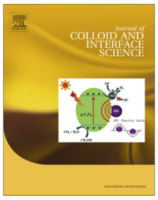
Journal of Colloid and Interface Science 505 (2017) 341–351

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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



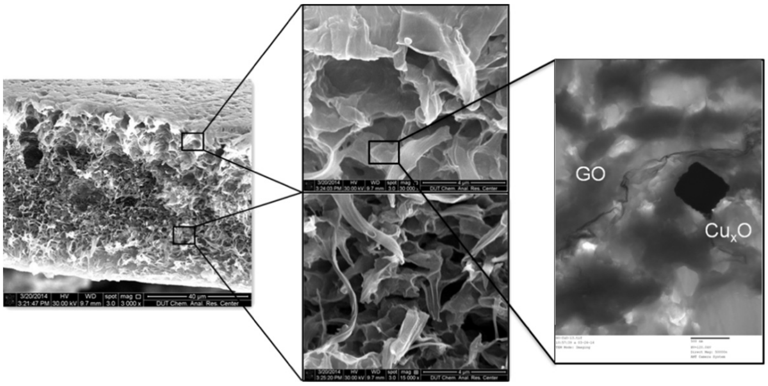
Regular Article

Highly antifouling and antibacterial performance of poly (vinylidene fluoride) ultrafiltration membranes blending with copper oxide and graphene oxide nanofillers for effective wastewater treatment

Chuanqi Zhao [a,*], Jinling Lv [b], Xiaochen Xu [b], Guoquan Zhang [b], Yuesuo Yang [a], Fenglin Yang [b]

[a] *Key Lab of Eco-restoration of Regional Contaminated Environment, Ministry of Education, Shenyang University, Shenyang 110044, China*
[b] *Key Lab of Industrial Ecology and Environmental Engineering, Ministry of Education, School of Environmental Science and Technology, Dalian University of Technology, Dalian 116023, China*

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 March 2017
Revised 19 May 2017
Accepted 23 May 2017
Available online 25 May 2017

Keywords:
Graphene oxide (GO)
Copper oxide
Hydrophilic modification
Antibacterial activity
Antifouling

ABSTRACT

Innovation and effective wastewater treatment technology is still in great demand given the emerging contaminants frequently spotted from the aqueous environment. By blending with poly (vinylidene fluoride) (PVDF), the strong hydrophilic graphene oxide (GO) and antibacterial copper oxide (Cu_xO) were used as nanofillers to develop the novel, highly antifouling composite membranes via phase inversion process in our latest work. The existence and dispersion of GO and Cu_xO posed a significant role on morphologies, structures, surface composition and hydrophilicity of the developed composite membranes, confirmed by SEM, TEM, FTIR and XPS in depth characterization. The SEM images showed that the modified membranes presented a lower resistant structure with developed finger-like macrovoids and thin-walled even interconnected sponge-like pores after adding nanofillers, much encouraging membrane permeation. The XPS results revealed that Cu_xO contained Cu_2O and CuO in the developed membrane and the Cu_2O nanoparticles were dominant accounting for about 79.3%; thus the modified membrane specifically exhibited an efficient antibacterial capacity. Due to the hydrophilic and bactericidal membrane surface, the composite membranes demonstrated an excellent antifouling performance, including higher flux recovery rate, more resistant against accumulated contaminants and lower filtration resistance, especially lower irreversible resistance. The antifouling property, especially anti-irreversible fouling, was significantly improved, showing a significant engineering potential.

---

* Corresponding author.
E-mail address: zcqbs@aliyun.com (C. Zhao).

http://dx.doi.org/10.1016/j.jcis.2017.05.074
0021-9797/

1. Introduction

Membrane separation technology is more effective and advantageous compared with conventional wastewater treatment process [1], in terms of space saving, improve effluent quality, high reliability and easy manipulation. However, high cost related to membrane materials/replacement and performance maintenance due to the severe membrane fouling restricted wider application of the membrane technology [2]. Membrane fouling results from interaction between the membrane materials and treated waters, consisting of a combination of the precipitates of inorganic and organic matters, as well as microbial deposits [3,4]. Fouling itself could occur in two ways, one is that foulants in wastewater directly adsorbed onto the membrane surface or plugged into the membrane pores/walls. Numerous studies show that membrane fouling is expected to be more severe for hydrophobic rather than hydrophilic membranes due to the hydrophobic interactions occurring between solutes, microbial cells and membrane materials [3,5]. Therefore, much effort has been focused on increasing membrane hydrophilicity through membrane modification [6–8]. Another way is biofouling, which is often considered irreversible because the adhered bacteria can grow and reproduce to form a biofilm and eventually cover the entire membrane surface [9]. Membrane biofouling is initiated by bacterial adhesion to the membrane surface, followed by growth and multiplication of the sessile cells; an effective strategy for preventing biofouling is thus to confer the membrane surface with antibacterial function [10,11]. Accordingly, developing a membrane with excellent surface hydrophilicity and outstanding antifouling (anti-organic fouling and antibacterial) properties is very significant for practical applications of the membrane technology.

Graphene oxide (GO), a two-dimensional carbon material, consists of a considerable number of covalently attached oxygen-containing groups such as hydroxyl, epoxy group, carbonyl and carboxyl groups [12]. These characteristics make the GO sheets strongly hydrophilic [13]. The intrinsic properties of the GO nanosheets, including strong hydrophilicity, superior chemical stability, and high surface area much enhance the feasibility of using these nanosheets as an additive for polymer membrane [14,15]. Hence it has been incorporated into the ultrafiltration membranes to obtain targeted properties via the solution-blending method. Jin et al. employed GO nanosheets as nanofillers to improve the hydrophilicity and antifouling ability of the polyethersulfone (PES) membranes [8]. Zhao et al. researched the improvement of hydrophilicity and mechanical properties of polyvinyl chloride (PVC) membranes modified with GO [15]. Li et al. developed poly (vinylidene fluoride) (PVDF) composite membranes containing GO-Ag nanoparticles (NPs) as antibacterial materials, showing excellent hydrophilicity, permeability and antibacterial property [16]. Our previous works also demonstrated that GO doped into polymer matrix could result in enhanced hydrophilicity, improved water flux and antifouling performances of the PVDF membrane [17,18]. Meanwhile, the GO nanosheets are ideal for surface modification of membranes due to the two-dimensional structure and functional groups. Wang et al. created a hydrophilic GO layer on hydrolyzed polyacrylonitrile (H-PAN) substrate via layer-by-layer (LbL) assembly, and obtained high rejection [19]. However, the potential for these nanocomposites in preventing biofouling has not been studied extensively. In particular, the antibacterial property of GO nanosheets is controversial and further investigation is needed. Liu et al. reported that GO dispersion showed the highest inactivation activity toward *E. coli* among the investigated graphene-based materials, including graphite, graphite oxide, graphene oxide and reduced graphene oxide (rGO). They found that the inactivation activity was time and concentration dependent [20]. In contrast, Ruiz et al. clearly demonstrated that GO could not present any antibacterial properties. Furthermore, they thought that GO acted as an enhancer of life, increasing not only mammalian cell growth but also bacterial growth [21]. The different conclusion maybe caused by the difference of GO size, the former was 0.56 μm, and the latter was several micrometers in diameter.

It is well known that a number of inorganic materials, such as nano-silver [22,23], copper [11,24,25], ZnO [26], TiO_2 photocatalysts [27,28] and single-walled carbon nanotube [29,30], display excellent antibacterial properties. Among these nano-materials, copper showed more superiority due to its low-cost and easy availability. Many studies have demonstrated the high antimicrobial activity of copper ions [31], metals and alloys [32], and oxides [24,33]. Chen et al. prepared PES hybrid membranes via phase inversion method containing halloysite nanotubes and copper ions as nanofillers, and resultantly the biofouling of membrane was efficiently controlled [11]. In particular, Cu-NPs were immobilized onto membrane surface via *in situ* formation method for biofouling control in several recent studies, showing strong antibacterial activity [34–36]. However, no systematic study has been undertaken in immobilization of the solid state copper oxide (Cu_xO) in a membrane matrix for improving antibacterial treatment. Here, we propose a novel hydrophilic inorganic/organic composite membrane incorporating excellent antibacterial property by using GO and Cu_xO NPs as nanofillers, for emerging wastewater treatment. The morphologies, surface characteristics and antibacterial performance of the novel PVDF/Cu_xO/GO composite membranes were systematically studied; and the permeability and antifouling performance of the Cu_xO/GO modified membranes were also investigated in detail.

2. Experimental section

2.1. Materials

Poly (vinylidene fluoride) (FR904, $M_w = 2 \times 10^6$, $M_n = 4.7 \times 10^5$) was obtained from Shanghai 3F New Materials Co., Ltd. N,*N*-dimethylacetamide (DMAc) was purchased from Shanghai Chemical Reagent Company. Bovine serum albumin (BSA, $M_n = 68{,}000$) was supplied by Beijing Solarbio Science & Technology Co., Ltd. Phosphate buffered saline (PBS solution, 0.01 M, pH = 7.4) was prepared with KH_2PO_4 and $Na_2HPO_4{\cdot}12H_2O$. Sulphuric acid (98%) and hydrochloric acid were purchased from Beijing Chemical Works. Natural graphite powder (<20 μm, with purity >99.85 wt.%) was purchased from Sinopharm Chemical Reagent Co., Ltd (China). Hydrogen peroxide and potassium persulfate were supplied by Tianjin Guangfu Fine Chemical Research Institute. Potassium permanganate, sodium nitrate and phosphorus pentoxide were purchased from Tianjin Damao Institute of Chemical. Cupric sulfate and sodium hydroxide were supplied by Shenyang Chemical Reagent Factory. The deionized (DI) water was used in the samples preparation and for pure water flux measurements.

2.2. Development of the novel composite membranes

Graphene oxide (GO) was prepared with natural graphite powder by modified Hummers method [37]. Cuprous oxide (Cu_2O) was firstly prepared using $Cu(OH)_4^{2-}$ as precursor and glucose as reducing agent in the presence of dispersant under ultrasonic radiation [33]. Due to the instability of Cu_2O, the Cu^+ would be partly oxidized to Cu^{2+}, therefore Cu_xO could be considered as a mixture of Cu_2O and CuO NPs.

The novel PVDF/Cu_xO/GO composite membranes were then prepared by phase inversion method with PVDF as the bulk material, DMAC as the solvent, GO and Cu_xO as the additive and deionized