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Full Length Article

Anti-irreversible fouling of precisely-designed PVDF-ZnO membrane: Effects of ion strength and co-existing cations

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ABSTRACT

In this work, the atomic layer deposition-zinc oxide (ALD-ZnO) modified membrane was fabricated and the effects of ionic strength, co-existing Ca^{2+} and Mg^{2+} on its fouling potential were systematically investigated. Results showed excellent anti-irreversible fouling performance of PVDF-ZnO modified membrane with co-existing cations. Attractively, the values of declined membrane flux dropped by 25.7%, 25.9% and 22.3% after ZnO modification in the presence of 50 mM NaCl, 1.0 mM Ca^{2+} and 1.0 mM Mg^{2+}, respectively. Besides, Ca^{2+} was prone to cause membrane fouling than Mg^{2+}. Furthermore, fitting of multistage filtration models revealed that membrane fouling was ascribed to dynamic adsorption initially, followed by surface and pores deposition when filtrating BSA with or without Mg^{2+}. However, the modified membrane experienced reverse process with higher ionic strength or Ca^{2+} addition due to BSA molecular cluster. Moreover, the reduced repulsive energy induced by charge screening and calcium bridging resulted in slight aggravation of membrane fouling. Interestingly, the flux of PVDF-ZnO fouled membrane was easily recovered after physical cleaning. These findings provided deep insight into practical application of ALD modified membrane in wastewater remediation.

1. Introduction

Membrane technology is regarded as a promising strategy for water treatment due to its satisfactory separation efficiency and less land occupation [1,2]. Nevertheless, membrane fouling results in operation cost escalation and membrane lifespan reduction, which poses a major obstacle to the advancement of membrane-based water treatment technique [3]. In order to address this severe problem, effective measures should be taken to inhibit foulant deposition and accumulation for sustainable application of membranes in water purification.

The membrane surface properties such as hydrophilicity/hydrophobicity and charge potentials play significant roles in membrane fouling [4,5]. Thus, membrane modification was considered as an effective route to realize fouling alleviation by membrane functionalization. Thus far, great efforts have been devoted to membrane modification involving various physical and chemical approaches [6–8]. Because of the inhomogeneous distribution and instability of modified material as well as uncontrollable modification process, it is difficult to achieve widespread exploitation of traditional methods (e.g. blending modification, surface coating and chemical grafting) [9,10]. Instead, the emerging modification strategy of atomic layer deposition (ALD) integrated the outstanding advantages of precisely-controlled self-limitation and self-saturation [11,12]. The deposited layer was proved to be uniform and conformal, benefiting for improvement of membrane hydrophilicity and anti-fouling performance without sacrificing permeability [13]. For example, Wang et al. found that the ALD-TiO_2 modified polyvinylidene fluoride (PVDF) membrane exhibited two times enhancement of hydrophilicity and 25% anti-fouling improvement to BSA foulant [14]. It has been demonstrated that ALD is a desirable modification technique for membrane fouling mitigation.

In addition to membrane properties, the feed solution chemistry also contributes to membrane fouling significantly [15,16]. The membranes are commonly challenged with various foulants in the presence of co-existing anions and cations. The composition of feed solution such as ion strength of medium and co-existing ions have significant effects on membrane fouling [17]. The charge potential of foulant molecules and membrane surface would be altered in solution with different ion strengths [18]. This behavior affects the resistance of foulants when moving onto the membrane surface. Besides, cross-linking might be occurred between co-existing ions and foulant molecules, forming cake/gel layer on membrane surface and thus accelerating fouling process [19]. Since the antifouling property of ALD modified membrane

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was enhanced by improving hydrophilicity, systematic investigation of the anti-fouling behavior in various foulant media is indispensable to identify the practicability of ALD modified membrane. However, information regarding the effects of ion strength and co-existing cations on anti-fouling property of ALD modified membrane is still scarce. Moreover, the interaction between foulants and membrane surface has a central function in the initial fouling of filtration process [20]. This interaction is strongly correlated with irreversible adsorption of foulants [21], which can predict the fouling trend of ALD modified membrane. Knowledge in this respect is imperative to fundamentally understand the mechanism of membrane fouling alleviation. To the best of our knowledge, the cryptic mechanism governing filtration of diverse foulant media, typically the interactions between foulants and ALD modified membrane still remain unknown.

Herein, the commonly used PVDF microfiltration (MF) membrane in membrane bioreactor (MBR) was selected for hydrophilic modification by ALD. Zinc oxide (ZnO), as an effective material for fouling inhibition owing to its stable and hydrophilic nature, was applied for membrane modification. The protein was considered as the dominating contribution to membrane fouling in MBR [22]. The model protein foulant of bovine serum albumin (BSA) was widely utilized in previous literatures [23–25], which was also employed for fouling test in this study. The effects of solution characteristics on anti-fouling property of ALD-ZnO modified membrane were systematically investigated. The major focuses of this study were: (1) to study the filtration resistance of BSA foulant with various ion strengths and co-existing cations; (2) to determine the fouling patterns and trends of ALD-ZnO modified membrane; (3) to analyze the interaction energy between foulants and modified membrane for deep insight into the fouling mechanism; (4) to further investigate the anti-irreversible fouling property of the modified membrane in BSA system. This work provided valuable information for the practical application of ALD modified membrane in complex water media. The obtained results contributed to promote the ALD-based modification strategy in membrane water treatment process.

2. Materials and methods

2.1. Chemicals and materials

The commercial PVDF flat sheet membranes were purchased from Merck Millipore (US) (pore size 0.28 μm, diameter 47 mm). The diethyl zinc (DEZ) with purity of 99.9% was supplied by Aldrich and deionized (DI) water was produced using a DI water machine (XXA-I-10 T). High purity nitrogen (N_2, 99.9%) and nitrogen dioxide (NO_2, 99.9%) were brought from Liming Gas Co., Ltd. The bovine serum albumin (BSA, ≥98%) as a model foulant was provided by Sigma-Aldrich. Other common chemicals including HCl, NaOH, NaCl, KCl, $MgCl_2$ and $CaCl_2$ were analytical reagents and supplied by Shanghai Aladdin Bio-Chem Technology Co., LTD. All solutions were prepared using DI water as solvent.

2.2. Membrane modification process

Surface modification of the PVDF membrane was carried out in a professional ALD reactor (530, MNT Micro and Nanotech) via deposition of ZnO hydrophilic layer. This process consisted of membrane activation and subsequent hydrophilic modification. First, DEZ and NO_2 were applied as Zn and O precursors for surface functionalization. These two precursors were pulsed into the ALD chamber alternately and chemisorbed on PVDF membranes. The residual precursors and byproducts were purged away from the chamber at each cycle to realize pure deposition. After 10 cycles, the activation process finished with an ultrathin ZnO layer generated on membrane surface. Second, DEZ and DI water as Zn and O precursors were pulsed to the chamber for hydrophilic modification of the functionalized membrane. A certain thickness of ZnO layer was formed after repeating the deposition cycle. In accordance to preliminary experiment, the optimal ALD cycle number was identified as 100 to realize better performance of the modified membrane. Additional information regarding the modification process was presented in the supplementary material (SM).

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.apsusc.2018.08.009.

2.3. Characterization methods

The surface morphology of membranes was observed by field emission scanning electron microscopy (FESEM, HELIOS 600 NanoLab, US). Before observation, the membranes were coated with an ultrathin gold layer to enhance conductivity. Besides, in order to study the distribution status of deposited layer, elemental mapping of Zn and O was conducted on ZnO modified membrane. The membrane pore size was determined by a pore size analyzer (3H-2000PB, BeiShide Instrument, CHN). The water contact angle (WCA) was determined using an apparatus (OCA15, Dataphysics, Germany). The WAC images were captured by a video camera and further processed by the image analysis system. Two polar liquids (formamide and DI water) and one apolar liquid (diiodomethane) were employed in this process. Five different sites were randomly chosen on each sample for WAC measurement. The flux data was collected by a dead-end cell combined with an electronic balance and computer (Fig. S1). The transmembrane pressure (TMP) was fixed at 0.1 bar. Before data collection, the membrane sample was first compacted by DI water filtration for 60 min.

2.4. Fouling experiments

The fouling behavior of membranes was investigated by BSA filtration using the stirred dead-end cell. The TMP and stirring speed were maintained at 0.1 bar and 250 rmp. In this process, the DI water was applied for filtration during the first 60 min to compact the membrane. After that, 20 mg/L BSA solution with different NaCl concentrations and co-existing Ca^{2+} and Mg^{2+} were added into the filtration cup. The ionic strength was adjusted to 5 mM using NaCl solution during the study of membrane fouling with co-existing bivalent cations. The corresponding flux data were collected via the electronic balance and computer. The relative flux can be defined as J/J_0, where J and J_0 represent instantaneous and initial fluxes respectively. Several traditional blocking models including standard blocking, intermediate blocking, complete blocking and cake filtration were used to fit the flux data for understanding the fouling potential and patterns.

2.5. Successive filtration and membrane cleaning

Successive membrane filtration was also carried out using BSA solution with co-existing NaCl, Ca^{2+} and Mg^{2+}. The TMP and stirring speed were kept at 0.1 bar and 250 rmp respectively. The membrane was washed physically after collecting 300 mL filtrate, followed by another filtration cycle. The flux data were recorded by a balance combined with a computer. Membrane cleaning was performed to study the ability of flux recovery. The fouled membrane after one cycle of filtration was immersed in DI water for 3 h with rinsing for several times. Then the membrane was washed with DI water again for 5 min. Before next cycle of filtration, the membrane was compacted with DI water filtration for 60 min.

2.6. Membrane resistance and interaction energy calculation

The membrane resistance during BSA filtration was estimated based on Darcy's equation [26]. Besides, the interaction energy between foulant and modified membrane was evaluated according to Young equation and extended Derjaguin-Landau-Verwey-Overbeek (XDLVO) theory [27]. Detailed processes about membrane resistance and interaction energy calculation were summarized in SM.