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Regular Article

Versatile polyvinylidene fluoride hybrid ultrafiltration membranes with superior antifouling, antibacterial and self-cleaning properties for water treatment

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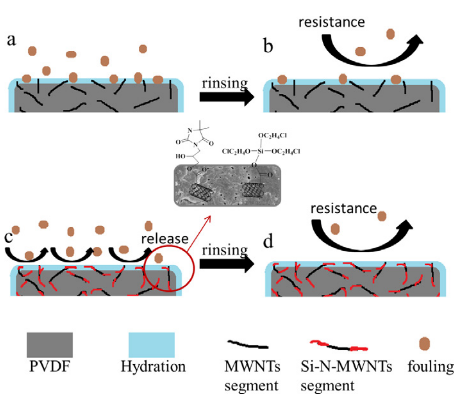
GRAPHICAL ABSTRACT



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ABSTRACT

Novel ultrafiltration membranes with both superior antibacterial and self-cleaning properties were fabricated. By using a non-solvent induced phase separation method (NIPS), N-halamine epoxide and siloxane were grafted onto the multi-walled carbon nanotubes (N-Si-MWNTs) to fabricate polyvinylidene fluoride (PVDF) hybrid membranes. The membrane morphology was observed under a field emission scanning electron microscopy. The results demonstrated that the PVDF hybrid membranes had an asymmetrical structure, and their hydraulic permeability was evidently enhanced with the addition of modified MWNTs. When compared with the primitive PVDF membrane, the hybrid membranes presented improved surface hydrophilicity. After three ultrafiltration–regeneration cycles with bovine serum albumin as model biofoulant and pure water as detergent, the PVDF hybrid membranes exhibited a high flux recovery ratio (FRR). Furthermore, when compared with other membranes, the membrane containing N-Si-MWNTs displayed the highest FRR value of above 96.5% after the entire fouling and cleaning experiment. The fabricated PVDF/N-Si-MWNTs hybrid membranes had excellent antibacterial efficacy, presenting maximum antibacterial efficacy of 98.0% and 95.6% against *Staphylococcus aureus* and *Escherichia coli*, respectively. Thus, the PVDF/N-Si-MWNTs membranes fabricated in this study are environment-friendly with both benign antibacterial and self-cleaning properties.

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Nomenclature

ω_1	wet weights of the membrane
ω_2	dry weights of the membrane
l	the membrane thickness (m)
d_w	the water density (0.998 g/cm^3)
R	the solute rejection rate (%)
C_p	the concentrations of permeate (g/L)
C_F	the concentrations of feed solutions (g/L)
Q	volumetric flow rate (m^3)
a	valid membrane area (m^2)
J_{BSA}	BSA aqueous solution permeation flux (m/s)
J_R	water flux of cleaned membrane after each cycle (m/s)
J_w	initial pure water flux (m/s)
FRR	pure water flux recovery ratio
PWP	pure water permeation (L m^{-2}bar^{-1} h^{-1})
J	membrane permeation flux in filtration process (m/s)
ΔP	trans-membrane pressure (bar)
μ	filtrate viscosity (Pa S)
R_t	total permeation resistance of membrane (m^{-1})
R_m	intrinsic membrane resistance (m^{-1})
R_r	irreversible resistance (m^{-1})
R_{ir}	reversible resistance (m^{-1})
N	the normality of the consumed NaS_2O_3 in the titration (equiv. L^{-1})
V	the volume of the consumed NaS_2O_3 in the titration (L)
W	the weight of membrane sample (g)
E	sterilization ratio (%)
A	the number of visible bacterial colonies contacting with membrane
B	the number of visible bacterial colonies without contacting membrane

1. Introduction

Ultrafiltration technology has been widely used as an effective approach for applications in drinking water treatment and waste water drainage and reuse treatment. However, membrane fouling, including biofouling and organic fouling, decreases the ultrafiltration efficiency and shortens membrane life. Therefore, membrane surfaces with both superior antibacterial and self-cleaning properties are the most attractive owing to their long-standing diverse functions. Moreover, fabrication of novel membranes based on these features would promote surface-governed or surface-based technologies for industrial, medical, environmental, and marine applications. The key to achieve superior antibacterial and self-cleaning properties is to design rational material and prepare homologous membranes [1,2]. Currently, antibacterial and self-cleaning properties are often achieved separately. While modified multi-walled carbon nanotubes (MWNTs), metal nanoparticles, and, particularly, amphiphilic nanofillers have been widely used to fabricate antibacterial membranes [3–5], hydrophilic antifouling surfaces and hydrophobic self-cleaning surfaces have been utilized to develop low-fouling and non-fouling surfaces [6].

Various approaches have been employed to fabricate antifouling and self-cleaning membranes. For example, zwitterionic monomer ([3-(methacryloylamino)propyl]-dimethyl(3-sulfopropyl) ammonium hydroxide inner salt) and side-chain fluorinated methacrylate monomer with sodium dodecyl sulfate (SDS) as emulsifier were used to prepare amphiphilic copolymers via aqueous phase emulsion polymerization, and the product was used as an additive to fabricate antifouling and self-cleaning membranes. The permeation flux recovery of the resultant membranes reached nearly 100% [6]. In another study, hydrophilic poly (ethylene oxide) (PEO) and polydimethylsiloxane (PDMS) segments were constructed via free-radical polymerization. The resultant fabricated membranes presented antifouling and self-cleaning properties, and also exhibited a visible decline in irreversible and reversible flux and complete retention of permeation flux recovery [7].

Nowadays, polyvinylidene fluoride (PVDF) is widely used for the development of ultrafiltration membrane owing to its good chemical resistance, thermal and hydrolytic stability, and mechanical strength. However, its hydrophobicity often leads to organic fouling and biofouling. Several nanofillers such as aluminum oxide, titanium dioxide nanoparticles, zinc oxide, silicon oxide, and silver nanoparticles have been utilized to modify PVDF membranes [8–16], and have presented positive effects on membrane properties. In recent years, MWNTs have been considerably used in modifying membranes because of their outstanding properties such as high specific area, prominent mechanical properties, and workability [17–20]. Nevertheless, crude MWNTs are difficult to disperse in casting solution owing to electrostatic influence, and opportune chemical modifications have been used to overcome this limitation. Strong acid has been commonly utilized to oxidize MWNTs and increase their dispersion and workability [21–24].

Currently, metal ions, quaternary ammonium salts, and N-halamines are widely employed to fabricate antimicrobial membranes. Among them, N-halamines are outstanding antibacterial agents owing to their excellent stability, biocidal efficacy, low toxicity, low corrosion of surfaces, and relatively economical properties [25–28]. Several tethering, grafting, and polymerization methods have been employed to anchor the antibacterial N-halamine moieties to membrane surfaces [4]. In general, chemical cleaning is commonly used to regenerate fouled membranes. Although chemical cleaning usually achieves a relatively high pure water flux recovery ratio (FRR), it destroys membrane properties and structure. Membrane cleaning with pure water alone may not achieve the desired FRR, and low surface energy architecture is generally employed in self-cleaning surfaces. For instance, hydrophobic polymers such as silicone-based and fluorinated polymers have been widely used through coating or grafting [29–31]. The mechanism of self-cleaning is to prevent the deposition and adsorption of foulants. As low surface energy architecture could decrease the interaction between membrane surfaces and foulants, the foulants could be rinsed using low water pressure, which has been generally recorded as fouling release [2,32,33]. Some of the recent representative studies on antifouling, self-cleaning, or antibacterial membranes are summarized in Table 1.

In the present study, novel PVDF ultrafiltration membranes simultaneously possessing antifouling, antibacterial, and self-cleaning properties were fabricated. In brief, MWNTs were oxidized by nitric acid steam (O-MWNTs), grafted with N-halamine and siloxane (N-Si-MWNTs), and used as nanofillers to fabricate PVDF hybrid membranes by non-solvent induced phase separation method (NIPS). Addition of N-halamine (derived from 5, 5-dimethylhydantoin) and siloxane ensured both antibacterial and self-cleaning properties. The effects of N-Si-MWNTs addition on the morphology, permeation, antibacterial performance, and self-cleaning efficiency of the final fabricated membranes were studied. To confirm the self-cleaning property of the resultant membranes, deionized water was used to rinse the fouled membranes. The bacteriostatic rates of the fabricated membranes were evaluated