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Modeling of combined particles and natural organic matter fouling of ultrafiltration membrane

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ABSTRACT

In this study the combined particles and organic matter (OM) fouling was investigated using kaolinite clay and humic substances. Results confirm the occurrence of a synergistic effect between the particles and the OM leading to a stronger flux decline than the one predicted by the resistance in series model. Moreover, a higher organic matter transmission through the membrane was observed when filtered with kaolinite particles compared to organic matter alone. Experimental data were successfully fitted, thanks to a phenomenological model. The developed model based on the contributions of the two components filtered separately introduces the filtration coefficient describing the capability of the cake layer being formed to hinder or capture OM. Model application to experimental data and data extracted from literature shows a better agreement than values predicted by the classical resistance in series model.

1. Introduction

Membrane processes are widely accepted as an efficient technology to produce high quality water or to recycle valuable compounds in several chemical processes. However, their development is still hindered by the complexity of fouling phenomena and the difficulty to predict critical conditions leading to water production decrease. As previously demonstrated by intensive research work, membrane fouling strongly depends on the membrane and filtered suspensions characteristics [1,2]. Even if important understanding knowledge has been gained from previous studies, most of this knowledge is limited to single foulant with homogeneous physicochemical conditions [3–8]. However, fouling in industrial case applications will be induced by one or more foulants with different properties (size, electrostatic charge). As previously emphasized, the filtration of suspension consisting of several foulants (defined here as "*mixed*" suspension) cannot be well described by existing theory [9–13]. Indeed, the common theory called resistance in series (RIS) model gives in many cases a poor description of the membrane's permeate flux decline. As recently reviewed by Shi et al., fouling during mixed feed suspension will be influenced by foulant–foulant, foulant–membrane and foulant–water/ions interactions [14,15]. As discussed by these authors an even more complex picture, involving all possible interactions in the system, is often needed to fully understand fouling phenomena in "*mixed*" feed filtration.

Compared to studies performed on single compounds filtration, only few work was dedicated to the understanding of fouling mechanisms in "*mixed*" feed suspension, defined here as combined fouling. In such cases, combined fouling induced by colloids (organic or inorganic) and soluble organic compounds could be differentiated into two mechanisms. The first one is the *Filter-aid* situation where the colloids induce a second membrane that could prefilter/adsorb soluble compounds or structure soluble compounds fouling layer. Guell et al. demonstrated the positive impact of a yeast cake layer in the microfiltration of protein suspension [16]. More recently, Kuberkar et al. provided a mathematical model describing the reduction by yeast particles of the membrane clogging induced by bovine serum albumin (BSA) [17]. The developed model includes depth filtration theory and was used to predict various filtration cases involving yeast and BSA protein. Their model stands on the prefiltration of BSA protein within the yeast cake thickness, reducing the BSA concentration (similar to a first order decay mechanism) responsible to the pore blockage phenomena. Similarly, Teychene et al. demonstrated that the addition of organic colloids (latex 500 nm) to the membrane bioreactor's sludge supernatant did not prevent fouling by organic matters (OM) but conducted to non-compressible fouling layers [18]. Moreover, it was widely demonstrated that the addition of adsorbent colloids (e.g. activated carbon or zeolites) might reduce fouling by reducing the soluble foulant concentration or by scouring effects due to colloids shearing at the membrane surface [19–22].

The second situation commonly observed in "*mixed*" feed

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filtration is the synergistic effect (also called *over clogging* situation). In such case, the colloids and soluble organic compounds lead to a stronger flux decline that cannot be easily described by the RIS model. Jerman et al. observed a significant stronger flux decline during the filtration of mixed suspensions, consisting of Aldrich humic substances ($2\ \mathrm{mg\,L^{-1}}$) and clay colloids ($100\ \mathrm{mg\,L^{-1}}$ kaolinite, 400 nm) suspension, in comparison to separately compound filtration [23,24]. Similar results were also obtained by Zularisam et al. during the filtration of humic substances ($10\ \mathrm{mg\,L^{-1}}$) and kaolinite clay particles ($10\ \mathrm{mg\,L^{-1}}$) [25]. These authors attributed the stronger permeate flux decline to the stabilization of clay particles due to OM adsorption leading to a more compact fouling layer. The soluble OM might penetrate or might be entrapped into the cake layer filling its porosity and consequently increasing its hydraulic resistance. Several authors also observed similar phenomena during the filtration of silica colloids and organic soluble compounds (BSA, alginate, humic substances) [13,26,27]. According to these works, the synergistic effect was attributed to the reduction of the back diffusion transport at the membrane surface due to the colloids cake layer. More precisely, this phenomenon refers to the cake enhanced polarization concentration (CECP) forcing soluble compounds to accumulate at the membrane surface or to increase their transport through the membrane. The CECP might be theoretically expressed by the modification of the soluble OM's bulk diffusion coefficient related to the porosity and tortuosity of the cake layer [13]. As recently demonstrated by Tian et al. the CECP mechanisms is strongly influenced by the size and concentration of the studied colloids [27].

As emphasized by this brief literature review, fouling induced by mixed feed suspension is not fully understood and there is a clear lack of phenomenological model describing permeate flux decline. Therefore, the aim of this study is to develop a new phenomenological model describing the "synergistic effect" observed during mixed feed suspension filtration. For this, several lab-scale dead-end filtrations of kaolinite clay particles and humic substances suspensions were performed on ultrafiltration membranes at various transmembrane pressures (TMP). The developed model was then applied to experimental data and results extracted from articles cited above.

2. Theory

As discussed previously, the synergistic effect is still not well understood and according to literature it depends on the characteristics of the filtered suspensions (type of OM, particles), the concentration ratio between particles and OM and the TMP. The goal of this section is to rationalize the "*synergistic effect*" by developing a filtration model that could evaluate the impact of particles on the filtration mechanisms of OM. As discussed above, the particles cake layer built up during filtration might decrease the back diffusion transport of OM to bulk solution and might promote the transport of OM to the membrane surface. So the developed model aims to determine the additional resistance resulting in the called "*synergistic effect*". For that, the model development was based on work reported by Kuberkar et al. using parameters obtained from the separate filtration of particles and OM [17]. The model considers a bidispersed system of large particles totally rejected by the membrane and inducing only cake layer formation. The OM was considered as small particles that could block the membrane pore and build a fouling layer.

It is commonly accepted that in the first stage of filtration, OM blocks the membrane pores and then build a fouling layer at the membrane surface [28,29]. As previously reported by Hermans and Bredee, the complete pore blocking model (f_b) represents the fraction of pores blocked and could be expressed as Eq. (1) [30]

$$df_b = \alpha C_{OM} dV \tag{1}$$

With V the specific filtration volume ($\mathrm{m^3\,m^{-2}}$), C_{OM} the OM carbon concentration in feed suspension ($\mathrm{kg_C\,m^{-3}}$) and α the pore blockage parameter in $\mathrm{m^2\,kg_C{}^{-1}}$ representing the area of blocked pore.

After a certain period of time, the pore blockage mechanism stops and is replaced by cake layer formation which is described by classical filtration law (Eq. (2)) [31].

$$\frac{J}{J_0} = \frac{1}{\frac{1}{(1-f_b)} + \frac{R_{OM}}{R_{mem}}\cdot C_{OM}\cdot V} \approx \frac{1}{1 + \frac{R_{OM}}{R_{mem}}\cdot C_{OM}\cdot V} \tag{2}$$

With R_{OM} the specific OM fouling resistance ($\mathrm{m\,kg_C{}^{-1}}$) and R_{mem} the clean membrane resistance ($\mathrm{m^{-1}}$), J and J_0 are the permeate flux and the pure water flux in $\mathrm{m^3\,m^{-2}\,s^{-1}}$, respectively.

As often reported the resistance induced by pore blockage is neglected and the clean membrane resistance value is used (Eq. (2)). Indeed, as usually observed the pore blockage only occurs during the very initial stage of filtration and consequently the resulting pore blockage resistance is much lower than the fouling layer resistance at higher filtered volume.

Similarly, during large particles filtration only cake building is expected, thus the flux decline for large particle might be described as Eq. (3) [31].

$$\frac{J}{J_0} = \frac{1}{1 + \frac{R_{part}}{R_{mem}}\cdot C_{part}\cdot V} \tag{3}$$

With R_{part} the particles cake layer specific resistance in $\mathrm{m\,kg^{-1}}$ and R_{mem} the membrane hydraulic resistance ($\mathrm{m^{-1}}$). C_{part} the particles concentration in feed suspension (in $\mathrm{kg\,m^{-3}}$).

During mixed suspension filtration, the induced fouling layer will consist of particles and OM. In literature, this combined fouling is often described by the RIS model (Eq. (4)).

$$\frac{J}{J_0} = \frac{1}{1 + \frac{R_{OM}}{R_{mem}}\cdot C_{OM}\cdot V + \frac{R_{part}}{R_{mem}}\cdot C_{part}\cdot V} \tag{4}$$

As shown in the RIS model (Eq. (4)), the two components' contribution to fouling are added separately without describing any possible interaction which is not suitable to describe a potential synergistic effect.

Indeed, at initial stage during combined fouling, OM is expected to block the membrane's pores while large particles will build a cake layer. As explained by Kuberkar et al., the deposited particles will hinder the OM's transport to the membrane surface [17]. Thus, at a given filtration time, the amount of OM which could block membrane's pores will be reduced.

Consequently, the OM concentration variation within the cake layer might be described as follows (Eq. (5)). As reported by Kuberkar et al., it is assumed here that the OM concentration followed a first order decay mechanism (Eq. (5)) [17]. More complex equation (including for example particle detachment) might be also used as often performed in depth filtration works [32,33].

$$\left(\frac{\partial C}{\partial z}\right)_t = -\gamma_t C \tag{5}$$

With z the cake layer thickness (m). γ_t the classical filtration coefficient ($\mathrm{m^{-1}}$) [34] and it could be considered as the capability of the cake layer to collect OM. γ_t values will depend on the particles properties (particles size, shape, electrostatic charges) found in the cake layer and OM characteristics (molecular weight, electrostatic charges). As described in Eq. (5), the filtration coefficient will depend on the filtration time (underscript t in Eq. (5)). Indeed,