Polyvinylidene fluoride ultrafiltration membrane blended with nano-ZnO particle for photo-catalysis self-cleaning

Junming Hong *, Yang He

College of Chemical Engineering, Huaqiao University, Xiamen 361021, China

HIGHLIGHTS

- Modify PVDF ultrafiltration membranes by addition nano-ZnO particles.
- Improve the membrane hydrophilicity with supplementation of nano-ZnO particles.
- Promote mechanical properties and thermal stability for PVDF–ZnO composite membrane.
- Show promising photo-catalytic self-cleaning capability PVDF–ZnO membranes.

ARTICLE INFO

ABSTRACT

A novel photo-catalysis polyvinylidene fluoride ultrafiltration membrane was successfully fabricated via phase inversion method. The membrane matrix was supplemented with nano-ZnO of different content for membrane modification. Filtration experiments, contact angle measurements, scanning electron microscope/energy dispersive X-ray spectrometer analysis, and mechanical tests were conducted to characterize the modified membranes. The photo-catalysis tests clearly showed that the modified PVDF membranes had significant photo-catalysis self-cleaning capability. PVDF-1 (adding 1.0% nano-ZnO with PVDF) membranes achieved 94.8% water flux recovery after exposure to low-pressure 10 W UV-C mercury lamp irradiation for 30 min, whereas the raw membrane only reached 63.3% recovery. The implantation of nano-ZnO on the inner surface of the membrane (i.e., the pore wall) may have been responsible for the enhancement of the photo-catalysis self-cleaning property. The pure water flux of the PVDF-1.5 (adding 1.5% nano-ZnO with PVDF) membrane was nearly five times as great as that of pure PVDF. Supplementation of nano-ZnO could improve the mechanical properties of the membrane, but excessive supplementation of nano-ZnO could cause a decline in the membrane mechanical properties.

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1. Introduction

Membrane filtration is one of the most promising technologies for application in water and wastewater treatment. In fact, membrane fouling is one of the major obstacles to widespread application of membranes, from the economic and technical point of view [1–4]. In particular, most polymer membranes applied to water treatment have been hydrophobic polymers. Polyvinylidene fluoride (PVDF) has excellent chemical stability and inertness to several corrosive materials owing to its fluorinated structure. However, application of PVDF membranes remains limited due to the hydrophobic property of the membrane surface. When conventional hydrophobic polymer membranes come into contact with protein-containing solutions during filtration, an inevitable fouling of solute proteins took place on both sides of the membrane surface and in the walls of the pores [5]. Therefore, modification of the PVDF membrane to improve hydrophilicity and performance

through physical blending, chemical grafting, and surface modification has been performed [6].

Recently, studies on PVDF-blended modifications have focused on blending the polymers with inorganic materials. The preparation of membranes formed by uniformly dispersed inorganic particles in a polymer matrix has been performed for years. Due to their unique physico-chemical properties, nanoparticles have attracted attention for their usefulness in manufacturing membranes with low fouling and a tunable structure as well as wide functionality [7]. In order to improve the properties of membranes, researchers have studied many types of additive nanoparticles, including alumina [8–10], silica (SiO_2) [11,12], clay [13], zirconia [14], and TiO_2 nanoparticles [15–17].

Recently, multifunctional inorganic nano-particle ZnO has been attracting significant attention due to its outstanding physical and chemical properties, including promising catalytic activity and efficient antibacterial and bactericidal capabilities. With one-fourth the cost, nano-ZnO is clearly more economical than TiO_2 and Al_2O_3 nanoparticles [18]. Since nano-ZnO particles can be embedded well in a solid matrix (the membrane), a stable operating system that simultaneously

* Corresponding author. Tel./fax: +86 592 6162300.
E-mail address: mhong@hqu.edu.cn (J. Hong).

promotes the physical properties and chemical characteristics of the membrane may be developed. Supplementing nano-ZnO particles into the membrane can also improve its hydrophilicity and the mechanical properties of the polymer matrix [19].

In fact, Balta et al. [7] pointed out that blending with ZnO nanoparticles led to a significant improvement in the ability of PES (polyethersulfone) nanofiltration membranes to attenuate the fouling effect. Moreover, the addition of nano-ZnO particles into polysulfone membranes also led to a reduction in fouling by oleic acid [20]. Liang et al. [18] reported that the PVDF membranes blended with nano-ZnO particles displayed significant anti-irreversible fouling properties. Our previous studies [21,22] also showed that prepared composite PVDF–ZnO ultrafiltration and microfiltration membranes with supplementation of 0.1% nano-ZnO particles exhibited promising mechanical properties and improved BSA (Blood serum albumin) rejection, compared to pure PVDF membranes. However, how to use nano-ZnO particles for UF membrane modification to maximize photo-catalytic efficiency of membranes and membrane fouling resistance analysis remains an open question.

The novelty of these works is to investigate how and why the synthesis of nano-ZnO enhanced membranes significantly enhances aspects of membrane ultrafiltration ability, including photo-catalysis self-cleaning and low fouling resistance. In addition, filterability properties and detailed membrane morphology were also studied in this work.

2. Material and methods

2.1. Membrane formation

PVDF was purchased from Shanghai 3F New Materials Co. Ltd (China). Blood serum albumin (BSA) was provided from Sinopharm Chemical Reagent Co. Ltd. Nano-ZnO particles (ca.50 nm, Fig. 1) were obtained from Star Nano Scientific and Technological development Co. Ltd. (China). For polymer precipitation, distilled water was used as the non-solvent.

PVDF–ZnO composite membranes were prepared via the phase inversion method. Casting dopes were prepared by dissolving the PVDF and nano-ZnO particles in the DMAc at 323.1 K, and the casting dopes were stirred for 24 h. Then, the casting dopes were maintained in dark for at least 24 h to remove air bubbles. The compositions of casting dopes are shown in Table 1 [23].

The casting dopes were casted uniformly onto a glass plate with 2.00×10^{-4} m of casting knife. After 45 s air exposure, the glass plate was immersed in a bath filled with distilled water. The membranes were then soaked in distilled water.

2.2. Membrane performance

2.2.1. Pure water fluxes (PWF) and rejection of BSA

All filtration experiments were carried out in a dead-end ultrafiltration cell without stirring. The capacity and the effective surface area of
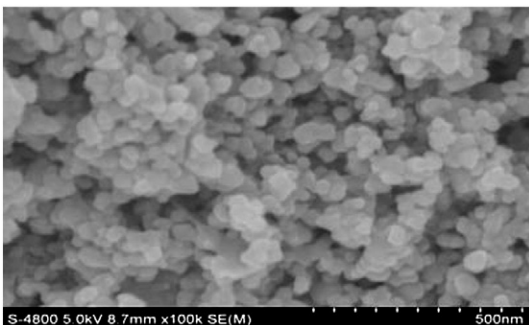

Fig. 1. SEM of nano-ZnO particles.

Table 1
Compositions of casting solution.

PVDF (wt.%)	PEG 600 (wt.%)	ZnO (wt.%)	DMAc (wt.%)	Labeled as
17	3	0	80	PVDF-0
17	3	0.001	79.999	PVDF-0.001
17	3	0.01	79.99	PVDF-0.01
17	3	0.1	79.9	PVDF-0.1
17	3	1	79	PVDF-1
17	3	1.5	78.5	PVDF-1.5

the cell were 3.00×10^{-4} m^3 and 3.85×10^{-3} m^2, respectively. Pure water flux was measured at 1.00×10^5 Pa when the flux was steady. It could be computed with Eq. (1).

$$J = \frac{V}{A \cdot t}, \qquad (1)$$

where J is the pure water flux (m^3·m^{-2}·s^{-1}), V the permeate volume (m^3), A is the membrane area (m^2) and t is the time (s).

Rejection was characterized with 0.50 kg·m^{-3} BSA aqueous solution after the membrane was previously filtered via pure water. The rejection ratio (R) was evaluated with Eq. (2) [9].

$$R = \left(1 - \frac{C_p}{C_j}\right) \times 100, \qquad (2)$$

where R is rejection ratio of BSA aqueous, C_p is the concentration of the permeate and C_j is the concentration of the feed.

2.2.2. Reclaimed water treatment, photo-catalysis efficiency and membrane fouling analysis

The reclaimed water was taken from secondary effluent of Xiamen wastewater treatment plant. Operating pressure of ultrafiltration cell was controlled with nitrogen. Reclaimed water was permeated with ultrafiltration cell. Permeated water was collected at 1.00×10^5 Pa when the flux was steady. COD concentration of the feed and permeation water of raw membrane and composite membranes was determined by the method of potassium dichromate [22].

The membrane fouling analysis procedure included: (1) The pure water flux (J_w, m^3·m^{-2}·s^{-1}) of membranes was measured; (2) The membrane was treated by reclaimed water; (3) The reclaimed water flux (J_{fw}, m^3·m^{-2}·s^{-1}) was measured; (4) The membranes were rinsed by shaking membrane continuously (approx. 100 r·min^{-1}) in the shaking table; (5) The pure water flux (J_{rw}, m^3·m^{-2}·s^{-1}) of fouled membrane was measured; (6) Then, the membrane surface was exposed to a low-pressure 10 W UV-C mercury lamp irradiation for 30 min since the strong adsorption of pollutant on membrane pore wall or surface would be removed by photo-catalyst process; (7) At the last, the final pure water flux (J_f, m^3·m^{-2}·s^{-1}) of membranes was measured.

The photo-catalytic efficiency of membranes could be defined as in Eq. (3).

$$\delta = \frac{J_f}{J_w} \times 100, \qquad (3)$$

where δ is the photo-catalytic efficiency of membranes, J_f is the final pure water flux and J_w is the pure water flux.

The degree of membrane fouling was quantitatively calculated using the resistance in series model as Eq. (4).

$$R_t = \frac{TMP}{\mu_p J_{fw}} = R_m + R_c + R_f + R_b, \qquad (4)$$

where TMP is trans membrane pressure (Pa), μ_p is the viscosity of permeate (Pa·s) after the fouling of the membrane, R_t is the total filtration resistance (m^{-1}) and J_{fw} is the reclaimed water flux. It is also postulated that total filtration resistance was the sum of intrinsic membrane