Journal of Industrial and Engineering Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Novel organic-inorganic hybrid polyvinylidene fluoride ultrafiltration membranes with antifouling and antibacterial properties by embedding *N*-halamine functionalized silica nanospheres

Han Wang[a], Zuo-Ming Wang[b], Xi Yan[a], Jun Chen[b], Wan-Zhong Lang[a,*], Ya-Jun Guo[a]

[a] The Education Ministry Key Laboratory of Resource Chemistry and Shanghai Key Laboratory of Rare Earth Functional Materials, Department of Chemistry and Chemical Engineering, Shanghai Normal University, 100 Guilin Road, Shanghai 200234, China
[b] College of Life and Environment Sciences, Shanghai Normal University, 100 Guilin Road, Shanghai 200234, China

ARTICLE INFO

Article history:
Received 23 January 2017
Received in revised form 27 March 2017
Accepted 31 March 2017
Available online xxx

Keywords:
Polyvinylidenefluoride (PVDF)
Ultrafiltration
N-halamine functionalized silica nanospheres (HFSNs)
Silica nanospheres
Antibacterial

ABSTRACT

Novel polyvinylidene fluoride (PVDF) hybrid ultrafiltration membranes with antifouling and antibacterial properties are prepared by embedding *N*-halamine functionalized silica nanospheres (HFSNs). With the addition of HFSNs, the antifouling properties of PVDF membranes are significantly improved. The results reveal that the highest pure water permeation flux of 559.8 L m^{-2} bar^{-1} h^{-1} is attained when the 0.6 wt% HFSNs is added in the casting solution. The membrane of M-3 with 0.9 wt% HFSNs addition shows the highest sterilization ratios of 97.1% and 97.0% against (escherichia coli) *E. coli* and (staphylococcus aureus) *S. aureus* respectively. After 6 times of inhibition-activation cycles, the membrane still remains 72.3% against *E.coli*.

Introduction

As a green and efficient technology, ultrafiltration has been widely used for separation and purification in the environmental, chemical, medicine and other industries. Currently, poly(vinylidene fluoride) (PVDF) ultrafiltration membranes have received intensive interest due to its good chemical and thermal stability, and mechanical properties [1,2]. However, because of their inherent hydrophobic property, PVDF membranes tend to be fouled by many organisms and biomolecules, among which bacteria is one of the most important species. Therefore, to reduce or eliminate the fouling and improve the membrane performances is an interesting work in membrane field. Many studies were devoted to improving the hydrophilicity of polymeric membranes with inorganic nanoparticles such as carbon nanotubes [3–5], TiO_2 [6], Al_2O_3 [7], SiO_2 [8,9] and so on. For example, Zhang et al. [5,10] prepared PVDF/perfluorosulfonic acid (PFSA)/oxidized multiwall carbon tubes (O-MWNTs) membranes with improved surface hydrophilicity and permeation flux by introducing O-MWNTs in membrane matrix. Shen et al. [9] prepared PES-SiO_2 hybrid membranes by phase inversion method within nano-SiO_2 as additive, and the pure water permeation flux and antifouling property of hybrid membranes were obviously enhanced. In addition, the membrane is prone to be contaminated by bacterial [11] and results in reduced membrane flux. Herein, it is necessary to endow membrane with anti-bacterial capacity. Several modification methods are employed to endow PVDF ultrafiltration membranes with antibacterial ability. Many antibacterial agents have been involved to prepare antimicrobial membranes, such as silver ions [12–14], copper ions [15,16], TiO_2 [17], halloysite nanotubes (HNTS) [18],*N*-halamine [19] and others. Pan et al. [20] prepared a PVDF membrane with antifouling and antibacterial properties through dip-coating method, and the in-situ formed silver nanoparticles were immobilized with silica nanoparticles. Nevertheless, to date, no reports have appeared concerning PVDF membranes with silica-functional nanoparticles to endow the improved permeability and antibacterial property simultaneously.

N-halamine is one antibacterial compound with several superiorities, such as super-active antibacterial activity, low toxicity and good regenerability [21,22] and shows strong antimicrobial action against a broad spectrum of microorganisms [23–27]. For example, Zhou and Kan [28] modified cotton fabric with 5, 5-dimethylhydantoin (DMH) to endow it antibacterial properties against *S. aureus* and the antibacterial ability is regenerable. One *N*-halamine precursor was synthesized and

* Corresponding author. Fax: +86 21 64321951.
E-mail address: wzlang@shnu.edu.cn (W.-Z. Lang).

http://dx.doi.org/10.1016/j.jiec.2017.03.059
1226-086X/

Nomenclature

w_1	The weight of wet membrane (g)
w_2	The weight of dry membrane (g)
$V_{membrane}$	The volume of flat membrane (m^3)
d_w	The pure water density (g/m^3)
ε	The membrane porosity (%)
J_{w1}	Pure water permeation flux ($L\,m^{-2}\,h^{-1}\,bar^{-1}$)
Q	The volume of pure water (L)
P	The nsmembrane pressure (bar)
A	The effective membrane area (m^2)
R	The rejection of solute
C_P	The concentrations of permeate (g/L)
C_F	The concentrations of feed solutions (g/L)
J_{p1}	The BSA aqueous permeability ($L\,m^{-2}\,h^{-1}\,bar^{-1}$)
FRR	Flux recovery ratio (%)
J_{w2}	Pure water permeation flux after washing with NaClO solution ($L\,m^{-2}\,h^{-1}\,bar^{-1}$)
R_t	Total flux decline ratio (%)
R_r	Reversible flux decline ratio (%)
R_{ir}	Irreversible flux decline ratio (%)
Cl^+%	Oxidative chlorine content
N	The normality of the consumed $Na_2S_2O_3$ in the titration (eqv/L)
V	The volume of the needed $Na_2S_2O_3$ in the titration (L)
W	The weight of membrane sample in the titration (g)
E	The percentage of bacterial reduction (%)
N	The number of visible bacterial colonies with the membrane
M	The number of visible bacterial colonies with membrane (M-0)

tethered onto cotton fabric by Cheng et al. [29]. The results indicated that the treated cotton fabrics had excellent biocidal efficacies and exceptional stability toward washing cycles.

In this work, our principal interest was to enhance antifouling and antibacterial properties of PVDF ultrafiltration membranes. The regenerable antimicrobial *N*-halamine functionalized silica nanospheres (HFSNs) were fabricated according to the method proposed by Zhao et al. [30], and then organic-inorganic PVDF hybrid ultrafiltration membranes were prepared by embedding the HFSNs via non-solvent immersion phase separation (NIPS) method. The separation performance, antifouling and antibacterial properties and regenerability were investigated in detail. *E. coli* and *S. aureus* were employed to test the antibacterial activity of membranes.

Experimental

Materials

PVDF (Solef® 1015) in powder was purchased from Solvay Advanced Polymers. *N*-methyl-2-pyrrolidone (NMP), Polyvinylpyrrolidone (PVP) (MW = 24,000), potassium iodide, ammonia solution ($NH_3{\cdot}H_2O$, 25 wt%) are supplied by Shanghai Chemical Agent Company. Bovine serum albumin (BSA, MW = 67,000) was purchased from Shanghai Bio Co. Ltd. (China). Humic acid (HA) (Fulvic acid >90.0 wt%) is purchased from Shanghai Aladdin Chemical Agent Co., Ltd. (China). Tetraethoxysilane (TEOS), 3-chloropropyltriethoxysilane (CPS), 5,5-dimethylhydantoin (DMH), sodium ethoxide, sodium hypochlorite (NaClO), thiosulfate and starch were offered by Aladdin. *S. aureus* (CICC24065) and *E. coli* (CMCC44102) were obtained from Shanghai Institute of Materia Medica of the Chinese Academy of Sciences (China).

Preparation of N-*(3-triethoxysilylpropyl)-5,5-dimethylhydantoin (TS-DMH)*

N-(3-triethoxysilylpropyl)-5,5-dimethylhydantoin was synthesized according to the previous literature [31]. In brief, 100 mL of ethanol, 12.8 g of 5,5-dimethylhydantoin (DMH) and 6.8 g of sodium ethoxide were mixed, stirred and reacted for 1 h. Then ethanol was evaporated under reduced pressure. Then the corresponding sodium salt of DMH was added to 100 mL of anhydrous *N*,*N*-dimethylformamide (DMF), and the solution was stirred for 0.5 h. Then 24.1 g of 3-chloropropyltriethoxysilane (CPS) was added into the mixture drop by drop. Finally, the product was obtained after purification.

Preparation and characterizations of HFSNs

0.25 g of above product and 1.43 g of TEOS were added into ethanol under vigorous stirring. Then, ammonia water was added to the solution. After 6 h, the formed nanoparticles of silica/DMH (the precursor of HFSNs) were acquired. The precursor (silica/DMH) was dissolved in NaClO solution under stirring to obtain the HFSNs. For comparison, the pure silica nanoparticles were also synthesized by Stöber method [32]. The synthesis route diagram of TS-DMH and HFSNs is presented in Scheme 1.

The FTIR spectra of HFSNs and pure silica were collected upon ElectronCorp Nicolet 380. The XPS spectra of the prepared HFSNs were collected on Perkin-Elmer PHI 5000C ESCA using Al Kα radiation. The spectra were corrected using the C1s spectrum at 284.8 eV as an internal standard.

Preparation of organic-inorganic PVDF hybrid ultrafiltration membranes

The organic-inorganic PVDF hybrid ultrafiltration membranes with antifouling and antibacterial properties were fabricated via the nonsolvent induced phase separation (NIPs) method. In brief, PVDF (16 wt%), PVP (2 wt%) and HFSNs with different mass fractions (0.0 wt.%, 0.3 wt.%, 0.6 wt.% and 0.9 wt.% for M-0, M-1, M-2 and M-3 respectively) were dispersed in NMP. The homogeneous casting solution was cast onto a clean glass plate with a knife of 200 μm, and immediately immersed into a water bath at 25 °C. After the membranes were fully formed, they were taken out and thoroughly washed with deionized water. In addition, the PVDF hybrid membrane with pure silica nanoparticles (0.6 wt% in casting solution) was also prepared and named as M-4. The modified membranes were listed in Table 1 in details.

Characterizations of organic-inorganic hybrid PVDF ultrafiltration membranes

A rotational rheometer (Austria Anton Par MCR102) was used to measure the rheology properties of casting solutions at room temperature. In the steady shear measurements, the viscosity in terms of the shear rate was recorded. The shear rate region ranged from 0.001 s^{-1} to 10^3 s^{-1}.

The morphologies of organic-inorganic hybrid PVDF ultrafiltration membranes were detected upon a field emission scanning electron microscopy (FESEM, Hitachi S-4800). The cross-sections of membranes were obtained by immersing the samples in liquid nitrogen and quickly being fractured. The membrane porosity ε (%)

Please cite this article in press as: H. Wang, et al., Novel organic-inorganic hybrid polyvinylidene fluoride ultrafiltration membranes with antifouling and antibacterial properties by embedding *N*-halamine functionalized silica nanospheres, J. Ind. Eng. Chem. (2017), http://dx.doi.org/10.1016/j.jiec.2017.03.059