Natural organic matter removal and flux decline with PEG–TiO₂-doped PVDF membranes by integration of ultrafiltration with photocatalysis

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ABSTRACT

Ultrafiltration (UF) has become one of the best alternatives replacing conventional drinking water treatment technologies because of increasing stringent regulations for drinking water quality. However, membrane fouling is an important factor which restricts its widespread application. In this study, the modified PVDF membranes were prepared by adding different amounts of PEG and TiO₂ particles. The performances of PVDF–PEG membranes and PVDF–PEG–TiO₂ membranes were investigated by discussing NOM removal and flux decline in both dead-end and cross-flow filtration experiments. The effect of photocatalytic degradation on TiO₂-doped PVDF membranes was also evaluated. Results indicated that appropriate TiO₂-doped modification on PVDF membrane could be an effective way for better removal of NOM and reduction of membrane fouling at the same time. During the ultrafiltration on TiO₂-doped PVDF membrane, an equilibrium might be reached between the foulants deposited on the membrane surface and photocatalytic degradation of the foulants during cross-flow UF coupled with photocatalysis. TiO₂-doped PVDF membrane also shows good self-cleaning ability. The fouled membrane can be cleaned with irradiation and the foulants' photocatalytic degradation is most effective in the first 30 min.

1. Introduction

Ultrafiltration (UF) allows the removal of particle, turbidity, microorganism, variety of water born viruses, and certain amount of the dissolved organic matter. It has proved to be one of the best alternatives replacing conventional drinking water treatment technologies and is increasingly used in drinking water treatment. However, membrane fouling (manifested as the flux decline) is a critical issue in UF process, and several studies have shown that natural organic matter (NOM) is one of the major pollutants [1,2].

NOM is a complex matrix of organic compounds which are converted from dead animals and plants in the process of decomposition. Since it can generate disinfection by-products (DBPs) during chlorination, the removal of NOM effectively is of significant importance in meeting the stringent DBPs regulations and providing safe drinking water. A major fraction of NOM present in surface or ground waters is composed of humic substances (HS) [3]. Humic acid (HA) was found to have a high fouling potential and thus is used as a model compound for natural organic matter [4] in many researches.

Various means have been studied to mitigate membrane fouling by modifying membrane surface properties and/or optimizing the operating conditions. Modifying membrane surface to be more hydrophilic appears to be a more effective approach for the membrane having antifouling property [5–7]. Among various organic polymer materials, polyvinylidene fluoride (PVDF) is commonly used because of its excellent thermal stability and chemical resistance to radiation, organic solvents, acids, and bases [8]. PVDF membrane usually has a good tensile strength and proper asymmetric structure for separation [9]. However, it has hydrophobic characteristics. A neat PVDF membrane is easily fouled by contaminants in the water, which leads to the flux decline of the membrane [10].

Many studies have investigated improvements of the PVDF membrane performances by physical blending, chemical grafting, and surface modification [11,12]. Among these methods, the blending of polymers has an advantage of easy preparation by phase inversion method. In order to obtain the membrane with large pore size and high porosity, additive polyethylene glycol (PEG) is dissolved in the casting solution. In addition, PEG is widely used as the hydrophilic graft for amphiphilic graft copolymer due to its low cost and good biocompatibility [13,14]. The graft copolymers with PEG side chains often show an enhanced hydrophilicity

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and biocompatibility compared with the hydrophobic polymeric backbones [15].

In recent years, TiO$_2$ nanoparticles have been commonly used to degrade contaminants in water treatment processes [16,17]. Several studies have demonstrated that the combination of membrane and suspended TiO$_2$ is helpful to reduce membrane fouling significantly [18,19]. However, in these studies, membrane filtration was typically used to separate and recover TiO$_2$ nanoparticles after photocatalysis reaction. In addition, this integration process increases the operational complexity and cost in practical application compared with single ultrafiltration process. Unrecycled TiO$_2$ nanoparticles left in water also cause a concern to environment. Therefore, immobilization of TiO$_2$ photocatalyst in the membrane is possibly an applicable approach, since it could not only overcome the difficulty of recovering TiO$_2$ photocatalyst, but also integrate membrane separation and photocatalytic degradation of contaminants in a single membrane device. Blending PVDF polymer with TiO$_2$ to fabricate organic–inorganic composite membrane has recently gained more and more attention. Anderson et al. [20] investigated the pioneering possibility of coupling membrane separation and photocatalysis reaction with TiO$_2$-doped membranes. Then more and more studies were carried out to fabricate TiO$_2$ photocatalytic membranes [21–23]. Ma et al. [23] reported that the removal rate of model pollutant, dye Reactive Red ED-2B (RR ED-2B), was improved obviously using the inorganic membrane under UV irradiation in comparison with photocatalysis or membrane separation alone. Moreover, the membrane flux with UV illumination was increased approximately 30% after 4 h filtration compared to that without UV irradiation. Damodar et al. [24] prepared the modified PVDF membranes by adding different amounts of TiO$_2$ particles into the casting solution, and investigated their antibacterial, photocatalytic and antifouling properties. Results showed that TiO$_2$ addition significantly affected the pore size and hydrophilicity of the membrane and thus improved the flux and permeability of the modified PVDF/TiO$_2$ membrane. TiO$_2$-doped PVDF membrane also showed better bactericidal and antifouling abilities under UV light exposure compared with the neat PVDF membrane.

In this study, composite PEG–TiO$_2$-doped PVDF membranes were prepared by adding different amounts of PEG and TiO$_2$ nanoparticles to the PVDF casting solution. The modified PVDF membranes were characterized by contact angle, scanning electron microscope (SEM), atomic force microscope (AFM) and energy dispersive spectroscopy (EDS). The objective of this study was to investigate the performance of PEG–TiO$_2$-doped membranes by discussing NOM removal and flux decline in both dead-end and cross-flow filtration experiments. The effects of photocatalytic degradation on TiO$_2$-doped PVDF membranes in the static UV irradiation and cross-flow UF coupled with photocatalysis were also evaluated.

2. Materials and methods

2.1. Experimental materials

A variety of asymmetric composite PVDF membranes were prepared by the phase inversion process (PIP) method. Casting solutions were made with different concentrations of PVDF (SOLEF® 6020, Solvay Ltd.), additive PEG (molecular weight of 600 Da) and TiO$_2$ particles P25 with average size of 20–30 nm (Degussa Corp.) in N,N-dimethylacetamide (DMAc) solvent at 40 °C. The casting solution was cast on a glass plate at 1.2 m/min and 40 °C with a casting knife of 200 μm space. Then, the membrane was immediately immersed in a tap water coagulation bath at room temperature. After complete coagulation, this membrane was transferred to a deionized (DI) water bath for 1 day at room temperature to remove the remaining solvent from the membrane structure. The membrane characterization was then followed. The flux of DI water was evaluated for the clean membrane, and pepsin (molecular weight of 34.5 kDa) solution of 1 g/L was used to evaluate its rejection.

Humic acid (Aldrich Corp.) was dissolved in DI water and considered as the humic acid solution of 2 mg/L for filtration experiments. Before filtration experiments, the pH value of the humic acid solution was adjusted to pH 7.5 using small amounts of either HCl or NaOH as needed. All the chemicals used in this study were analytical reagent from Sinopharm Chemical Reagent Corp. (SCRC), China, otherwise being noted.

2.2. Experimental methods

The characterization of prepared membrane was conducted in a 25 mm dead-end stirred cell (Model 8010, Amicon Corp.), connected to a nitrogen-pressurized solution reservoir. The pure water flux was measured at 0.1 MPa by timed collection with filtrate mass determined using an analytical balance, and the retention rate of pepsin was determined by the concentration ratio of filtrate solution to feed solution in the first 5 min of filtration experiments.

Dead-end UF experiments of humic acid were also conducted in this dead-end stirred cell. Each membrane was flushed with approximately 100 L/m^2 of DI water prior to remove any agents. Then the stirred cell and reservoir were filled with the humic acid solution at 69 kPa (10 psi). The water flux was measured by timed collection, with filtrate samples collected periodically for subsequent analysis. The schematic diagram of dead-end UF experiment is shown in Fig. 1.

After dead-end UF experiment, fouled TiO$_2$-doped membranes were immerged in DI water and irradiated for a certain time by a 6 W UV lamp (λ_{max} = 254 nm, Yalien Corp., China) with light intensity at membrane surface of 0.04 mW/cm^2 to explore whether the
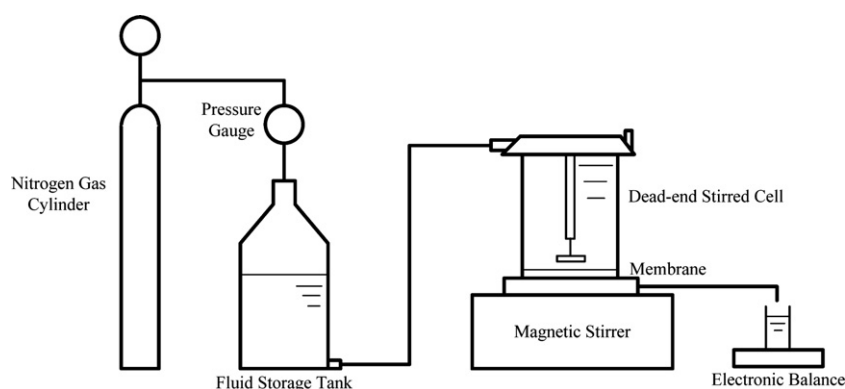

Fig. 1. Schematic diagram of dead-end UF experiment.