Cake Layer Fouling Potential Characterization for Wastewater Reverse Osmosis via Gradient Filtration

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Abstract: It is of great importance to quantitatively characterize feed fouling potential for the effective and efficient prevention and control of reverse osmosis membrane fouling. A gradient filtration method with microfiltration (MF 0.45 μm) → ultrafiltration (UF 100 kDa) → nanofiltration (NF 300 Da) was proposed to extract the cake layer fouling index, I, of different feed foulants in this study. MF, UF, and NF showed high rejection of model suspended solids (kaolin), colloids (sodium alginate and bovine serum albumin), and dissolved organic matters (humic acid) during constant-pressure individual filtration tests, where the cake layer was the dominant fouling mechanism, with I showing a good linear positive correlation with the foulant concentration. MF → UF → NF gradient filtration tests of synthetic wastewater (i.e., model mixture) showed that combined models were more effective than single models to analyze membrane fouling mechanisms. For each membrane of gradient filtration, I showed a positive correlation with the targeted foulant concentration. Therefore, a quantitative assessment method based on MF → UF → NF gradient filtration tests of synthetic wastewater (i.e., model mixture) showed that combined models were more effective than single models to analyze membrane fouling mechanisms. For each membrane of gradient filtration, I showed a positive correlation with the targeted foulant concentration. Therefore, a quantitative assessment method based on MF → UF → NF gradient filtration, the correlation of combined fouling models, and the calculation of I would be useful for characterizing the fouling potentials of different foulants. This method was further successfully applied for characterizing the fouling potential of real wastewater (i.e., sludge supernatant from a membrane bioreactor treating dyeing and finishing wastewater).

Keywords: gradient filtration; single and combined membrane fouling models; cake layer fouling index; fouling potential; model foulants; real wastewater; reverse osmosis

1. Introduction

A reverse osmosis (RO) membrane with a nonporous dense structure has the highest rejection performance (theoretically rejects any substance except for water molecules) among pressure-driven membranes for water and wastewater treatment [1]. Thus, the RO process has gained successful full-scale application in seawater desalination [2–5] and high-quality reclaimed water production, mainly from biologically treated wastewater [6–8], due to its intrinsic advantages of stable and excellent permeate quality, compact structure and small footprint, ease of automatic operation, etc. However, membrane fouling is an inevitable problem during RO membrane operation, resulting in a reduction in membrane flux and rejection performance, thus restricting its technical economy [9–11]. Membrane fouling is essentially affected by the complex interactions between the membrane and foulants and among different foulants [12–14]. It is of great importance to accurately and quickly characterize the fouling potential of RO feed to select an appropriate pretreatment
to effectively and efficiently prevent and control RO membrane fouling [15,16]. Thus, a fouling index is proposed to quantitatively characterize the fouling potential of RO feed [17–19].

The silt density index (SDI) was first developed to predict the fouling potential of particles (including suspended solids and some colloids) in RO feed [20]. It measures the plugging rate of a microfiltration (MF) membrane (mean pore size of 0.45 µm and diameter of 47 mm) in a constant-pressure (207 kPa) dead-end filtration mode. Lots of statistical data have demonstrated the significant positive correlation between RO membrane fouling and the SDI of RO feed [20]. The SDI of RO feed has been listed as one of the key feed quality parameters by RO membrane manufacturers. Based on field experience, the SDI of RO feed is generally required to be less than 4 or 5 for a spiral-wound module and less than 3 for a hollow-fiber module. However, the SDI is inherently an empirical parameter characterizing the MF fouling rate in constant-pressure dead-end filtration and thus lacks a theoretical basis. Many studies have shown the reliability issue of SDI testing and the limitations of SDI application (e.g., the lack of a fouling mechanism, no intrinsic linear relationship between the SDI value and the concentration of colloid and suspended solids, and not covering most colloids with sizes significantly less than 0.45 µm) [21–23].

The modified fouling index (MFI) was derived directly from the improvement of the SDI, where the same MF process and a new calculation method based on a cake layer fouling mechanism were adopted [24]. Thus, the MFI is better than the SDI to characterize the particulate fouling potential of RO feed. Some RO membrane manufacturers have required feed MFI less than 1 s/L², which is equivalent to an SDI less than 3 according to the standard method for MFI measurement [24]. As a relatively new index, the MFI still needs time to accumulate field data for setting the target value of RO feed. In addition, pore blocking and cake layer fouling mechanisms usually occur simultaneously during the constant-pressure dead-end MF process [24], thus affecting MFI measurement. A new double-MFI measurement (i.e., raw feed for the first measurement and the first permeate for the second measurement) was proposed to eliminate the effects of pore blocking [25].

Considering that SDI and MFI measurements are based on an MF membrane with a mean pore diameter of 0.45 µm that cannot reject colloids and dissolved organic matters (i.e., the important foulants causing RO fouling) effectively, an ultrafiltration (UF) membrane with a molecular weight cut-off (MWCO) of 13 kDa (approximate pore size of 5–8 nm) and a nanofiltration (NF) membrane with an MWCO of 1.5 kDa were proposed for MFI measurements, resulting in MFI-UF [26] and MFI-NF [27]. MFI-UF has been developed under both constant-pressure and constant-flux dead-end filtration modes [28,29]. MFI-UF with a crossflow sampler has been further developed to simulate the hydraulic selective deposition of particulates and colloids during real crossflow filtration of an RO membrane [30]. MFI-NF with a cake resistance simulator has been further proposed to simulate the same salt concentration close to the RO membrane surface and filtration pressure as the real RO process, resulting in the same specific cake resistance [31]. It should be noted that the last two improvements require a complex measuring device and methodology, take a long time, and need more field data verification.

There are generally multiple potential foulants with sizes of several nanometers to several hundred micrometers (i.e., particulates, colloids, and dissolved organic matters) in RO feed (e.g., seawater and biologically treated wastewater), resulting in very complex fouling phenomena, and thus it is very difficult to characterize its fouling potential via only one index associated with one membrane. Thus, a multiple membrane array system with gradient filtration of MF → UF → NF was proposed to characterize the cake layer fouling potentials of particulate matters, colloids, and dissolved organic matters via MFI-MF, MFI-UF, and MFI-NF, respectively, for a seawater RO application [32,33]. Although it is a promising methodology to characterize the fouling potential of RO feed, the gradient filtration of MF → UF → NF requires further development, including membrane and pressure selection, the extraction methodology of the real cake layer fouling potential, and verification from seawater as well as biologically treated wastewater.
In this study, an MF → UF → NF gradient filtration methodology was systematically investigated to characterize the fouling potential of biologically treated wastewater as a targeted RO feed. The positive correlations between the cake layer fouling index and the targeted foulant concentrations were first demonstrated for individual MF, UF, and NF tests. Then, single and combined membrane fouling models were employed to analyze the fouling mechanism of each membrane (MF, UF, and NF) filtration process in the MF → UF → NF gradient filtration of a model foulant mixture, resulting in a new extraction method based on combined models for the cake layer fouling index. Thus, the MF → UF → NF gradient filtration methodology was proposed because the cake layer fouling index showed a positive correlation with feed quality for each membrane. Finally, the MF → UF → NF gradient filtration methodology was successfully employed to characterize the fouling potential of biologically treated dyeing and finishing wastewater.

2. Materials and Methods

2.1. Experimental Setup for Gradient Filtration

In this study, a lab-scale low-pressure MF/UF dead-end filtration setup (shown in Figure 1) and a high-pressure NF cross-flow filtration setup (shown in Figure 2) were used for gradient filtration tests. Through pretests, a polyvinylidene fluoride flat-sheet MF membrane (model name of MF045) with a nominal pore size of 0.45 μm, a polyvinylidene fluoride flat-sheet UF membrane (model name of UF100) with an MWCO of 100 kDa, and a composite polyamide flat-sheet NF membrane (model name of NF200) with an MWCO of 300 Da (MF and UF from RisingSun Membrane Technology, Beijing, China and NF from Dow Chemical, Midland, MI, USA) were selected for the gradient filtration tests of MF → UF → NF, where the corresponding operating pressures were selected as low values of 0.5, 1, and 10 bar, respectively, considering the potential occurrence of cake layer compression and balance recording malfunction under high pressure and the associated high initial permeate flow. All membrane surfaces were hydrophilic, and the pure water fluxes at 20 °C of the MF, UF, and NF membranes were measured as 7200, 168, and 3.1 L/m²·h/bar, respectively, in this study. The surface mean roughness of the NF membrane was reported as 5.2 nm in a previous study [34].

![Figure 1. Low-pressure MF/UF dead-end filtration setup.](image)

Prior to the beginning of the low-pressure MF/UF dead-end filtration test, compressed nitrogen was first employed to pressurize the water sample to be filtered in a stainless-steel tank with an effective volume of 10 L to a preset pressure value. Then, the exhaust valve of the filtration cell with a membrane area of 41.8 cm² (Amicon 8400, Millipore, Burlington, MA, USA) was opened to vent the residual air in the pipe and filtration cell. The constant-pressure dead-end filtration was thus started. The weight of the filtrate was weighed in real time by an electronic balance (ME4002E, Mettler Toledo, Greifensee, Switzerland) and sent to a computer for recording. According to the measured temperature of the filtrate (20 ± 1 °C), the density was calculated, and the weight was further converted into volume. Finally, the instantaneous filtration rate was obtained by the numerical differentiation...
of the filtrate volume and the filtration time, and the instantaneous membrane flux was further calculated.

![Diagram](image)

Figure 2. High-pressure NF crossflow filtration setup.

The NF cross-flow filtration setup was composed of a high-pressure plunger diaphragm pump, a flat-sheet NF membrane with an area of 96 cm², an inlet/concentrate bucket, a thermostatic bath, two pressure gauges, a regulating valve, a balance for measuring effluent weight, and a computer. The high-pressure pump provided a constant-pressure cross-flow filtration mode. The pressure was adjusted by the regulating valve. The thermostatic bath maintained the water sample at a constant temperature of 20 ± 1 °C through a heat exchange jacket. The filtrate was automatically weighed and recorded by the balance connected to the computer and further processed according to the above-mentioned method.

2.2. Wastewater Sample and Analytical Method

The model foulants of kaolin (mean diameter of 2.5 μm), a mixture of sodium alginate (mean MWCO of 150 kDa) and bovine serum albumin (mean MWCO of 66 kDa), and humic acid (mean MWCO of 3 kDa) from Macklin (Shanghai, China) were employed to simulate suspended solids, colloids, and dissolved organic matters in biologically treated wastewater. The synthetic kaolin solution (10, 50, and 100 mg/L), the mixed solution of sodium alginate (10, 50, and 100 mg/L) and bovine serum albumin (10, 50, and 100 mg/L), and the humic acid solution (10, 50, and 100 mg/L), fully mixed or dissolved by stirring, were prepared for the individual MF, UF, and NF tests, respectively. The synthetic wastewater (SWW) sample for the gradient filtration test of MF → UF → NF was a mixture of the model foulants. High- and low-concentration samples containing kaolin (10 and 5 mg/L), sodium alginate (1 and 0.5 mg/L), bovine serum albumin (1.5 and 0.75 mg/L), and humic acid (7.5 and 3.75 mg/L), respectively, were prepared to simulate high- and low-concentration biologically treated wastewater as SWW samples. The sludge supernatant from a membrane bioreactor (MBR) treating dyeing and finishing wastewater in a local wastewater treatment plant was prepared via gravitational sedimentation as a real wastewater (RWW) sample.

The turbidity and absorbance at 254 nm (UV₂₅₄) of the wastewater samples were measured by a portable turbidimeter (WGZ-4000B, Xinrui, Shanghai, China) and an ultraviolet-visible spectrophotometer (T6, Puxi, Beijing, China), respectively. The raw wastewater samples containing suspended solids were prefiltred by a 0.45 μm syringe filter to measure dissolved organic carbon (DOC) with an organic carbon analyzer (TOC-L, Shimadzu, Kyoto, Japan). The DOC values of membrane permeate samples were directly measured.

2.3. Membrane Fouling Mechanism Analysis

Table 1 lists the single and combined membrane fouling models that can be used to describe the constant-pressure filtration process [23,35,36]. In this study, Origin software (2018, OriginLab, Northampton, MA, USA) was used to fit the filtration data with the model
equations for analyzing the membrane fouling mechanism. The linear and nonlinear fitting for single and combined membrane fouling models, respectively, were conducted based on the equations in Table 1. On the basis of passing the model F test and the parameter t test ($p < 0.1$), a coefficient of determination, $R^2$, of more than 0.95 could be considered as a successful fitting.

### Table 1. Membrane fouling models for constant-pressure filtration.

| Model Name               | Equation * | Characteristic Parameters | Schematic Diagram |
|--------------------------|------------|---------------------------|-------------------|
| Cake layer               | $\frac{t}{V/A} = \frac{1}{J_0} + \frac{K_c}{A} (V/A)$ | $K_c$ (s/m²)      |                   |
| Complete blocking        | $\frac{d(V/A)}{dt} = J_0 - K_\theta (V/A)$ | $K_\theta$ (s⁻¹) |                   |
| Intermediate blocking    | $\frac{d}{dV} = \frac{1}{J_0} + K_i t$ | $K_i$ (m⁻¹)       |                   |
| Standard blocking        | $\frac{d}{dV} = \frac{1}{J_0} + \frac{K_s}{A} t$ | $K_s$ (m⁻¹)       |                   |
| Complete blocking–Cake layer | $\frac{V}{A} = \frac{K_i}{K_\theta} \left(1 - \exp\left(\frac{K_c}{K_\theta (V/A)} \right) \right)$ | $K_c$ (s/m²), $K_\theta$ (s⁻¹) |   |
| Intermediate blocking–Cake layer | $\frac{V}{A} = \frac{1}{K_\theta} \ln \left(1 + \frac{K_c}{K_\theta (V/A)} \right)$ | $K_c$ (s/m²), $K_i$ (m⁻¹) |   |
| Complete blocking–Standard blocking | $\frac{V}{A} = \frac{K_i}{K_s} \left(1 - \exp\left(\frac{K_s}{2K_i J_0} \right) \right)$ | $K_i$ (s⁻¹), $K_s$ (m⁻¹) |   |
| Intermediate blocking–Standard blocking | $\frac{V}{A} = \frac{1}{K_s} \ln \left(1 + \frac{2K_i J_0}{K_s} \right)$ | $K_i$ (m⁻¹), $K_s$ (m⁻¹) |   |
| Standard blocking–Cake layer | $t = \frac{1}{K_s \left(\frac{V}{A}\right)^2} \left(K_c \frac{V}{A} \right)^2 - \frac{(\frac{V}{A})}{J_0} - \frac{2\left(\frac{V}{A}\right)^2}{J_0}$ | $K_c$ (s/m²), $K_s$ (m⁻¹) |   |

*: $t$ is filtration time (s), $V$ is permeate volume (m³), $A$ is membrane area (m²), $J_0$ is initial membrane flux (m³/m²·s).

Based on the cake layer fouling model in Table 1, the MFI is calculated from Equation (1) to evaluate the fouling potential of the cake layer [24].

$$\frac{t}{V} = \frac{1}{A J_0} + \frac{K_c \mu R_m}{2 A^2 V} = \frac{\mu R_m}{A \Delta P} + \frac{\mu J}{2 \Delta P A^2} V = \mu \frac{R_m}{A \Delta P} + \frac{\mu a C}{2 \Delta P A^2} V$$

(1)

where $\Delta P$ is the filtration pressure (N/m²), $\mu$ is the filtrate viscosity (N·s/m²), $R_m$ is the pure membrane resistance (m⁻¹), $I$ is the fouling index of the cake layer (1/m²), $a$ is the specific resistance of the cake layer (m/g), $C$ is the particulate matter concentration (mg/L), and MFI is the modified fouling index (s/L²). $K_c$ can be obtained by linear fitting, and the MFI and $I$ can be further calculated according to $A$, $\Delta P$, and $\mu$. In this study, the MFI values for the filtration tests of MF, UF, and NF were not directly comparable due to the different pressure and membrane area applied, while $I$ was the product of $a$ and $C$ and thus directly characterized the cake layer formed on the membrane surface. Therefore, the cake layer fouling index, $I$, of MF, UF, and NF in MF → UF → NF gradient filtration could be used to quantitatively compare the cake layer fouling potential of suspended solids, colloids, and dissolved organic matters, respectively.
3. Results and Discussion

3.1. Response of Cake Layer Fouling Index, I, to Targeted Fouulant Concentrations for Individual MF, UF, and NF Tests

The turbidities of the kaolin solutions with concentrations of 10, 50, and 100 mg/L were 0.83, 2.86, and 5.48 NTU, respectively; the turbidities of the MF permeates were 0.32, 0.40, and 0.61 NTU, respectively; and the turbidity rejection rates of MF were 62.8, 86.0, and 90.0%, respectively, indicating that the MF membrane with a nominal pore size of 0.45 μm used in the study could effectively reject suspended solids, represented by kaolin. The MF process closely followed the cake layer model in this study. Taking the filtration of a 10 mg/L kaolin solution as an example, the cake layer model fit well ($R^2 > 0.95$, $p < 0.01$, shown in Figure 3a). From the relationship between $I$ and the feed kaolin concentration in the MF process (shown in Figure 3b), $I$ gradually increased from $2.58 \times 10^{10}$ to $3.69 \times 10^{10}$ to $4.80 \times 10^{10}$ m$^{-2}$ with feed kaolin concentrations from 10 to 50 to 100 mg/L, respectively. The linear fitting showed a very good linear positive correlation between $I$ and the feed kaolin concentration ($R^2 > 0.99$, $p = 0.04$), with the slope of $2 \times 10^8$ m/g characterizing the cake layer specific resistance.

![Figure 3. Cake layer model fitting for the MF process of a 10 mg/L kaolin solution (a) and the correlation between $I$ and the feed kaolin concentration (b).](image)

The DOC values of mixed sodium alginate and bovine serum albumin solutions with concentrations of 10, 50, and 100 mg/L were 5.21, 22.60, and 42.72 mg/L, respectively; the DOC values of UF permeate were 1.73, 4.68, and 12.36 mg/L, respectively, and the DOC rejection rates of UF were 66.8, 79.3, and 71.1%, respectively, indicating that the UF membrane with an MWCO of 100 kDa used in the study could effectively reject colloids, represented by sodium alginate and bovine serum albumin. The UF process closely followed the cake layer model in this study. Taking the filtration of a mixed 10 mg/L sodium alginate and 10 mg/L bovine serum albumin solution as an example, the cake layer model fit well ($R^2 > 0.99$, $p < 0.01$, shown in Figure 4a). From the relationship between $I$ and the feed colloid concentration in the UF process (shown in Figure 4b), $I$ gradually increased from $1.08 \times 10^{14}$ to $5.18 \times 10^{14}$ to $1.02 \times 10^{15}$ m$^{-2}$ with feed colloid concentrations from 20 to 100 to 200 mg/L, respectively. The linear fitting showed a very good linear positive correlation between $I$ and feed colloid concentrations ($R^2 > 0.99$, $p < 0.01$), with the slope of $5 \times 10^{12}$ m/g characterizing the cake (or gel) layer specific resistance.

The UV$_{254}$ values of the humic acid solutions with concentrations of 10, 50, and 100 mg/L were 0.332, 1.834, and 3.433 cm$^{-1}$, respectively, while the UV$_{254}$ values of the NF permeates were 0.025, 0.032, and 0.045 cm$^{-1}$, respectively, and the UV$_{254}$ rejection rates of NF were 92.5, 98.3, and 98.7%, respectively, indicating that the NF membrane with an MWCO of 300 Da used in the study could effectively reject dissolved organic matters, represented by humic acid. The NF process closely followed the cake layer model in this study. Taking the filtration of a 10 mg/L humic acid solution as an example, the cake layer
model fit well ($R^2 > 0.99, p < 0.01$, shown in Figure 5a). From the relationship between $I$ and feed humic acid concentration in the NF process (shown in Figure 5b), $I$ gradually increased from $3.42 \times 10^{13}$ to $5.16 \times 10^{13}$ to $8.65 \times 10^{13}$ m$^{-2}$, with feed humic acid concentrations from 10 to 50 to 100 mg/L, respectively. The linear fitting showed a very good linear positive correlation between $I$ and the feed humic acid concentration ($R^2 > 0.98, p = 0.08$), with the slope of $6 \times 10^{11}$ m/g characterizing the cake (or gel) layer specific resistance.

The filtration processes of the MF, UF, and NF membranes feeding their respective targeted foulants (i.e., suspended solids, colloids, and dissolved organic matters) in this study closely followed the cake layer model, and the cake layer fouling index, $I$, showed a good linear positive correlation with the foulant concentration, demonstrating that $I$ could serve as a quantitative index to characterize the membrane fouling potential, thus laying a theoretical foundation for the subsequent investigation of the gradient filtration of MF → UF → NF for wastewater samples. The linear fitting relationship between $I$ and the feed foulant concentration showed that the specific resistance ($5 \times 10^{12}$ m/g) of the UF cake layer formed by colloids (i.e., sodium alginate and bovine serum albumin) per unit concentration > the specific resistance ($6 \times 10^{11}$ m/g) of the NF cake layer formed by dissolved organic matters (i.e., humic acid) per unit concentration >> the specific resistance ($2 \times 10^8$ m/g) of the MF cake layer formed by suspended solids (i.e., kaolin) per unit concentration.
3.2. Development of Cake Layer Fouling Potential Assessment Methodology in Gradient Filtration Based on SWW

3.2.1. Rejection Performance during the Gradient Filtration of SWW

Figure 6 shows the feed and permeate quality of each membrane in the gradient filtration of SWW containing high- and low-concentration model foulant mixtures. The turbidity, DOC, and UV$_{254}$ of low- and high-concentration SWW (i.e., MF feed) were 1.71 and 6.98 NTU, 2.51 and 4.24 mg/L, 0.16 and 0.36 cm$^{-1}$, respectively. For low- and high-concentration SWW, the turbidity rejection rates of MF, UF, and NF in gradient filtration were 69.8 and 78.2%, 13.5 and 18.6%, and 2.2 and 22.6%, respectively. The high turbidity rejection rate of MF verified its high rejection of the targeted foulants—suspended solids (i.e., kaolin). For low- and high-concentration SWW, the DOC rejection rates of MF, UF, and NF in gradient filtration were 1.9 and 2.4%, 74.9 and 58.1%, and 22.0 and 55.0%, respectively. The high rejection rate of DOC by UF verified its high rejection of the targeted foulants—colloids (i.e., sodium alginate and bovine serum albumin). For low- and high-concentration SWW, the UV$_{254}$ rejection rates of MF, UF, and NF in gradient filtration were 5.1 and 14.4%, 40.3 and 42.8%, and 71.2 and 69.6%, respectively. The high UV$_{254}$ rejection rate of MF verified its high rejection of the targeted foulants—dissolved organic matters (i.e., humic acid). It should be noted that turbidity, DOC, and UV$_{254}$ were not solely specific to suspended solids, colloids, and dissolved organic matters, respectively, in this study. For example, sodium alginate and bovine serum albumin could generate turbidity, humic acid could generate DOC, and bovine serum albumin could generate UV$_{254}$. This was why UF showed significant rejection on UV$_{254}$ and NF showed significant rejection on DOC.

![Figure 6](image-url)  
**Figure 6.** Turbidity (a), DOC (b), and UV$_{254}$ (c) during gradient filtration of low- (Δ) and high-concentration (■) SWW.
3.2.2. Membrane Fouling Mechanism Analysis in Gradient Filtration Based on Single Models

Figure 7 shows the fitting results of single models for the MF process in the gradient filtration of SWW. Benefitting from the high-frequency recording of permeate weight every 10 s in this study, the dense data points formed smooth curves for all subfigures. Based on the general standard of $R^2 > 0.95$ employed in this study, the cake layer, standard blocking, and intermediate blocking models showed good linear fitting ($R^2 > 0.95, p < 0.01$) for both low- and high-concentration SWW. The complete blocking model also showed good linear fitting ($R^2 = 0.9691, p < 0.01$) for low-concentration SWW. If setting a very good linear fitting standard (e.g., $R^2 > 0.99$), it was still achievable via selecting partial data (e.g., the final/initial third of data points for high/low-concentration SWW) to make good linear fittings for all four single models. The same methodology was employed for the UF and NF processes. Table 2 summarizes the linear fitting $R^2$ of single models for the MF, UF, and NF processes in gradient filtration ($p < 0.01$). The simultaneous occurrence of two or more membrane fouling mechanisms not only existed in the MF process but also in the UF and NF processes. For example, during the NF process of low-concentration SWW, four single models (i.e., cake layer, standard blocking, intermediate blocking, and complete blocking) fit well, indicating the occurrence of statistical illusion in judging the fouling mechanism in the filtration process simply via single models [36–38].

![Figure 7. Linear fitting of single models, including cake layer (a), standard blocking (b), intermediate blocking (c), and complete blocking (d) for MF process during gradient filtration of low- (□) and high-concentration (×) SWW.](image-url)
### Table 2. $R^2$ of single model fitting for gradient filtration of SWW.

| Membrane  | Low-Concentration SWW | High-Concentration SWW | Low-Concentration SWW | High-Concentration SWW | Low-Concentration SWW | High-Concentration SWW | Low-Concentration SWW | High-Concentration SWW |
|-----------|-----------------------|------------------------|-----------------------|------------------------|-----------------------|------------------------|-----------------------|------------------------|
| MF        | 0.9494                | 0.9862                 | 0.9995                | 0.9868                 | 0.9958                | 0.9955                 | 0.9691                | 0.8441                 |
| UF        | 0.9996                | 0.9771                 | 0.9704                | 0.9419                 | 0.9783                | 0.9739                 | 0.8213                | 0.8116                 |
| NF        | 0.9529                | 0.8367                 | 0.9776                | 0.8242                 | 0.9786                | 0.7607                 | 0.9698                | 0.8024                 |

#### 3.2.3. Membrane Fouling Mechanism Analysis in Gradient Filtration Based on Combined Models

Taking the MF process in the gradient filtration of low-concentration SWW as an example, Figure 8 shows the fitting results of the combined models of intermediate blocking–standard blocking and standard blocking–cake layer. The calculated values of the models were in very good agreement with the experimental values ($R^2$ of 0.9998 and 0.9994, respectively, $p < 0.01$). Only one combined model fit well in the other membrane filtration processes ($R^2 > 0.98$, $p < 0.01$). Table 3 summarizes the fitting results of the combined models in the gradient filtration processes ($p < 0.01$). For the MF process of the gradient filtration of low-concentration SWW, two combined models (i.e., intermediate blocking–standard blocking and standard blocking–cake layer) fit well, indicating the simultaneous occurrence of intermediate blocking, standard blocking, and cake layer fouling mechanisms. According to the characteristic parameters ($K_c$, $K_i$, $K_s$, and $K_b$) of nonlinear fitting, the contribution of each single fouling mechanism to flux reduction could be calculated [35,36]. In the combined model of intermediate blocking and standard blocking, the contributions of intermediate blocking and standard blocking were 91.3% and 8.7%, respectively, while in the combined model of standard blocking and cake layer, the contributions of standard blocking and cake layer were 64.1% and 35.1%, respectively. Therefore, three fouling mechanisms coexisted in the MF process of the gradient filtration of low-concentration SWW, and the cake layer was not the dominant fouling mechanism, which might be related to the interaction (e.g., noncovalent interaction and spatial effect) between suspended solids and colloids or dissolved organic matters in the SWW [14]. For the MF process of the gradient filtration of high-concentration SWW, only the combined model of complete blocking and cake layer fit well. The quantitative calculation showed that the contributions of complete blocking and cake layer were 88.2% and 11.8%, respectively, indicating that the cake layer was the absolute dominant fouling mechanism.

#### 3.2.4. Evaluation of Cake Layer Fouling Potential of SWW Based on Gradient Filtration

Figure 9 shows the cake layer fouling index, $I$, of each membrane filtration process in the gradient filtration of SWW according to the above combined model fitting. The $I$ values in the MF process of gradient filtration with low- and high-concentration SWW were $6.08 \times 10^{10}$ and $1.44 \times 10^{12} \text{m}^{-2}$, respectively, and the corresponding feed turbidity values of MF were 1.71 and 6.98 NTU, respectively. The $I$ values of the UF process were $5.77 \times 10^{12}$ and $1.02 \times 10^{13} \text{m}^{-2}$, respectively, and the DOC values of UF feed (i.e., MF permeate) were 2.46 and 4.14 mg/L, respectively. The $I$ values of the NF process were $1.40 \times 10^{14} \text{m}^{-2}$ and $2.16 \times 10^{14} \text{m}^{-2}$, respectively, and the UV$_{254}$ values of NF feed (i.e., UF permeate) were 0.09 and 0.18 cm$^{-1}$, respectively. The $I$ of each membrane had a positive correlation with its targeted feed foulant concentration, indicating that the $I$ values of the MF, UF, and NF processes could quantitatively evaluate the cake layer fouling potential of suspended solids, colloids, and dissolved organic matters, respectively. The order of $I$ values in the different membrane filtration process was NF >> UF >> MF. Further considering the foulant
concentration ratio in SWW (suspended solids/colloids/dissolved organic matter ratio of 4:1:3), it could be roughly estimated that the specific resistance order of the cake layer formed by foulants was NF > UF >> MF (i.e., dissolved organic matters > colloids >> suspended solids), similar to previous studies [32,33]. This was different from the order of specific resistance of the cake layer (i.e., UF > NF >> MF or colloids > dissolved organic matters >> suspended solids) in Section 3.1, where individual membranes and targeted foulants were applied. This could be related to the interactions of different foulants in SWW [14].

![Figure 8. Nonlinear fitting of the combined models of intermediate blocking–standard blocking (a) and standard blocking–cake layer (b) for the MF process during the gradient filtration of low-concentration SWW.](image)

**Table 3. Fitting results of combined models during gradient filtration of SWW.**

| Concentration                    | Gradient Filtration | Combined Model                              | Parameter Value       | Nonlinear Fitting $R^2$ |
|----------------------------------|---------------------|--------------------------------------------|-----------------------|-------------------------|
| **low-concentration SWW**        | MF                  | Intermediate blocking–Standard blocking     | $K_i = 2.30 \text{ m}^{-1}$ |
|                                  |                     | Standard blocking–Cake layer               | $K_s = 0.223 \text{ m}^{-1}$ |
|                                  | UF                  | Intermediate blocking–Cake layer           | $K_i = 1.836 \text{ m}^{-1}$ |
|                                  |                     |                                              | $K_s = 1.223 \text{ s/m}^2$ |
|                                  | MF                  | Complete blocking–Cake layer               | $K_i = 5.8 \times 10^4 \text{ s/m}^2$ |
|                                  |                     |                                              | $K_s = 1.41 \times 10^5 \text{ s/m}^2$ |
|                                  |                     |                                              | $K_c = 0.0178 \text{ s}^{-1}$ |
| **high-concentration SWW**       | MF                  | Intermediate blocking–Cake layer           | $K_i = 2.89 \times 10^4 \text{ s/m}^2$ |
|                                  |                     |                                              | $K_s = 1.74 \times 10^7 \text{ m}^{-1}$ |
|                                  | NF                  | Intermediate blocking–Cake layer           | $K_i = 1.03 \times 10^5 \text{ s/m}^2$ |
|                                  |                     |                                              | $K_s = 1.85 \times 10^{-11} \text{ m}^{-1}$ |
|                                  |                     |                                              | $K_c = 2.17 \times 10^5 \text{ s/m}^2$ |

3.3. Cake Layer Fouling Potential Assessment via Gradient Filtration of RWW

3.3.1. Rejection Performance in Gradient Filtration of RWW

Figure 10 shows the feed and permeate qualities of each membrane in the gradient filtration of RWW (i.e., the supernatant of MBR treating dyeing and finishing wastewater) with two different DOC concentrations sampled in different seasons. The DOC, turbidity, and UV254 values of low- and high-DOC RWW were 29.22 and 38.03 mg/L, 1.42 and 0.81 NTU, and 1.17 and 1.77 cm$^{-1}$, respectively. The higher turbidity in low-DOC than high-DOC RWW was mainly due to the worse sludge settleability when sampling MBR sludge. The turbidity rejection rates of low- and high-DOC RWW by MF, UF, and NF were 42.0% and 6.2%, 27.9% and 6.2%, and 40.4% and 6.1%, respectively, indicating that higher turbidity in RWW could result in higher rejection by membranes. The DOC rejection
rates of low- and high-DOC RWW by MF, UF, and NF were 20.1% and 13.4%, 13.4% and 13.3%, and 78.5% and 57.8%, respectively. The DOC rejection order of NF >> MF > UF might be related to the bimodal distribution of organics in the MBR supernatant [39,40], where the minor submicron biopolymers could be rejected directly by MF and the major low-molecular-weight organics less than 1 kDa could only be rejected by NF, thus resulting in low rejection by UF in this study. The UV$_{254}$ rejection rates of low- and high-DOC RWW by MF, UF, and NF were 5.5% and 0.6%, 5.8% and 9.9%, and 84.5% and 85.5%, respectively. The high rejection of both DOC and UV$_{254}$ by NF indicated that low-molecular-weight organic compounds with benzene rings and unsaturated bonds (e.g., humic and fulvic substances) could be the major components of RWW in this study.

Figure 9. Cake layer fouling index, $I$, during gradient filtration of SWW.

Figure 10. Turbidity (a), DOC (b), and UV$_{254}$ (c) during gradient filtration of low- ($\triangle$) and high-DOC (■) RWW.
3.3.2. Membrane Fouling Mechanism Analysis and Cake Layer Fouling Potential Evaluation in Gradient Filtration of RWW

Table 4 shows the linear fitting results of single models for the gradient filtration of RWW. Similar to SWW, the linear fitting of single models for the gradient filtration of RWW showed the simultaneous occurrence of multiple fouling mechanisms caused by the statistical illusion, with the only exception being the NF process of low-DOC RWW, where none of the single models fit well.

Table 4. R² of single model fitting for gradient filtration of RWW.

| Membrane | Cake Layer | Standard Blocking | Intermediate Blocking | Complete Blocking |
|----------|------------|-------------------|-----------------------|------------------|
|          | Low-DOC RWW | High-DOC RWW | Low-DOC RWW | High-DOC RWW | Low-DOC RWW | High-DOC RWW | Low-DOC RWW | High-DOC RWW |
| MF       | —          | 0.9986          | 0.9967          | 0.9934          | 0.9823          | 0.9913          | 0.9117          | 0.9644          |
| UF       | 0.9748      | 0.9913          | 0.9518          | 0.9851          | 0.6943          | 0.804           | 0.8857          | 0.9207          |
| NF       | 0.8930      | 0.968           | 0.8809          | 0.9811          | 0.8554          | 0.953           | 0.8824          | 0.9681          |

Table 5 presents the nonlinear fitting results of the combined models for RWW. For the MF process of low-DOC RWW, only the combined model of intermediate blocking and standard blocking fit well. The contribution of intermediate blocking was calculated as 84.7%, indicating the dominant intermediate blocking fouling in the MF process that neither the standard blocking fitted by single models nor the cake layer generally considered, which might be due to very low concentration of suspended solids in RWW [23]. For the UF process of low-DOC RWW, only the combined model of intermediate blocking and cake layer fit well. Although the fitting characteristic parameter, $K_i$, of the intermediate blocking model did not pass the $t$ test, the contribution of intermediate blocking could be neglected, considering the very small order of magnitude of $K_i$, resulting in the dominant cake layer fouling in the UF process. For the NF process of high-DOC RWW, the MF rejected DOC values of the UF and NF processes showed a positive correlation with foulant concentration, indicating their capability to characterize the fouling potential of RWW quantitatively. A further comparison between $I$ and the rejected DOC of the UF and NF processes for both low- and high-DOC RWW showed that the fouling layer formed on the NF membrane by dissolved organic matters had a significantly higher specific resistance than that formed on the UF membrane by colloids. For high-DOC RWW, the $I$ of the MF process was $5.1 \text{ mg/L}$. A further comparison
between \( I \) and the rejected DOC values of the MF and UF processes for high-DOC RWW showed that the fouling layer formed on the MF membrane by dissolved organic matters had a far lower specific resistance than that formed on the UF membrane by colloids. These results were also in agreement with the above-mentioned SWW.

**Table 5.** Fitting results of combined models during gradient filtration of RWW.

| Type          | Gradient Filtration | Combined Model                      | Parameter Value                      | Nonlinear Fitting R² |
|---------------|---------------------|-------------------------------------|--------------------------------------|----------------------|
| Low-DOC RWW   | MF                  | Intermediate blocking–Standard blocking | \( K_i = 3.88 \text{ m}^{-1}, K_c = 0.70 \text{ m}^{-1} \) | 0.9988               |
|               | UF                  | Intermediate blocking–Cake layer     | \( K_i = 9.05 \times 10^{-10} \text{ m}^{-1} \) | 0.9914               |
|               | NF                  | Intermediate blocking–Cake layer     | \( K_i = 2.36 \times 10^{-6} \text{ m}^{-1} \) | 0.9913               |
| High-DOC RWW  | MF                  | Intermediate blocking–Cake layer     | \( K_i = 0.0516 \text{ m}^{-1}, K_c = 3226 \text{ s/m}^2 \) | 0.99997              |
|               | UF                  | Standard blocking–Cake layer         | \( K_i = 0.468 \text{ m}^{-1}, K_c = 2532 \text{ s/m}^2 \) | 0.99996              |
|               | NF                  | Intermediate blocking–Cake layer     | \( K_i = 2.24 \times 10^{-11} \text{ m}^{-1} \) | 0.9978               |
|               |                     |                                     | \( K_c = 3.67 \times 10^{5} \text{ s/m}^2 \) | 0.9999               |
|               |                     |                                     | \( K_c = 5.97 \text{ m}^{-1} \) |                      |
|               |                     |                                     | \( K_c = 6.47 \times 10^{5} \text{ s/m}^2 \) |                      |

*: failed the \( t \) test at the significance level of 0.05.

![Figure 11](image.png)  
Figure 11. Cake layer fouling index, \( I \), during gradient filtration of RWW.

4. Conclusions

The gradient filtration of MF (0.45 \( \mu \text{m} \)) → UF (100 kDa) → NF (300 Da) with combined model correlation and the calculation of the cake layer fouling index, \( I \), was developed to quantitatively characterize the feed fouling potential for RO fouling prevention and control in this study. The following conclusions could be drawn:

The rejection rates of MF, UF, and NF for individual targeted model foulants (i.e., kaolin representing suspended solids, sodium alginate and bovine serum albumin representing colloids, and humic acid representing dissolved organic matters) were 79.6%, 72.4%, and 96.5%, respectively, during constant-pressure filtration tests where the cake layer was the dominant membrane fouling mechanism and the cake layer fouling index, \( I \), showed a positive linear correlation with feed foulant concentration. In the MF → UF → NF gradient filtration of low- and high-concentration SWW (i.e., model foulant mixture), the rejection rates of MF, UF, and NF for turbidity, DOC, and UV254 were 69.8% and 78.2%, 74.9% and 58.1%, and 71.2% and 69.6%, respectively. A single-model analysis showed that two or more models fit well for each membrane filtration process due to statistical illusion. A combined-model analysis confirmed the occurrence of multiple fouling mechanisms, and the contribution of each fouling mechanism could be further quantified. In the MF process...
of SWW, the cake layer was not the dominant fouling mechanism due to the interaction between suspended solids and colloids or dissolved organic matters. In the UF and NF processes of SWW, the cake layer was the dominant fouling mechanism. In MF \(\rightarrow\) UF \(\rightarrow\) NF gradient filtration, the \(I\) values of each membrane were positively correlated with the corresponding targeted foulant concentrations (suspended solids, colloids, and dissolved organic matters). The orders of \(I\) and the cake layer specific resistance were NF >> UF >> MF and NF > UF >> MF. Thus, the gradient filtration method was preliminarily established to quantitatively characterize the cake layer fouling potential of different foulants.

RWW (i.e., the sludge supernatant of MBR for dyeing and finishing wastewater treatment) was employed to verify the applicability of the proposed MF \(\rightarrow\) UF \(\rightarrow\) NF gradient filtration method. For low- and high-DOC RWW, the rejection rates of MF, UF, and NF for turbidity were 42.0% and 6.2%, 27.9% and 6.2%, and 40.4% and 6.1%, respectively; the rejection rates of MF, UF, and NF for DOC were 20.1% and 13.4%, 13.4% and 13.3%, and 78.5% and 57.8%, respectively; and the rejection rates of MF, UF, and NF for UV\(_{254}\) were 5.5% and 0.6%, 5.8% and 9.9%, and 84.5% and 85.5%, respectively. Similar to SWW, single models failed to identify fouling mechanisms, but combined models successfully performed this task. In the MF process of low-DOC RWW, the cake layer was not formed, possibly due to the very low concentration of suspended solids. Similar to SWW, the \(I\) values of the UF and NF processes showed a positive correlation with foulant concentration. The order of \(I\) was NF >> UF >> MF, and the order of cake layer specific resistance was NF > UF >> MF. Therefore, the proposed MF \(\rightarrow\) UF \(\rightarrow\) NF gradient filtration would be promising for quantitative cake layer fouling potential evaluation.

**Author Contributions:** Conceptualization, C.-H.W. and K.X.; methodology, R.O. and B.H.; software, B.H.; validation, H.R., H.Y. and F.Q.; investigation, R.O. and B.H.; writing—original draft preparation, R.O. and B.H.; writing—review and editing, C.-H.W., K.X. and X.H.; supervision, C.-H.W. and K.X.; funding acquisition, C.-H.W. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was jointly supported by the National Natural Science Foundation of China (No. 51778599 and 52170071), the Natural Science Foundation of Guangdong Province (No. 2022A1515011909), the Youth Innovation Promotion Association CAS (No. 2019172), the Open Project of State Key Joint Laboratory of Environmental Simulation and Pollution Control in Tsinghua University (No. 21K05ESFCT), and the Science and Technology Planning Project of Guangzhou (No. 202102010417).

**Institutional Review Board Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** The authors acknowledge the suggestions and comments from reviewers.

**Conflicts of Interest:** The authors declare no conflict of interest.

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