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Optimization of preparation conditions of poly(vinylidene fluoride)/graphene oxide microfiltration membranes by the Taguchi experimental design

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HIGHLIGHTS

- The preparation conditions of PVDF/GO membranes were optimized by Taguchi design.
- The optimal conditions were 12 wt.% PVDF, 5 wt.% PVP and 3 wt.% GO in DMAC.
- The solution type was the most effective factor.
- The introduction of GO improved antifouling properties of composite membranes.

ARTICLE INFO

ABSTRACT

Poly(vinylidene fluoride) (PVDF)/graphene oxide (GO) microfiltration membranes were prepared via phase inversion process. The Taguchi experiments were designed to optimize the preparation conditions of composite membranes. PVDF content, solution type, GO content, and poly-(N-vinyl-2-pyrrolidone) (PVP) content were chosen as important effecting parameters. Membrane filtration resistance was optimized by calculating the signal-to-noise (S/N) ratio of the parameters. The group of PVDF = 12 wt.%, solution type = N, N-dimethylacetamide (DMAC), GO = 3 wt.%, and PVP = 5 wt.% was the optimal combination, and solution type was the most effective factor. Scanning electron microscope (SEM) images showed that all membranes had thicker finger-like substructures. To further investigate the influence of GO on antifouling and mechanical properties, the pure PVDF and PVDF/GO composite membranes (3.0 wt.%) were prepared according to the optimum conditions. The PVDF/GO composite membranes presented better antifouling performances due to the improvement of membrane hydrophilicity. The tensile strength and Young's modulus reached values of 10.33 and 148.47 MPa, which corresponded to a 55.11% and 67.14% increase, respectively.

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1. Introduction

Membrane bioreactors (MBRs) are effective and advantageous in treating municipal and industrial wastewaters over the conventional process because of the advantages including small space occupation, better effluent qualities, higher sludge concentration/low yield of surplus sludge, the sludge residence time and the hydraulic residence time separated [1]. The major drawback and restriction of MBRs come from the high cost in preventing performance deterioration caused by progressive membrane fouling and the high cost of membrane [2], which are the most challenging issues for the further development of MBRs [3]. Several characteristic parameters of membranes such as hydrophilicity, surface roughness, pore size and surface charge can affect the membrane antifouling properties [4]. Many efforts, such as physical

blending, plasma treatment, polymer grafting and chemical reaction, have been made to improve antifouling properties of membranes [5–7]. The most effective modification method is blending with inorganic nanoparticles such as Al_2O_3 [7], TiO_2 [8–10], SiO_2 [11], and $Mg(OH)_2$ [6]. Introducing inorganic nanoparticles in the membrane matrix can improve the hydrophilicity, the strength and stiffness, the water permeability and the antifouling properties.

Graphene oxide (GO) sheets are abundant with oxygen-containing functional groups (e.g., hydroxyl, carboxyl, carbonyl, and epoxy groups), which make them having strong hydrophilicity [12]. Meanwhile, the intrinsic properties of GO nanosheets, such as, good chemical stability, innocuity, and high surface area, make them feasible as additives for the fabrication of composite membranes [12–15]. Wang et al. report that the GO nanosheets, as a hydrophilic modifier, could obviously improve the water flux of prepared PVDF ultrafiltration membranes [14]. Ganesh et al. find that the GO doping into polymer matrix has resulted in enhanced hydrophilicity, water flux, and salt rejection property of

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the polysulfone (PSF) membrane [15]. However, a comparative study of the optimized preparation conditions and antifouling performances of PVDF/GO microfiltration membranes has not been reported.

Many factors such as polymer content, solution type, hydrophilic additives, coagulation bath temperature and membrane thickness, have an influence on the membrane properties during the preparation process. A large number of experiments need to be carried out to optimize the preparation conditions. It is a complex and tedious process. The Taguchi experimental method, which is a less complicated method requiring a much smaller number of experiments to be conducted for identifying the effect of all the possible combinations of the factors [16,17], can be used to optimize the preparation conditions through the settings of designed parameters and reduce the sensitivity of the system performance to sources of variation [18].

In this study, the preparation condition of antifouling microfiltration membrane was optimized based on Taguchi experimental design. The selected parameters were polymer content, solution type, GO amount, and pore-former content. Moreover, the effect of GO nanosheets on antifouling and mechanical properties was further probed.

2. Materials and methods

2.1. Materials

Poly(vinylidene fluoride) (PVDF, FR904) was obtained from Shanghai 3F New Materials Co. Ltd. N,N-dimethylacetamide (DMAc), N-methyl-2-pyrrolidone (NMP) and N,N-dimethylformamide (DMF) were purchased from Shanghai Chemical Reagent Company. Poly(N-vinyl-2-pyrrolidone) (PVP-K30, MW = 40,000) was purchased from Sigma Aldrich. Natural graphite powder (<20 μm, with purity >99.85 wt.%) was purchased from Sinopharm Chemical Reagent Co., Ltd. Sulphuric acid (98%) and hydrochloric acid were purchased from Beijing Chemical Works. 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. Dried yeast was purchased from Guangdong Danbaoli Instant Yeast Co., Ltd., which was washed thoroughly with water and then dispersed in deionized water using in membrane separation. The average yeast cell size was 5.9 ± 0.9 μm (range of 3.1–12.5 μm) determined by a Mastersizer 2000 particle size analyzer (Malvern, UK). The deionized (DI) water was used in the sample preparation and for pure water flux measurements.

2.2. Preparation of graphene oxide (GO)

Graphene oxide (GO) was prepared with natural graphite powder through a modified Hummers method [19]. The graphite powder (10 g) was put into cold (4 °C) concentrated H_2SO_4 (300 mL) maintained by an ice-bath. $NaNO_3$ (5 g) and $KMnO_4$ (30 g) were added gradually and slowly, so that the temperature of the mixture was not allowed to reach 20 °C. The mixture was then stirred at 35 °C for 2 h, and distilled water (250 mL) was added. The temperature would rise to more than 98 °C, maintaining for 1 h and then terminated by the addition of distilled water (250 mL) and 30% H_2O_2 solution (50 mL), after which the color of the mixture changed to bright yellow. The mixture was washed with a 1:10 HCl solution and a large amount of deionized water until there were no metal ions and acids. The viscous and brown mixture was treated with ultrasonic exfoliation for several hours, followed by centrifugation at 12,000 rpm for 15 min. At last the supernatant was dried at 70 °C for several hours. Exfoliated GO product was obtained.

2.3. Preparation of composite membranes

The PVDF/GO composite membranes were prepared by general phase inversion method. In this method, PVDF was used as bulk material, GO nanosheets as the additive, PVP as the pore-making agent and

distilled water as the nonsolvent coagulation bath. Prior to compounding, all powder reagents were dried at 80 °C in vacuum oven for 12 h to remove the absorbed water. The GO nanosheets were accurately weighed and dispersed in different solutions following sonication for more than 10 h to make homogeneous solutions, and then PVDF and PVP were dissolved in GO solution at 70 °C and stirred for 24 h. After the solution was fully degassed, the PVDF/GO composite membranes of 400 μm thickness on the clean polypropylene nonwoven fabric (PP-NWF) were cast accurately using a casting knife. Exposing to air for 20 s, the membranes were immersed into a coagulation bath (distilled water at 20 °C). The resultant membranes were kept in deionized water for 24 h to remove all the residual solvent and preserved in deionized water before all the characterization tests.

2.4. Characterization of membranes

The top surface and cross-section morphologies of membranes were examined by a scanning electron microscopy (SEM) (JEOL Model JSM-5600LV, Japan). The samples were cut into pieces of small sizes and cleaned with deionized water. These pieces were fractured in liquid nitrogen and coated with a thin gold layer under vacuum before test.

The hydrophilicity of membranes was evaluated by measuring water contact angle of the membrane top surface using the Drop Shape Analysis System (DSA100, Kruss Company, German). Briefly, a water droplet was deposited on a flat membrane surface and the contact angle of the droplet with the surface was measured. The instantaneous contact angle obtained within 0.2 s (ensuring observable vibration of the liquid drop on the membrane surface had already ceased) was recorded. The reported data of contact angle were averaged from at least five measurements at different locations for each sample.

The membrane porosity ε (%) is considered as the ratio between the volume of membrane pores and the total volume of the porous membrane. It can be determined by gravimetric method and is usually defined as [6]:

$$\varepsilon = \frac{(m_1 - m_2)/\rho_w}{(m_1 - m_2)/\rho_w + m_2/\rho_p} \tag{1}$$

where m_1 is the weight of the wet membrane, m_2 is the weight of the dry membrane, ρ_w is the density of pure water (0.998 g/cm^3) and ρ_p is the density of polymer membrane. In this paper, ρ_p is approximate to the density of PVDF (1.765 g/cm^3) due to the small GO content in the composite membranes.

Mean pore size is determined by the filtration velocity method. According to the Guerout–Elford–Ferry equation [11], r_m can be calculated as follows:

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta lQ}{\varepsilon \times A \times \Delta P}} \tag{2}$$

where η is the water viscosity (8.9×10^{-4} Pa·s), l is the membrane thickness (m), Q is the volume of the permeate water per unit time (m^3/s), A is the effective area of the membrane (m^2) and ΔP is the operational pressure difference (0.025 MPa).

Maximum pore size (r_{max}) could be obtained by bubble point method. According to Laplace's equation, maximum pore size could be calculated [11]:

$$r_{max} = \frac{2\sigma \times \cos\theta}{P} \tag{3}$$

where σ was the surface tension of water (71.96×10^{-3} N·m^{-1}), θ was the contact angle of water to membrane (°) and P was the minimum bubble point pressure (Pa).

A self-made dead-end stirred cell filtration system (effective area of 34.2 cm^2) connected with a peristaltic pump was used to evaluate membrane permeation flux and antifouling properties. At least 3