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Preparation and antifouling property of polyethersulfone ultrafiltration hybrid membrane containing halloysite nanotubes grafted with MPC via RATRP method

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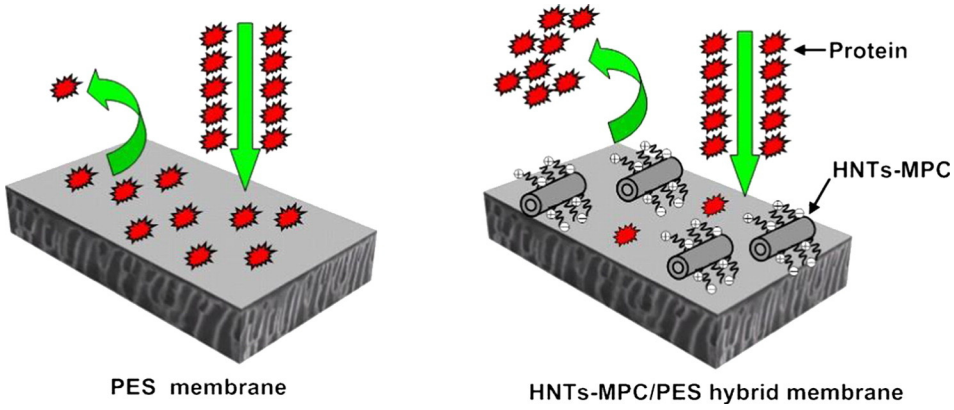
HIGHLIGHTS

- HNTs-MPC were synthesized by chemical modification of HNTs with MPC via RATRP.
- The hybrid membranes containing HNTs-MPC possessed higher water flux.
- The hybrid membranes showed good antifouling performance and stability.

GRAPHIC ABSTRACT



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ABSTRACT

Polyethersulfone ultrafiltration hybrid membrane containing halloysite nanotubes grafted with 2-methacryloyloxyethyl phosphorylcholine (HNTs-MPC) was prepared via phase inversion method for the purpose of enhancing the antifouling property of the membrane. HNTs-MPC were synthesized by chemical modification of HNTs with MPC via reverse atom transfer radical polymerization (RATRP). The performance and morphology of the membranes were characterized by water contact angle and SEM. The hybrid membrane was shown to be more hydrophilic with a higher pure water flux. The thickness of the thin separating layer on the top tended to decrease with the addition of HNTs-MPC. The BSA adsorption experiment indicated that the adsorption amounts of bovine serum albumin (BSA) on the membrane were dramatically decreased. BSA ultrafiltration experiment also showed that the antifouling ability of the membrane with the addition of HNTs-MPC was better than the pure PES membrane. Meanwhile, the long term ultrafiltration experiment showed that the hybrid membrane had an ideal stability.

1. Introduction

Polyethersulfone (PES) membrane has been widely used in biomedicine, food and water purification, etc. [1]. PES is one of the most important membrane materials because of its excellent heat-aging

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resistance, environmental endurance and easy processing [2]. However, the performance of the membrane is affected seriously due to the membrane fouling, which is likely associated with the hydrophobic character of PES. Membrane fouling occurs on the hydrophobic surface as a result of protein adsorption, denaturation and aggregation [3,4]. What is worse, membrane fouling is a serious problem in the practical applications such as membrane bioreactor and ultrafiltration systems [5,6].

It is generally accepted that the increase of the hydrophilicity could improve the antifouling property of the membranes [5,7]. Recently, the hydrophilization of the membrane has been considered as a promising approach to reduce membrane fouling. So the surface modification of the membrane is very important [8]. Coating, surface grafting, and blending as the methods of modification have been developed to increase the hydrophilicity of the membrane surface [3,9]. Boributh et al. studied the modification of hydrophobic membrane by chitosan solution to reduce protein fouling. The results indicated that the modified membrane had higher hydrophilicity and better antifouling property than the unmodified membrane [10]. Zhang et al. prepared photochemical modification-PES/PVDF blend membrane. The modified membrane showed better fouling resistance and better flux recovery and the adsorption amounts of BSA decreased from 159 ± 2 μg/cm^2 to 13 ± 2 μg/cm^2 [11].

Although hydrotropic modification of the membrane is a method to reduce protein fouling, non-fouling of the membrane surface is still not achieved. Ostuni et al. proposed four molecular-level characteristics of non-fouling membrane surface: hydrophilic, including hydrogen-bond acceptors, without hydrogen-bond donors and electric neutrality [12]. While the kinds of modifier of non-fouling membrane surface are numbered, there are poly (ethylene glycol) (PEG) and its derivative as well as zwitterionic polymer. Wang et al. studied PVDF microporous membrane with surface-immobilized PEG. The results indicated that the flux decreased with the increase of PEG and the modified membrane had good antifouling property [13]. Nie et al. improved the antifouling property and biocompatibility of polyacrylonitrile membrane by the immobilization of PEG on the membrane surface. It was found that the membrane showed higher solution flux, lower BSA adsorption and better flux recovery [14]. Hucknall et al. showed the protein resistant or non-fouling surface. The article indicated that polymer brushes synthesized by surface initiated polymerization were extremely resistant to protein adsorption and cell adhesion [15]. Su et al. studied the synthesized phosphorylcholine copolymer MPC-BMA and blended with PES to fabricate antifouling ultrafiltration membrane. The results showed that the hydrophilicity of the modified membrane was improved and the adsorption amounts of BSA were dramatically decreased compared with the pure membrane. Ultrafiltration experiments showed that the rejection ratio of BSA was decreased and the flux recovery ratio was obviously increased [16]. Ye et al. designed a novel CA membrane blended with MPC copolymer to improve the blood compatibility of CA membrane. The CA blended membrane showed both good water and solute permeabilities in comparison with the pure CA membrane [17].

Nowadays, nanoparticles are the major hydrotropic substance to modify the membrane in order to reduce protein fouling, such as TiO_2 [18,19], SiO_2 [20,21], Al_2O_3 [22,23], CNT [24,25], and HNTs [26]. The halloysite (formula: $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$) often occurs as an ultramicroscopic hollow tubule with a multi-layer wall in nature. Halloysite nanotubes (HNTs) have been widely used as catalyst support, nanoreactors and adsorbents [27,28]. Moreover, HNTs are easy to be dispersed in a polymer matrix due to their well-crystallized structure, low density of hydroxyl functional groups and their tubular shape [29]. MPC [30–32], an artificially synthesized monomer, has received more and more attention and many MPC-based materials are effective to resist protein adsorption. In this study, HNTs grafted with MPC were prepared to improve the antifouling performance of the membrane.

In the present study, PES ultrafiltration membranes were modified by blending with HNTs-MPC. HNTs-MPC were synthesized by chemical modification of HNTs with MPC via RATRP. The results indicated that the hybrid membranes containing HNTs-MPC possessed higher water flux. Meanwhile, the hybrid membranes showed good antifouling performance and stability.

2. Experiment

2.1. Materials

Halloysite nanotubes (HNTs) were refined from clay minerals in Henan province, China. 2-methacryloyloxyethyl phosphorylcholine (MPC) was used for the chemical modification of HNTs and purchased from J&K. Polyethersulfone (PES) was supplied by BASF Company. PVP (Mw = 40,000 Da) was purchased from Sinopharm Chemical Reagent Co. Ltd. Other reagents were all of analytical grade and used without further purification. The used water is deionized water.

2.2. MPC grafted onto HNTs

The reaction principle of preparing HNT-MPC nanoparticles is shown in Fig. 1. Firstly, chemical modification of HNTs by 3-chloride propyl triethoxy silane was achieved by applying the steps as follows: 3-chloride propyl triethoxy silane (9 g) and triethylamine (1 mL) were dissolved in toluene (100 mL) by shaking and then HNTs (6 g) were poured into the solution. The resulting mixture was then refluxed at 125 °C for 48 h under rigorous stirring. Then, the surface modified HNTs were washed with isopropanol and collected by centrifugation. The product was dried in a vacuum oven at 60 °C.

Then, the silane-modified HNTs (1.5 g), MPC (6.5 g), $CuCl_2$ without water (0.06724 g), 2, 2-bipyridyl (0.1562 g) and ethyl alcohol (40 mL) were mixed in a three-necked flask. Azodiisobutyronitrile (AIBN) (0.0821 g) was dissolved in ethyl alcohol (20 mL) and the mixture was transferred into the constant pressure funnel. The constant pressure funnel was placed in the three-necked flask. The equipment was vacuumized and filled with nitrogen for three times and stirred continuously at 30 °C for 10 min. AIBN solution was instilled and stirred continuously at 30 °C for 6 h. After the exchange, the sample was washed with methanol for one time and deionized water for three times. Then, the product was collected by centrifugation and dried in a vacuum oven at 60 °C.

2.3. Preparation of the membrane

Pure PES membrane and HNTs/PES hybrid membrane were prepared via the phase inversion method. Casting solution of the PES dissolved in DMAc was prepared using PVP as pore former by stirring

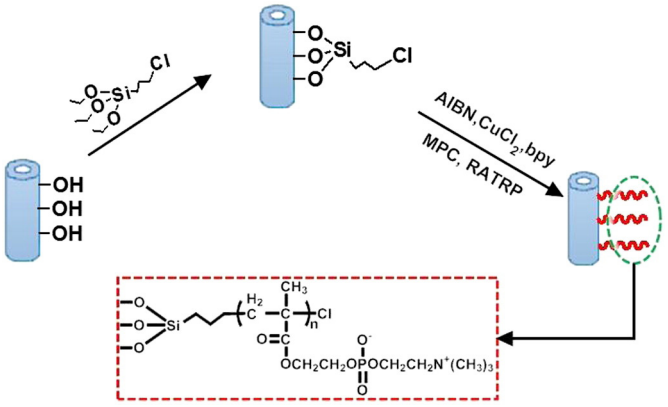

Fig. 1. Preparation process of HNTs-MPC via reverse atom transfer radical polymerization.