A novel ZnO nanoparticle blended polyvinylidene fluoride membrane for anti-irreversible fouling

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ABSTRACT

Irreversible membrane fouling is harmful for long-term operation of filtration. In this study, a novel anti-irreversible fouling polyvinylidene fluoride (PVDF) membrane was successfully fabricated using the wet phase separation methods. Nano-ZnO, with different dosages ranging from 6.7% to 26.7% (percentage of PVDF weight), was blended as an additive into the membrane matrix for the modification of the internal surfaces of membrane pores. A series of tests, such as filtration experiments, contact angle measurements, scanning electron microscope (SEM)/energy dispersive X-ray spectrometer (EDS) analyses and mechanical tests, were performed to characterize the modified membranes. The multi-cycle filtration experiments showed that the modified PVDF membranes demonstrated significant anti-irreversible fouling property. All the modified membranes achieved almost 100% water flux recovery after physical cleaning, whereas the raw membrane only reached 78% recovery. This promotion might be related to the increase of membrane hydrophilicity. The implantation of nano-ZnO into membrane inner surface (i.e., pore wall), as indicated by SEM/EDS tests, might be responsible for the enhancement of anti-irreversible fouling property. The water permeability of the modified membrane almost doubled by adding 6.7% nano-ZnO which was determined as the optimum dosage (within the dosage range in this study) for PVDF membrane modification. Additionally, the mechanical strength was found reinforced for modified membranes, which should also benefit the filtration application.

1. Introduction

Membrane filtration is one of the most promising technologies for application in water and wastewater treatment systems. However, it has been widely accepted that membrane fouling is one of the most stubborn problems hindering the practical application of membrane technologies [1–8]. A great variety of researches have been carried out for a better understanding of the complex membrane fouling mechanisms [4,9–11] and the fouling control strategies to maintain the predominant filterability of membranes [2,12–15]. In the microfiltration and ultrafiltration processes, membrane fouling includes reversible fouling and irreversible fouling [16]. The fouling that can be removed by physical cleaning methods, mainly refers to hydraulic cleaning methods (e.g. cross-flushing), is generally defined as reversible fouling [6,16,17]. Whereas, the fouling caused by adsorption and entrapment of dissolved pollutant into the membrane pores, which can scarcely be removed by physical cleaning methods and is thought to be harmful for the long-term operation of the filtration techniques [18,19], is here defined as irreversible fouling or physically irreversible fouling. In general,

the irreversible fouling can only be removed by chemical cleaning [20]. However, the chemical cleaning should be limited to a minimum frequency because repeated chemical cleaning may shorten the membrane lifespan [16]. Therefore, it is of great significance that the irreversible membrane fouling be efficiently controlled.

Membrane modification is an effective way to tune the surface characteristics, which closely correlates with anti-fouling properties. Hydrophilicity is one of the desirable surface properties of membrane which can mitigate membrane fouling. Unfortunately, most polymeric materials used for membrane fabrication is only weakly hydrophilic [21]. One example is polyvinylidene fluoride (PVDF) which possesses excellent mechanical and thermal strength, and is widely used in membrane bioreactors. Therefore, extensive efforts have been devoted to increasing the hydrophilicity of membranes via physical or chemical methods [22–24]. The incorporation of inorganic materials into the organic polymer matrix with blend strategy has attracted great interests due to their completely hydrophilic characteristic. Recent advances in nanotechnology have greatly expanded the ideas of membrane modification by introducing the nanoparticles to fabricate various kinds of nanoparticles-based-membranes [24]. Beneficial effects of certain types of nanoparticles on membrane modification have been reported, such as the amelioration of surface hydrophilicity and enhancement of antifouling property [25–30]. But most of the

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attentions were focused on membrane surface modification. The surface property of internal pores, which is directly related with irreversible fouling, is barely concerned. Furthermore, the mainly used nano-materials in previous studies, such as TiO_2 and Al_2O_3 nanoparticles, are relatively expensive for practical applications in future.

Zinc oxide, with the completely hydrophilicity, is one of the most common raw materials in industry and suitable to be used to improve the hydrophilicity of the membrane. Furthermore, nano-sized zinc oxide (nano-ZnO) possesses not only the antibacterial nature [31] but also the valuable ultravioresistant property [32,33], which might potentially benefit the antifouling performance and extend the service life and application field of membranes. More-over, nano-ZnO is much cheaper than TiO_2 and Al_2O_3 nanoparticles (~1/4 price according to the Chinese market quotes). However, the related application of nano-ZnO for membrane modification has not been reported.

In this research, a novel anti-irreversible fouling PVDF mem-brane, with nano-ZnO blended as an additive, was successfully fabricated using the non-solvent induced phase separation (NIPS) method [34]. The modification of internal surface of membrane pores was primarily concerned. Different dosage of nano-ZnO rang-ing from 6.7% to 26.7% (percentage of PVDF weight) was adopted for membrane modification. The filterability and anti-irreversible fouling property of the resultant membranes were evaluated through testing the water permeability, flux recovery and long-term filtration performance. A series of experiments, such as water contact angle (CA) measurements, scanning electron microscope (SEM)/energy dispersive X-ray spectrometer (EDS) analyses and mechanical tests, were carried out for membrane characterization. Through all of the experiments, an optimum dosage of nano-ZnO was proposed, and the mechanism of membrane filterability improvement caused by blending nano-ZnO was investigated.

2. Materials and methods

2.1. Materials

The materials used for membrane fabrication include PVDF (Solef 6010, Solvay S.A., Belgium), polyvinylpyrrolidone (PVP, Amresco, USA), glycerol (Amresco, USA), N-methyl-2-pyrrolidone (NMP, Sinopharm Chemical Reagent Co., Ltd., China) and nano-ZnO (nominal size ~25 nm, Beijing Goodwill Metal Technology Co., Ltd., China).

Bovine serum albumin (BSA), humic acid, sodium alginate and sodium azide, used to prepare the synthetic wastewater, were all purchased from Sigma–Aldrich (USA). Ultrapure water (Milli-Q water, Millipore Mili-Q reference ultrapure water purification system, USA) was used in this study. All reagents were used as received.

2.2. Membrane fabrication

Cast solutions (Table 1) were prepared using the following steps. 1 g of PVP, 3 g of glycerol and a certain quantity of nano-ZnO were dissolved into 84 g of NMP in an ultrasonic bath (KQ-250DE, Kun-shan Ultrasonic Instruments, Jiangsu, China) at 30 °C for at least 5 h, which facilitated the dispersion of the nano-ZnO. 15 g of PVDF was then added into the solution followed by an 8 h stirring at 30 °C. At the end of the mixing process all the polymer chemicals were con-vincingly dissolved. The cast solutions were then sealed and stored at room temperature for up to 9 h to remove bubbles. Solvent loss by evaporation was negligible due to the high boiling points of NMP (202 °C) [21].

In this research, PVP was used to enhance the porosity of PVDF membranes [35,36], and it might increase membrane hydrophilic-ity due to the residue trapped in the membrane matrix [37,38]. It is commonly accepted that a hydrophilic membrane performs better in anti-fouling than a hydrophobic membrane. Therefore, to highlight the special contribution of nano-ZnO in anti-fouling, a hydrophilic raw membrane was fabricated as a control by proper over-dosage of PVP (added 6.7% PVP, percentage of PVDF weight, determined after several tests).

The membranes were fabricated by the NIPS method [34]. The cast solution was cast onto a glass plate to form a liquid film using a motorized machine (Elcometer 4340, Elcometer Ltd., UK) equipped with a film applicator (Elcometer 3530, set at a thickness of 250 μm, UK). After a 30 s exposure in the air, the plate was immersed into a Milli-Q water bath at 50 °C, where the membrane formed slowly through precipitation. After 10 min, the membrane was detached from the glass plate and kept in another fresh Milli-Q water bath for 1 h. Subsequently, the membrane was annealed for 15 min in an 80 °C Milli-Q water bath, and then washed under running water for 1 min. Prior to the further tests, all the membranes will filter 700 g Milli-Q water as the final washing step. Several pieces of mem-branes of each kind (Table 1) were freeze-dried (LGJ-12, Beijing Song Yuan Hua Xing Co., Ltd., China) and kept at room temperature for SEM/EDS and water CA measurements. To prepare the samples for mechanical property tests, the wet membranes were directly dried in the air at room temperature. The residual membranes were kept in Milli-Q water for filtration tests.

2.3. Filtration experiments

2.3.1. Dead-end filtration system

The water permeability and anti-fouling property of the membranes were evaluated through a series of batch filtration experiments in a dead-end filtration system. The sample mem-brane disk was precisely installed in a stirred dead-end cell (Amicon 8400, USA) with an effective membrane area of 41.8 cm^2 and con-stant stirring speed of 200 rpm. The constant filtration pressure was allowed by using a digital electronic pressure transducer and con-troller (EL-PREESS series, Bronkhorst HIGH-TECH, Netherlands). The effluent was collected into a beaker on the balance (Mettler Toledo, PL2002, USA), which was connected to a PC for data logging. All experiments were conducted at room temperature (25 ± 2 °C).

2.3.2. Determination of water permeability

Prior to each filtration, membranes were pre-compacted by Milli-Q water (more than 350 g) until the flux reached a plateau. Water permeability ($m^3\,m^{-2}\,s^{-1}\,kPa^{-1}$) of the membrane was tested by filtering the Milli-Q water at a constant pressure (10 kPa) using the dead-end filtration system. The rate of water flow was recorded for further calculation. The membrane resistance was determined according to Darcy's equation [7,39]. Both of the water permeability and membrane resistance were averaged from three membrane coupons.

2.3.3. Fouling and physical cleaning

Fouling experiments were performed in the dead-end filtration system using synthetic wastewater as the feed solution, which was prepared according to Table 2. NaN_3 was used to inhibit the growth of bacteria and minimize the decomposition of the organic com-ponents. $CaCl_2/MgCl_2$, $NaHCO_3$ and NaCl were used to control the hardness, basicity and ionic strength of the solution, respectively. The pH of the synthetic wastewater was kept stable at 7.8, and the conductivity at 2.2 mS cm^{-1}. The filtration was carried out at the pressure of 10 kPa and the stirring speed of 200 rpm. Permeate volume was around 300 mL when the filtration ended.