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Preparation and characterization of SLS-CNT/PES ultrafiltration membrane with antifouling and antibacterial properties

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ABSTRACT

Carbon nanotubes (CNTs) were functionalized by a simple non-covalent modification with sodium lignosulfonate (SLS), and the hybrid polyethersulfone (PES) ultrafiltration membranes were prepared by phase inversion method with different ratios of functionalized carbon nanotubes (f-CNTs). SEM analysis indicated that obvious finger-like pores appeared in f-CNT/PES hybrid membranes. The f-CNTs were uniformly dispersed on the membrane surface, causing super hydrophilicity and high water flux of the f-CNT/PES hybrid membranes. Filtration and protein adsorption tests indicated that the antifouling performances were dramatically increased, the amount of protein pollutants adsorbed by the hybrid membranes was significantly lower than the nascent membranes, and most of the water flux can be recovered after three cycles of the BSA solution fouling process. The antibacterial tests confirmed that no prepared membranes showed excellent antibacterial properties to Escherichia coli (*E. coli*). However, the hybrid membrane showed good antibacterial properties treated with a low-voltage electric field (direct current (DC), about 1.5 V cm^{-1}), and the antibacterial rate (AR) closed to 100% after testing for 3 h.

1. Introduction

Ultrafiltration is widely used for the purification of natural waters and wastewaters. Usually, the pre-treatment of seawater and the drilling reuse of shale-gas produced water both need ultrafiltration technology [1–3]. At present, most ultrafiltration membranes are made from hydrophobic membrane materials such as polyethersulfone (PES), polyvinylidene fluoride (PVDF) and polysulfone (PSF) [4–7].

PES is a kind of commonly used ultrafiltration membrane material, because of its thermal stability and mechanical strength and other valuable performances [8,9]. However, the hydrophobic surface and many pores of PES membranes are very easy to adsorb organic pollutants in the water resulting in the membrane fouling. Membrane fouling is widely found as a big challenge in the practical application of ultrafiltration membranes [10]. Membrane fouling involves reversible and irreversible fouling, decreasing the irreversible fouling is an effective way to ameliorate the antifouling properties [11]. There have been some excellent research in improving the antifouling performance of PES membranes [12,13]. In general, improving surface hydrophilicity is effective for enhancing the antifouling ability of ultrafiltration membranes, among these methods, blending with hydrophilic nanoparticles is considered being an excellent method [10,14,15]. Arsuaga et al. modified the PES membrane with the nanoparticles of TiO_2, Al_2O_3 and ZrO_2, and found the continuously stable flux and antifouling properties of the modified membranes [16]. Arumugham et al. fabricated the nano MgO/sulfonated polyphenyl sulfone (SPPSU)/polyphenyl sulfone (PPSU) membranes for oil removal from water, they found that the ultrafiltration membrane produced a greater antifouling ability [17]. Zinadini et al. prepared the grapheme oxide (GO)/PES nanofiltration membrane and found that the membrane had super antibiofouling property and reusability [18].

Furthermore, bio-fouling is another problem that hinders the development of ultrafiltration membranes [19,20]. There have been many studies on antibacterial membranes [21,22]. Among these studies, the membranes containing Ag or its ionic state have long been known to own antibacterial properties. Ihsanullah et al. synthesized silver-doped CNTs membranes with high water permeation fluxes and strong antimicrobial properties [23]. Vatanpour et al. prepared PES mixed matrix membrane with rGO/Ag nanosheets, leading to the increase in antibacterial properties of the membranes [24]. However, Ag and its ionic state may threaten human health due to their release into the environment. Therefore, it is necessary to develop efficient and by-product-free technologies to effectively remove organisms or pathogens in the water.

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As a kind of nano-materials of advanced performance, CNTs can effectively transport water molecules due to their great aspect ratio and smooth inner walls, it is showed that CNTs have valuable application prospects in membrane technologies [25,26]. Chan et al. prepared CNT nanocomposite membranes to make a successful study on water desalination [27,28]. Ghaemi et al. pointed out that CNT/PES mixed matrix nanofiltration membrane can effectively remove dyes in water [12]. However, CNTs intrinsically tend to bundle or aggregate, it is necessary to carry out the surface modification of CNTs. The modification includes covalent reactions and non-covalent effects. Covalent modification can generate some functional groups on the surface of CNTs through some chemical reactions, but the chemical reactions may damage the CNT structure and cause some adverse effects [29,30]. Compared to covalent modification, non-covalent methods are attractive in terms of stability and uniformity. Recently, many high-performance devices have been developed by the non-covalently modified CNTs [31,32]. Cha et al. fabricated CNT/Epoxy nanocomposites with enhanced mechanical properties by PSS and PAS non-covalent functionalized CNTs [33]. Various non-covalent methods and the applications of the modified CNTs are summarized by Fujigaya et al. [31].

Previous research has demonstrated the antibacterial properties of CNTs [34–36]. However, the antibacterial performance of CNT composite membranes is controversial. Chi et al. pointed out that the antibacterial effect of CNT has a strong relationship with the nutrient in aquatic system [34]. Akhavan et al. found that the hydrazine reduced graphene oxide nanowalls (GONWs) exhibited more antibacterial activities [37]. In many respects, the CNTs have a striking resemblance to graphene nanosheets. Su et al. discovered that the water flux in CNT increased significantly under the action of electric field [38]. Fan et al. noted that electrochemical assisted CNTs/Al_2O_3 membranes have surprising flux and antifouling ability [39]. Kang et al. showed that Norovirus could be efficiently separated in a membrane-based electrical separation study [40].

In our work, hybrid membranes were prepared with different amount of f-CNTs and applied in the ultrafiltration tests. We studied the antifouling and antibacterial properties in depth, and investigated the synergistic antibacterial effect of the hybrid membranes and electric field under a low-voltage electric field. The prepared CNTs and membranes were characterized by a series of experiments, such as Scanning electron microscopy (SEM), water contact angle (CA) and Atomic force microscopy (AFM). In addition, the mechanism of membrane antifouling performance and the synergistic antibacterial effect between electric field and hybrid membranes were researched.

2. Materials and methods

2.1. Materials

Polyethersulfone (PES, Ultrason E6020P with Mw = 58 kDa) was purchased from BASF, Germany. N,N-dimethylacetamide (DMAc, ≥99.5%, reagent) was obtained from Tianjin Kermel Chemical Reagent Co., Ltd., China. Bovine serum albumin (BSA) was purchased from Beijing Solarbio Science & Technology Co. Ltd China. Sodium lignosulfonate (SLS) and polyvinyl pyrrolidone (PVP) were provided by Tianjin Guangfu Fine Chemical Research Institute, China. The pristine multiwalled carbon nanotubes (MWCNTs, outside diameter 10–20 nm, length 10–30 μm, purity ≥98%) were purchased from Times Nano Ltd., Chengdu. The used water is deionized water.

2.2. Preparation of SLS functionalized MWNTs

Jeong et al. prepared the SLS functionalized MWCNTs successfully by a non-covalent method [41]. In this study, the method was improved to functionalize MWCNTs more effectively. 1 g MWCNTs, 4 g SLS and 10 ml deionized water were mixed in a mortar and ground for 1 h by hand. After thorough grinding, the mixture was sonicated at room temperature for 1 h (40 kHz, 80 W). Afterwards, the mixed solution was separated by filtration and the excess SLS was removed by rinsing with deionized water several times. The prepared SLS functionalized MWCNTs were dried under vacuum for use.

Table 1
The composition of f-CNT/PES composite membranes.

Samples	Additives		PES (wt %)	PVP (wt %)	DMAC (wt %)
	f-CNT	Amounts (wt %)			
M−0	–	–	19	1	80.0
M-C−3	Pristine CNT	1.5	19	1	78.5
M-S−1	SLS-CNT	0.5	19	1	79.5
M-S−2	SLS-CNT	1.0	19	1	79.0
M-S−3	SLS-CNT	1.5	19	1	78.5
M-S−4	SLS-CNT	2.0	19	1	78.0
M-S−5	SLS-CNT	2.5	19	1	77.5

2.3. Preparation of f-CNT/PES ultrafiltration membranes

Nascent PES membranes and hybrid membranes were fabricated in coagulation bath by phase inversion method [18,22]. Precise amounts of f-CNT and PVP were first added into DMAc to prepare homogeneous mixture under ultrasound treatment for 1 h. After sonication, PES was added in the mixture by magnetic stirring at 60 ℃ for 12 h. As the PES was completely dissolved, the air bubbles in the solution was removed by a sonication method for 10 min. In order to sufficiently remove the bubbles in the casting solution, the solution was kept in a vacuum oven at 25 ℃ for more than 6 h. Subsequently, the solution was coated onto a glass plate using a self-made scraper (thickness: 150 mm), and the glass plate was immediately immersed in deionized water (10 ℃). Finally, the membranes were naturally dried at room temperature after complete phase separation. Table 1 shows the compositions of various membranes.

2.4. Characterization of f-CNT

2.4.1. Transmission electron microscopy (TEM)

A Hitachi H7650 transmission electron microscope (HITACHI, Japan) was used to research the SLS functionalized MWCNTs. The f-CNTs were dispersed in ethanol by means of ultrasound and were dried on a copper grating (300 meshes).

2.4.2. Fourier transforms infrared spectroscopy (FTIR)

FTIR spectra were analyzed by Thermo Nicolet iS50 spectroscope (Thermo Nicolet Corporation, USA) within the confines of 400–4000 cm^{-1} (at 2 cm^{-1} resolution).

2.4.3. Energy dispersive X-ray (EDX)

In order to confirm whether the SLS molecules were still wrapped on the surface of CNT after membrane formation, the element ratios of f-CNT were tested by energy dispersive X-ray (EDX) analysis using a Hitachi S4800 SEM instrument (HITACHI, Japan).

2.5. Characterization of membranes

2.5.1. Structure of membranes

The membrane structure was inspected using a Hitachi S4800 SEM instrument (HITACHI, Japan). Cleaned samples were ruptured in liquid nitrogen to keep the original structure, and were observed at 10 kV after sputtering gold.

As for surface roughness, the samples (0.5 cm × 0.5 cm) were fixed on a glass substrate and were tested by an Agilent-S5500 scanning probe optical microscope (AGILENT, USA), and the areas of 10 μm ×