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Performance enhancement of polyvinyl chloride ultrafiltration membrane modified with graphene oxide

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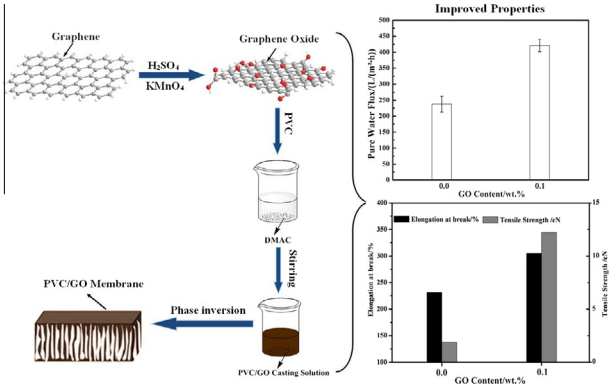
GRAPHICAL ABSTRACT



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ABSTRACT

A novel polyvinyl chloride (PVC) membrane was modified with graphene oxide (GO) via phase inversion method to improve its hydrophilicity and mechanical properties. The GO presented a large amount of hydrophilic groups after the modification through the modified Hummers method. It was observed that with the addition of low fraction of GO powder, the GO/PVC hybrid membranes exhibited a significant enhancement in hydrophilicity, water flux, and mechanical properties. With optimal dosage (0.1 wt%), the pure water flux of GO/PVC membrane increased from 232.6 L/(m^2 h bar) to 430.0 L/(m^2 h bar) and the tensile strength increased from 231.3 cN to 305.3 cN. The improved properties of the PVC/GO hybrid membranes are mainly attributed to the strong hydrophilicity of functional groups on the GO surface, indicating that GO has a promising candidate for modification of PVC ultrafiltration membranes in wastewater treatment.

1. Introduction

Ultrafiltration (UF) membrane technology has been widely applied in the processes of water purification, wastewater

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treatment, food and pharmaceutical industry [1,2]. As an important strategy to improve UF membrane performance, polymer matrix materials as backbone have been intensively investigated in many studies [3,4]. Presently, variable polymer materials are proposed as backbone for the fabrication of UF membranes, such as cellulose acetate, polysulfone, polyacrylonitrile, polyethylene, poly-ether-sulfone, and polyvinylidene fluoride (PVDF). Especially, among them, PVDF has been widely developed as polymer matrix for UF membrane synthesis due to its high resistance to chlorine [5]. However, the high cost of these aforementioned polymer materials and their membrane modules substantially hinder the application of UF membrane in the rural area of developing countries, especially Africa, which suffer from the severe water shortage and security risk. Currently, the membrane cost is still a great concern for the world-wide application of UF membrane. Polyvinyl chloride (PVC) is an outstanding polymer for the fabrication of ultrafiltration membrane due to its lower cost and similar chemical stability with PVDF [6]. Generally, the PVC polymer is abundant in the plastic markets with a very low price which is less than 1/10 of that of PVDF polymer [7]. Thus, the PVC polymer is more competitive than other polymers for membrane fabrication, in view of its worldwide application in rural areas.

During the application of UF membrane, it is subjected to the membrane fouling, which can severely deteriorate the membrane flux and permeate quality [8]. In general, the strong hydrophilicity of membrane surface is favorable to resist the membrane fouling caused by the adsorption of soluble nature organic matters and microorganisms. On the other hand, the excellent mechanical property is urgently required to prolong the lifespan of UF membrane during backwashing or air flushing for membrane cleaning once the fouling occurs. Therefore, enhancement of the hydrophilicity and mechanical property for the PVC ultrafiltration membrane is of great concern for its potentially practical application in the rural areas [9].

Over the past decade, the effort on modification of polymer membrane through the incorporation of inorganic nanoparticles has been intensively made [10–12]. Many studies have confirmed that the incorporation of nanoparticles (i.e., SiO_2, TiO_2, ZrO_2, ZnO, Al_2O_3, etc.) with an appropriate content has a significant improvement in the hydrophilicity and permeability of synthesized membranes through changing the membrane structure [8,13–20]. In most cases, a relatively high proportion (1–4 wt%) of inorganic nano-materials is proposed to enhance the mechanical strength of synthesized membranes, which potentially exhibits the high risk of membrane blockage and thus conversely deteriorates the membrane flux [13,14,21].

Presently, carbon nano-materials have attracted substantial attention as promising additives for membrane modification [22,23]. For instance, carbon nanotube (CNT)/organic hybrid membranes show the stronger hydrophilicity and higher water flux, compared to the pristine membrane [24,25]. Practically, the optimal dosage of the CNT for membrane modification remains at the level ranging from 0.25 wt% to 2 wt% [7,26]. Thereby, the cost of applied CNT material poses a great concern for its engineering practice in membrane modification. Another carbon nano-material, namely graphene oxide (GO), contains a large amount of hydrophilic oxygen functional groups on its basal planes and edges [27]. Given the extraordinary 2D nanoplate structure, excellent mechanical properties and strong hydrophilicity, GO has been regarded as a desired candidate to design the advanced membranes [28–30]. As reported, several novel methods have been developed to prepare GO with low cost, making it more competitive and accessible than CNT [31,32]. Preferentially, a small dosage of GO is strongly recommended to reduce the cost for the fabrication of GO-modified hybrid membranes with improved performance. Currently, very limited literature reports the modification of UF membrane by blending GO with the small content. Zinadini et al. claimed that the permeation flux and anti-biofouling property of PES/GO membranes can be significantly enhanced with the addition of 0.5 wt% GO [33]. The blended PVDF/GO membranes can yield an improved filtration performance when the GO amount of 0.2% was applied [34]. Given the potential application of PVC membrane, it is of paramount importance to investigate the performance of PVC membrane doped with ultra-low concentration of GO. To the best of our knowledge, such study focusing on the doping of GO with ultra-low content in PVC polymer matrix has not been reported yet.

In this study, GO was prepared from expanded graphite through modified Hummers method to obtain a highly dispersed GO solution. Then novel GO modified PVC membranes were prepared by blending ultralow concentration of GO (0–0.15 wt%) via non-solvent induced phase separation procedure. The synthesized PVC/GO hybrid membranes were comprehensively characterized, in terms of the membrane morphology, mechanical property and permselectivity. Additionally, the antifouling property of the PVC/GO hybrid membranes was investigated as well.

2. Experimental section

2.1. Materials

PVC (M_w = 80,000 g/mol, Shenyang Chemical Industry Co. Ltd., China) was employed as the base polymer. N,N-dimethyl acetamide (DMAC, >99.5%, AR, Bodi Co., Ltd, China), polyvinyl pyrrolidone (PVP, AR) and flake natural graphite powder were obtained from Qingdao Tianhe Co. Ltd., (China). H_2SO_4 (98%), sodium nitrate ($NaNO_3$), hydrogen peroxide solution (5%), $KMnO_4$ and ethanol purchased from Fuyu Co. Ltd., (China) were applied in GO preparation as received. The distilled water was used throughout the experiment.

2.2. Preparation of GO dispersion

In this study, the modified Hummers method was employed to prepare graphene oxide (GO) [34]. Under the condition of ice bath, 5.0 g flake natural graphite powder was gradually added to cool H_2SO_4 with vigorous stirring for 50 min. Subsequently, 30 g $KMnO_4$ and 3.0 g $NaNO_3$ were added step wisely with stirring and cooling for 3 h at lower than 10 °C. The mixture was then heated to 35 °C and stirred at for 45 min. Afterwards, 220 mL deionized water was added into the mixture and heated to 95 ± 2 °C, and the color of suspension started to turn from black to brown· H_2O_2 (5%) solution was added to reduce the excess $KMnO_4$ until the color of the mixture turned from dark-brown to golden-yellow. Finally, the sample was obtained by centrifugation with washing by deionized water for several times and then dispersed by ultrasound for 1 h.

2.3. Preparation of GO-blended ultrafiltration membranes

GO-blended PVC ultrafiltration membranes were prepared via the immersion phase inversion method, which is described anywhere else [35]. 12 wt% PVC polymer and 5 wt% PVP in DMAC solvent was applied as the polymer matrix. The GO-modified PVC membranes were fabricated by fully dispersing different amounts of GO through mechanical stirring at 5000 rmp and 25 °C. Before dissolving PVC polymer, different loadings of GO (i.e., 0.05, 0.1, 0.15, and 0.2 wt%) was adequately dispersed in DMAC solvent with ultrasonic treatment for 1 h. Subsequently, the PVC polymer was added to the solution, stirred for 12 h to obtain homogeneous solutions for casting. And then the solutions were placed in a vacuum oven for 12 h to remove air bubbles and casted on a glass