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Biofouling resistance of reverse osmosis membrane modified with polydopamine

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HIGHLIGHTS

- Polydopamine was deposited on RO membrane to improve antibiofouling potential.
- Surface hydrophilicity and charge density of modified membrane were not affected.
- The antiadhesion property of modified membrane against bacteria was improved.
- Polydopamine modified membranes showed antibacterial property.
- Polydopamine coating could improve membrane biofouling resistance.

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ABSTRACT

It has been reported that surface modification with polydopamine (PDA) increases the hydrophilicity and the negative charge density of membrane surfaces, which improves their antifouling potential against organic foulants. Thus, in this paper, we attempted to modify a reverse osmosis (RO) membrane with PDA to improve antibiofouling potential. The deposition of PDA was confirmed by several methods, including X-ray photoelectron and Fourier-transform infrared spectroscopy. However, increases in hydrophilicity and negative charge density were not clearly observed. Nevertheless, the improvement of antibiofouling properties was confirmed by cross-flow filtration of a bacterial (*Pseudomonas putida*) suspension. The high antiadhesion property of the PDA-modified membrane was confirmed by scanning electron microscope surface images after 1200 minute continuous filtration of the bacterial suspension. In addition, it was confirmed by using a shake flask test with *Escherichia coli* that the PDA-modified membrane had a bactericidal property. Using shake flask tests in the different pH solutions, it was concluded that the antibiofouling property of PDA-modified membranes could be attributed to the bactericidal property of protonated amine groups of PDA deposited on the membrane surface.

1. Introduction

Biofouling is the undesired attachment of microorganism communities to a membrane surface. Bacteria adhered to the surface release extracellular polymeric substances (EPS) and consequently, a biofilm EPS matrix with embedded bacteria is formed. Because biofilms reduce salt rejection and flux [1,2], biofouling is a serious obstacle in reverse osmosis (RO), and other membrane processes. Several methods have been reported to overcome membrane biofouling. Most of these methods have been based on enhancing the antimicrobial and antiadhesion properties [3–5]. An antimicrobial property improves bacteria lysis, while the antiadhesion property increases the adhesion resistance of the surface against bacterial attachment.

Surface modifications such as coating, deposition and grafting are general approaches that improve membrane biofouling resistance by increasing antimicrobial or antiadhesion properties. Using organic and inorganic antimicrobial agents is a common method to increase the antibacterial property of the membrane surface. The adhesion resistance against bacteria could be improved by improving hydrophilicity and smoothness, and also by increasing the negative charge density of the membrane surface [6–8].

To improve the antibacterial properties, silver is an inorganic agent used in many studies as a strong biocide. Silver nanoparticles can release Ag ions, which are biocidal and consequently lyse the bacteria [4,9–11]. Sawada et al. enhanced the antibiofouling properties of a polyethersulfone (PES) hollow fiber (HF) membrane by forming an acrylamide surface layer embedded with silver nanoparticles [10]. In our previous study, the antibacterial property of a commercial RO membrane was improved by silver nanoparticles embedded into polyelectrolyte multilayers using the Layer-by-Layer (LbL) method [4]. Metal hydroxides such as $Ca(OH)_2$, $Mg(OH)_2$ and $Cu(OH)_2$ were also used as

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inorganic antimicrobial agents [12–14]. We recently reported that the antibacterial property of an RO membrane surface was improved by the deposition of $Cu(OH)_2$ particles that released Cu ions [14]. The other approach to improve the antibacterial property is the formation of a material surface with antibiotic functional groups such as antimicrobial peptides or compounds that present positive charges such as the quaternary ammonium (QA) group. Razi et al. improved the antibiofouling properties of a PES-HF membrane by grafting (2-dimethylamino) ethyl methacrylate methyl chloride quaternary salt (DMAEMAq) onto the membrane surface [15]. The QA groups have positive charges that penetrate the cell wall of bacteria or induce disruption of the cell membrane integrity and lyse the cell.

Many investigations have reported that the improvement of membrane surface hydrophilicity improves the antiadhesion property and effectively reduces membrane biofouling [4,16,17]. Surface modification with hydrophilic substances such as zwitterions is a promising method. Zwitterionic monomers, such as methacryloyloxyethyl phosphorylcholine (MPC), are electrically neutral chemicals with cationic and anionic groups on their backbone structures. We coated a commercial RO membrane surface with polyzwitterion (PZ) using the LbL method and improved the antiadhesion property of the membrane surface [4]. Organic fouling and biofouling resistances of a PES-HF membrane were also improved by grafting zwitterionic monomers [17].

However, the methods mentioned above have a number of shortcomings, such as high cost (e.g. silver or PZ), risks to human health (low value of secondary maximum contaminant level, for example, 0.1 mg/L for silver), complexity (such as LbL method), low reproducibility and poor stability. Thus, an attractive method should feature low toxicity, simplicity, low cost and good stability in addition to good antiadhesion and antimicrobial properties.

Dopamine coating is a relatively new surface modification method. A polydopamine (PDA) layer is formed on any substrate that is immersed in dopamine solution [18]. Surface modification with PDA has been reported for several kinds of membranes, including electrodialysis (ED) [19], microfiltration (MF) [20], ultrafiltration (UF) and RO membranes [20–22]. It is well known that PDA is a super-hydrophilic material that improves the hydrophilicity of hydrophobic surfaces such as polyethylene (PE), poly (vinyl fluoride) (PVDF) and polytetrafluoroethylene (PTFE) [23–26]. The PDA layer tightly adheres to the surface by strong covalent and non-covalent interactions with the substrate, giving a highly stable PDA coating [27]. Xi et al. showed that PDA had very good stability on the membrane surface [23]. Kasemset et al. showed that the organic fouling resistance of a commercial RO membrane was sufficiently improved by PDA modification [21]. Also, Azari and Zou showed that the organic fouling resistance of an RO membrane was enhanced by L-PDA coating through a marked improvement of hydrophilicity [22].

Considering the experimental results shown above, surface modification with PDA would also be a promising modification method to improve the antibiofouling potential of an RO membrane. The PDA coating is a simpler method than the LbL method we used for the surface modification with silver nanoparticles and PZ. The dopamine is cheaper than silver and PZ. In addition, it is expected that the PDA coating is more stable than the $Cu(OH)_2$ coating we have already reported, since $Cu(OH)_2$ adsorbed by physical adsorption. Furthermore, recently, PDA has attracted considerable interest for various types of biomedical applications [28] indicating that PDA can be used safely to modify membranes for producing drinking water. To the best our knowledge, the improvement of antibiofouling properties of RO membranes with PDA coating has not been reported. So in this paper, we attempted to improve the antibiofouling properties of an RO membrane by PDA coating. The optimal conditions and mechanism behind the improvement of the antibiofouling performance are discussed. Finally, we show, for the first time, the antibacterial property of PDA.

2. Experimental

2.1. Materials

A commercial RO membrane (ES20, Nitto Denko, Osaka, Japan) was used as the base membrane. This is an ultra-low pressure RO membrane with an aromatic polyamide selective layer. The nominal value of rejection stated in the company catalog is 99.7% for 0.05% NaCl. NaCl (Wako Pure Chem. Ind., Osaka, Japan) was used as an electrolyte. Glutaraldehyde, ethanol and [Bis(trimethylsilyl)amine] (Wako Pure Chem. Ind.) were used in antiadhesion experiments. Dopamine hydrochloride (Sigma-Aldrich, St. Louis, MO, USA) was used for surface modification of the RO membrane. The chemical structure of dopamine is shown in Fig. 1. Tryptic Soya Broth (TSB) and Difco Nutrient Broth (NB) (Becton, Dickinson and Company, Franklin Lakes, NJ, USA) were used as nutrient agents. *Escherichia coli* (*E. coli*) (NBRC 3310) and *Pseudomonas putida* (*P. putida*) (NBRC 100650) (Biological Resource Center at the National Institute of Technology and Evaluation, Shibuya, Japan) were used as model Gram-negative bacteria, because most bacteria in water treatment processes are Gram-negative bacteria [29]. Syto 9 and Syto propidium iodide (PI) (Life Technologies Corporation, Tokyo, Japan) were used as molecular probes for bacteria. All chemicals were used without further purification. Milli-Q water (18.2 MΩ·cm) (Millipore, Billerica, MA, USA) was used to prepare all solutions and for rinsing.

2.2. Membrane modification

The RO membrane was modified by dopamine. Dopamine solutions were prepared by dissolving dopamine hydrochloride at several concentrations (i.e., 0.1, 0.5, 1, 1.5, and 2 kg/m^3) in 15 mM Tris–HCl buffer (pH 8.8). Dopamine spontaneously polymerizes and forms PDA by contacting with oxygen in an alkaline aqueous solution [30]. Fig. 1 shows a mechanism for dopamine oxidative self-polymerization [18,31–34]. The PDA interacts with membrane surface by covalent and noncovalent interactions [27], and strongly adheres to the membrane surface. A membrane was fixed to a customized fixture [14] and only the active layer was exposed to the aqueous dopamine solution since the fouling takes place only on the active layer of membrane. Otherwise PDA coating deposited on the support layer will lead to a decline in membrane performance. The fixture was horizontally placed in a beaker containing 600 ml of dopamine solution, and then the solution was thoroughly stirred for the desired modification time (i.e., 1.5, 3, 6, 15 and 24 h) at 28 °C.

After modification for the desired time, the membrane was removed from the beaker and rinsed three times with fresh water. To remove excess or weakly-bound PDA from the membrane surface, the modified membrane was immersed in 25% (v/v) isopropyl alcohol (IPA) solution for 10 min. The membrane was then thoroughly rinsed with Milli-Q water for 1 day.

2.3. Characterization

2.3.1. FT-IR and XPS

The surface chemical structures of the unmodified membrane and PDA-modified membranes were analyzed by Fourier-transform infrared spectroscopy (FT-IR) and the chemical composition by X-ray photoelectron spectroscopy (XPS). FT-IR measurements were carried out by an FT-IR spectrometer (ALPHA, Bruker Co., Billerica, MA, USA) with attenuated total reflectance (ATR). XPS measurements were carried out with an ESCA-850 spectrometer (Shimadzu Co., Kyoto, Japan). The sample surface was irradiated by Mg Kα radiation, generated at 8 kV and 30 mA. The membranes were dried in a freeze dryer (FDU-1200 EYELA; Tokyo Rikakikai Co. Ltd., Tokyo, Japan) overnight prior to FT-IR and XPS measurements.