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Effect of polymer template on structure and membrane fouling of TiO_2/Al_2O_3 composite membranes for wastewater treatment

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ABSTRACT

A series of photocatalytic TiO_2 membrane was prepared on macroporous Al_2O_3 support via sol–gel route using polymer templates including Pluronic block copolymers of P123, F127 and poly(vinyl chloride) (PVC) homopolymer. The TiO_2 layer on Al_2O_3 support reduced permeability due to pore size reduction regardless of polymers applied. The TiO_2/Al_2O_3 composite membrane under UV light reduced organic fouling. The PVC based-homopolymer showed highest adsorption capacity and catalytic function with TiO_2/Al_2O_3 composite membrane. Organic removal efficiency of 90% was achieved by PVC based TiO_2/Al_2O_3 composite membrane. The precoating with the PVC polymer template led to uniform TiO_2 film by mitigating pore infiltration.

Introduction

Membranes are effective tool for the removal of contaminants from wastewater. The wider use of membrane filtration, however, is hindered by membrane fouling caused by colloidal and organic deposit on membrane surface and/or within membrane pores [1–6]. Significant efforts have been made to reduce membrane fouling. However, external functionalities, for example, operational conditions, are still limited to control membrane fouling due to complexity and variety of feed waters.

Recently, interests in functional membrane or self-cleaning membrane which can degrade foulants on the membrane surface or that can catalyze reactions that degrade foulants are growing rapidly. Photocatalytic membrane is to combine membrane material with photocatalytic activity for simultaneous filtration and degradation of organic foulants through membrane [1,4,7–9]. Nanocrystalline photocatalysis such as TiO_2 is developed on macroporous inorganic support such as alumina (Al_2O_3) [10–14]. The TiO_2 layer on inorganic support confines photocatalytic activity of the membrane with desired fouling control [4,15]. Structure and morphology of TiO_2 layer on macroporous inorganic support plays an important role in photocatalytic activity and antifouling properties [16–18]. As a result, morphological properties of TiO_2 layer affects photocatalytic functionality by controlling not only light abundance but also transport of foulant to the layer on membrane significantly [19].

There have been limits to develop well-organized TiO_2 layer on inorganic support exhibiting large surface area and high membrane porosity. Block copolymers have been used as structure directing agent to develop well-defined photocatalytic layer on membrane [11,20,21]. The Pluronic block copolymer increased photocatalytic degradation efficiency of the TiO_2 membrane in wastewater treatment [22–24]. The porous and fine-tuned structure of photocatalytic layer on ceramic support was formed by altering the amounts of Pluronic block copolymer such as P123 [11]. The self-assembled block copolymer also enhanced structure of TiO_2 layer with improved photocatalytic activity [19]. Nevertheless, tailoring membrane surface to fuse photocatalytic coating layer without densification still requires intensive research.

In this study, we applied a cost-effective, hydrophobic polyvinyl chloride (PVC) homopolymer with high molecular weight (97,000 g/mol) alternative to block copolymer template to develop photocatalytic membrane. A series of photocatalytic membrane was prepared by immobilizing TiO_2 coating on macroporous Al_2O_3 support via sol–gel route using the PVC polymer template. Experimental works were also performed to compare performance of photocatalytic membrane with Pluoric block copolymers including P123 and F127 polymer template.

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Experimental

Materials

Poly(vinyl chloride) (PVC, weight-average molecular weight (M_w) = 97,000 g/mol, number-average molecular weight (M_n) = 55,000 g/mol), titanium(IV) isopropoxide (TTIP, 97%), hydrogen chloride solution (HCl, 37 wt%), poly(ethylene glycol)$_{106}$-block-poly(propylene glycol)$_{70}$-block-poly(ethylene glycol)$_{106}$ (F127, M_n = 12,700 g/mol), poly(ethylene glycol)$_{20}$-block-poly(propylene glycol)$_{68}$-block-poly(ethylene glycol)$_{20}$ (P123, M_n = 5800 g/mol), poly(vinyl pyrrolidone) (PVP, M_w = 40,000 g/mol) were purchased from Sigma–Aldrich. Tetrahydrofuran (THF) and ethanol were obtained from J.T. Baker. Congo red dye was supplied from Showa chemicals, Japan. All chemical reagents were used without any further purification and treatment. The macroporous alumina disk support (α-Al_2O_3, diameter = 30 mm, thickness = 2 mm, pore size = 100 nm) was obtained from Nano Pore Materials Co., Ltd.

Preparation of TiO_2 membranes

To prepare photocatalytic TiO_2 membrane, a PVP solution (10 wt% in ethanol) was first spin-coated on the bare Al_2O_3 support at 500 rpm for 20 s and completely dried at 50 °C as shown in Fig. 1. This step is important to obtain smooth even surface of the support by minimizing deep penetration of the TiO_2 solution. Then 0.03 g of three kinds of polymer (i.e. PVC, P123 and F127) was dissolved in 1.5 mL of THF by magnetic stirring at room temperature. To prepare the TiO_2 precursor solution, HCl was added into TTIP drop by drop and then H_2O was added to the solution with vigorous stirring. The solution was mixed for 30 min. The ratio of solution was fixed at TTIP:HCl:water = 2:1:1 wt. 0.2 mL of the prepared precursor solution was mixed with the polymer dissolved in THF for 3 h. The mixture solution was spin-coated on the PVP-coated Al_2O_3 membrane and calcinated at 450 °C for 30 min. During the calcination, all organic materials were completely decomposed and TTIP precursor was crystallized to pure TiO_2.

Characterization of photocatalytic TiO_2 membranes

The surface and cross-section morphologies of membranes were analysed with field emission scanning electron microscope (FE-SEM, SUPRA 55VP, Carl Zeiss, Germany). The morphology and crystalline structure were characterized with high resolution-transmission electron microscope (HR-TEM, JEM-3010, JEOL, Japan). To confirm the crystalline phase, TiO_2 films on the substrate was scratched with slide glass and characterized with X-ray diffraction spectroscopy (XRD, generator: 40 kV, 40 mA, D8 ADVANCE with DAVINCI, BRUKER, Germany, wavelength(l): Cu kα1 – 1.5418 Å, 2 theta range: 10–80°). The surface images of the TiO_2 on alumina membrane were obtained by atomic force microscopy (AFM, XE-Bio, Park Systems).

Filtration tests with photocatalytic membrane

To investigate the performance of photocatalytic membranes, dead-end filtration was performed using Congo-red dye compound having 100 mg/L concentration. The organic solution was prepared by diluting 0.5 g/L of Congo-red dye stock solution. The stock solution was prepared every two weeks using deionized (DI) water from ultrapure water production system (STS-8l, Human Science, Korea). Membrane fouling and photocatalytic activity were evaluated by using the photocatalytic membrane reactor, as illustrated in Fig. 1(a). The bench-scale, photocatalytic membrane reactor consists of feed reservoir having 5 L of effective volume in which magnetic bar is stirred. The feed reservoir was connected to the membrane module consisting of quarts specifically designed for this study. Circular type of ceramic membrane was equipped into the membrane module (effective surface area is 4.5 cm^2). The membrane was irradiated directly by the UV lamp (254 nm, Philips TUV 4W SLM, Poland) which was installed above the membrane surface having 2 cm distance between the membrane surface and UV lamp. A 1.5 bar was provided as an applied pressure by using a compressed oxygen gas tank connected to the feed reservoir. The permeate weight produced by the photocatalytic membrane module was measured on an electric balance (Ohaus Corporation, Pine Brook, NJ, USA) and recorded with filtration time by data acquisition system. The changes in the concentration of dye compound in membrane permeate during membrane filtration were measured with filtration time by measuring the absorbance at 510 nm with a UV–visible spectrophotometer (SCINCO, S-3100, South Korea).

The photocatalytic activity of TiO_2/Al_2O_3 membrane with highest antifouling property (i.e., PVC-based TiO_2/Al_2O_3

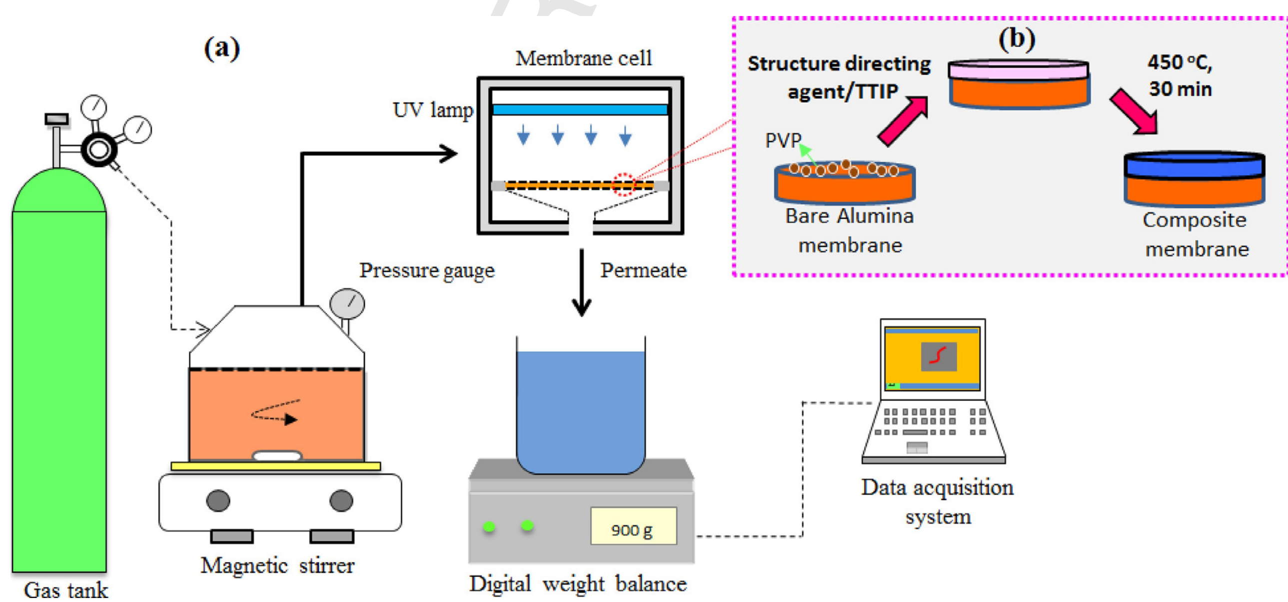

Fig. 1. (a) Schematic illustration for the preparation of composite membrane, (b) experimental setup for photocatalytic membrane reactor.