Internal, partial and surface fouling modeling is carried out in this paper to confirm this assumption. Another important issue that could explain this phenomenon is the charge effects of the membrane surface.

A typical decrease of the permeate flux was observed during the UF operation before reaching a steady state after 2 hours for all the membranes as shown in Fig. 3. The highest flux of about 200 l/h.m^2 was obtained by the CZ membrane. In the subsequent experiments, the CZ membrane with a cutoff 3×10^5 Daltons gave maximum permeate flux and it was a total barrier for oil used.

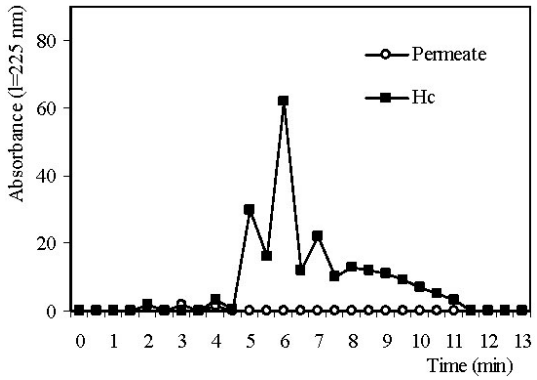

Fig. 2. Chromatogram of hydrocarbon (Hc) emulsion at 2 g/l and of the permeate, CZ M, 25°C, 2 bars, 1.2 m/s.

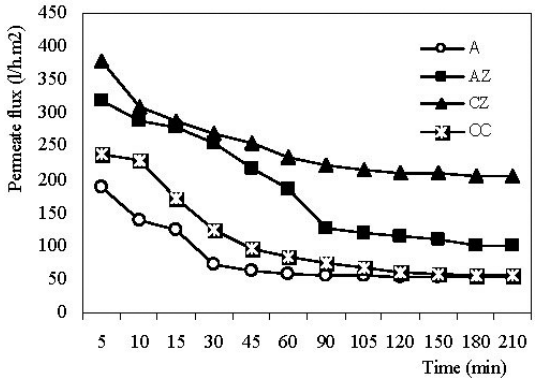

Fig. 3. Permeation flux against time for different membranes, oil: 1.5 g/l, 25°C, 2 bars, 2 m/s.

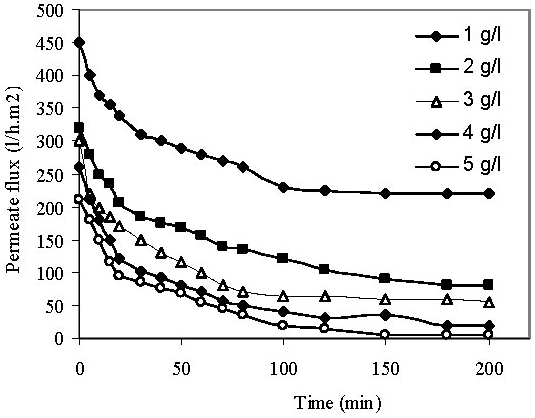

Fig. 4. Permeation flux against time for different feed concentrations, 2 bars, 25 oC, 1.2 m/s.

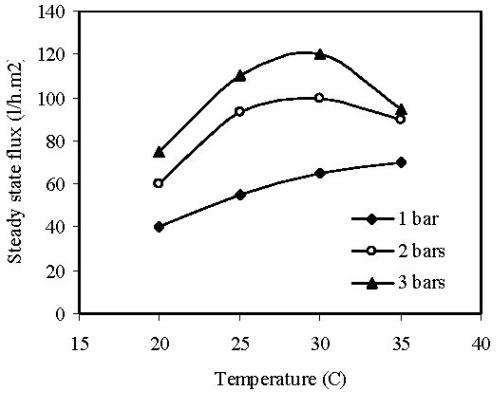

Fig. 5. Influence of temperature on steady state flux for different pressures, oil: 2 g/l, 1.2 m/s.

3.2. Influence of the operating parameters on steady state flux

The flux decreases with time and an increase of feed concentration, diminishing faster in the beginning but then leveling of somewhat before reaching a steady state. The results are depicted in Fig. 4. The increase of feed concentration decreases the steady state flux and induces a drastic fouling rending the membrane practically difficult to clean. When the feed concentration is increased more than 5 g/l, the steady-state flux is almost nil but has practically no influence on the permeate quality which remains limpid. The accumulation of oil droplets on the membrane surface forms a cake layer with high concentration which is strongly adsorbed and resistant to shear. The collisions between droplets become more frequent and form aggregates which become more numerous and larger when the interactions between droplets increase [3]. This result shows that a pretreatment process to reduce the concentration by removing large particles and free oil is necessary to protect UF membrane.

The temperature is the main parameter conditioning the filtration process, as this determines the droplet size distribution which is found highly dispersed at any temperature leading to standard deviations of the same order of magnitude as or even larger than the mean diameters; the measuring results have been gathered in Table 2. Higher temperatures result in a decrease of the larger droplet frequency which means a lower flux. The maximum flux obtained at 30°C could be explained by the conservation of some larger droplets which were still able to protect the active layer (Fig. 5). The highest gap was observed from 20 to 25°C where the mean size diameter decreases from 65 to 10 μm. At a higher emulsion pressure, the effect of temperature on permeation flux becomes more complicated as shown in Fig. 5 due to the decrease of droplets size when temperature increases. This result is different from the fundamental study on droplet size at different stages of UF, which was undertaken by Lipp et al. [13], in which they showed that the droplets were about the same order of size.

The viscosity of the feed solution affects the permeation flux as predicted by Darcy's equation. The effect of feed temperature on the process is due to the physical proprieties of the solution, even though the feed concentration is relatively high. The decrease of droplets sizes when temperature increases could be due to the decrease of viscosity, the increase of solubility and the changes of

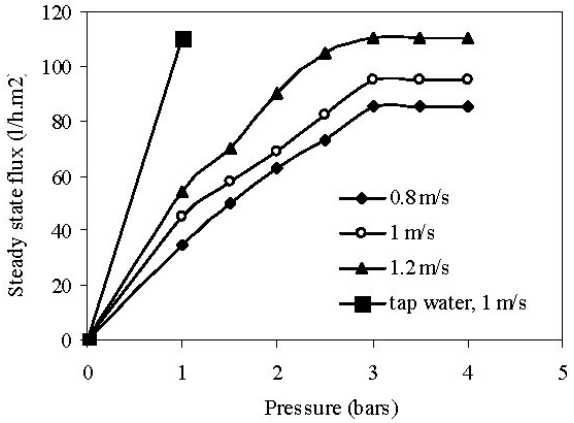

Fig. 6. Influence of driving pressure on steady-state flux for different velocities, oil: 2 g/l, 25°C.

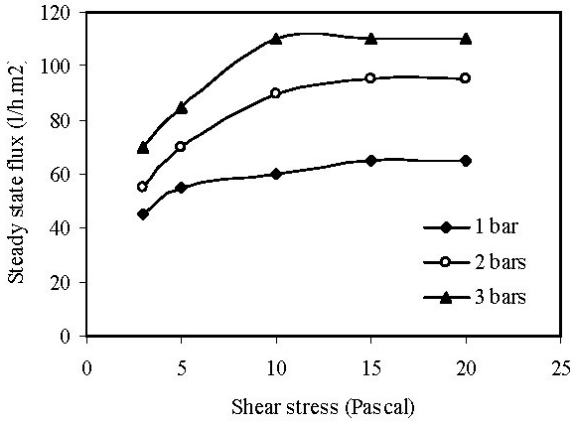

Fig. 7. Influence of shear stress on steady-state flux for different pressures, oil: 2 g/l, 25°C.

the surface tension which favor the droplets splitting. On the contrary, the decrease in temperature favors droplet coalescence, thus larger sizes.

The permeation flux for a pure water or tap water, which does not contain suspended solids, oil droplets or high molecular weight substances, is directly proportional to the trans-membrane pressure (Fig. 6) because the net filter resistance is governed only by the intrinsic membrane resistance. In the case of emulsion, however, accumulated oil droplets form a cake layer on the membrane surface, and the permeation flux therefore decreases in UF operation. If the filtration run is continued, oil droplets continue to be supplied, and the cake layer increases in thickness before a gel layer is formed. However, the thickness of the cake layer is also governed by the fluid shear stress, which is closely related to the cross-flow velocity in the unit [10]. Therefore, the permeation flux at a given velocity becomes a constant, regardless of the driving pressure, as shown in Fig. 6.

Nystrom [5] found that an increase of driving pressure decreases the flux and then the flux is restored when pressure is released. This is due probably by the fact that at high pressure some oil droplets are found in the permeate which means an internal fouling occurs even though the pore size is much smaller than the droplet size (in this case penetration of oil droplets through the pores should not occur). The effect of pressure increases the concentration polarization that makes the oil droplets coalesce on the membrane surface. It seems that the driving pressure exceeds the capillary pressure in certain pores so that the droplets can be deformed and forced to penetrate into the membrane pores [3], which explains the decreasing flux when the pressure increases. This result depends on the emulsions nature and the type of membrane.

The experimental results presented in Fig. 7 show that the steady state flux increases along with an increase of shear stress and become independent from 15 Pascal, corresponding to a Reynolds number of 12×10^3 and therefore to a turbulent flow. We notice that for low pressure the flux is slightly influenced by the shear stress. The influence of cross flow velocity on flux seems to be a very important factor, which is quite natural as an increase in flow velocity decreases the concentration polarization and leads to the formation of a uniform layer.

3.3. Membrane fouling

In order to better understand the flux decline and identify the irreversible and reversible fouling mechanisms, different models and characterization were used.

The pressure required to force the oil flow through the membrane pores is given by the following equation [3,4]:

$$\Delta P=\frac{4\gamma\cos\theta}{d_p} \quad (1)$$

where ΔP is the transmembrane pressure, γ is the interfacial tension between the oil and the solvated surface, θ is the contact angle and d_p is the pore diameter. To confirm the absence of HC in the permeate and within the membrane structure, internal and partial fouling models were used.

It is assumed that all pores are cylinders of the same length and the same diameter, and all the droplets carried by a filtrate volume dV were retained on the pore walls as a monolayer if the droplets are very small compared to the pore radius r_p. Then the pore radius decreases and it is related to filtrate volume by:

$$\ln(-2\pi r_p\, dr_p) = X_o dV \quad (2)$$

where L is the pore length, X_o is the volumic fraction of

droplets in the suspension and N is the number of pores. Using Poiseuille's law and the integration of Eq. (2), we obtain:

$$\sqrt{\frac{Q_0}{Q}}=1+k_i\frac{Q_0 t}{2} \tag{3}$$

with

$$k_i=\frac{2X_0}{N\pi r_0^2 L} \tag{4}$$

where Q and Q_0 are respectively the filtrate flow-rate at any time and the initial filtrate flow-rate, t is the time, r_0 is the initial pore radius and k_i is the internal clogging coefficient.

The plot of $(Q/Q_0)^{1/2}$ against $Q_0t/2$ is a straight line for different pressures (Fig. 8). But the coefficient k_i is a function of pressure and is independent of concentration which is contrary to the theory [Eq. (4)]. This could be because of the absence of internal fouling in the experiments or because this model considers only the transient state and is directly derived from the classical relationships established for deal-end filtration [14]. Since permeate is completely free of hydrocarbon droplets for any operating range and the smallest droplet size is much larger than the pore size, the assumption of absence of internal fouling is valid. However, there is a possibility that the smallest droplets penetrated the membrane structure and blocked some pores partially without passing through the membrane; these droplets could make these membrane surfaces hydrophobic and increase the contact angle.

Since the possibility of an internal fouling process is eliminated, let us assume that the partial clogging occurs. The droplets accumulate outside the pores, probably coalesce to form bigger droplets and spread over the membrane surface and partially block them.

During the partial clogging stage some pores are partially clogged and the variation of the filtering surface area is calculated by:

$$-\mathrm{d}A=\sigma'\frac{A}{A_0}\mathrm{d}V \tag{5}$$

where σ′ is a coefficient having the dimension of a specific area, A is the active filtering surface area and A_0 is the initial active surface area.

Integration and the use of Darcy's law results in:

$$\frac{1}{Q}=\frac{1}{Q_0}+k_p t \tag{6}$$

with

$$k_p=\frac{\sigma' P}{\mu R_m Q_0} \tag{7}$$

where R_m is the intrinsic membrane resistance, μ is the dynamic viscosity and k_p is the partial clogging coefficient.

The plot of $(1/Q)$ against time for different pressures should give a single straight line. But different straight lines are obtained for each pressure (Fig. 9). In addition, Fig. 10 shows that k_p is inversely proportional to the driving pressure, which is contrary to Eq. (7). Consequently, these results indicate that no partial clogging is happening. The main limiting process is then simply a mass accumulation against the membrane surface evidencing a lack of affinity of the oil towards the membrane material.

The specific cake resistance is inversely proportional to the transmembrane pressure and the feed concentration. Coalescence of oil droplets is probably favored by increase in concentration and the pressure which favors the coalescence of the deposited droplets and diminishes the deposit specific area. On the other hand, the specific cake resistance is independent of temperature and cross-flow velocity. The velocity stabilizes the deposit without provoking a significant coalescence.

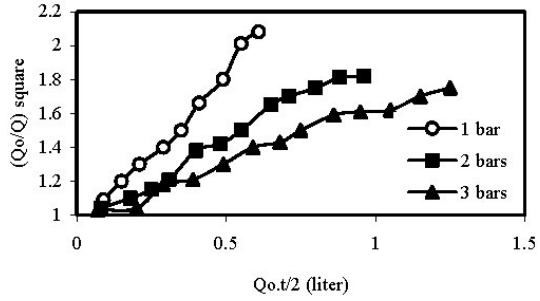

Fig. 8. Internal clogging for different pressures, 1.2 m/s, 25°C, oil: 2 g/l.

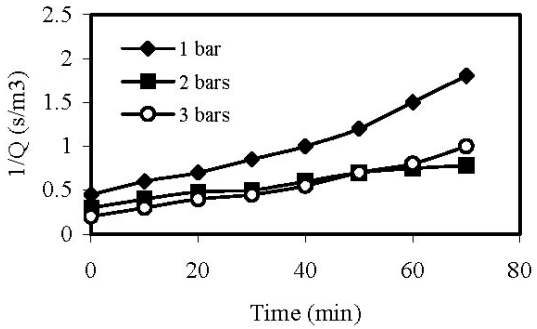

Fig. 9. $1/Q$ vs. time for different pressures.

When oil of bulk concentration X_0 is fully rejected by the membrane, the interfacial concentration X_m increases with the flux as predicted by the following equation deduced from film theory.

$$J = k \ln \frac{X_m}{X_0} \quad (8)$$

where $k = D/\delta$ is the conductance depending of the system hydrodynamics conditions and the physico-chemical proprieties of the solution. D is the solute diffusivity coefficient of solute in water due to cross-flow and δ is the thickness of the film layer on the membrane surface. X_m is the volume fraction occupied by droplets at the membrane wall.

Considering the range of operating conditions for which the flux is independent of the applied pressure, it was suggested in the case of UF of a solution that the limiting flux corresponds to an interfacial concentration X_g that is high enough to turn into a gel [8,14]. This assumption, together with film theory, leads to the following expression for the limiting flux J_l.

$$J_l = k \ln \frac{X_g}{X_0} = k \ln X_g - k \ln X_0 \quad (9)$$

It is not realistic to assume that the oil could form a gel. However, a gel model is valid if a straight line is obtained when the experimental limiting fluxes are plotted against the logarithm value of the bulk concentration which is effectively observed (Fig. 11). The limiting concentration X_g is therefore not a gel concentration but corresponds to a mass accumulation beyond which the flux cannot be increased by pressure. Our approach is very satisfactory with the experimental data and explains the reason for obtaining a critical flux when the driving pressure increases.

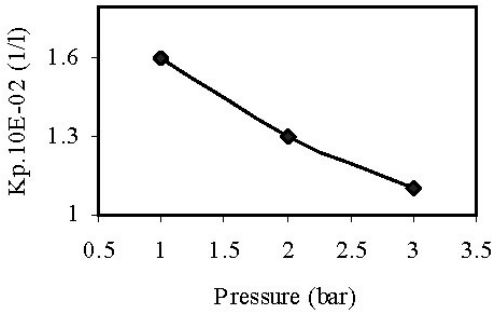

Fig. 10. k_p coefficient vs. pressure.

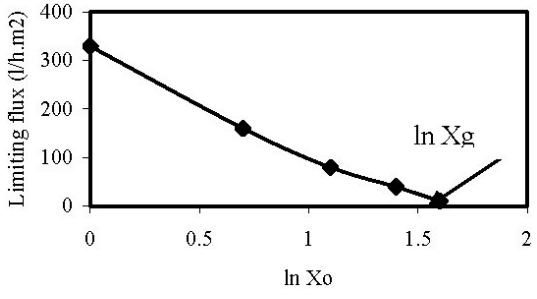

Fig. 11. Limiting flux against $\ln X_0$, 1.2 m/s, 2 bars, 25°C.

4. Conclusions

1. All tested membranes were a total barrier for oil below a feed concentration of 20%. Beyond this value, around 50 ppm oil is found in the permeate except for the CZ membrane where the permeate was limpid for any feed concentration.

2. The tubular CZ membrane was selected after it proved to be a total barrier for oil and gave the highest permeation flux.

3. The total oil rejection depends of the membrane nature and the type of the emulsion.

4. Flux performance depends on the droplet size distribution, which depends strongly on temperature. The effect of feed temperature on the process is due to the physical proprieties of the emulsion, even though the feed concentration is high.

5. Increased feed concentration severely decreased the permeate flux, but transmembrane pressure and shear stress had relatively little effect on the flux decline.

6. The permeate flux is maximized at 200 l/h.m^2 for a feed concentration of 1.5 g/l and with optimal operating parameters.

7. The specific cake resistance strongly depends on the pressure and the concentration and is independent of the temperature and cross-flow velocity due to shearing forces.

8. The CZ membrane is fully blocked for high feed concentrations, over 5 g/l, and it is practically difficult to clean.

9. A supplementary second stage of treatment (RO or MD) after UF as proposed by several authors is not needed.

10. The membrane fouling modeling is satisfactorily quantified for the experimental data.

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