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Nanostructured mesoporous carbon polyethersulfone composite ultrafiltration membrane with significantly low protein adsorption and bacterial adhesion

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ABSTRACT

A novel polyethersulfone (PES) ultrafiltration membrane containing 0.05–2.00 wt% of synthesized mesoporous carbon nanoparticles (MCNs) was prepared via the phase inversion technique. The structures and properties of MCNs were characterized using a variety of analytic techniques. The MCNs showed the surface area of 1396.8 m^2/g and the highest pore size of around 1 nm. The effect of incorporation of MCNs on the composite membrane morphology and performance was investigated through pure water flux, protein adsorption, and bacterial adhesion resistance tests. The membrane's anti-fouling performances were determined under constant-pressure operation at 100 kPa in a dead-end module. The as-prepared nanocomposite membranes were also studied in terms of morphology, structure and surface chemistry. Generally, the incorporation of MCNs into the polymeric membrane improved the pure water flux. The composite membrane containing 0.20 wt% MCNs exhibited the highest antifouling, protein adsorption resistance, and bacterial attachment inhibition property. The incorporation of the MCNs into the membranes introduces a different strategy of inhibiting biomolecule adsorption and bacterial attachment to the membrane surface, instead of killing the bacteria which may lead to more severe membrane fouling by the intracellular substances.

1. Introduction

Polymer membrane based filtration process has been widely applied for water and wastewater treatment [1]. One of the key issues in membrane-assisted separation processes is the membrane fouling, especially the formation of biofilm and biofouling. Biofilm is developed by the gradual bacterial deposition and proliferation on the membrane surface, and it would significantly reduce the membrane permeability [2–4]. As a result, it is crucial to control both the initial attachment of bacteria and the subsequent growth on the membrane surface.

Enabling the membrane surface bacteriostatic properties via surface modification has been regarded as an effective approach to inhibit the growth of microorganisms. A promising solution is to integrate antibacterial agent into polymer membrane matrix to suppress the bacterial colonization. This can be achieved via blending, dip-coating, grafting and interfacial polymerization process [5–7]. The most extensively studied antibacterial agent is silver nanoparticles [8]. The Ag-polymer composite membranes usually exhibit satisfactory initial antibacterial efficiency [9]. However, due to the poor interfacial affinity between the Ag and polymer membrane, the gradual detachment of the inorganic nanoparticles would lead to the loss of antimicrobial efficiency of the membrane, especially during the membrane filtration process when excessive shear force is applied [10]. Leaching and dissolution over time are also frequent issues. To solve this problem, the

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inorganic nanoparticles or polymer membranes need to be modified to improve their interfacial compatibility. However, this makes the membrane fabrication process more complex and could lead to the loss of antibacterial efficiency of the inorganic nanoparticles.

Titania nanoparticles also have been used to render membranes antibacterial characteristics [11]. The focus is to apply the UV irradiation for photocatalytic degradation of the foulants prior to their attachment to the membrane surface. Although UV-assisted TiO_2 nanocomposite membranes have shown certain potential to prevent biofouling, it is not attractive by industry due to the difficulty of providing UV light inside membrane modules with high packing densities. As a result, it is ideal to prepare antibacterial membranes with the materials that are inexpensive and naturally compatible with the polymer matrix, thus can be adapted for large-scale industrial applications. Another important aspect of the antibacterial membrane is the long-term operational stability. Even though bacteria can be killed when contacting with the antibacterial membrane surface, the release of the intracellular substances from dead cells still have high tendency to foul the membrane, and the fouling layer would provide an ideal substrate for further bacterial colonization. It will eventually lead to a more severe membrane fouling [12]. As a result, providing the membrane surface an anti-adhesion property to prevent the initial attachment of the microorganisms seems to be a more effective approach than the antimicrobial method which aims at killing bacteria already attached to the membrane surface. The design of the anti-biofouling membrane should be accompanied by the consideration of membrane antifouling properties (e.g. protein fouling). However, the synergy between anti-adhesion and antimicrobial coatings has not been as well-studied to date.

Recently, the carbon-based antibacterial agents, like carbon nanotubes (CNT), graphene oxide (GO), hollow carbon sphere and mesoporous carbon, have attracted increasing attention for desalination [13], water treatment and purification [14,15], and antibacterial agents [3,16,17]. These materials possess unique structural and electronic properties: the nanoscale edges of the carbon-based materials can protrude through the bacterial cellular membranes, and the formation of superoxide anion could further react with the bacteria to damage its integrity. More importantly, these materials can be easily combined with various polymeric materials for nanocomposite membrane preparation due to their good interfacial compatibility [18]. The resultant membranes usually possess improved performances, such as better antifouling performance, higher water flux, and improved salt rejection [3]. As a result, the carbon-based materials are promising candidates to prepare the highly efficient membranes with good anti-biofouling performance. So far, CNT and GO have been extensively investigated for this purpose. However, the potential of mesoporous carbon nanoparticles (MCN) has not been explored to prepare the antibacterial membranes. Its large surface area could ensure good contact with bacteria for highly efficient antibacterial performance. Comparing to GO and CNTs, the high specific surface area (SSA) of MCN makes it a very efficient candidate for preparing mixed matrix membranes. In addition, due to the simplicity of synthesis of MCN, the vast variety of micro/macro and mesoporous carbon with different SSA, pore size and size distribution already have been industrialized in mass production scale. Financially, MCN is a better nominee as a filler for scaling up the procedure of fabrication mixed matrix membrane rather than CNT and GO, considering the promising results which had been reported. Moreover, its hydrophilicity could potentially promote the membrane antifouling behavior. In order to create the desired anti-adhesion characteristics such as prevent bacterial attachment and biofilm formation on a surface, the physicochemical properties of the surfaces should be carefully regulated, as the protein adsorption and cell adhesion can behave differently on such surfaces. Introducing a hydrophilic surface with nanoscale roughness may lead to an anti-biofouling membrane [19].

In this work, polyethersulfone (PES) was applied for ultrafiltration membrane preparation. PES is commonly used to prepare microfiltration [20], ultrafiltration [21] as well as nanofiltration [22] membranes. Its wide application is a result of good chemical and thermal resistance, easy processing and environmental stability [21,23,24]. MCNs particles were blended into PES membrane matrix to promote its antibacterial attachment properties. The blending process is applied as it is the most feasible approach for large scale membrane fabrication. Different MCN loadings into PES membranes were compared in terms of membrane structure, surface morphology, and filtration performance. Membrane surface antifouling properties are crucial for the preparation of the long-term anti-biofouling membrane. It is well-known that if a surface shows protein adsorption resistance it frequently shows resistance to bacterial attachment and biofilm formation [25]. Hence, the protein adsorption and biofilm formation resistance of the nanocomposite membranes were investigated to provide a better understanding of the effect of MCN on membrane anti-biofouling performance.

2. Experimental

2.1. Materials

Polyethersulfone (PES; Ultrason E6020P, 51 kDa) was purchased from BASF Co. Ltd., Germany for membrane matrix preparation. Polyvinylpyrolidone (PVP; 40 kDa), *N*-methyl-2-pyrrolidone (NMP) was provided by Merck, and bovine serum albumin (BSA; 66 kDa) was purchased from Sigma-Aldrich. Sodium dihydrogen phosphate, sulfuric acid, disodium hydrogen phosphate, nutrient broth (NB) bacterial culture media and Coomassie Blue g-350 were purchased from Sigma-Aldrich (Germany). Sodium hydroxide (NaOH) pellets, ethanol 85%, hydrochloric acid, sucrose, hydrofluoric acid, zeolite 4A, and phosphoric acid were purchased from Merck, Germany. Potassium nitrate (KNO_3) pellets were purchased from Merck Millipore. Davicat SI-1403 silica powder was supplied by Grace-Davison and Mesoporous Silica MSU was in-house synthesized. Three strains of bacteria containing *Staphylococcus epidermidis* ATCC 35984, *Pseudomonas aeruginosa* PAO1, *Staphylococcus aureus* ATCC 25923 as biofilm former were provided from a local provider. All other chemicals were of the highest purity and used without further purification.

2.2. Synthesis of mesoporous carbon

The mesoporous carbon was in-house synthesized through the following procedures [17–19]. Briefly, a 50 ml aqueous solution of sucrose (approximately 10 g) containing 1 g of the template (industrial silica powder) and 50 μl of concentrated sulfuric acid (99.99%) as a catalyst was prepared. After stirring for 24 h at 70 °C, the suspension polymerization of resulting gel has been performed at 100 °C for 3 h followed by another 3 h treatment at 160 °C. The powdery material obtained was placed in a tubular furnace and heated at 700 °C for 3 h under N_2 atmosphere (by the flow rate of 100 mL/min). The gas flow rate was 350 mL/min and the initial heating rate of samples was 5 °C min^{-1}. The resulted sample was washed with a mixture of 30 vol % of hydrochloric acid and 70% of hydrofluoric acid to remove the templates. Finally, the sample was activated with the water steam (by the flow rate of 200 mL/min) at 550 °C for 45 min. The treatment with concentrated acid would increase the hydrophilicity by introducing carboxyl groups on the MCN surface [20].