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In situ surface functionalization of reverse osmosis membranes with biocidal copper nanoparticles

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HIGHLIGHTS

- A method for *in situ* functionalization Cu-NPs of thin-film composite RO membranes is presented.
- In situ loading of Cu-NPs had minor impact on membrane water permeability and selectivity.
- Functionalized TFC membranes exhibit strong antibacterial activity.
- Cu-NPs can be cost-effective for *in situ* TFC membrane functionalization.

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ABSTRACT

Biofouling may lead to severe operational challenges that can significantly impair membrane desalination processes. In recent years, copper-based nanoparticles (Cu-NPs) have gained increased attention as a potentially viable anti-biofouling agent in membrane processes, due to their strong antibacterial activity and relatively low cost. This study presents a novel and facile method to attach biocidal Cu-NPs on the surface of a thin-film composite reverse osmosis membrane. Herein, we suggest a method for membrane surface functionalization with Cu-NPs that is performed without disassembling the membrane module, which highlights its practicality and potential application for reverse osmosis desalination plants. The loading of Cu-NPs on the membrane was confirmed both by scanning electron microscope imaging and X-ray photoelectron spectroscopy analysis, indicating that the deposited nanoparticles were composed of either metallic copper or copper-oxide. The impact of the *in situ* Cu-NP modification on membrane transport properties was found to be minor, with only a slight increase of the water and salt permeability. Furthermore, except for a slight increase in hydrophobicity, the modified membrane exhibited surface properties comparable to those of the pristine membrane. Finally, the *in situ* formed Cu-NPs imparted a strong antibacterial activity to the membrane surface, leading to 90% reduction in the number of attached live *Escherichia coli* bacteria on the modified membrane compared to the pristine reverse osmosis membrane. This study demonstrates that *in situ* grafting of Cu-NPs on reverse osmosis membranes is a potential alternative to reduce biofouling.

1. Introduction

The progress in membrane desalination processes and the worldwide construction of mega desalination plants in the past decades were achieved by intensive scientific and industrial research that tackled many of the engineering process challenges [1,2]. However, biofouling continues to be a severe operational hurdle in membrane-based water treatment processes [3–5]. Biofouling refers to the formation of a biofilm composed of bacteria and extracellular polymeric substances on the membrane surface and/or membrane spacer. It is a spatial–temporal problem [6], exacerbated in warm waters [7] that contain high nutrient concentrations such as secondary effluent [8], tropical seawater [9], or water during seasonal algal blooms [10,11].

A densely formed biofilm inside the membrane module may result in negative operational consequences, such as an increase in the pressure drop along the module, exacerbation of concentration polarization effects, and deterioration of permeate water quality [12–15]. Mitigating biofilm formation during desalination of feed waters with high biofouling potential requires frequent chemical cleaning procedures, which lead to shorter membrane life span and significant increase of process cost. Thus, there is a need for the development of innovative methods that will improve and expand the engineering toolbox for combating biofouling in membrane desalination processes.

In reverse osmosis (RO), a multi-barrier approach is usually used to abate the potential development of biofouling inside the membrane

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module during the desalination process. Pretreatment methods of filtration and disinfection are employed to significantly reduce the number of live bacteria that are conveyed to the membrane module [16,17]. Also, frequent chemical cleaning is applied in an attempt to prevent the development of a biofilm at early stages [18]. However, to date, there is no effective method of bacteria inactivation that will complement pretreatment and frequent chemical cleaning by continuous disinfection of the feed water inside the membrane module during the desalination process. This lack stems mostly from the high sensitivity of the predominant type of desalination membranes (*i.e.*, polyamide thin-film composite (PA-TFC) membrane) to commonly used oxidants, such as chlorine, chlorine derivatives, and ozone [19], which degrade the polyamide layer of the membrane [20]. Consequently, there is a critical need for a novel, non-destructive, and cost-effective method to impart biocidal activity inside the membrane module during the separation process.

Among different proposed anti-biofouling approaches in desalination technologies, the use of biocidal metal nanoparticles (Me-NPs) has gained substantial momentum in the past decade [21–23]. The strong antibacterial activity of some Me-NPs (*e.g.*, silver [24,25], copper [26], and zinc [27,28]) toward many diverse types of bacteria and other microorganisms is well established. However, an understanding of the potential to apply these biocidal Me-NPs for biofouling mitigation in reverse osmosis has not been well established, mostly because of the lack of a practical method to load the biocidal Me-NPs inside the membrane module. Controlled localized loading of the biocidal Me-NPs in the vicinity of the module spacers and the membrane surface will require less metal and therefore will be more cost-effective than injecting the Me-NPs directly into the feed tank before the RO module.

The inevitable dissolution of Me-NPs during module operation must also be considered. Particle dissolution will likely be aggravated during periodic cleaning operations. Therefore, localized loading of biocidal Me-NPs on the membrane must also be able to replenish the Me-NPs after their dissolution. Such reloading must be performed in the desalination site without disassembling the membrane module, requiring minimal loading time and limited chemical reagents.

Recently, we have demonstrated a new method for loading silver nanoparticles on TFC RO membranes, *via in situ* formation of Ag-NPs [29]. The method is simple and rapid (a 15-minute procedure), requiring the use of a very low concentration of silver salt and reductant (sodium borohydride). However, the relatively high price of silver will increase the operating cost [30], leading to the adjustment of the *in situ* formation method to incorporate other less expensive alternative Me-NPs with efficient anti-biofouling properties.

In recent years, the use of copper nanoparticles (Cu-NPs) as biocides in membrane filtration has received increasing interest [22,31,32]. Compared with silver, copper is relatively inexpensive and abundant [30], and is extensively utilized as a wood preservative [33], as a fungicide for vineyards or other agricultural crops [34], as a disinfectant in swimming pools [35], and as a major component of anti-biofouling paint to protect ship hulls [36]. The use of copper salt as an anti-biofouling agent in desalination processes also has been reported [37,38]. Thus, copper-based NPs offer a potential agent for biofouling mitigation in reverse osmosis, if a practical loading method for NPs inside the membrane module could be introduced.

This study presents a novel *in situ* protocol for loading biocidal Cu-NPs on TFC-RO membrane. The modified membrane was extensively characterized to confirm the successful loading of Cu-NPs on the membrane surface and to assess the impact of the Cu-NP *in situ* formation reaction on the water and salt transport properties. Surface properties such as hydrophilicity, roughness, and surface charge (zeta potential) were evaluated prior to and after surface functionalization. Finally, we demonstrate the imparted strong antibacterial activity to the membrane surface by the *in situ* formed Cu-NPs.

2. Materials and methods

2.1. Chemicals

Copper sulfate ($CuSO_4$), nitric acid (HNO_3), and potassium chloride (KCl) were purchased from Sigma Aldrich (St. Louis, MO). Sodium chloride (NaCl), sodium hydroxide (NaOH), and 2-propanol (isopropyl alcohol, $CH_3CHOHCH_3$) were purchased from J. T. Baker (Phillipsburg, NJ). Potassium bicarbonate ($KHCO_3$), sodium bicarbonate ($NaHCO_3$), and sodium borohydride ($NaBH_4$) were obtained from Fisher Scientific (Fair Lawn, NJ). Potassium hydroxide (KOH) was purchased from Aventor Performance Materials (Center Valley, PA). Bacto agar and Luria-Bertani (LB) broth were received from BD Biosciences (Sparks, MD) and American Bioanalytical (Natick, MA), respectively. Unless specified, all solutions were prepared in deionized (DI) water produced by the Milli-Q ultrapure water purification system (Millipore, Billerica, MA).

2.2. Model bacteria strain

Kanamycin resistant *Escherichia coli* (*E. coli*) BW26437 was received from the Yale Coli Genetic Stock Center (New Haven, CT). The *E. coli* culture was maintained on LB agar plates and grown in LB media 25 mg/L with kanamycin sulfate (American Bioanalytical) prior to any experiments.

2.3. In situ formation of Cu-NPs on the membrane

Dried sheets of seawater TFC-RO membrane (Dow Filmtec SW30XLE) were received from OctoChem, Inc. The dried membrane coupons were wetted through immersion in a mixture of 20v/v% isopropanol in DI water for 20 min. The membranes were rinsed and soaked three times in DI water for 24 h and stored at 4 °C until use.

The following protocol for *in situ* formation of Cu-NPs is modified from our previous report of *in situ* formation of Ag-NPs [29]. A schematic diagram of the modification procedure is shown in Fig. 1. Initially, the membrane was placed between a glass plate and a rubber frame (inner hole size: 7.5 cm × 12 cm) designed to hold the solutions on the active layer of the membrane. Ten milliliters of $CuSO_4$ solution (50 mM) reacted with the isolated active layer for 10 min (Fig. 1B). Subsequently, the $CuSO_4$ solution was discarded, leaving only a thin layer of $CuSO_4$ solution on the membrane surface (Fig. 1C). Then, the membrane active layer was allowed to react with a $NaBH_4$ (50 mM) solution for 15 min (Fig. 1D), forming copper nanoparticles. After the formation of Cu-NPs, the $NaBH_4$ solution was removed from the membrane (Fig. 1E), and the prepared *in situ* Cu-NP modified membrane was rinsed for approximately 10 s with DI water. Unless otherwise specified, all the modification experiments were conducted at an ambient temperature of 23 °C.

2.4. Confirmation of the Cu-NP loading on the membrane surface

Visual characterization of the modified and the pristine membrane surfaces was carried out with scanning electron microscopy (SEM; Hitachi Ultra-High-Resolution Analytical Field Emission Scanning Electron Microscope, FE-SEM, SU-70). Prior to SEM measurement, the membrane was dried and sputter-coated (Denton Vacuum, DESK V) with a chromium layer of approximate 10 nm. X-ray photoelectron spectroscopy (XPS; Surface Science Instruments model SSX-100-SPECS) measurements for surface elemental analysis were performed with monochromatized Al-Ka X-ray source.

2.5. Characterization of membrane properties

The transport properties of the membrane were examined on a bench-scale RO filtration system [39]. Two measurements were taken