

광촉매 반응기용 세라믹 막에의 TiO₂ 층 형성과 성능평가

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(2017년 6월 23일 접수, 2017년 8월 17일 수정, 2017년 8월 28일 채택)

In-situ TiO₂ Formation and Performance on Ceramic Membranes in Photocatalytic Membrane Reactor

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(Received June 23, 2017, Revised August 17, 2017, Accepted August 28, 2017)

요약: 메조포러스 공극구조를 갖는 광촉매 멤브레인은 다양한 환경기술에 적용될 수 있다. 본 연구에서는 TiO₂ 층을 형성시킨 광촉매 반응기용 세라믹 멤브레인을 개발하고 이를 염색용액 처리에 적용하였다. 높은 공극률과 균질성을 지닌 TiO₂ 광촉매층을 그래프트 공중합체를 사용하여 제조하였다. 멤브레인은 광촉매 반응기와 멤브레인 여과를 결합시킨 하이브리드 광촉매 반응기에 성공적으로 적용하였다. 실험결과 정렬된 구조의 TiO₂ 층이 Al₂O₃ 지지체에 형성되었다. TiO₂ 층 형성 후 제조된 세라믹 분리막의 순수 투과도는 형성된 광촉매 층 저항으로 감소하였다. 정렬된 구조의 TiO₂ 층은 UV 결합 시 5시간 안에 완벽한 염색용액 분해를 달성시킬 수 있었다. 광촉매 멤브레인의 염색용액 분해는 Langmuir-Hinshelwood 흡착 모델로 잘 설명할 수 있었다. 또한 TiO₂ 층이 고정화된 세라믹 멤브레인의 model Congo Red에 대한 1차 속도상수는 Al₂O₃ 지지체 단독인 경우에 비해 약 6배 정도 큰 값을 나타내었다(0.0081 vs. 0.0013 min⁻¹).

Abstract: Fabricating photocatalytic composite membrane with a mesoporous and tailored morphological structure would have significant implication for environmental remediation. In this study, we reported hybrid TiO₂ immobilized photocatalytic membrane and its application for the treatment of dye solution. Photocatalytic film with high porosity and homogeneity was fabricated by graft copolymer as polymer template. Hybridization of membrane filtration with photocatalysis was successfully achieved by photocatalytic membrane reactor developed. Result showed that membrane permeability was significantly reduced after immobilizing the TiO₂ film on bare Al₂O₃ support. The membrane characterization indicated that well organized TiO₂ film was successfully formed on Al₂O₃ support. Benefiting from the controlled morphology of TiO₂ film, the composite membrane exhibited almost complete degradation of organic dye within 5 h of filtration under UV illumination. Langmuir-Hinshelwood model explained degradation of organic dye. First-order rate constant was approximately six times with TiO₂ immobilized composite ceramic membrane, higher than the one with the bare Al₂O₃ support (0.0081 vs. 0.0013 min⁻¹).

Keywords: Photocatalytic membrane reactor, TiO₂ film, catalytic reactions, organic dye, photocatalysis

1. Introduction

There are upsurge of interests in membrane for industrial wastewater treatment[1,2]. However, significant

amount of contaminants could still merely be separated from the water, requiring additional treatment process for the removal of them[3-5]. Photocatalytic membrane reactor (PMR) combines the benefits of membrane sep-

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aration and photocatalysis. Ceramic membrane is very attractive to PMR application because of excellent chemical membrane resistances against strong oxidants. The PMR containing photocatalyst (i.e., TiO₂) in suspension has been widely studied[6,7]. The suspended type configuration has been successfully adopted for degradation of carcinogenic dyes in wastewater treatment[8]. Congo Red dye is an azo dye which is capable to cause allergic reaction and can be metabolized to benzidine, known as a human carcinogen[9]. Although the suspended type configuration gained much attention of researchers, however complete recovery of the photocatalyst from the treated water is a big hurdle. In addition, the photocatalyst in suspension can act like foulants on membrane surface, thereby reducing membrane reactivity[10].

Functional membrane immobilized with photocatalyst exhibits both physical separation and degradation of organic contaminants simultaneously under reaction promoters[11-13]. Combining nanocrystalline TiO₂ film on macroporous metal oxide support such as alumina (Al₂O₃) has been extensively studied for photocatalytic ceramic membrane applications due to their excellent physical and chemical properties[13-17]. In general, nano-TiO₂ particles are coated on membrane surface to improve surface reactivity by dipping method, but they can be released easily during membrane filtration. In addition, it is difficult to achieve homogenous coating layer on the membrane. The TiO₂ layer immobilized onto a macroporous inorganic support provides beneficial effects such as confinement of photocatalyst in the membrane, improvement of membrane hydrophilicity or in-situ degradation of the contaminants on membrane surface[7,18]. Intrinsic properties of inorganic support against chemical reagent enable the photocatalytic membrane to withstand the concomitant attack of strong oxidants produced by photocatalytic activity such as hydroxyl radicals[13]. As such, the structural characteristics of immobilized photocatalyst film need considerable attention because the well-organized photocatalytic film should be related closely with photocatalytic membrane activity.

Currently, much attention has been given to control the morphology of the photocatalytic membranes. The use of different surface directing agents has provided better control over structural characteristics of photocatalytic membranes. The Pluronic block copolymer based photocatalytic membrane with fine-tuned and porous structure showed higher removal efficiency of organic dye compound[15]. Well-organized photocatalyst film with enhanced catalytic activity was also fabricated by using self-assembled block copolymer[19]. The photocatalytic membranes typically based upon Pluronic block copolymer have been investigated widely. However, applying graft copolymer for developing photocatalytic membranes still requires further studies.

In this paper, we reported the development and the application of TiO₂ immobilized photocatalytic composite membrane using TiO₂ precursor and the poly(vinyl chloride)-graft-poly(oxyethylene methacrylate) (PVC-g-POEM) graft copolymer as polymeric template. The prepared membrane was characterized and their photocatalytic activity was evaluated by using Congo Red dye compound.

2. Experimental

2.1. Fabrication of composite membrane

The TiO₂ immobilized hybrid photocatalytic composite membranes were prepared as described in our previous study[13]. Briefly, the poly(vinyl chloride)-graft-poly(oxyethylene methacrylate)(PVC-g-POEM) graft copolymer as surface directing agent for photocatalytic film was first synthesized via atom transfer radical graft polymerization (ATRP). The prepared graft copolymer was diluted in tetrahydrofuran (THF, J.T. Baker) and then precipitated in methanol for the purification. The purification cycle was carried three times. The purified (PVC-g-POEM) graft copolymer precipitates were completely dried in an oven at 50°C.

For the fabrication of composite membranes, poly(vinyl pyrrolidone) (PVP, average molecular weight: 40,000 g mole⁻¹, Sigma Aldrich) was first pre-coated

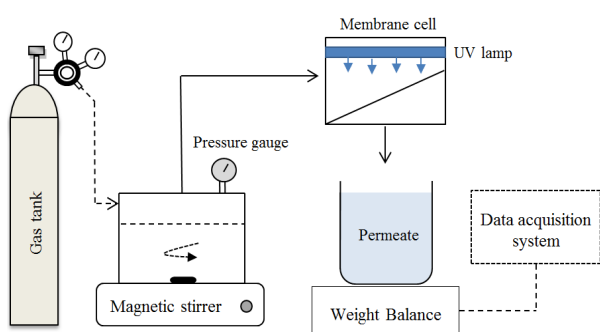


Fig. 1. Schematics of experimental set-up of photocatalytic membrane reactor.

on bare Al_2O_3 support (nominal pore size 100 nm). The TiO_2 precursor solution with molar ratio of TTIP : H_2O : HCL = 2 : 1 : 1, was prepared. A 0.1 mL aliquot of as prepared TiO_2 precursor solution was added to polymer solution (0.03 g of PVC-g-POEM graft copolymer in 1.5 mL of THF) and stirred for 3 h. Finally, the resulting polymer and precursor solution was spin coated on PVP pre-coated Al_2O_3 support followed by calcination at 450°C for 30 min.

2.2. Membrane characterization and performance

In order to confirm the successful fabrication of hybrid photocatalytic composite ceramic membranes, the surface of membranes was analyzed using field emission scanning electron microscopy (FE-SEM, SUPRA 55VP, Carl Zeiss, Germany). The performance of the membranes was evaluated by using a photocatalytic membrane reactor developed in this study, as illustrated in Fig. 1. The specially designed reactor equipped with circular type membrane (effective surface area : 4.5 cm^2) was operated in dead-end filtration mode. The membrane surface was directly irradiated by a UV lamp (254 nm, Philips TUV 4W SLM, Poland) which was placed 2 cm above the membrane. The feed solution containing 100 mg/L of Congo Red dye (Showa Chemical, Japan) solution in organic-free water was placed in pressure vessel and oxygen gas was supplied at constant pressure of 1.5 bar to derive feed solution towards membrane module. The permeation through membranes was investigated by measuring the weight of water permeated through membrane using data acquis-

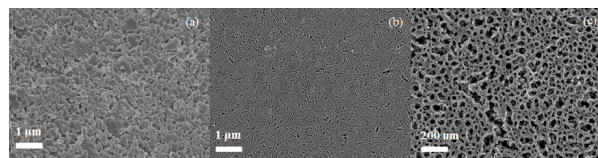


Fig. 2. Surface SEM images of (a) bare Al_2O_3 membrane, (b) TiO_2 immobilized hybrid composite membrane, and (c) magnified image of (b).

ition system. Prior to investigating photocatalytic membrane reactivity, the membranes were pre-adsorbed by the dye solution first by filtering the feed solution under dark condition (without UV irradiation). The adsorption capacity of bare membrane was also completely saturated with dye compound until its concentration in membrane permeate was equal to the feed solution.

The effect of photolysis on membrane fouling and dye adsorption efficiency was also studied. For this experiment, 1 L of feed solution containing 100 mg/L of Congo Red dye solution was illuminated during 12 h followed by membrane filtration for 30 h under dark conditions. The concentration of Congo Red in membrane permeate was measured at wavelength of 510 nm using UV visible spectrophotometer (SCINCO, S-3100, South Korea).

3. Results and Discussions

3.1. Structural characteristics of membrane

Fig. 2 compares the surface morphology of bare and TiO_2 immobilized hybrid composite ceramic membrane. The pore of bare Al_2O_3 support as provided from the supplier (Nano Pore Materials Co., Ltd.) was 100 nm. A uniform, mesoporous and well organized TiO_2 film with 50-70 nm pore size was immobilized on bare Al_2O_3 support as demonstrated in Fig. 2 (b and c). The pre-coating of PVP on bare Al_2O_3 support provided a flat platform for the development of photocatalytic film with least pore-infiltration, hence homogenous surface coverage was observed as shown in Fig. 2 (b). Meanwhile, the amphiphilic PVC-g-POEM copolymer helped to form mesoporous TiO_2 structure during sol-gel and calcination process.

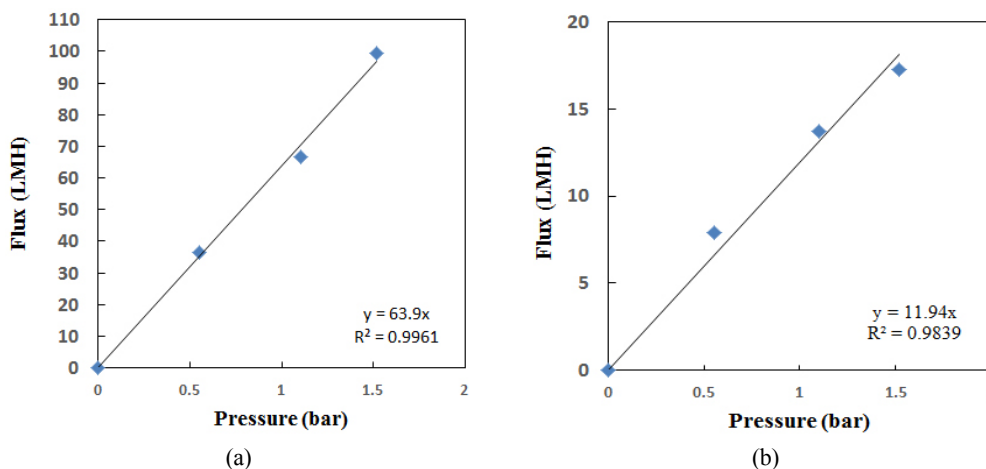


Fig. 3. Comparison between the permeability of (a) bare Al₂O₃ support and (b) TiO₂ immobilized hybrid composite membrane.

3.2. Water permeation and photocatalytic activities

Before the treatment of feed solution, the permeability of bare Al₂O₃ support and TiO₂ immobilized hybrid composite ceramic membranes was compared. As shown in Fig. 3, the permeability of bare Al₂O₃ support was decreased significantly after the immobilization of TiO₂ film on it. The permeability of bare Al₂O₃ support was observed to be 63.9 L m⁻² h⁻¹ bar⁻¹, but it decreased to 11.9 L m⁻² h⁻¹ bar⁻¹ with TiO₂ immobilized hybrid composite membrane. The corresponding values of membrane resistances for bare and TiO₂ immobilized hybrid composite membrane were 6.2×10^{12} and 4.9×10^{13} m⁻¹, respectively. The membrane resistance was calculated using Darcy's equation as given below[20] :

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

Our SEM observation confirmed that the pore size of membranes decreased from 100 nm to 50-70 nm for the bare Al₂O₃ and TiO₂ composite ceramic membrane, respectively. This result indicates that the pore size reduction should provide resistance against permeate flow through membrane[21].

The influence of photolysis with organic dye compound on membrane fouling and its removal efficiency

through membrane was investigated by filtering the Congo Red solution after 12 h photolysis. Results are shown in Fig. 4. The membrane filtration under dark conditions (without UV illumination) revealed that the ratio of J/J_0 was slightly higher after photolysis of dye compound than before it, as shown in Fig. 4 (a). Approximately 21% and 26% flux decline was observed by the filtration of dye solution before and after photolysis, respectively. The same trend was observed that the removal of dye compound through TiO₂ composite ceramic membrane was slightly increased after the photolysis of dye compound. The removal efficiency of dye compound increased from 43% (before photolysis) to 54% (after photolysis). Possible explanation is that the intermediate products during photolysis of dye compound should be formed and they may competitively adsorb in the membrane due to their smaller size[22,23]. The intermediate product may also form by the photolysis of water molecules, producing reactive radicals such as HO·, H·, and the hydrate electron[24]. The interaction of these strong radicals with Congo Red dye molecules has found to produce hydroxyl and naphthalene intermediate compounds[25]. Further works in analyzing intermediate after photolysis of dye compound through membrane are required.

In order to examine the photocatalytic activity only of TiO₂ immobilized composite ceramic membrane de-

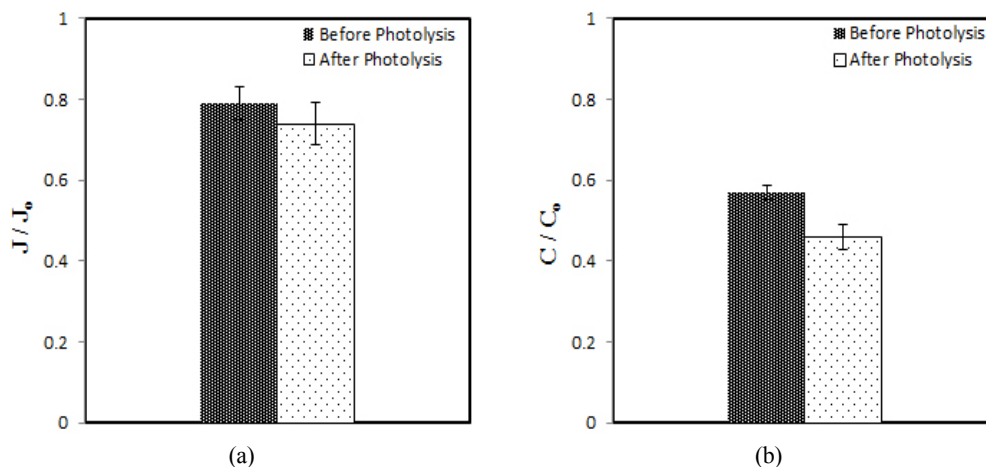


Fig. 4. Effect of filtering feed solution through TiO_2 immobilized hybrid composite membrane after 12 h photolysis on (a) membrane fouling, and (b) organic dye removal (without UV; filtration time: 30 h), J_0 is initial permeate flux and J is permeate flux after 30 hr filtration.

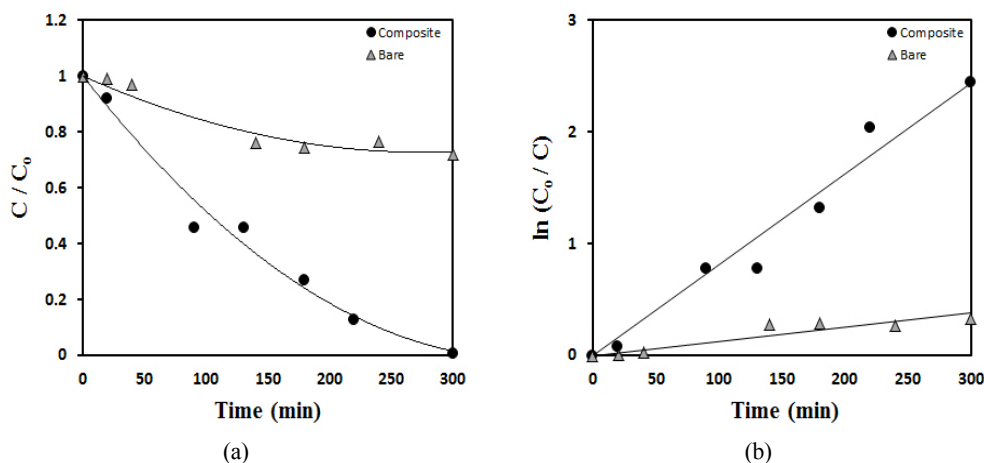


Fig. 5. (a) Photocatalytic degradation profile of Congo Red and (b) kinetic linear fitting curves of Congo Red degradation through bare Al_2O_3 support and TiO_2 immobilized hybrid composite membrane under UV illumination.

veloped in this study, the photocatalytic degradation of the organic dye through the pre-adsorbed membranes was observed. Fig. 5 demonstrates the significance of TiO_2 film with respect to the degradation efficiency of organic compound. During the 5 h membrane filtration under UV illumination, degradation of dye compound was achieved almost completely with TiO_2 immobilized composite ceramic membrane. However there was only 28% of organic removal efficiency with the bare Al_2O_3 support as shown in Fig. 5 (a). The higher removal efficiency of organic compound through TiO_2 immobi-

lized composite ceramic membrane can be attributed to the photocatalytic degradation of dye compound on the membrane under UV illumination[26]. To further elucidate the photocatalytic degradation rate of the membranes towards Congo Red, the kinetic study was carried out using Langmuir-Hinshelwood pseudo-first-order kinetic model[27]. The Langmuir-Hinshelwood model equation has been proven to appropriate model to estimate the simple photodecomposition rate as shown in eq. 2[28].

Table 1. Comparison of Rate Constant Between the Bare Al₂O₃ Support and TiO₂ Immobilized Hybrid Composite Membrane Under UV Illumination

Membrane	k (min ⁻¹)	R ²
Bare Al ₂ O ₃ support	0.0013	0.86
TiO ₂ composite ceramic membrane	0.0081	0.97

$$\ln\left(\frac{C_o}{C}\right) = kt \quad (2)$$

Where C_o (mg/L) represents the initial concentration of Congo Red tested, C (mg/L) denotes the concentration of Congo Red in membrane permeate at time t (min) and k is the rate constant (min⁻¹).

Table 1 provides the comparison of rate constant between the bare Al₂O₃ support and TiO₂ hybrid composite ceramic membrane. The rate constants were 0.0013 (min⁻¹) and 0.0081 (min⁻¹) for the bare Al₂O₃ support and TiO₂ hybrid composite ceramic membrane, respectively. The associated correlation coefficients (R^2) were found to be 0.86 and 0.97 in the case of bare and composite membrane, respectively. This result confirms the beneficial aspect of TiO₂ immobilized composite ceramic membrane fabricated with graft co-polymer combined with UV irradiation for the treatment of organic dye compounds.

4. Conclusion

The TiO₂ immobilized hybrid composite ceramic membrane was successfully fabricated using PVC-g-POEM graft copolymer as polymeric template. The permeability of the membrane was reduced by the formation of TiO₂ film on Al₂O₃ support. The evaluation of membrane characterization revealed that the pore size of the Al₂O₃ support decreased after TiO₂ immobilization. The TiO₂ immobilized composite ceramic membrane showed excellent photocatalytic activity and almost complete dye degradation was achieved within 5 h of filtration under UV illumination. The kinetic degradation was consistent with the Langmuir-Hinshelwood model and rate constant with TiO₂ im-

mobilized hybrid composite membrane was approximately 6 times higher than with the bare Al₂O₃ support (0.0081 vs. 0.0013 min⁻¹). Future works in analyzing intermediates through membrane filtration and observing performance of the TiO₂ immobilized composite ceramic membrane developed by other types of graft copolymer are needed.

Acknowledgements

This research was supported by the project titled "Manpower training program for ocean energy" funded by the Ministry of Oceans and Fisheries, Korea.

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