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Cecilia M. C. Law[a]; Xiao-Yan Li[a]; Qilin Li[b]
[a] Department of Civil Engineering, The University of Hong Kong, Hong Kong, China [b] Department of Civil and Environmental Engineering, Rice University, Houston, TX, USA

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The Combined Colloid-Organic Fouling on Nanofiltration Membrane for Wastewater Treatment and Reuse

Cecilia M. C. Law,[1] Xiao-Yan Li,[1] and Qilin Li[2]
[1]*Department of Civil Engineering, The University of Hong Kong, Hong Kong, China*
[2]*Department of Civil and Environmental Engineering, Rice University, Houston, TX, USA*

Nanofiltration (NF) has been increasingly used for wastewater reuse purposes. However, membrane fouling is still the major barrier for this technology. Colloidal particles and soluble organic substances are the two main types of foulants present in wastewater effluent. However, little investigation has been conducted on the combined effect of colloids and organic on membrane fouling. The present study addresses the combined fouling effect by colloidal particles and organic substances on the NF membrane. The results show that the combined colloid-organic fouling occurred at a considerably faster rate than the sum of individual colloidal fouling and organic fouling rates.

Keywords combined colloid-organic fouling; membrane; nanofiltration; wastewater reuse

INTRODUCTION

Scarcity of water resources and pollution of natural water resources call for more reuse of secondary effluent from municipal wastewater treatment plants. Membrane filtration has been increasingly applied for this purpose. Nanofiltration (NF) is effective in removing turbidity, organics, micro-organisms, and disinfection by-product (DBP) precursors and to comply with more stringent regulations (1–3); thus, it is being increasingly used in wastewater treatment and reuse (4,5). However, membrane fouling is still the major barrier to the wide application of NF membrane technology (6,7). Membrane fouling causes filtration flux decline, which requires frequent cleaning or even replacement of the membrane and hence increases the operational and maintenance cost. Fouling of the membrane may also affect the permeate quality.

Membrane fouling has been a subject of many investigations. However, because of the complex nature of natural water and wastewater effluent, almost all studies on the membrane fouling in water and wastewater treatment have focused on one type of the foulants, either colloidal foulant or organic foulant (2,3,5). There is little understanding about the effect of colloid-organic interactions on the fouling process. The objective of this study is to systematically characterize the fouling phenomenon in a system containing both colloidal particles and dissolved organics, in comparison with the system containing only one type of the foulant. A crossflow flat-sheet membrane setup was used for the filtration and fouling experiments on the combined colloid-organic fouling effects. Artificial wastewater was prepared for the laboratory study, and the quality of the permeate was analyzed for the performance of the filtration system.

THEORY

Calculation of Membrane Resistance R_m

Membrane hydraulic resistance R_m can be determined from the flux of clean water filtration. R_m was calculated for each set of the fouling experiments by the following equation using the data in the membrane compaction stage

$$R_m = \Delta P/(\mu J_w), \tag{1}$$

where ΔP is the trans-membrane pressure of the system and μ is the dynamic viscosity of feed liquid ($\mu = 1.002 \times 10^{-3}\,\mathrm{N\,s/m^2}$ for water at 20°C).

Determination of the Initial Osmotic Pressure $\Delta\pi_m$

When salt is present in the NF system, concentration polarization would be formed, resulting in a gradient of salt concentration across the membrane and an associated osmotic pressure ($\Delta\pi_m$). In the conditioning stage, before adding the foulants, the cake resistance is negligible and the permeate flux v_0 may be expressed by rearranging Darcy's Law. Thus, the osmotic pressure caused by the salt constituents can be determined as follows.

$$\Delta\pi_m = \Delta P - \mu v_0 R_m. \tag{2}$$

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Address correspondence to Xiao-Yan Li, Department of Civil Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, China. E-mail: xlia@hkucc.hku.hk

Determination of the Salt Concentration in the Membrane Surface C_m

As the concentration polarization happened at the surface of the membrane, the salt concentration at the membrane surface, C_m, would be much higher than that in the bulk solution. Thus, it can be written as

$$\Delta\pi_m = f_{os}(C_m - C_p), \tag{3}$$

where f_{os} is the osmotic coefficient that can be found by van't Hoff equation under low salt concentrations, and C_p is the salt concentration in the permeate. Using Eq. (3), the salt concentration C_m can be estimated.

Determination of the Cake Enhanced Osmotic Pressure $\Delta\pi_m^*$

The intrinsic salt rejection of the membrane is assumed to be constant under any circumstances and the value obtained can be used for the calculation of the cake enhanced osmotic $\Delta\pi_m^*$. By substituting the values into Eq. (3) for the situation after the cake layer formation, $\Delta\pi_m^*$ in the fouling stage can be determined.

Determination of the Cake Resistance R_c

Lastly, in the fouling stage after all the other parameters are obtained, using the modified cake resistance model below, the cake resistance during the membrane filtration process can be calculated,

$$R_c = \frac{\Delta P - \Delta\pi_m^*}{\mu v} - R_m. \tag{4}$$

MATERIALS AND METHODS

NF-270 Membranes

A thin film composite NF membrane, denoted as NF-270 by the manufacturer (Dow-Film Tec Corp, Minneapolis, MN), was used for all the filtration experiments. It is a semi-aromatic (8), polypiperazine-based amide membrane with a molecular weight cut off at 200 kDa. It was supplied in a large flat sheet (1.5 m × 1.5 m) and was cut into coupons of the size required by the cross-flow filtration apparatus. The NF-270 membrane samples for the fouling tests were stored in deionized (DI) water at 4°C, with DI water being replaced weekly before use of the membrane. Alkaline pretreatment of the membrane was conducted right before the filtration experiment, as instructed by the manufacturer. All membrane samples were rinsed thoroughly with DI water prior to use. The membrane resistance before each set of the fouling tests was calculated using Eq. (1) described in the theory section. The NF-270 membrane resistance ranged from 2.01 to $3.15 \times 10^{13}\,\mathrm{m}^{-1}$ with an average of 2.75 (±0.39) $\times 10^{13}\,\mathrm{m}^{-1}$. The observed salt rejection of the membrane filtering a solution of 15 mM NaCl and 1.5 mM $CaCl_2$ was 16.0–33.3% for Na^+ and 41.3–75.1% for Ca^{2+}.

Model Protein, Polysaccharide and Standard Colloidal Particles

Bovine serum albumin (BSA, Acros Organics, New Jersey, USA) and sodium alginate (NaAlg) (BDH Laboratory Supplies Poole, BH15 1TD, England) were used as the model protein and polysaccharide, respectively. Both chemicals were obtained as dry powders. The molecular weight of BSA is 66,500 Da, and NaAlg has a molecular weight ranging from 10,000 to 60,000 Da. The stock solution of each model organic foulant at the concentrations of 5 g/L for BSA and 2 g/L for NaAlg was made by dissolving the chemical in DI water under vigorous stirring and then stored at 4°C in a refrigerator. Silica colloid, denoted as ST-XL (Nissan Chemical America, Houston, TX) was used as the model colloidal foulant. The particle size ranged from 40 to 60 nm as specified by the manufacturer. The model foulants were added to DI water at different combinations to make synthetic wastewaters for the NF fouling experiments.

Analytical Methods

In the membrane conditioning stage, the pressure, the cross flow rate, the pH, and the temperature were monitored. During the filtration experiment, samples from the feed and permeate were collected at designated intervals. The liquid samples were analyzed for UV_{280nm} absorbance using a spectrometer and dissolved organic carbon (DOC) using an O-I Corporation Model 1010 Analytical TOC Analyzer (College Station, TX). The concentrations of Na^+ ion and Ca^{2+} ion were measured using an inductively coupled plasma (ICP) atomic adsorption optical spectrometer (Optima 3000 DV, Perkin Elmer, Woodbridge, ON, USA) for determining the ion rejection efficiency of the NF membrane.

Experimental Protocol

Each filtration experiment included three different and consecutive stages, namely compaction, conditioning, and filtration. For compaction, the membrane was flushed by DI water at 100 psi (689.5 kPa) for at least 5 hours to ensure a stable clean water flux being obtained. After compaction, the background electrolyte solution (15 mM NaCl and 1.5 mM $CaCl_2$) was prepared by adding the concentrated stock solution to DI water. Prior to the filtration test, the membrane was conditioned with the electrolyte solution for at least 9 hours. No membrane would be reused after each filtration-fouling experiment.

The fouling experiments were conducted using a laboratory scale crossflow flat-sheet membrane apparatus consisting of two rectangular plate-and-frame membrane cells in parallel (9). Each cell contained a flat-sheet membrane, placed in a rectangular channel that has a dimension (L × W × H) of 6.35 × 2.54 × 0.51 cm. A schematic diagram of the setup can be found elsewhere (6).

During the filtration experiment, the flowrate of the retentate was monitored by a floating disc rotameter, and the feed pressure and crossflow velocity were controlled using a bypass valve and a back pressure regulator. The permeate flux was monitored continuously by a digital flow meter interfaced with a PC for recording at 10 s interval. The permeate was fed back to the feed reservoir that had a volume of 20 L to maintain the same concentration levels of the substances in the feed solution during a filtration test. The temperature of the feed water was kept at about 20°C by a recirculating heater/chiller (VWR, West Chester, PA). The pressure, the crossflow rate, the permeate flux, the pH and the temperature were monitored throughout the filtration-fouling experiment.

The fouling experiment was carried out under the same hydraulic conditions, and the initial permeate flux was set at 2×10^{-5} m/s while the crossflow rate was set at 1 L/min. The feed water was an artificial wastewater containing 15 mM NaCl and 1.5 mM $CaCl_2$ and different model foulants at pre-determined concentrations. The applied pressure was varied from 90 to 98 psi in order to reach the initial permeate flux. The organic foulant concentration was 20 ppm each while the colloid concentration was 150 ppm. Water samples from the feed and permeate were collected once per 250 ml permeate production for analysis.

RESULTS AND DISCUSSION

Permeate Flux and Cake Resistance

The fouling results for different combinations of the foulants in the feed wastewater are summarized in Fig. 1. The results show that the flux decline rate by the combined fouling was considerably faster than the sum of individual colloidal fouling and organic fouling. For further analysis, the fouling experiment results are put into groups, each of which has at least one identical foulant as the base foulant. The results in the permeate flux decline and the cake resistance increase are depicted separately. The initial NF membrane filtration resistances were found to be much lower than the cake resistances observed later during the fouling experiments.

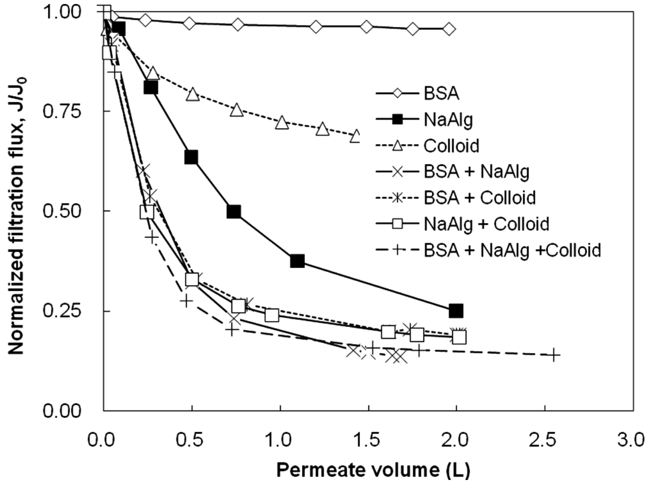

FIG. 1. Normalized flux of the membrane filtration-fouling experiments with different foulant combinations.

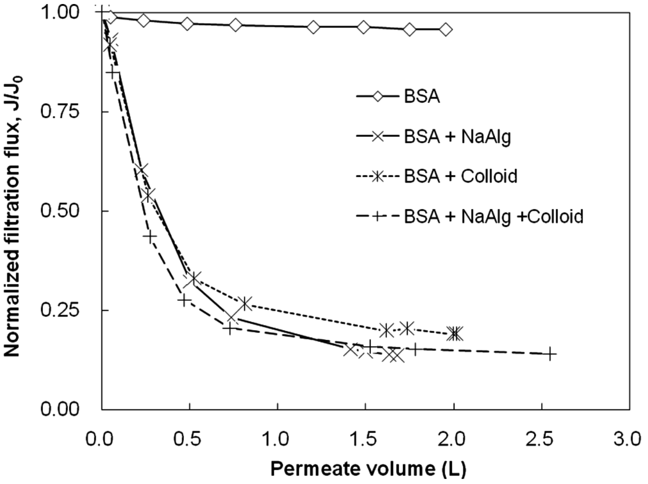

FIG. 2. Normalized flux of the membrane fouling experiments for BSA-based feed solutions.

Colloid-Organic Fouling with BSA

The permeate flux associated with the colloidal-organic fouling with BSA as the base substance is shown in Fig. 2, while the calculated cake resistance is given in Fig. 3. BSA alone did not foul the NF membrane very much, as shown

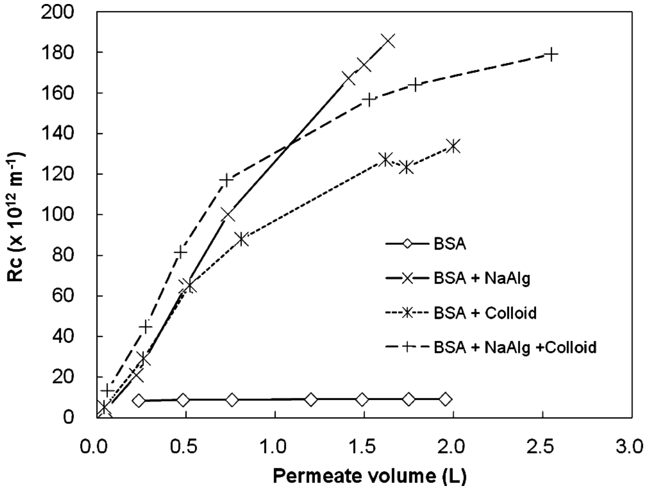

FIG. 3. Cake resistance determined for fouling experiments on BSA-based feed solutions.

by the little decrease in the permeate flux. However, when NaAlg and/or colloids were added to the feed solution, serious membrane fouling was observed. BSA apparently aggregated with NaAlg, increasing the effective size of the foulants. NaAlg also formed an impermeable gel layer with Ca^{2+} on the membrane surface, which caused an enormous increase in cake resistance. BSA could be adsorbed onto the surface of the colloids, which would reduce the surface charges and thus the electrostatic repulsion between colloidal particles. The reduction in electrostatic repulsion would allow a faster fouling layer formation on the membrane surface.

When all BSA, NaAlg, and colloid were found in the feed solution, the combined colloid-organic fouling caused the worst fouling rate with the most prominent initial flux decline. The cake layer formed by colloids alone is porous with a high permeability. However, with the existence of smaller organics like BSA and NaAlg, the combined fouling would greatly increase the cake resistance. Moreover, the formation of the cake layer would greatly hinder the back diffusion of foulants back to the bulk solution, resulting in a much higher foulant concentration at the membrane surface. This phenomenon, termed as cake enhanced concentration polarization (CECP), is believed to be another major cause of flux decline in NF membrane filtration.

Colloid-Organic Fouling with NaAlg

The permeate flux associated with the colloidal-organic fouling with NaAlg as the base substance is given in Fig. 4, while the cake resistance is shown in Fig. 5. NaAlg alone could foul the membrane to a great extent when compared to BSA or colloids alone. This is mainly because the NaAlg formed a complex with Ca^{2+} forming an impermeable gel layer at the membrane surface. The gel layer formation contributed to the rapid decline in filtration flux. Combining NaAlg with BSA resulted in an immediate sharp decrease in flux. When the feed contains both NaAlg and colloids, both the flux decline and cake resistance increased greatly. The cake resistance increased continuously with the filtration process. As expected, when BSA, NaAlg, and the colloid existed together in the feed solution, the fouling situation became the worst.

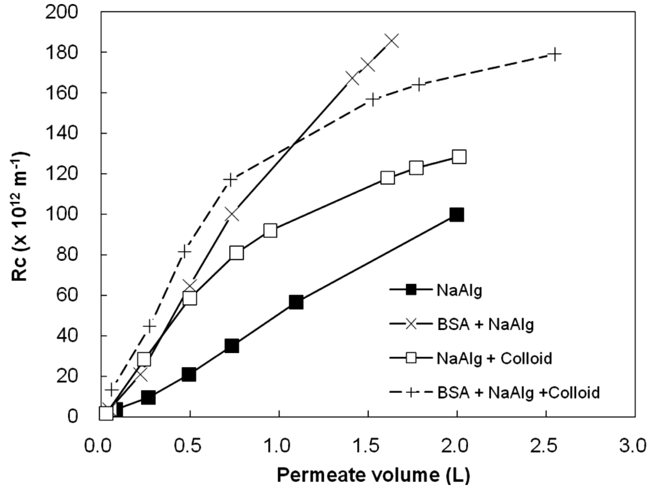

FIG. 5. Cake resistance determined for fouling experiments on NaAlg-based feed solutions.

Colloid-Organic Fouling with Colloids

The permeate flux associated with the colloidal-organic fouling with colloid as the base substance is shown in Fig. 6, while the cake resistance is shown in Fig. 7. Colloids alone could also cause a certain decrease in filtration flux. However, the resistance of the cake formed by only colloidal particles did not increase much. When one of the organics,

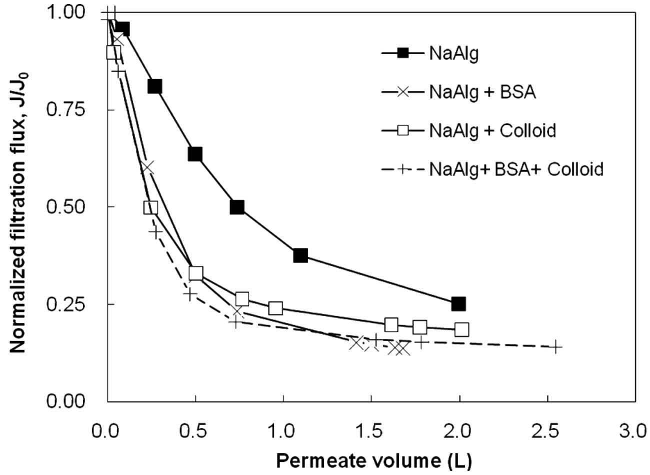

FIG. 4. Normalized flux of the membrane fouling experiments for NaAlg-based feed solutions.

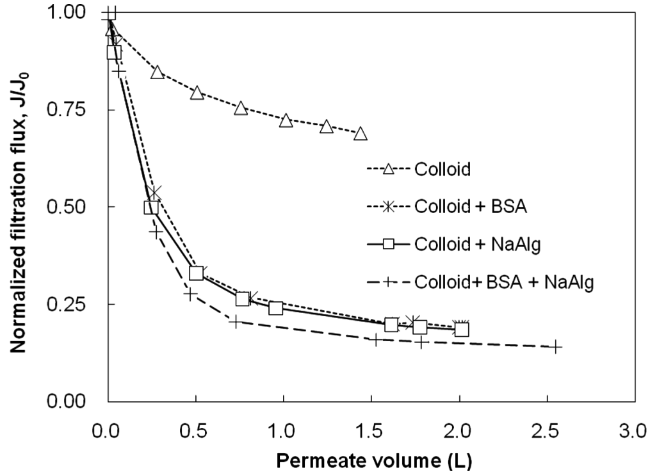

FIG. 6. Normalized flux of the membrane fouling experiments for colloid-based feed solutions.

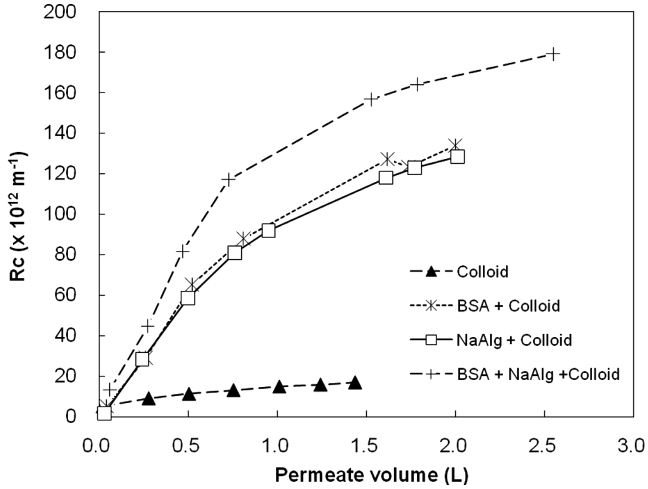

FIG. 7. Cake resistance determined for fouling experiments on colloid-based feed solutions.

BSA or NaAlg, was added to the colloidal suspension, the flux decline and the cake resistance increased greatly but with little difference between the two types of organics. It is expected that the organic filled in the pores between the colloids in the cake layer, resulted in a considerable increase in cake resistance and decrease in permeability. Also, the organic adsorbed onto the colloidal surface would decrease the repulsion between the colloids and membrane. With the co-existence of all three types of foulants, the fouling was the most serious for the NF membrane filtration.

Salt Rejection

The change of salt rejection during filtration is shown in Fig. 8. It can be found that the salt rejection of Ca^{2+} was always about 20% higher than that of Na^+. The rejection ratios for both salts decreased during filtration with all the combinations of BSA, NaAlg, and the colloid, except

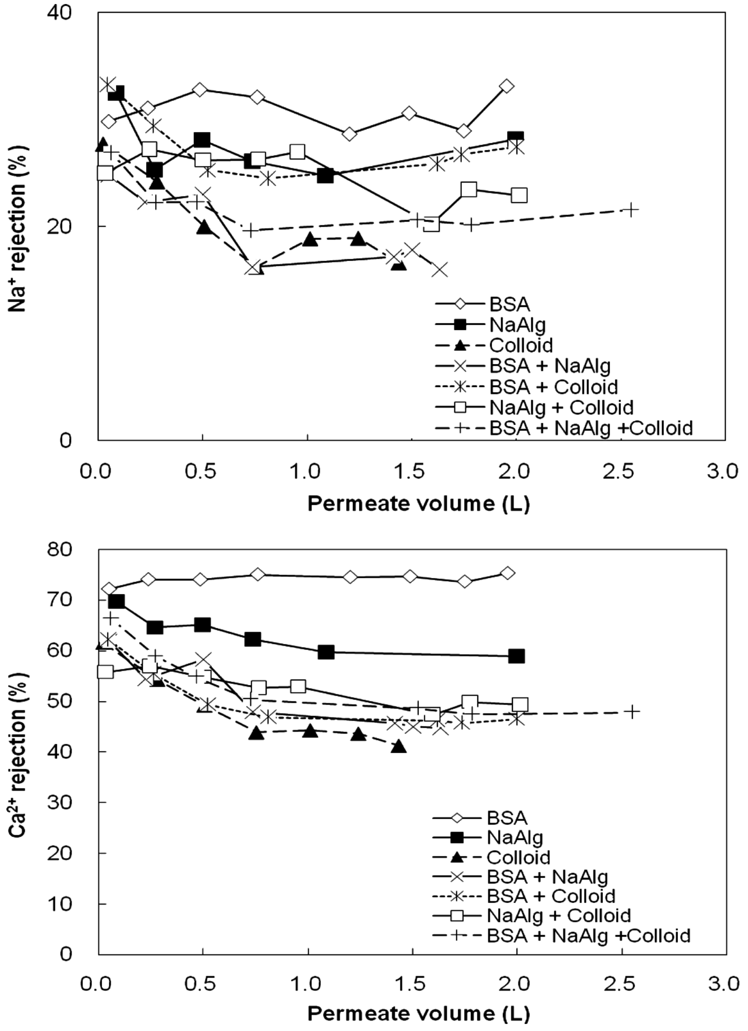

FIG. 8. Change of (a) Na^+ and (b) Ca^{2+} rejection ratios during the filtration experiments for different foulant combinations.

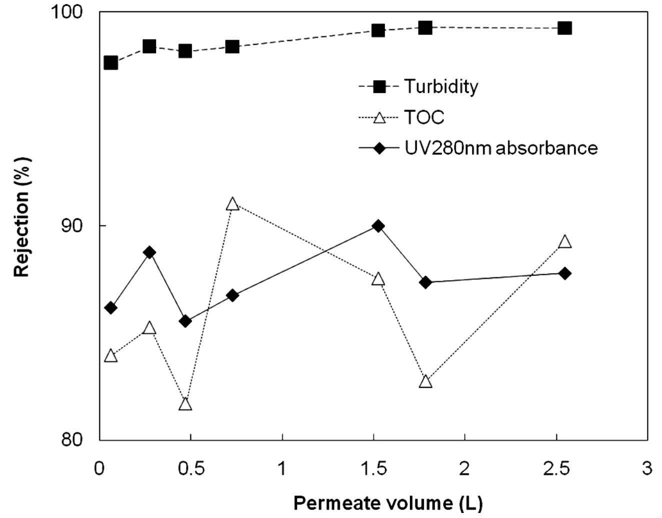

FIG. 9. Rejections of the foulants during filtration of the feed solution with 20 ppm BSA, 20 ppm NaAlg and 150 ppm colloids.

for BSA alone. This is an evidence that the cake-enhanced concentration polarization occurred during the fouling experiments. The cake layer formed by BSA alone apparently did not hinder the back diffusion of salts significantly for the CECP effect.

Foulant Rejection

The rejections of the foulants were calculated from the concentration difference between the feed and the permeate (Fig. 9). In general, the NF membrane showed an increase in the foulant rejection ratio during the filtration, or a decrease in foulant concentration in the permeate. This is different from a CEOP-based prediction. In comparison with BSA, the rejection of NaAlg appeared to be more constant during the filtration. The increase in rejection of total organics may mainly be caused by the increase in BSA retention in the cake layer resulting from the colloid-organic fouling.

CONCLUSIONS

The colloidal particles and dissolved organics exhibited a synergistic effect on the fouling development during NF membrane filtration. The synergistic fouling effects are confirmed by the increase in the cake resistance of combined foulants when compared to the sum of individual fouling rates. The extent of the fouling evolution enhanced by the synergistic effect, however, varied largely for different foulant combinations. The greatest combined fouling effect was found for the fouling with the combination of BSA, NaAlg, and colloids, followed by the combination of NaAlg and colloids. The fouling mechanisms for various combinations of organic and colloidal foulants include increased cake resistance, hindered back diffusion, and alternation of the colloidal surface properties. The foulant rejection ratio was in a general increase throughout the filtration experiment, while the salt rejection decreased gradually during the filtration process.

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