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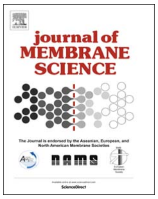

An iron (II) phthalocyanine/poly(vinylidene fluoride) composite membrane with antifouling property and catalytic self-cleaning function for high-efficiency oil/water separation

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ABSTRACT

To endow poly(vinylidene fluoride) (PVDF) membranes with the performance of fouling resistance and the capability of catalytic degradation of organic contaminants, iron (II) phthalocyanine (FePc) as a modifier was incorporated into PVDF matrix to prepare a novel FePc/PVDF composite membrane via non-solvent induced phase separation technique. ATR-FTIR spectroscopy, XPS, SEM, streaming potential analysis, contact angle measurement and cross-flow filtration test were employed to investigate the influence of modification on membrane property and performance. It was found that the introduction of FePc in PVDF membrane matrix resulted in improved porosity, mean pore size, surface hydrophilicity and negative charge of as-prepared composite membranes, and thereby enhanced membrane permeability and antifouling property. Owing to the presence of Fenton-like catalyst FePc, the composite membranes are imparted the catalytic degradation function for adsorbed organic foulants in soaking H_2O_2 solution. The catalytic self-cleaning capability of the composite membrane with 2.5 wt% FePc was further proved by fluorescence probe technique which was employed to detect the generation of ·OH radicals in catalytic self-cleaning process. This indicates that the FePc/PVDF composite membrane has a potential application in water treatment with its combined advantage of membrane separation and catalytic self-cleaning.

1. Introduction

Membrane separation technology has emerged as an effective approach for applications in the water purification and wastewater treatment fields in view of its outstanding performance in the removal of various water contaminants [1]. Actually, membrane fouling is one of the major obstacles to widespread application of membranes, leading to a sharp decrease in permeate flux and increase in operation cost [2,3]. PVDF is one of the most promising membrane materials for the fabrication of ultrafiltration (UF) and microfiltration (MF) membrane for industrial application owing to its high mechanical strength, good thermal stability and chemical resistance as well as film-forming properties compared to other commercialized polymeric materials [4,5]. Nevertheless, the highly hydrophobic PVDF membranes are susceptible to fouling due to the adsorption of organic matter. This leads to lower permeability and reduced membrane life span. Therefore, it is necessary to design and synthesize a composite PVDF membrane material with the ability to alleviate membrane fouling and increase the permeate flux of the membrane [6].

A recent trend in membrane filtration processes is the development of a PVDF composite membrane with additional functions that not only possess enhanced hydrophilicity, but also can provide better removal of refractory organic pollutants accumulated in various treatment processes [7–11]. The introduction of nanoparticles with catalytic properties into PVDF membranes, such as TiO_2 [12], graphene oxide/TiO_2 [1], ZnO [13], Ag [14] and Fe_2O_3 [7], has been proven to be a simple and effective strategy to enhance hydrophilicity and self-cleaning capability. [15]. Among these, nano-sized TiO_2 has been extensively applied in membrane modification because of its high hydrophilic and photocatalytic effects [16]. Several studies have demonstrated that membranes with TiO_2 effectively immobilized degrade organic foulants and inactivate bacterial cells, thus enhancing membrane separation performance [17–19]. Unfortunately, exhibition of the improvement in membrane hydrophilicity, fouling resistance and self-cleaning is limited due to the agglomeration of nanoparticles, which inevitably leads to the lower modification efficiency [4].

Metallophthalocyanines (MPcs) are highly conjugated macro-cyclic compounds, which have been extensively studied as catalysts for a

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variety of applications in green chemistry, organic synthesis and environmental treatment [20–22]. MPcs are very attractive as catalysts not only owing to structural analogy with porphyrin complexes but also because of their accessibility in terms of the cost, their simple large-scale preparation and their chemical and thermal stability [23,24]. Sorokin and co-workers reported that an efficient oxidative dechlorination and aromatic cycle cleavage of 2,4,6-trichlorophenol by H_2O_2 catalyzed by iron tetrasulfophthalocyanine (FePcS) [25]. Zhu and others prepared a polyacrylonitrile-supported FePc nanofiber catalyst by electrospinning, which exhibited high catalytic activity and excellent catalytic degradation ability for wastewater containing Carbamazepine and Rhodamine pollutants [26]. Most previous reports concerning FePc-H_2O_2 as a future catalytic system focused on the oxidative removal of pollutants. However, few studies have been performed regarding the introduction of FePc into the PVDF matrix to prepare a novel PVDF composite membrane with remarkable water permeability, antifouling property and catalytic cleaning capability.

In this work, we innovatively incorporated an environmentally friendly FePc into the PVDF matrix to fabricate a FePc/PVDF composite membrane through solution casting and phase inversion method. For the first time, FePc as a membrane modifier was used in catalytic degradation of organic pollutants in membrane cleaning process. The surface chemical composition, morphological structure, hydrophilicity as well as charge of the resulting membrane were rigorously characterized to illustrate the influence of FePc addition on PVDF membrane performance. Membrane permeation and fouling resistance were evaluated by cross-flow filtration experiments with model foulants of bovine serum albumin (BSA) by measuring the time-dependent water flux. More significantly, the catalytic self-cleaning capability of the composite membranes was also investigated in treating oily wastewater, and the flux recovery ratio of 100% for the membrane fouled by oil contaminants was achieved based on the catalytic degradation of organic foulants by decomposition of H_2O_2 to hydroxyl (·OH) radicals in the presence of FePc. The highly effective antifouling and catalytic self-cleaning properties impart the FePc/PVDF composite membranes with potential application in oil/water separation and wastewater treatment containing oil.

2. Materials and methods

2.1. Materials

PVDF powder (solef 1015, Mn = 238,000 Da, Mw = 573,000 g mol^{-1}) was supplied by Solvey Company of Belgium. Bovine serum albumin (BSA, Mn = 68,000 Da) and iron (II) phthalocyanine (FePc) were purchased from Aladdin (China). N,N-dimethylacetamide (DMAc) was provided by Tianjin Yongda Chemical Co., Ltd. The phosphate-buffered saline (PBS, pH = 7.4) was obtained by the addition of prepackaged buffer salts (Aldrich) to deionized water. All other chemicals were of commercial analytical grade and were used without further purification. Water used in all experiments was deionized water.

2.2. Preparation of FePc/PVDF composite membranes

The FePc/PVDF composite membranes were prepared via a non-solvent induced phase inversion method from casting solutions containing PVDF, FePc and DMAc according to the compositions listed in Table 1. To begin with, a certain amount of the FePc ranging from 0.0 to 3.5 wt% was dissolved in DMAc using magnetic stirring for several hours to ensure a complete dissolution. Afterwards, corresponding amounts of PVDF was added into the above solution to form a homogeneous solution under constant stirring for 12 h at 60 °C. After releasing the bubbles completely, the homogeneous solutions were cast onto polyethylene terephthalate nonwoven fabric placed on a glass plate using an automatic film applicator cast-knife. Subsequently, the glass plate was immersed into a coagulation bath of deionized water at 35 °C. Upon complete coagulation, the nascent membranes were soaked with deionized water to remove the residual solvent and preserved in deionized water prior to further utilization. Membranes prepared with different FePc contents of 0.0, 0.5, 1.5, 2.5 and 3.5 wt% hereinafter are referred to as M0, M1, M2, M3 and M4, respectively.

Table 1
Compositions of casting solution.

Membrane	PVDF (g)	FePc (g)	DMAc (g)
M0	15.0	0	85.0
M1	14.5	0.5	85.0
M2	13.5	1.5	85.0
M3	12.5	2.5	85.0
M4	11.5	3.5	85.0

2.3. Characterizations of membranes

Membrane surface chemical structure and composition were analyzed using Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet Avatar 370 FTIR spectrometer, USA) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha instrument, USA) [27]. Membrane morphology in terms of surface and cross-section structure was observed through a field emission scanning electron microscopy (FE-SEM, Hitachi S-4800, Japan). Membrane surface hydrophilicity was evaluated by determining the static contact angle of deionized water on the dried surface of the membrane with DSA10-MK2 contact angle measurement (KRUSS BmbH, Germany) at 25.0 °C [28]. Membrane surface zeta potential was measured with a streaming electrokinetic analyzer (EKA, Anton Paar GmbH, Austria) using 0.001 mol L^{-1} KCl aqueous solution at 25.0 °C and pH range of 3.0–9.0. The surface zeta potential was calculated from the measured streaming potential according to the Helmholtz–Smoluchowski equation [29].

The overall porosity (ε) of membrane was defined as the volume of the pores divided by the total volume of the membrane. The porosity ε (%) was determined by using dry-wet weight method that was calculated through the following equation [30]:

$$\varepsilon = \frac{(w_1 - w_2)/\rho_w}{(w_1 - w_2)/\rho_w + w_2/\rho_p} \tag{1}$$

where w_1 is weight of wet membrane; w_2 is weight of dried membrane; ρ_p and ρ_w are the density of PVDF and deionized water, respectively.

Mean pore radius r_m of membrane was determined by filtration velocity method and was calculated from the Guerout–Elford–Ferry equation [31]:

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta l Q}{\varepsilon \times A \times \Delta P}} \tag{2}$$

Herein, η denotes water viscosity (8.9×10^{-4} Pa s), ε signifies membrane porosity (%), l is membrane thickness (m), Q is the volume of permeate water per unit time ($m^3\ s^{-1}$), A is the membrane active area (m^2), and ΔP is the operation pressure (0.1 MPa).

2.4. Filtration experiments and antifouling properties evaluation

The permeability, retention and antifouling properties of the FePc/PVDF composite membranes were evaluated through a cross-flow filtration system with an effective membrane area of 23.75 cm^2. The schematic diagram of the experimental setup was shown in our previous work [27]. The rejection and antifouling tests were performed with an aqueous solution of BSA (1.0 g L^{-1}, pH value was 7.4 buffered by phosphate-buffer solution). All the filtration process were carried out at 25.0 °C under a constant pressure of 0.1 MPa and the permeate flux was recorded every 5 min.