

Self-cleaning and antifouling properties of plasma-grafted poly(vinylidene fluoride) membrane coated with ZnO for water treatment



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ABSTRACT

Fouling is the main drawback in using membranes for water purification. This study focused on the investigation of coating ZnO onto the poly (vinylidene fluoride) (PVDF) membranes in order to alleviate fouling through the photooxidation process. Poly (acrylic acid) (PAA) was plasma-grafted on the PVDF to introduce functional groups on the membrane surface to support the adhering catalyst. ZnO particles were synthesized by co-precipitation of zinc acetate with oxalic acid at 60 °C. The synthesized ZnO was loaded on the membrane surface at varying dope concentrations (0.5, 1.5 and 3.0 wt% ZnO). Results showed that the membrane hydrophilicity was tremendously enhanced by the self-assembly of ZnO and the highest water flux was found at 0.5% ZnO. The membranes were then severely fouled on filtration of alginate (1 wt%) and the ZnO-coated membranes were able to fully recover their original fluxes upon UV irradiation for 30 min. Furthermore, the modified membranes exhibited excellent photocatalytic activity, wherein PVDF-g-PAA/ZnO-3% membrane could decolorize 86% of remazol black B under UV irradiation of 5 h. This indicates that PVDF-g-PAA/ZnO has a potential application in water treatment with its combined advantage of membrane filtration and photocatalytic oxidation to minimize membrane fouling and improve reusability of ZnO.

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1. Introduction

During the past decade, membrane process has been widely used for separation and concentration of various compounds in food processing, biotechnology industries, and water treatment [1–3]. This is due to its high separation efficiency and energy saving capability. However, long-time membrane filtration is often hindered by membrane fouling which involving the adsorption and accumulation of foulants present in the feed solution onto the surface or within the membrane matrix, leading to a sharp decrease in permeate flux and increase in operation cost.

The nature of membrane material has played an important role in membrane fouling [4]. Currently, most commercially available membranes are made of poly (vinylidene fluoride) (PVDF), polysulfone (PSf), polyimide (PI), and polyethylene sulfone (PES) polymers because of their high mechanical strength, thermal stability, and

chemical resistance. However, due to the hydrophobic nature and low surface energy of these materials, adsorption of organic pollutants on the membrane surface is triggered which therefore results to severe fouling. Thus, it is necessary to improve the hydrophobicity of these membranes in order to alleviate fouling and increase permeate flux, which allows for their widespread application.

Recently, incorporation into membrane of inorganic nanoparticles such as Al₃O₄, SiO₂, Fe₃O₄, ZrO₂, TiO₂, has gained significant interests as it can make hydrophobic membranes strongly hydrophilic [5–7]. Among these, TiO₂ has been extensively used to modify membrane because of its photocatalytic and superhydrophilic effects. Many studies have revealed that the photocatalysis of TiO₂ under UV light is effective to break down organic pollutants [8,9] and inactivate bacteria cells [10]. Thus, combining TiO₂ with membrane material can offer a new hybrid material that has the potential use in water and wastewater treatment [11,12].

ZnO is the second most studied catalyst for photocatalysis after TiO₂. It was reported that ZnO has the same, or even better, photocatalytic activity as TiO₂ [13–15] and it is slightly cheaper, making it a promising alternative to TiO₂ in photocatalysis. Currently,

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the related application of ZnO nanoparticles for membrane modification is still limited to ZnO mixed matrix membrane [16–20], which is prepared by blending ZnO into casting solution to improve mechanical strength and lower membrane fouling tendency. However, excess amount of particles in the membranes often lead to the reduction of membrane stability and performance because of the agglomeration effect of the particles that limits free space for the movement of polymer chains [21].

Surface modification of inorganic nanoparticles via coating or chemical grafting a functional layer on the membrane surface was found to be more effective than the blending method in maintaining membrane hydrophilicity and chemical properties such as the photocatalytic activity of TiO₂. By simply dip coating TiO₂ on alkaline treated PES membrane, Mansourpanah et al. [22] obtained a hydrophilic TiO₂/PES ultrafiltration membrane. Pourjafar et al. [23] prepared nanocomposite by grafting poly vinyl alcohol (PVA) on membrane surface to improve binding force of TiO₂ on the hydrophobic PES membrane. Feng et al. [24] utilized dopamine as coupling ligands to immobilize TiO₂ onto PSf polymer, creating a membrane that exhibits excellent self-cleaning properties and durability. This is due to the polydopamine (PDA) interlayer acting as a free radical scavenger to capture free radical produced for photocatalysis. In our previous study, self-cleaning TiO₂/PAA/PVDF membrane was also successfully fabricated by self-assembly of TiO₂ (PVDF) on plasma-grafted polyacrylic acid (PAA) onto PVDF membrane [25,26].

In this study, we explored the possibility of using ZnO instead of TiO₂ to prepare a self-assembled ZnO modified PVDF membrane surface via plasma-grafted induced polymerization of PAA. First, PVDF membrane surface was treated with argon plasma to oxidize membrane surface for graft polymerization of PAA layer on the membrane. Subsequently, grafted membrane was directly coated with ZnO particles in varying concentrations from 0.5 to 3.0 wt%. All modified membranes were investigated for photocatalytic activity, antifouling and self-cleaning properties, as compared to the pristine PVDF membrane. Surface hydrophilicity and microstructure of modified membranes were characterized using contact angle and scanning electron microscopy, respectively.

2. Experimental

2.1. Materials

Zinc acetate dehydrate (99% purity) was purchased from Alfa Aesar. Oxalic acid (99% purity) was supplied from Merck. Ethyl alcohol (95% purity) was obtained from Taiwan Tobacco & Liquor Co. (TTL). Alginate acid from brown algae (98.5% purity) and anionic azo dye of remazol black B, RB (55% purity) were purchased from Sigma Aldrich. Fig. 1 illustrates chemical structure of the RB. The dye has two sulfonate groups and another two sulfato-ethyl-sulfone groups. It has negative charges when dissolving in the water. Ultrapure water was used for preparation of solution throughout this study.

2.2. Preparation of ZnO photocatalyst

ZnO nanoparticles were synthesized through a simple precipitation-thermal decomposition method as previously described by Subash et al. [27]. In this procedure, zinc acetate solution (0.4 M, 100 mL) and oxalic acid solution (0.6 M, 100 mL) were pre-heated to 90 °C in an oil bath. The oxalic acid solution was slowly added into the zinc acetate solution to form ZnO sol under continuous stirring at 60 °C. After 2 h, the ZnO particles were separated from the aqueous solution by centrifugation and washed several times with water before drying in an oven at 100 °C for 12 h. Calcination of ZnO was performed in a muffle

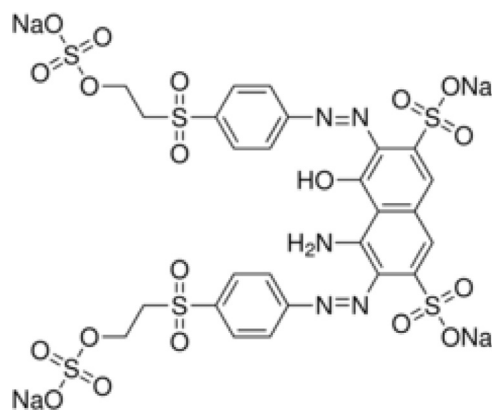


Fig. 1. Chemical structure of anionic azo remazol black B (RB).

furnace (Thermo-Thermolyne, type F6000, USA) at a constant temperature of 500 °C for 5 h. The calcinated ZnO catalyst powders were collected and stored in an airtight bag for further characterization and preparation of hybrid membranes.

2.3. Preparation of self-assembled PVDF-g-PAA/ZnO membranes

The modified PVDF-g-PAA/ZnO membranes were prepared as described in our previous study [25]. The commercial PVDF flat sheet membrane with average pore size of 0.45 μm (Durapore™, Millipore) was cut into 10 × 10 cm and placed in the reaction chamber. Under the vacuum condition, plasma from argon gas (20 sccm) was generated using Dressler PFG-600 (USA) at a power of 125 W. After 150 s, the membranes were exposed to O₂ gas (60 sccm) for 420 s to produce free radicals. Then, the plasma-treated membranes were immersed into 70 wt% acrylic acid monomer (pH 7.5), which was initially purged with N₂ gas for 60 min in order to remove dissolved oxygen. The plasma-induced self-polymerization of PAA on the membrane surface was performed at 60 °C in a water bath for 2 h. The unreacted monomer and PAA polymer were washed out using water and the membranes were used as a substrate for dip-coating ZnO at ambient conditions.

Self-assembled ZnO onto PAA-grafted membrane was fabricated using a simple dip-coating method. To prevent aggregation of the nanocatalyst, ZnO was first dispersed in water and sonicated for 20 min. The grafting modified membranes were dipped into 100 mL of ZnO solution (varying concentrations of 0.5, 1.5 and 3.0 wt%) for 30 min and air-dried for 60 min. This step was repeated one more time before the weakly bound ZnO particles was removed by water, and then air-dried for 1 h. These membranes were denoted as PVDF-g-PAA/Zn-0.5%, PVDF-g-PAA/Zn-1.5%, and PVDF-g-PAA/Zn-3.0% for plasma-grafted membrane coated with 0.5, 1.5, and 3.0 wt% ZnO, respectively throughout the study. The membrane thickness of all the studied membranes was measured and the values were noted between 105 and 112 μm.

Microstructure of all prepared membranes were further characterized using field emission scanning electron microscopy (FESEM) (Hitachi, S 3000, Japan) and static sessile drop method carried out on automatic interfacial tensiometer (Kyowa Interface FACE PD-VP, Japan) for water contact angle.

2.4. Determination on the photocatalytic activity of modified membranes

In this study, RB was used as a model organic pollutant to evaluate the photocatalytic activity of the modified membranes. Two UV lamps (254 nm, 15 W) were immersed in a 1 L beaker

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