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A novel composite nanofiltration membrane prepared with PHGH and TMC by interfacial polymerization

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ABSTRACT

A novel nanofiltration membrane prepared by interfacial polymerization of purposefully synthesized polyhexamethylene guanidine hydrochloride (PHGH) with antibacterial property and trimesoyl chloride (TMC) on polysulfone (PSf) ultrafiltration membrane was investigated. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscope (SEM) and atomic force microscopy (AFM) were employed to characterize the chemical structures and morphologies of the active layers of obtained membranes. The effects of monomer concentrations, reaction time, curing temperature and time on filtration performance of the composite nanofiltration membranes were discussed. It was found that the membrane rejections to different salts followed the order of $\text{MgCl}_2 > \text{MgSO}_4 > \text{Na}_2\text{SO}_4 > \text{NaCl}$. Dyes rejection results further showed the feasibility for the membranes to separate small organic molecules with a molecular weight cut-off (MWCO) of around 700 Da. Antibacterial experiments indicated that the newly prepared composite nanofiltration membrane had effective inhibition against *Escherichia coli*. Furthermore, a 50 h fouling test using high concentration of bacteria solution also demonstrated an enhanced anti-biofouling performance of the composite nanofiltration membrane.

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1. Introduction

Nanofiltration (NF) is a pressure-driven membrane separation technology between ultrafiltration (UF) and reverse osmosis (RO) [1–3]. With the advantages of low operation cost, relatively high flux and high retention of multivalent ions or small organics, NF membranes have been widely utilized in drinking water treatment, pre-treatment of seawater for desalination, pharmaceutical concentration and dye removal [4–7]. Nevertheless, growth of membrane fouling, particularly biofouling, still remains as a serious problem [8–10], because the undesired biofilm formed on membrane surface would damage chemical structure of membrane materials and affect membrane permeability, thus limiting the widespread application of NF membranes [11]. Membrane biofouling is usually induced by the adsorption and deposition of microorganisms on membrane surface or in membrane pores, then followed by microorganisms reproduction and ultimately sticky biofilm formation (Fig. 1) [12,13]. Autopsy studies exhibited

that more than 50% (w/w) of dry fouling layer on fouled NF membranes was biological origin [14,15]. Commercially available NF membranes are primarily derived from cellulose acetate (CA) and polyamide (PA) at present. The major deficiency of CA membranes is their poor resistance to microbiological attack in water [16,17]. Furthermore, the PA membranes are susceptible to membrane fouling and unstable in the continual presence of disinfectants, such as chlorine [18,19]. Therefore, it is very important to develop NF membranes with high anti-biofouling for the practical application.

Attempts have been made to improve the anti-biofouling property of NF membranes. For example, Singh et al. [14] reported phosphonic acid functionalized 1,3,4-oxadiazole based antibacterial organic–inorganic nanocomposite membrane derived by acid catalyzed sol–gel in aqueous media and the anti-biofilm forming studies revealed that membrane showed better microbial growth inhibiting properties. In addition, antibacterial nanoparticles such as copper and silver have been widely used for membrane fabrication. Tang et al. [20] synthesized an LBL-assembly-based silver nanocomposite NF membrane and investigated influence of different AgNPs doping routines on membrane performances. It was demonstrated that the incorporation of silver in membranes

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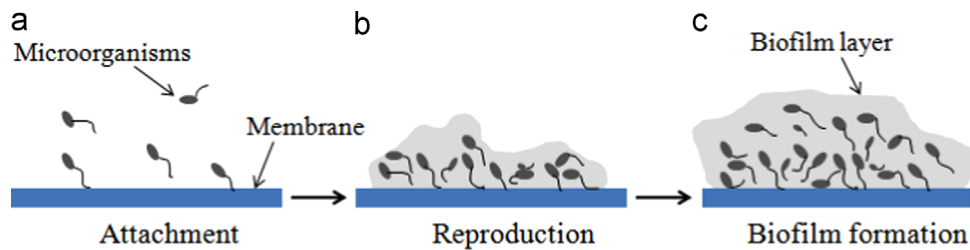


Fig. 1. Schematic process of biofilm formation on membrane surface.

exhibited excellent antibacterial properties against both Gram-positive *Bacillus subtilis* and Gram-negative *Escherichia coli*. Isloor et al. [21] immobilized copper onto polysulfone/modified polyisobutylene alt-maleic anhydride blend NF membrane surface as a biofouling protective layer by physical vapor deposition method. The copper coated membrane showed good resistance towards microbial attack while maintaining good salt rejection and appreciable flux. However, a high concentration of nanoparticles in the dope solution is usually required due to their easy leaching from membrane surface, which may lead to a regulatory risk in water treatment field [11,22].

Recently, the cationic polyguanidine oligomers have been extensively used because of their broad-spectrum antibacterial activity and low toxicity to humans [23,24]. The high antibacterial activity of polyguanidine oligomers is ascribed to the progressive interaction between the lipid bilayer of bacterial cell membrane and guanidine groups, which causes the lipid bilayer to lose fluidity or dissolution, inhibits cell growth and eventually leads to the death of the bacteria [25,26]. There are some reports about polyguanidine oligomers immobilization on different materials. Guan et al. [23] grafted guanidine polymer PHGH onto cellulose fibers via in situ copolymerization using ceric ammonium nitrate (CAN) as an initiator and the cellulose fibers exhibited an excellent antibacterial activity against *E. coli*. Mei et al. [24] functionalized the surface of electrospun polyacrylonitrile (PAN) nanofibrous membranes with PHGH through hydrophilic flexible spacers. The modified PAN nanofibrous membranes exhibited significantly enhanced antibacterial and easy-cleaning properties.

In this work, the PHGH was synthesized by polycondensation of hexamethylenediamine and guanidine hydrochloride. Then a novel composite NF membrane was successfully prepared via interfacial polymerization of TMC and PHGH on the surface of PSf support membrane. Various membrane fabrication conditions were systematically investigated to evaluate their effects on the performance of the composite NF membranes. At the end, gram-negative *E. coli* was used to investigate membrane antibacterial and anti-biofouling properties. As far as we know, this is the first study reporting the preparation of composite NF membranes with PHGH.

2. Experimental

2.1. Materials

1,6-Hexamethylenediamine (HDA) and guanidine hydrochloride were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Trimesoyl chloride (TMC) was purchased from Acros Co. Ltd. (Belgium), and n-hexane was purchased from Xingyue Chemical Co., Ltd. (Tianjin, China). Triethylamine (TEA) was purchased from Fuyu Fine Chemical Co., Ltd. (Tianjin, China). Inorganic salts ($MgCl_2$, NaCl, $MgSO_4$ and Na_2SO_4), NaOH and HCl (36.6–38.6 wt%) were used as received. Molecular dyes including Brilliant Blue, Congo Red and Methyl Orange were used without

further purification. *E. coli* was purchased from Institute of Microbiology, Chinese Academy of Sciences (Beijing, China). Beef extract, peptone, yeast extract power and agar power were purchased from Aoboxing Bio-tech Co., Ltd. (Beijing, China). D-glucose was purchased from Kermel Chemical Agent Co., Ltd. (Tianjin, China). PSf ultrafiltration membrane was fabricated via immersion-precipitation method [27] and used as the support membrane with pure water flux of about $150 L/m^2 h$ under 0.1 MPa. Deionised water with conductivity less than $10 \mu S/cm$ was used in our experiments.

2.2. Synthesis of polyhexamethylene guanidine hydrochloride

The PHGH was synthesized according to the literatures [26,28]. Equimolar amounts of HDA and guanidine hydrochloride were mixed in a vacuumed 250 ml three-necked flask under mechanical stirring. The mixture reacted first at $100^\circ C$ for 1 h, and then went on at $170^\circ C$ for 3 h. The byproduct of ammonia during the polycondensation reaction was neutralized by dilute HCl solution. After that the generated white viscous liquid sample was put in a vacuum oven at room temperature to further remove residual ammonia. Finally, a solidified white PHGH sample was obtained. The synthetic process of polyhexamethylene guanidine oligomer is illustrated in Fig. 2.

2.3. Preparation of composite NF membranes

The composite NF membranes were fabricated by the conventional interfacial polymerization technique. A series of aqueous phase solutions were prepared with variable PHGH concentrations (from 0.5 to 2.0 wt% with an interval of 0.5 wt%) and TEA (0.2 wt%) in deionized water. Meanwhile, the organic phase solutions were prepared by dissolving TMC with different concentrations (from 0.05 to 0.20 wt% with an interval of 0.05 wt%) in n-hexane. The PHGH aqueous solutions were first poured on top of the flat sheet PSf support membranes for about 15 min to ensure that PHGH can diffuse into porous support membranes. The excess solution on the membrane surface was drained off with filter papers. Then, the organic phase solutions of TMC were poured on PSf support membranes for a certain time to carry out the polymerization reaction, which resulted in a thin film formed on the surface of the membranes. After removing excess TMC solution, the composite membranes underwent heat treatment with different temperatures (60 – $90^\circ C$) in an oven for further polymerization reaction and hexane evaporation to achieve the desired membrane performance. Finally, the PHGH and TMC composite NF membranes, designated as PHGH–TMC/PSf composite NF membranes were washed thoroughly with deionized water and then stored in deionized water before use. The HDA and TMC composite NF membrane with a fixed HDA concentration of 0.5 wt% (designated as HDA–TMC/PSf composite NF membranes) was also prepared and served as a control sample in terms of filtration and antibacterial performance.

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