DEAD END FILTRATION OF NATURAL ORGANIC MATTER: EXPERIMENTAL EVIDENCE OF CRITICAL CONDITIONS

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Abstract

Development of membranes technologies led industrials and researchers to focus on the way to optimize filtration processes in terms of quality and costs of production. In this way, this paper presents a study about determination of low fouling operating conditions in dead-end ultrafiltration of natural organic matter which leads to the definition of sustainable conditions for filtration by limiting formation of irreversible layer. The reversibility of fouling is studied in respect to a break in the driving force and the effect of the duration of the break is underlined by comparing reversibility after an instantaneous rinsing and a 24 hours soaking. The existence of a critical filtered volume (below which the mass accumulation is reversible and above which a significant irreversible fouling exists) is experimentally demonstrated. Results show that it is possible to avoid the formation of irreversible fouling layer when operating parameters (the pair filtered volume and applied pressure) are suitably chosen.

1. Introduction

Separation by membrane is now used in a wide range of industrial applications. This rapid development lead researches to be focused on the optimisation of processes in term of quality and cost of production. This improvement implies a better understanding of fouling phenomena (inherent to the separation process) and ways to evaluate, anticipate and possibly control it.

In the filtration of natural surface water, there is a wide variety of components in terms of size and surface properties (charge, hydrophilic or hydrophobic interactions ..) as it contains as well soluble organic matter as particles or colloids. Fouling is the result of several contributions:

- the *concentration polarization phenomena*: during a filtration, accumulated particles remaining in a dispersed phase at the interface membrane/suspension or deposit/suspension provide a pressure in opposition to the separation force by the way of the osmotic pressure. This resistance is reversible by simply decreasing the driving force.
- the *cake or gel formation*: cohesive multilayer fouling can form on the membrane: when the concentration at the membrane reach a critical point, the particles become interlinked in irreversible deposit or gel presenting several degrees of compactness. This kind of fouling needs a back flush or an important shear stress to be removed.
- the *adsorption*: physico-chemical interactions between the various organic substances and the membrane can lead to irreversible fouling (reversibility can only be achieved by chemicals). This phenomenon is exacerbated by the local over concentration at the membrane inherent to the separation.
- the *internal fouling*: particles can be blocked because of shape properties or adsorbed in the pore of the membrane. This contribution of fouling is irreversible in regard to a decrease in the separation force and can be partly removed with a back flush.

The fouling and its irreversibility represents a limiting and really complex phenomena as it was found to be dependant on the membrane [1], solution characteristics [2] and operating parameters [3]. An essential key to improve separation processes is to be able to define simply and rapidly the operating parameters leading to sustainable operations where fouling consequences are limited to the minimum.

In this way, the concept of critical flux has been developed [4, 5] to describe low fouling conditions in cross-flow filtration (when a steady state is reached). This parameter, associated to a cross flow velocity, marks off the formation of irreversible multilayer fouling on the membrane surface. For dead-end filtration, operation continually in transient state, this description can not be directly applied. With the aim to depict the formation of a deposit in dead-end filtration, it was developed the idea of the existence of a critical accumulated mass below which irreversible layer deposition can be avoid [5], this study was run with spherical latex suspensions which led to consider only surface fouling with membrane pore size used.

The aim of this paper is to investigate the idea that it may be possible to avoid irreversible fouling formation in dead-end filtration, even if the suspension studied contains organic matters. Experiments are performed by rinsing membrane after filtration of different volume in order to quantify variation of fouling reversibility with filtered volume. Effects of pressure and break time on the fouling mechanisms are studied and analysed through the specific flux and the distribution in reversibility of fouling resistances.

## 2. Materials and methods

2.1. Feed suspensions

This study presents experiments run with natural surface water from the Yorkshire Albert Water Treatment Works.
This water presents a high organic content (9.0 mg l^{-1} of dissolved organic carbon, 42.5 m^{-1} of ultra-violet absorbance at 254 nm) and a low particle content (turbidity of 2.3 NTU), so fouling is expected to act mainly by the way of adsorption or internal fouling. The water was stored at a constant temperature of +4°C until use and brought to the room temperature before the experiment. The characteristics of the water were constant during the experiment campaign.

2.2. Experimental device

The filtration experiments were performed with a bench scale unit (fig. 1) using home made ultrafiltration flat sheet membranes allowing an average removal of 18 % of dissolved organic carbon. The rig was composed of a 0.2 l filtration cell (model KST 47, Advantec MFS Inc. Dublin, USA) providing a surface of 12.5 cm^2. The pressure was kept constant via a 50 l buffer tank supplied by compressed air.
The permeate was collected in a beaker placed on an electronic balance and the filtrate mass recorded via the software RegKey with a 5 s frequency. The permeate temperature was measured at the end of the experiment to take into account the possible variation in viscosity.
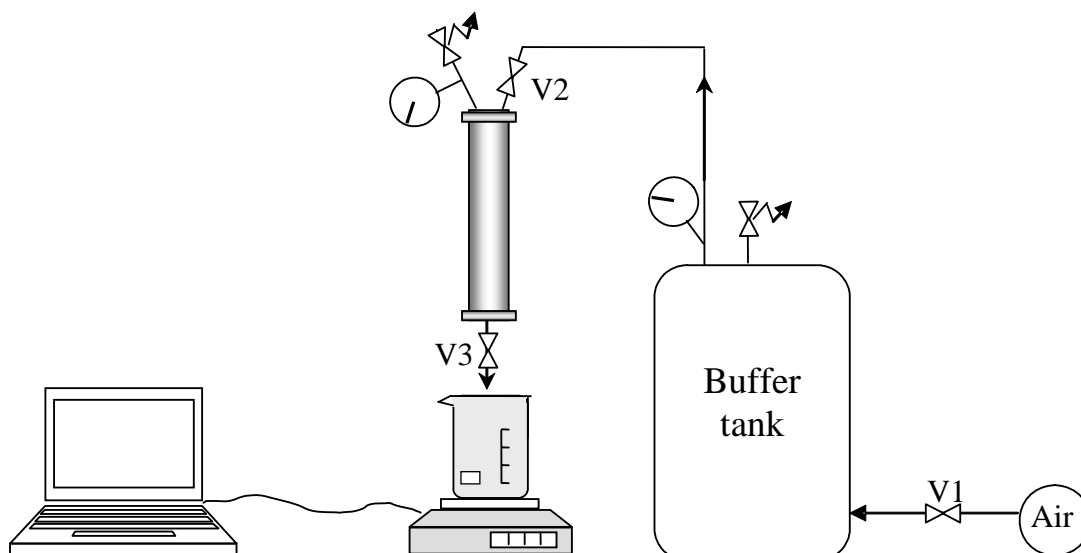
2.3. Processing

The identification of the formation of an irreversible layer and its sensibility to time was done using three steps (fig. 2):

1) first the <u>filtration</u> period leading to the concentration of the suspension at the membrane surface: the filtration cell is filled with the studied suspension, the required pressure (0.6 and 1.0 b) is stabilised via the valve V1. The filtration starts when opening V3 and its duration is defined by the mass of permeate collected (between 50 and 200 ml, corresponding to a range between 40 and 160 l m^{-2}). The pressure is relaxed and the permeate valve V3 closed. This filtration period leads to the formation of the total fouling resistance R_{t1}, defined as the difference between the total resistance and the membrane resistance.

2) a <u>rinsing</u> phase to determine the instantaneous reversibility of fouling: the remaining suspension is removed and the filtration cell is carefully filled with ultrapure water and gently manually stirred; this step was repeated three times, to ensure the removal of the dispersed phase, before measuring the clean water flux of the fouled membrane, which allows determination of resistance of the remaining deposit R_{c2}.

3) a <u>soaking</u> phase to evaluate the effect of time on the compact layer: after the rinsing phase, the membrane is delicately removed and stored during 24 hours in 400 ml of ultrapure water at +4°C. Then, the water flux is measured to determine the residual cake resistance R_{c3}.
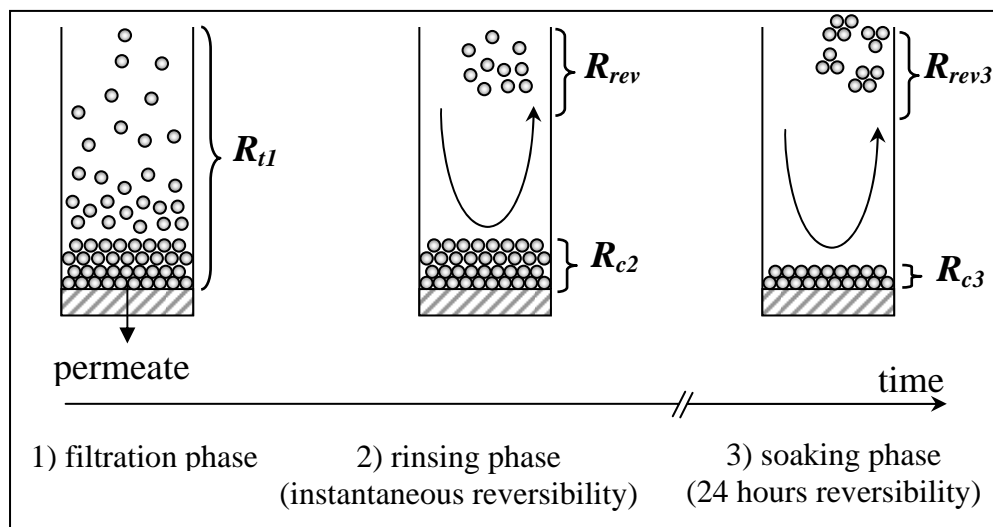
Fig. 2 : reversibility determination procedure

According to Darcy's law, the permeate flux *J* can be access using eq. 1:

$$J = \frac{\Delta P}{\mu(T) \cdot R} \qquad (1)$$

where μ is the viscosity at the experiment temperature T, ΔP the transmembrane pressure and R is the global hydraulic resistance which can be split up in different contributions, according steps defined previously:

$$R = R_m + R_{t1} = R_m + R_{rev2} + R_{c2} = R_m + R_{rev2} + R_{rev3} + R_{c3} \qquad (2)$$

where R_m is the clean membrane resistance whereas others resistances can be defined as:

R_{t1} total fouling resistance after filtration

R_{c2} deposit resistance remaining after the rinsing phase

R_{rev2} resistance removed by the rinsing step

R_{c3} deposit resistance remaining after the soaking phase

R_{rev3} resistance removed by the soaking step

as schematically described in fig. 2.

3. Experimental results

Fouling reversibility was measured by a sequence of experiments as described in the previous section. Two filtration pressures with several filtered volumes before the rinsing phase were studied. The experimental results are presented in term of normalized flux during the filtration and after the different "cleaning" phases in figure 3. The three steps of the protocol bring each some complementary information:

- fouling during the filtration is more pronounced for the higher pressure; indeed, for the same filtered volume (120 l m^{-2}), the time needed for the filtration is not inversely proportional to the operating pressure as it was 23 and 33 min for 1.0 and 0.6 bar respectively. The normalized flux resulting is always higher for the lower pressure.

- the rinsing phase makes it possible to evaluate the fraction of fouling which is instantaneously reversible; assuming that this operation do not provoke any significant shearing at the membrane surface, the reversible contribution can then be attributed to the matter presents in a dispersed phase, whereas irreversible resistance is chargeable to a multilayer cohesive deposit.

- the soaking phase put in light the effect of time on the cohesion of the compact layer: the 24 hours delay leads either to the relaxation of the gel (or deposit) or to the slow desorption of solutes possibly adsorbed on or in the membrane. The effect of pressure on the compactness of the fouling is demonstrated as for the low pressure, the initial flux can be almost recovered (92 %) when filtering 120 l m^{-2} whereas for 1 bar, the final flux is only 75% of the clean membrane flux.
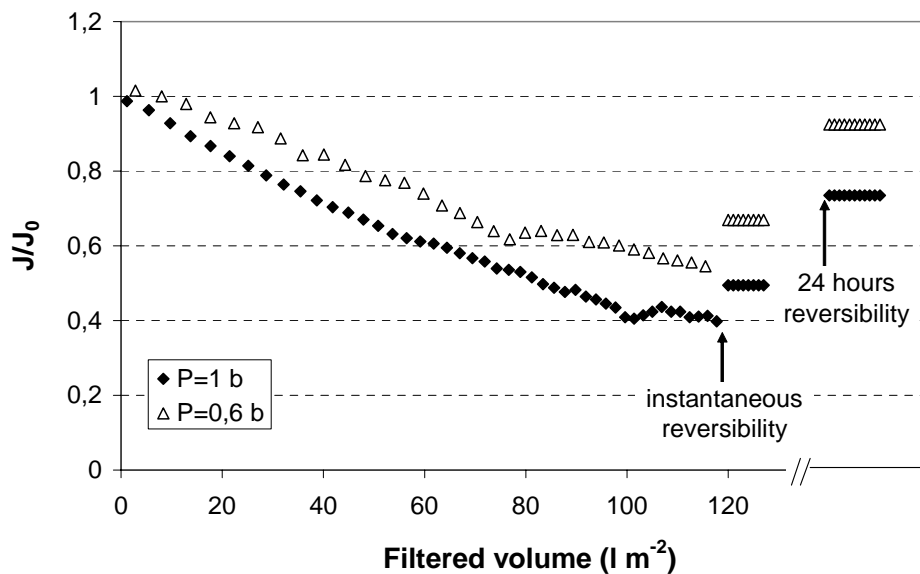
Fig. 3 : evolution of normalized flux versus filtered volume – effect of pressure – 120 l m^{-2}

The results of the whole experimental campaign (two pressures with 4 filtered volumes each) are summarized in table 1 and 2 for 1.0 and 0.6 bar respectively, in terms of resistance defined for each step of the procedure as illustrated in fig. 2.

Vf (l m^{-2})	Phase 1	Phase 2		Phase 3	
	Rt (10^{12} m^{-1})	Rrev2 (10^{12} m^{-1})	Rc2 (10^{12} m^{-1})	Rrev3 (10^{12} m^{-1})	Rc3 (10^{12} m^{-1})
40	0.26	0.26	0	0	0
80	0.53	0.30	0.23	0.19	0.04
120	1.00	0.34	0.66	0.43	0.23
160	1.84	0.42	1.43	0.87	0.56

Table 1 : Depict of fouling resistance versus the filtered volume - P=1.0 bar

Vf (l m^{-2})	Phase 1	Phase 2		Phase 3	
	Rt (10^{12} m^{-1})	Rrev2 (10^{12} m^{-1})	Rc2 (10^{12} m^{-1})	Rrev3 (10^{12} m^{-1})	Rc3 (10^{12} m^{-1})
40	0.16	0.16	0	0	0
80	0.45	0.30	0.15	0.11	0.04
120	0.64	0.32	0.32	0.27	0.05
160	1.14	0.54	0.60	0.49	0.11

Table 2 : Depict of fouling resistance versus the filtered volume - P=0.6 bar

One can deduce the part of reversible and residual resistance after each operation. The evolution of the residual resistance with the filtered volume gives information about non fouling conditions.

4. Discussion

4.1. Critical filtered volume (CFV)

Fouling hydraulic resistances are plotted versus the filtered volume during phase 1 in fig. 4 a) and 4 b) for 0.6 and 1.0 bar respectively. In this figure appears the total hydraulic resistance, R_{t1}, the residual resistance after the rinsing, R_{c2}, and the soaking, R_{c3}. Such a graph allows then to split the different fouling contributions : a difference of colour is used to easily

distinguish these contributions in term of instantaneously reversible (clear part), reversible after one days soaking (grey) and totally irreversible (dark part) fouling for a specified filtered volume.

It can be notice that the instantaneously reversible resistance is almost constant, whereas when the filtered volume becomes more important, the parts of partially and totally irreversible fouling increase appreciably. This can be an essential point to run filtration operation as it opens the possibility to work with very low irreversible fouling conditions. As depict in fig. 4b) below a filtered volume of $40 \, l \, m^{-2}$ fouling is totally reversible, between 40 and 80 $l \, m^{-2}$ weakly reversible fouling and a significant irreversible fouling for filtered volume superior to 80 $l \, m^{-2}$. It can be filtered up to 40 $l \, m^{-2}$ without forming any irreversible layer; this volume will be defined as the critical filtered volume as it represents the maximum volume before which no irreversible fouling occurs (by analogy with the concept of the critical flux which is defined as a flux below which no irreversible fouling occurs).

This draw presents the same trend whatever the pressure studied even if the totally irreversible fouling is much more important for the 1.0 bar operation.

a)   b)
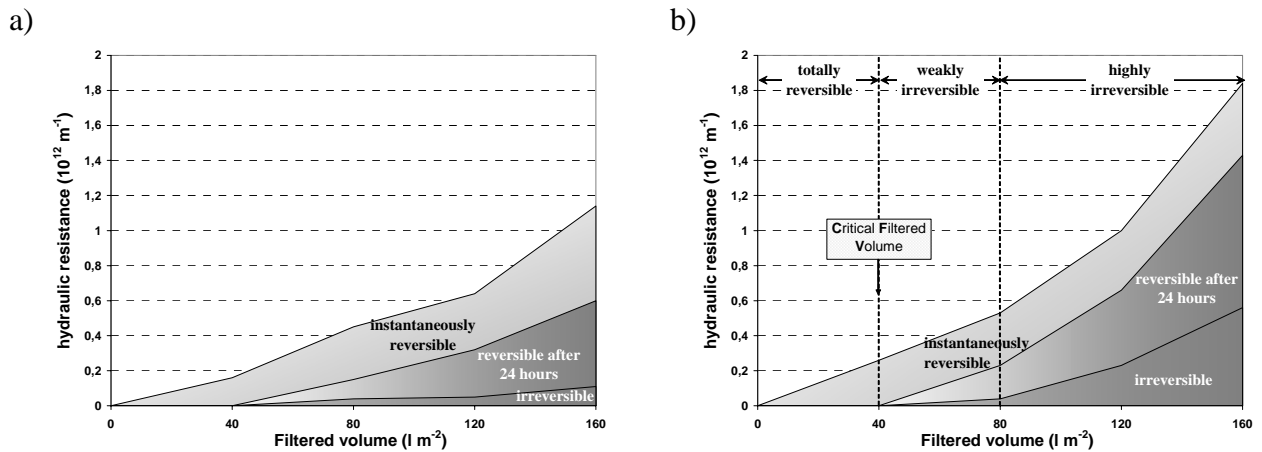
Fig. 4: contribution of resistance according to the filtered volume. a) P=0.6 bar – b) P=1.0 bar.

Those results put in light that it is possible to avoid or at least to greatly limit irreversible deposition in dead-end filtration of natural organic matter. Indeed, even if adsorption is likely to occur, a suitable frequency of devolution operation allows maintaining the constituents at the membrane surface at a concentration lower to the one leading to irreversible multilayer fouling.

4.2. Time and pressure dependence of reversibility

The influence of time and pressure in reversibility is illustrated in Fig. 5 for a filtered volume of 120 $l \, m^{-2}$ where degree of reversibility is defined as the percentage of reversible fouling over the total fouling
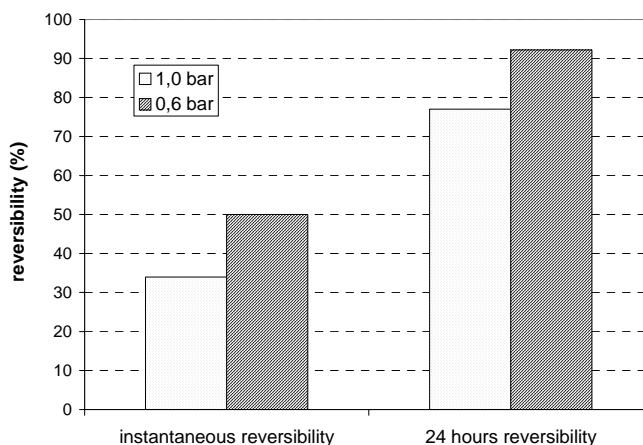
Fig. 5: effect of time and operating pressure on reversibility – filtered volume = 120 l m^{-2}.

This representation put in light that a 24 hours relaxation before measuring the residual resistance allows to recover a well greater part of the flux: for the 0.6 bar operation, the reversibility after 24 hours is more than 90% whereas it starts to 47 % when measured just after the filtration phase. One can guess that time allows the relaxation or a slow desorption of fouling layer on the membrane allowing its removal by a rinsing.
Furthermore, it can be noted the significant effect of pressure on long term irreversibility: the experiment under 1 bar leads to 31% of irreversibility for the higher filtered volume even after 24 hours. That last point underline the effect of pressure on the cohesion of the fouling formed during the filtration period.

4.3. Critical set: pressure –filtered volume

Figures 6 a) and 6 b) present the degree of reversibility as a function of both the applied pressure (x axis) and the filtered volume (y axis). Isocurves in these figures correspond to iso-degree of reversibility: shading becoming darker when the degree of reversibility decreases. These isocurves result of the interpolation of data of reversibility (table 1 and 2) which are given in white boxes. Figure 6A) and 6 b) are relative to instantaneous and 1 days reversibility respectively.
It can be clearly seen by comparing figure 6 a) and 6 b) that the degree of reversibility depends on fouling rest time before rinsing. Furthermore, it can be noted that low degree of reversibility always correspond to high applied pressure and important filtered volume. This last point means that the criticality (in term of fouling reversibility) seems to be correlated to a pair of operating conditions: applied pressure and filtered volume. The higher is the pressure the lower is the critical filtered volume. Such a critical pair of operating conditions has already been underlined [5] for latex suspension and further experimental evidence concerning its existence have been put in light for clays particles in dead end filtration mode with a constant flux [6].
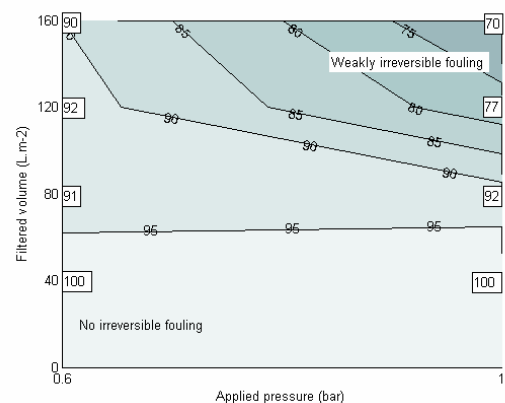
a)
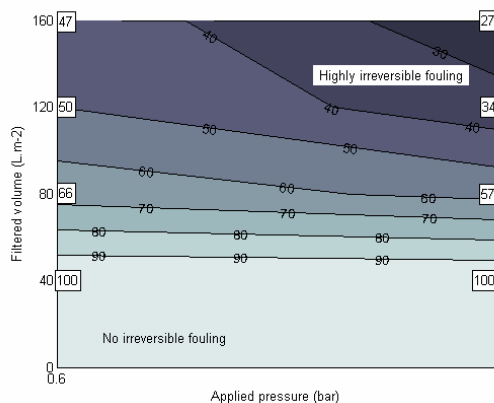
b)

Figure 6: Degree of reversibility (in percentage) as a function of the applied pressure (x axis) and the filtered volume (y axis) when considering instantaneous reversibility a) and reversibility after 24 h b). Values of reversibility in white boxes corresponds to the experiments summarized in tables 1 and 2.

5. Conclusion

The study presented here shows the possibility to work with low fouling conditions in dead-end filtration even when treating natural surface water: indeed, it clearly appeared that for a given pressure, it exists an associated critical filtered volume below which the whole part of additional hydraulic resistance is reversible by rinsing whereas above this critical filtered volume a significant part of fouling is irreversible.

The effect of the rest time before rinsing on the irreversibility was demonstrated. This increase of reversibility could be the consequence of the relaxation or slow desorption of fouling layer during the 24 hours soaking. This recovering in flux was found to be strongly linked to the operating pressure: the relaxation being less pronounced when filtration were realised with more important pressure surely due to the formation of more compact fouling layers.

The critical fouling conditions, defining a critical change in fouling irreversibility, seems relative to the pair of operating conditions: applied pressure/filtered volume. A significant fouling irreversibility appears for higher filtered volume when filtering with a lower applied pressure.

Acknowledgement

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