MODELING THE STEADY STATE FLUX OF OIL/WATER AND SUSPENDED SOLIDS SEPARATION BY CROSS-FLOW ULTRAFILTRATION

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ABSTRACT

The Oil Refinery Company TOTAL produces wastewater containing 20 mg/l hydrocarbons (HC) and 30 mg/l suspended solids (SS). The new International standards will require less than 5 mg/l HC and less than 10 mg/l SS. Such standards could be met by an ultrafiltration operation. The M9 Carbosep membrane was selected after this inorganic membrane proved to be a total barrier for the HC and giving highest water flux. A systematic study of the influence of the different operational parameters was then affected with a mixed suspension (MS) containing HC and biological solids sampled from an activated sludge plant. The importance of the temperature is emphasized as it determines the droplet size distribution. The major limiting processes conditioning the fouling are evidence and explained by the mean droplet size distribution. Aggregation processes of HC on the bacterial flocks were observed leading to larger particles with an optimal HC/SS ratio. Progressive fouling can be limited by use of helical baffles introduced in the membrane. Experimental data were fitted to a model of cake deposition with retroflux while the steady state results were recalculated in terms of two dimensionless quantities whose experimental values are linearly correlated. A relationship for the limiting flux is fitted to the experimental data.

Keywords: *Separation Techniques; Ultrafiltration; Fouling; Barrier Membranes; Mixed suspension, Water treatment*

الملخص

ينتج عن تكرير النفط في شركة TOTAL الفرنسية مياه مستعملة تحتوي على ٢٠ مغ/ل هيدروكربونات و ٣٠ مغ/ل مواد صلبة عالقة ، ولكن المواصفات (المعايير) العالمية الجديدة تتطلب أقل من ٥ مغ/ل هيدروكربونات وأقل من ١٠ مغ/ل مواد صلبة عالقة . هذه المواصفات يمكن الحصول عليها باستخدام عملية الانتشار الغشائي المساعد بالضغط. في هذه الدراسة تم اختيار غشاء Carbosep M9 الغير العضوي بعد أن أثبتت التجارب أنه حاجز شامل للهيدروكربونات مع الحصول على أعلى معدل سريان للماء. تم إنجاز دراسة منهجية على المتغيرات العملية لخليط يحتوي على هيدروكربونات ومواد صلبة عالقة مأخوذة من محطة تنقية مياه الصرف. إتضح أن لدرجة الحرارة أهمية في تحديد حجم قطرات المستحلب الموزعة. تبين أن توزيع الحجم المتوسط للقطرات يخضع للمتغيرات العملية المحددة لظاهرة الالتساخ. لوحظ في هذا البحث زيادة في حجم الجزيئات نتيجتا لعملية تجمع الهيدروكربونات مع القطع

البكتيرية وهذا بدوره يؤدي إلى الحصول على أفضل نسبة للهيدروكربونات إلى المواد الصلبة العالقة. يمكن التقليل من تراكم الالتساخ باستعمال الحواجز الحلزونية داخل الغشاء. تم محاكات نتائج التجارب باستعمال نموذج طبقة الكعكة بينما نتائج حالة الاتزان تم حسابها بدلالة كميتين لا بعاديتين تربط مقاديرهما التجريبية علاقة خطية تبادلية وكذلك تم ربط علاقة التدفق النهائي بمعطيات التجارب.

1. INTRODUCTION

The oil refinery wastewater conventionally treated still contains about 20 ppm total hydrocarbons (HC) and 30 ppm suspended solids (SS) sloughed from biological reactor and their temperature is about 30 ^{o}C. However, the new European standards will require less then 5 ppm HC and less then 10 ppm SS. Such standards are out of the reach of classical treatments but they could easily be met by an ultrafiltration operation. Nevertheless, the development of membrane processes for industrial wastewater treatment is hampered by the relatively low flux performances due to fouling. Although there have been several studies of the membrane separation of oil/solvent in water emulsions, there is a lack of understanding of the basic phenomena which determine flux performance and oil rejection in these systems to an extent which could impede engineering developments. The oil refinery TOTAL has implemented an academic research program to improve the basic knowledge of the limiting processes.

The first step towards the design of an efficient and economical treatment is a screening research to identify a convenient membrane, keeping in mind that in such operational conditions, an inorganic membrane is more adapted than an organic one. The M9 Carbosep membrane was selected after this membrane proved to be a total barrier for the HC contained in a synthetic emulsion made with crude oil while giving the highest filtrate flux. The second step was a systematic study of the influence of the different operational parameters on the transient and steady flux performances obtained with the M9 membrane at different temperatures focusing on the processes which limit the mass transfer when oil is the sole solute [Villarroel Lopez et al., 1994]. It was then demonstrated that the flux performances strongly depend on temperature to such an extent that is seemed necessary to decrease the wastewater temperature prior to an industrial operation. This work is devoted to the results obtained with mixed suspensions containing oil and suspended solids simultaneously.

2. MATERIAL AND METHODS

2.1. Unit

The experimental unit provided by the manufacturer Tech-Sep operates on a 40 cm long and 6 mm diameter tubular Carbosep membrane in a closed loop, where the permeate and the retentate are both recirculated (Fig. 1). The selected M9 membrane is an inorganic composite membrane whose zirconia- active layer was deposited on a carbon support. The thickness of

the membrane is 4 mm and the membrane cut-off as given by the manufacturer is 300 000 Daltons. In some runs, helical rode type baffles are introduced in the membrane tube in such conditions that there are contact points between the helix and the membrane wall, which constitutes a significant difference with the configuration proposed by Gupta et al. with no helix-wall contact [Villarroel Lopez et al., 1994]. The duration of each experiment range between 70 and 80 minutes.

No HC were detected in the permeate for any experiment by extraction and infrared absorptiometry effected with an oil content analyzer OCMA-220 Horiba, HC are therefore fully rejected. Besides, the dissolved organic carbon abatement is about 45 % without taking into account the HC abatement.

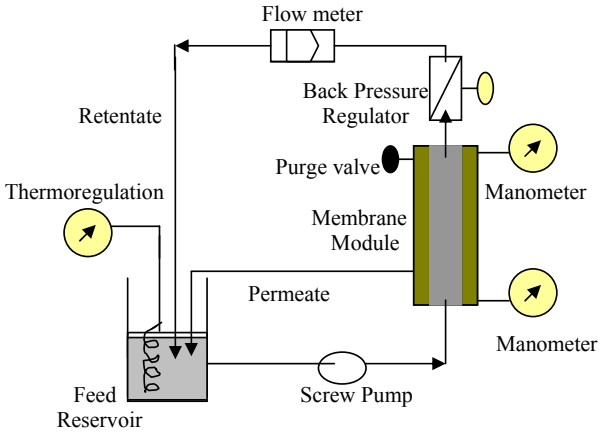

Figure 1: Experimental unit

2.2. Suspensions

The suspensions are made with an Iranian crude oil having a density of 860 kg/m^3, which may be mixed with SS collected from a settler of the activated sludge plant of Montpellier, France. The oil and/or the solids are diluted with the settler supernatant. The suspension is continuously stirred and thermoregulated in a storage tank at a concentration corresponding to the required permeate concentration keeping in mind that an industrial effluent has a concentration ratio SS/HC of about 1.5.

2.3. Determinations

Particle numbers quantifies the particle size distribution with a Malvern Mastersizer/E laser granulometer, which gives distribution. Filtration flow-rate is determined by measuring the time required to collect a given filtrate volume. Dissolved organic carbon concentration is obtained after filtration through a 40 μm membrane and measurement with a TOC-meter 5000 Shimadzu.

2.4. Membrane regeneration

Between two runs, the membranes were regenerated by the following procedure:

1. 30 min static washing with a 3% sodium hydroxide solution at 50°C;
2. Tap water static washing;
3. 30 min static washing with a 3% in volume nitric acid solution;
4. 1 h static washing;
5. Tap water static washing.

The initial water flux (tap water) of the membrane should be obtained after each regeneration and allowed to calculate the membrane resistance R_m.

3. RESULTS AND DISCUSSION

3.1. Influence of Operating Parameters

The presence of biological solids produces an increase of the mean size of the particles (Fig. 2). At 35 °C, the mean size of HC droplets alone in suspension is 2 μm whereas the biological solids alone have a mean size of 60 μm; in the mixed suspension, the mean size becomes 80 μm. Microscopic observations show that there is an agglomeration of droplets on the biological particles, which tend to flocculate. This process limits the fouling as higher fluxes are observed in presence of solids. The maximum flux is reached when the SS concentration has the same value as the HC concentration expressed in mass per volume (Fig. 3).

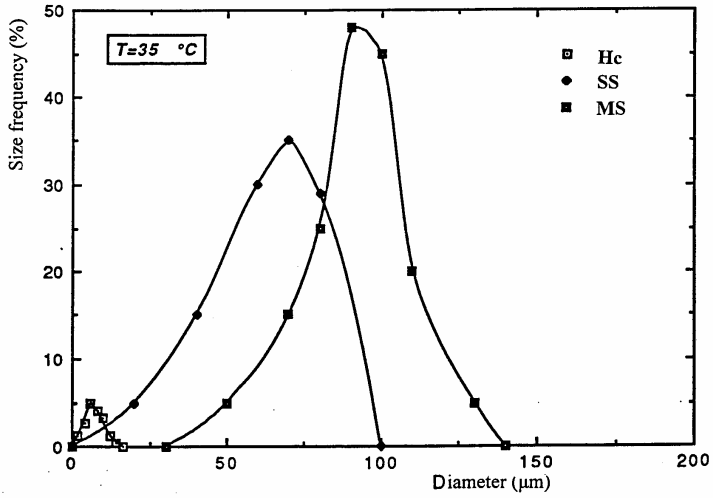

Figure 2: Size distribution of HC droplets, SS particles and MS particles

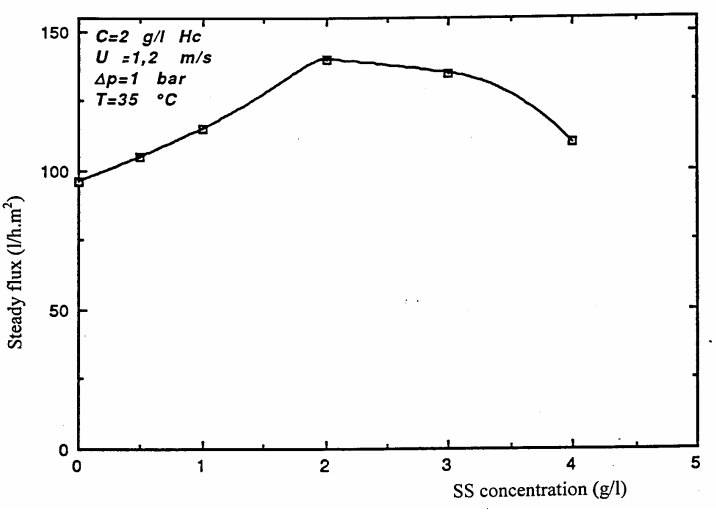

Figure 3: Influence of SS concentration on steady flux

The shear stress τ against the membrane wall depends on the energy degradation regime [Le Gof, 1979]; it is calculated by the following relationship:

$$\frac{f}{2} = \frac{\tau}{\rho u^2} \qquad (3\text{-}1)$$

Where f/2 is the friction factor whose value is a function of the Reynolds number $R_e=\rho ud/\mu$, ρ being the liquid density, u the cross-flow velocity, d the filtration element internal diameter and μ the liquid dynamic viscosity. The friction factor is then obtained by one of the following relationships:

$$\frac{f}{2} = \frac{8}{R_e} \quad \text{For } R_e \leq 2500\text{-}4000 \qquad (3\text{-}2)$$

$$\frac{f}{2} = 0.023 R_e^{-0.2} \quad \text{For } 5000 \leq R_e \leq 200\,000 \qquad (3\text{-}3)$$

The experimental data show that a plateau is reached for a low shear stress of 5 Pascal, which is independent of the biological solids addition (Fig. 4). There is therefore some irreversibility of the oil deposit, which cannot be transported towards the bulk of the suspension by hydrodynamic effects. This result is not easy to explain, as the operated membrane should be oleophobic.

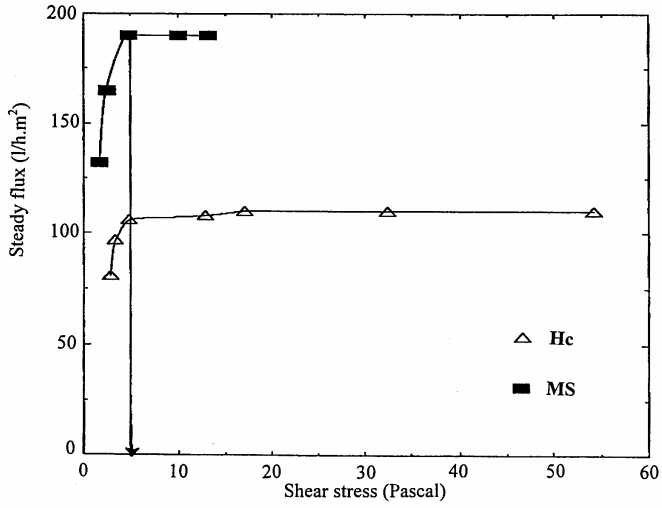

Figure 4: Permeate steady flux against shear stress, 2 g/l HC, 3 g/l SS, 35°C and 2 bars

3.2. Retroflux Model

A general model for particle microfiltration was proposed by Liu (1992). This model takes into account the different particle fractions: the particles which are deposited against the membrane wall, the particles which contribute to an internal clogging and the particles which are transported from the deposit to the bulk of the liquid phase by a retroflux process. The filtration flow-rate Q is then given as a function of time t and filtered volume V:

$$\frac{Q_o}{Q} = k_d(V - k_p t) + \frac{1}{[1 - k_i(V - k_p t)]^2} \qquad (3\text{-}4)$$

Where:

$$k_d = \frac{\alpha x_o}{AR_m}, \qquad k_p = \frac{Q_r}{x_o} \text{ and } \quad k_i = \frac{2x_o}{Nr_o^2 \pi L} \qquad (3\text{-}5)$$

Where Q_o is the initial flow-rate and k_d, k_i and k_p are respectively linked to the deposition, the internal clogging and the retroflux. r_o being the initial pore radius; L is the pore length, N the number of pores. Q_r is the retroflux flow-rate and x_o the volume fraction occupied by particles in the bulk of the suspension, A is the filtering surface area, R_m the initial membrane resistance and α the specific resistance per unit length of deposit. This model allows calculating a steady flux reached when ($V - k_p t$) becomes constant. This approach will be used to quantify the ultrafiltration data. In this case, there is no evidence of internal clogging by HC as they are fully rejected. The equation (3-4) is then simplified under a form easy to use:

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$$\frac{\frac{Q_o}{Q}-1}{V} = k_d - k_d k_p \frac{t}{V} \qquad (3\text{-}6)$$

The plot of $(Q_o/Q–1)/V$ against t/V are a straight line allowing calculating both of the parameters (Fig. 5).

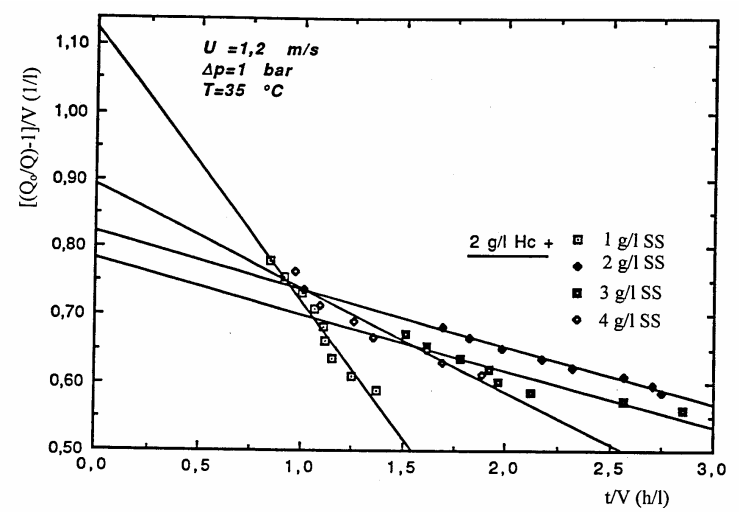

Figure 5: Flux modeling, 2 g/l HC and variable SS concentration

3.3. Use of Helical Baffles

When helical baffles are introduced, the model still applies. The higher flux is observed when the baffle has 3 helices per 4 cm. No additional pressure drop is observed and a critical flux of 150 l/hm^2 nearly steady is obtained for 0.5 bar (Fig. 6).

3.4. Steady flux

The steady flux is the flux obtained in a filtration run when the permeate flow-rate reaches a plateau while the limiting flux is observed when the flow-rate becomes independent of pressure.

When oil of bulk concentration x_o is fully rejected by the membrane, the interfacial concentration x_m increases with the flux J as predicted by the following equation deduced from the film theory:

$$J = k \ln \frac{x_m}{x_o} \qquad (3\text{-}7)$$

Considering the range of operating conditions for which the flux is independent of the applied pressure, it was suggested in the case of ultrafiltration of a solution that the limiting flux J_l

corresponds to an interfacial concentration x_g high enough for the solution to turn into a gel [Aimar et al., 1986]. This assumption, together with the film theory, leads to the following expression for the limiting flux:

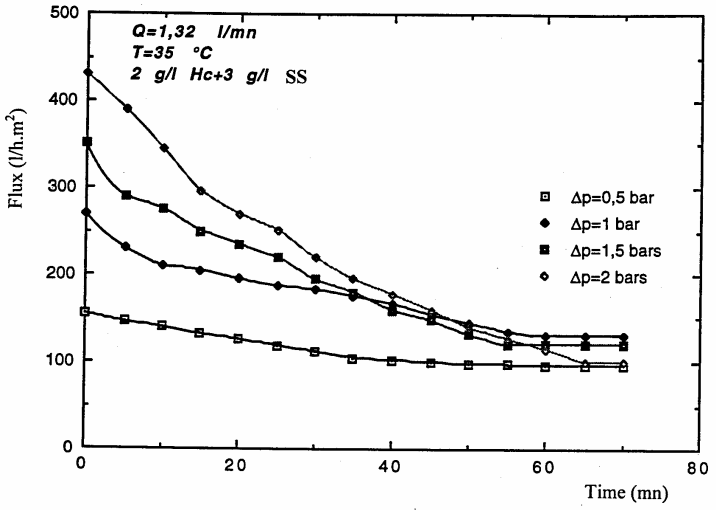

Figure 6: Flux against time at various pressures in presence of helical baffles

$$J_l = k \ln \frac{x_g}{x_o} \qquad (3\text{-}8)$$

Where the mass transfer coefficient k depends on the hydrodynamics.

It would not be realistic to assume that HC could form a gel. However, equation (3-8) predicts that a straight line is obtained when the experimental limiting fluxes are plotted against the bulk concentration, which is effectively observed (Fig. 7). 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.

Besides, the steady flux increases when cross-flow velocity is increased and reaches a plateau at about 2 m/s corresponding to a Reynolds number of 12.10^3 and therefore to a turbulent regime (Fig. 8). Before reaching the plateau, the limiting flux is proportional to $u^{0.54}$, which means a transfer in laminar and transient conditions (Fig. 9) [Wiley and al., 1985].

The limiting flux can therefore be expressed by the following relationships:

$$J_l = K u^{0.54} \ln \frac{x_g}{x_o} \qquad \text{For } u<2 \text{ m/s} \qquad (3\text{-}9)$$

$$J_l = k \ln \frac{x_g}{x_o} \qquad \text{For } u>2 \text{ m/s, k being constant} \qquad (3\text{-}10)$$

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From the experimental data, it is derived that $K=3.6.10^{-5}$ $m^{0.46}s^{-0.46}$, $k=4.10^{-5}$ m/s and $x_g=6.10^{-3}$ corresponding to about 5 g/l oil in water.

These results are confirmed by calculating and plotting x_m/x_o against the driving pressure (Fig. 10). All the points belong to one curve whose shape includes a point of inflection. The point corresponds to a change in the limiting transfer phenomenon. The hydraulic resistance is the physical barrier of the membrane which limits the major process below this point of inflection and the transfer. For data located beyond the point of inflection, the membrane has less influence on transfer than the boundary layer [Aimar et al., 1986]. Besides, the asymptote value confirms the validity of the x_g calculation.

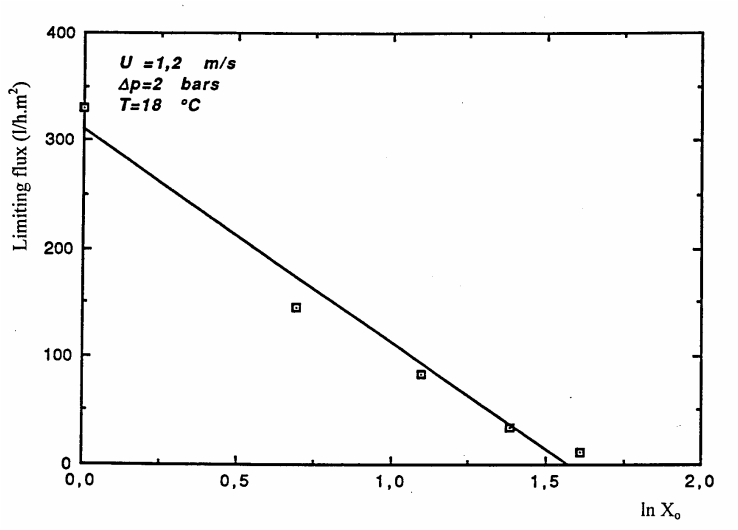

Figure 7: Limiting flux against ln x_o

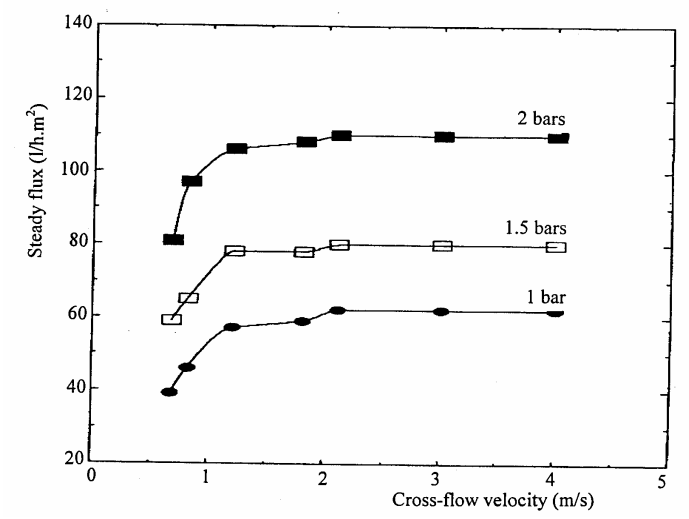

Figure 8: Steady flux against cross-flow velocity, 2 g/l HC, 18 °C

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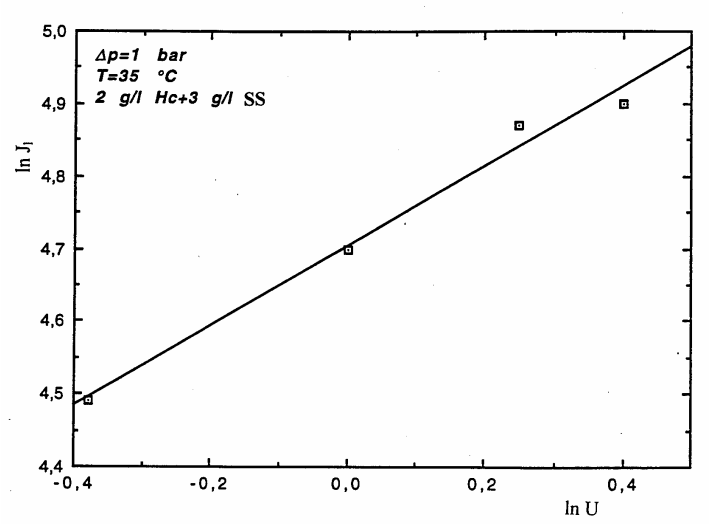

Figure 9: ln J_l against ln u

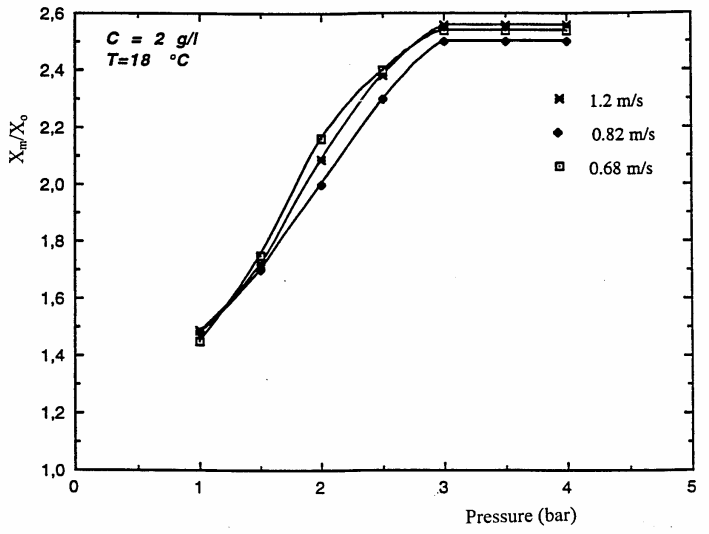

Figure10: x_m/x_o against driving pressure

The steady state data are interpreted with the dimensional analysis proposed by Assadi et al. (1992). In this approach two dimensionless quantities are used: $E = \rho u^2 / P$ and $F = R_d / u P$ where R_d is the resistance due to the fouling and P the driving pressure. The quantity E is similar to the inverse of an Euler number or of a Number of Energy Units NEU (Le Goff, 1979). Whereas F is equal to u / J_d, J_d is being the flux through media having the resistance

R_d; F therefore compares the convective flux to the flux through the fouling layer. The experimental results recalculated in terms of these dimensionless groups give satisfactory plots, which are straight lines of positive slope (Fig. 11). Assadi et al. found straight lines of negative slope with microfiltration data. The meaning here is that there is no cross-flow velocity value which eliminates completely the fouling. The higher slope is obtained while filtering HC combined with biological solids. The intermediate slope for the membrane operated with baffle is explained by the steady flux decrease, which occurs, in this case, at pressure higher than 1 bar (Fig. 12).

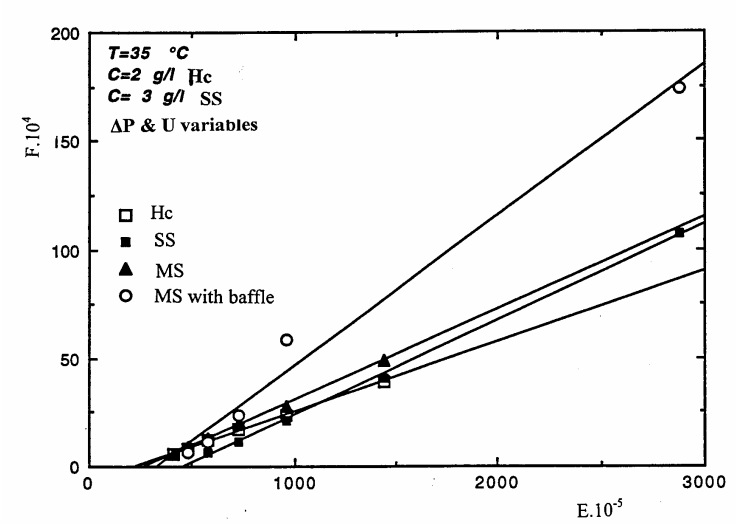

Figure 11: Dimensionless plots of steady state data

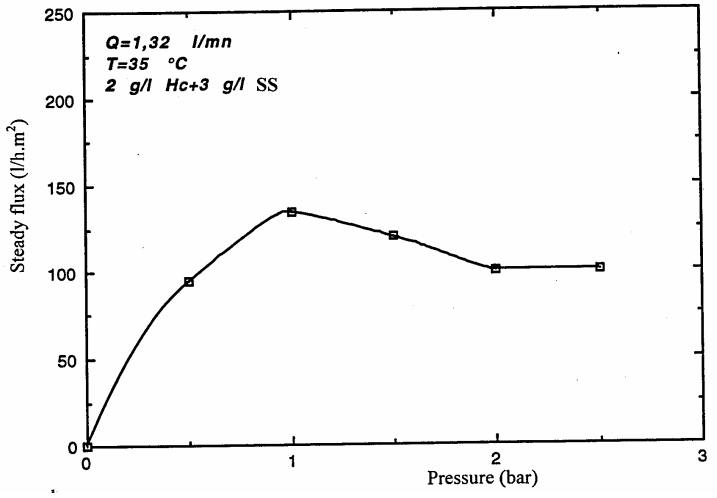

Figure 12: Steady flux against pressure with baffle

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4. CONCLUSIONS

1. The hydrocarbons agglomerate on the biological solids maximizing the flux when a stoichiometric ratio is reached
2. In presence of a helical baffle, the flux is increased to some 40 %. There is then a critical flux of 150 l/hm^2 at 0.5 bar
3. The flux curves can be modeled by a deposition process associated with a retroflux towards the bulk of the liquid phase
4. The transient and the limiting flux are satisfactorily quantified
5. Two dimensionless groups take into account all the experimental steady data and can give a basis for estimating the optimal parameters

ACKNOWLEDGEMENTS

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