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Regenerable antimicrobial activity in polyamide thin film nanocomposite membranes

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ABSTRACT

Control of microbial growth at the membrane surface on a continuous basis is needed to mitigate biofouling in long term membrane applications. In this study, a regenerable antimicrobial nanocomposite membrane was developed for sustainable membrane biofouling control via slow release of silver. Nanozeolites attached to the surface of a commercial polyamide nanofiltration membrane by covalent binding served as carriers for Ag^+ or $\text{Ag}(0)$. At a silver loading of $7.18 \pm 0.62 \text{ mg/m}^2$, the nanocomposite membranes effectively inhibited growth of *P. aeruginosa* for up to seven 24 h exposure cycles, and the antimicrobial efficacy correlated well with silver release kinetics data. The release of silver strongly depended on the Cl^- concentration in the solution. At low Cl^- concentrations, the low aqueous solubility of silver controlled silver release; the Ag^+ and $\text{Ag}(0)$ loaded membranes showed similar release rate. At high Cl^- concentration, silver release from the $\text{Ag}(0)$ loaded membrane was notably more stable and longer lasting as $\text{Ag}(0)$ oxidation became the rate-limiting step. After depletion, reloading silver via a simple physisorption protocol resumed the antimicrobial activity. The regenerated membranes had similar silver loading and antimicrobial activity as the freshly prepared membranes, demonstrating the potential of this approach in long-term control of membrane biofouling.

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1. Introduction

Biofouling is a serious operational issue impeding the application of membrane technology in water and wastewater treatment [1]. It is caused by the formation of a biofilm on a material surface by bacteria and other microorganisms. In a membrane system, biofouling reduces membrane permeability and contaminant rejection, increases chemical cleaning frequency, causes membrane material degradation and hence shortens membrane life. Removal of a fully-established biofilm can be very difficult, due to its high resistance to hydraulic shear and antimicrobial chemicals [2,3]. Control of biofouling is especially challenging in nanofiltration (NF) and reverse osmosis (RO) systems as polyamide membranes are highly sensitive to oxidation by disinfectants such as chlorine [4]. Due to the lack of sensitive biofouling detection methods in NF and RO systems, biofouling can often lead to spoilage of the membrane or the entire module before recognized.

Current practice of biofouling control focuses on pretreatment of the feed water to reduce the bacteria population and nutrient

concentration [5]. This approach has obvious disadvantages and is only marginally effective [6]. Use of high concentration of disinfectants such as chlorine generates disinfection byproducts and requires chlorine removal before the feed water enters the NF or RO modules. In NF or RO systems, nutrients are retained and concentrated at the membrane surface. Since absolute sterilization of the system is impractical, the small number of survived bacteria will still be transported to the membrane, proliferate, and eventually foul the membrane.

Development of biofouling resistance membranes has focused on membrane surface modification to reduce adhesion of bacteria or biopolymers, or inhibition of bacterial growth using antimicrobial chemicals. Membrane surface coating of hydrophilic and non-adhesive polymers is a common strategy for biofouling control in both laboratory studies and industrial applications [7,8]. Numerous research have studied coating of hydrophilic polymers on membranes [1]. The coating reduces attachment of bacteria cells on the membrane surface and hence delays the onset of biofouling. However, it is unable to prevent the formation and development of biofilm in the long term.

Membrane modification with antimicrobial materials directly inhibits bacterial growth on the membrane surface. It uses less antimicrobial chemicals and is expected to be more effective than disinfecting the feed water. Several studies have incorporated

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antimicrobial nanoparticles in membranes. A commonly used method is to disperse the nanoparticles in the polymer solution during the membrane formation process. Zodrow et al. [9] added silver nanoparticles (AgNPs) to the polysulfone solution and synthesized AgNP impregnated polysulfone membranes by wet phase-inversion. The membrane significantly inhibited growth of both *E. coli* and *P. mendocina* in stationary batch experiments. Kim et al. [10] prepared AgNP impregnated polyamide membranes by dispersing AgNPs in the aqueous reagent solution used in the interfacial polymerization of polyamide. The membrane showed drastically reduced attachment of *P. aeruginosa* in batch antifouling experiments. Lind et al. [11] incorporated silver ion loaded nanozeolite into the polyamide active layer of a lab synthesized RO membrane, but the membrane did not show significant antimicrobial activity. It was suspected that Ag^+ was lost due to leaching via ion exchange during the interfacial reactions and the low areal density of silver loaded zeolite particles did not generate significant silver concentration at the membrane surface [11]. Huang et al. [12] fabricated PES based nanocomposite ultrafiltration membrane by dispersing silver loaded sodium zirconium phosphate nanoparticles in the casting solution. The generated membrane showed antimicrobial activity towards *E. coli*. There is also patent document that explored the utilization of carrier particles in membrane modification [13]. Similar as other studies, they incorporate the carrier particles within the low-pressure membrane matrix by dispersing them in the casting solution and demonstrated good antimicrobial behavior. Albeit simple and effective, direct mixing of nanoparticles with membrane polymer has obvious disadvantages. The membrane polymer covers the nanoparticles, thus the dissolution and release of Ag^+ is hindered and the bioavailability of silver is reduced. For ultrafiltration and microfiltration membranes, Ag^+ is also lost to the membrane permeate during filtration. Furthermore, dissolution of the silver NPs leaves voids in the membrane that may affect its integrity.

Antimicrobial nanoparticles have also been incorporated into membranes via surface grafting. Mauter et al. [14] coated AgNPs with polyethyleneimine and grafted them on polysulfone ultrafiltration membrane surface via amide bond. The coated membrane showed an inactivation rate as high as 99.9% for a kanamycin resistant *Escherichia coli* K12 strain. Yin et al. [15] covalently attached AgNPs on polyamide membrane surface using cysteamine and demonstrated antimicrobial activity towards *E. coli*. Single-walled carbon nanotubes (SWNTs) were covalently grafted on polyamide membranes in a study by Tiraferri et al. [16], and achieved up to 60% inactivation of *Escherichia coli* K12 within 1 h of contact time. The surface coating approach circumvents the limitations of incorporating nanoparticles within the polymer matrix. However, its long-term efficacy has not been demonstrated and is expected to be limited. AgNPs will be depleted as silver dissolves over time. Nanoparticles that do not dissolve such as SWNTs require contact with bacteria cells to impart antimicrobial activity. Fouling of the coating by organic matter or cell debris will reduce their antimicrobial efficacy.

In the current study, a regenerable slow release mechanism was utilized to achieve sustainable biofouling control. Zeolite nanoparticles loaded with Ag^+ or $\text{Ag}(0)$ nanoparticles were covalently attached to a commercial nanofiltration membrane. We demonstrated that stable, slow release of silver provided sustained antimicrobial activity against a model biofilm forming bacterium *P. aeruginosa*. Upon depletion of the silver loading, the antimicrobial efficacy was regenerated by reloading the zeolite with Ag^+ via a simple physisorption protocol. To our knowledge, this is the first study that demonstrates regenerable antimicrobial activity in nanocomposite membranes.

2. Experimental

2.1. Materials

ACS grade AgNO_3 , NaCl, citric acid, isopropanol, 99% NaBH_4 , 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and N-hydroxysuccinimide (NHS) were purchased from Fisher Scientific (Pittsburg, PA). Ethanol (200 proof) was purchased from Decon Laboratory, Inc. (King of Prussia, PA). 3-aminopropylmethyldiethoxysilane (APMDES, 95%) was purchased from Gelest, Inc. (Morrisville, PA). Nanozeolite particles were purchased from Nanoscape (Munich, Germany). The nanozeolite used in this study was a FAU type X zeolite crystal with a particle diameter of ~ 150 nm and pore opening of ~ 7 Å, according to the information provided by the vendor. All solutions and suspensions were prepared using ultrapure water (≥ 18.0 M Ω -cm) generated by an E-pure system (Barnstead, IL).

The bacterium used was *Pseudomonas aeruginosa* (*P. aeruginosa*, ATCC# 700829). *P. aeruginosa* is a model bacterium known to form robust biofilm and is commonly used in biofouling studies [17]. Growth media, including Trypticase Soy Broth (TSB), Luria-Bertani (LB), phosphate buffered saline (PBS), and agar were purchased from Fisher Scientific (Pittsburg, PA).

The membrane used was a commercial thin film composite nanofiltration membrane Filmtec NF 90 (Dow Water and Process Solutions, Minneapolis, MN). The membrane was cut into small pieces, rinsed thoroughly with ultrapure water, and stored in ultrapure water in dark at 4 °C for at least 24 h before use.

2.2. Methods

2.2.1. Silver-zeolite coating

To covalently bind the Ag^+ -loaded nanozeolite on membrane surface, the nanozeolite was firstly functionalized with amine functional groups, followed by loading with Ag^+ , and then attached to the membrane surface via an amide bond formed with the carboxyl groups on the membrane. To generate the $\text{Ag}(0)$ -zeolite coated membrane, Ag^+ loaded in the nanozeolite coated membrane was reduced to $\text{Ag}(0)$. The detailed coating procedure is described below.

2.2.1.1. Grafting of amine functional groups on nanozeolite. To attach nanozeolite to the membrane surface through an amide bond, zeolite nanoparticles were grafted with amine functional groups (Fig. 1) in order to react with the carboxyl groups on the membrane surface [18]. Firstly 0.05 g nanozeolite was sonicated in 5 mL isopropanol for 30 min, and transferred into a round bottom flask. APMDES was then added drop-wise to reach a concentration of 26 mM. Constant stirring was provided. A condenser was then put on the flask and the mixture was purged with argon for 4 h. After Ar purging, the system was sealed and left to react for another 20 h under ambient temperature.

After the reaction, the mixture was centrifuged at 7500 rpm ($\sim 6680 \times g$) to recover the nanozeolite, which was washed twice with 200 proof ethanol, and dried overnight in a vacuum oven (Isotemp Model 281 A, Fisher Scientific) at 80 °C.

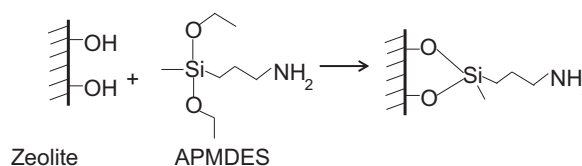


Fig. 1. Grafting reaction between the hydroxyl groups on zeolite and APMDES.

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