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On an experimental method to measure critical flux in ultrafiltration

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Abstract

The following study presents an improvement of previous techniques to determine critical flux in ultrafiltration. The data treatment allows having accurate values of the critical flux and the rate of irreversibility of the created deposit on the membrane. Measures of critical flux were run with different hydrodynamic conditions and were in accordance with the expected results (critical flux increases with hydrodynamics). To confirm this method, the experiments were run with stable suspensions of PVC latex in water with different ionic strength to induce a change in stability. A significant difference was noticed in the measure of critical flux showing the sensibility of the method.

Keywords: Critical flux; Latex; Ultrafiltration; Experiment; Membrane; Colloid

1. Introduction

Improvement of membrane pressure-driven technologies allows one to use these kinds of techniques in a large number of industrial activities, for example, water treatment, production of paint and coating, biotechnology and many others.

However, nowadays, the major part of the running cost in membrane processes is linked to membrane fouling. This cost appears in two different ways: a direct one due to flux reduction (or an increase in energy to maintain the same flux) and an induced cost linked to the cleaning of membranes. According to the treated fluid, the cleaning will necessitate either a mechanical cleaning (back-

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washing) or chemical cleaning. Hydrodynamics of the system and the physical chemistry of the treated fluids rule this fouling; thus, adapting the filtration conditions to the processed fluid appears essential. It emerges that the critical flux, defined as the lowest flux that creates an irreversible deposit on the membrane, seems to be a key parameter in the control of membrane processes as it allows distinguishing two distinct zones, one where no deposit build-up appears on the membrane and thus does not need to be cleaned and another one for which cleaning will be necessary.

The theoretical prediction of critical flux of the main industrial solutions from physico-chemical properties is still impossible as the theory dealing with surface interactions cannot be applied to complex fluid. As it is obvious that the stability of solution is hardly controllable in filtration plants and is highly dependent on the preparation of the fluid, the development of material and of a systematic method to measure critical flux appears essential. Those procedures should be able ones in an industrial operation to choose the operating parameters in order to better control the fouling of membranes.

2. Background

2.1. Resistances to permeation

In filtration, the permeation flux is usually described as a function of the transmembrane pressure. It is necessary to define the various resistances opposite to the flux:

$$J = \frac{\Delta P - \Delta \pi}{\mu(R_m + R_c)} \quad (1)$$

Where ΔP is the transmembrane pressure, $\Delta \pi$ is the osmotic pressure opposite the apply pressure, μ is the viscosity of the permeate and R_m and R_c are the resistance of the membrane and of the deposit, respectively.

2.2. Critical flux

As soon as a separation of solute occurs, an accumulation of matter appears on the membrane. The critical flux J_{crit} [1] defines the permeate flux above which an irreversible deposit appears. The critical flux results in a force balance between drag forces and surface interaction in a mass boundary layer and then, depending on surface interactions, of the hydrodynamics and the position along the membrane. As the concentration in the boundary layer increases along the membrane, in crossflow filtration this critical flux appears where the conditions are the worst. Under given conditions for separation and with a low-pressure drop along the membrane, critical flux appears where the boundary layer is the thickest [2], that is, at the exit of the membrane channel.

Above the critical flux, the fouling phenomenon is self-regulated. An increase of pressure leading to a flux higher than the critical flux generates a growth in the deposit until a decrease in flux reaches its critical value. On the other hand, the limiting flux is the maximum flux that can be achieved at steady state in an operation; it corresponds to a value of flux for which the critical flux is reached at all points of the membrane surface.

3. Experimental

3.1. Materials

The ultrafiltration set-up is shown in Fig. 1. The permeate is measured with a balance (Adventurer Ohaus) with computer acquisition. The pressure is controlled by a current-to-pressure transducer (CPT, Rosemount accuracy: 0.02 bar) and regulated with a PID regulator. The acquisition can be run in two modes: an automatic one that detects stability of the flux (steady state) and a manual mode; the accuracy of the time measure is within 0.1 s. The temperature is controlled in the loop at 25°C with a cryostat having an accuracy of $\pm 0.5^\circ\text{C}$. Crossflow velocity is measured with a flowmeter (Endress-Hausser Promag A) with a precision of 3%.

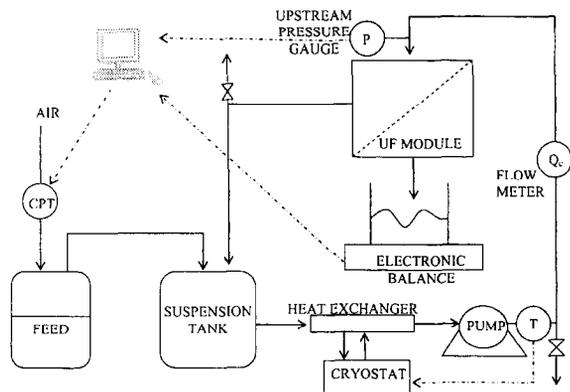


Fig. 1. Schematic of the experimental apparatus.

The ultrafiltration module contains one membrane with one inner skin (Carbosep tubular membrane, Orelis, Miribel, France). The active membrane layer is of $ZrO_2 TiO_2$ with a cut-off of 15 kDa. Latexes used in experimental studies are 100% rejected.

The total membrane surface is 0.0226 m^2 , and the hydraulic diameter is 6 mm. The flow rate can vary from $0.29 \text{ m}\cdot\text{s}^{-1}$ to $0.98 \text{ m}\cdot\text{s}^{-1}$. The associated Reynolds numbers are 1952 and 6506, respectively.

3.2. Methods

The standard filtration procedure proposed here is to alternate positive and negative pressure changes, as shown schematically in Fig. 1. Anytime the pressure is set to any new value, the

flux is monitored and the system waits until the flux stabilizes over time. A new pressure value can then be set. By comparing the steady-state flux obtained at steps 1 and 4 (in Fig. 2), one can deduce if a flux limitation observed in step 3 is due to an irreversible fouling or to reversible phenomena (polarization layer). For example, if the flux in step 4 is on point b, fouling is 100% irreversible, and, if the flux is on point a, fouling is totally reversible; therefore, a fraction of reversibility can be ascribed according to the flux value at step 4 (included on segment a–b).

Such a procedure makes possible the differentiation between reversible fouling (mainly due to osmotic pressure limitation) and a deposit all along a range of pressure and flux. This procedure is then an improvement of previous techniques developed for searching critical flux [3–5] as a decrease in pressure after each increasing pressure step allows determining fouling irreversibility.

3.3. Suspension

The latex used here is of PVC, stabilized with surfactant (from Atofina); its diameter is 124 nm with a mass fraction in the stock liquor of 0.41. For each experiment, the pH was measured at the beginning and at the end of the run on retentate and permeate. The pH of the solution ranges from 6.4 to 7.1, corresponding to an average zeta potential of -49 mV (Zetasizer 4 combined with a pH titrator, Malvern, Orsay, France) with the associated error of 5.8 mV.

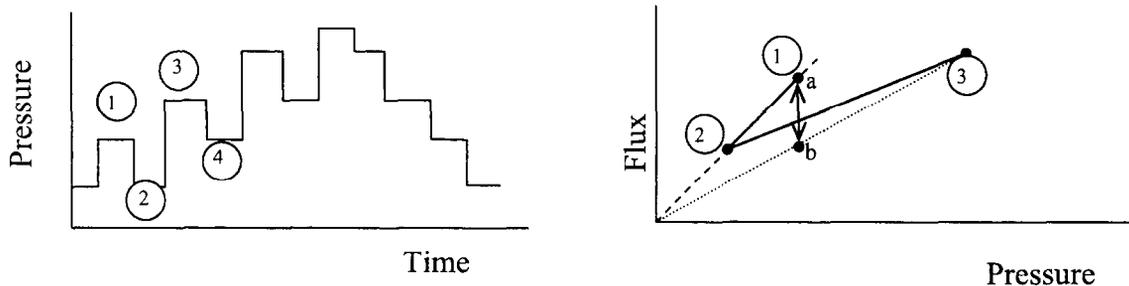


Fig. 2. Pressure vs. time, pressure step used to measure the critical flux, and corresponding flux vs. pressure, the flux of step 4 is included on the segment a-b.

The critical coagulation concentration is experimentally determined between 0.1 M (stable suspension) and 0.5 M (fast aggregation) of KCl. The latex solution is diluted in distilled water ($5 \mu\text{S}\cdot\text{cm}^{-1}$). Suspension was made without salt and with 10^{-2} M to have high and low repulsions, respectively, between particles without any aggregate in both cases.

4. Results and discussion

Different experiments were carried out within three different crossflow velocities: 0.29, 0.59 and $0.98 \text{ m}\cdot\text{s}^{-1}$ without salt, at 0.59 and $0.98 \text{ m}\cdot\text{s}^{-1}$ with KCl at 10^{-2} M. Results appear in terms of pressure vs. time and flux vs. time (Fig. 3), with details of the pressure step used during the filtration procedure.

Data are presented in Fig. 4 in terms of stationary flux (average on the 10 last values on each pressure step corresponding to 5 min) vs. pressure and compared with the previous water flux. A difference is observed between the initial flux of latex and the water flux at the same pressure.

As this difference was observed in all experiments, a results analysis was performed as a function of the initial permeability of the latex solution,

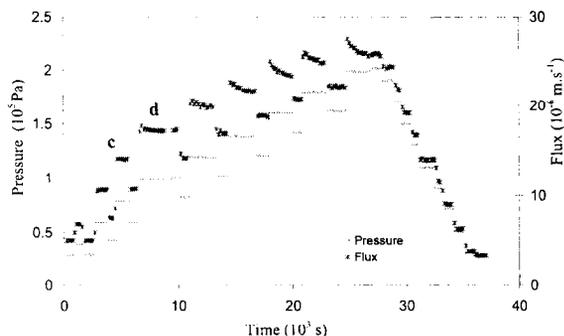


Fig. 3. Flux and pressure vs. time at a crossflow velocity of $0.98 \text{ m}\cdot\text{s}^{-1}$ with a PVC latex concentration of $7.1 \times 10^{-4} \text{ g}\cdot\text{L}^{-1}$ without salt. c and d represent the zone where the critical flux appears and are represented in the figures that follow.

and a new initial resistance (R_i) is included in Eq. (1) and is rewritten as follows:

$$J = \frac{\Delta P}{\mu(R_m + R_c + R_i)} \quad (2)$$

A hypothesis could attribute this decrease to the blocking of the widest pores in the first instant of the filtration.

A relevant representation for critical flux determination is presented in Fig. 5 and consists of a plot of $(R_c + R_i) / R_m$ as a function of the water flux. In comparison with Fig. 4, the critical flux appears to be much more readable on Fig. 5. The critical flux is then taken between two experimental points: here c and d, and an average is taken of the two fluxes J_{oc} and J_{od} . Furthermore, the resistance remains constant when the pressure is reduced. This irreversibility in resistance indicates that the osmotic pressure resistance contribution is negligible for the studied suspension.

Such experiments have been conducted for different operating conditions. In order to see the evolution and the effect of particle interactions on the critical flux, results are presented (Fig. 6)

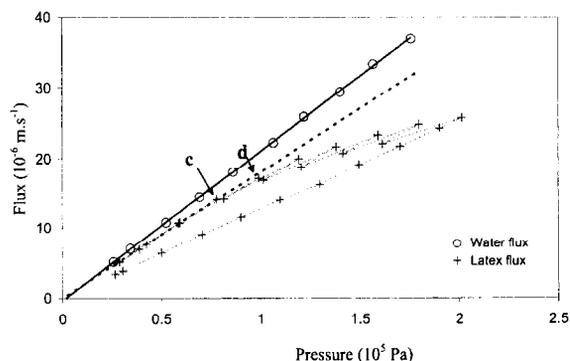


Fig. 4. Relationship between applied flux and transmembrane pressure plotted as flux vs. transmembrane pressure for the filtration of water (circle) and of PVC latex at $7.1 \times 10^{-4} \text{ g}\cdot\text{L}^{-1}$ (cross) without salt; the crossflow velocity is of $0.98 \text{ m}\cdot\text{s}^{-1}$ ($R_e = 6507$). The dotted line corresponds to the permeability measured on the first points of the filtration of latex; points c and d corresponds to the range of critical flux.

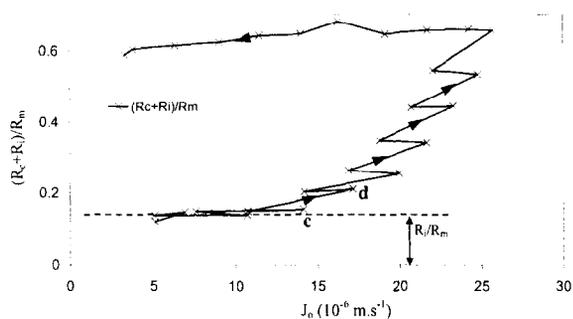


Fig. 5. Evolution of the resistance along the increased and decreased pressure steps; cross corresponds to $(R_c + R_i)/R_m$ vs. water flux J_0 ; c and d correspond to the zone of the critical flux.

in terms of critical flux vs. the crossflow velocities for the two different ionic strengths of the suspension.

The increase of critical flux is noticed with the increase of crossflow velocity. The critical flux at 0.98 m.s^{-1} is more than twice the value of critical flux at 0.29 m.s^{-1} as expected for the most stable solution. The solution at 10^{-2} M also shows an increase with hydrodynamics but is less important. The effect of salt is notable; the critical flux is smaller by 25% at 0.98 m.s^{-1} compared with the suspension without salt. That confirms the screening of charges of the latexes in solution due to the KCl ions and its effect on membrane fouling. To control the relevance of the critical flux, a manipulation of 8 h with subcritical flux [5] was run. Crossflow velocity was 100 L.h^{-1} and the concentration was $7.1 \times 10^{-4} \text{ g.L}^{-1}$; treated volume solution was 10 L. No reduction of flux was noticed during this experiment.

5. Conclusions

Here is presented an improvement of the previous apparatus and data treatment allowing accurate measures of critical flux. Indeed, the material presented here makes possible any easy systematic detection of critical flux. The automatic

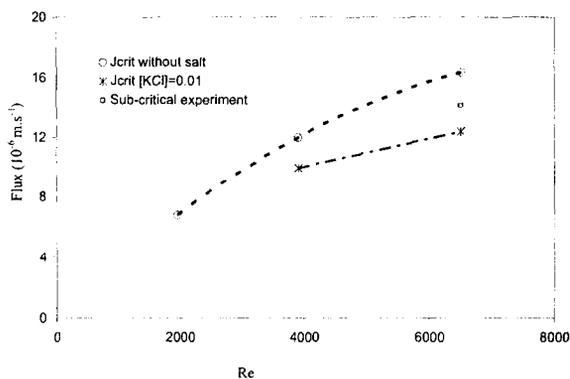


Fig. 6. Critical flux J_{crit} vs. the Reynolds number for the filtration of PVC latex with a concentration of $7.1 \times 10^{-4} \text{ g.L}^{-1}$ with and without KCl; the subcritical flux experiment was run without salt during 8 h without fouling.

detection of steady state allows one to optimize the time of measure of the critical flux. Furthermore, the associated method to analyze the data allows one to find a critical flux value and gives the fraction of deposit reversibility. The experiments run confirm the critical flux sensibility as a function of solution and hydrodynamic stability. As experiences were run on an industrial membrane with hydrodynamics and pressure that are close to industrial conditions, it can easily be transposable.

That opens areas in terms of choice of operating conditions (crossflow velocity and transmembrane pressure). The operating conditions can be precisely adjusted and controlled whenever the treated fluid changes and hence reduce running costs linked to fouling.

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