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Preparation of anti-adhesion and bacterial destructive polymeric ultrafiltration membranes using modified mesoporous carbon

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ABSTRACT

Satisfactory ultra-high biofilm formation resistant polymeric interfaces have yet to be realized. A new application of mesoporous carbon (MPC) via the loading of silver nanoparticles into its matrix was successfully introduced for the fabrication of biofouling resistant polyethersulfone ultrafiltration membranes. MPC not only solved the silver nanoparticle detachment issue, as the most significant scaling up challenge of new materials modified by silver, but it also led to an anti-adhesion interfacial layer for microorganisms. The effect of the incorporation of MPC on biofouling mitigation and the performance of the composite membranes was examined through bacterial adhesion resistance. The composite membrane containing the optimized 0.20 wt% MPC doped with an Ag ratio of 1:99 (w/w) easily dispatched microorganisms. Bacterial attachment on the membrane surface was reduced dramatically. Furthermore, the remaining attached bacterial cells were dealt with via the bactericidal properties of the silver nanoparticles, up to 93%. Rendering of the flow cytometry results showed that MPC amplified the effect of the negligible amount of Ag (0.002 wt% of the membrane) and induced apparent bacterial damage of *Bacillus subtilis* (92.94%) and *Escherichia coli* (93.21%). The polymeric mixed matrix membrane entirely mitigated biofouling over 99% by the combination of the bactericidal effect of silver and the anti-adhesion properties of MPC.

1. Introduction

Polymeric membrane-based filtration processes have been widely applied for water treatment [1]. Membrane fouling is one of the most critical issues in membrane-assisted separation processes. The operating condition optimization has an enormous impact on membrane fouling alleviation [2,3]. A well-designed pre-treatment section with in time backwashing and chemical cleaning can be used to optimize the lifespan of the membranes and minimize the extra operational costs [4]. However, the initial investment of such a professional water purification system is invariably escalated and must be operated by experienced technicians. The most crucial fouling type, including organic [5,6], scaling, biofouling [7] and colloidal [8], in membrane science is biofouling (biofilm formation and subsequently biofouling). Biofilms are developed by the gradual deposition and proliferation of bacteria, whether dead or alive, on the membrane surface [9]. Biofilms significantly reduce the membrane permeability. Hence, it is vital to alleviate both the primary attachment of bacteria and the subsequent growth on the membrane surface.

Biofilm formation rapidly enhances the energy consumption and consequently, permeates the cost of the biofouled membrane. The fabrication of mixed matrix membranes (MMMs) has been successfully accomplished via two- and three-dimensional [10,11] inorganic materials [12–14]. In the last decade, the study of biofouling mitigation of polymeric membranes has been performed by means of blending, grafting, coating [15] and electrospinning [16]. The spread of polymeric membrane applications for water and wastewater treatment has led to several types of research to minimize the challenges, such as biofouling and maximizing the advantages [17]. As previously mentioned, biofouling alleviation solutions can be divided into modifications of membranes and the process control. Considering the low compactness of membrane modules that are photocatalytically modified, appropriate membrane modification remedies act via two core functions, antibacterial, and anti-adhesion. The former can be addressed by enabling bacteriostatic features by adding silver nanoparticles, a topic that has been broadly studied. Silver composite membranes usually exhibit satisfactory primary antibacterial efficiency [18]. However, their weak interfacial affinity with polymer causes gradual detachment of the inorganic nanoparticles and a loss in antimicrobial ability, and more importantly, it could also cause secondary

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contamination [19], particularly during the industrial membrane filtration process where excessive shear force is applied.

To solve this problem, the inorganic nanoparticles or polymeric membranes need to be modified to improve their interfacial compatibility. For rendering antibacterial characteristics, titania nanoparticles also have been widely used [20]. However, the low packing densities for applying ultraviolet irradiation for photocatalytic degradation of the foulants before their attachment to the membrane surface is not favorable for the industry. As a result, it is ideal to prepare high membrane packing densities with antibacterial materials that are highly compatible with the polymer matrix and thus can be adapted for long-term operational stability. In summary, providing a membrane surface with an anti-adhesion property to prevent the initial attachment of microorganisms can be a more effective approach than the antimicrobial method alone. Therefore, the design of a membrane that benefits from both anti-adhesion and antibacterial properties is in high demand and is the subject of this work.

Carbon-based materials, such as graphene oxide (GO), nanoporous carbon [21], carbon nanotubes (CNTs) and hollow carbon spheres, have attracted increasing attention for desalination [22], water treatment and purification, and as antibacterial agents [23]. Moreover, these materials can be easily combined with various polymeric materials for nanocomposite membrane preparation due to their excellent interfacial compatibility [24]. These MMM membranes have improved performances, such as better bacterial adhesion resistance, higher water flux and improved salt rejection [25,26]. Accordingly, carbon-based materials are promising candidates to prepare highly efficient membranes with low bacterial attachment. Formerly, CNTs and GO have been investigated for synergetic antibacterial effects [27,28]. However, the potential of modified mesoporous carbon (MPC) has not been studied for the preparation of antibacterial membranes. In comparison to GO and CNTs, the higher specific surface area of MPC not only makes it a highly efficient candidate for making MMMs with a stable affinity, but it also develops a desirable space for doping other nanoparticles to produce a multifunctional filler [29]. Likewise, due to the simplicity of MPC synthesis, a vast variety of micro, macro and mesoporous carbons with different specific surface areas, pore sizes, and size distributions have already been industrialized on a mass production scale. MPC provides anti-adhesion characteristics to prevent bacterial attachment and subsequently biofilm formation on the surface. Moreover, the Ag dopants will damage the probable microorganisms to create a synergy between the anti-adhesion and antimicrobial effects of Ag-doped mesoporous carbon poly(ether sulfone) (PES) ultrafiltration (UF) membrane, in addition to the long-lasting antibacterial effectiveness [30,31].

This study focused on the biofouling alleviation of fabricated and characterized MPCAg blended flat sheet membranes. MPCAg was blended into a PES UF membrane matrix to enhance its antibacterial properties and resistance to bacterial adhesion attachment. Different Ag loadings into the highly biofouling resistant MPC amount of 0.2%, which was well defined in our recent research as an anti-biofilm adhesion membrane filler [32], were compared with regards to membrane structure, surface morphology, and filtration performance. Furthermore, the protein adsorption and biofilm formation resistance of the nanocomposite membranes were investigated via static bovine serum albumin (BSA) adsorption and flow cytometry, respectively, to provide a better understanding of the effect of the dopant on membrane biofouling mitigation.

2. Experimental section

2.1. Materials

To prepare the doped MPC (20–40 mesh), MPC was bought from Supelco, Inc., USA, and silver nanopowder (< 100 nm) was purchased from Sigma–Aldrich (CAS No.: 7440-22-4). The membrane matrix preparation, performed via PES (Radel A-300, 51 kiloDalton [kDa]), was provided by Solvay Advanced Polymers, LLC., USA. Polyvinylpyrrolidone (PVP) (40 kDa) and *N*-methyl-2-pyrrolidone (NMP) were procured from Merck. Two different strains of bacteria as biofilm formers, *Bacillus subtilis* 168 (B168) and *Escherichia coli* DH5 alpha (DH5α), were purchased from Shanghai Seebio Biotech, Inc. (Shanghai, China). All other chemicals, namely, ethanol, glycerin and deionized water, were of the highest purity and were commonly used without additional purification and enrichment procedures.

2.2. Preparation of Ag-doped MPC

Concisely, to prepare the Ag-doped MPC, PVP coated silver nanoparticles (1 mg/mL) were vigorously stirred in methanol for 72 h and intermittently dispersed by shearing, sonication, and probe sonication. Subsequently, the addition of MPC to the diluted (0.1 mg/mL) and redispersed Ag suspension was performed to attain five different ratios of 1:99, 3:97, 5:95, 10:90, and 30:70% (w/w) under ultrasonic mixing for 30 min to obtain a homogeneous black suspension. This procedure was followed by stirring in the absence of direct light for 24 h. As discussed, the weight ratio of Ag to MPC was controlled to be 1%, 3%, 5%, 10%, or 30%, and the obtained samples were labeled as MPCAg1, MPCAg3, MPCAg5, MPCAg10, and MPCAg30, respectively. The Ag-impregnated samples were dried into powder in a rotatory evaporator for 2 h under an air atmosphere at 100 °C, followed by 30 min of drying under a vacuum at the same temperature. Finally, the as-prepared MPCAg fillers have formed a suspension in 2 g NMP and was mixed with a honey-like PES solution.

2.3. Preparation of membranes

The PES membrane was made of 16 wt% PES, 4 wt% PVP and 80 wt% NMP as the solvent. The nanocomposite membrane compositions are given in Table 1. Six different concentrations of AgMPC (0, 1, 3, 5, 10 and 30 wt%) were incorporated into the PES membrane (as presented in Fig. A.1) for manufacturing the composite membrane containing 0.20 wt% MPC (hereafter referred to as PES MPC), to understand the effect of Ag on enhancing the PES MPC membrane performance. Virgin PES, PES MPC and PES MPCAg membranes made via wet phase inversion technique.

2.4. Characterization

The surface and cross-sectional morphology of PES MPCAg samples and particles were characterized with field-emission scanning electron microscopy (FESEM, Hitachi S-4800). Moreover, atomic force microscopy (AFM, Bruker, Dimension Icon equipped with ScanAsyst) was used to illustrate the surface roughness and morphology of the membranes, which were divided into 5 mm × 5 mm sections in tapping-mode. Ag-doped MPC samples were examined with X-ray diffraction (XRD, Rigaku, Smartlab-9KW) using Cu Kα radiation in the range of 2–90° with an increment of 0.5° at room temperature. JEM-2010 HR JEOL high-resolution transmission electron microscopy (HRTEM) was

Table 1
Compositions of casting solutions for PES, PES MPC, and PES MPCAg nanocomposite membranes.

Samples	PES (wt%)	PVP (wt%)	NMP (wt%)	MPC (wt%)	Ag (wt%)
PES virgin	16.00	4.00	80.00	0.00	0.00
PES MPC	16.00	4.00	79.80	0.20	0.00
PES MPCAg1	16.00	4.00	79.80	0.20	0.002
PES MPCAg3	16.00	4.00	79.80	0.20	0.006
PES MPCAg5	16.00	4.00	79.79	0.20	0.01
PES MPCAg10	16.00	4.00	79.78	0.20	0.02
PES MPCAg30	16.00	4.00	79.74	0.20	0.06