Humic substances fouling in ultrafiltration processes

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Abstract

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Membrane fouling by humic substances (HS) is a major problem in UF water treatment. The complex phenomena involved have been the subject of numerous investigations. HS fouling is attributed to accumulation of particles in the feed water on the membrane surface forming a cake layer and adsorption of small particles in the inner pores thus constricting or blocking the pore mouth. The exact contribution of each of these mechanisms to membrane fouling and to flux reduction is not sufficiently clear. While there is a substantial qualitative agreement on various fouling aspects in studies focusing on commercial humic acid solutions, the extensive literature on fouling by natural organic matter (NOM) is less coherent. The major deficiency in the available information is the lack of reliable predictive models. This paper presents a systematic review of scattered literate information and outlines HS fouling aspects that await elucidation.

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1. Introduction

Ultrafiltration is considered to be one of the leading techniques in water purification processes. The efficiency of the process largely depends on the ability to restrict the extent of fouling to a manageable degree. A widely encountered fouling species in surface waters is natural organic matter (NOM) which mainly consists of humic substances (HS). At the current state of the art, HS fouling is not easily controlled. Due to the complexity of the phenomena involved, fouling predictive abilities are limited despite vast research efforts. These efforts include many fundamental studies using the readily analyzed humic acid as a model foulant. The objective of this review is to compile systematically scattered information so as to facilitate identification of...
the effect of specific parameters on HS fouling and to indicate major issues that require further research.

2. Humic substances chemistry

The natural organic matter (NOM) of soil, peats and water consists of a mixture of plant and animal products in various stages of decomposition together with substances synthesized biologically and chemically. NOM is usually divided into two groups: non-humic substances and humic substances. The non-humics include a large number of relatively simple compounds of known structures belonging to well-known groups: hydrocarbohydrates, proteins, peptides, amino acids, fats, waxes, resins, pigments and other low molecular weight organic substances. In general, these compounds are easily attacked by microorganisms and have a relatively short survival rate so that the bulk of organic matter consists of humic substances [1], whose properties are described below.

2.1. Chemical properties

Humic substances are very abundant in the environment. Though their origin is microbial decomposition of plant and animal tissues, they are more stable than their precursors. The apparently large molecular size of humic substances is actually a supramolecular structure of small bio-organic molecules of a molecular mass smaller than 1000 Da, held together by weak forces, such as Van der Waals force [2].

Humic materials vary in their composition, structure, molecular weight, number and position of functional groups, depending on their origin and age. The authoritative ACS monograph of Gaffney et al. [3] describes the structure, chemical characterization, metal bindings and organic pollutants interactions of humic and fulvic acids.

Traditionally, humic substances are classified into three main categories, according to their solubility in water [4]:

- **Fulvic acids**: soluble in water at all pH values; average molecular weight less than 2000 Da; average length of macromolecules of 60 nm and average diameter of 2 nm.
- **Humic acids**: insoluble at acidic pH values (pH<2) and soluble at higher pH levels; average molecular weight in the range of 2000 to 5000 Da; chemical structure dominated by phenol groups and long carboxylic fatty acids; more hydrophobic in comparison with fulvic acids.
- **Humins**: insoluble at all pH values; consist mainly of bitumens, coupled with fatty acids and humic acids.

No sharp division exists among humic acids, fulvic acids and humins since the differences among them stem from variations in the acidity and hydrophobicity of the molecules (Fig. 1).

The elemental composition of humic materials is approximately 40–60% carbon, 30–50% oxygen, 4–5% hydrogen, 1–4% nitrogen, 1–2% sulfur and 0–0.3% phosphorus. The molecular sizes of humic acids present in water place them in the colloidal range; therefore humic concentration, pH and ionic strength control the colloidal structure. At high concentrations (>3.5 g/lit), low pH (<3.5) and high ionic strength (>0.05 M), humic materials are rigid uncharged colloidal particles. At low concentrations, high pH and low ionic strength, humic materials are flexible linear polyelectrolytes [3].

Humic substances are endowed with aromatic and aliphatic characteristics which contribute to surface charge and reactivity mainly by the phenolic and the carboxylic groups. Humic substances may chelate multivalent cations such as Mg²⁺, Ca²⁺, and Fe²⁺.

2.2. Analytical methods

The main techniques used for the characterization of HS content are determinations of TOC (total organic carbon), DOC (dissolved organic carbon) [4–16] and light absorbance [4,6,13,15,17–26].

According to Thurman (cited in [27]), the DOC value is approximately 50% of the amount of the dissolved organic matter (DOM). The accuracy of DOC results is poor, especially at low concentrations, due to the deficiency of the analytical method used and the risk of sample contamination [15].

Measurements of light absorption in both the ultraviolet range (254 nm) and the lower part of the visible range (400–600 nm) have often been applied for a simple quantification of the NOM or DOM. The absorption of light at these wavelengths by humic substances is due to both their aromatic rings and conjugated unsaturated bonds and to the presence of free electron pairs on heteroatoms [27].

Contrary to the TOC/DOC techniques, the UV absorbance analysis depends on the structure of the organic molecule, the UV-absorbing molecules tending to be larger and more aromatic. It is therefore not a reliable method for determining the concentrations of HS in the feed and the permeate [15]. Since larger molecules tend to be less permeable, the rejection fraction determined by the UV technique will be biased towards the smaller molecules.

3. Parameters affecting humic substances fouling

HS membrane rejection and fouling are governed by three types of variables:

- Parameters related to the HS characteristic (molecular weight, aromaticity, hydrophobicity and charge)
- Membrane properties (molecular weight cut-off, hydrophobicity, charge and porous structure)
- Hydrodynamic operating conditions (flow geometry, permeate flux and mass transfer coefficient).

The complexity of HS parameters affecting the fouling process has been aptly portrayed by noting that “a huge pull of chemistry is involved” [27]. The fundamental mechanisms of fouling lie in the intermolecular interaction between the membrane and the various feed components. The interactions involve short range attraction forces, electrostatic interactions and polarization forces. The interactions manifest themselves by adsorption processes and particles deposition that lead to pore blockage, pore constriction and cake filtration. Correlation of HS fouling data is reviewed in Section 6.

Fouling is influenced not only by physico-chemical factors but also by hydrodynamic parameters. The most obvious parameter is the degree of concentration polarization which is dictated by the hydrodynamics of the system. The level of the concentration polarization affects the degree of fouling and rejection and the reversibility of the fouling process as discussed in Section 3.5.

Two main types of HS fouling studies are reported in the literature: experiments carried out with synthetically extracted humic acid (HA), predominantly supplied by Aldrich and the International Humic Substance Society (IHSS), and experiments conducted with naturally occurring aquatic humic substance. Because of the variability of naturally occurring humic substances it is difficult to identify the NOM fraction responsible for irreversible membrane fouling [7].

Fig. 1. A schematic structure of HA molecule.

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3.1. Presence of divalent ions

It is generally agreed that the presence of divalent ions enhances HS fouling [5,7,15,18,21,22,27]. Of particular interest is the presence of Ca$^{2+}$ which is most abundant in natural waters. The effect of Ca$^{2+}$ is illustrated in Fig. 2 showing normalized flux decline ($\frac{J}{J_0}$) with time in the absence and presence of 1 mM Ca$^{2+}$. The discontinuities denote flux recovery by periodic backwash. It is seen that the flux decline is significantly higher in the presence of Ca$^{2+}$.

The negative effect of Ca$^{2+}$ on membrane permeability is considered to arise from its reaction with the acidic functional group of the NOM, forming a cross linked structure of a very dense cake layer [5,7]. The degree of complexation of NOM with Ca$^{2+}$ increases with pH due to the increased dissociation of the carboxylic groups [28]. Also, at high pH and high Ca$^{2+}$ content, calcite may precipitate and the NOM may then adsorb on the crystal surfaces [12].

Studies related to the effect of Ca$^{2+}$ on HS fouling are summarized in Table 1 and provide substantial evidence on the deleterious fouling effect of Ca$^{2+}$.

3.2. Effect of solution pH

Except of the study of Costa et al. [5], it is generally agreed that HS fouling is more severe at low pH levels. The pH level affects the charge of both the membrane surface and the HA macromolecules. These charge effects can cause different membrane materials to display different fouling propensities.

Fig. 3 illustrates the flux decline occurring at the low pH level of 3 relative to that at the higher pH level of 7. At the low pH level, the HA macromolecules are less charged. This induces a reduced electrostatic repulsion between the HA in solution and the clean membrane and between the HA in solution and the pre-formed HA fouling layer. As a result, HA deposition is enhanced leading to an intensified flux decline.

Studies on the effect of solution pH on HS fouling are summarized in Table 2.

<table>
<thead>
<tr>
<th>Researchers [ref]</th>
<th>Effect studied</th>
<th>Membrane MWCO and material</th>
<th>Feed conc. ppm (supplier)</th>
<th>Ca$^{2+}$ Conc. mM</th>
<th>Results</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aoustin et al. 2001 [15]</td>
<td>Flux decline; HS rejection</td>
<td>10 kDa regenerated-cellulose 100 kDa regenerated-cellulose</td>
<td>12.5 ppm DOC (IHSS)</td>
<td>0.5–4</td>
<td>For identical permeate volumes, flux decline occurred only in the 100 kDa membrane. DOC rejection in 10 kDa membrane deteriorated as Ca$^{2+}$ content increased from 0.5 mM to 2.5 mM and then increased again at 4 mM. In all cases, rejection increased with time. DOC rejection with 100 kDa membrane lower than with 10 kDa membrane.</td>
<td>100 kDa membrane pores are large enough to facilitate pore blocking by aggregates. As charge repulsion between ionized negative groups on HA is lowered by Ca$^{2+}$, HA molecules tend to curl up to smaller molecular sizes and are thus rejected less effectively. Alternatively, charge neutralization by Ca$^{2+}$ reduces repulsion between negatively charged membrane and HA molecules thus lowering rejection. At 4 mM rejection is enhanced due to HA coagulation and improved retention of larger molecules. Rejection increases with time due to accumulation of organics and due to pore closure or blockage.</td>
</tr>
<tr>
<td>Costa et al. 2006 [5]</td>
<td>Flux decline</td>
<td>2 kDa CA 75 kDa CA</td>
<td>100 (Aldrich)</td>
<td>0.3–1</td>
<td>No increased fouling detected with 0.3 mM Ca$^{2+}$ with both membranes; significantly increased fouling with 1 mM Ca$^{2+}$. Ca$^{2+}$ slightly increased the flux decline but diminished backwashability. With Aldrich HA, presence of Ca$^{2+}$ reduced backwashability with PES membrane but not with PAN membrane. With natural water, no effect of Ca$^{2+}$ was observed with both membranes. Ca$^{2+}$ up to 2 mM hindered backwash efficiency; Ca$^{2+}$ at 4 mM affected only slightly backwash efficiency.</td>
<td>Ca$^{2+}$ enhances fouling; attributed to augmented adhesion between foulants in bulk solution and the fouling layer.</td>
</tr>
<tr>
<td>Jermann et al. 2007 [23]</td>
<td>Flux decline; backwashability</td>
<td>100 kDa PES 100 kDa PES</td>
<td>2 mg-C/L (IHSS)</td>
<td>0–1.25</td>
<td>Differences in the effect of Ca$^{2+}$ between Aldrich HA solution and natural water attributed to the more hydrophobic nature of Aldrich HA molecules; Ca$^{2+}$ promotes aggregation of the Aldrich hydrophobic molecules; pore clogging by these aggregates induces more severe fouling than with natural water. As Ca$^{2+}$ concentration increases, HA aggregates grow larger in size forming a backwashable cake layer.</td>
<td></td>
</tr>
<tr>
<td>Yamamura et al. 2007 [7]</td>
<td>Flux decline; backwashability</td>
<td>100 kDa PAN 100 kDa PES</td>
<td>Natural water 3 (Aldrich)</td>
<td>0.2</td>
<td>Yes increased fouling detected with 0.3 mM Ca$^{2+}$ with both membranes; significantly increased fouling with 1 mM Ca$^{2+}$. Ca$^{2+}$ slightly increased the flux decline but diminished backwashability. With Aldrich HA, presence of Ca$^{2+}$ reduced backwashability with PES membrane but not with PAN membrane. With natural water, no effect of Ca$^{2+}$ was observed with both membranes. Ca$^{2+}$ up to 2 mM hindered backwash efficiency; Ca$^{2+}$ at 4 mM affected only slightly backwash efficiency.</td>
<td>Ca$^{2+}$ enhances fouling; attributed to augmented adhesion between foulants in bulk solution and the fouling layer.</td>
</tr>
<tr>
<td>Katsoulidou et al. 2005, 2008 [21,22]</td>
<td>Flux decline; backwashability</td>
<td>150 kDa PES</td>
<td>10 (Aldrich)</td>
<td>0–4</td>
<td>Differences in the effect of Ca$^{2+}$ between Aldrich HA solution and natural water attributed to the more hydrophobic nature of Aldrich HA molecules; Ca$^{2+}$ promotes aggregation of the Aldrich hydrophobic molecules; pore clogging by these aggregates induces more severe fouling than with natural water. As Ca$^{2+}$ concentration increases, HA aggregates grow larger in size forming a backwashable cake layer.</td>
<td></td>
</tr>
</tbody>
</table>

For identical permeate volumes, flux decline occurred only in the 100 kDa membrane. DOC rejection in 10 kDa membrane deteriorated as Ca$^{2+}$ content increased from 0.5 mM to 2.5 mM and then increased again at 4 mM. In all cases, rejection increased with time. DOC rejection with 100 kDa membrane lower than with 10 kDa membrane.

Costa et al. [5], it is generally agreed that HS fouling is more severe at low pH levels. The pH level affects the charge of both the membrane surface and the HA macromolecules. These charge effects can cause different membrane materials to display different fouling propensities.

Fig. 3 illustrates the flux decline occurring at the low pH level of 3 relative to that at the higher pH level of 7. At the low pH level, the HA macromolecules are less charged. This induces a reduced electrostatic repulsion between the HA in solution and the clean membrane and between the HA in solution and the pre-formed HA fouling layer. As a result, HA deposition is enhanced leading to an intensified flux decline.

Studies on the effect of solution pH on HS fouling are summarized in Table 2.
3.3. Ionic strength

It is generally agreed that HS fouling is more severe in a high ionic strength environment. Fig. 4 illustrates the effect of increased ionic strength on the normalized flux decline. It is seen that a higher ionic strength increases the flux decline at all pH levels tested.

The reason for the deleterious effect of solution high ionic strength is that at high ionic strength HS molecules are smaller and their configurations are more spherical leading to augmented diffusivities. This promotes significant diffusion of HS into the membrane pores, leading to enhanced flux decline due to pore adsorption. High ionic strength may also compress the double layer of the HS macromolecules, leading to intensified aggregation and cake formation.

Table 3 displays studies investigating the effect of solution ionic strength on HS fouling.

3.4. Commercial HA vs. NOM

Two main types of HS fouling studies are reported in the literature: experiments carried out with synthetically extracted HA [4,5,7,9,13,17–19,21–25,27,29], predominantly supplied by Aldrich and the IHSS and experiments conducted with naturally occurring aquatic humic substances [4,7,8,10,11,14,19,20,24,25]. Compared to the HS found in natural waters which is dominated by fulvic acids, the Aldrich HA is considered to have larger molecular sizes and higher aromatic and metal contents [20].

Since humic substances of natural waters are heterogeneous mixtures of degradation products, they differ in properties affecting membrane fouling. The differences are mainly in TOC/DOC, hydrophobicity, aromaticity, charge, molecular configuration and size.

Model HA solutions are prepared by dissolving in distilled water the required amount of commercial HA, obtained usually by alkaline extraction of soil. The solution may then be adjusted to a desired pH level, to a required ionic strength by adding either NaCl or KCl and to a required divalent cations concentration, if necessary. While the use of a model HA solution has the advantage of a defined feed solution composition, an uncertainty remains due to variability in the properties of commercial HA extracted from different soil sources.

It is generally recognized that fouling is more severe in the filtration of natural water than in the filtration of commercial HA while rejection is higher for the commercial, larger HA molecules. Papers investigating commercial HA fouling vs. natural water fouling are summarized in Table 4. The augmented fouling of natural water is illustrated in Fig. 5 which compares permeate flux decline of natural water with that of a commercial HA solution.

Table 2
Effect of pH level on HS fouling.

<table>
<thead>
<tr>
<th>Researchers [ref]</th>
<th>Effect studied</th>
<th>Membrane MWCO and material</th>
<th>Feed conc. ppm (Supplier)</th>
<th>pH studied</th>
<th>Results</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kulovaara et al. 1999 [27]</td>
<td>Flux decline</td>
<td>50 kDa PS</td>
<td>Natural water 25 Nordic reference HA</td>
<td>4.5 5.5 6.5</td>
<td>Rate and extent of flux decline were significantly higher at low pH.</td>
<td>PS membrane is most positively charged at pH 4.5 resulting in a strong HA – membrane attraction. When pH increases, HA molecules are still negatively charged but are more soluble due to increased polarity. Membrane is negatively charged resulting in decreased fouling: fouling still formed by hydrophobic adsorption. Results explained by different electrostatic interactions at various pH levels.</td>
</tr>
<tr>
<td>Yuan and Zydney 2000 [18]</td>
<td>Static adsorption; Flux decline</td>
<td>30 kDa PES</td>
<td>2 (Aldrich)</td>
<td>3 7</td>
<td>Rate and extent of flux decline and static adsorption degree were significantly higher at the low pH. Rejection was lower at low pH.</td>
<td>Electrostatic interactions affect reversible and irreversible fouling resistances.</td>
</tr>
<tr>
<td>Jones and O’Melia 2001 [29]</td>
<td>Static adsorption; Flux decline</td>
<td>30 kDa regenerated-cellulose</td>
<td>25 (IHSS)</td>
<td>4.7 10</td>
<td>Rate and extent of flux decline and the degree of static adsorption were significantly higher at the low pH.</td>
<td></td>
</tr>
<tr>
<td>Costa et al. 2006 [5]</td>
<td>Flux decline</td>
<td>2 kDa CA 5 kDa CA</td>
<td>100 (Aldrich)</td>
<td>4.2 8.2</td>
<td>Rate and extent of flux decline were comparable at both pH levels.</td>
<td>Disparity of observed pH effect with literature results is attributed to differences in HA compositions.</td>
</tr>
</tbody>
</table>
It may be noted that insufficient attention has been given to the control of solution composition such that commercial and natural solutions have comparable concentrations of the fouling species.

3.5. Hydrodynamic parameters

A major fouling parameter is the foulant concentration on the membrane surface. This concentration is governed by the concentration polarization \( \frac{C}{P} \) level which according to the commonly used film model is given by:

\[
\frac{C}{P} = \frac{C_m - C_p}{C_B - C_p} = e^{k \Delta P/k}
\]  

where \( C_m \), \( C_p \), and \( C_B \) are the solute concentration on the membrane surface, of the bulk solution and of the permeate, respectively; \( J_v \) is the permeate flux and \( k \) is the mass transfer coefficient.

Eq. (1) shows that the major parameters governing the \( C/P \) level are the permeate flux \( J_v \) and the mass transfer coefficient \( k \) which can be evaluated by several methods [29].

Amy and Cho [8] compared the flux decline and flux recovery by caustic cleaning of three UF membranes at the same \( J_v/k \) ratio of 2, operated with a NOM source. Slight differences in flux decline and in recovery were observed with the three membranes. As may be anticipated, increase of the \( J_v/k \) level induced a flux decline due to fouling and decreased the rejection.

In their study on the effect of operating conditions on membrane fouling, Crozes et al. [11] found that one of the important control parameters is the concentrate velocity. It was found that irreversible fouling could be contained by applying short-term filtration cycles operated at increased concentrate velocities, at reduced fluxes and at frequent backwash cycles. The result of this study indicates that there is scope for investigating the possibility of containing HS fouling by applying the “critical flux” concept [30] which presumes the existence of a flux level below which no significant fouling is anticipated.

An investigation of HS deposition using the critical flux concepts was made by Bowen et al. [26]. Their main effort was to demonstrate the superior performance of membranes made of blends of polysulphone and sulphonated poly(ether ether ketone) (PSU/SPEEK). A plot of fractional deposition rate of particles vs. \( J_v/k \) provided linear relationships. For a 2 kDa cellulose acetate membrane and 4 kDa aromatic polyether sulphone membrane, the fractional deposition curves passed through the origin, signifying that particle deposition on the membrane occurred at all fluxes. However, for the S5-20 PSU/SPEEK membrane, the straight line crossed the x axis at \( J_v/k = 4.6 \) for the T5-20 PSU/SPEEK membrane, the straight line crossed the x axis at \( J_v/k = 6.4 \). These results were considered to indicate a critical flux of 34.8 Lm/h for the S5-20 membrane below which no particle deposition is anticipated and of 16.9 Lm/h for the T5-20 membrane.

3.5.1. Pressure limited fouling model

A group of researchers in the University of Budapest [24,25] attempted to determine the mass transfer coefficient of HA in a well defined geometry system of a hollow fiber module, on the basis of the gel layer model which relates the pressure limited flux \( J_v \) to mass transfer coefficient \( k \) by:

\[
(J_v)_{\text{max}} = k \ln \frac{C_f}{C_B}
\]  

where \( C_f \) is the feed concentration and \( C_B \) is the gel concentration. Values of \( k \) were determined from linear plots of \( (J_v)_{\text{max}} \) vs. \( \ln C_B \).
<table>
<thead>
<tr>
<th>Researchers [ref]</th>
<th>Effect studied</th>
<th>Membrane MWCO and material</th>
<th>Commercial HA conc. ppm</th>
<th>Natural water</th>
<th>Results Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maartens et al. 1999 [19]</td>
<td>Flux decline; HS rejection</td>
<td>40 kDa PSM (Fluka)</td>
<td>80</td>
<td>Natural water characterized by light absorbance data</td>
<td>Flux decline was slightly greater with natural water. Rejection was lower with natural water and improved with time. Rejection was higher with commercial HA and constant with time. Commercial HA solution has mainly large molecules. Natural water is more heterogeneous in nature, having both large and small molecules. Rejection improvement is due to evolvement of pore constriction that hinders the passage of smaller particles.</td>
</tr>
<tr>
<td>Kulovaara et al. 1999 [27]</td>
<td>Flux decline</td>
<td>50 kDa PS (Nordic reference HA)</td>
<td>25</td>
<td>Lake water 15–20 ppm DOC</td>
<td>Rate and extent of flux decline was higher with natural water relative to commercial HA. Under comparable hydrodynamic conditions, notably same C/P levels, flux decline was similar for all waters at relatively low C/P conditions; at high C/P level, a small increase in flux decline was observed at increasing aromaticity (SUVA level). Rejection was higher as the humic content and aromaticity level were higher. Natural water is assumed to contain either abiotic or biotic components that enhance fouling inside the pores or on the membrane.</td>
</tr>
<tr>
<td>Amy and Cho 1999 [8]</td>
<td>Flux decline; HS rejection</td>
<td>3 kDa CEL; 8 kDa PA; 10 kDa PES; 20 kDa PES</td>
<td>–</td>
<td>5 sources of natural waters, high to low TOC levels (2–48 ppm) and aromaticity (SUVA range of 2.4 to 5.7 L/m mg)</td>
<td>Flux decline was higher with natural water relative to commercial HA. Rejection improvement is due to evolvement of pore constriction that hinders the passage of smaller particles.</td>
</tr>
<tr>
<td>Yuan and Zydney 2000 [18]</td>
<td>Flux decline; Membrane surface properties</td>
<td>30 kDa PES; 50 kDa PES; 100 kDa PES; 300 kDa PES</td>
<td>2 (Soil-base Aldrich); pH = 7</td>
<td>–</td>
<td>Under comparable hydrodynamic conditions, notably same C/P levels, flux decline was similar for all waters at relatively low C/P conditions; at high C/P level, a small increase in flux decline was observed at increasing aromaticity (SUVA level). Rejection was higher as the humic content and aromaticity level were higher. It is claimed that low C/P enables NOM molecules to diffuse away from the membrane resulting in a decreased flux decline and an increased rejection.</td>
</tr>
<tr>
<td>Domany et al. 2002 [4]</td>
<td>HS rejection</td>
<td>5 kDa PAES; 6 kDa PES; 15 kDa PES; 100 kDa PES</td>
<td>9 (Aldrich)</td>
<td>Well water 11 ppm TOC</td>
<td>With all membranes, rejection of commercial HA was at a higher level (90%) than the rejection of HS of natural water (60–70%). Authors recommend improving removal efficiency by adding a flocculent or using membranes with smaller pore sizes.</td>
</tr>
<tr>
<td>Galambos et al. 2005 [24] Ciszar et al. 2006 [25]</td>
<td>Estimation of mass transfer coeff.; Evaluation of gel concentration</td>
<td>1 kDa PS; 2 kDa PS</td>
<td>11.8 (Aldrich)</td>
<td>Three well waters of 11–23 ppm TOC</td>
<td>It was claimed that HA flux decline obeys the pressure limited UF/MF gel model; gel concentration of 2.4 g/L was obtained for the commercial HA solution and 18–54 g/L for the natural water solutions. It was claimed that conventional mass transfer correlations are in agreement with experimental measurements. A mass transfer model for transient flow was proposed. The paper does not provide adequate evidence to support their conclusions.</td>
</tr>
<tr>
<td>Yamamura et al. 2007 [7]</td>
<td>Fouling irreversibility due to presence of Ca</td>
<td>100 kDa PAN; 100 kDa PES</td>
<td>3 mg-C/L (Aldrich) Ca(^{2+} = 8) ppm</td>
<td>Chitose river 2.2 mg-C/L Ca(^{2+} = 8) ppm</td>
<td>With Aldrich HA, presence of Ca affected backwashability with PES membrane but not with PAN membrane. With natural water, no effect of Ca(^{2+}) was observed with both membranes. Difference in fouling effects of Ca(^{2+}) between Aldrich HA and natural water attributed to the more hydrophobic nature of Aldrich HA molecules; Ca promotes aggregation of the Aldrich hydrophobic molecules. Pore clogging by these aggregates induces more severe fouling than in natural water.</td>
</tr>
</tbody>
</table>

Table 4
Commercial HA fouling vs. natural water fouling.
and compared to values predicted from classical mass transfer correlations.

The authors do not provide sufficient experimental information. No evidence is given in support of their basic premise that HA fouling is a pressure limited process and that indeed their tested system provided a constant $C_C$ value, regardless of the membrane used.

4. Membrane aspects

Membrane characteristics exert a profound influence on the extent of fouling. The dominant property is not the membrane material per se but its physico-chemical attributes such as:

- adsorption propensity which depends on membrane properties – charge, hydrophobicity etc.
- porous structure which characterizes MWCO of the membrane and permeate flux.

4.1. Pore size and MWCO

One of the main drawbacks of studies aiming to investigate the effect of MWCO on HS fouling and rejection lies in the inadequate definition of the pore size distribution and overall membrane porosity. Differences in the performance of membrane MWCO are due not only to average pore size but also to pore size distribution and membrane overall porosity. Deeper insight on MWCO effects could be obtained by tests on membranes of well defined porous structures.

The effect of pore size and MWCO on the fouling intensity was investigated in studies summarized in Table 5. Virtually all studies except that of Lowe and Hossain [13] found that fouling is more severe in the more porous high MWCO membranes than in the less porous low MWCO membranes.

Fig. 6 illustrates the flux reduction after 2 h, measured by Yuan and Zydney [18] at a pressure of 69 kPa, in four membranes having MWCO of 30, 100, 300 kDa and in a 0.16 μm microfiltration membrane. The mean initial fluxes of the 30, 100, 300 kDa and 0.16 μm various membranes were: 7.25, 20.9, 31.9 and 128.1 ($\times 10^5$ m/s), respectively. The decrease in fouling with the MWCO level is evident with the two different HA feeds examined. This result has generally been attributed to differences in the fouling mechanisms; a membrane with larger pore size enables pore constriction in addition to cake formation while a tight membrane is more likely to form a cake layer only [8,9,17,18,31 – cited in 5]. The more severe flux decline in a porous membrane is due to the greater flow resistance imposed by adsorption of small particles within pores than the resistance induced by cake build-up.

It should be realized however that experiments conducted under identical applied pressures rather than identical fluxes are strictly not comparable. The higher permeation flux obtained with the more porous membrane is by itself a factor leading to enhanced transport of the fouling species towards the membrane. Tests under identical permeation fluxes are more instructive.

There is an agreement that fouling encountered in experiments carried out under either identical pressures or identical fluxes, involves both pore constriction and cake formation. The experimental evidence indicates that the increased fouling propensity of high MWCO membranes at comparable permeate fluxes is due to the more rapid pore constriction process and an earlier inception of cake formation. However, clearer insight into these phenomena awaits further research.

4.2. Membrane charge and hydrophobicity

Due to electrostatic interactions, membrane charge is expected to influence fouling formed by charged particles such as humic particles; conversely, such fouling may modify the membrane charge. Membrane rejection is an indicator to these electrostatic interactions. For instance, rejection may be lowered when colloids are attracted to the membrane surface due to opposite charges.

Zeta potential [31] is a useful indicator of the membrane surface charge. A change in the zeta potential value may indicate fouling formation because deposit surface properties can differ from clean membrane surface properties.

Membrane hydrophobicity/hydrophilicity is commonly determined by measuring the membrane surface contact angle. A change in the contact angle may indicate fouling formation because of differences in surface properties of the deposit and the clean membrane. Contact angles are commonly measured by the sessile drop method [32]. A goniometer is used to determine the contact angle of the water droplet on the membrane surface in the ambient air. A low contact angle indicates high water affinity.

Table 6 summarizes studies investigating the effects of membrane charge and hydrophobicity on the fouling extent.

5. Membrane cleaning and fouling reversibility

Membrane fouling is detected by the decrease in permeate flux. The flux decline is induced by the accumulation of fouling species either on the membrane surface or inside the membrane pores or in both locations. Flux restoration is a crucial issue. Most membrane configurations allow partial permeate flux recovery by applying a counter flow (backwash). Backwash usually removes fouling species deposited on the membrane surface so that non-adherent matter on the membrane is considered to be reversible fouling. However, the material trapped inside the pores cannot be usually dislodged by backwash and is therefore considered to be irreversible fouling. Moreover, after a long period of operation, a reversible fouling tends to lose its reversibility and the irreversible fouling fraction gradually increases [11].

Irreversible fouling may sometimes be eliminated by chemical cleaning. However, the frequency of such a costly procedure should be limited because repeated cleaning tends to shorten membrane life and the disposal of spent chemicals poses environmental difficulties. Prevention of irreversible fouling is clearly an important goal. However, currently there is insufficient understanding on the parameters governing the extent of irreversible fouling.

The success of a cleaning procedure is usually measured by the extent of permeate flux restoration [19]. The effectiveness of a backwash operation is characterized by the frequency and duration of each cycle and that of a cleaning procedure, by the composition of the cleaning solution and the frequency of its application.

The actual backwash or cleaning procedure used has a major influence on the effectiveness of the operation so that care should be therefore taken in comparing results. In general, a caustic soda solution of about 0.1 N is used to dissolve HA residuals. Cakes formed...
Table 5
Effect of membrane pore size on HS fouling.

<table>
<thead>
<tr>
<th>Researchers [ref]</th>
<th>Effect studied</th>
<th>Membrane MWCO and material</th>
<th>Feed conc. ppm (supplier)</th>
<th>Constant ΔP</th>
<th>Constant Jc [lmh]</th>
<th>Results</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yuan and Zydney al. 2000 [18]</td>
<td>Flux decline; HS rejection; Membrane surface properties</td>
<td>30 kDa PES 50 kDa PES 100 kDa PES 300 kDa PES</td>
<td>2 (Aldrich) 2 (BSS)</td>
<td>69 kPa –</td>
<td>–</td>
<td>A similar flux decline was observed with the 30 kDa membrane in both types of feed water; minor differences found in larger pore size membranes. An uncommon phenomenon was the significant increase in rejection with filtration time in the large pore size membrane (from less than 20% to about 80% in 30 minutes).</td>
<td>A similar flux decline was observed with the 30 kDa membrane in both types of feed water; minor differences found in larger pore size membranes. An uncommon phenomenon was the significant increase in rejection with filtration time in the large pore size membrane (from less than 20% to about 80% in 30 minutes).</td>
</tr>
<tr>
<td>Domany et al. 2002 [4]</td>
<td>HS rejection</td>
<td>5 kDa PAES 6 kDa PES 15 kDa PES 100 kDa PES</td>
<td>9 (Aldrich) 11 ppm TOC well water</td>
<td>1–6 bar –</td>
<td>–</td>
<td>All UF membranes exhibited with commercial HA a higher rejection (85–90%) compared with the rejection of natural well water HS (62–70%). Except for the low rejection observed with the MWCO membrane of 100 kDa, results of all other membranes were in substantial agreement with those of the Domany et al. [4].</td>
<td>All UF membranes exhibited with commercial HA a higher rejection (85–90%) compared with the rejection of natural well water HS (62–70%). Except for the low rejection observed with the MWCO membrane of 100 kDa, results of all other membranes were in substantial agreement with those of the Domany et al. [4].</td>
</tr>
<tr>
<td>Galambos et al. 2004 [6]</td>
<td>HS rejection Continuation of Domany et al. study [4]</td>
<td>1 and 2 kDa unspecific material 5 kDa PAES 6 kDa PES 15 kDa PES 100 kDa PES</td>
<td>Natural water 10 (Aldrich)</td>
<td>0.5–20 bar –</td>
<td>–</td>
<td>A linear relationship between flux and pressure was observed for tight membranes (2.3–20 kDa); non-linear relationship was observed in the more porous membranes (50–75 kDa) with evidence for the existence of a limiting flux. A higher flux decline was observed in the porous membranes. The tight membranes showed almost 100% rejection regardless of solution chemistry. Rejection was found to decrease with increasing ionic strength in the more porous membrane.</td>
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</tr>
<tr>
<td>Costa and de Pinho 2005 [9]</td>
<td>Permeate flux decline; HS rejection</td>
<td>2.3 kDa CA 9 kDa CA 20 kDa CA 50 kDa CA 75 kDa CA</td>
<td>10 (Aldrich)</td>
<td>1–4 bar –</td>
<td>–</td>
<td>Linear relationship between flux and pressure was observed for tight membranes (2.3–20 kDa); non-linear relationship was observed in the more porous membranes (50–75 kDa) with evidence for the existence of a limiting flux. A higher flux decline was observed in the porous membranes. The tight membranes showed almost 100% rejection regardless of solution chemistry. Rejection was found to decrease with increasing ionic strength in the more porous membrane.</td>
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</tr>
<tr>
<td>Costa et al. 2006 [5]</td>
<td>Flux decline</td>
<td>2 kDa, CA 75 kDa, CA</td>
<td>100 (Aldrich)</td>
<td>– ~100</td>
<td>–</td>
<td>A more pronounced flux decline was observed with the larger pore size membrane.</td>
<td>Pore blocking is the dominant fouling mechanism at the initial filtration stage in both membranes. Subsequently, transition from pore blocking to cake formation occurs faster with the more permeable membrane.</td>
</tr>
<tr>
<td>Mousa, 2007 [17]</td>
<td>Membrane resistance</td>
<td>10 kDa PS 50 kDa PS 100 kDa PS 20 kDa PAN 100 kDa PAN</td>
<td>1–20 (Aldrich)</td>
<td>35 kPa –</td>
<td>–</td>
<td>In the case of the PS membranes, flux reduction decreased with the reduction in membrane pore size. In the case of the PAN membranes, an opposite trend was observed.</td>
<td>In the case of the PS membranes, flux reduction decreased with the reduction in membrane pore size. In the case of the PAN membranes, an opposite trend was observed.</td>
</tr>
<tr>
<td>Lowe and Hossain 2008 [13]</td>
<td>Flux decline; HS Rejection</td>
<td>3.5,10 kDa Regenerated Cellulose 10–50</td>
<td>0.5–4.5 bar</td>
<td>–</td>
<td>–</td>
<td>All tested membranes showed a high rejection level, amounting to 80–90%. Contrary to results of others, fouling was more severe in tighter membranes (3 and 5 kDa) than in the larger pore size membrane (10 kDa).</td>
<td>All tested membranes showed a high rejection level, amounting to 80–90%. Contrary to results of others, fouling was more severe in tighter membranes (3 and 5 kDa) than in the larger pore size membrane (10 kDa).</td>
</tr>
</tbody>
</table>

Table 7 summarizes studies investigating the effect of operating conditions on fouling reversibility.

6. Correlation of HS fouling data

Although the qualitative effects of natural organic matter on the performance of membrane systems are now reasonably well understood, there is still considerable disagreement over the actual mechanisms involved in the fouling process [18]. Most correlations on the membrane surface are often removed by backwashes applied every 30–90 min.

The complexity of the phenomena involved in the formation of irreversible as opposed to reversible fouling may be illustrated by the study of Yamamura et al. [7] on the influence of Ca²⁺ on the evolution of irreversible fouling. The addition of Ca²⁺ to commercial HA solution promoted formation of aggregates which plugged membrane microspores. Fig. 7 shows that backwashing was unable to restore the permeate flux to its original level thus indicating that the fouling was irreversible.
aiming to model HS fouling data are based on expressions derived from the blocking filtration laws, discussed below.

6.1. Blocking filtration models

The filtration blocking expressions assume the porous membrane matrix to consist of a set of parallel capillaries conforming to Poiseuille flow. Four distinctive blocking mechanisms, illustrated in Fig. 8, are considered to be involved in the filtration process:

A) Cake filtration — particles accumulate as a cake layer whose resistance is proportional to its thickness.
B) Intermediate blocking — particles settle on previously deposited particles; each location has an equal probability of being occupied; thus, the probability of a particle settling on a free site equals the ratio of free to occupied sites ([34]).
C) Standard blocking (pore constriction) — particles settle inside cylindrical pores causing a progressive restriction of the free pore volume; the occupied pore volume is proportional to the filtered volume ([35]).
D) Complete blocking — it is assumed that the porous medium consists of uniform capillary tubes, that each capillary pore is completely blocked by an individual particle and that no cake deposits are on the membrane ([35]).

Hermans and Bredée showed that for constant pressure filtration all blocking models are derived from the following unique differential equation relating filtration time t with filtrate volume V [35–40]:

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

The different blocking mechanisms are distinguished by values of the parameter n: n = 0 for filtration of an incompressible cake, n = 1 for intermediate blocking, n = 1.5 for standard blocking and n = 2 for complete blocking.

Table 6

<table>
<thead>
<tr>
<th>Researchers [ref]</th>
<th>Effect studied</th>
<th>Membrane</th>
<th>Clean membrane measured values:</th>
<th>Feed conc. ppm (supplier)</th>
<th>Results</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cho et al. 1999 [10]</td>
<td>HS rejection</td>
<td>8 kDa PA 10 kDa PES 20 kDa PES 3 kDa CEL 8 kDa TFC</td>
<td>CEL — 8.5 mV; rest: –13 to –22 mV CEL 13°; rest: 51° to 62°</td>
<td>2—48 ppm DOC Six natural water sources</td>
<td>Higher rejection at the higher MWCO membrane. The more hydrophobic membrane exhibited a more severe flux decline.</td>
<td>The higher rejection level exhibited by higher MWCO membranes of higher negative surface charge indicates that membrane charge dominates rejection. The more hydrophobic membrane exhibits a more severe flux decline due to the hydrophobic nature of the HS substances in the feed water. Solution pH affects both the membrane charge and the colloids charge thus strongly influencing rejection and flux decline. When the membrane and the colloids have an opposite charge, rejection is lowered and fouling is enhanced. The zeta potential increase is attributed to HS adsorption inside the pores; the contact angel increase is attributed to the deposition of a cake layer on the membrane.</td>
</tr>
<tr>
<td>Amy and Cho 1999 [8]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kulovaara et al. 1999 [27]</td>
<td>Flux decline</td>
<td>50 kDa PS 25 (Nordic-reference HA) 15–20 ppm DOC Lake water</td>
<td></td>
<td></td>
<td>At decreasing pH, HA deposition decreased membrane zeta potential: At pH 6.5, ( \Delta \zeta = -5 ) to (-10 ) mV At pH 5.5, ( \Delta \zeta = -10 ) to (-20 ) mV At pH 4.5, ( \Delta \zeta = -21 ) to (-34 ) mV Flux reduction was highest at the lowest pH level. HA deposition significantly increased the zeta potential, by 15–50%. HA deposition significantly increased the contact angel, by 20–70°.</td>
<td>The higher rejection level exhibited by higher MWCO membranes of higher negative surface charge indicates that membrane charge dominates rejection. The more hydrophobic membrane exhibits a more severe flux decline due to the hydrophobic nature of the HS substances in the feed water. Solution pH affects both the membrane charge and the colloids charge thus strongly influencing rejection and flux decline. When the membrane and the colloids have an opposite charge, rejection is lowered and fouling is enhanced. The zeta potential increase is attributed to HS adsorption inside the pores; the contact angel increase is attributed to the deposition of a cake layer on the membrane.</td>
</tr>
<tr>
<td>Yuan and Zydney 2000 [18]</td>
<td>Flux decline: HS rejection; Membrane surface properties</td>
<td>30 kDa PES 300 kDa PES 30 kDa: –16 to –12 mV 300 kDa: –22 mV 30 kDa: 44°</td>
<td>2 (Aldrich) 2 (IHSS)</td>
<td></td>
<td>In the absence of Ca(^{2+}) the change in membrane zeta potential due to HS deposition was higher: ( \Delta \zeta = -28.7 ) at 0 ppm Ca(^{2+}) ( \Delta \zeta = -23.3 ) at 1.25 mM Ca(^{2+})</td>
<td>In the presence of Ca(^{2+}), negatively charged HA particles are neutralized by the Ca(^{2+}) ions.</td>
</tr>
<tr>
<td>Jermann et al. 2007 [23]</td>
<td>Effect of Ca(^{2+}) on membrane zeta potential</td>
<td>100 kDa PES</td>
<td>-16.1 mV</td>
<td>2 ppm (IHSS)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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complete blocking. The coefficient $k_n$ embodies parameters characterizing the specific fouling mechanism.

Table 8 [41] provides model equations for flux reduction at constant filtration pressure, according to the various blocking mechanisms. The equations are presented in a more instructive way than commonly published in the literature [36–39] by highlighting the rate of flux decline caused by fouling according to the various blocking mechanisms.

Fouling correlations have been made either according to the basic differential equation [Eq. (3)] or according to the integrated expressions given in Table 8. The slope $n$ can serve to identify the fouling mechanism according to Eq. (3) if the experimental data

<table>
<thead>
<tr>
<th>Researchers [ref]</th>
<th>Effect studied</th>
<th>Membrane MWCO and material</th>
<th>Feed conc. ppm (supplier)</th>
<th>Results</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crozes et al. 1997 [11]</td>
<td>Operating flux; Backwash frequency</td>
<td>100 kDa Cellulosic derivative</td>
<td>Natural water</td>
<td>Pilot testing provided evidence that irreversible fouling could be controlled by limiting short-term reversible fouling through increase of concentrate velocity, flux reduction (AP–0.85–1.0 bar) and increasing backwash frequency.</td>
<td>Important conclusion of the paper is that irreversible membrane fouling depends not only on physico-chemical parameters but also on operating parameters.</td>
</tr>
<tr>
<td>Maartens et al. 1999 [19]</td>
<td>Efficiency of various cleaning agents,  analyzed by constant pressure normalized flux decline</td>
<td>40 kDa PSM 80 (Fluka)</td>
<td>Detailed data provided on the pure water flux restoration after cleaning with 6 different cleaning solutions. Some cleaning solutions increased flux above its original value but rejections were concomitantly decreased indicating a deleterious effect of the cleaning solution.</td>
<td>The increase in ionic strength decreases the hydration double layer surrounding molecules. This promotes coating and compaction of the molecules, leading to enhanced pore plugging. Compared to the membrane pore size, humic–iron aggregates are not big enough to be completely retained by the membrane. The cleaning efficiency of a simple wiping operation indicated that the fouling was mainly located on the membrane surface.</td>
<td></td>
</tr>
<tr>
<td>Kulovaara et al. 1999 [27]</td>
<td>Ionic strength, analyzed by constant pressure normalized flux decline</td>
<td>50 kDa PS</td>
<td>25 (Nordic reference HA)</td>
<td>Increase in ionic strength converted part of the reversible fouling to irreversible fouling. Coagulant dosage (Fe ions) increased irreversibly fouling without significantly affecting the reversible fouling.</td>
<td></td>
</tr>
<tr>
<td>Yuan and Zydny 2000 [18]</td>
<td>Membrane pore size, analyzed by hydraulic permeability decline at constant pressure</td>
<td>30 kDa PES 300 kDa PES</td>
<td>10 (Aldrich)</td>
<td>The 30 kDa membrane showed a flux decline of 27%; physical cleaning (wiping) restored the flux to 91% of its original value. The 300 kDa membrane showed a higher flux decline of 65% and a lower flux restoration, to 49% of its original value. Alkaline cleaning had practically no effect on the 30 kDa membrane and had some effect on the 300 kDa membrane.</td>
<td></td>
</tr>
<tr>
<td>Taniguchi et al. 2003 [20]</td>
<td>Feed concentration; Feed prefiltration; Membrane pore size Analyzed by flow resistance after withdrawal of 10 gram of permeate at constant pressure</td>
<td>10 kDa PES 30 kDa PES 50 kDa PES 70 kDa PES 100 kDa PES 300 kDa PES 500 kDa PES 1000 kDa PES</td>
<td>Natural water</td>
<td>Irreversible fouling noted only in membranes with MWCO up to 100 kDa. Reversible fouling was practically the same for all membranes. Dilution of the feed concentration by 50% or feed prefiltration through 0.45 μm filter reduced the reversible fouling by 50% in membranes of MWCO up to 100 kDa; a higher reduction in reversible fouling was observed in the larger pore size membranes and the irreversible fouling extent also diminished.</td>
<td>Irreversible fouling does not form on large MWCO membranes because NOM particles are able to pass through the pores. Irreversible fouling occurs in the low MWCO membranes by passing through of small NOM particles. Aggregates contribute to reversible fouling. Similar backwashable cake layers formed by aggregates are observed in all membranes regardless of their MWCO. Prefiltration is able to remove some of the species that contributed to irreversible fouling.</td>
</tr>
<tr>
<td>Yanamura et al. 2007 [7]</td>
<td>Ca$^{2+}$ addition, analyzed by normalized flux decline at constant pressure</td>
<td>100 kDa PAN 100 kDa PES</td>
<td>3 mg-C/L (Aldrich) pH = 7 Ca = 8 ppm Natural water</td>
<td>Ca$^{2+}$ in commercial HA solution promoted aggregates formation, plugging micropores and inducing severe irreversible fouling. Ca$^{2+}$ in natural water promoted irreversible fouling only in some of the membranes. No irreversible fouling was detected with PAN membranes.</td>
<td>Ca$^{2+}$ facilitates aggregation of small hydrophobic molecules of commercial HA; the aggregates can block membrane pores and lead to severe irreversible fouling. Membrane material has a great influence on the degree of irreversible fouling. The reason for lack of irreversible fouling in PAN membranes is not clear.</td>
</tr>
<tr>
<td>Jermann et al. 2007 [23]</td>
<td>Ca$^{2+}$ addition, analyzed by normalized flux decline at constant pressure</td>
<td>100 kDa PES 2 ppm (IHSS)</td>
<td>Normalized irreversible flux decline somewhat increased by the presence of Ca$^{2+}$; (42–54% in the absence of Ca$^{2+}$; 71–82% in the presence of 1.25 mM Ca$^{2+}$).</td>
<td>Most of the HA fouling is of irreversible nature due to adsorption. Ca$^{2+}$ induces stronger interactions between HA molecules and the membrane.</td>
<td></td>
</tr>
<tr>
<td>Katsoufidou et al. 2005, 2008 [21,22]</td>
<td>Ca$^{2+}$ addition; Feed prefiltration Analyzed by normalized flux decline at constant pressure</td>
<td>150 kDa PES 10 (Aldrich)</td>
<td>Flux decline was more severe in the absence of backwash. Ca$^{2+}$ reduced flux recovery by backwash; at high Ca$^{2+}$ concentration backwash provided a minor flux recovery. Feed prefiltration reduced the extent of flux decline at all Ca$^{2+}$ concentrations but did not provide full flux recovery.</td>
<td>In the presence of Ca$^{2+}$, a more cohesive gel layer is formed on the membrane.</td>
<td></td>
</tr>
</tbody>
</table>
display a linear plot of $\log \frac{dV}{dt}$ vs. $\log \frac{dt}{dQ}$ However, it is well known that even a first differentiation of data magnifies considerably the experimental error and a double differentiation, even more so. Nevertheless this technique seems to have yielded useful results. This is illustrated in Fig. 9 which shows the analysis of Costa et al. [5] on the effect membrane pore size on HA fouling mechanism. Flux decline data were measured with two cellulose acetate membranes: CA1 membrane having a MWCO of 2 kDa and CA5 membrane of MWCO of 75 kDa. It is seen that at short filtration times which correspond to low values of $dt/dV$, the data of both membranes yield a linear relationship with a slope of 2, indicating that filtration was governed by pore blocking. At higher values of $dt/dV$, the CA1 curve reaches a plateau indicating a slope of $n=0$, suggesting a cake formation mechanism. No explanation was given for the sharp negative slope observed with membrane CA5.

The more widely used technique for identifying fouling mechanisms is by searching which of the model equations listed in Table 8 fits the experimental data. The difficulties involved are illustrated in hypothetical plot of $t/V$ vs. $V$, shown in Fig. 10. The initial curve depicting a gradual reduction in the slope with increasing permeate volume can result from either a pore constriction or a pore blocking mechanism. The second linear curve characterizes well the filtration mechanism of an incompressible cake. The final curve which indicates a considerable increase in flow resistance can arise either from formation of a compressible cake or from subsequent clogging of cake flow passages.

Despite the wide use of the above simple fouling models to analyze flux decline data, it was pointed out by van Reis and Zydnei [43] in their authoritative review that there is considerable experimental evidence that changes in mechanism often occur invalidating this simple approach. More sophisticated models are described in Section 6.2.

### Table 8

<table>
<thead>
<tr>
<th>$n$</th>
<th>Fouling mechanism</th>
<th>Flow rate</th>
<th>Fouling rate</th>
<th>Initial Fouling rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Cake filtration</td>
<td>$Q = \frac{dV}{dt} = \frac{Q_0}{\sqrt{1 + \frac{t}{\tau}}} \alpha$</td>
<td>$-\frac{dQ}{dt} = \frac{\alpha Q_0^2}{\left[1 + \frac{t}{\tau} \alpha \right]}$</td>
<td>$-\frac{dQ}{dt}_{t=0} = \frac{\alpha Q_0^2}{\left[1 + \frac{t}{\tau} \alpha \right]}$</td>
</tr>
<tr>
<td>1</td>
<td>Intermediate law</td>
<td>$Q = \frac{dV}{dt} = \frac{Q_0}{1 + \frac{t}{\tau}}$</td>
<td>$-\frac{dQ}{dt} = \frac{\alpha Q_0^2}{\left[1 + \frac{t}{\tau} \alpha \right]}$</td>
<td>$-\frac{dQ}{dt}_{t=0} = \frac{\alpha Q_0^2}{\left[1 + \frac{t}{\tau} \alpha \right]}$</td>
</tr>
<tr>
<td>1.5</td>
<td>Standard law</td>
<td>$Q = \frac{dV}{dt} = Q_0 \exp \left[-\frac{\alpha t}{\tau} \right]$</td>
<td>$-\frac{dQ}{dt} = \frac{\alpha Q_0^2}{\left[1 + \frac{t}{\tau} \alpha \right]}$</td>
<td>$-\frac{dQ}{dt}_{t=0} = \frac{\alpha Q_0^2}{\left[1 + \frac{t}{\tau} \alpha \right]}$</td>
</tr>
<tr>
<td>2</td>
<td>Complete blocking</td>
<td>$Q = \frac{dV}{dt} = Q_0 \exp \left[-\frac{\alpha t}{\tau} \right]$</td>
<td>$-\frac{dQ}{dt} = \frac{\alpha Q_0^2}{\left[1 + \frac{t}{\tau} \alpha \right]}$</td>
<td>$-\frac{dQ}{dt}_{t=0} = \frac{\alpha Q_0^2}{\left[1 + \frac{t}{\tau} \alpha \right]}$</td>
</tr>
</tbody>
</table>

6.2. Combined blocking models

Models based on a single blocking mechanism have been justly criticized by Katsou et al. [21,22] claiming that fouling generally involves several simultaneous mechanisms. They proposed a model combining pore constriction, pore mouth blocking and cake formation (Fig. 11). The increase in membrane resistance $R_m$ due to adsorption within the pores and to blocking of pore mouths was given by:

$$R_m = R_{mo} \left(\frac{D_0}{D}\right)^4 / \phi_p$$

where $D_0$ is the initial diameter; $R_{mo}$ is the initial membrane resistance and $\phi_p$ is the fraction of the free pores, governed by the intermediate pore blockage mechanism.

The increased cake resistance was evaluated by:

$$R_c = R_s H$$

where $R_s$ is the specific cake resistance. The change in the cake height $H$ was evaluated from the mass balance:

$$\frac{dH}{dt} = J_{fl} / \phi_c$$

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where \( J \) is the water flux, \( \phi_{Lb} \) is the bulk concentration of large particles and \( \phi_c \) is the cake volume fraction.

Experimental data were measured in dead-end filtration of commercial HA at a concentration of 10 ppm through a 150 kDa PES membrane. The data were correlated by the model using five adjustable parameters.

Yuan et al. [44] correlated HS fouling data by a different model based on pore blocking and cake formation, developed and successfully applied by Ho and Zydney [45] in their protein fouling study. The model analyzes dead-end filtration and assumes that the initial flux decline is due to pore blocking caused by physical deposition of large HA aggregates on the membrane surface. A cake is then formed on those regions that have been covered by the aggregates. The expression derived for filtrate flux is:

\[
\frac{J}{J_0} = \exp\left(-\frac{\alpha \Delta P C_{kt}}{\mu R_m t} \right) + \frac{R_m}{R_m + R_c} \left[1 - \exp\left(-\frac{\alpha \Delta P C_{kt}}{\mu R_m t} \right)\right]
\]  

where the first term is the flow rate through the open pores according to the classical pore blocking model and the second term describes the flow through the blocked pores. \( J_0 \) is the initial flux through the unfouled membrane and \( R_c \) is the resistance of the cake that forms over the membrane surface. Analysis of HA experimental data according to the above model indicated that there is a flux below which cake formation becomes negligible.

The same Ho and Zydney [45] model was also used by Taniguchi et al. [20] in their study of the effect of pretreatment on HA fouling mechanisms. Analysis of the fouling data indicated that for filtration carried out with membranes of large pore size, pretreatment of the raw water alters the fouling mechanism from the cake filtration to pore blocking.

The inherent difficulty in indentifying the mechanism governing a fouling process is highlighted by the study of Chang and Benjamin [14]. As shown below, three different models were able to provide a reasonable correlation of the data.

NOM filtration experiments were carried out in a dead-end mode through a 100 kDa membrane. The progress of the observed fouling is described in Table 9. The data showed a linear increase of total resistance with time; this was ascribed to the formation of a fouling gel layer having a resistance \( R_{gel} \).

Three independent fouling models were examined. The first model attributed the fouling to an increase of the effective pore length by an
amount equal to the thickness of the NOM gel layer that forms on the membrane surface. The membrane resistance $R_m$, assumed constant, was evaluated by:

$$R_m = \frac{32 \delta_m}{f_p D_{p,m}}$$  \hspace{1cm} (8)

where $\delta_m$ is the membrane thickness, $f_p$ is the porosity and $D_{p,m}$ is the diameter of the pores. The resistance of the fouling layer $R_{fgel}$ was evaluated by:

$$R_{fgel} = \frac{32 \delta_{fgel}}{f_{fgel} D_{fgel,m}}$$  \hspace{1cm} (9)

where $\delta_{fgel}$ is the fouling layer thickness, $f_{fgel}$ is the porosity of the fouling layer and $D_{fgel,m}$ is the diameter of the pores inside the fouling layer. The observed linear relationship between $R_{fgel}$ and the measured gel thickness $\delta_{fgel}$ indicated that $f_{fgel} D_{fgel,m} = 8.7 \times 10^{-6}$ m$^2$. The membrane parameters $f_p = 9.4\%$ and $D_{p,m} = 9.6$ nm conform to the value measured in the gel layer, giving support to the assumption of gel layer thickening at constant porosity.

The second model assumed that the gel layer was formed as a continuous porous cake rather than an impermeable film containing discrete pores. The Carman–Kozeny relationship was used to characterize the resistance of the fouling layer of thickness $\delta_{fgel}$ formed by particles of spherical diameter $d_{eq}$.

$$R_{fgel} = \frac{K (6/d_{eq})^2 (1-e)^2}{e^2} \delta_{fgel}$$  \hspace{1cm} (10)

where $K$, the Carman–Kozeny constant, is commonly assumed to equal 5 and $e$ is the void volume of the layer. The experimental values of $R_{fgel}/\delta_{fgel}$ provided possible combinations of $d_{eq}$ and $e$. For a reasonable range of cake porosities ($0.2$–$0.5$), the range of equivalent diameters for the particles comprising the cake was $10$–$60$ nm. However, most NOM molecules have a characteristic length of less than $10$–$20$ nm. Hence, this model implied that the primary particles comprising the cake layer were aggregates of NOM molecules.

The third model described fouling as a pore constriction phenomenon and assumed that the number of pores and the length of each pore remain constant while the pressure drop across the cake layer is negligible. The flux decline over 20 h of operation could then be attributed to a constriction of $32\%$ of the effective pore diameter of the pores. This decline corresponds to the coating of pores of initial diameter of $5$, $10$ and $20$ nm by a uniform layer of $0.8$, $1.6$ and $3.4$ nm thickness, respectively. All these values are within the range of the diameter of a single NOM molecule.

The conclusion of the authors was that the alternate analyses did not favor any of the models and that possibly, all three models can be involved in a fouling process.

7. Concluding remarks

This review of HS fouling in ultrafiltration highlights the complexity of the phenomena involved. Extensive survey of published experimental data demonstrates that the fouling extent is influenced by numerous parameters which include physico-chemical properties of the humic substances, membrane properties and hydrodynamic conditions.

Analysis of available data shows qualitative agreement on several effects. Most studies found that divalent ions (notably Ca$^{2+}$) enhance HS fouling and that HS fouling is more severe at low pH levels. It is also agreed that HS fouling is more severe at high ionic strengths, in large pore size membranes and with humics of natural waters.

However, quantitative conclusions are difficult to draw since data obtained under comparative conditions are insufficient for formulating generalized correlations. Also, modeling efforts have so far not yielded generally accepted results.

The need for generalized correlations and for reliable predictive models is well recognized and will no doubt be reflected in future HS fouling studies.

References


