



EMPIRICAL MODELING OF UF MEMBRANE FOULING IN REMOVAL OF ORGANIC MATTERS FROM SURFACE WATER

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Abstract: Fouling due to organic matters from surface water has been always of concerns as it affects the water production and membrane lifespan. It's the fouling that hinders the wide application of membrane technology in water treatment field. This study aims to investigate the fouling mechanism, which mostly impacts the water permeability via empirical modeling. Normally, there are four different physical-based types of fouling: complete blocking, intermediate blocking, cake filtration and standard blocking or adsorption. It was revealed that fouling by organic matters on ultrafiltration membranes' surfaces behaved like loose nanofiltration membranes, which mostly involved in intermediate or complete pore blocking. A combined cake formation and pore constriction model simulated even better the fouling mechanism for those tested membranes. The nature of membrane surface characteristics including roughness or hydrophobicity influenced the fouling to some certain extent.

Keywords: Empirical modeling, fouling, ultrafiltration membrane, surface water treatment.

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1. Introduction

Organic matter in surface water is a very important factor during the ultrafiltration of surface water treatment. Organic matter appears almost in surface water sources and its amount and properties depend on climate, ground shape and transformations that occur during its transport in lakes and rivers [1]. This is a mixture of high molecular weight (proteins, carbohydrates, humus) and low-molecular weight (simple organic acids) organic compounds [2] and it is responsible for the membrane fouling, leading to the decrease of a permeate stream during the filtration with membranes.

In analysis of membrane fouling, an empirical model of the system can often be built as a hypothesis of how the system could work or try to predict how an unforeseeable factor could affect the system. Two main types of empirical modeling have been widely used to describe the fouling phenomenon occurring on membrane surface: Fouling Resistance Modeling and Fouling Mechanism Modeling. According to the first modeling approach, fouling can be quantified by the resistance appearing due to formation of cake or gel layer on membrane's surface during the filtration and the resistance removal can be determined via cleaning [3]. The total resistance (m^{-1}) often includes the effects of membrane itself, solute adsorption, gel formation, cake formation, etc. The second modeling approach is to study the mechanisms leading to membrane fouling. The common assumes that one of the four fouling mechanisms (e.g., cake formation, intermediate blocking, pore constriction/adsorption (standard blocking) and complete blocking) takes place. The differential rate laws corresponding to all possible fouling mechanisms were proposed by [4]. As a single model sometimes did not simulate well the fouling data, [5] developed a model that combines cake formation and pore constriction for dead-end filtration and they found that it fit better than did the single cake formation model. [6] later modified it for cross-flow filtration mode by incorporating a back transport term since for ultrafiltration and microfiltration, the cross-flow filtration mode prevails.

The key objective of this study is to understand better the fouling mechanism during the removal of organic matters from river water using tailor-made ultrafiltration membranes via empirical modeling approach.

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2. Methodology

2.1 Mathematical modeling

A mathematical model uses mathematical language to describe a system by a set of variables and a set of equations that establish relationships between the variables. Two types of empirical modeling were used in this research to describe the fouling phenomenon occurring on membrane surface: Fouling Resistance Modeling and Fouling Mechanism Modeling.

Fouling Resistance Modeling

According to the first modeling approach, fouling can be quantified by the resistance appearing due to formation of cake or gel layer on membrane's surface during the filtration and the resistance removal can be determined via cleaning [3]. The flux (J) through the cake and membrane can be described by Darcy's law:

$$J = \frac{\Delta P}{\mu R_t} \quad (1)$$

where J is solute-containing water flux ($\text{L}/\text{m}^2/\text{h}$); ΔP is transmembrane pressure (N/m^2); μ is viscosity of water at temperature T ($\text{N}\cdot\text{s}/\text{m}^2$); R_t is total resistance (m^{-1}), may include the effects of membrane itself, soluteadsorption, gel formation, cake formation, etc.

$$R_t = R_m + R_f \quad (2)$$

Whereas R_m membrane resistance. This index refers to the resistance of membranes with pure water only.

$$R_m = \frac{\Delta P}{\mu J_{wo}} \quad (3)$$

where J_{wo} is Initial flux with ultra pure water ($\text{L}/\text{m}^2/\text{h}$); R_f is resistance appears after fouling with solute-containing water.

$$R_f = \frac{\Delta P}{\mu J_{wf}} \quad (4)$$

J_{wf} is flux at the end of fouling test period ($\text{L}/\text{m}^2/\text{h}$)

Empirical modeling of membrane fouling

Basically, there are four different physical-based types of fouling: complete blocking of the pores (pore plugging), intermediate blocking (long term adsorption), cake filtration or boundary layer resistance and standard blocking or pore constriction (direct adsorption) (Fig. 1).

Complete blocking occurs when each particle arriving to the membrane blocks entirely one or more pores with no superposition of particles. Intermediate blocking takes place as each particle settles on other previously-arrived particles already blocking some pores or directly blocking some membrane areas. During cake filtration, each new foulant particle adheres to (or rests on) one or more previously arrived foulant particles that are already blocking some pores. However, in cake filtration there is no direct contact between the newly arrived foulant particles and the membrane's surface. When each particle arriving to the membrane is deposited into the internal pore walls, leading to a decrease in the pore volume, it is called standard blocking. Given these descriptions and that there will be an

uneven distribution of different membrane pore sizes as well as solute molecular sizes, it is clear that all the above mechanisms may predominate at various times for a filtration cycle. For the first three mechanisms, the solute molecules are bigger than membrane pore sizes, thus fouling occurs outside of pore walls. For the standard blocking, however, the particles (solute molecules) deposit along the pore walls since they are smaller than membrane pores.

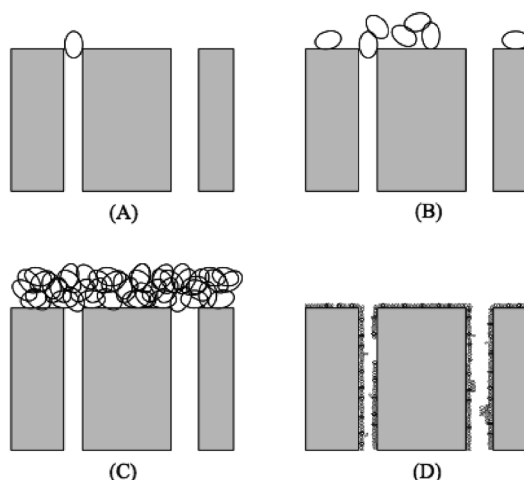


Figure 1. Four types of fouling mechanisms (A) complete blocking, (B) intermediate blocking, (C) cake formation, (D) standard blocking /adsorption [7]



Identification of the controlling fouling mechanism is often conducted via modeling the flux reduction using mathematical modeling as followings:

General fouling equation

To study the mechanisms leading to membrane fouling, the common practice consists of assuming that one of the four fouling mechanisms (e.g., cake formation, intermediate blocking, pore constriction and complete blocking) takes place. The differential rate laws corresponding to all possible fouling mechanisms were proposed by Hermia [4] for dead-end filtration under constant applied pressure:

$$\frac{dJ}{dt} = kJ(J)^{2-n} \quad (5)$$

where k is a fouling coefficient and n is a dimensionless filtration constant, which depends on the type of filtration. n has values of 0, 1, 1.5 and 2 for cake filtration, intermediate blocking, standard blocking and complete blocking, respectively.

Single mechanism

The filtration experiments in this study however used cross-flow mode. Cross-flow mode has been claimed to enhance mass transfer processes that induce back transport from the membrane's surface, leading to lower net flux of foulant to the membrane's surface [6]. The unifying equation for cross-flow filtration applied in this study was:

$$\frac{dJ}{dt} = -k(J - J^*)(J)^{2-n} \quad (6)$$

where J^* is a critical flux and n can take the same values as in equation [1].

Determination of k , J^* with corresponding n was performed using MATLAB 7.0 (Math Works, Natick, MA).

Combined mechanisms

The single mechanism modeling in some cases does not fit well the experimental data due to the possible fact that more than one mechanism affecting membrane fouling.

In simulation of cross-flow filtration mode, the area of open pores was expressed as:

$$A_{open} = A_T \exp \left[-\alpha C_b t \left(\frac{\Delta P}{\mu R_m} - J^* \right) \right] \quad (7)$$

where $A_T (= A_{open} + A_{blocked})$ is the nominal membrane area (m^2); A_{open} is area of unblocked or open pores (m^2); $A_{blocked}$ is area of membrane blocked by foulant (m^2); α is pore blockage parameter (m^2/kg); C_b is bulk concentration of the solute (kg/m^3); ΔP is applied pressure (Pa); μ is solution viscosity ($kg/m/s$); R_m is membrane resistance (m^{-1}).

The rate of cake resistance, which is assumed to be equal to the mass of solute transported to the surface, was integrated analytically from $R_{c,0}$ to R_c :

$$\frac{dR_c}{dt} = \alpha_c (A_T - A_{open}) C_b \left(\frac{\Delta P}{\mu (R_m + R_c)} - J^* \right) \quad (8)$$

where α_c is specific resistance of the cake ($m^{-1}kg^{-1}$); $R_{c,0}$ is resistance of the initial deposit (m^{-1}).

Finally the modeled flux was calculated with the equation:

$$J_T = \frac{A_{open} \Delta P}{\mu R_m} + \frac{(A_T - A_{open}) \Delta P}{\mu (R_m + R_c)} \quad (9)$$

Parameters such as α , α_c , R_c and J^* were optimized using Microsoft Excel Solver and MATLAB 7.0 (Math Works, Natick, MA).

2.2 Testing membranes and testing protocol

Three kinds of membranes (0.5LSMM, 0.25SMM and 0.5SMM) were used for the test. They were polyethersulfone PES based membranes integrated with 0.5% by weight of additives LSMM (hydrophilic molecular surface modifying macromolecules), 0.25% and 0.5% by weight of additives SMM (hydrophobic molecular surface modifying macromolecules), respectively. The membranes were fabricated in the lab by a method which was described in details elsewhere [8,9]. The "Control" membrane was the PES based membrane having no additives incorporated. All these membranes were cleaned thoroughly in ultra pure

water and cut into 52-mm diameter coupons for testing in the ultrafiltration system. The ultrafiltration system for testing was also described in previous research [10]. The membranes were characterized in terms of roughness (via SEM - scanning electron microscopy) and hydrophobicity (via contact angle measurement). The contact angle of membrane surfaces was measured using VCA Optima goniometer (AST Products, Inc., Billerica, MA). Morphological examination of the top surface was made using scanning electron microscopy (SEM, model JSM-6400, Japan Electron Optics Limited, Japan).

For the pure water permeation test, the system was run for 50 hours with ultra pure water under the pressure of 50psi, and then permeation flux J_w was measured. For fouling test, river water was replaced by ultra pure water and run under an operating pressure of 345 kPa gauge (50 psig) and at a feed flow rate of 0.4 Lpm in 50 hours. The initial fluxes $J_{w,i}$ and final flux $J_{w,f}$ were measured at the beginning and at the end of the fouling run. All filtration tests were conducted in duplicate.



3. Results and Discussions

3.1 Characteristics of tested membranes and feed water

The characteristics of tested membranes are presented in Table 1.

It can be seen in Table 1 that the 0.5LSMM-PES based membranes are more hydrophilic (contact angle $<90^\circ$), and they are smoother accordingly. Normally, the smooth membranes shall be less prone to adhering to the foulants. Besides, the hydrophilic membranes trend to allow more water penetration through membranes, less susceptible to fouling and easier to be cleaned [8].

The feed water was a river water with low alkalinity (44mg CaCO_3/L), low hardness (46mg CaCO_3/L), low turbidity (7.57 ± 0.002 NTU), low conductivity (0.11 mS/cm), pH of 7.5 but was highly colored (50 Pt/Co color unit). Dissolved organic carbon (DOC) concentration was 6.78 ± 0.01 mg/L.

3.2 Resistance of tested membranes

The intrinsic membrane resistance, determined using pure water as a feed, is not only useful for modeling purposes, but also for evaluating the stability of the membrane [12]. This value was evaluated after the 50-hr filtration using ultra-pure water.

Fig. 1 depicts the resistances of Control, 0.5LSMM and 0.5 SMM PES based membranes, which are on average of $1.5 \times 10^{13} \text{ m}^{-1}$, $2.2 \times 10^{13} \text{ m}^{-1}$ and $2.6 \times 10^{13} \text{ m}^{-1}$, respectively. It seems that the incorporation of LSMM/SMM made the pore size smaller [8,9], leading to higher solute resistance. In general, higher solute resistance shall increase the solute removal capacity of the membranes due to the solute-solute repulsion in nature.

3.3 Fouling Mechanism Modeling

After the filtration test for 50 hours with river water, the data for each kind of membranes was obtained and was plotted in terms of Flux versus time (hours). Using MATLAB 7.0 software, the coefficients of k , J^* with corresponding n were determined based on equation (6) for single mechanism or equations (7-9) for combined fouling mechanism. With the found coefficients of k , J^* , we plotted again the Flux vs Time graph and check the MSR (mean square regression) to see the best fit model. It should be noted that the lower MSR is, the better fit of the model shall be.

Single mechanism modeling

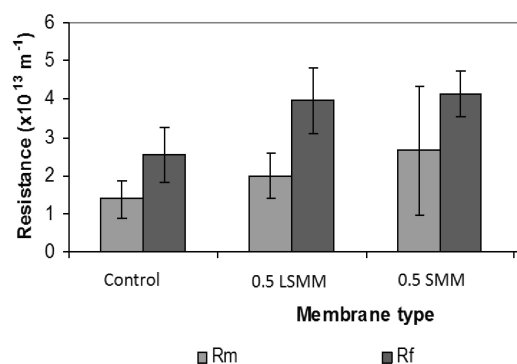
Table 2 presents the regressed model coefficients as well as MSR for single mechanism modeling. It appears that the best fitted (i.e., has the lowest MSR) mechanism varies for every single case. For instance, for 0.5LSMM hydrophilic membranes, standard blocking ($n=1.5$) was dominant fouling mechanism while for

Table 1. Characteristic of tested membranes

Type of membranes	Roughness (nm)	Contact angles ($^\circ$)
0.5LSMM	1.1	70.4
0.25SMM	2.4	90.8
0.5SMM	2.8	91.6

Note: If contact angle is more than 90° , it is considered hydrophobic [11]

Figure 1. R_m and R_f of PES-LSMM membranes





0.5SMM hydrophobic membranes, intermediate blocking or complete blocking best described how foulants deposited on membrane surface. Fig. 2 shows the data fitting for the case of 0.5 LSMM-PES membranes during the filtration test, where the blank circles represent the experimental data while the lines represent the fitted curves for different fouling mechanisms. It can be seen that the brown dash-double-dot line follows the blank circles most closely. Mosqueda et al., [13] found in their study that cake formation was the best fitted model which was definitely not for this case. The difference may be raised from different membranes and testing protocols even though the similar feed of water was used.

It is observed that good fit came along with smooth curve of data. It is worth noting that the values of J^* which is the critical flux were close to the final fluxes after 50-hour testing period. In addition, when the degree of fouling became more serious (from $n=0$ to $n=2$), the fluxes often decreased more slowly and k constant was observed decreasingly. In other words, the smaller values of k represent less dramatic flux decline. It was confirmed in several studies [6,13].

Increasing concentration of SMM affected the fouling mechanism since the best fit model changed without routine. Although the data was not fully analyzed for all the cases, however, increasing concentration of SMM led to rougher surface, smaller mean pore size [9], thus the chances of pore constriction or completely blocking were higher. In addition, these tight UF membranes with small pore size and low MWCO (especially at high concentration 1.5% of SMM) can be considered as loose nanofiltration (NF) membranes, for which the major fouling mechanism was found to be intermediate or complete blocking [14].

In other studies, it was claimed that the mechanism of fouling which occurs during ultrafiltration was based on the adsorption of substances inside pores of a membrane, which resulted in the decrease of an internal pores diameter. It could lead to the increase of the efficiency of substances removal including medium- and low-molecular weight compounds [1].

Combined mechanism modeling

Mosqueda et al., [13] found that for PES based membranes, the combined mechanism fitted the experimental data better than the single one with a smaller mean square error (MSR). It is confirmed again by this study (Fig. 3).

The MSR of combined-mechanism model (Table 3) are all smaller than those of single mechanism model (Table 2), proving the combined simulates better the fouling mechanism. Autopsy of fouled membranes suggested that the irreversible fouling layer was initially formed by pore blocking of small particles followed by strong interaction of fouling layer with mainly dissolved materials and by fouling layer compaction due to permeation drag [15].

According to Table 3, the specific cake resistance parameter αc , pore block parameter α and the resistance of the initial fouling layer $R_{c,0}$ seem to be slightly affected with the increasing concentration of SMM.

To assess the correlation of possible pore restriction due to organic matters and the removal efficiency of organic matters by membranes, DOC (Dissolved organic carbon-represents organic matters present in the water) removal capacity was calculated as below:

Table 2. Fitting parameters for single fouling mechanism model

	n	k	J^*	MSR
0.5LSMM-PES				
	0.0	0.0001	45.3169	4.0400
	1.0	-0.0004	10.0524	1.8932
	1.5	-0.0184	50.4742	0.2712
	2.0	-0.1083	45.9350	0.8980
0.25SMM-PES				
	0.0	0.0009	6.9391	0.4376
	1.0	-0.0017	2.4673	0.4177
	1.5	-0.0362	6.5900	0.3281
	2.0	-0.0379	6.4376	0.4286
0.5SMM-PES				
	0.0	0.0003	6.3364	1.0663
	1.0	-0.0211	10.5017	0.5231
	1.5	-0.0185	10.6172	0.9807
	2.0	-0.2672	10.5195	0.5843

Figure 2. Flux reduction with time for different single mechanism model with 0.5 LSMM membranes

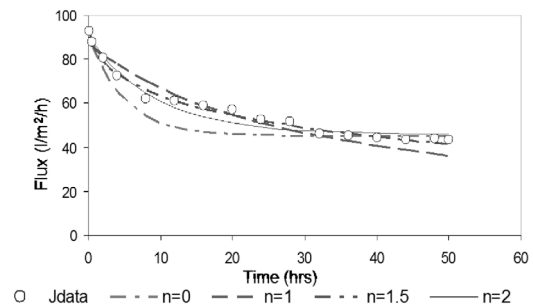
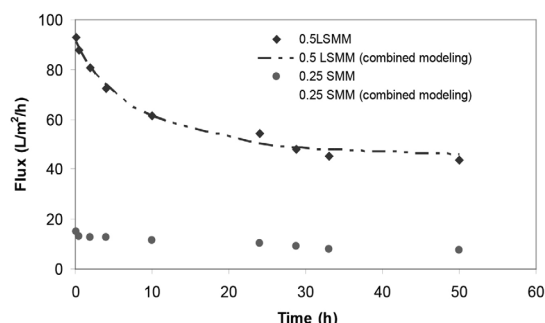
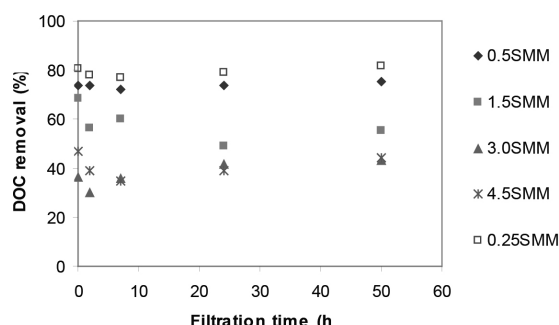


Table 3. Fitting parameters for combined fouling mechanism model

Membranes	α	αc	$R_{c,0}$	J^*	MSR (Combined)	MSR (Single)+
0.5 LSMM	0.2849	3.59E+18	1.45E+16	45.212	0.039	0.271
0.25 SMM	0.2786	8.50E+19	1.00E+17	7.412	0.086	0.328
0.5 SMM	0.3020	1.05E+20	1.01E+17	10.255	0.011	0.523


Figure 3. Flux reduction with time for combined mechanism model for different types of PES based membranes

Figure 4. DOC removal as a function of filtration time

$$\text{DOC removal (\%)} = (1 - \text{DOC}_p / \text{DOC}_f) \times 100 \quad (10)$$

in which: DOC_p and DOC_f : dissolved organic carbon concentrations in the permeate and feed, measured by TOC analyzer equipment.

One would be expected that with increasing SMM additives, the pore size would be smaller, then the organic matters would be retained more on the membrane surface, or organic matters in the permeate would be reduced, leading to higher DOC removal. Fig. 4 presents the DOC removal efficiency of PES based membranes with 0.5 SMM and 0.25 SMM additives and others (1.5 SMM, 3.0 SMM and 4.5 SMM-PES based membranes, referred from previous study [16]). It was revealed that DOC removals were lower for the higher SMM concentration (Fig. 4). The possible explanation for that phenomenon lies on the chemical reaction impacts of the additive on membrane surfaces. It was observed during the film hardening period that the solvent exchange took long time and it happened strongly. Moreover, the roughness of membranes would probably play the key role in solute separation other than pore screening. As the membranes become rougher (with increasing SMM additives), they would be more susceptible to compression under long filtration at high pressure (50 psi), making membranes with more defects than the un-modified membranes. The solute (organic matters) retain, therefore, would be not as good as the un-modified one, accordingly.



4. Conclusion

Fouling of organic matters on membrane surface can be described in many fouling modeling with different mechanisms: cake formation, intermediate blocking, pore constriction/adsorption and complete blocking. In effort of investigating the impact of surface modifying additives on membrane surface and fouling mechanism, a single modeling and a combined modeling were tried. It was revealed that the fouling by organic matters of these hydrophobic membranes involved in most intermediate or complete pore blocking when single fouling mechanism modeling was applied. A combined cake formation and pore constriction model simulated even better the fouling mechanism for those membranes.

During the filtration with river water, organic matters penetrated through the membrane to the permeate side increased with the increase of SMM additives probably due to the morphology of SMM-PES membranes. The rougher SMM-PES membranes more likely to deform under pressure, leading to gap appearance and more organic matter penetration. Moreover, the roughness of membranes would probably play the key role in solute separation other than pore screening in this particular study. Further study on the impacts of different factors such as type of organic matters, flowrate and transmembrane pressure, etc., would help understand the conditions that fouling mechanism least occurs. Also, kind of cleaning for each type of fouling mechanism would be of interest to help recover the membranes to the original state.



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