FULL PAPER

Effect of SiO2 coating on alumina microfiltration membranes on flux performance in membrane fouling process

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Inorganic surface modification was performed using a SiO2 sol–gel technique to mitigate the fouling of alumina microfiltration membranes. A positively charged alumina membrane was coated with SiO2 to generate a negative charge, and as a result, electrostatic repulsion prevented the serious adsorption (or deposition) of model foulants on the membrane. Upon the formation of the SiO2 layer, small changes in the surface morphology, pore size, and surface roughness were detected. In particular, as the pore size decreased, the pure water permeability gradually decreased. When the membrane fouling was accelerated with model foulants, the highest normalized flux level and the lowest flux decline ratio (%) were observed in the smallest SiO2-coated microfiltration membrane (0.1 M SiO2). In summary, the SiO2 coating contributed to the optimization of the antifouling properties of the ceramic membranes, although the pore size was reduced.

Key-words : Ceramic membrane, Sol–gel process, Surface modification, Flux decline, Antifouling

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1. Introduction

Ceramic membranes [especially microfiltration (MF) and ultrafiltration (UF) membranes] have been widely used to physically eliminate suspended particles with sizes of 0.01–10 μm from water.1) These ceramic membranes are usually composed of three layers that have gradual pore structures consisting of support, intermediate, and separation layers.2) Ceramic membrane technology is widely applied in water/wastewater purification and as pretreatment in the nanofiltration/reverse osmosis process.3) Alumina (Al2O3),4) zirconia (ZrO2),5) titania (TiO2),6) silica (SiO2),7) carbon,8) and zeolite9) have been mainly investigated as materials for ceramic membranes. The development of membrane manufacturing technology using low-cost ceramic raw materials has also been investigated in an effort to reduce the cost of raw materials and reduce the temperature of the sintering processes (>1,300°C).10,11) Even though ceramic membranes are more expensive than polymeric membranes, they are essential in applications where chemical and thermal durability are required. Examples of successful commercial-scale applications of ceramic MF/UF membranes include the purification and concentration of valuable components in the biotechnology, food, and petrochemical industries.12-14) The unique advantages of ceramic membranes are mainly attributed to the intrinsic features of ceramics: (1) outstanding chemical/mechanical/thermal stability, (2) a controllable pore size distribution and high porosity, and (3) hydrophilicity.15,16) The most serious issue in developing an efficient membrane processes for water purification is membrane fouling (especially irreversible fouling) during permeation.17) The mechanism of membrane fouling involves three key elements: (1) pore adsorption, (2) pore blockage, and (3) cake formation. Solutes with pore diameters similar to those of the membrane pores completely block them, while solutes of larger pore diameters form a cake layer on the surface of the membrane.18) As a result, membrane fouling reduces the permeate flux and water quality, increasing the transmembrane pressure (TMP) and the operational costs.19) Thus, mitigating the adsorption (or deposition) of foulants on the membrane surface is essential for the development of ceramic membranes with superior fouling resistance. Numerous surface modification techniques have been reported for polymeric membranes.20) In comparison, the surface modification of ceramic membranes has received less attention, because of the limited modification methods available to date.

In our previous work, SiO2 was surface-modified via a sol–gel process on a positively charged alumina support
mentioned alumina support layers.22) A table-top dip coater samples were sintered at 1,600°C for 1 h (heating rate of 210, Sumitomo Chemical Co. Ltd., Japan). Then, the alumina powder with a mean particle size of 4.8 and the pH was adjusted to 9.0 using 0.1 M NH4OH. The mean particle size of 0.27

Electrostatic repulsion thus occurred between the membrane to reduce the surface charge at a pH of 6.5.21) Inorganic surface modification on alumina MF membranes (in contrast to macroporous support membranes). The physicochemical properties of SiO2-coated MF membranes were characterized, including the surface morphology, pore size distribution, and root-mean-square (RMS) roughness. Notable fouling resistance to model foulants was demonstrated by the time-dependent flux pattern achieved during the membrane permeation procedures.

2. Materials and methods

2.1 Fabrication of alumina MF membranes

Alumina support layers were manufactured using α-alumina powder with a mean particle size of 4.8 μm (AM-210, Sumitomo Chemical Co. Ltd., Japan). Then, the samples were sintered at 1,600°C for 1 h (heating rate of 5°C/min). A normal coating procedure was employed to prepare for alumina MF membranes using the aforementioned alumina support layers.23) A table-top dip coater (E-flex, Republic of Korea) was utilized to produce an alumina separation layer on an alumina support layer. The coating slurry was composed of 10 wt% α-alumina with a mean particle size of 0.27 μm (AKP-30, Sumitomo Chemical Co. Ltd., Japan), polyvinyl alcohol (Junsei Chemical, Japan), glycerol (Sigma–Aldrich, USA), 2-propanol, ethyl alcohol, and deionized (DI) water. The alumina support layers were dip-coated for 10 s and then withdrawn at a speed of 1 mm/s. The coated samples were dried under ambient conditions overnight and subsequently sintered at 1,300°C for 1 h with a heating rate of 3°C/min.

2.2 Coating alumina MF membranes with SiO2

Tetraethyl orthosilicate (TEOS) was chosen to introduce unique surface characteristics to the alumina MF membranes according to our previous study, which revealed that inorganic surface modification with amorphous SiO2 enhances the antifouling properties of pristine alumina membranes.21) An ethanol/DI water mixture was prepared, and the pH was adjusted to 9.0 using 0.1 M NH4OH. The TEOS was then dissolved in the aforementioned mixture and stirred to obtain SiO2 sol solutions of different molar concentrations (0.1, 0.15, and 0.2 M). The pristine alumina MF membrane was immersed in the SiO2 sol solution for 10 min at the ambient temperature. This process was conducted under vacuum to form a uniform SiO2 coating layer. Thus, the SiO2 coating was homogeneously applied to the entire MF membranes, regardless of the TEOS concentrations. Next, the membranes were washed with ethanol and dried in an oven. Finally, the SiO2-coated membranes were calcinated at 400°C for 6 h. The pristine alumina MF membranes were thus modified using inorganic SiO2. These membranes were denoted as 0.1 M SiO2, 0.15 M SiO2, and 0.2 M SiO2 according to the molar concentration of the SiO2 sol solution.

2.3 Characterization of SiO2-coated alumina MF membranes

The alumina MF membranes that underwent surface modification and membrane fouling were evaluated to investigate their physicochemical properties. The surface morphology of the alumina MF membranes was measured using a field-emission scanning electron microscope (SEM, JSM-6700F, JEOL, Japan) at magnifications ranging from 1,000× to 50,000×. The crystalline structure was analyzed via X-ray diffraction (XRD, Rigaku, D/MAX 2500, Japan). The pore size distributions of the MF membranes were characterized via mercury intrusion porosimetry (Autopore IV 9510, Micromeritics, USA). The surface topography of the alumina MF membranes was measured using atomic force microscopy (AFM, XE-100, Park Systems, Republic of Korea). The AFM images were obtained in the non-contact mode with a scan area of 5.0 × 5.0 μm². The RMS method was employed to estimate the surface roughness of the alumina MF membranes.

2.4 Membrane permeation test of SiO2-coated alumina MF membranes

Membrane permeation tests were performed on the alumina MF membranes using a cross-flow MF system (Lab-MPT, SeppraTek Membrane System, Republic of Korea).23,25) The feed solution was supplied at 25°C using a circulating bath (JEIO TECH, Republic of Korea). The permeation tests were then conducted at a TMP of 2.0 bar with a fluid velocity of 2.5 L/min. The weight of the permeate was periodically measured using an electronic mass balance (CAS, Republic of Korea) for the calculation of flux data. The membrane fouling procedure comprised four steps. In step 1, the membranes were permeated using DI water for 30 min to obtain a stable baseline flux (J0). In step 2, two model foulants [HA and Bovine Serum Albumin (BSA)] were supplied to induce membrane fouling for 1 h (Jfr). They were dissolved to 10 mg/L for HA (pH 6.5) and 0.5 g/L for BSA (pH 7.4). In step 3, the fouled membranes were subjected to backwashing for 10 min with a 10 mM sodium dodecyl sulfate solution (pH 11, Sigma–Aldrich, USA). In step 4, DI water was introduced again for 30 min to obtain a stable flux (Jf). These fouling processes were conducted in triplets using three separate membranes, and the mean values were employed for the analysis. On the basis of the flux data obtained, the antifouling properties, such as the flux decline ratio (%) and flux recovery ratio (%), were determined using the following equations.

Flux decline ratio (%) = \( \left( 1 - \frac{J_f}{J_0} \right) \times 100 \) (1)

Flux recovery ratio (%) = \( \left( \frac{J_f}{J_0} \right) \times 100 \) (2)
Here, \( J_0 \) is the DI water flux in step 1, \( J_p \) is the flux of the foulant solutions in step 2, and \( J_1 \) is the DI water flux in step 4.

For additional characterization of the antifouling properties, the membrane fouling ratio (\( \% \)) was considered. The membrane permeation test was performed in the circulation mode, i.e., an HA or BSA solution (1 L) was added to the feed tank in step 2, and the permeate was sent back to the feed tank. The permeate (10 mL) in the feed tank was collected every 10 min. The concentration of foulants could then be measured at 254 or 280 nm via ultraviolet-visible spectroscopy (Cary 5000, Agilent Technologies, USA). The membrane fouling ratio (\( \% \)) was determined using the following equation.

\[
\text{Membrane fouling ratio (\%)} = \left( 1 - \frac{C_f}{C_0} \right) \times 100 \quad (3)
\]

Here, \( C_0 \) is the initial concentration of foulants, and \( C_f \) is the concentration of the permeates in step 2.

3. Results and discussion

3.1 Characterization of SiO\(_2\)-coated alumina MF membranes

In our previous study, alumina support membranes (pore size: 0.80 \( \mu \)m) were modified with a SiO\(_2\) coating layer via a sol–gel process by following the same procedure described in section 2.2.\(^{21}\) The resultant membranes were characterized with regard to their surface morphology, pore size distribution, pure water permeability, zeta-potential, and permeation flux for an HA solution. The effectiveness of the newly formed SiO\(_2\) layer was evidenced by the increased flux values. For more advanced studies, we endeavored to apply the SiO\(_2\) sol–gel process to alumina MF membranes. The results of the characterization of the SiO\(_2\)-coated membranes are as follows.

In this study, the alumina support layers were dip-coated using a nanosized alumina slurry and heat-treated at 1,300°C to obtain pristine alumina MF membranes. Thus, an asymmetric ceramic MF membrane was successfully generated with two different pore structures. A cross-sectional image of the pristine MF membranes is presented in Fig. 1(A), which shows the support layer (consisting of the coarse alumina particles) and the separation layer (consisting of the fine alumina particles).

To determine the optimized TEOS concentration for the inorganic surface modification of the alumina MF membranes, three TEOS concentrations (0.1, 0.15, and 0.2 M) were selected. The surface morphology of the pristine and SiO\(_2\)-coated MF membranes was measured at a high magnification of 50,000 \times \([\text{Fig. 1(B)}]\). Larger pore volumes (between the nanosized alumina particles) were observed in the pristine alumina MF membranes compared to those in the SiO\(_2\)-coated MF membranes (0.1 M SiO\(_2\) and 0.15 M SiO\(_2\)). The two smaller SiO\(_2\)-coated MF membranes (0.1 M SiO\(_2\) and 0.15 M SiO\(_2\)) had slightly smaller pore sizes owing to the newly formed SiO\(_2\) layer, but it was difficult to distinguish the microporous structure in the SEM images. On the other hand, the largest SiO\(_2\)-coated MF membrane (0.2 M SiO\(_2\)) was fully covered with a SiO\(_2\) layer, and the microporous structure was not observed, primarily because of the high concentration of the TEOS solution. Moreover, it was difficult to conduct the normal MF membrane performance test. Therefore, the two smaller SiO\(_2\)-coated MF membranes (0.1 M SiO\(_2\) and 0.15 M SiO\(_2\)) are suitable for inorganic surface modification because the micropore reduction of the alumina MF membrane is minimal. Compared to that of our previous study, the SiO\(_2\) coating on the alumina support membrane did not distinctly alter the membrane morphology; thus, the inorganic surface modification had only a minimal effect.\(^{21}\)

XRD analysis of the SiO\(_2\)-coated alumina MF membranes was performed to prove the stable formation of the SiO\(_2\) layer (Fig. 2). The amorphous SiO\(_2\) phase was broadly distributed near the 2\( \theta \) value of 23°, indicating that a SiO\(_2\) coating layer was newly formed on the alumina MF membrane. However, there was no peak fluctuation with the increase or decrease of the TEOS concentration. The TEOS concentrations used in the experiment (0.1, 0.15, and 0.2 M) were considered to be sufficient to change the surface characteristics of the alumina MF membranes.

The pore size distributions of the alumina MF membranes were analyzed using mercury intrusion porosimetry to examine the effect of the SiO\(_2\) coating process (Fig. 3).
Figures 3(A) and 3(B) show two typical peaks for the separation and support layers, which exhibited similar pore size distributions. The average pore sizes of the pristine MF membrane were found to be 0.830 μm (support layer) and 0.134 μm (separation layer). Therefore, it is evident that the support layer (having a coarse pore structure at the bottom) and the separation layer (having a dense pore structure at the top) were well-aligned. Because of the SiO2 coating on the membrane surface, the pore size of the SiO2-coated membranes gradually decreased with the increase of the TEOS concentration. In the separation region [Fig. 3(A)], the average pore size of the SiO2-coated membranes decreased in the following order: 0.134 μm (pristine) > 0.107 μm (0.1 M SiO2) > 0.095 μm (0.15 M SiO2) > 0.095 μm (0.2 M SiO2). The same trend of pore size reduction is observed in the support region [Fig. 3(B)]. For example, the pore size decreased in the order of 0.830 μm (pristine) > 0.675 μm (0.1 M SiO2) > 0.670 μm (0.15 M SiO2) > 0.660 μm (0.2 M SiO2). We thus performed a quantitative analysis of the reduction of the micropore size due to inorganic surface modification.

For comparison with the SEM morphological analysis (Fig. 1), an AFM topological analysis was performed. The three-dimensional (3D) AFM images are shown in Fig. 4(A), and the RMS roughness is shown in Fig. 4(B). As the TEOS concentration increased from 0.1 to 0.15 M, the RMS roughness increased in the order of 88 nm (pristine) < 93 nm (0.1 M SiO2) < 117 nm (0.15 M SiO2). Thus, the SiO2 coating on the sintered alumina particles increased the RMS roughness. On the other hand, when the TEOS concentration reached the maximum of 0.2 M, the membrane surface was completely covered with the SiO2 layer. The RMS roughness was then rapidly reduced to 72 nm. These results are consistent with the SEM morphological images [Fig. 1(B)] and imply that the newly formed SiO2 coating layer filled the surface pores between the alumina particles and flattened the surface, reducing the roughness of the membrane surface.

The pure water permeability of the SiO2-coated alumina MF membranes was assessed because it is a major parameter for estimating the membrane productivity and efficiency (Fig. 5). The pristine alumina MF membrane showed the highest pure water permeability of 414 ± 24 L/m²·h·bar. However, as the pore size (especially in the separation region) decreased owing to inorganic surface modification, the pure water permeability gradually de-
...In the two smaller SiO₂-coated membranes (0.1 M SiO₂ and 0.15 M SiO₂), the pure water permeability was maintained at 326 ± 10 and 252 ± 34 L/m²·h·bar, respectively. When the TEOS concentration reached 0.2 M (0.2 M SiO₂), the pure water permeability became very low: 130 L/m²·h·bar. For the largest SiO₂ coating (0.2 M SiO₂), a considerable portion of the membrane surface was coated with SiO₂, and the membrane was expected to have a low pure water permeability. These results explain the basic operation principle of membranes for water treatment. In the constant-TMP mode, a smaller micropore size yields less water permeation.

In contrast to the small decrease in the pore sizes of the separation region (0.134 to 0.095 μm), the pure water permeability significantly decreased from 414 to 130 L/m²·h·bar. This is because the surface morphologies of the largest SiO₂-coated membranes (0.2 M SiO₂) varied significantly. That is, the membrane surface was fully covered with a SiO₂ layer, and the microporous structure could not be observed. It is considered that the thick SiO₂ coating was present throughout the entire membrane, the average pore size of the separation region would be significantly smaller than 0.095 μm. Therefore, the thick SiO₂ coating on the membrane surface (0.2 M SiO₂) caused a larger reduction of the pure water permeability compared to the two smaller SiO₂-coated MF membranes (0.1 M SiO₂ and 0.15 M SiO₂).

Previous studies on organic surface modification have also revealed a correlation between the pore size and the pure water permeability of alumina MF membranes. An increase of the extent of surface grafting (or coating) leads to a reduction of the pore size, surface roughness, and water permeability. In spite of the many merits of organic/inorganic surface modification, it sometimes gives rise to a reduction in the flux level owing to the "pore-filling" effect.

In this study, the SiO₂ coating did not severely influence either the physical properties or the water permeability of the alumina MF membranes. Moreover, some membrane properties, such as the pore size distribution, surface roughness, and water permeability, could be regulated by changing the TEOS concentration. We therefore aimed to identify the optimal SiO₂ coating conditions that would not only diminish the variations of the surface morphology/pore size and water permeability but also encourage the evolution of fouling resistance against model foulants.

### 3.2 Fouling resistance of SiO₂-coated alumina MF membranes

A schematic showing of the SiO₂-coated alumina MF membrane and its interaction with model foulants (HA and BSA) is presented in Fig. 6. As explained in section 2.2, the pristine alumina MF membrane was surface-modified using a SiO₂ sol solution. Strong negative charges were generated through the SiO₂ sol–gel process. According to our previous work, the surface charge of the SiO₂-coated membrane was −130 mV at a pH of 6.5, and that of the pristine alumina membrane was +28 mV at the same pH.

Two model foulants [HA (IEP: 4.7) and BSA (IEP: 4.7)] were introduced for simulating soluble humic substances and proteins that are ubiquitous in secondary treated effluents. The membrane fouling pattern can differ depending on the physicochemical properties of the foulants. Owing to the electrostatic repulsion between the SiO₂-coated alumina MF membrane and the negatively charged foulants (HA and BSA), the SiO₂ coating was expected to prevent
foulant adsorption (or deposition) on the membrane pore surfaces, as well as the subsequent flux decline. The normalized time-dependent flux pattern of the SiO2-coated MF membranes in each step of the process is shown in Fig. 7 (step 1: DI water; step 2: HA or BSA solution; step 3: backwashing; and step 4: DI water). The membrane permeation tests were performed three times for each MF membrane to acquire reliable outcomes. All the MF membranes retained a stable flux level in step 1. As the HA solution was added in step 2 [Fig. 7(A)], a very rapid decline of the flux occurred for each MF membrane, followed by a slower decrease with time. The flux level decreased in the order of 0.15 M SiO2 > 0.1 M SiO2 > pristine MF membrane > 0.2 M SiO2. On the contrary, the flux decline ratio (%) increased in the order of 0.15 M SiO2 < 0.1 M SiO2 < pristine MF membrane < 0.2 M SiO2 (Table 1). The 0.2 M SiO2 membranes had even lower flux values (higher flux decline ratios) than the pristine MF membranes, and the 0.15 M SiO2 membrane exhibited the highest flux level. As demonstrated in section 3.1, the membrane permeation is closely associated with the surface morphology (Fig. 2) and membrane pore size (Fig. 4).

Because of the SiO2 coating effect on the membrane permeation (Fig. 7), the inorganic surface modification reduced the pore sizes to a minimal range. However, it allowed the pores to be easily blocked by low-molecular-weight foulants and subsequently diminished the flux levels. Specifically, the largest SiO2-coated MF membrane (0.2 M SiO2) showed a morphology in which the top surface was completely covered with the SiO2 layer owing to the highest TEOS concentration, resulting in the smallest pore size. Thus, the largest SiO2-coated MF membrane (0.2 M SiO2) exhibited the lowest flux level. Accordingly, the smaller SiO2-coated MF membranes (0.1 M SiO2 and 0.15 M SiO2) had higher fouling resistance against the HA solution owing to the reduced effect of the pore size restriction and electrostatic repulsion. In step 4, DI water was fed again after backwashing for 10 min, and the flux recovery ratios (%) were estimated (Table 1). With the exception of the largest SiO2-coated MF membrane (0.2 M SiO2) (84%), most of the MF membranes exhibited excellent flux recovery ratios (93–95%), indicating that the primary cause of membrane fouling was reversible fouling rather than irreversible fouling. The flux loss (%) due to irreversible fouling was approximately 5–7%.

Membrane fouling tests were also performed using a BSA solution [Fig. 7(B)]. The decreasing trend of the flux

Table 1. Membrane filtration performance of the pristine alumina membrane and SiO2-coated alumina membranes using HA (10 mg/L) and BSA (0.5 g/L) solutions throughout the entire membrane fouling process (steps 1 to 4). The flux decline ratio (%) and flux recovery ratio (%) were calculated using the Eqs. (1) and (2) presented in section 2.4.

|          | Flux decline ratio (%) | Flux recovery ratio (%) |
|----------|------------------------|------------------------|
|          |                        |                        |
| HA solution |                        |                        |
| Al2O3     | 46 ± 3                 | 93 ± 3                 |
| 0.1 M SiO2| 37 ± 1                 | 94 ± 2                 |
| 0.15 M SiO2| 34 ± 2               | 95 ± 2                 |
| 0.2 M SiO2| 65 ± 1                 | 84 ± 2                 |
| BSA solution |                        |                        |
| Al2O3     | 36 ± 3                 | 92 ± 2                 |
| 0.1 M SiO2| 23 ± 1                 | 97 ± 2                 |
| 0.15 M SiO2| 41 ± 3               | 91 ± 1                 |
| 0.2 M SiO2| 57 ± 3                 | 90 ± 1                 |
The membrane fouling ratios (less than approximately 20%) of SiO2-coated MF membranes were smaller (Table 1). The smallest SiO2-coated MF membranes were maintained at 90% decline ratios, which were consistent with those for the HA solutions [Fig. 8(B)].

In this study, the antifouling properties were demonstrated by the membrane permeation patterns (Fig. 7) and membrane fouling ratios (Fig. 8) using two model foulants. The effects of natural organic matter on membrane fouling have been previously described in detail.27-29) The molecular-weight distribution of the model foulants (HA and BSA) should be considered for comparison with the membrane pore sizes. The HA solution contained a wide molecular-weight distribution (approximately 10 kDa to 0.45 μm).27) In particular, the proportion of components >0.1 μm in size was approximately 8%. These large-molecular-weight components, whose sizes were close to or larger than those of the membrane pores, led to pore blockage and cake formation.20) This caused a rapid flux decline in the early stage and a gradual subsequent decline [Fig. 7(A)]. Even larger membrane fouling ratios (%) were observed for the HA-fouled membranes, regardless of the inorganic surface modification [Fig. 8(A)]. On the other hand, the BSA solution had a lower molecular-weight distribution (67 kDa) and contained no components larger than 0.1 μm.27,30) For this reason, the BSA solution, whose particles were smaller than the membrane pore sizes, either passed through the MF membranes or were deposited on the membrane pores, leading to a gradual flux decline [Fig. 7(B)]. Consequently, in the case of BSA, the membrane fouling ratios (%) remained constant, specifically below 20% [Fig. 8(B)].

The SEM morphology for the fouled/backwashed MF membranes was analyzed, as shown in Fig. 9. The early MF membranes were seriously fouled but mostly cleaned through backwashing. For the HA-fouled MF membranes [Fig. 9(A)], the gross images are also presented, for evaluation of the effective fouling resistance of the SiO2-coated MF membranes. The pristine MF membrane became dark brown in step 2, which is mostly attributed to the extreme HA fouling. However, the membrane fouling patterns of the SiO2-coated MF membranes varied in color with respect to the TEOS concentration. The largest SiO2-coated MF membranes (0.2 M SiO2) exhibited the least fouling, followed by the other two membranes in the order of the decreasing TEOS concentration (0.15 M and 0.1 M SiO2). Nonetheless, the smallest SiO2-coated MF membrane (0.1 M SiO2) showed even higher fouling resistance than the pristine alumina MF membrane, and this was consistent with the corresponding SEM images. A lower flux was observed at a higher TEOS concentration [Fig. 7(A)], even though the fouling resistance was higher, as shown in Fig. 9(A). This result is explained by the pore size restriction after inorganic surface modification. In general, there are optimized TEOS concentrations that can not only maintain the microporous structure of the membrane but also promote the fouling resistance. The gross images for the BSA solution are not provided, because this solution was transparent [Fig. 9(B)]. However, the fouling resistance was identical to the results for the HA solution with regard to the fouling/backwashing processes.

level in step 2 was slightly different from that for the HA solution: 0.1 M SiO2 > pristine MF membrane > 0.15 M SiO2 > 0.2 M SiO2. However, the normalized flux (J/J0) for the BSA solutions decreased gradually with membrane permeation time and maintained higher levels than for the HA solutions. Consequently, the flux decline rates (%) were smaller (Table 1). The smallest SiO2-coated MF membrane (0.1 M SiO2) exhibited the highest flux recovery ratio (97%). The flux recovery ratios of the other membranes were maintained at 90-92%.

As another standard to estimate the antifouling properties, the membrane fouling ratios (%) of the SiO2-coated MF membranes were analyzed (Fig. 8). All the MF membranes were severely fouled by the HA solution at the initial stage of permeation before reaching steady levels [Fig. 8(A)]. The pristine MF membranes exhibited the largest membrane fouling ratio (99%), and the other membranes followed in the order of 0.1 M SiO2 (97%), 0.15 M SiO2 (96%), and 0.2 M SiO2 (95%), with only slight differences. A larger SiO2 content (more negatively charged) on the membrane surface led to a smaller membrane fouling ratio (%). In comparison, the MF membranes fouled by BSA solutions exhibited significantly lower membrane fouling ratios (less than approximately 20%), but the profile was consistent with those for the HA solutions [Fig. 8(B)].

Fig. 8. Evaluation of membrane fouling (%) on the pristine alumina membrane and SiO2-coated alumina membranes. The (A) HA solution (10 mg/L, pH 6.5) and (B) BSA solution (0.5 g/L, pH 7.4) were filtered out in a circulation mode (step 2), and the concentrations in the bulk and permeate were measured for calculations.
4. Conclusions

The effectiveness of SiO₂-coated alumina MF membranes was demonstrated with regard to their fouling resistance against model foulants (HA and BSA). This study is initiated from our previous research, in which we applied a SiO₂ sol–gel coating to alumina support membranes for enhancing the fouling resistance. In the present study, we extended the inorganic surface modification technique to alumina MF membranes. The efficacy of the SiO₂ coating was proven for smaller SiO₂-coated MF membranes (0.1 M SiO₂ and 0.15 M SiO₂), which exhibited the greatest flux levels (the smallest flux decline) through the membrane fouling procedures. However, the reduced pore sizes due to the dense SiO₂ coating (0.2 M SiO₂) caused a larger flux decline.

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