



Improvement in fouling resistance of silver-graphene oxide coated polyvinylidene fluoride membrane prepared by pressurized filtration

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ARTICLE INFO

Keywords:

Nanocomposite coating
Pressurized filtration
Hydrophilicity
Surface roughness
Fouling resistance

ABSTRACT

Polyvinylidene fluoride (PVDF) membranes are widely used in microfiltration and ultrafiltration because of their high chemical resistance, thermal stability, and mechanical strength. However, the hydrophobicity and high roughness of the PVDF membrane surface make it vulnerable to membrane fouling. Therefore, engineered nanomaterials such as graphene oxide (GO) have been coated to the membranes to improve its fouling resistance. In this study, PVDF membranes were coated with different concentrations of silver functionalized graphene oxide (Ag-GO) nanocomposite suspensions ($0.01\text{--}0.3\text{ mg ml}^{-1}$) via pressurized filtration process. The fouling resistance of Ag-GO coated PVDF membranes was significantly enhanced due to increased hydrophilicity and smoother membrane surface. The initial feed water flux of modified membranes increased up to 53% when compared to that of the pristine PVDF membrane. Also, the flux recovery rate and antibacterial properties of Ag-GO/PVDF membranes were higher than that of the pristine membrane. Ag-GO was stably coated on the membrane surface and the enhanced performance resulting from modification with Ag-GO was maintained after the membrane backwash. We expect that our results could contribute to the development of highly reusable anti-fouling membranes coated with inorganic nanocomposites.

1. Introduction

Membrane fouling incurred by organic, inorganic, and biological substances during the membrane operation causes dramatic and often irreversible decrease in permeate flux and requires higher pressure and energy for the operation [1,2]. Therefore, previous studies have focused on the reduction of such adverse effects of membrane fouling through physical and chemical cleaning, fouling detection techniques, and membrane modifications [3–6]. Among these approaches, membrane modification via application of engineered nanomaterials can be effective in increasing the fouling resistance of the membranes [7].

Graphene oxide (GO), which has a two-dimensional structure, is one of the nanomaterials that are widely used in membrane modification. Due to its various oxygen-containing functional groups and large surface area, GO can be well assembled with membranes [8,9]. To mitigate the adhesion of organic and inorganic substances that causes membrane fouling, GO has been applied to modify the polyethersulfone (PES) membrane surface. Hydrophilic membrane resulting from such modification shows better anti-adhesive properties and thus can impede the adsorption of foulants which are mostly hydrophobic in nature [6,10].

Moreover, the application of GO on membranes reduced the surface roughness of polyvinylidene fluoride (PVDF) membrane and resulted in higher fouling resistance compared to that of the pristine membrane [11]. In addition, due to the antibacterial characteristics of GO [12], GO can prevent the formation of biofilm by inactivating the bacterial cells attached on the membrane surface [13]. Such inactivation occurs by direct contact of bacterial cells with GO and oxidative stress caused by reactive oxygen species generated by GO [14]. Polyamide (PA) membrane modified by GO also showed anti-adhesive and antibacterial properties [15].

Along with GO, silver nanoparticles (Ag NPs) are also widely applied in membrane modifications. Ag NPs are well known antibacterial agent and membranes modified with Ag NPs show high antibacterial activities. For example, the total biofilm formed on PES membranes modified by Ag NPs was 70% lower in protein content than that of the pristine membrane [16]. Also, significantly less *E. coli* attached on the surface of PES membranes modified with silver-PEGylated dendrimer nanocomposite when compared to that on the pristine membrane surface [17]. Such antibacterial properties of modified membranes were mainly due to Ag ions (Ag^+) released from Ag NPs [18]. However, fast

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dissipation of Ag NPs may cause the loss of function and limit its long-term application [19]. Also, Ag NPs are likely to form large aggregates which can block the pores of the membrane and decrease the water permeability of the membrane [20]. Therefore, previous studies have combined GO and Ag to solve such problems and to obtain the maximum antibacterial effects of Ag [21,22]. GO acts as a great supporting structure by dispersing and fixing Ag NPs, and thus increase the stability of Ag NPs attached to GO [22]. Significantly lower amount of Ag⁺ was released from PVDF membranes modified with silver functionalized GO (Ag-GO) when compared with those modified with Ag NPs, which indicated the potential for long-term operation of Ag-GO modified membrane [19]. In addition, due to the synergetic effects of GO and Ag NPs, Ag-GO nanocomposites provided enhanced fouling resistance and antibacterial properties to various membranes such as cellulose acetate (CA) [23], polysulfone (PSU) [24], polyamide thin-film composite (PA-TFC) [9], and PVDF membranes [25].

Diverse methods such as blending [25], interfacial polymerization [20], grafting [18], and cross linking [9] are used to modify membranes with GO, Ag, and Ag-GO. These membrane modification techniques offer strong interactions between the membrane components and the nanomaterials. However, the process is time consuming and the cost of engineered nanomaterials is high, so these techniques have been only applied on small scale filtrations to date [26,27].

Therefore, in this study, we focused on using simple and low cost pressurized filtration method for membrane modification, which has a great potential to be applied in large scale membrane modifications. Coating a thin layer of water dispersible nanoparticles via filtration is a simple and fast method to increase the hydrophilicity and decrease the surface roughness of the membranes [28]. It is relatively easy to apply on commercial membranes with a large effective area, since the nanomaterials can be simply coated on the membrane surface through existing filtration system by adding them in the feed clean water. Previous studies have used the filtration method to modify diverse membranes including CA [23], PSU [29], PES [30], and PVDF membranes [31] with GO or Ag-GO. PVDF membrane, which was used in this work, is widely applied in microfiltration, ultrafiltration, and membrane bioreactor (MBR) because of its high chemical resistance, thermal stability, and mechanical strength [32]. However, the hydrophobic surface of PVDF membrane makes them vulnerable to membrane fouling [6]. Application of GO [11,33,34] or Ag-GO [25] on PVDF membrane can modify the membrane surface to be more hydrophilic, and this improves the fouling resistance.

In this study, Ag-GO nanocomposites were coated on the surface of commercial PVDF microfiltration membranes via simple pressurized filtration method to improve fouling resistance and antibacterial activity. The objectives of our study were to (1) modify PVDF membranes with Ag-GO through pressurized filtration process and quantify the amounts of Ag-GO coated on the membrane; (2) compare the physicochemical characteristics between pristine and Ag-GO coated PVDF membranes; (3) verify the improvement in anti-fouling and antibacterial properties of Ag-GO coated PVDF membranes; (4) evaluate the reusability of Ag-GO coated membranes; (5) analyze the stability of Ag-GO nanocomposites coated on membrane surface by measuring the concentration of Ag-GO and Ag⁺ released. Results of this study suggest that membrane coating via simple filtration process can improve the performance of commercial membranes, and can contribute to furthering the applications of Ag-GO in manufacturing safe and reusable anti-fouling membranes at a large scale.

2. Experimental

2.1. Preparation and characterization of Ag-GO nanocomposites

GO was prepared by modified Hummers method described elsewhere [35,36]. Ag-GO was prepared by glucose reduction method [37] with modifications. Homogeneous GO suspension (50 ml, 0.5 mg ml⁻¹)

was prepared in distilled water by bar sonication. Polyvinylpyrrolidone solution (10 ml, 4 mg ml⁻¹, MW ~ 29,000, Aldrich) and α-D-glucose (800 mg, 96%, Aldrich) was added to this, and then silver-ammonia solution (10 ml) was added at 45 °C. Silver-ammonia solution was prepared by adding 2 wt% ammonia aqueous solution (28.0–30.0%, NH₃, Sigma-Aldrich) into silver nitrate solution (20 mg ml⁻¹, ≥ 99.0%, AgNO₃, Sigma-Aldrich). After 7 min of reaction, Ag-GO was separated by centrifugation at 10,000 rpm for 10 min, washed with water, dried at 80 °C overnight, and ground into powder. The morphology of Ag-GO was determined by high-resolution transmission electron microscopy (HR-TEM, Tecnai 20, FEI, USA), and the particle size distribution and average particle size of Ag NPs from the TEM image using ImageJ software. Functional groups of Ag-GO were analyzed by Fourier transform infrared spectroscopy (FT-IR, NICOLET iS10, Thermo Fisher Scientific, USA).

2.2. Modification of PVDF membrane by Ag-GO nanocomposites

2.2.1. Membrane modification via pressurized filtration method

PVDF microfiltration membrane was purchased from Millipore (pore size 0.22 μm, surface area 33.18 cm²). Ag-GO nanocomposites were coated on the surface of PVDF membrane by pressurized filtration method. Ag-GO suspensions were prepared by 2 h of bath sonication. A batch type dead-end cell system, further described in Section 2.4.2, was used for the filtration process. After placing the membranes on the filtration cell, 10 ml of suspensions were filtered by the feed pressure of 20 kPa. Membranes were washed with deionized water to remove uncoated Ag-GO and washed water was collected to calculate the quantity of Ag-GO coated on the surface of each membrane. Ag-GO coated PVDF membranes were oven dried at 40 °C for 1 h before use.

2.2.2. Measurement of the quantity of Ag-GO coated on membranes

The quantity of Ag-GO coated on the membrane surface was measured via spectroscopy [38]. Standard curve ($R^2 = 0.9998$) was obtained by measuring the absorbance of Ag-GO standards in a clear 96-well microplate (Corning, 3370) using Synergy HT Multi-Mode Microplate Reader (BioTek, USA) at a wavelength of 650 nm. The amounts of Ag-GO coated were calculated by the following equations:

$$\text{Uncoated Ag-GO (mg)} = C_w \times V_w \quad (1)$$

$$\text{Coated Ag-GO (mg)} = \text{Ag-GO dose (mg)} - \text{uncoated Ag-GO (mg)} \quad (2)$$

where C_w indicates the concentration of Ag-GO in the washed water (mg ml⁻¹) and V_w indicates the volume of washed water (ml).

2.3. Membrane characterization

The membrane samples were coated with platinum and the surface was observed using field emission scanning electron microscopy (FE-SEM, S-4200, HITACHI, Japan). The presence of Ag-GO nanocomposites on the membrane surface was determined by energy dispersive spectroscopy (EDS). Membrane hydrophilicity was analyzed by measuring the water contact angle (CA, Pendant Drop Tensiometer, DSA100, KRÜSS, Germany). Photos of the water droplets (3 μl) were taken right after the water contact, since the contact angle changed with time due to the absorption of water drop to the membrane. Results presented are the average of the contact angles of both sides. Surface roughness and area were analyzed using atomic force microscope (AFM, XE-100, Park Systems, Korea) at a scan size of 10 μm × 10 μm.

The overall porosity (ϵ) of the membranes was analyzed by gravimetric method, using the following equation [39]:

$$\epsilon = \frac{W_1 - W_2}{A \times l \times d_w} \times 100\% \quad (3)$$

where W_1 and W_2 indicates the wet and dry weights of the membrane, respectively. A indicates the membrane effective area (33.8 cm²), l the

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