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The anti-biofouling properties of thin-film composite nanofiltration membranes grafted with biogenic silver nanoparticles

Shasha Liu [a], Fang Fang [a], Junjie Wu [b], Kaisong Zhang [a,*]

[a] Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China
[b] School of Engineering and Computing Sciences, Durham University, Durham DH1 3LE, UK

HIGHLIGHTS

- Biogenic silver nanoparticles (AgNPs) were grafted on TFC NF membranes.
- Biogenic AgNPs enhanced hydrophilicity and water flux of TFC NF membranes.
- Better membrane stability was achieved with grafted biogenic AgNPs than chemical AgNPs.
- Biogenic AgNP grafted NF membrane shows better antibacterial ability.

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ABSTRACT

Biofouling is still one of the most challenging issues of nanofiltration. One of the practical strategies to reduce biofouling is to develop novel anti-biofouling membranes. Herein, biogenic silver nanoparticles ($BioAg^0$-6) with the averaged diameter of only 6 nm were firstly grafted on the surface of polyamide NF membrane. The effect of grafted $BioAg^0$-6 on the performance of thin-film composite (TFC) NF membranes was systematically investigated with a comparison to the grafted chemical AgNPs. $BioAg^0$-6 grafted membrane (TFC-S-BioAg) increased the hydrophilicity of the TFC membrane and water permeability, while maintaining the relatively high salt rejection. The result of silver leaching experiment indicated that the grafted $BioAg^0$-6 had a better stability on the membranes, the ratio of remained silver in the TFC-S-BioAg membrane was 95%, after soaked in pure water for 50 days. After 4 month immersion, the rejection of TFC-S-BioAg membrane remained more than 90% of initial rejection. The results of disk diffusion test revealed that both of TFC-S-BioAg membrane and TFC-S-ChemAg membrane showed effective anti-bacterial ability to inhibit *Pseudomonas aeruginosa* and *Escherichia coli* growth, the TFC-S-BioAg membrane showed more excellent and longer lasting antibacterial property. Therefore, $BioAg^0$-6 grafted TFC membranes could be potential as an effective strategy to decrease biofouling in nanofiltration process.

1. Introduction

Biofouling is one of the most challenging problems in membrane separation processes which hinders wider applications of thin-film composite (TFC) nanofiltration (NF) membrane in wastewater treatment system [1,2]. Biofouling begins with the bacterial adhesion on the membrane surface [3]. Once bacteria attach to the membrane surface, bacteria will produce a bio-film, which is difficult to be eliminated and often causes irreversible damage to membrane structure with the decline in the permeate quantity [4,5]. Antifouling strategies of TFC membranes are normally carried out either by feed stream pretreatment, cleaning-in-place program or by membrane surface modification [6,7]. Physical pretreatment and chemical pretreatment are able to control inorganic and a part of the organic fouling. However, most antifouling efforts by pretreatments are not effective in eliminating biofouling in membrane separation process [8]. The application of biocide such as chlorine in the feed stream was reported, which could effectively decrease the membrane biofouling. However, even 99.99% removal of bacteria from the feed water cannot guarantee the elimination of bacterial growth on the membrane surface because the remaining bacteria can still migrate and multiply rapidly [9]. Besides, the biocides added in the feed streams have often been found to damage the membrane structure [10]. Hence, the most immediate method to control biofouling is applying antifouling efforts to membranes directly.

Inorganic additives were incorporated into polymeric membranes with the purpose of reducing membrane fouling [11–13]. Silver compounds and silver ions have been known to exhibit strong inhibitory and bactericidal effects as well as a broad spectrum of anti-microbial activities [14]. Due to their excellent biocidal properties and low toxicity

* Corresponding author.
E-mail address: kszhang@iue.ac.cn (K. Zhang).

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towards mammalian cells [15,16], silver nanoparticles (AgNPs) have been widely applied in TFC reverse osmosis (RO) membrane fabrication. Lee et al. [17] added AgNPs in the oil phase to form polyamine thin-film layer during the interfacial polymerization. Kim et al. [18] combined AgNPs into the aqueous solution during the interfacial polymerization to improve antifouling properties of TFC membrane. AgNPs were also attached to the surface of TFC membrane effectively via covalent bonding, and the AgNPs showed good stability [19]. These reports indicated that AgNPs could be immobilized to the TFC membrane effectively and improved the antibacterial and antifouling properties. AgNPs with diameter of 15–100 nm are reported to synthesize via chemical reduction method, which is the most commonly used [20]. However, chemically produced silver nanoparticles often have problems with particle stability and tend to aggregate at high concentrations or when the average particle size is less than 40 nm [21].

In our previous work, novel biogenic silver nanoparticles were obtained using dried *Lactobacillus fermentum* biomass [22,23]. The biogenic AgNPs with an average diameter of ~6 nm (Bio-Ag^0-6) exhibited excellent antibacterial performance. Some studies suggested that the antibacterial properties of AgNPs might be size dependent, with smaller particles having a greater bactericidal effect [24]. But the smaller AgNPs synthesized in traditional approaches are often less stable than larger ones and tend to aggregate faster at high concentrations [25]. For Bio-Ag^0-6, the attachment of bacterium fragment on the surface of nanoparticles might prevent the AgNPs from aggregating. Therefore, Bio-Ag^0-6 showed a very high stability in aqueous solution [22], which is the advantage that normal chemical particles cannot afford.

In this study, Bio-Ag^0-6 was grafted onto the surface of freshly fabricated TFC NF membrane for the first time, in contrast with the commercial chemical AgNPs. The AgNPs showed good stability on the surface of TFC membrane though chemical covalent bonds. The surface of freshly prepared membranes were investigated by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy and water contact angle apparatus. The silver release from the membranes in both static immersion and dead-end filtration were evaluated. Furthermore, the AgNP grafted membranes were soaked in pure water for 4 months to assess the effect of silver release on the long term filtration performance. The antibacterial and antibiofouling performances were also evaluated by the disk diffusion method and bacterial suspension filtration experiment.

2. Experimental section

2.1. Materials

Polysulfone (PS Solvay P3500) was bought from BASF (China) Co. Ltd. polyvinylpyrrolidone (PVP-K30), N-methyl pyrrolidone (NMP; ≥99%) triethylamine (TEA; ≥99%), sodium dodecyl sulfate (SDS; 99%), N-hexane (99%), sodium sulfate (Na_2SO_4; 99%), Ammonia solution (analytical grade), silver standard solution (1000 mg L^{-1}) were supplied by Sinopharm Chemical Reagent Co., Ltd. Silver nitrate ($AgNO_3$; analytical grade) was purchased from Shanghai Shenbo Chemical Co., Ltd. Bovine serum albumin (BSA, 67 KDa), cysteamine (H_2N-$(CH_2)_2$-SH, 95%), piperrazine (PIP; 99%), and trimesoyl chloride (TMC; 98%) were purchased from Aladdin Co. Ltd. Chemical AgNPs (diameter of 20 nm, 99.95%) were purchased from Beijing Dk Nano technology Co. Ltd.

2.2. Preparation of PS supporting membrane

The PS support membrane was prepared via immersion precipitation phase inversion method. Firstly, the blend solution was prepared by dissolving 17.5 wt.% PS, 0.5 wt.% PVP-K30 in NMP at 80 °C. After stirring for 12 h, the homogeneous solution was kept at the room temperature to remove air bubbles for around 12 h. Then the dope solution was casted onto a non-woven fabric (thickness 120 μm) using a casting knife, followed by dipping the membrane into a DI water bath for immediate phase inversion. The wet film thickness was controlled at ~220 μm. After 30 min in a gelation medium, the membrane was taken out and kept in DI water.

2.3. Synthesis and characterization of biogenic silver nanoparticles (Bio-Ag^0-6)

The biogenic silver nanoparticles (Bio-Ag^0-6) were synthesized with *L. fermentum* LMG 8900 as reported in a previous work [22,26]. The detailed procedure was as followed: dried biomass was dissolved in Milli-Q water in an Erlenmeyer flask, with NaOH and diamine silver added sequentially. The final concentration of biomass, silver, and $[OH]^{-1}$ was controlled to 10 g L^{-1}, 10 g L^{-1}, and 0.2 mol L^{-1} respectively. After incubating in a shaking incubator at 30 °C (200 rpm) for 24 h, the solution was centrifuged at 5000 rpm for 6 min. The biogenic silver hydrosol was separated and centrifuged at 6000 rpm for 10 min for further concentration and purification. Finally, the biogenic AgNPs with a diameter of 6 nm were obtained.

2.4. Preparation of TFC NF membranes

The TFC NF membrane was prepared by interfacial polymerization of PIP and TMC as described elsewhere [27]. Firstly, the PS support layer was immersed in a 1.6 wt.% PIP aqueous phase for 1 min. The excess solution was removed from the soaked surface by a rubber roller. Then the organic solution of TMC (0.35 wt.%) in n-hexane was poured over the membrane for 20 s to finish the interfacial polymerization reaction. The PS membrane was taken out from the n-hexane solution and heated in an oven at 50 °C about 3 min, for a better polymerization reaction. Finally, the prepared TFC membranes were rinsed with pure water and then ethanol before the surface grafting.

Newly fabricated TFC membranes were immediately immersed in a H_2N-$(CH_2)_2$-SH ethanol solution (20 mM, 40 mL) for 6 h. Then the membranes (labeled as TFC-S) were moved out from the ethanol solution, washed with pure ethanol and DI water, and incubated with the selective layer in contact with biogenic AgNPs, chemical AgNP suspension (0.1 mM, 40 mL) for 12 h, respectively. Finally, the membrane samples (labeled as TFC-S-BioAg, TFC-S-ChemAg) were rinsed with DI water and store in DI water for future tests.

2.5. Membrane characterization

Surface morphologies of the composite membranes were observed by a field emission scanning electron microscope (FESEM, HITACHI S-4800) equipped with an X-ray energy dispersive spectroscope (EDS) system. The accelerating voltage of SEM is 5 kV. Before SEM analysis, all membrane samples were dried in vacuum oven at 80 °C for more than 48 h and then coated with gold. The presence of silver nanoparticles was confirmed by energy dispersive X-ray spectra (EDS) and elemental mapping.

Functional groups of membrane surfaces were identified by ATR FT-IR spectroscopy, which was conducted on the Nicolet iS10 (Thermo Fisher Scientific) equipped with multi-reflection Smart Performer ATR accessory. All spectra included the wave numbers from 500 to 4000 cm^{-1} with 64 scans at a resolution of 4.0 cm^{-1}.

Hydrophilicity of the membrane surface was assessed according to the pure water contact angle, which was measured by the sessile drop method on a video contact angle system (DSA100, German KRUSS). The contact angle was measured automatically by a video camera in the instrument using the drop shape analysis software. At least five