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Dead-end filtration of natural organic matter: experimental evidence of critical conditions

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Abstract

The development of membrane technology has reached a state whereby operational optimisation is becoming the major issue to both researchers and industrial operators. A key focus is towards sustainable operation where fouling is limited and cleaning is greatly reduced. The paper presents an example of such an approach for the filtration of natural organic matter (NOM) in a dead-end ultrafiltration cell. Sustainable operation has been assessed in relation to the application of a cessation period followed by a gentle rinse. The work demonstrates the existence of a critical filtered volume below which the mass accumulated at the membrane's surface is reversible and above which significant fouling occurs. Further, appropriate selection of operating conditions (filtered volume and applied pressure) makes it possible to avoid the formation of an irreversible fouling layer.

Keywords: Fouling; NOM; Critical flux; Critical filtered volume; Irreversibility

1. Introduction

Industrial use of membrane processes for physical separation has now become an established process option. Inherent to all membrane processes is a reduction in productivity due to the accumulation of material in and on the membrane's surface, normally termed "fouling". In the filtration of natural surface water, there is a wide variety of components (soluble organic matter,

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particles, colloids) leading to heterogeneity in terms of size and surface properties (charge, hydrophilic or hydrophobic interactions). Consequently, fouling can occur through a number of mechanisms:

• concentration polarization phenomena: during filtration, accumulated particles remaining in the dispersed phase at either the membrane/suspension or deposit/suspension interface provide a pressure in opposition to the separation force in terms of osmotic pressure. This

resistance is reversible by simply decreasing the driving force.

- cake or gel formation: cohesive multilayer fouling can form when the concentration at the membrane reaches a critical point. The particles become interlinked in an irreversible deposit or gel presenting several degrees of compactness. This kind of fouling needs a back flush or a significant shear stress to be reversed.
- adsorption: physicochemical interactions between the various organic substances and the membrane can lead to irreversible fouling. This phenomenon is exacerbated by high local concentrations at the membrane's surface.
- internal fouling: particles can block internal pores due to differences in the shape of the foulant material or adsorption. This contribution of fouling is irreversible in regard to a decrease in the separation force and can be partly removed with a back flush.

Studies in the literature have shown fouling and its irreversibility to be a complex phenomenon which is dependent on the membrane [1], solution characteristics [2] and operating parameters [3]. Improvement in such separation processes requires rapid and straightforward identification of operating conditions that lead to a sustainable process.

A classic example of this is the concept of critical flux, which has been developed [4,5] to describe low fouling conditions in cross-flow filtration (when a steady state is reached). More recently the concept has been refined into three separate concepts described as critical, transitional and sustainable flux. In the current study the most appropriate refinement relates to sustainable flux which is defined as a flux policy in which fouling is minimised and maintained in a pseudo-steady state. The flux policy relates to whatever combination of flux rate, cross flow rate and cleaning regime is required to generate a stabilised operation. However defined, the para-

meter refers to the point prior to the onset of the irreversible multilayer fouling on the membrane's surface. For dead-end filtration, operating continually in a transient state, this description cannot be directly applied. Instead the concept of a critical accumulated mass is considered below where an irreversible layer deposition can be avoided [6].

The aim was 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 material. Experiments were performed by rinsing the membrane after filtration of different volumes in order to quantify variation of fouling reversibility with filtered volume. Effects of pressure and soaking on the fouling mechanisms were studied and analysed through the specific flux and the distribution in reversibility of fouling resistances.

2. Materials and methods

2.1. Feed suspensions

The current investigation was conducted on real raw water from a water treatment works in the north of England. The water is characterised as high DOC (9 mg L^{-1}), high UV absorption (42.5 m^{-1} at 254 nm) and low turbidity (2.3 NTU). Consequently, the main fouling mechanism was expected to be adsorption based. The water was stored at a constant temperature of +4°C and brought to room temperature before the experiment. The characteristics of the water were constant during the experiments.

2.2. Experimental device

The filtration experiments were performed with a bench-scale unit (Fig. 1) using ultrafiltration flat-sheet membranes provided by Aquasource (Toulouse, France) allowing an average removal of 18% of DOC. The rig was composed of a 0.2 L filtration cell (model KST 47, Advantec
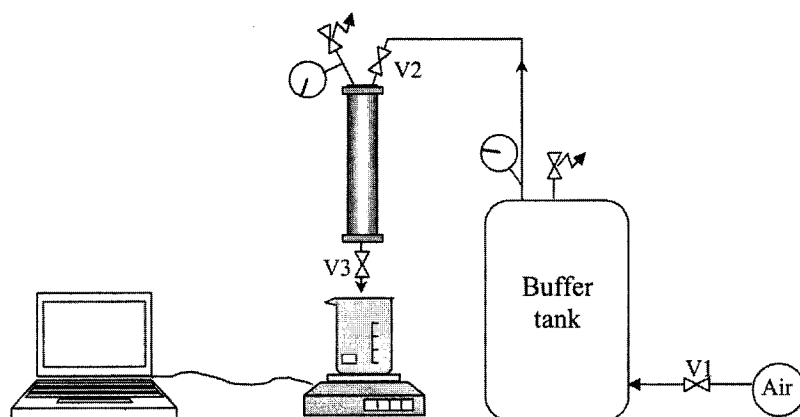
Fig. 1. Schematic of the filtration bench scale unit.

MFS, Dublin, USA) providing a surface of 12.5 cm². 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 evolution as a function of time were investigated in a three-step procedure (Fig. 2):

- Step 1, the filtration period leading to the concentration of the suspension at the membrane surface: the filtration cell was filled with the studied suspension, the required pressure (0.6 and 1.0 bar) was stabilised via the valve V1. The filtration was started by opening V3 and its duration was defined in terms of the mass of permeate collected (between 50 and 200 ml, corresponding to a range between 40 and 160 L m⁻²). The pressure is then relaxed and the permeate valve V3 closed. This filtration period leads to the formation of the total fouling resistance R_{f1}, defined as the difference between the total resistance and the membrane resistance.

- Step 2, a rinsing phase to determine the instantaneous reversibility of fouling: the remaining suspension was removed and the filtration cell was 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}.

- Step 3, a soaking phase to evaluate the effect of time on the compact layer: after the rinsing phase, the membrane was delicately removed and stored during 24 h in 400 ml of ultrapure water at +4°C. The water flux was then measured to determine the residual cake resistance R_{c3}.

According to Darcy's law, the permeate flux J can be accessed using Eq. (1):

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

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

$$R = R_m + R_{f1} = R_m + R_{rev2} + R_{c2}$$
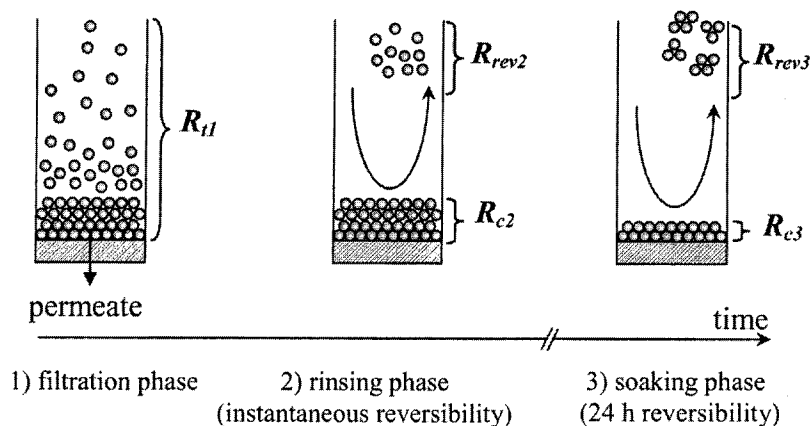$$= R_m + R_{rev2} + R_{rev3} + R_{c3} \tag{2}$$
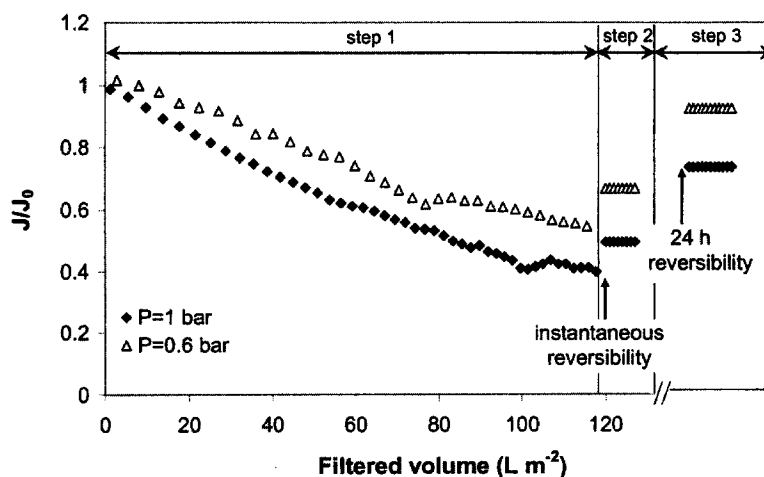
Fig. 2. Reversibility determination procedure.

Fig. 3. Evolution of normalized flux vs. filtered volume — effect of pressure — 120 L m^{-2}.

where R_m is the clean membrane resistance and others resistances can be defined as: R_{f1}, 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; and R_{rev3}, resistance removed by the soaking step — as schematically described in Fig. 2.

3. Results

The experimental results are presented in terms of normalized flux (Fig. 3). A comparison of the flux profiles during the filtration phase revealed that operation at higher pressures led to an increase in fouling. For instance, in the case of a total filtered volume of 120 L m^{-2}, the time required for filtration increased from 23 to 33 min for operating pressures of 1.0 and 0.6 bar respectively. Consequently, the normalised resulting flux is always higher for the lower operating pressure. Rinsing of the membrane led to a recovery of flux at all applied pressures and filtered volume (Table 1). Soaking of the membrane for 24 h further reduced the resistance to filtration although the degree of recoverability appeared to be

Table 1
Fouling resistance vs. the filtered volume ($P = 1.0$ bar)

V_f (L m^{-2})	Step 1	Step 2		Step 3	
	R_{f1} (10^{12} m^{-1})	R_{rev2} (10^{12} m^{-1})	R_{c2} (10^{12} m^{-1})	R_{rev3} (10^{12} m^{-1})	R_{c3} (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 2
Fouling resistance vs. the filtered volume ($P = 0.6$ bar)

V_f (L m^{-2})	Step 1	Step 2		Step 3	
	R_{f1} (10^{12} m^{-1})	R_{rev2} (10^{12} m^{-1})	R_{c2} (10^{12} m^{-1})	R_{rev3} (10^{12} m^{-1})	R_{c3} (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

pressure related. For instance, at an applied flux rate of 120 L m^{-2}, the initial flux was almost completely recovered (92%) at 0.6 bar compared to only 75% at 1.0 bar.

A comparison of the different resistances measured according to the outline protocol is given in Tables 1 and 2.

4. Discussion

4.1. Critical filtered volume (CFV)

Assessment of the hydraulic resistances as a function of filtered volume during Step 1 revealed that the instantaneously reversible resistance is relatively constant whereas, when the filtered volume becomes progressively more important, the part of partially and totally irreversible fouling increases appreciably (Fig. 4). For example, in the case of the 1 bar experiments, fouling is totally reversible below a filtered volume of 40 L m^{-2}, weakly reversible between

40 and 80 L m^{-2}, and significantly irreversible when the filtered volume exceeds 80 L m^{-2} (Fig. 4b). Consequently, a CFV can be defined as the point beyond which irreversible fouling occurs, i.e., as the volume corresponding to the concentration at the membrane's surface leading either to adsorption phenomena or to aggregation of particles. Such an approach is analogous with the concept of critical flux commonly used in cross flow membrane filtration. The same overall trend is observed at both pressures with a critical volume identified between 40 and 80 L m^{-2}. However, differences were observed in terms of the total irreversible resistance. To illustrate, as a filtered volume of 160 L m^{-2} the total resistance was 0.11×10^{12} to 0.56×10^{12} m^{-1} in the case of filtration at operating pressures of 0.6 to 1.0 bar, respectively.

The results demonstrate that it is possible to avoid — or at least to greatly limit — irreversible deposition in dead-end filtration of NOM. Further, intermittent dilution to reduce the
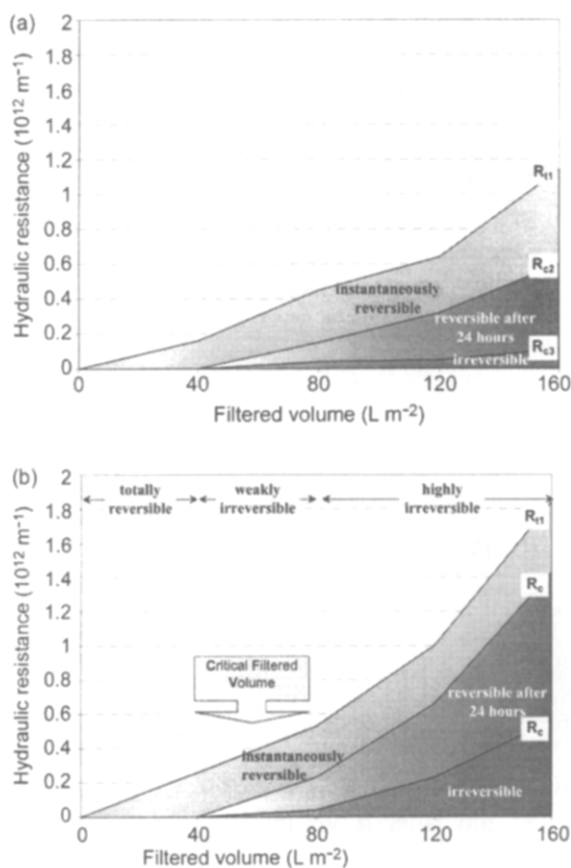
Fig. 4. Contribution of resistance R_{f1}, R_{c2} and R_{c3} according to the filtered volume. (a) $P = 0.6$ bar; (b) $P = 1.0$ bar. Clear part: instantaneous reversible; grey part: reversible after 1 day of soaking; dark part: totally irreversible.

Fig. 5. Effect of time and operating pressure on reversibility — filtered volume = 120 L m^{-2}.

concentration of the material at the membrane's surface to below the level which produces irreversible multilayer fouling, should prolong the operational cycle of the membrane.

4.2. Time and pressure dependence of reversibility

A consistent trend was observed with regard to the influence of time and pressure on the reversibility such that the degree of recoverability was enhanced when a prolonged relaxation period was applied. To illustrate (Fig. 5), in the case of
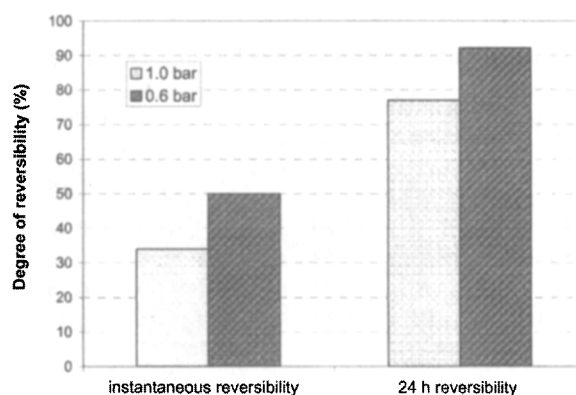
the 0.6 bar experiment, the reversibility after 24 h is more than 90% compared to 47% when measured just after the filtration phase. Furthermore, the impact of relaxation appears to be pressure sensitive as demonstrated by the fact that during the 1 bar experiments the flux recovery only reached 31% and 76% immediately after filtration and 24 h later, respectively. It is possible that this represents a propensity for slow desorption of adsorbed species or gel or a deposited layer relaxation which displays a pressure-sensitive attribute.

4.3. Critical combination of parameters: PFV

Previous investigation into critical fouling during dead-end filtration has highlighted the importance of considering the combination of operating conditions (flux and accumulated mass) when filtering latex solutions [6]. Further experimental evidence concerning the existence of a critical combination of parameters has been highlighted for clays particles in the dead-end filtration mode with a constant flux [7]. Incorporating such an approach into the current investigation enables the degree of reversibility to be described by the combination of applied pressure (x-axis) and filtered volume (y-axis) (Fig. 6). Iso-curves
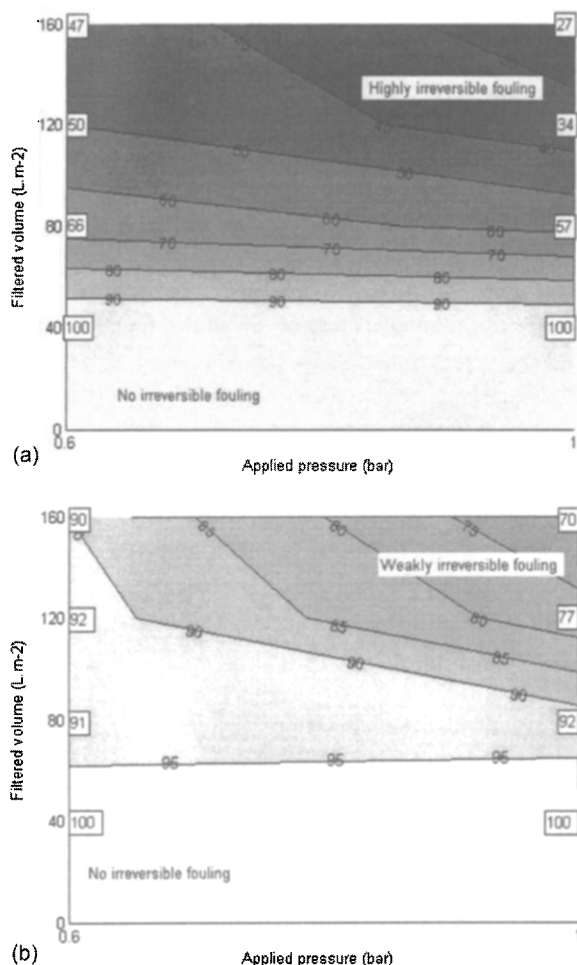
Fig. 6. Degree of reversibility (in percentage) as a function of the applied pressure (x axis) and the filtered volume (y axis) when considering instantaneous reversibility (a) and reversibility after 24 h (b). Values of reversibility in white boxes correspond to the experiments summarized in Tables 1 and 2.

can be drawn, which connect the point of the same level of reversibility. The iso-curves result from the interpolation of the reversibility data outlined in Tables 1 and 2 such that plots related to highly reversible (clearest parts) and irreversible (darkest parts) fouling are shown. A comparison of the graphs indicates that the degree of reversibility depends on the rest time before rinsing. Furthermore, the low degree of reversi-

bility always corresponds to high applied pressures and filtered volume. Interestingly, this suggests that the criticality (in terms of fouling reversibility) is correlated to a pair of operating conditions: applied pressure and filtered volume. High pressures result in low critical filtered volumes.

5. Conclusions

The results indicate that for a given pressure there exists an associated critical filtered volume, below which fouling is reversible by rinsing whereas above this critical filtered volume a significant part of fouling is irreversible. The effect of the relaxation time before rinsing on the irreversibility was demonstrated to increase the degree of reversibility attainable. The recovery in flux was found to be strongly linked to the operating pressure. The critical fouling conditions, defining a critical change in fouling irreversibility, seem to relate to the combination of operating conditions: applied pressure/filtered volume.

Acknowledgement

References

[1] J. Cho, G. Amy and J. Pellegrino, Membrane filtration of natural organic matter: initial comparison of rejection and flux decline characteristics with ultrafiltration and nanofiltration membranes. Water Res., 33 (1999) 2517–2526.

[2] K.L. Jones and C.R. O'Melia, Ultrafiltration of protein and humic substances: effect of solution chemistry on fouling and flux decline. J. Membr. Sci., 193 (2001) 163–173.

[3] B. Espinasse, P. Bacchin and P. Aimar, On an experimental method to mesure critical flux in ultrafiltration. Desalination, 146 (2002) 91–96.

[4] R.W. Field, D. Wu, J.A. Howell and B.B. Gupta, Critical flux concept for microfiltration fouling. J. Membr. Sci., 100 (1995) 259–272.

[5] P. Bacchin, P. Aimar and V. Sanchez, Model for colloidal fouling of membranes. AIChE J., 41 (1995) 368–376.

[6] P. Harmant and P. Aimar, Coagulation of colloids retained by porous wall. AIChE J., 42 (1996) 3523–3532.

[7] Y. Bessiere, P. Bacchin and N. Abidine, Low fouling conditions in dead-end filtration: evidence for a critical filtered volume and interpretation using critical osmotic pressure. Submitted for publication.