Chemical Engineering Journal 315 (2017) 509–515

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Sodium persulfate based PVDF membrane for concurrent advanced oxidation and ultrafiltration of ofloxacin in water

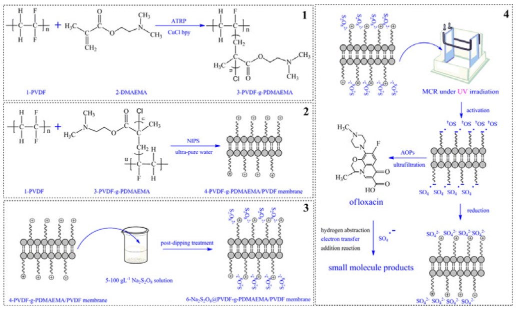
Guowen Wang [a,b,*], Dong Wang [c], Xiaoli Dong [a], Xiufang Zhang [a], Hongchao Ma [a]

[a] School of Light Industry and Chemical Engineering, Dalian Polytechnic University, No. 1 Qinggongyuan, Ganjinzi District, Dalian 116034, PR China
[b] Swette Center for Environmental Biotechnology, Biodesign Institute, Arizona State University, 727 E Tyler St, Tempe, AZ 85287, USA
[c] College of Marine Science-Technology and Environment, Dalian Ocean University, No. 52 Heishijiao, Shahekou District, Dalian 116023, PR China

HIGHLIGHTS

- A novel method for preparing inorganic–organic composite membrane is proposed.
- Combining the filtration and oxidation of membrane may enhance pollutant removal.
- Positively charged and hydrophilic property of DMAEMA is explored in membrane modification.
- Concurrent sulfate radical oxidation and PVDF ultrafiltration is investigated in MCR.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 November 2016
Received in revised form 15 January 2017
Accepted 16 January 2017
Available online 17 January 2017

Keywords:
Amphiphilic polymer
Composite PVDF membrane
Persulfate
MCR

ABSTRACT

Flat $Na_2S_2O_8$@PVDF-g-PDMAEMA/PVDF inorganic–organic composite membrane was prepared by sequential use of atom transfer radical polymerization (ATRP), non-solvent induced phase inversion separation (NIPS) and post-dipping treatment. The membrane was tested in a membrane chemical reactor (MCR) system for concurrent advanced oxidation and ultrafiltration of ofloxacin (OFLX) under UV irradiation. Results indicated that the production of sulfate radicals ($SO_4^{\cdot-}$) from persulfate can achieve 54% removal efficiency of OFLX, outperforming single advanced oxidation processes (AOPs) or ultrafiltration treatment. The best performance, was secondary to the combination of high redox potential of the $SO_4^{\cdot-}$, hydrophilicity of N,N-dimethylaminoethyl methacrylate (DMAEMA) and molecular cutoff of polyvinylidene fluoride (PVDF) ultrafiltration membrane. This study also identified factors related to successfully preparing composite membranes with concurrent positive charges and hydrophilicity. Characterization using XRD, FTIR and EDS showed that introducing PDMAEMA into the polymer mixture and post-dipping were both required to obtain a multifunctional membrane, which can electrostatically attract negative $S_2O_8^{2-}$ species. Judging from SEM results, the formation mechanisms of the composite membrane structure were derived from instantaneous liquid–liquid demixing.

1. Introduction

Antibiotic ofloxacin (OFLX) in aquatic bodies is a common but underinvestigated problem causing significant adverse impacts on public health and ecosystems [1]. Environmental and health concerns associated with OFLX-contaminated aquatic systems have prompted study into effective and efficient treatment technologies, especially AOPs or membrane filtration [2]. Given the complementary treatment capacity of these two processes, coupling them would enhance overall performance. Most of the AOPs evaluated for OFLX degradation with worse biodegradability generate hydroxyl radicals as the main oxidizing species [3,4].

---

* Corresponding author at: School of Light Industry and Chemical Engineering, Dalian Polytechnic University, No. 1 Qinggongyuan, Ganjinzi District, Dalian 116034, PR China.

E-mail address: wanggw@dlpu.edu.cn (G. Wang).

http://dx.doi.org/10.1016/j.cej.2017.01.059
1385-8947/© 2017 Elsevier B.V. All rights reserved.

While other AOPs are still used frequently, $Na_2S_2O_8$ is the most commonly used, especially for in situ chemical oxidation (ISCO) [5]. The principal pathways for $SO_4^{\cdot-}$ formation are via heat, metal-catalyst, alkaline, or UV activation of $S_2O_8^{2-}$ or HSO_5^-. Moreover, the radical quantum yields of $S_2O_8^{2-}$ from UV254 nm are higher than those of HSO_5^- and H_2O_2 [6,7]. Hence, UV-activated $S_2O_8^{2-}$ is effective in abolishing water pollutants [8]. However, to employ $S_2O_8^{2-}$ in wastewater ISCO, $S_2O_8^{2-}$ immobilization is needed. While we are concerned in applying $S_2O_8^{2-}$ in a heterogeneous system, the membrane is a perfect supporter. Moreover, MCR was produced by our experimental design because, like other heterocatalysis systems, it can carry or retain $S_2O_8^{2-}$ and selectively extract reactants due to its separation side [9,10].

To achieve $S_2O_8^{2-}$ immobilization onto a common, flat PVDF membrane, the conventional PVDF membrane must be modified to carry positive species [11]. Therefore, the interface of the inorganic–organic membrane can form via electrostatic interaction between the inorganic $S_2O_8^{2-}$ groups and the organic PVDF membrane support surface. Among direct preparation methods for positive amphiphilic graft copolymers from PVDF, atom transfer radical polymerization (ATRP) has been widely studied [12]. As a "grafting-from" technique, ATRP can effectively provide hydrophilic properties to the parent PVDF polymer [13]. When preparing a $S_2O_8^{2-}$-based PVDF membrane, considering that these grafted amphiphilics may improve hydrophilicity of membrane is important, as well as the effects of the positive group of amphiphilics on electrostatic attraction performance with negative $S_2O_8^{2-}$. Furthermore, DMAEMA is an amphiphilic polymer that can be used as a flocculant and an ion exchange resin because of its positive dimethylamino group [14]. In the casting solution, DMAEMA is expected to enhance the solvent-non-solvent exchange by increasing the affinity of the casting solution and water, thereby creating favorable conditions for instantaneous liquid–liquid demixing. However, the versatility of DMAEMA in improving hydrophilicity and carrying positively charged dimethylamino group may have been underestimated.

By taking the advantages of concurrent oxidation and ultrafiltration of MCR, we aimed to fabricate a $Na_2S_2O_8$@PVDF-g-PDMAEMA/PVDF flat membrane by: (1) using the ATRP method to prepare a graft copolymer PVDF-g-PDMAEMA, (2) casting dopes using NIPS, and (3) post-dipping PVDF-g-PDMAEMA/PVDF membrane in 10% $Na_2S_2O_8$ solution. The PVDF-g-PDMAEMA/PVDF membrane is designed for concurrent oxidation and filtration, which is important in synthesizing inorganic–organic multifunctional sheets. The major goal was to achieve a comprehensive evaluation of the MCR system for antibiotic treatments, which can help develop better wastewater treatment strategies. Research on composite membrane characteristics using various analysis methods would elucidate the $Na_2S_2O_8$@PVDF-g-PDMAEMA/PVDF prospect.

2. Materials and methods

2.1. Chemicals and reagents

$Na_2S_2O_8$ (99%) was purchased from Sigma-Aldrich Co. LLC. (China). Commercial polymer PVDF Kynar HSV 900 was purchased from Arkema Inc., and was dried at 50 °C under vacuum for at least 1 day before use. Dimethylacetamide (DMAc, AR, 99%) and polyvinylpyrrolidone (PVP-K30, Mw = 58,000) from Aladdin Industrial Corporation (Shanghai, China) were used as solvents and an additive respectively in casting solutions for NIPS step. Ultra-pure water was employed as the non-solvent, prepared using a Millipore (Bedford, MA) Milli-Q filtration system and had a resistivity of 18 MΩ*cm. 1-Methyl-2-pyrrolidinone (NMP, AR, 99%), DMAEMA, 99%, copper(I) chloride (CuCl, AR, 97%), and 2,2′-Bipyridyl (bpy, AR, 99%) were purchased from Aladdin for ATRP step. Ofloxacin (98%) was purchased from Ruibio. The other substances were of the highest purity available.

2.2. Synthesis of graft copolymer PVDF-g-PDMAEMA

In ATRP step, we referred to a similar study described by Hester [15]. PVDF (1 g) was dissolved in NMP (8 mL) in a small conical flask at 50 °C. The solution was cooled to room temperature, after which DMAEMA (5 mL), CuCl (0.008 g, 0.08 mmol), and bpy (0.04 g, 0.26 mmol) were added and the flask was sealed with a rubber septum. Nitrogen gas was bubbled through the reaction mixture for 15 min while stirring. The reaction vessel was then placed into an oil bath preheated to 90 °C, and the reaction was allowed to proceed for 24 h. The graft copolymer was precipitated into a mixture of 1 part methanol, 1–2 parts petroleum ether, and a small amount of HCl and recovered by filtration. The polymer was purified by thrice redissolving in NMP and reprecipitating in methanol and petroleum ether. Finally, the polymer was dried under vacuum overnight at room temperature.

2.3. Preparation of $Na_2S_2O_8$@PVDF-g-PDMAEMA/PVDF membrane

$Na_2S_2O_8$ based PVDF composite membranes (labeled as 1#–6#) were prepared via NIPS method and further dipped in 100 g L^{-1} $Na_2S_2O_8$ solution for 30 min. Casting dopes were prepared by dissolving the mixture (PVDF: PVDF-g-PDMAEMA in a weight ratio of 4:1 and 2:1) in the DMAc at room temperature and adding PVP-K30 to the casting dopes under stirring. The weight proportion of the mixture (PVDF and PVDF-g-PDMAEMA), DMAC and PVP K-30 was 15%, 80% and 5% by weight of the polymer dopes, respectively. In order to obtain optimal dispersions of the every ingredient in the casting solutions, agitation was required for at least 24 h. After removing air bubbles in casting dope, an appropriate amount of the dope was scraped uniformly on a glass plate (casting knife gap distance = 200 μm) for 30 s exposure to air, then the glass plate was immediately immersed in a coagulation bath only containing ultra-pure water. The labeled as 7#–10# were prepared by directly blending $Na_2S_2O_8$ and polymer dopes for comparing with 1#–6#. Details of the membranes compositions are shown in Table 1. The membranes were washed with, and soaked in, water until they were used for characterization.

2.4. Performance investigation of $Na_2S_2O_8$@PVDF-g-PDMAEMA/PVDF membrane

Experimental configurations for measuring and displaying oxidation and filtration performance of the composite membranes in MCR are sketched in Fig. 1. In this bench scale system, $Na_2S_2O_8$@PVDF-g-PDMAEMA/PVDF membranes were investigated in a dead-end membrane system setup, with a reactor volume of L (12 cm) × W (8 cm) × H (14 cm). The effective membrane area was 9 cm^2. Negative pressure was provided by peristaltic pump. The trans-membrane pressure (TMP) used in experiments was 0.05 MPa. One low pressure UV lamp with principal monochromatic light emission of λ_{max} = 395 nm was fixed in the cell.

2.5. Characterization and analysis

The concentration of OFLX was quantified on a Varian Pursuit C18 column (analytical column 250 × 4.6 mm, 5 μm), with an eluting system consisting of a mixture of CH_3CN: CH_3OH: citric acid 0.4 mol L^{-1} = 7:15:78% (v/v). Detection was performed with a UV detector at 288 nm [16]. X-ray measurements were performed using monochromatic Cu Kα radiation (Lab X XRD-6100, Shimadzu) to identify and analyze the PVDF and $Na_2S_2O_8$ crystalline phases based on the ICDD. Patterns were recorded over