



Review of fouling by mixed feeds in membrane filtration applied to water purification

Xiafu Shi, Robert Field, Nicholas Hankins*

*Department of Engineering Science, The University of Oxford, Parks Road, Oxford, OX1 3PJ, UK
Email: nick.hankins@eng.ox.ac.uk*

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ABSTRACT

Fouling is, and will remain, a significant problem in membrane filtration. Most previous fouling studies have determined the effects caused by a single type of foulant. However, in many water purification applications, the feed solutions are often complex, containing multiple foulant types. Existing analyses based on the contribution of individual foulant types do not suffice to explain the complex interactions which occur during mixed-feed fouling behaviour. This article presents a review of fouling studies for feeds containing a mixture of foulant types, with an emphasis on microfiltration and ultrafiltration systems for water purification. Two types of mixed-feed fouling systems are considered: mixtures of different types of macromolecules (such as NOM and polysaccharides); and mixtures of macromolecular and colloidal particles (such as kaolinite). The presence of metallic ions and organic solutes is also considered. Macromolecular adsorption often initiates the fouling, and leads to irreversible flux decline; the presence of cations may or may not exacerbate this phenomenon. The behaviour of combined macromolecule and colloidal particle systems is complex and interactive, and cannot easily be inferred from the behaviour of the individual components; this behaviour may be synergistic (greater than the sum) or it may, in some cases, be compensatory (less than the sum). Such synergy results from macromolecule-particle interactions, affecting colloid stability and macromolecular deposition onto the membrane, as well as leading to altered cake resistance and hindered back diffusion of macromolecules through the cake. Mixed feeds are found to have significant effects on the critical flux phenomenon, and this remains a poorly understood area.

Keywords: Mixed fouling; Membrane filtration; Water purification; Organic foulant; Colloids; Foulant interactions

1. Introduction

The provision of clean water and energy are amongst the most pervasive challenges of the 21st century. Problems with water stress are expected to grow worse in the coming decades, with water scarcity occurring globally, even in regions currently considered water-rich [1,2].

Membrane technology, due to its separation efficiency, is now playing an increasingly important role in the water cycle. Processes such as micro- (MF), ultra- (UF) and nanofiltration (NF) are commonly used in surface water treatment to remove turbidity, hardness, chlorine resistant pathogens and natural organic matter (NOM) [3,4]. The distinction between these processes is somewhat arbitrary; their differences are defined chiefly by the approximate size range of the particles or solutes

*Corresponding author.

in solution which they are capable of rejecting [5,6]. In NF, membrane-solute molecular interactions also play a role.

Membrane fouling results from interactions between the membrane and the various components in the feed solution through deposition, reaction, precipitation, and/or microbiological processes. It leads to the irreversible loss of system productivity over time; it has long been a serious issue, and is still one of the most critical factors hindering the uptake of membrane technology [5–8]. Membrane fouling consists of the accumulation of rejected material, either: (i) on the top surface of the membrane (external fouling) or (ii) at the openings of pores or (iii) within the pores themselves (internal fouling) [9,10]. The build-up of foulants may take one of the following forms [6,11,12]:

- **Adsorption:** adsorption occurs when attractive interactions exist between the membrane surface and the solutes or particles, which can happen without convection.
- **Pore blockage:** membrane pores are closed completely or partially by foulants.
- **Cake formation:** an external fouling layer of rejected particles forms over the entire membrane surface and grows layer by layer, leading to an additional hydraulic resistance.
- **Gel formation:** In UF or NF, particularly at high trans-membrane pressure (TMP), the level of concentration polarisation (CP) may cause macromolecules to form an external gel layer on the membrane surface.

Although significant advances in the understanding of fouling mechanisms have been gained from previous studies, most of this knowledge is limited to a single, well characterized model foulant with homogenous physicochemical properties [13]. Membrane fouling in water treatment is strongly influenced by natural water characteristics. As all feed waters withdrawn from rivers, lakes and aquifers are, by their nature, complex mixed systems, fouling in the water industry is almost always caused by more than one type of foulant with various particle sizes and surface characteristics [13]. The interactions between different foulant species may be significant, and this has already been confirmed in several systematic studies [14]. Even the poly-dispersity of the influent feed can drastically change the nature of foulant layers [15–17].

Recent studies on membrane fouling by both inorganic colloids and dissolved NOM have shown that fouling behaviour differs under varying solution conditions with different membrane types [13]. Moreover, the fouling behaviour of mixed systems cannot be adequately described by existing theories.

A simple additive superposition of individual foulant contributions fails to depict the complex, synergistic phenomena arising when multiple foulants are present [14,18]. Still, an integrated understanding of key fouling mechanisms in mixed foulant systems remains in great demand for the development and application of fouling control strategies, especially in the water purification industry [14].

2. Mixed fouling concepts

2.1. Mixed fouling definition

Separation processes deal with mixtures. In setting out to define the potentially wide scope of mixed fouling, an attempt to do so is likely to be unnecessarily restrictive at this stage. It is preferable to describe the range of systems to which the term ‘mixed’ applies [19].

In water purification, membrane filtration is used to separate drinkable ‘pure’ water from various other components. The feed-water can be a simple solution. For example, the brine water in desalination mainly comprises of microsolute (inorganic ions) and water. In this work, the notion of a mixed system will be restricted to a system containing solutes and complex colloidal dispersions with different species of macromolecules and/or colloidal particles, as illustrated in Fig. 1. Typical surface waters are good examples of such complex feeds, containing natural organic matter (NOM), metal ions, low molecular weight organics, micro-organisms, mixed complexes, and inorganic colloids [20]. All the components in the feed-water, along with the membrane itself, have the potential to cause flux decline behaviour in membrane filtration [13,21]. Thus, the term *mixed fouling* is used here for water purification in a general and non-specific way.

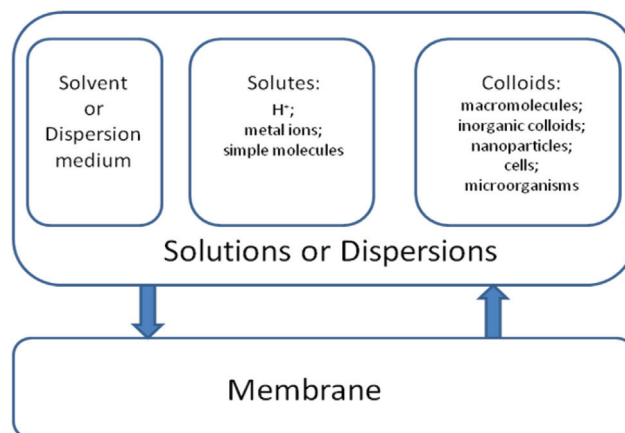


Fig. 1. Schematic of a typical example of mixed systems in membrane filtration for water purification.

2.2. Complexity of mixed fouling

Membrane fouling itself is a complicated phenomenon. Almost all system variables, such as foulant properties, solution chemistry, membrane properties, and system hydrodynamics could have a potential impact on the overall fouling behaviour. Some interactions are common to different size scales in all systems, including [22]:

- Foulant-membrane interactions: ligand exchange reactions, electrostatic interactions, van der Waals interactions, and hydrophobic interactions [23].
- Foulant-ion interactions: ion-binding can alter the conformation and hence the effective size of the molecules, as well as reducing the effective charge of particles (see Section 3.3).
- Foulant-water interaction: this is also related to the effect of pH and ionic strength.

This picture is even more complicated for a complex feed, due to the interactions between different foulants, i.e., foulant A-foulant B interactions. Ultimately, the complexity of a mixed fouling system may involve complex foulant A-foulant B-cation/anion-water-membrane interactions.

2.3. Foulant speciation

Foulants are categorized in this paper by their material type; see Table 1. It is difficult to make a sharp distinction for every single species. For surface water treatment, macromolecules and colloidal particles are often considered as the main foulants [24]. Thus, these two groups naturally inform the structure of this section.

2.3.1. Macromolecules

Macromolecules range in molecular weight from a few thousand to a million, or even larger for non-volatile organics. In producing drinking water, NOM, essentially the biological remnants of live and dead flora and

fauna, is generally accepted as the main foulant, which can occur in both surface waters and ground waters [5,26,27]. NOM is a heterogeneous mixture of numerous organic carbon compounds, such as humic substances, amino acids, carbohydrates such as polysaccharides, lipids, lignins, waxes and organic acids [28]. Therefore, organic fouling is fairly complicated, because specific interactions between different species of foulants or between foulants and chemical functional groups on the membrane surface may occur. Many previous studies have considered that flux decline behaviour is initially controlled by specific interactions (chemical or electrical attraction/repulsion) between the foulants and membrane surface, but is later determined by foulant-foulant interactions [20,29–31]. Thus, the physicochemical characteristics of organic foulants – size, hydrophobicity, charge density, isoelectric point, chemical functionality, and molecular conformation – play important roles in organic fouling [18].

2.3.2. Humic substances

The large fraction of NOM present in surface or ground waters is composed of humic substances, which account for the numerous chemicals affecting the colour and tint of water [8]. They have been suggested as the most detrimental constituent in causing severe membrane fouling [26,32–35]. Humic substances are complex macromolecules, having a molecular weight (MW) greater than 2,000 Da, and are conveniently divided into three categories: humic acids (HAs), fulvic acids (FAs), and humins, according to their solubility in acidic solution [28]. HAs refer to the fraction of humic substances not soluble in water under acidic conditions (pH<2) but soluble at higher pH. The exact structure of HAs can change, but it is generally agreed that HAs are heterogeneous mixtures of large and complex molecules, with a number of aromatic rings as well as aliphatic components. They contain three main functional groups: carboxylic acids (–COOH), phenolic alcohols (–OH), and methoxy carbonyls (C=O) [8]. FAs have generally similar structures, but are more polar.

The negative charge of HAs and FAs is mainly due to the deprotonation of carboxylic and phenolic groups at high pH, and this makes NOMs exhibit a distinct anionic character with a strong propensity for the attraction of cationic species, such as metal ions [36,37]. HAs occur as long linear chains at high pH and low ionic strength, due to charge repulsion of the functional groups, and as coiled, spherical molecules at low pH and high ionic strength, due to stronger intra-molecular (such as hydrophobic) interactions [20]. Calcium and other divalent cations are known to form complexes with humic substances, and can neutralize part of their surface charge, especially at neutral pH, reducing the size of the molecule

Table 1
Foulant categorization (adapted from [25])

Foulant material type categories based on:

Size

Molecular, macromolecular, colloidal or particulate

Chemical type

Inorganic or organic

Origin

Microbial (autochthonous), terrestrial (allochthonous) or man-made (anthropogenic)

and exposing hydrophobic chains to the aqueous solution. This leads to enhanced aggregation [20], which has been reported to cause more pronounced fouling [38]. Li and Elimelech used atomic force microscopy (AFM) to confirm the existence of NOM-NOM and membrane-NOM interactions by calcium-enhanced complexation and by the subsequent formation of intermolecular bridges among organic foulant molecules [39].

2.3.3. Polysaccharides

Besides humic substances, polysaccharides have also been recognized to cause membrane fouling [40]. Polysaccharides are hydrophilic and primarily neutral, polar compounds [34,41]. A study identified polysaccharides, along with some amino sugars and proteins, as the principal fouling materials in treating water from several natural reservoirs and remaining on the membrane even after chemical cleaning [42]. Another study determined that alginate, a microbial polysaccharide, mainly fouls the membrane surface by pore blocking and consequent cake building, and only a little adsorption takes place [30].

Polysaccharides are the main components in extracellular polymeric substances (EPS), which significantly affect the fouling in membrane bioreactor (MBR) systems [34]. Also, EPS from algae have been found to cause significant flux decline and fouling on UF membranes when source water from eutrophic reservoirs were filtered [40].

2.3.4. Proteins

Proteins are also important components in EPS. They have lower molecular weights and a narrower molecular weight distribution than polysaccharides [34,41]. Proteins have complex molecular structures, and are multi-polar with multiple charge points, and the overall net charge depends on the solution pH [22]. The ionic strength affects the active size and shape of the protein and the interactions between protein molecules [22]; intra-molecular hydrogen bonding determines their tertiary structure. Protein UF study has shown the rate and extent of protein fouling is strongly dependent on the feed-water composition, such as protein concentration, pH and ionic strength [43].

MF has been a popular method for separating proteins from fermentation broths. Though protein molecules are much smaller than the pores of MF membranes, severe fouling can nevertheless occur under dynamic conditions [44]. Deposition of large protein aggregates are thought to cause the initial fouling [45,46]. Pore blockage is associated with the deposition of these aggregates on the membrane surface [7]. These aggregates in the bulk protein solution can be generated during the initial protein preparation, or they may be formed by shear

forces in the cross-flow filtration system. Alternatively, they can be formed by the high local shear rates that can exist in the concentrated layer near the membrane surface or in the membrane pores [7,47–49]. As filtration progresses, native or non-aggregated protein molecules chemically attach to the growing deposit of protein aggregates, via the intermolecular thio-disulfide interchange reaction involving a free sulhydryl group in the native protein [50]. Thus, the initial stages of the deposition of protein aggregates are described by pore blockage, while the later stages are described by cake formation [51,52]. Based on this, Duclos-Orsello et al. developed a three mechanism model, including pore constriction, pore blockage and cake filtration. The pore constriction accounts for internal fouling caused by protein adsorption [53].

2.3.5. Particulate matter

Besides macromolecules, particulate (colloidal) matter is another type of major foulant. This includes a cocktail of inorganic materials, lipids and other fatty or oily particles, latex, cellular debris and other organic particles, as well as oil droplets in emulsions [7]. In some process applications, contaminants such as pigments, cellular debris, rust, etc. will also find their way to the membrane surface [4]. In this paper, the main concern in this category will be large inorganic colloids and cells, which have relatively large size and a more rigid shape than macromolecules.

Size exclusion is typically the principle governing the MF or UF of large colloids. When a suspension contains particles which are too large to enter the membrane pores, such particles are retained by sieving and accumulate on the membrane surface, gradually forming a cake layer. Such a cake layer provides an additional resistance to filtration, which causes the permeate flux to decline with time [7]. Morphology of the fouling cake layer dictates the flux decline, and the layer-membrane interactions determine the fouling reversibility [5]. The cake layer morphology and interactions themselves are affected crucially by particle characteristics, such as size, charge, and surface chemical stability [54,55].

The formation of the colloidal cake layer is dependent on a wide range of factors, including the physico-chemical properties of the membrane surface (surface charge, roughness, and hydrophobicity); the characteristics of the colloidal material (particle size, charge and hydrophilicity); solution chemistry (solution pH, and ionic strength); and system hydrodynamics (cross-flow velocity, and TMP) [7,54]. The surface charges of the membrane and of the colloidal particles determine the electric double layer (EDL) interactions between membrane surface and colloidal foulants, as well as between colloidal particles themselves; the same interactions

also strongly depend on the total ionic strength and pH of the feed solution [54]. For chemically inert colloidal materials, such as silica, colloidal particles are held in the cake layer by non-specific interactions (mainly electrical double layer and van der Waals interactions, and by TMP). Consequently, the resistance of such a fouling layer is usually low, and the resultant fouling is likely to be reversible [18].

3. Fouling by macromolecules

3.1. Macromolecule-membrane interactions

Organic matter can adsorb onto the membrane, which affects the initial fouling stage. Such adsorption can be crucial, as conformational and chemical changes in the initial adsorbed layer can modify membrane surface chemistry, including membrane surface roughness, hydrophobicity and charge [21]. For instance, the adsorption of HA, alginate and bovine serum albumin (BSA) were observed on a commercial NF thin-film composite membrane of low salt-rejection. Such adsorption altered the membrane surface properties in terms of the shifted zeta potential (ZP). The membrane possessed a negative ZP value in pure water. HA and alginate made the ZP even more negative, as these two foulants were highly negatively charged, while BSA significantly reduced the negativity of the ZP, due to its lower charge density [13].

The continual adsorption of protein onto membrane may close off smaller pores, causing redistribution of flow throughout the membrane structure. This can cause retention of an increasing fraction of the feed, resulting in severe CP and a resultant rapid flux loss in MF [21]. However, some observations on NF didn't show the continual adsorption to have a lasting effect on the apparent flux decline [13].

HAs adsorption on a polyethersulfone (PES) membrane causes considerable irreversible fouling when filtered alone [30]. Mixed filtration of HAs with particles such as kaolinite doesn't considerably affect the irreversibility of the fouling, even though HA can adsorb onto these particles [33].

3.2. Macromolecule-macromolecule interactions

Jermann et al. studied the interplay of HA and alginate fouling mechanisms during UF (PES, 100 kDa) [30]. Based on the observations and experimental results, fouling models (see Fig. 2) have been proposed for different combinations of substances. When HA and alginate are filtered together, HA can function as a bridge between alginate and the membrane surface, leading to a more stable and less reversible fouling layer.

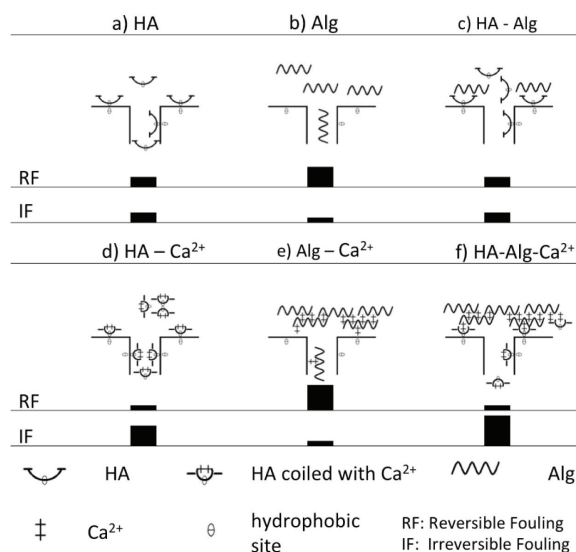


Fig. 2. Mechanistic model of foulant-foulant and foulant-membrane interactions for humic acid (HA) and alginate (Alg) and their associated fouling characteristics: a) HA filtered only (initially fast and substantial adsorption onto the clean and fouled membrane surface and in the pores by hydrophobic interactions); b) Alginate filtered only (cake formation on the membrane by pore blockage, marginal adsorption and relatively reversible due to strong electrostatic repulsion); c) HA and alginate filtered together (heterogeneous fouling cake formed and anchored on membrane surface via HA adsorption); d) HA filtered with calcium ions (increased adsorption and coiled HA molecules by Ca^{2+}); e) Alginate filtered with calcium ions (gel formation induced by Ca^{2+} complexation with alginate, low adsorption); f) HA, alginate and calcium ions filtered together (heterogeneous HA-alginate gel formation and enhanced adsorption of HA on membrane surface in the presence of Ca^{2+}). Adapted with permission from [30].

Ye et al. used alginate to determine the fouling contribution of polysaccharide-like matter via testing its rejection, specific cake resistance and compressibility as a function of pressure and membrane morphology in MF [34]. This study investigated the change in fouling mechanisms and specific cake resistance when BSA was added as a model protein to form a mixed system with alginate. Their results showed that the presence of protein did cause higher alginate rejection and a slightly lower specific resistance of the cake layer than when filtering alginate alone. This would suggest that protein in the mixture feed lowers the strength of binding within alginate aggregates and hence the mixed protein-alginate cake has lower hydraulic resistance.

3.3. Effect of solution chemistry on macromolecular fouling

Solution ionic strength, pH, and metal ion concentration have important effects on membrane fouling rates and mechanisms [18,56]. The decrease of pH or increase

of ionic strength will screen and reduce electrostatic interactions between HA molecules, which can promote more adsorption or the formation of macromolecular gel [57]. Metal ions, particularly divalent cations, can attach to deprotonated acidic functional groups of NOM, e.g., carboxylic acids, causing electrostatic charge shielding [32]. In molecular modelling studies, such strong associations between NOM carboxyl groups and divalent ions were found to form metal-humic complexes [58,59], by which divalent ions can cause macromolecules, such as HA, to adopt a small, coiled conformation via intramolecular complexation. In addition, the organic molecule may cross-link to its surrounding materials via intermolecular bridging [39].

Many filtration studies have observed an exacerbated membrane fouling in the presence of divalent cations. Ca^{2+} can promote aggregation of macromolecules, and change membrane fouling behaviour, though the specific mechanism may vary for particular cases in terms of different foulant species and surrounding conditions [18,30,60–62]. In the UF experiments conducted by Katsoufidou et al., Ca^{2+} enhanced HA fouling by forming a more cohesive gel layer, whereas Ca^{2+} led to a more labile alginate gel layer that is more easily removable by shear [63]. This latter is unlike the result of Jermann et al.'s study, in which Ca^{2+} caused a very compact fouling layer of alginate by the complexation between Ca^{2+} and alginate, which can be highly resistant to hydrodynamic forces and a subsequently higher flux decline [30]. In UF of mixtures of the three components (HA, alginate and calcium), the calcium-induced denser alginate gel layer is less permeable to water and hinders entry of HA molecules. Meanwhile, calcium also formed HA- Ca^{2+} -alginate associations, as calcium can interact with both. Such linkage tightened the gel layer onto the membrane via HA-membrane hydrophobic interactions (see Fig. 2) [30].

The presence of cations can also reduce the overall flux decline, to some extent. By reducing the electrostatic repulsion, Ca^{2+} can destabilize NOM-coated particles and enhance their aggregation to form a fouling cake layer with relatively high porosity and low hydraulic resistance (see Fig. 2), although the irreversibility of fouling increased in the presence of Ca^{2+} [5]. Moreover, by either an intra-molecular complexation mechanism or neutralization of acidic surface groups to cause NOM compaction [32,64], NOM molecules are coiled and small enough to pass through the UF membrane pores, and hence the flux decline is reduced [65]. However, sometimes the effect is insignificant when foulants do not bind specifically with Ca^{2+} . With this, the fouling layer of organic macromolecules bridged together by Ca^{2+} can be disturbed by foulants inert to Ca^{2+} [18]. This just indicates the complication of filtration behaviour in an environment of mixed species, including metal ions.

Metal ions can mitigate the electrostatic repulsion. The classic Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloidal stability tells us that particle-particle interactions depend on the electrolyte concentration and valency. This reveals that very fine aggregates will remain dispersed at low ionic concentrations and high pH as a result of substantial interparticle repulsive forces. On the other hand, when ionic strength is sufficiently high to compress a double layer of counter-ions, the energy barrier between particles will be nullified, allowing the van der Waals attraction forces to dominate [65,66]. It has been observed that the diffusivity of NOM increases with decreasing pH and increasing Ca^{2+} concentration, due to molecular compaction [64]. Chen and Elimelech reported that HA adsorption on fullerene nanoparticles led to increased stability of the nanoparticles by steric repulsion at $<10 \text{ mM } \text{Ca}^{2+}$, while higher Ca^{2+} concentration (40 mM) could cause enhanced aggregate growth by bridging effects (firstly, Ca^{2+} bridges unadsorbed HA to form aggregates; then these aggregates bridge the nanoparticles) [67]. Moreover, in respect of higher ionic strength, divalent cations can screen charges more effectively and therefore have a greater effect on reducing double layer repulsion than monovalent cations [39]. With different divalent ions, the effect on fouling is varied. In the study conducted by Kimura et al., iron and manganese were observed to enhance the irreversible fouling caused by polysaccharides on a hydrophobic polysulfone membrane, but neither aluminium nor calcium had such an effect [68].

4. Fouling by mixtures of macromolecules and colloidal particles

Fouling caused by filtration of macromolecules and colloidal particles together has recently been termed 'combined fouling'. The term specifically refers to that type of fouling in which colloidal particles and macromolecules are both present in the feed stream, and both contribute to the flux decline in membrane filtration [13,14,18,61].

4.1. Filter-aid and over-clogging

Hughes and Field proposed two broad categories of combined fouling by particles and soluble components in complex feeds [69]. One is the *filter-aid* situation, in which cake-like deposits beneficially screen out components that have a high fouling potential at the membrane surface (a compensatory effect); the other is the *over-clogging* situation, in which components increase the specific resistance of cake-like deposits and have a higher impact than if they are present on their own (a synergistic effect).

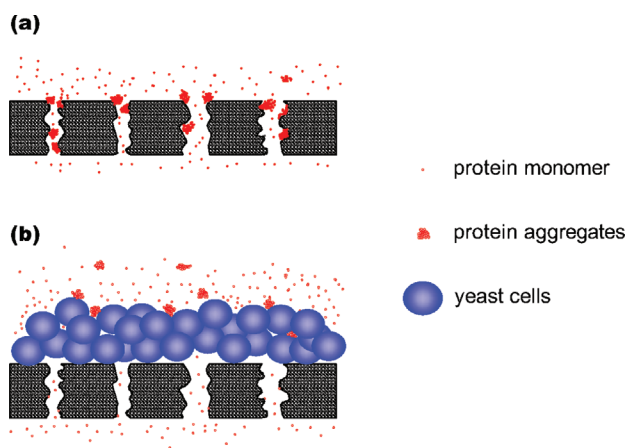


Fig. 3. Proposed mechanisms for microfiltration membrane fouling by protein aggregates (a) without and (b) with yeast cells. Reproduced with permission from [44].

The *filter-aid* situation occurs when particles can act as a secondary membrane or a prefilter, removing smaller foulants that would otherwise have a high fouling impact at the membrane surface. In the study of MF of yeast cells and protein mixtures by Guell et al., it was observed that the yeast cake which forms on top of the primary membrane acts as a prefilter which prevents protein aggregates from entering the internal structure of the MF membrane (see Fig. 3) [44]. This reduces fouling on the primary membrane and pore blocking. Higher protein transmission and higher flux was achieved in the presence of the yeast cake than in its absence.

In an NF combined fouling study conducted by Lee et al., results showed the extent of flux decline for combined fouling was less than the sum of the individual contributions of silica particles (300 nm) and NOM [61].

The *over-clogging* category was demonstrated in many combined fouling studies, which manifested a considerably higher flux decline rate than the sum of the respective rates ascribed to individual foulants [5,13,18,33]. Such a fouling characteristic is termed a *synergistic* effect. Jermann et al. observed combined fouling synergistic effects to a significant level during UF experiments on combined particles (kaolinite) and organic matter (HA and/or alginate), which was far greater than the sum of particle and organic fouling alone [5,33]. Furthermore, mixtures of alginate, HA and kaolinite caused the most detrimental total fouling. Similar results have also been reported by Li and Elimelech in a loose NF system, when both colloidal (two different sized silica particles (300 nm and 30–40 nm)) and organic foulants (HA) were present in the feed solution [18].

4.2. Macromolecule-particle interactions

Colloids or particles can affect the initial deposition of the macromolecules by adsorbing them onto their surfaces or providing a secondary layer as a prefilter [21]; macromolecules can affect colloidal particle stability in the feed stream and bind the particles together, and the latter can then fill up the interstitial spaces between the deposited colloids. These interactions all have a potential impact on overall fouling behaviour. Generally, the underlying mechanisms are based on chemical interactions and mutual steric effects between macromolecules and particles.

4.2.1. Effect of macromolecular adsorption onto particles

Adsorption of organics onto particles can lead to a transformation of the particle surface characteristics. For instance, proteins such as BSA are able to significantly adsorb onto negatively charged colloidal silica surfaces. This can drastically lower the negative surface zeta potential of silica and hence reduce the electrostatic repulsion between particle and membrane, as well as that between silica particles. However, HA did not adsorb onto the same kind of silica colloids (ST-XL, 60 nm) in Contreras et al.'s study [13].

The adsorption of macromolecules can facilitate the transport of natural and model colloids in porous media and their aggregation kinetics [13,66,67]. HA can adsorb onto particles and affect particle stability (stabilization in the case of kaolinite), decrease the aggregate size, and smooth out their surface heterogeneity. Kaolinite particles have negatively charged base faces but conditionally charged edges, resulting in face-to-edge aggregation with a porous polyhedral structure. Once HA has adsorbed onto kaolinite, particles are more likely to be aggregated via face-to-face linkage [70,71]. This forms a more compact cake rather than the porous polyhedral structure, leading to a higher resistance and, hence, a synergistic effect of mixed fouling [33]. However, HA has minimal effect on the stability of particulate quartz and silica, as there is negligible adsorption of HA onto such particles [72].

Therefore, the particle stability (aggregation/destabilization or stabilization) as affected by macromolecules is a crucial factor. Stabilized particles lead to a denser cake, with a higher resistance than aggregated particles [5]. Nanoparticles such as black carbon, a material discharged by various human activities into the environment, is usually negatively charged and stably dispersed in natural water. The UF of such self-dispersable carbon particles suffers significant flux declines, due to membrane pore blocking by superimposition of the nanoparticles from the initial stages of filtration, but such that pore blocking could be eliminated by promoting rapid

aggregation with NOM [73]. Carbon particles adsorb to the hydrophobic parts of NOM via π - π interactions (hydrophobic association) at the aromatic surfaces of its particles [74], but can also associate with the carboxylic functional groups of hydrophilic compounds by intermolecular bridging in the presence of calcium cations [64,65]. The NOM/particle ratio affects particle stability and initial deposition of macromolecules onto the membrane surface [5]. This is possibly due to the competitive adsorption for macromolecules between particles and the membrane surface.

Alginate has been reported to be able to form alginate-coated particles with, for example, hematite and kaolinite [66,75]. The interactions were assumed to be induced by electrostatic forces, van der Waals forces, and hydrogen bonding, leading to the bridging and destabilization of suspensions in the solution [75]. Jermann et al. used two filtration methods to investigate the interactions between substances in the feed solution; by “premixed” filtration (the compounds were mixed and kept for at least 4 h, sufficient to reach interaction equilibrium, before filtration), and during the fouling process by “subsequent” filtration (kaolinite was filtered prior to the NOM) [33]. Comparison of the flux decline between the two methods showed that the alginate-kaolinite interactions were considered not to be the main cause of synergistic fouling on UF, but the dominant mechanism was a simultaneous cake-layer build-up of both kaolinite and alginate, without requiring previous substance mixing. On the other hand, the leading mechanism in the case of combined HA and kaolinite fouling, as mentioned above, is the formation of stabilized colloids led by HA adsorption on kaolinite (see Fig. 4b).

4.2.2. Steric effects

Small macromolecules have the potential to penetrate and adsorb into a colloidal cake layer and membrane structure [21] (see Figs. 2 and 3). On the other hand, macromolecules can be entrapped in the cake layer during its formation when filtering mixtures together, due to mutual physical effects such as size exclusion. The penetrated or entrapped organic macromolecules can fill up the interstices of the particle layer to form a heterogeneous fouling cake with low porosity [33]. In the case mentioned in Jermann’s studies, alginate entrapment by the dynamic fouling layer, due to its high molecular weight (12–80 kDa compared to 100 kDa MW of PES membrane) and longitudinal shape, dominated the fouling characteristics and caused a significant synergistic effect, which is the interplay of the individual fouling behaviour of alginate and kaolinite (see Fig. 4) [5,33].

4.3. Cake enhanced concentration polarisation

Besides specific interactions, the transport of solutes in pressure-driven filtration is mainly determined by the hydrodynamic effects including the permeate drag force, tangential-flow shearing force, and back diffusion of the solutes [18]. Back diffusion includes Brownian (thermodynamic entropy) and shear-induced (hydraulic stress) types [76]. The active diffusion pattern depends on the particle size. For small particles ($<1\ \mu\text{m}$), shear-induced diffusion is negligible [7,11] and their back transport is driven by the gradient diffusion resulting from the concentration polarisation – the increased concentration of rejected or retained solutes at the membrane surface [6].

When the feeds contain both colloids and solutes, the colloid-solute interactions near the membrane surface have an influence on the back diffusion of solutes. The deposit layer of colloids on the membrane surface may counteract the back flux of solutes to the bulk solution because the solutes need to travel through tortuous paths within the fouling layer and, hence, the back diffusion of solutes is hindered. The slower back diffusion leads to faster accumulation of the smaller solutes, and hence a higher concentration in the CP layer and an enhanced osmotic pressure of solutes at the membrane wall [13,77]. This phenomenon refers to the *cake-enhanced concentration polarisation* (CECP) or *cake-enhanced osmotic pressure* (CEOP) effect, which has been identified as a significant contributor to the permeability loss in NF and RO when colloids and salts were filtered together [78–80]. In addition, the CECP may cause the deterioration of permeate quality as it can push more solute contents passing through the membrane [81].

As the rejection of macromolecules and low-molecular-weight solutes in UF is considerably high, the osmotic pressure imposed by these foulants may be significant. Therefore, CEOP could occur in UF while MF is generally unaffected because particulate feeds do not exert large osmotic pressure [6,82]. In fact, UF of kaolinite-alginate mixtures has shown the exacerbated flux decline resulting from such effect of hindered back-diffusion of alginate molecules within the kaolinite cake layer [5,33].

Theoretical work on CEOP/CECP has proposed models for combined filtration of colloid and solute for salt-rejecting membranes [14,78,80]. The gradient diffusion coefficient is a complex function of the solute concentration and colloidal interactions [82,83]. However, in the bulk solution, the Stokes-Einstein equation can be used to estimate the diffusion coefficient of small, spherical solutes [13]:

$$D_0 = \frac{k_B T}{3\pi\mu d_p} \quad (1)$$

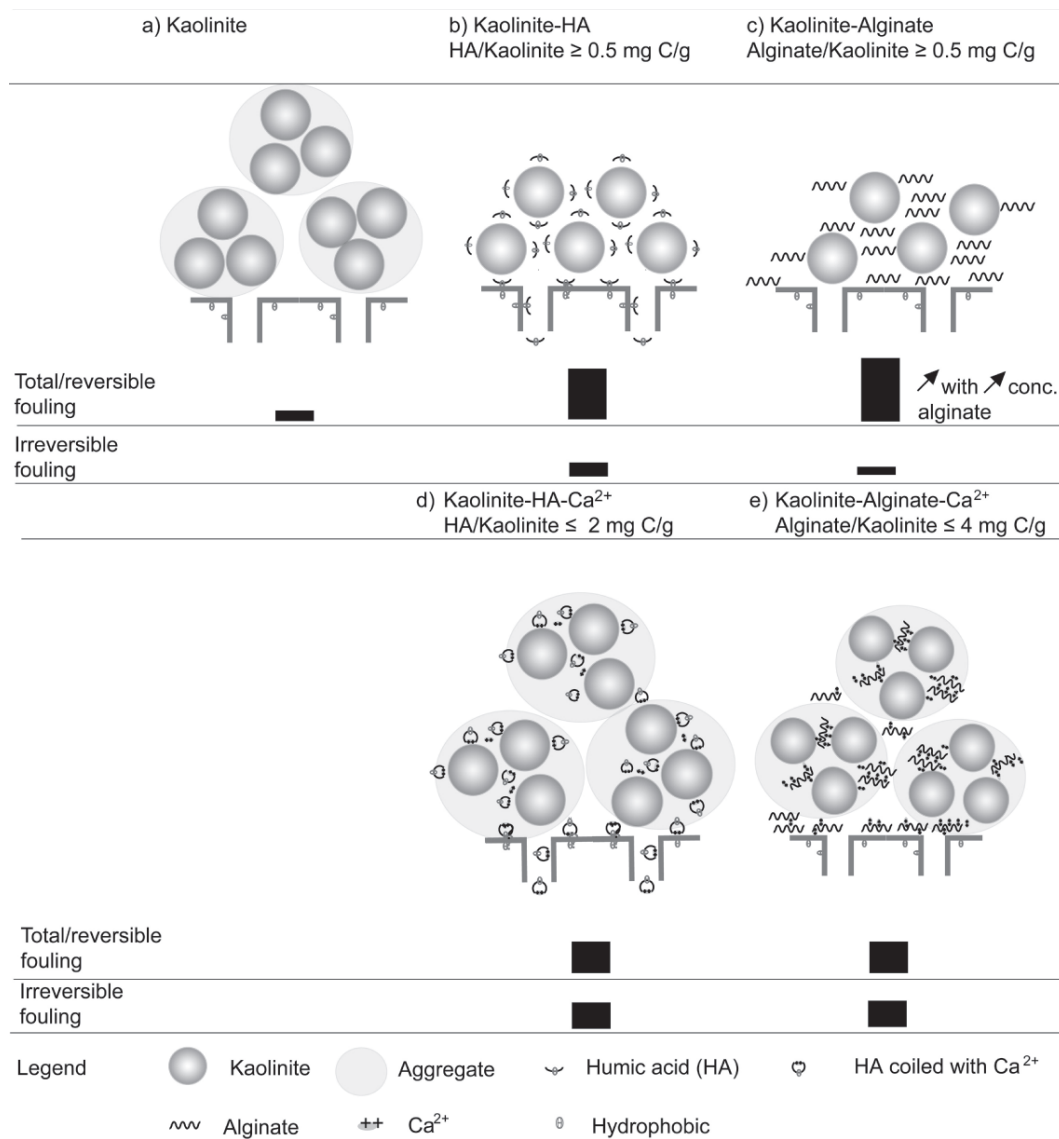


Fig. 4. Schematic fouling model of (a) kaolinite, (b) HA and kaolinite in the absence of calcium, (c) alginate and kaolinite in the absence of calcium, (d) HA and kaolinite in the presence of calcium, and (e) alginate and kaolinite in the presence of calcium. Reproduced with permission from [5].

where D_0 is the bulk diffusion coefficient, k_b is the Boltzman constant, T the absolute temperature, μ the fluid viscosity, and d_p is the particle diameter. Thus, the hindered diffusion coefficient, D' , related to the cake layer porosity (ϵ) and the cake tortuosity (τ) can be estimated from [78]:

$$D' = \frac{D_0 \epsilon}{\tau^2} \quad (2)$$

where τ can be calculated from ϵ using [84]

$$\tau^2 = 1 - \ln \epsilon^2 \quad (3)$$

Over the range of typical porosity values, the effective diffusion coefficient may be reduced to between 10 and 40% of the bulk diffusion coefficient (see Fig. 5), leading to a significantly increased salt concentration at the membrane surface [79]. Thus, the hindered back diffusion and hence the CECF/CEOP effect cannot be neglected when mixtures contain both colloidal particles and dissolved organics or salts.

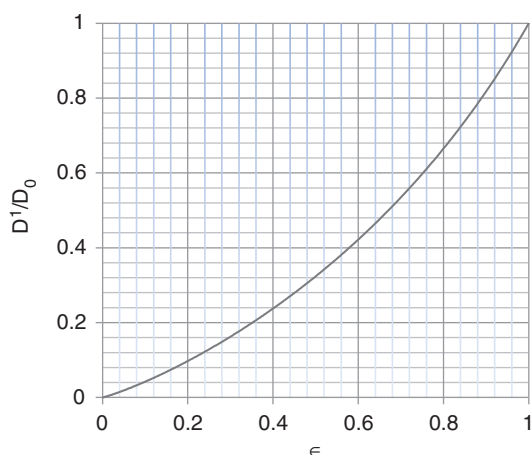


Fig. 5. Ratio of the cake-hindered back diffusion coefficient to the bulk diffusion coefficient against porosity predicted by equation 2. Adapted from [79].

4.4. Reversibility

Hydraulically irreversible fouling is caused by foulant-membrane adsorption, especially during NOM fouling [30]. For example, HA can lead to membrane-HA-kaolinite association, which makes the retained HA-kaolinite mixed fouling layer quite irreversible compared to a one component colloidal cake layer. On the other hand, the presence of the kaolinite particle doesn't affect the irreversibility of NOM fouling significantly [5,33].

As discussed above, Ca^{2+} can increase the adsorption of HA onto the membrane and cause more severe irreversible fouling [30]. However, such effects can be mitigated by the presence of particles. In a study by Lohwacharin et al., NOM fouling was observed to have been eliminated by carbon black in the presence of calcium [65]. This could be explained as follows: the increased adsorption of hydrophilic base/neutral compounds (64% of total DOC) by BC due to the addition of Ca^{2+} reduced the total adsorbed NOM on the membrane. Some other researchers have suggested that the competition between organic matter and particles for calcium could have mitigating effects on HA-membrane association [5].

In the study conducted by Kimura et al., the constituents in surface water responsible for irreversible fouling were evaluated in a long-term (5 months) pilot scale study of UF, using a low-pressure hydrophobic polysulfone membrane (MWCO = 750 kDa) [68]. The irreversible fouling layer was desorbed and extracted by various chemical reagents, followed by different analyses, including chemical, adsorptive fractionation, fluorescence excitation-emission matrix (EEM) and

Fourier-transform infra-red (FTIR) spectral analysis. The results indicated that organic matter was the main culprit in the development of the irreversible fouling phenomena, and, moreover, different fractions of it had different affinities with the membrane surface, among which polysaccharide-like matter preferentially adsorbed on the hydrophobic membrane and mainly caused the irreversible fouling.

4.5. Effect of complex feeds on critical flux

A critical flux exists below which a decline of permeability with time does not occur and above which fouling is observed [85]. The definition implies that, at critical flux, the convective forces just balance the back transport of the solute [86]. The critical flux depends on the back transport provided by the cross-flow or the turbulence generated by imposed liquid flow and/or bubbling, as well as the specific solute-membrane interactions, which are affected by charge and hydrophobicity [21]. A higher back transport rate means a higher critical flux [87]. Critical flux can also be defined as one of two types, the strong and weak form. The strong form of critical flux exists when the membrane resistance does not change from that observed with clean water, while the weak form exists if the relationship between TMP and flux is linear, but the slope of the line differs from that for clean water [88].

For particles in the micro-size range, the critical flux is increased with particle size. For a mixture of different sizes of particles, the cake formed in crossflow would preferentially contain the smaller particles, as these have lower critical fluxes [86]. Madaeni used latex particles of 1.0 and 0.1 μm size and their 50:50 mixture to test their respective critical flux values, which gave results of 120, 105 and 88 $\text{l/m}^2\text{h}$ respectively, i.e., the mixture gave the lowest critical flux [89]. However, in a later study by Zhang et al., significant increases in critical flux were recorded by the addition of bigger particles into the feed suspensions (latex particles of 5.0 + 3.0 μm , or 10 + 5.0 μm) [86]. The percentage improvement increased with the concentration of bigger particles added. This has been explained through the larger particles influencing the shear-induced diffusivity by increasing momentum transfer of bulk components through particle-particle collision.

In filtering mixed particle and macromolecule systems at constant flux, a zero rate of TMP increase is generally not attained. Membrane fouling occurs even at low flux rates, but changes dramatically when a certain value of flux is reached [21]. This is likely to be due in part to background adsorption of organic macromolecules taking place even without convection. Moreover, multi-stage TMP increases may occur in combined fouling, because of the variety of foulant species and fractionation.

Table 2
Fouling mechanisms in some mixtures

Foulants	Membrane types	Fouling characteristics	Fouling mechanisms	References
HA + silica (colloids)	NF	Slight reduction of initial flux decline rate; Continually increasing synergistic effect with filtration time.	HA adsorption onto membrane (increasing surface ZP) but no adsorption on silica colloids, initially increasing electrostatic repulsion between membrane and colloids. Potentially high hindered back diffusion and/or high mixed cake resistance with HA interspersed in the colloid layer.	[13]
Dextran (polysaccharides) + silica (colloids)	NF	Very slight increasing flux decline rate shown in the later stage of filtration compared to silica fouling alone. Dextran alone caused minor flux decline.	Dextran filling in the interstitial pore space of the colloidal cake layer. Little hindered back diffusion.	[13,14]
Alginate (polysaccharides) + silica (colloids)	NF	Strong synergism. Flux dropped fast in the beginning and gradually decreased afterwards, Stable salt rejection.	Strong hindered back diffusion of silica colloids as alginate solution is more viscous.	[13,14]
BSA (protein) + silica (colloids)	NF	Flux kept declining fast. Great synergistic effect with the filtration time. Feed water turbidity increasing over time. Large fluctuation of salt rejection.	BSA adsorption on silica colloids and membrane, reducing electrostatic repulsion between colloids as well as colloids and membrane. Compressible fouling layer that increases in resistance over time. Silica aggregation in CP or cake layer, leading to dynamic cake layer. Complex interplay of chemical and sterical fouling mechanisms.	[13,14]
NOM + carbon black + Ca ²⁺	UF	Substantial flux decline.	Transform from pore-plugging to cake formation.	[65]

This phenomenon is worthy of further investigation. A summary of fouling behaviour for mixed macromolecule-particle systems is given in Table 2.

5. Conclusions

Mixed fouling occurs naturally when surface water is filtered and it is an extremely complicated phenomenon. The interaction between different species of foulants is

important for an integrated understanding of the flux decline involved with complex feeds. This is important for membrane applications in water purification; for surface waters and many ground waters, macromolecules in NOM, and soluble microbial products and particulate matter are seen to cause fouling together.

Macromolecular adsorption on the membrane surface is thought to initiate fouling, and is usually the cause of the irreversibility of flux decline. The molecular

interactions between different macromolecular foulants can cause mutual effects among their individual fouling mechanisms. Divalent cations, among which Ca^{2+} has been mostly identified, can promote more detrimental and irreversible fouling by their ability to complex with macromolecular foulants and some functional group on membrane surface.

Combined fouling by both macromolecules and particles is rather complex. On the one hand, the presence of particles can have a positive effect on reducing the severity of organic fouling by adsorbing organics to reduce the amount adding to membrane surface. On the other hand, combined particle-macromolecule filtration can also lead to a synergistic effect, which more or less worsens the flux decline. The synergy of combined fouling is due to the macromolecule-particle adsorption, which can affect particle stability and surface characteristics, as well as the deposition of macromolecules onto/into the membrane. It can also result from the macromolecule-particle steric effect, which causes an increased cake layer resistance due to smaller macromolecules filling in the interstices of particle cakes, and the hindered back diffusion due to the colloidal cake layer counteracting the back diffusion of macromolecules or other solutes. These mechanisms can interplay in mixed systems to a very complex degree, varying contributions to the overall fouling behaviour. Due to the complex nature of mixed feeds and the interactions between system variables, there is lack of consistency in conclusions reported in the literature.

Different particle sizes and polydispersity are natural features of mixed fouling, and have an important impact on fouling behaviour; they must be incorporated into any quantitative modelling development for mixed fouling. Furthermore, mixed feeds have a significant effect on the critical flux phenomenon, and this area has not been well studied.

Overall, a great deal remains to be explored in the area of mixed fouling.

Symbols

Math symbols

d_p	—	particle diameter (m)
D_0	—	solute diffusion coefficient in free space (bulk solution) (m^2/s)
D'	—	hindered diffusion coefficient (m^2/s)
k_B	—	Boltzmann constant (8.314 J/mol K)
T	—	absolute temperature (K)

Greek symbols

ε	—	cake layer porosity
μ	—	viscosity (Pa s)

ρ_p	—	particle density (kg/m^3)
τ	—	diffusive tortuosity of the cake layer

Abbreviations

CECP	—	cake enhanced concentration polarisation
CEOP	—	cake enhanced osmotic pressure
CP	—	concentration polarisation
DOC	—	dissolved organic matter
EPS	—	extracellular polymeric substances
FA	—	fulvic acid
HA	—	humic acid
MF	—	microfiltration
NF	—	nanofiltration
NOM	—	natural organic matter
PES	—	polyethersulfone
RO	—	reverse osmosis
TMP	—	trans-membrane pressure
UF	—	ultrafiltration
ZP	—	zeta potential

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