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Surface modification of thin film composite RO membrane for enhanced anti-biofouling performance

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ABSTRACT

Anti-adhesion and antimicrobial coatings were prepared and applied on commercial thin-film-composite (TFC) polyamide (PA) membrane to enhance anti-biofouling performance. Polyvinyl alcohol (PVA) coating was modified with cationic polyhexamethylene guanidine hydrochloride (PHMG) polymer to obtain antimicrobial performance. ATR-FTIR, SEM and AFM investigated the surface chemistry and morphology of the coated membranes. The contact angle measurement was used to determine hydrophilicity and surface energy. All coated membranes revealed more hydrophilic and lower surface roughness compared to uncoated membrane. Lower number of adhered *Pseudomonas aeruginosa* (*P. aeruginosa*) bacteria was detected on coated membranes, indicating anti-adhesion performance. The colony forming unit (CFU) and diffusion inhibition zone (DIZ) tests determined antimicrobial activity of the coated membranes against *Escherichia coli* (*E. coli*) and *Bacillus subtilis* (*B. subtilis*), showing the antimicrobial performance of PHMG. The results suggested that an optimal anti-fouling surface could be obtained applying a coating, which combines anti-adhesion and antimicrobial performance.

1. Introduction

Reverse osmosis (RO) membranes are widely applied for seawater desalination and wastewater reclamation. However, biofouling of RO membranes remains as a critical challenge in these applications. Biofouling is initiated by the adhesion and accumulation of planktonic microorganisms followed by their primary colonization and growth [1]. The attachment of microorganisms together with their extracellular polymeric substance (EPS) decreases membrane permeability and therefore, increases the energy consumption of RO processes [2].

Biofouling can be affected by various factors, including feed water characteristics, hydrodynamic conditions, and membrane surface properties. Pre-treatment of feed water with disinfection, coagulation, filtration and/or adsorption are adopted to remove/inactivate microorganisms and to reduce organic/nutrient loading [2,3]. In addition, operating at moderate flux level seems to be effective in preventing severe biofouling at the initial fouling stage [4]. However, the growth and colonization of micro-organisms on membranes after initial attachment remains an unsolved issue [3]. Membrane surface properties play also a key role in affecting biofilm formation. In many cases, anti-fouling membrane is achieved as combination of the surface physiochemical properties, such as increased hydrophilicity, lowered surface roughness and neutralised surface charge [5]. It has been shown that surfaces are more easily fouled for membranes with high peaks or deep valleys [2,5]. Furthermore, the type of surface texture has essentially affected to the biofouling tendency [6,7].

Recently, surface modification of RO membranes has gained increasing attention [8]. For example, some of the commercial thin-film-composite (TFC) polyamide (PA) membranes are coated by additional thin PVA layer to introduce hydroxyl groups to the PA surface [9]. In the laboratory experiments, the surface modification of commercial TFC PA membrane has been carried out by depositing or grafting various hydrophilic polymeric substances on PA surface, such as hydrogels, surfactants or monomers [10–12]. Furthermore, these anti-adhesion surfaces can be prepared using contact active amphiphilic, microbe-repelling or anti-adhesive polymers [13–15]. In addition, active antimicrobial coatings with bactericidal effects have been prepared using heavy metal nanoparticles, such as silver, copper and zinc [16,17]. However, the heavy metal based antimicrobial coatings may have certain disadvantages: (1) uncontrolled leaching of the metal ions to the

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surroundings decreases the self-life of the anti-fouling membrane [18], and (2) these metal ions may raise questions concerning their safety to environment [19]. In this regard, polymer based anti-microbial coatings may be favoured.

The current study aimed to develop surface coating method to enhance anti-biofouling performance of RO membranes. Polyvinyl alcohol (PVA) and cationic polyhexamethylene guanidine hydrochloride (PHMG) coatings were used to obtain hydrophilic and smooth surfaces to enhance membrane anti-adhesion properties. In addition, the PHMG coating was shown to have antimicrobial effect.

2. Experimental

2.1. Materials and chemicals

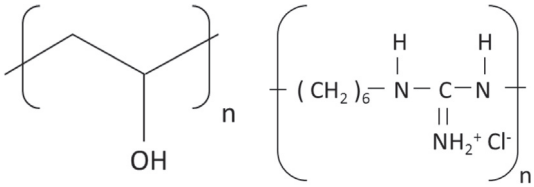
The commercial TFC PA membrane DOW™ FILMTEC™ LE-400, purchased from HOH Separtec Oy (Finland), was used as a substrate for the coatings. The following chemicals were used for the membrane surface modification. PVA (Mw 9000–10,000 g/mol, 80% hydrolysed) was purchased from Sigma-aldrich. PHMG, polyhexamethylene guanidine hydrochloride ($C_7N_3H_{15}\cdot HCl$, Mw=8000–10,000 g/mol) was provided by Soft Protector Oy. The chemical structures are presented in Scheme 1.

2.2. Membrane surface modification

The preparation of PVA coatings was done by mixing 2 wt% of PVA into milliQ water at 60 °C. After a complete mixing, the solution was cooled down to room temperature. The PVA–PHMG solutions were similarly prepared as described above, by adding PHMG to the PVA solution after the cooling step. PVA–PHMG solutions were prepared in ratios 95:5 and 99:1 (PVA:PHMG) with a total polymer content of 2 wt%. The pure PHMG solution (2 wt%) was prepared by mixing PHMG with milliQ water to reach the targeted concentration. PVA, PVA–PHMG and PHMG solutions were applied on the membrane coupons using dispersion coating method with K Control Coater K202 device (R K Print-Coat Instruments Ltd.). The device was equipped with glass bed and close wound K202 meter bar No. 0 was used to apply wet films with a thickness of 4 μm. The applied coatings were heat-treated at 110 °C for 2 min to evaporate the water and to increase the coating stability using thermal cross-linking [20].

2.3. Membrane characterizations

ATR-FTIR measurement was carried out to analyse the surface chemistry of uncoated and coated membranes. Perkin Elmer spectrum BX II FT-IR (Fourier transform IR) system was equipped with vertical-ATR (Attenuated total reflectance) and KRS-5 crystal. In a typical analysis 50 scans were collected from 500 to 4000 cm^{-1} at 4 cm^{-1} resolution. A background spectrum of pure KRS-5 was collected before running the samples.



Polyvinyl alcohol (PVA) Polyhexamethylene guanidine hydrochloride (PHMG)

Scheme 1. Chemical structure of polyvinyl alcohol (PVA) and polyhexamethylene guanidine hydrochloride (PHMG).

The microscopic imaging of uncoated and coated membranes was conducted using scanning electron microscope (SEM) JEOL JSM-6360 LV 11 kV on high vacuum mode. Membrane cross sections were prepared by fracturing samples in liquid nitrogen. All SEM samples were sputter coated with gold before imaging.

The surface topography of uncoated and coated membrane samples was characterised using non-contact mode atomic force microscopy (NC-AFM). The NC-AFM analysis was performed using Park Systems XE-100 AFM equipment with cantilever 905M-ACTA (purchased from ST Instruments B.V.). Typically, the scan rate was 0.4–0.6 Hz and the measured area was 5×5 μm^2. Six replicate measurements were performed to determine the roughness value root-mean-square roughness R_{RMS}.

The measurements of the static contact angle were conducted by using Optical Tensiometer Theta T200 device (Attension, Biolin Scientific). The measurements were performed in a controlled atmosphere (RH 50%, temperature 23 °C) and the results are given as an average of five parallel measurements. The water contact angle values, expressed as °, are presented at the time of 30 s from the moment the drop contacts the surface. The surface energy values were obtained by measuring the contact angle of three different probe liquids, including water (H_2O, γ=72.80 mN/m), di-iodomethane (CH_2I_2, γ=50.80 mN/m) and formamide (CH_3NO, γ=58.20 mN/m). The total surface energy values, as summary of polar and dispersive surface energies, were determined from the measured contact angle data using the Fowkes theory [21].

2.4. Membrane anti-adhesion performance

Biofilm formation was demonstrated by analysing the attachment of *Pseudomonas aeruginosa* on uncoated and coated membranes. *P. aeruginosa* is Gram-negative, aerobic, rod-shaped bacterium, which is widely used as the model microbe for biofilm formation study [22–25]. Therefore, *P. aeruginosa* was selected as model bacterium in our study to provide comparable data related to the attachment of bacteria.

Bacteria attachment test was conducted by submerging the membranes (Ø4.7 cm) in bacterial suspension consisted of standard seawater ASTM D1141-98 (2008) [26]. Furthermore, the suspension was inoculated with overnight culture of *P. aeruginosa* (VTT E-96726) cultivated in 37 °C Trypticase soy broth solution, harvested by centrifugation (3000 rpm, 10 min) and washed with PBS (10 mM). The cell density was approximately 1×10^8 CFU/mL determined by plate count on TSA (37 °C, 1 d). The exposure of membranes was conducted in a rotary shaker (75 rpm) at room temperature for 1 d. The number of adhered cells on the membranes was determined after swabbing by plate count on TSA (37 °C, 1 d). It was aimed to describe the anti-adhesion performance. Results are presented as colony forming units per membrane area (CFU/cm^2). Three replicate membrane samples were examined for each membrane type.

2.5. Membrane antimicrobial performance

2.5.1. Colony forming unit (CFU) test

Antimicrobial performance of uncoated and coated membranes were analysed using colony forming unit (CFU) test for the two rod shaped model microorganisms, Gram-positive bacteria *Bacillus subtilis* (ATCC 6633) and Gram-negative bacteria *Escherichia coli* (ATCC 8739). These bacteria are extensively used to investigate surface antimicrobiality [27,28].

Bacteria cultivation was conducted by following the instruction of the producer, ATCC (24 h cultivation for *B. subtilis* in 30 °C nutrient broth solution and 12 h cultivation for *E. coli* in 37 °C