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Combined effects of organic matter and calcium on biofouling of nanofiltration membranes

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ABSTRACT

Biofouling of nanofiltration (NF) membranes is a major impediment in wastewater reclamation. However, research on the fouling process, including conditioning and subsequent biofouling in complicated systems, is limited. In this study, the combined effects of organic matter (OM) and calcium on *Pseudomonas aeruginosa*-induced fouling are systematically investigated and verified through an analysis of permeate flux, foulants, and membrane surface properties (roughness, surface charge, hydrophobicity). Sodium alginate (SA), bovine serum albumin (BSA), and humic acid (HA) are selected as model organics for polysaccharides, proteins, and humic substances in wastewater, respectively. Results show that approximately 8% of permeability is lost during organic-free conditioning in the absence and presence of Ca^{2+}. However, subsequent biofouling is reduced at 5 and 8 mM Ca^{2+}. In the presence of OM, Ca^{2+} plays an important role in organic conditioning and subsequent biofouling. SA and HA accelerate organic conditioning with the increase in Ca^{2+} concentration but inhibit subsequent biofouling. By contrast, severe biofouling occurs in the presence of BSA at 2 mM Ca^{2+}, as revealed by both flux decline and the biomass accumulation. Organic conditioning significantly influences membrane surface properties and results in biomass retention on hydrophobic and rough surfaces conditioned with BSA.

1. Introduction

Biofouling of high-pressure spiral wound membranes, such as nanofiltration (NF) and reverse osmosis (RO) membranes, is the most serious constraint in wastewater reclamation because it results in permeate flux decline and pressure drop increase with deteriorating water quality as well as increased operating and maintenance costs [1–3]. The dynamic process of biofouling has been generally accepted; this process includes (i) membrane surface conditioning by organic and inorganic matter present in the bulk liquid [3–5], (ii) adhesion and attachment of microorganisms on the conditioned surface, (iii) growth of deposited cells by utilizing organics previously attached to the membrane surface and production of extracellular polymeric substances (EPS, including polysaccharides, proteins, and humic substances), and (iv) biofilm formation and biofouling occurrence [6–8]. Therefore, biofouling is a very complicated process and cannot be completely eradicated as only a few initial colonies on membrane surface are required to form a mature biofilm [9]. Biofouling is affected by many factors [10,11], including membrane surface properties (roughness, surface charge, and hydrophobicity), operating conditions (flow velocity and applied pressure), solution chemistry (pH, ionic strength, multivalent cations, and organic foulants), and cell surface properties (surface charge and hydrophobicity).

Pseudomonas aeruginosa (PA), a gram-negative aerobic bacterium, is a common model bacterium for membrane biofouling studies [2,12]. The bacterial deposition/adhesion behavior is highly related to cell surface characteristics and the conditioning film pre-absorbed onto the membrane surface, which are both influenced by the presence of divalent cations [13–15]. Organic matter (OM), such as polysaccharides, proteins, and humic substances, are known to be the most problematic organic foulants in wastewater that form a conditioning film on membrane surface [16–18]. Organic conditioning modifies membrane surface properties, which are believed to have a significant impact on bacterial deposition and the subsequent development of biofilms [14,15,19]. Therefore, investigating the effects of different organic foulants on membrane surface properties as well as the effects of biofouling behavior on organic conditioned membranes is critical.

Multivalent cations, particularly calcium ions (Ca^{2+}), are present in wastewater. Organic conditioning and subsequent biofouling are influenced by the presence of Ca^{2+} in a solution. Many

Abbreviations: NF, nanofiltration; RO, reverse osmosis; PA, *Pseudomonas aeruginosa*; SA, sodium alginate; BSA, bovine serum albumin; HA, humic acid; EPS, extracellular polymeric substances; OM, organic matter; ATP, adenosine triphosphate; TDC, total direct cell count; SEM, scanning electron microscopy; AFM, atomic force microscopy; CFU, colony forming unit; RFR, relative flux reduction; CP, concentration polarization; CEOP, cake-enhanced osmotic pressure; BEOP, biofilm-enhanced osmotic pressure

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studies have analyzed the influence of Ca^{2+} on organic fouling by using model organics, such as sodium alginate (SA), bovine serum albumin (BSA), and humic acid (HA) [16,17,20]. However, the impact of Ca^{2+} on biofouling of nanofiltration (NF) membranes remains unknown, although many studies have revealed enhancement in the adhesion and aggregation of bacteria and biopolymers in the presence of Ca^{2+} [7,15,21]. The simultaneous effects of OM and calcium on intricate systems that include both microbial cells and conditioning films also remain unclear despite previous investigations. Hence, the combined effects of organic foulants and Ca^{2+} on organic conditioning and subsequent biofouling and the mechanisms responsible for biofouling on organic conditioned membranes with different conditioning types and Ca^{2+} concentrations should be systematically investigated.

In this study, we investigated the *Pseudomonas aeruginosa*-induced fouling of NF membranes as a function of organic conditioning types and Ca^{2+} concentrations. The combined effects of OM and calcium were verified through a systematic analysis of permeate flux, biomass (ATP, live/dead cells), and membrane surface properties. Fouling experiments were conducted with commercial SA, BSA, and HA as surrogates for polysaccharides, proteins, and humic substances in wastewater, respectively. The fouled membranes were characterized in terms of membrane morphology and roughness through scanning electron microscopy (SEM) and atomic force microscopy (AFM); membrane surface charge and membrane hydrophobicity were determined through zeta-potential measurement and contact angle measurement, respectively. The result of this study provides novel insights into the membrane biofouling process in the reuse of wastewater in complex systems.

2. Materials and methods

2.1. Model bacterial strain and media

The model bacterium (PA), purchased from China General Microbiological Culture Collection Center (CGMCC), was utilized in all the experiments. A fresh single colony of PA was grown in a nutrient agar (NA) medium and harvested at the exponential growth phase to serve as inoculum for an overnight culture grown in NA broth. This overnight culture was rediluted in NA broth and allowed to grow to the late exponential phase, with a final optical density (OD) of 1 using a UV/visible spectrophotometer (UV 2450, Shimadzu, Japan) at a wavelength of 600 nm, to be used subsequently as inoculum for the biofouling experiments [12].

An enriched synthetic wastewater medium was utilized for bacterial growth in the NF test unit. To achieve accelerated biofouling behavior, a relatively large amount of carbon (as citrate) and a small amount of NA broth (1:1000 dilution) were supplemented to the wastewater media according to the procedure of Herzberg and Elimelech [12]. The feed solution was as follows: 0.8 mM sodium citrate, 2 mM NH_4Cl, 0.2 mM KH_2PO_4, 0.2 mM $MgSO_4 \cdot 7H_2O$, 0.2 mM $NaHCO_3$, $CaCl_2 \cdot 2H_2O$ at five different concentrations (0–8 mM), and an appropriate amount of NaCl to adjust the final ionic strength of 140 mM. In addition, 60 mg/L of the model OM (SA/BSA/HA, except control experiments) was added. The final pH of the synthetic wastewater was 7.2. SA (Sigma-Aldrich, USA), BSA (Biosharp, China), and HA (Sigma-Aldrich) were employed as model OM. The other chemicals were of ACS grade. Milli-Q water was produced by an ultrapure water purification system (Milli-Q PLUS, Milli-pore, Japan).

2.2. Nanofiltration unit and experimental protocol

2.2.1. NF membrane and crossflow test unit

A commercial polyamide composite NF membrane, NFW (Synder, USA), was utilized as the model membrane for the experiments. The pure water flux was 45 L/m^2 h (LMH), and the resistance of the virgin membrane was 7.38×10^{13} m^{-1} at 25 °C, crossflow velocity of 2.5 cm/s, and pressure of 8.27 bar (120 psi). According to the manufacturer, the membranes have a molecular weight cut off (MWCO) of 300–500 Da. The crossflow test unit (Synder, USA) consists of a membrane test cell with effective filtration area of 40 cm^2 (8 cm length and 5 cm width), a high-pressure pump, a feed water reservoir, a chiller equipped with a temperature control system, and a data acquisition system to acquire the permeate flux in real time. Inflow and retentate flow were monitored with a floating disk rotameter. The permeate and retentate were recirculated back to the feed reservoir while maintaining the influent concentration at the same condition (as shown in Fig. S1 in Supporting information).

2.2.2. Experimental protocol

The conditioning experiment was conducted to simulate the actual NF process, in which residual organic and inorganic matter from the pretreatment process are adsorbed onto the membrane surface to form a conditioning film. Therefore, the clean membrane was initially exposed to the feed solution without microorganisms in the absence or presence of OM to promote initial nutrient adsorption onto the membrane surface (Scheme S1) [3].

The NF unit was disinfected and cleaned before and after each fouling experiment [12]. Prior to each experiment, the NF membrane was soaked in Milli-Q water at 4.0 °C for 24 h and then compacted with Milli-Q water at a pressure of 10.34 bar (150 psi) for 1 h after the cleaning step. Following membrane compaction, fouling experiments were conducted for 24 h at constant pressure (8.27 bar, 120 psi), constant temperature (25 °C), and constant crossflow velocity (2.5 cm/s). Each fouling experiment included three phases (Scheme S1). In the first phase, baseline phase (t=0–1 h), 1 h baseline performance with Milli-Q water was examined to correct the virgin membrane flux under operational conditions of the subsequent fouling experiment. In the second phase, conditioning phase (t=1–5 h), the feed solution with 60 mg/L OM (control experiments without OM) was added to the feed reservoir after attaining stable flux with Milli-Q water. The system was preconditioned for 4 h with this synthetic wastewater to obtain the conditioned membranes. In the third phase, biofouling phase (t=5–24 h), a culture of PA was centrifuged for 15 min at 4000 rpm and 4 °C and resuspended in Milli-Q water. The resuspended culture was inoculated into the synthetic wastewater described above to achieve an initial cell concentration of 10^8 colony forming units (CFU) mL^{-1}. The system was operated for a continuous period of 19 h to obtain the biofouled membranes.

2.3. Analysis methods

The membranes were carefully removed from the unit at the end of the conditioning and biofouling experiments, and membrane autopsy was performed. A membrane specimen was cut into sections with sterilized scissors, and the foulants on the membrane were resuspended with 40 mL of phosphate buffer for biomass and organic foulant measurement, as shown in Supporting information [22–24].

2.3.1. Organic foulants

Total polysaccharide content was determined according to the phenol–sulphuric acid method with SA as the standard [11]. Total protein content was measured through the bicinchoninic acid (BCA) method with a BCA assay kit (Sangon Biotech, Shanghai) [25]. Total HA content was quantified through UV spectrometry (UV 2450, Shimadzu, Japan) at a characteristic wavelength of 254 nm, where the extinction coefficient was determined to be