RETENTION IN BACKFLUSHED
CROSS-FLOW MICROFILTRATION

Jiří CAKL[1] and Ivo BAUER
Department of Chemical Engineering, University of Pardubice,
CZ-532 10 Pardubice

Crossflow microfiltration with rapid membrane backflushing has been investigated to quantify and optimize the effects of backflushing on the solute retention under varying operating conditions. Experiments were performed on asymmetric, multilayered, ceramic membranes with the mean pore diameter of active layer equal to 0.1 μm. The feeds were the commercial emulsifier stabilized metal-working oil emulsion and the aqueous solutions of the anionic emulsifier itself. The basic mechanism which affects the solute retention has been found and described. In addition, starting theoretical relationships describing the process are presented and discussed. The results demonstrate that rapid membrane backflushing is a useful tool for increasing the emulsifier transmission.

---

[1] To whom correspondence should be addressed.

Introduction

Membrane microfiltration with ceramic membranes is a promising technique for the removal of various macromolecular compounds, emulsions, and particulates present in process streams as well as in wastewaters. The process can be exploited either to concentrate dispersed matter up to contents of 20 to 70% vol. or to separate some active components (e.g. alkalis, detergents, and proteins) from the dispersed phase. This enables a reduction of the cost associated with the consequent processes and, in some cases, recyclisation of process water and/or a part of the active components. However, performance limitations may be encountered during the microfiltration due to the well-documented phenomenon of concentration polarization and/or membrane fouling [1,2]. Thus, for successful operation of the microfiltration unit, these must be minimized by choosing a suitable membrane and establishing proper operating conditions.

The backflushing process represents an efficient approach to minimizing both the concentration polarization and fouling problem in microfiltration systems. The process is carried out by periodic reversing the direction of flow of the permeate. This is achieved by applying pressure on the permeate side of the membrane. The clear permeate is then forced in reverse direction through the membrane, thereby lifting off the boundary layer and washing it out of the membrane surface. Within each backflushing cycle the flux starts to decline until a backpulse is imposed to restore the flux. The reverse direction of the backpulse is reflected in the negative flux. Although backflushing decreases the effective operating time and gives a loss of permeate back to the feed stream, it was reported in literature, e.g. [3–11,13,14] that the average flux per cycle may be much higher than that in the long-time flux without backflushing.

Very little has been published on the process selectivity although the variations of the concentration at the membrane surface should alter the potential for pulsing to change not only permeate flux but also the observed retention. Most of the experiments reported in the literature were carried out at the conditions of complete rejection of the particles or solute, e.g. [4–6,8,10,13]. Nevertheless, there have been a few studies that considered backflushing using feeds containing mixtures (mainly proteins with other matrices) with partial transmission of a component through the membrane used [9,11,13,16]. They concluded that boundary layer removal during permeate backflushing led to improved transmission and recovery of protein products. It was also documented that rapid backpulsing had greater impact on solute retention than slower backpulsing because the boundary layer was removed from the membrane before it had been fully formed or compacted.

Further work is needed to quantify and optimize the effects of backflushing on the solute retention under varying conditions. Thus the purpose of this work was to choose an experimental system and to obtain experimental data of backflushing

under various operating conditions with the goal of finding the basic operative mechanism which affects the solute retention. In addition, starting theoretical relationships of the process are presented and discussed.

Theory

The average permeate flux, J_{AVG}, during the pulse period (one cycle) can be expressed [4] as

$$J_{AVG} = \frac{\int_0^{t_F} J_F(t)\,dt - \int_{t_F}^{t_F+t_R} J_R(t)\,dt}{t_F + t_R} \tag{1}$$

where J is permeate flux and t is time; index F refers to the forward filtration period while index R refers to the reverse flow period. Similarly the average permeate solute concentration $(C_P)_{AVG}$, during the pulse period can written as

$$(C_P)_{AVG} = \frac{\int_0^{t_F} J_F(t)(C_P)_F(t)\,dt - \int_{t_F}^{t_F+t_R} J_R(t)(C_P)_F\,dt}{J_{AVG}(t_F + t_R)} \tag{2}$$

In practice, the observed retention coefficient, R_{obs}, is used as a measure of the membrane selectivity for a given component

$$R_{obs} = 1 - \frac{C_P}{C_B} \tag{3}$$

Here C_B and C_P denote bulk and permeate solute concentrations, respectively (see Fig. 1). Combining Eqs (2) and (3), we can express the selectivity of the entire operation of backflushed microfiltration

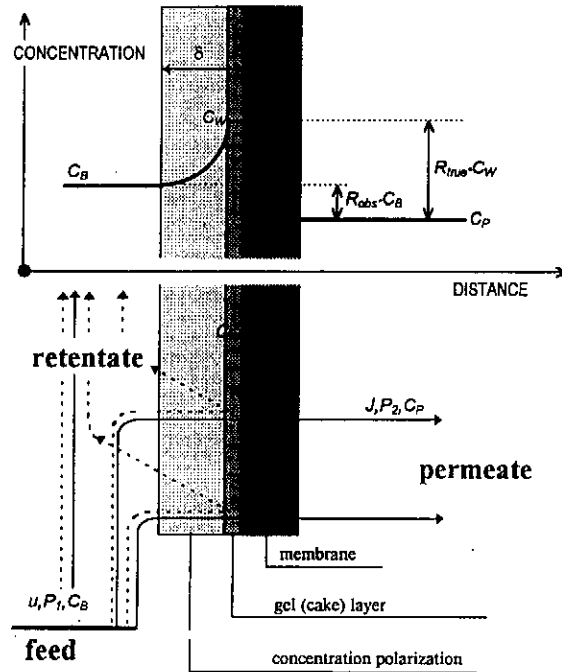$$(R_{obs})_{AVG} = 1 - \frac{(C_P)_{AVG}}{C_B} \tag{4}$$

Fig. 1   Schematic representation of the concentration polarization boundary layer

The knowledge of both the initial flux decline $J_F(t)$ and variation of permeate concentration $(C_P)_F(t)$ during this process period is crucial for the determination of the average observed retention $(R_{obs})_{AVG}$.

Effect of Concentration Polarization

The observed retention is a function of many process variables that affect the structure of the boundary layer. In order to describe how the membrane itself actually operates, attempts have been made to estimate the concentration at the membrane surface C_W and to express membrane selectivity by the true retention R_{true} that is defined with C_W instead of C_B

$$R_{true} = 1 - \frac{C_P}{C_W}$$ (5)

However, the value of C_W is hard to obtain directly by experiments, and in practice it is calculated as a fitting parameter of various mathematical models describing the mass transfer in membrane systems. The best known is the stagnant film model in which it is assumed that (in the steady state) the change from concentration at the membrane surface to bulk concentration occurs in the boundary layer of thickness δ immediately adjacent to the membrane surface (see Fig. 1). Taking the concentration at a general point within the concentration boundary layer to be C and solute diffusivity D, one obtains for permeate flux the relationship [1]

$$ J = \frac{D}{\delta} \ln\left(\frac{C_W - C_P}{C_B - C_P} \right) \tag{6} $$

Combining Eqs (5) and (6) we can express the solute concentration in the permeate stream under steady state conditions as

$$ C_P = C_B \left(1 - \frac{1}{\exp\left[\dfrac{J}{D/\delta} + \ln\left(\dfrac{1 - R_{true}}{R_{true}} \right) + 1 \right]} \right) \tag{7} $$

From the point of view of backflushing process, the concentration C_P given by Eq. (7) represents the upper concentration limit under given hydrodynamic conditions in the retentate channel. For purposes of modeling the backflushing process the variation of permeate concentration $(C_p)_F(t)$ during the initial flux decline period is also needed. Assuming the true retention during forward filtration phase to be constant (for a given solute and membrane), the changes of permeate concentration are tied with the concentration on the membrane surface C_W. In order to predict $C_W(t)$ during concentration polarization build-up, the more complicated differential convection — diffusion equation and the momentum equations must be solved numerically. It can be shown that the farther off the steady state, the lower solute concentration is in the vicinity of the membrane surface. Therefore, the general trend is an increase of solute permeate concentration as the polarization layer develops. As a consequence, retention $(R_{obs})_{AVG}$ increases for the rapid backflushing in which steady state concentration polarization layer is avoided. In this connection it is necessary to note that under typical conditions in microfiltration systems the time scale for development of the concentration polarization layer is approximately 1 s [5,8]. Thus rapid backflushing with a frequency higher than 1 Hz is needed to operate the system in the transient region of concentration polarization build-up.

Effect of Membrane Fouling

During cross-flow microfiltration, there are numerous reasons for a dispersed particle to settle irreversibly on the membrane surface or inside the pores. To describe the effect of fouling, the modified blocking (reduction in the number of pores or reduction in the average pore radius) or cake-based models are used [12,14,15]. However, they are not often discussed in terms of solute retention. The main consequence is a decline in flux, but also a change in the retention is possible. The general trend following from experiments is an increase of retention by fouled membranes as compared to clean ones. Therefore, permeate backflushing as a method of membrane cleaning therefore offers a possibility of decreasing of solute retention in fouling-controlled systems.

Effect of Multi-Component Feed

Retention of individual solutes from a mixture is more complicated. Because some larger components are retained by the membrane, they form a layer which is retentive for smaller components. Without this "dynamic secondary membrane" the smaller component would pass the primary membrane. Thus rapid permeate backflushing is potentially suitable for increasing the transmission of small components.

Experimental

Materials

The experiments were performed on asymmetric, multi-layered, ceramic membranes (SCT Bazet, France, subsidiary of US Filter). They were configured as single cylindrical tubes 0.25 m long, 7 mm ID and 10 mm OD (the active membrane area of 48.4 cm^2), consisting of a thin zirconia layer deposited on the internal surface of the tubular α-alumina support. The mean pore diameter of active layer reported by the membrane producer was 0.1 μm.

The feeds to microfiltration unit investigated in this study were the commercial emulsifier stabilized metal-working oil emulsion PARAMUL ERO-SB (Paramo Pardubice, the Czech Republic) and the aqueous solutions of the anionic emulsifier itself. The mass fraction of dispersed matter varied from 0.5 to 5% (w/w).

Apparatus

As shown in Fig. 2 the unit can be divided into two major parts consisting of the circulation loop and the backflushing system.
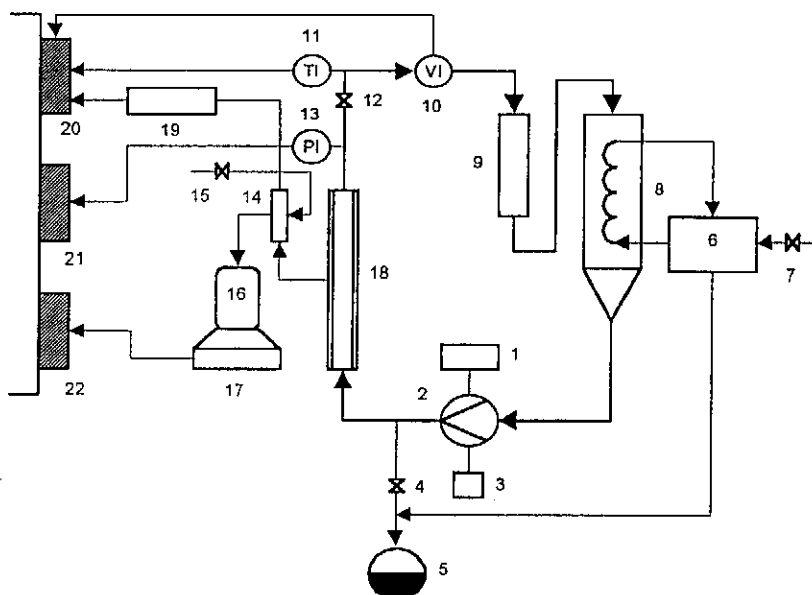

Fig.2 Set up of experimental apparatus: 1,19 – switches, 2 – pump, 3 – pump speed controller, 4,7,12,15 – valves, 5 – to sink, 6 – temperature regulating system, 8 – retentate container, 9,10 – flowmeter, 11 – temperature indicator, 13 – pressure indicator, 18 – membrane module, 14 – backflushing unit, 16 – permeate reservoir, 17 – electronic balance, 20,21,22 – computer acquisition system

The velocity and pressure in the retentate loop were varied independently by means of pump controller and an appropriate needle valve. The resulting feed velocities and average transmembrane pressures reached up to 5.8 m s^{-1} and 0.4 MPa, respectively. The circulation loop was constructed of stainless steel and contained a five-liter retentate container, a diaphragm pump, membrane module, and flow control valve at the module outlet. The loop was also equipped with a thermal regulation system, and a pressure and a flow monitoring system. The permeate was collected in a reservoir placed on an electronic balance, which was connected to a personal computer.

The backflushing system made use of an air driven piston mechanism mounted on the permeate port of the membrane housing. Further the system contained a timer for setting the frequency and duration of the pulses (computer

controlled) and pneumatic valves. The setup was capable of handling pulse times of 100 ms and larger. In the beginning of each backflushing cycle the first stage of the piston stroke closed the permeate outlet; then there followed the second stage in which piston pushed the permeate back through membrane. The amount of permeate used for backpulsing could be varied in the range from 0 to 5.2×10^{-6} m^3.

Procedure

After the membrane was placed in the membrane module, distilled water was circulated in the test loop at a moderate operating pressure for about 2 hours. During this time a stabilization of the membrane was observed giving a relatively stable water permeability. A concentrate of feed substance was then introduced to the unit, preheated to the desired temperature (25 °C), and the operating pressure as well as retentate velocity were adjusted by the regulation system. The flux through membrane was measured by weighting the permeate and timing the collection period (using a balance interfaced with a computer). Both the retentate and the permeate were recirculated back into the retentate container. Therefore, the concentration in the recirculation loop remained virtually constant. After each set of experiments the circuit and membrane were rinsed with water and the pure water flux was measured again under the conditions of initial testing until the steady state was obtained. The differences between the initial and final steady-state pure water flux were taken as a measure of the fouling tendency of the membrane. A chemical cleaning was needed periodically to recover the permeate flux. For this purpose alkaline detergent with hypochlorite was used.

The flux was recorded as a function of time and both permeate and retentate samples were analysed for COD and oil content. Repeated experiments for selected conditions showed good reproducibility of the data measured.

Results and Discussion

The results of permeate flux measurements are summarized and discussed in details in Ref. [17]. The experimental data showed a trend with higher average permeate flux for backflushed microfiltration compared with the standard cross-flow set up. The steady-state which was reached in all sets of experiments was lower than the pure water flux; it ranged from 10 to 95% of the pure water flux. It was hypothesized that permeate pulsing affected boundary layer development. If this postulate is correct, then permeate flow variations should alter the potential for pulsing to change also the transmission of a component through the membrane. Analyses of the permeate composition showed a nearly complete retention of the oil substances ($R_{obs} > 0.98$). The observed retention of emulsifier varied from

0.748 to 0.92 depending on the feed and operation conditions. At first sight the retention changes seem not to be so important. However, the emulsifier concentration in permeate becomes three times larger if the emulsifier retention decreases from 0.92 to 0.75.

Emulsifier-Distilled Water Systems

The membrane-emulsifier interaction was initially studied in standard crossflow systems without backflushing. The retentate cross-flow velocity and transmembrane pressure difference were found to be important factors influencing both the permeate flux and separation efficiency. The well known limiting flux behavior was observed which suggests that there is little advantage to be gained (in terms of flux) from operation at higher pressure differences than 250 kPa. The emulsifier retention data are presented in Fig. 3 as a function of permeate flux. The same values of retention were obtained for a given permeate flux no matter whether the flux was reached as a result of changes in transmembrane pressure difference or retentate cross-flow velocity. The increase in emulsifier retention with decreasing permeate flux suggests the membrane retention probably due to physical adsorption and/or to micelle formation in the mouth of the membrane pores. This is typically one of the several fouling mechanisms, leading to a pore size narrowing and/or to the blocking of the pore. The shear forces induced by the permeate flow through these modified membrane pores during filtration were strong enough to overcome partially this attraction for permeate fluxe higher than $100 \, l \, m^{-2} \, hr^{-1}$. For this conditions the breaking of the fouling agglomerates led to lower emulsifier retention.

This phenomenon was much more pronounced in microfiltration with permeate backflushing. The results of testing of the process under varying duration of the forward filtration are shown in Fig. 4. It can be seen that the effect of backpulsing was the more evident, the shorter the forward filtration time was. This is not surprising considering that in the initial period of forward filtration the permeate flux is very high and prevents the build-up of agglomerates. Also shear forces induced during the reverse flow through the pores of fouled membrane exceed those one in forward filtration.

Oil Emulsion Systems

Experiments were performed with an emulsion of cutting oil concentrate ERO-SB (80% wt.oil and 20% wt. emulsifier) in distilled water. The feeds were prepared with an emulsifier concentration equal to that in experiments without oil. In relation to the permeate flux the experimental results are summarized and discussed in Refs [14,17]. The presence of oil emulsion, free emulsifier molecules and emulsifier mi-

Cakl J., Bauer I./Sci. Pap. Univ. Pardubice Ser. A 5 (1999) 301–312
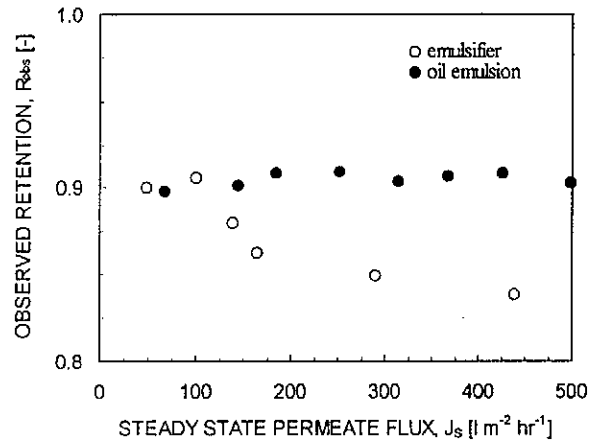
309

Fig.3   Variation of observed emulsifier retention with permeate flux in the system without membrane backflushing
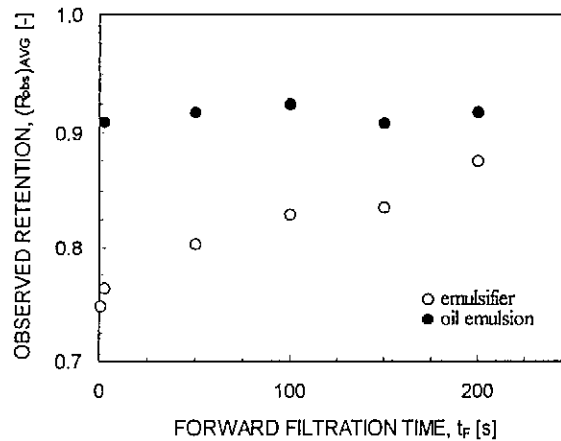

Fig.4   Variation of observed average emulsifier retention with the forward filtration time in backflushed microfiltration (u = 2   m s^{-1}, ΔP_F = 300   kPa, ΔP_R = 400   kPa, t_R = 0.1 s, emulsifier: 0.1% wt, emulsion: (0.1% wt. emulsifier and 0.4 % wt. oil)

celles caused considerable permeate flux drop in comparison with the pure water flux. The oil retention was found to be independent of operating parameters. Observed oil retention was consistently higher than 98%, indicating permeate oil concentrations to be less than 10 mg l^{-1}. The total organic carbon rejection was 96 to 98%. Emulsifier retention was enhanced in the presence of oil. A possible

explanation is that the free emulsifier concentration in the feed stream was lower in the presence of oil (because of emulsification). The experimental results for both standard and backflushed modes are depicted in Figs 3 and 4. In contrast to the experiments with emulsifier alone it can be seen that emulsifier retention is not considerably affected by operating conditions.

Conclusion

Microfiltration studies with emulsifier-water and emulsifier-oil-water systems indicate that adsorption and/or micelle formation of emulsifier molecules in the membrane pores cause substantial retention increase of the emulsifier. However, this process is influenced by shear stress within the pores. When the shear stresses are greater, the attachment of the emulsifier to the membrane material is not sufficiently strong to prevent convection of emulsifier through the membrane. As a consequence, the observed emulsifier retention depends on the operating conditions during microfiltration. The experimental results demonstrate that rapid membrane backflushing is a useful tool for increasing the emulsifier transmission.

Acknowledgements

Symbols

C concentration
d inner diameter of the tube, m
D solute diffusivity, $m^2\,s^{-1}$
J permeate flux, $m\,s^{-1}$ ($l\,m^{-2}\,h^{-1}$)
ΔP transmembrane pressure difference, Pa
R retention
t time, s
u retentate velocity, $m\,s^{-1}$
δ thickness of boundary layer, m

Subscripts

0 initial value
AVG average

B bulk
F forward filtration
obs   observed
P permeate
R reverse flow
W wall

References

1. Belfort G., Davis R.H., Zydney A.L.: J. Membrane Sci. **96**, 1 (1994).
2. Mikulášek P.: Collect. Czech. Chem. Commun., **59**, 743 (1994).
3. Masamuto K., Katsuyama M., Ohya H.: J. Ferment. Technol. **66**, 199 (1988).
4. Redkar S.G., Davis R.H.: AIChE J. **41**, 501 (1995).
5. Roger V.G.J., Sparks R.E.: J. Membrane Sci. **68**, 149 (1992).
6. Xu Y., Dodds J., Leclerc D.: Chem. Eng. J. **57**, 247 (1995).
7. Galaj S., Wicker A., Dumas J.P.: Le Lait **64**, 129 (1984).
8. Redkar S.G., Kuberkar V., Davis R.H.: J. Membrane Sci. **121**, 229 (1996).
9. Jonsson G., Wenten I.G.: *Control of Concentration Polarization, Fouling, and Protein Transmission of Microfiltration Processes within the Agro Based Industry*, Presented at the Workshop on Membrane Technology in Agro Based Industry, Kualalumpur, 1994
10. Mallubhotla H., Belfort G.: Ind. Eng. Chem. Res. **35**, 2920 (1996).
11. Wilharm C., Rodgers V.G.J.: J. Membrane Sci. **121**, 217 (1996).
12. Field R. Wu D., Howell J.A., Gupta B.B.: J. Membrane Sci. **100**, 259 (1995)
13. Parnham Ch.S., Davis R.H.: J. Membrane Sci. **118**, 259 (1996).
14. Cakl J., Doleček P.: *Boundary Layer Phenomena in Backflushed Cross-Flow Microfiltration*, 13th International CHISA Congress, Prague, 1998
15. Hermia J.: Trans. Inst. Chem. Eng., **60**, 183 (1982).
16. Parnham C.S., Davis R.H.: Biotechnol. Bioeng., **47**, 155 (1995).
17. Cakl J., Bauer I., Doleček P., Mikulášek P.: Desalination, in press.