Effects of coagulation on filtration mechanisms in dead-end ultrafiltration

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Abstract Filtration mechanisms occurring during ultrafiltration of coagulated and non-coagulated surface water were investigated using the general blocking filtration laws. The sharp decline in permeate flux in the first 10–20 minutes of filtration was largely due to a combination of the blocking filtration mechanisms. However, a distinction between “complete”, “standard” and “intermediate blocking” mechanisms was not possible as a large degree of overlap existed between the mechanisms and the transition from one type of blocking to another was very smooth. Coagulation appeared to retard blocking and consequently, the duration of the “blocking phase” was twice as long for coagulated water compared with non-coagulated water. The “transition phase”, where both blocking and cake filtration occurred simultaneously, was also extended in the case of coagulated water as continuous blocking of the membrane through the pores of the cake was observed. The modified fouling index-ultrafiltration (MFI-UF) was employed to examine the impact of coagulation on filter cake properties. Coagulation reduced the specific resistance of the filter cake by 50% at a TMP of 1.5 bar, and 35% at a TMP of 0.5 bar. Depth filtration was hardly evident at a TMP of 0.5 bar, but was very pronounced at a TMP of 1.5 bar as the specific resistance of the filter cake increased continuously, particularly in the absence of coagulant. The filter cake was sensitive to the applied TMP and the MFI-UF value increased by 130% for non-coagulated surface water and 55% for coagulated water due to compression of the cake, when the TMP increased from 0.5 to 1.5 bar.

Keywords Blocking; cake filtration; coagulation; compression; depth filtration

Introduction The combined treatment of coagulation and microfiltration (MF) or ultrafiltration (UF) is generally applied to aggregate foulants to form particles large enough to be rejected at the membrane surface (Wiesner et al., 1989; Lee et al., 2000; Soffer et al., 2000). The targeted foulants are dissolved organic matter and small colloids (< 1 µm), and they are the main cause of pore blocking and irreversible fouling in MF/UF systems. Increasing the size of such foulants in dead-end UF systems is expected to: (i) reduce their chance of penetrating membrane pores and adsorbing on the pore walls, (ii) form a porous cake on the membrane surface that can protect the membrane from further blocking, and (iii) simplify cleaning so that flushing and/or backwashing with product water can remove the permeable cake layer (Wiesner et al., 1989; Kennedy et al., 2001). Coagulation prior to membrane filtration has been reported to improve the flux of constant pressure membrane systems, as both membrane blocking and specific resistance of the filter cake are reduced (Wiesner et al., 1989; Lee et al., 2000). The aim of this study is to examine the effects of coagulation on the filtration mechanisms in hollow fibre UF systems.

Experimental Hollow fibre membrane
Polymeric hollow fibre ultrafiltration membranes (Norit Membrane Technology) made from polyethersulphone (PES) and coated with an anti-fouling layer of polyvinylpirrolidone were tested. The membrane characteristics are given in Table 1.
Surface water

Surface (canal) water was used for all UF tests performed. The surface water characteristics are presented in Table 2 (the values are averages of 10 surface water samples collected weekly over a 2–3 month period). The turbidity was measured using a turbidity meter, model LTP4 and expressed in NTU. TOC was quantified using a total organic carbon analyser (Analytica, model 7000).

Experimental set-up

A lab-scale UF unit presented in Figure 1, equipped with a single UF hollow fibre (1 m in length) was used for filtration purposes. The TMP was generated by gravity filtration from a storage tank and was constant throughout each test. Permeate (droplets) was collected from the front (50 cm) and the rear of the UF hollow fibre (50 cm) via two “permeate collectors”. Each “permeate collector” was placed on a balance (Mettler) connected to a computer and the cumulative volume of permeate was recorded automatically every 30 seconds for the duration of each test (100 minutes) using Mettler Toledo Balance Link 2.5 software.

Ultrafiltration tests

UF tests were carried out at a constant transmembrane pressure (TMP: 0.5 or 1.5 bar) in dead-end mode (retentate closed). The hollow fibre was de-aerated by flushing with Milli Q water for 30–40 seconds to remove all air bubbles from the fibre. Thereafter, the clean water flux was measured using Milli Q water at a TMP of 0.5 and 1.5 bar. Surface water (non-coagulated) was fed (via the storage take) to the hollow fibre and filtrated volume and temperature were recorded every 30 seconds. The hollow fibre was replaced after each filtration test and the procedure repeated. Surface water was coagulated by adding 0.75 mg/l Fe³⁺ (FeCl₃) to the storage tank. The coagulant was rapidly mixed with the surface water (300 rpm) for 1 minute and then slowly mixed for another 20 minutes (30 rpm). Thereafter, the coagulated water was fed to the UF fibre. The MFI-UF system was described in detail by Boerlage et al. (1998).

Data processing

Prior to calculating the first and second derivatives, the experimental t and V data were smoothened by non-linear regression (using Statistica 5.0 software) and the simulated t(V) functions obtained were derived correspondingly.

### Table 1  Characteristics of UF hollow fibres

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Polyethersulphone and polyvinylpirrolidone</td>
<td>–</td>
</tr>
<tr>
<td>Molecular weight cut-off (UFC)</td>
<td>150,000–200,000</td>
<td>Dalton</td>
</tr>
<tr>
<td>Fibre length</td>
<td>1.0</td>
<td>m</td>
</tr>
<tr>
<td>Internal fibre diameter</td>
<td>8.0 × 10⁻⁴</td>
<td>m</td>
</tr>
<tr>
<td>Membrane surface area</td>
<td>2.5 × 10⁻³</td>
<td>m²</td>
</tr>
<tr>
<td>Maximum operation pressure</td>
<td>2.0</td>
<td>bar</td>
</tr>
</tbody>
</table>

### Table 2  Surface (canal) water characteristics

<table>
<thead>
<tr>
<th>Turbidity (NFU)</th>
<th>pH</th>
<th>TOC (mg/L)</th>
<th>TSS (mg/L)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.3–22.9</td>
<td>7.5–7.6</td>
<td>18.8–22.8</td>
<td>18.6–21.1</td>
<td>5.8–12.7</td>
</tr>
</tbody>
</table>
Results and discussion

Effects of coagulant addition on permeate flux

Non-coagulated and coagulated surface water was fed to a UF hollow fibre at a constant TMP pressure of 0.5 and 1.5 bar. Permeate flux development (normalised to 20°C) as a function of time is presented in Figure 2 (a) and (b). The permeate flux decreased rapidly in the first 8–10 minutes of dead-end filtration, particularly at a TMP of 1.5 bar. This was attributed to the high flux of particles; colloids and macromolecules to the membrane at a TMP of 1.5 bar (initial flux of 570 l/m².hr) compared with a TMP of 0.5 bar (initial flux 190–200 l/m².hr). The addition of 0.75 mg/L Fe³⁺ improved permeate flux by 15 and 20% at a TMP of 0.5 and 1.5 bar, respectively.

The rate at which the instantaneous resistance increased with the filtered volume (or filtration time) is clearly different for coagulated and non-coagulated water. In Figure 3 (a), $\frac{dt}{dV}$, which is directly related to the actual resistance, is represented as a function of the cumulative volume. The rate of increase of the actual resistance was roughly twice as high for non-coagulated water compared with coagulated water, at a TMP of 1.5 bar (similar trends were found at a TMP of 0.5 bar). Two phenomena may explain the slower increase in filter resistance and the higher permeate flux, after coagulation. Firstly, membrane blocking may diminish as coagulation is expected to aggregate feed water particles so that they are rejected by the membrane, thus reducing pore blocking and the adsorption of colloids and macromolecules on the pore walls. Additionally, coagulation may increase the average size of colloids and macromolecules in the feed water so that a more porous and permeable cake is formed on the membrane (Wiesner et al., 1989; Lee et al., 2000).

Figure 1 Experimental set-up for a single UF hollow fibre

Figure 2 Permeate flux decline in a UF hollow fibre for coagulated and non-coagulated surface water at a TMP of (a) 0.5 bar; and (b) 1.5 bar
Effects of coagulation on blocking filtration

All filtration tests were performed at a constant TMP and in dead-end mode. Under these conditions, the blocking and cake filtration equations (Hermans and Bredée, 1936; Hermia, 1982; Bowen et al., 1995) can be used to investigate the filtration mechanisms. The general form of the second derivative equation relates the “rate of blocking” \( \frac{d^2t}{dV^2} \) with the instantaneous resistance (reciprocal flow rate, \( \frac{dt}{dV} \)), as follows (Hermia, 1982):

\[
\frac{d^2t}{dV^2} = k \left( \frac{dt}{dV} \right)^\beta
\]

\( t \) is the filtration time (s), \( V \) is the cumulative volume (l), \( k \) is a constant \( (s^{-1-\beta} l^{-2}) \) and \( \beta \) is the exponent. Depending on the values of the exponent (\( \beta \)), the equations can be used to indicate the specific blocking mechanism during constant pressure (unstirred filtration). For example, \( \beta = 2 \) (complete blocking), \( \beta = 1.5 \) (standard blocking), \( \beta = 1 \) (intermediate blocking) and \( \beta = 0 \) (cake filtration). The shape of the characteristic second derivative curves at a TMP of 1.5 bar are similar (Figure 3b) and indicate a rapid decrease of slope for both non-coagulated and coagulated water. Correspondingly, a rapid change in the filtration mechanism from blocking to cake filtration can be assumed for both non-coagulated and coagulated surface water. \( \beta \), which can be used to monitor the progression from blocking to cake filtration, was estimated by taking the logarithm of Eq. (1) (\( \beta \) is the slope of Eq. (2)). \( \beta \) versus time is presented in Figure 4 (a) and (b).

\[
\log \left( \frac{d^2t}{dV^2} \right) = \log k + \beta \log \left( \frac{dt}{dV} \right)
\]

\( \beta \) decreased rapidly from \( \approx 2 \) to around 0 in the first 10–20 minutes of filtration (Figure 4), suggestive of a rapid transformation from blocking to cake filtration for both coagulated and non-coagulated surface water. A distinction between the blocking mechanisms i.e. “complete”, “standard” and “intermediate blocking” was not possible as a large degree of overlap appeared to exist between them and the transition from one type of blocking to another was very smooth. Considering the wide range of particle sizes in surface water and the wide pore size distribution of polymeric UF membranes, blocking (complete and standard) and cake filtration probably occurred simultaneously from the beginning of a filtration cycle. In this case, blocking was assumed to be the main filtration mechanism for the first 15–20 minutes of filtration with cake filtration playing a secondary role only. Assuming that membrane blocking was finished when “complete”, “standard” and “intermediate blocking” had taken place (\( \beta = 1.0 \)), the duration of the “blocking phase” for non-coagulated and coagulated water was estimated. The duration of membrane blocking decreased as the TMP increased, e.g. blocking was complete after 5 minutes at a TMP of 1.5 bar compared with 10 minutes at a TMP of 0.5 bar for non-coagulated surface water. This was attributed to the higher flux of colloids and macromolecules to the membrane at the higher TMP of 1.5 bar (\( J_t = 200 \text{l/m}^2 \cdot \text{hr} \) at a TMP of 0.5 bar and 570 l/m²·hr at 1.5 bar).

![Figure 3](https://iwaponline.com/ws/article-pdf/3/5-6/109/419208/109.pdf)

Figure 3 (a) Variation in the actual filter resistance with the cumulative permeate volume for coagulated and non-coagulated water; and (b) characteristic curves of \( \frac{d^2t}{dV^2} \) vs \( \frac{dt}{dV} \), at a TMP of 1.5 bar.
Coagulation appeared to prolong the “blocking phase” as a longer filtration time (and filtrate volume) was required to complete membrane blocking due to a reduction in the amount of small colloids and macromolecules after coagulation. For example, membrane blocking appeared to be complete ($\beta = 1.0$) after 5 minutes of filtration for non-coagulated surface water compared with 10 minutes for coagulated surface water, at a TMP of 1.5 bar. Similarly, blocking filtration appeared to be complete after 10 minutes in the case of non-coagulated water, while 20 minutes was required for coagulated surface water, at a TMP of 0.5 bar. From the constant pressure blocking laws (Hermia, 1982), cake filtration occurred when $\beta = 0$. However, in this study the lowest value of $\beta$ recorded was 0.02 (after 100 minutes of filtration). Therefore, the principal filtration mechanism was assumed to be “cake filtration” when the slope of $\beta$ versus time was constant (and blocking was assumed to have a minor contribution at this stage). From Figure 4, approximately 40 minutes was needed to establish “cake filtration” in the case of non-coagulated water, while 60 minutes was required for coagulated water, at a TMP of 0.5 bar. Similarly, at a TMP of 1.5 bar, 60 minutes was required to establish cake filtration for non-coagulated water and 40 minutes was necessary for coagulated water.

A long period of “transition” appeared to exist, where both blocking and cake filtration occurred simultaneously. The duration of the “transition phase” was approximated based on the assumptions that: (i) membrane blocking was complete when $\beta = 1.0$, and (ii) cake filtration was the dominant filtration mechanism when the slope of $\beta$ versus time became constant. The duration of the transition phase was ca. 30 and 40 minutes for non-coagulated and coagulated water, respectively, at a TMP of 0.5 bar. Similarly, the duration of the transition phase was ca. 20 and 30 minutes for non-coagulated and coagulated water, respectively, at a TMP of 1.5 bar. The duration of the “transition phase” was longer in the case of coagulated water and this was due to the fact that coagulation prior to ultrafiltration retarded membrane blocking and consequently, the duration of the “blocking phase” was extended. Moreover, coagulation probably increased cake porosity, thus enhancing the passage of small colloids and macromolecules through the pores of the cake, allowing continuous blocking of the membrane even during the transition phase. This phenomenon may explain the higher $\beta$ values for coagulated water during the transition phase (Figure 4).

Many authors have pointed out that a good fit of the experimental data by any of the blocking laws does not mean that the true physical fouling mechanism has been identified (Gonsalves, 1950; Hlavacek et al., 1993) because the same curves may be obtained through completely different mechanisms. However, it may be safe to assume that the sharp decline in permeate flux (Figure 1) in the first 10–20 minutes of filtration was largely due to a combination of blocking filtration mechanisms.

**Effects of coagulation on cake filtration**

The modified fouling index ($\text{MFI}_{0.45\mu m}$) was developed by Schippers and Verdouw (1980), to predict the propensity of water to foul a membrane, and is based on the
occurrence of cake filtration without compression in dead-end filtration. The MFI is defined as the slope of the linear region of the \( t/V \) vs. \( V \) plot, derived from the general equation of cake filtration at constant pressure. The MFI-UF is calculated by correcting the MFI to specific conditions of pressure (\( \Delta p_0 = 2 \) bar), temperature (\( \mu \) at 20°C) and membrane surface area (\( A_0 = 0.1385 \) m\(^2\)).

\[
\frac{t}{V} = \frac{\mu R_m}{\Delta P A} + \frac{\mu \alpha C_b}{2 \Delta P A^2} V
\]

The slope of the linear region of \( t/V \) vs. \( V = MFI = \mu \alpha C_b / 2 \Delta P A^2 \), where \( \Delta P = \text{TMP} \).

The MFI-UF was developed by Boerlage et al. (1997, 2000) and employs an ultrafiltration membrane instead of a 0.45 \( \mu \)m membrane, in order to capture more of the small particles and colloids that contribute to membrane fouling. The MFI-UF was measured continuously for the duration of the filtration cycle (100 minutes) and is presented in Figure 5. The rapid increase in the MFI-UF in the first 10–20 minutes of filtration was attributed to blocking filtration. The addition of coagulant reduced the MFI-UF by 35%, from 17,112 to 11,068 s/l\(^2\) at a TMP of 0.5 bar (filtration time = 100 mins). The reduction in the MFI-UF value was due to a lower specific resistance of the filter cake (\( \alpha \)) as coagulant addition is expected to increase the average size of feed water particles, colloids and macromolecules that make up the cake. At a TMP of 0.5 bar, the MFI-UF value was stable and hardly increased (<5%), even in the absence of coagulant, during the last 60 minutes of filtration. Therefore, depth filtration did not play a significant role in increasing the specific resistance of the cake at a TMP of 0.5 bar (\( J_i = 80 \) lm\(^2\).hr), even without coagulant addition. Compression of the filter cake was unlikely, as the TMP was constant throughout the experiment.

At the higher TMP of 1.5 bar, coagulant reduced the MFI-UF by 50%, from 32,153 to 16,112 s/l\(^2\) (\( t = 100 \) minutes). The reduction in the MFI-UF was attributed to lower specific resistance of the filter cake after coagulation. However, the resistance of the cake was not stable and increased by 22% for non-coagulated water and 15% for coagulated water during the last 40 minutes of filtration, at a TMP of 1.5 bar. The continual increase in MFI-UF over time was attributed to depth filtration, where fine particles were continually trapped in the filter cake reducing cake porosity and increasing cake resistance. Depth filtration was more pronounced at high TMP because of the higher flux of particles, colloids etc., to the filter cake and in the absence of coagulant, because of the abundance of small colloids and macromolecules.

The MFI-UF, and thus the specific cake resistance, was roughly 50% higher for coagulated water and 130% higher for non-coagulated water when the TMP was increased from 0.5 to 1.5 bar. From Figure 5, the MFI-UF of coagulated water was 11,068 s/l\(^2\) at a TMP of 0.5 bar and 16,531 s/l\(^2\) at a TMP of 1.5 bar. Similarly, the MFI-UF of non-coagulated water was 16,112 s/l\(^2\) at a TMP of 0.5 bar and 32,153 s/l\(^2\) at a TMP of 1.5 bar. The fact that the MFI-UF value increased with increasing TMP suggests that the filter cake was sensitive to
the applied TMP and compression of the cake may have occurred above a TMP of 0.5 bar. If the filter cake was not sensitive to the applied pressure, then similar MFI values should have been observed, irrespective of the TMP applied.

Conclusions

• The sharp decline in permeate flux in the first 10–20 minutes of filtration was largely due to a combination of blocking mechanisms but a distinction between “complete”, “standard” and “intermediate blocking” was not possible as a large degree of overlap existed between the mechanisms and the transition from one type of blocking to another was very smooth.

• Coagulation appeared to retard blocking and consequently, extend the duration of the “blocking phase” by roughly 50%. The “transition phase”, where both blocking and cake filtration occurred simultaneously, was also extended in the case of coagulated water as continuous blocking of the membrane through the pores of the cake was observed, during the transition phase.

• Coagulation reduced the specific resistance of the filter cake by 50% at a TMP of 1.5 bar, and 35% at a TMP of 0.5 bar. Depth filtration was hardly evident at a TMP of 0.5 bar, but was very pronounced at a TMP of 1.5 bar as the specific resistance of the filter cake increased continuously, particularly in the absence of coagulant.

• The filter cake was sensitive to the applied TMP and the MFI-UF value increased by 130% for non-coagulated surface water and 55% for coagulated water, when the TMP increased from 0.5 to 1.5 bar.

List of symbols

\( A \): filter membrane surface area (m\(^2\))

\( C_b \): solute concentration in the bulk (kg/m\(^3\))

\( P \): filtration pressure (N/m\(^2\))

\( t \): filtration time (s)

\( V \): filtrate volume (m\(^3\))

\( \alpha \): specific cake resistance (m/kg)

\( \mu \): viscosity (N s/m\(^2\))

References


