Journal of Membrane Science 448 (2013) 81–92

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

# Synergetic effects of oxidized carbon nanotubes and graphene oxide on fouling control and anti-fouling mechanism of polyvinylidene fluoride ultrafiltration membranes

Jiguo Zhang [a], Zhiwei Xu [a,*], Mingjing Shan [a], Baoming Zhou [a], Yinglin Li [a], Baodong Li [b], Jiarong Niu [b], Xiaoming Qian [b,**]

[a] State Key Laboratory of Hollow Fiber Membrane Materials and Processes, Tianjin Polytechnic University, Tianjin 300387, People's Republic of China
[b] School of Textiles, Tianjin Polytechnic University, Tianjin 300387, People's Republic of China

ARTICLE INFO

*Article history:*
Received 29 May 2013
Received in revised form
25 July 2013
Accepted 26 July 2013
Available online 7 August 2013

*Keywords:*
Synergetic effects
Graphene oxide and oxidized carbon nanotubes
Permeability
Anti-fouling performance
Ultrafiltration membranes

ABSTRACT

This study investigated the remarkable synergetic effect between two-dimensional graphene oxide (GO) and one-dimensional oxidized carbon nanotubes (OMWCNTs) on permeation and anti-fouling performance of polyvinylidene fluoride (PVDF) composite membranes. Stacking of individual GO is effectively inhibited by introducing OMWCNTs. Long and tortuous OMWCNTs can bridge adjacent GO and inhibit their aggregation, which makes the materials achieve their highest potential for improving the anti-fouling performance of composite membranes. Ultraviolet–visible spectra and zeta potential study well demonstrated that the dispersion of hybrid materials is better than that of either GO or OMWCNTs. The morphology of different membranes demonstrated that modified membranes have bigger pore density, which undoubtedly played a positive role in permeation flux. Compared with the pristine PVDF (78°), the hydrophilicity of membranes with the ratio of 1:9 (GO/OMWCNTs) showed a marked improvement (52.5°) in contact angle. With a GO/OMWCNTs ratio of 5:5, the pure water flux is enhanced by 251.73% compared with pristine PVDF membranes, while improved by 103.54% and 85.68% for the PVDF/OMWCNTs and PVDF/GO membranes, respectively. The membrane fouling mechanism was studied by resistance-in-series model, and results indicated that membranes tended to be fouled by the cake layer. Additionally, an atomic force microscope (AFM) analysis with a BSA-immobilized tip indicated low adhesion force with the modified membranes, while the pristine PVDF membranes exhibited strong adhesion to the probe, consistent with the fouling properties of the membranes. The newly-developed modified membranes, especially the PVDF/GO/OMWCNTs membranes, demonstrated an impressive prospect for the anti-irreversible fouling performance in dead end filtration experiments. And the pure water flux recovery achieved 98.28% for membranes with the ratio of 5:5 (GO/OMWCNTs), which contributing to the synergistic effect of the hybrid samples. As a result, the optimum ratio of GO/OMWCNTs immobilizing membranes for ultrafiltration membrane application in terms of highest permeability and lowest fouling was 5:5. Conspicuously, the ease of synthesis and the exceptional permeability and anti-fouling performance render that the low-dimensional carbon nanomaterial modification is an attractive way of designing future ultrafiltration membranes in both conventional fields and new emerging areas.



## 1. Introduction

Despite its high hydrophobicity, poly (vinylidene fluoride) (PVDF) is still a popular membrane material due to its good chemical resistance, thermal stability and mechanical properties [1–3]. Nevertheless, PVDF membrane fouling results in substantial flux decline that necessitates frequent membrane cleaning and replacement. Consequently, efficient application of membrane technology in wastewater reclamation is significantly hampered by the phenomenon of organic fouling as wastewater effluent contains a considerable amount of organic substances. In recent years, in order to further reduce the susceptibility of PVDF membranes to biofouling or to enhance their anti-fouling performance, various methods to increase their surface hydrophilicity have been described, such as coating [4], adsorption [5], surface graft polymerization [6] and chemical modification of pristine PVDF [7]. Besides, blending modification is another

* Corresponding author. Tel./fax: +86 22 83955231.
** Corresponding author. Tel./fax: +86 22 83955051.
*E-mail addresses:* xuzhiwei@tjpu.edu.cn (Z. Xu), qianxiaoming@tjpu.edu.cn (X. Qian).

0376-7388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.memsci.2013.07.064

practical method without any pre-treatment or post-treatment procedures [8].

In recent years, several authors have shown the successful preparation of carbon nanotubes blended polymeric composite membranes and they have mainly studied the effects of carbon nanotubes on the performance of membranes [9,10]. In addition, former reports (including our previous work), have simply investigated the effects of graphene derivatives on the performance of composite membranes [11–13]. And results indicated that introducing low-dimensional carbon nanomaterials in the membrane matrix can improve the hydrophilicity, water permeability and the anti-fouling performance of polymer based nanocomposite membranes. However, like carbon nanotubes the problem of dispersion is strongly present for graphene derivatives as well due to strong Vander Waals forces and inter-planer stacking [14–16]. Consequently, the poor dispersion of carbon nanotubes and graphene in polymeric matrices may limit the extent of realizing potential improvements of composite membranes and the performance of low-dimensional nanomaterials-based composite membranes is hampered by the aggregation and stacking of either carbon nanotubes or graphene. It is known that by bringing together two nanofillers like carbon nanotubes and graphene derivatives they form a co-supporting network of both fillers like a hybrid net structure in which the platelet geometry shields the tube fillers from fracture and damage during processing whilst still allowing full dispersion of both during high-power sonication, thus causing improved properties [17]. Hence, we can expect that integrating one-dimensional oxidized carbon nanotubes (OMWCNTs) and two-dimensional graphene oxide (GO) resulted in a strong synergistic effect between the two materials, consequently leading to a superior ultrafiltration membrane with higher anti-fouling performance compared with the membranes modified by either GO or OMWCNTs. Furthermore, as is known in the art, the synergetic effect of OMWCNTs and GO on the membrane – foulant adhesion forces and membrane-fouling behavior as well as on the anti-fouling mechanism of PVDF ultrafiltration membranes has not yet to be systematically studied. And it is an open question to completely understand the synergistic effect brought about by the nanomaterial mixture of different ratios.

Based on these considerations and the body of previous research, the objective of this work is to synthesize composite membranes of different nanofiller ratios using a non-solvent induced phase separation method and determine the synergistic effects on the fouling control and anti-fouling mechanism of two highly-potent nanomaterials in the matrix. These results offer a novel yet simple and effective way of designing composite ultrafiltration membranes with extraordinary performance by incorporating two different low-dimensional carbon nanomaterials neither one of which alone might be essentially perfect for the required applications.

## 2. Experimental

### 2.1. Materials

The PVDF (FR904) was purchased from Shanghai 3F New Materials Co. Ltd. China. N, N-dimethylacetamide (DMAc, $>99.5\%$, reagent) and polyvinyl pyrrolidone (PVP) were purchased from Tianjin Weichen Chemical Reagent Co. Ltd. China. Multi-walled carbon nanotubes (MWCNTs, with diameters of 10–50 nm and length of 1–30 μm) were obtained from Nanjing XF Nanomaterial Science and Technology Co. Ltd. The purity of received MWCNTs is 95%. Oxidized carbon nanotubes (OMWCNTs) were synthesized by the previous reports [18]. Graphite oxide powders were prepared by improved Hummers' method [19]. Then the powders were suspended in pure water (1 mg/ml) and sonicated for 2.5 h to generate a graphene oxide (GO) suspension. Subsequently, the aqueous GO suspension was frozen into an ice cube in a refrigerator (258.15 K) for 8 h and then was freeze-dried using a FD-1A-50 lyophilizer (Boyikang Co. Ltd., China) with a condenser temperature of 223.15 K at an inside pressure of less than 20 Pa. After 48 h lyophilization and 48 h vacuum drying (318.15 K) process, low-density, loosely packed GO powder was finally obtained.

### 2.2. Preparation of membranes

All the membranes were prepared by the classical phase inversion method using PVDF and PVP as the solute materials, DMAc as the solvent, low-dimensional carbon materials as the additive, and distilled water at room temperature as the nonsolvent coagulation bath. The different ratios of GO and OMWCNTs mixtures with a total of 1 wt% (mass of low-dimensional carbon materials/mass of polymer) were first imported into DMAc solvent, and then the solution was sonicated for 30 min (40 kHz) before the addition of PVP (1 g) and PVDF (15 g) powders. Casting solution was then mechanically stirred at 323.15 K for at least 24 h. After fully degassing, the casting solution was spread onto clean glass plates with 200 μm gap and then immersed into coagulation bath (distilled water) for 30 min. After peeling off from the glass plates, the resultant membranes were rinsed in distilled water before ultrafiltration tests.

### 2.3. Characterization of low-dimensional carbon nanomaterials

Ultraviolet–visible (UV–vis) absorption spectra of GO, OMWCNTs and GO/OMWCNTs were recorded with a UV-1800 spectrophotometer. Zeta potential analyses were performed using a Delsa Nano instrument and all data were measured over five times. All the samples were dispersed by ultrasonic agitation in DMAc solution at 298.15 K for 1 h before tests.

### 2.4. Characterization of membranes

#### 2.4.1. Structure and functionality

The existence of OMWCNTs and GO in ultrafiltration membranes was characterized by Fourier-Transform Infrared spectroscopy (FTIR). To determine the stability of the hydrophilicity of membranes, the membranes were stirred in frequently changed pure water for 3 weeks and then dried in air. The contact angle (CA) change with the drop age of membranes was recorded by a water contact angle system (JC2000D2). Five different points of every sample were measured and the CA was the average of these measurements.

Permeation flux of the membranes was measured by ultrafiltration experimental equipments. The sample membranes were immersed in pure water before measurement. The measuring protocol was depicted as follows: for the first 30 min, the membranes were compacted at 0.1 MPa to get a steady flux; then the flux was recorded at 0.1 MPa every 5 min, and at least 5 readings were collected to obtain an average value. The permeation flux was defined using the following Eq. (1):

$$J = \frac{Q}{AT} \tag{1}$$

where $J$ was permeation flux of membranes for pure water ($L\,m^{-2}\,h^{-1}$), $Q$ was volume of permeate pure water (L), $A$ was effective area of membranes ($m^2$) and $T$ was the permeation time (h).