TiO₂ 나노입자로 표면침적된 Polyethersulfone 정밀여과 분리막의 자연유기물 파울링 감소

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Mitigations of Natural Organic Matter Fouling of Polyethersulfone Microfiltration Membrane Enhanced by Deposition of TiO₂ Nanoparticles

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요   약: 본 연구에서는 TiO₂ 나노입자로 표면침적된 polyethersulfone (PES) 정밀여과 분리막이 자연유기물로 인한 분리막 막힘현상(파울링)에 미치는 영향을 관찰하였다. TiO₂ 나노입자로 표면침적된 PES 정밀여과 분리막의 자연유기물 파울링 거동에 TiO₂ 나노입자의 결정구조와 용액의 pH 그리고 Ca⁺²이 미치는 영향을 관찰하였다. 연구결과, TiO₂ 나노입자로 표면 개질된 정밀여과 분리막은 자연유기물에 의한 파울링 현상을 현저하게 감소시킬 수 있음을 확인 할 수 있었다. 그러나 이와 같은 현상은 TiO₂ 나노입자의 결정구조와 용액의 성상에 매우 의존하는 것으로 나타났다. 자연유기물 파울링의 감소는 결정구조가 상대적으로 불안정한 anatase TiO₂ 나노입자를 분리막에 표면침적 시, 용액 중 Ca⁺²이 존재하지 않을 때 상대적으로 높은 pH에서 효과적인 것으로 관찰되었다. 그러나 Ca⁺²의 첨가 시 이와 같은 효과는 높은 pH에서 더욱 증가할 수 있음을 확인할 수 있었다. 반면, 결정구조가 상대적으로 안정한 rutile TiO₂ 나노입자의 경우 자연유기물의 파울링 감소는 용액의 조성에 큰 영향을 받지 않는 것으로 나타났다.

Abstract: In this study, the effect of surface deposition of TiO₂ nanoparticles at polyethersulfone (PES) microfiltraiton (MF) membrane on humic acid fouling was investigated. The effect was observed as a function of crystal structures of TiO₂ nanoparticles and solution chemistries including pH and divalent cation such as calcium. Our results showed clearly that TiO₂-deposited membrane could mitigate membrane fouling significantly. However, this effect was observed to be dependent upon crystal structures of TiO₂ nanoparticles and solution chemistries. In the absence of calcium, fouling mitigation was less pronounced for both anatase and hybrid TiO₂-deposited membrane than for rutile TiO₂-deposited membrane while opposite trend was observed after addition of calcium. In the presence of calcium, the adsorption of humic acid to TiO₂-deposited membrane can be reduced by electrostatic repulsions between humic acid and TiO₂ surface. Addition of calcium provided further beneficial effect on fouling mitigation particularly at higher pH for the anatase TiO₂ deposited membrane, implying that both increased hydrophilicity due to TiO₂ nanoparticles and negative surface charge of the membrane should affect fouling mitigation. However, rutile TiO₂ having more inertness generally than the anatase TiO₂ showed relatively robust effect on the fouling mitigation regardless of solution properties.

Keywords: TiO₂ nanoparticles, PES membrane, microfiltration, humic acid, fouling

1. Introduction

Although the applications of membrane technologies

in drinking water treatments have been growing rapidly, membrane fouling caused by deposition of foulant materials on membrane surface and/or adsorption of them within membrane pore matrix still remains a major problem [1]. Membrane fouling decreases membrane

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performance significantly by declining permeate flux with time under constant pressure mode of operation or increasing transmembrane pressure with time under constant flux mode of operation. As a result, membrane fouling reduces a frequency of chemical cleaning for the fouled membrane and requires replacement of it, thereby increasing operational and capital costs subsequently [2,3].

In membrane water treatment, the membrane fouling is attributed primarily to natural organic matter (NOM) and humic acid (HA) is major component of the NOM [4,5]. The NOM in water represents broad range of structural complexity, which is derived from the degradation of plants and microorganisms [6]. In particular, removal of NOM in the drinking water treatment is important because it can serve as precursors of disinfection by-products which are carcinogenic upon chlorination [7]. A large fraction of NOM has negative charge due to dissolution of carboxylic and hydroxy functional groups. Calcium and other multivalent cations are also known to form complexes with NOM and accelerate aggregation, thus increasing membrane fouling [8].

The NOM was found to be major foulant of the MF membrane in the drinking water treatment although this type of porous membrane is more suitable for the removal of suspended solids [9]. Howe and Clark showed that the compounds of NOM which is larger than 3 nm should be responsible for major fouling of MF membrane although this fraction was only 10~15% of total NOM [10]. They also concluded that the adsorption of NOM was the main mechanisms that lead to the fouling of the MF membrane. It was reported that hydrophobic fractions of NOM adsorbed the hydrophobic MF membranes preferentially. However, nature of NOM, water solution properties and types of the membranes all affected adsorptive fouling [6]. For instance, adsorption of humic acids particularly onto hydrophobic MF membrane was observed to be greater at lower pH and higher ionic strength, but hydrophilic membranes suffered less fouling than the hydrophobic membrane [6,8].

Recent advances in nanotechnology have expanded the range of methods available to membrane researchers to mitigate membrane fouling. The use of nanoparticles in the manufacturing membranes allows for both a high degree of control over membrane fouling and the ability to produce desired structure as well as their functionalities [11]. On this regard, titianum dioxide (TiO₂) nanoparticles have gained considerable attentions due to their photocatalytic and hydrophilic effects [12,13]. Several studies evaluated fouling mitigation effects of TiO₂ nanoparticles without UV exposure in membrane bioreactor applications [13,14]. It was observed that the effect of TiO₂ particles on fouling mitigation was significant and surface dipping of TiO₂ at membrane had a greater fouing mitigation effect than the embedding of them into the membrane pore matrix [13].

It is true that the most efficient way of the use of TiO₂-enhanced membrane can be achieved when the TiO₂ nanoparticles are combined with UV light illumination. However, better understanding interactions between NOM and TiO₂ nanoparticles as coating materials for the membrane are still lacking. To authors' knowledge, little information on the combined effect of different crystal structures of TiO₂ nanoparticles and solution properties including pH and Ca^{+2} on the NOM fouling of MF membrane deposited by TiO₂ nanoparticles is available.

The objectives of this study were to investigate the effects of TiO₂-deposited MF membrane on the membrane fouling caused by humic acid (HA) which constitutes major fraction of NOM. Due to low hydrophilicity of PES membrane, it has been known as the membranes having high fouling potential for aqueous NOM filtration. In this study, surface of the PES MF membrane was modified by the deposition of hydrophilic TiO₂ nanoaprticles at membrane surface and applied for the filtration of HA. The fouling mitigation effect by applying the TiO₂-deposited membrane was investigated as a function of crystal structures of TiO₂ nanoparticles and solution properties including pH and Ca^{+2}.
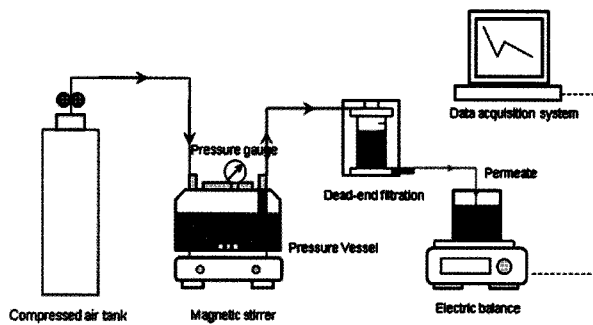
Fig. 1. Schematics of experimental set-up (constant pressure mode).

2. Experimental

2.1. Filtration Apparatus

In this study, filtration tests were performed at constant pressure mode of operation. The schematic diagram of filtration apparatus is shown in Fig. 1. The pressure vessel was pressurized at constant pressure by compressed air tank for providing feed solution to the dead-end filtration cell (effective volume is 50 mL). Transient behavior of permeate flux from the membrane equipped in the cell was monitored continuously by using electric balance and data acquisition system (Balance Talk, Labtronics, USA). The pore size of PES microfiltration membrane (Supor PES Membrane Disc Filter) tested in this study was 0.1 µm.

2.2. Feed Solution and TiO₂ Nanoparticles

Humic acid (HA) solution was prepared by dissolving 20 mg HA (Aldrich Inc.) in 1 L of deionized water. The solution pH was controlled by 0.01 M H_2SO_4 and 0.1 M NaOH, and 1 mM $CaCl_2$ was also added to the feed solution to investigate calcium effect on membrane fouling. The test HA solution was prefiltered by GF/C filter to remove impurities (Whatman, pore size is 1.2 µm) and stored at 4°C. Three types of TiO_2 nanoparticles were purchased from Aldrich (USA), Deajung (Korea) and Degussa P25 (Japan). To investigate crystal structure and size for each nanoparticle, XRD analysis (X-ray Diffractometer System, DMAX-2500, Rigaku) and microscopic analysis using scanning electron microscope (Field Emission

SEM, S-4200) and transmission electron microscope (CM200, Philips Inc.) were performed.

2.3. Surface Coating with TiO₂ Nanoparticles

To deposit the TiO_2 nanoparticles at membrane surface, dead-end filtration cell (Amicon 8000 series, effective volume: 50 mL) was used in this study. 50 mL of TiO_2 solution (TiO_2 concentration is 10 mg/L) was filtered through the PES membrane at about 4 psi by using the filtration cell. After depositing TiO_2 particles at membrane surface, the HA solution was fed subsequently into the same dead-end filtration cell at 8 psi from the pressure vessel connected to the cell. By doing this way, the HA filtration could be performed without damaging TiO_2 coating layer at membrane surface. The surface concentration of TiO_2 nanoparticles defined as the mass of TiO_2 particles per membrane surface area was about 0.5 mg/m².

This surface coating method has been performed by other researchers for coating alumina ceramic membrane with ferric oxide nanoparticles [13] although further considerations need to be made in terms of the immobilization of the nanoparticles at membrane surface. Nonetheless, it has been observed that the membrane surface could be coated by various metal oxide nanoparticles in relatively uniform fashion [13].

3. Results and Discussion

3.1. Characterizations of Crystal Structures of TiO₂ Nanoparticles

Fig. 2 shows the characterizations of three different types of TiO_2 nanoparticles tested in this study. Our SEM-XRD data provided the result that the TiO_2 nanoparticles purchased from Aldrich, Deajung and Degussa P25 were anatase, rutile and hybrid titania (anatase : rutile = 4 : 1), respectively. The microscopic observations also showed that the particle diameters of anatase and hybrid TiO_2 nanoparticles were about 25 nm while the particle size of rutile TiO_2 particles was about 100 nm. The TEM images in Fig. 3 also show that the nanoparticles are spherical and agglomerated, but no sig-
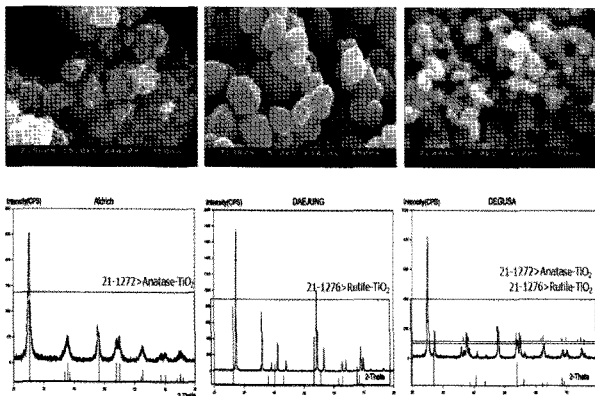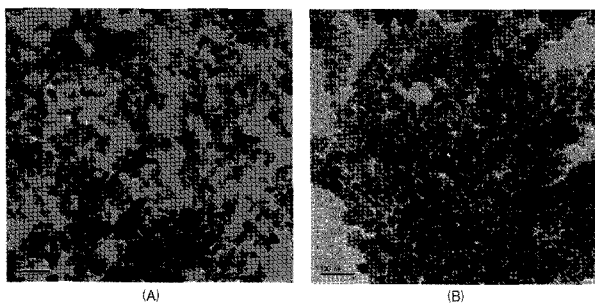
Fig. 2. SEM-XRD results of TiO₂ nanoparticles.

Fig. 4. Permeate flux decline without calcium at pH 5.8.

Fig. 3. TEM images of hybrid TiO₂ (A) and anatase TiO₂ (B).

nificant differences in the morphology of the each TiO₂ nanoparticles were observed. To increase the dispersibility of TiO₂ nanoparticles, the solution was sonicated for 30 min prior to depositing them at membrane surface.

Both anatase and rutile are known as being effective photocatalyst, but the anatase has shown greater photocatalytic activity because of its unstable crystalline structures [16]. Debates are still ongoing in research community about the photocatalytic activity of hybrid TiO₂. However, it has been observed that the hybrid TiO₂ had higher photocatalytic activity than the anatase or rutile TiO₂ particularly for the aromatic compounds [17]. Smaller TiO₂ nanoparticles have also been proven to provide higher photocatalytic functionality. However, investigating photocatalytic activity of each TiO₂ was beyond this study.
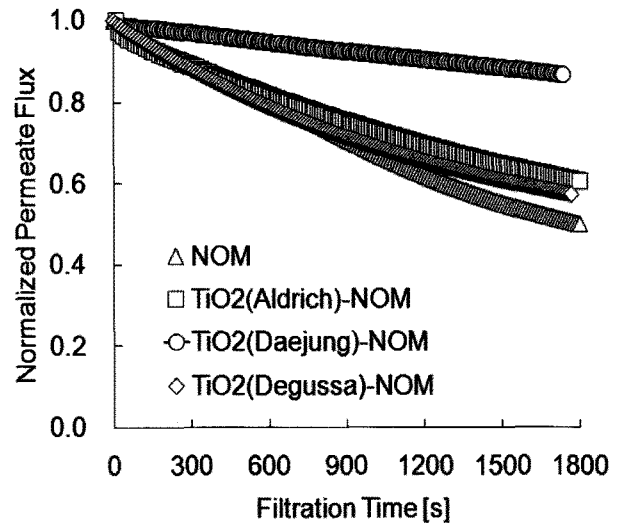
3.2. Effects of Surface Coating with TiO₂ Nanoparticles on Fouling Mitigations

After performing deposition of TiO₂ nanoparticles at membrane surface, fouling test was conducted further by filtering HA solution to observe membrane fouling for three different types of TiO₂ nanoparticles (anatase, rutile and hybrid TiO₂) as coating materials. The solution pH of the HA was 5.8 in the absence of Ca^{+2}. As shown in Fig. 4, the permeate flux with bare membrane was only about 50% of the initial value at 30 min of filtration time. However, permeate flux decline was reduced significantly as the membrane was deposited by rutile TiO₂ nanoparticles. Fouling mitigation effect was less pronounced for both anatase and hybrid TiO₂-deposited membrane than for rutile TiO₂-deposited membrane.

As for the TiO₂ nanoparticles, the HA adsorption onto the TiO₂ surface may play a critical role in membrane fouling. That is, adsorption of HA on anatase and hybrid TiO₂ should be more pronounced than the rutile TiO₂, thereby increasing membrane fouling. In addition, the rutile TiO₂ tends to have more hydrophilicity than the anatase one [18], implying that hydrophobic interactions between humic acid and rutile TiO₂ should also be reduced. At higher solution pH (=10), however, membrane fouling could be reduced significantly for both anatase and hybrid TiO₂-depo-sit-
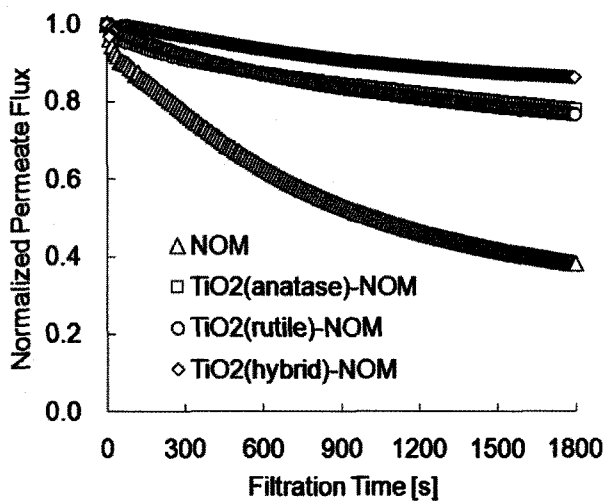
Fig. 5. Permeate flux decline without calcium at pH 10.

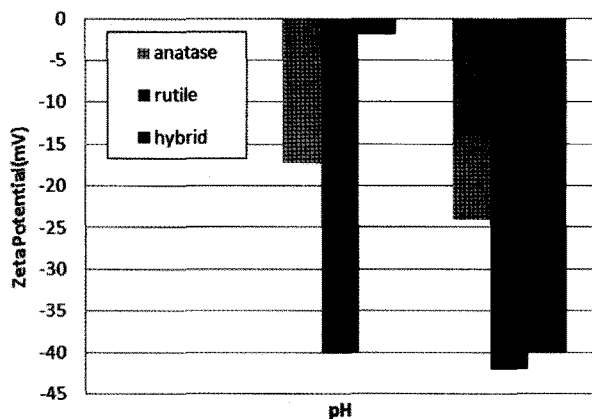Fig. 7. Permeate flux decline with calcium at pH 5.8.

Fig. 6. Zeta potential of TiO_2 nanoparticles at pH 5.8 and 10.

ed membranes as shown in Fig. 5.

Results might attribute to the different surface charge values for TiO_2 nanoparticles [18]. As shown in Fig. 6, the rutile TiO_2 was negatively charged at pH 5.8 and the portion of negative surface charge of the TiO_2 nanoparticles was higher than other two types of rutile TiO_2. Since the HA is negatively charged at this pH, more electrostatic repulsions between HA and rutile TiO_2 nanoparticles can be occurred. As the solution pH increased to 10, however, both anatase and hybrid TiO_2 became negatively charged while the extent of the increase in negative surface charge of the rutile TiO_2 was not significant. Therefore, anatase and hybrid TiO_2-deposited membrane is expected to provide higher
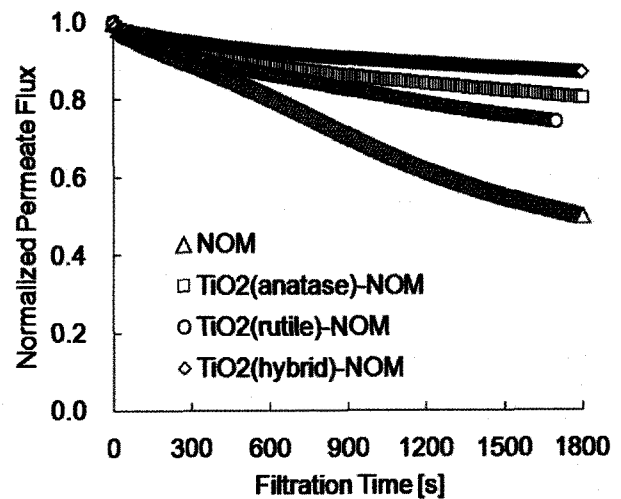
repulsive forces against HA at higher pH due to electrostatic repulsions between HA and TiO_2 nanoparticles.

3.3. Combined Effects of pH and Calcium on Fouling Mitigations

To observe Ca^{+2} effect as divalent cation on HA fouling of TiO_2-deposited membranes, the calcium was added as 1 mM $CaCl_2$ into the test solution. As shown in Fig. 7, the fouling mitigation effect in the presence of Ca^{+2} at pH 5.8 was higher for the anatase and hybrid TiO_2-deposited membrane than for the rutile TiO_2-deposited membrane. Opposite result was found under the same pH condition in the absence of Ca^{+2} (Fig. 4). This fouling behavior suggests that increased binding of Ca^{+2} due to complexation of it by carboxylate sites on the HA, and thus reducing the negative surface charge of it. As a result, adsorption of HA can be reduced by electrostatic repulsions between HA complexed with Ca^{+2} and TiO_2 surface which is less negatively charged (Fig. 6).

The transient behavior of the permeate flux of TiO_2-deposited membranes in the presence of Ca^{+2} at solution pH of 10 is shown in Fig. 8. Interestingly, addition of Ca^{+2} resulted in decreasing in HA fouling for the membranes deposited by all types of TiO_2 nanoparticles. In particular, the hybrid TiO_2 showed greatest mitigation effect on membrane fouling under these conditions. The effect of the addition of Ca^{+2} on
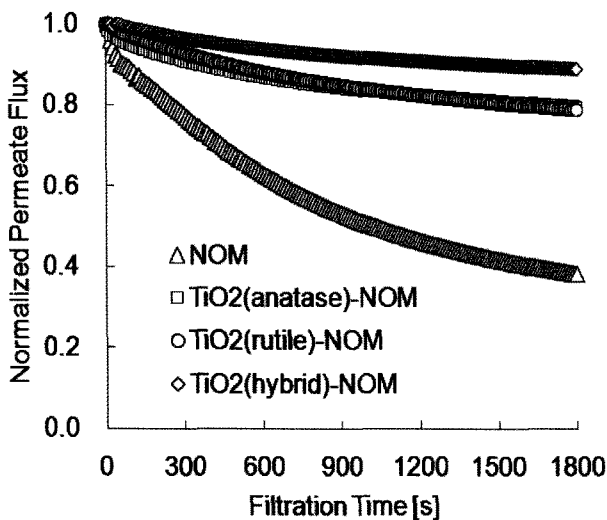
Fig. 8. Permeate flux decline with calcium at pH 10.

fouling mitigation at higher pH may not be explained only by electrostatic interaction between HA and TiO₂ nanoparticles. Both the increased hydrophilicity as a result of depositing TiO₂ nanoparticles or non-electrostaic forces may be responsible for the observed results [19].

4. Conclusions

Integrating TiO₂ nanoparticles with PES microfiltration membrane greatly reduced membrane fouling by humic acid. However, the crystal structure of TiO₂ nanoparticles, solution pH and Ca^{+2} could affect fouling mitigation. More rapid fouling occurred for anatase TiO₂-deposited membrane than for rutile or hybrid TiO₂-deposited membranes without Ca^{+2} at pH 5.8. However, the extent of HA fouling could be reduced significantly as the solution pH increased and this effect was improved further by the addition of Ca^{+2}. The fouling mitigation effect could be explained well by electrostatic interactions between HA and TiO₂ nanoparticles. However, increased hydrophilicity of TiO₂-deposited membrane or non-electrostatic forces can not be overlooked for better understanding interactions between HA and TiO₂ nanoparticles.

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