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Biogenic silver nanoparticles (bio-Ag^0) decrease biofouling of bio-Ag^0/PES nanocomposite membranes

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ABSTRACT

Biofouling is a major problem for the application of membrane technology in water and wastewater treatment. One of the practical strategies to decrease biofouling is the use of advanced anti-biofouling membrane material. In this study, different amounts of biogenic silver nanoparticles (bio-Ag^0) were embedded in polyethersulfone (PES) membranes, using the phase-inversion method. The effects of the bio-Ag^0 content on the structure of the membrane and its filtration performance were systematically investigated. The results demonstrated that silver-containing nanostructures were uniformly distributed on membrane surface. Bio-Ag^0 incorporation slightly increased the hydrophilicity of the PES membrane and increased the permeate flux. The anti-bacterial and anti-biofouling properties of the bio-Ag^0/PES nanocomposites membrane were tested with pure cultures (*Escherichia coli* and *Pseudomonas aeruginosa*) and a mixed culture (an activated sludge bioreactor), respectively. The bio-Ag^0/PES composite membranes, even with the lowest content of biogenic silver (140 mg bio-Ag^0 m^{-2}), not only exhibited excellent anti-bacterial activity, but also prevented bacterial attachment to the membrane surface and decreased the biofilm formation during a 9 weeks test.

1. Introduction

The reliability and ease of operation of membrane-based water filtration systems have led to their increasing use in water and wastewater treatment. However, membrane fouling remains to be an inevitable obstacle in the membrane process causing deterioration of the membrane performance and consequently, higher operation and maintenance costs for cleaning and replacing (Drews, 2010). Membrane fouling can be defined as the undesirable deposition of retained particles, colloids, macromolecules, salts, etc. at the membrane surface or at the pore wall inside the pores (Rana and Matsuura, 2010). From the viewpoint of fouling components, the fouling can be classified into three major categories: biofouling, organic fouling, and inorganic fouling (Paul et al., 2010). Among them, biofouling is the most complicated one which seriously hampers the application of membrane processes. Biofouling results from the accumulation of assimilable organics, biofilm formation and regrowth of microorganisms on the membrane surface (Hilal et al., 2004; Yang et al., 2009). Biofouling is difficult to eliminate because microbes are able to grow and multiply rapidly, even at low nutrient concentrations (Paul et al., 2010). Biofouling has a significant impact on decreasing the membrane flux, deteriorating the membrane structure, and increasing salt passage (Schneider et al., 2005). Hence, developing anti-fouling membrane materials has become the focus of many academic studies and industrial research since the early

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1960s, when industrial membrane separation processes emerged.

Recently, the combination of polymeric materials with biocides has attained much attention in membrane fabrication (Paul et al., 2010). Silver compounds and silver ions have been known to exhibit strong inhibitory and bactericidal effects as well as a broad spectrum of anti-microbial activities for a long time (Choi et al., 2008; Kim et al., 2008; Marius et al., 2011; Samberg et al., 2011). Due to their effective anti-bacterial properties and low toxicity toward mammalian cells (Choi et al., 2008), silver nanoparticles have become a typical example of biocides that are used for fouling mitigation in polymeric membranes. As reported by Zodrow et al. (2009) and Taurozzi et al. (2008), flat sheet porous polysulfone–silver nanocomposite membranes were synthesized by the wet phase-inversion method. All the membranes exhibited anti-bacterial activity against *Escherichia coli*, *Pseudomonas aeruginosa* and showed improved biofouling resistance and virus removal as well. Zhu and co-workers reported on the immobilization of ionic or reduced silver onto the chitosan membrane surface for better anti-biofouling performance (Zhu et al., 2010). The RO membrane and spacer were modified by a simple nanosilver-coating process (Yang et al., 2009), and performed better than the unmodified membrane and spacer, in terms of much slower decrease in permeate flux and total dissolved solids rejection, and also improved anti-microbial activity. Besides, silver filled polyethersulfone (Basri et al., 2010, 2011; Cao et al., 2010; Huang et al., 2012), polyimide (Deng et al., 2008), polyamide (Lee et al., 2007), polyacrylonitrile (PAN) (Yu et al., 2003), cellulose acetate (CA) (Barud et al., 2011; Chou et al., 2005) and chitosan (Liu et al., 2010; Zhu et al., 2010) composite membranes have also been fabricated.

Many methods exist to synthesize silver nanoparticles and chemical reduction methods are most commonly used (Jiang et al., 2006). However, chemically produced silver nanoparticles often have problems with particle stability and tend to aggregate at high concentration or when the average particle size is less than 40 nm (Mafune et al., 2000). In addition, there is a demand for more environment-friendly production methods in nanotechnology. To cope with these demands, biological processes have been developed using microorganisms.

Recently, lactic acid bacteria have been used as reducing and capping agent for the rapid, non-enzymatic, and extracellular production of nanoscale-sized Ag^0 particles (Sintubin et al., 2009). The association of the nanoparticles with the dead bacterial carrier matrix, called biogenic Ag^0 (bio-Ag^0), prevents them from aggregating, which is an advantage over chemically produced nanoparticles. De Gusseme et al. (2010) used biog-Ag^0 for disinfection of drinking water contaminated with enteric viruses (De Gusseme et al., 2010), and they later incorporated bio-Ag^0 into PVDF membranes as antiviral agent (De Gusseme et al., 2011). Both bio-Ag^0 in suspensions and the composite membranes with bio-Ag^0 showed improved antiviral activity and can be applied for the treatment of contaminated drinking water. However, there is little information on the impact of the silver content on the performance of bio-Ag^0/PVDF composite membranes in more complex conditions. It should be noted that the previous experiments were performed in a clean matrix (drinking water) (De Gusseme et al., 2011), which is far from the conditions of industrial application. In order to thoroughly examine biofouling, the more complex situation in membrane bioreactors should be considered. Moreover, the theoretical maximum silver content in the membranes for drinking water disinfection ranged from 250 mg bio-Ag^0 m^{-2} to 2500 mg bio-Ag^0 m^{-2}. Because of the high price of silver, the reported high content constitutes a major challenge for commercialization. Inevitably, lower silver contents and thus lower costs must be achieved for further application.

In this study, the anti-biofouling characteristics of PES ultrafiltration membranes embedded with bio-Ag^0 as anti-microbial agent were investigated. Polyethersulfone is one of the most attractive polymeric materials because of its outstanding thermal tolerance, chemical stability, oxidation resistance and mechanical characteristics (Abu Seman et al., 2009; Cao et al., 2010; Zhao et al., 2011). It was hypothesized that there might exist an optimal content of bio-Ag^0 to achieve good performances with lower costs. The effect of different contents of bio-Ag^0 on the permeate flux and anti-biofouling properties was systematically investigated. The anti-bacterial effect, the anti-adhesion properties and the consequent biofilm formation were examined in order to find an optimal condition for the bio-Ag^0/PES composite membranes. Furthermore, water contact angle measurements, SEM and TGA analyses and silver leaching tests were also carried out to investigate the membrane surface morphology, its structure and the stability of silver in the membrane.

2. Experiment

2.1. Materials

Polyethersulfone (PES, Ultrason E6020P, MW = 52,000 g mol^{-1}) was purchased from BASF. PES was dried at 120 °C overnight in a vacuum oven prior to dope preparation. N,N-Dimethylacetamide (DMAC) was obtained from Shanghai Jinshan Jingwei Chemical Co., Ltd and silver nitrate ($AgNO_3$, analytical grade) was purchased from Shanghai Shenbo Chemical Co., Ltd. Ammonia solution (analytical grade), silver standard solution (1000 mg L^{-1}) were supplied by Sinopharm Chemical Reagent Co., Ltd. The ultrapure water used in all experiments was supplied by a Milli-Q system (Millipore Corp., USA). The standard constituents of the Luria-Bertani medium and agar plates used for bacteria incubation were purchased from Oxoid.Ltd.

2.2. Synthesis of biogenic silver

Bio-Ag^0 was synthesized with *Lactobacillus fermentum* LMG 8900 (LMG culture collection, Ghent University, Belgium), provided by the Laboratory of Microbial Ecology and Technology (LabMET), Ghent University, according to Sintubin et al. (2009). *L. fermentum* biomass was harvested by centrifugation and washed three times with Milli-Q water. Subsequently, biomass was resuspended in Milli-Q and the OD_{600} was adjusted to obtain 5 g L^{-1} cell dry weight (CDW). Diamine silver complex was added to the alkalified biomass (pH 11.5) in