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Preparation and characterization of negatively charged PES nanofiltration membrane by blending with halloysite nanotubes grafted with poly (sodium 4-styrenesulfonate) via surface-initiated ATRP

Junyong Zhu, Ningning Guo, Yatao Zhang*, Liang Yu, Jindun Liu*

School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou 450001, PR China

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ABSTRACT

Sodium 4-styrenesulfonate was grafted onto the surfaces of halloysite nanotubes (HNTs) via surface-initiated atom transfer radical polymerization (SI-ATRP), and then negatively charged nanofiltration (NF) membranes were fabricated by blending various contents of HNTs-poly(sodium 4-styrenesulfonate) (HNTs-poly(NASS)) composites via phase inversion method. The grafting degree was effectively controlled by varying the reaction time and the amount of monomers. The results of FT-IR, TGA, and TEM indicated that HNTs-poly (NASS) composites were successfully synthesized and GPC results exhibited the linear relationship between number-average molecular mass (Mn) and reaction time. In addition, the membranes were characterized by SEM, static water contact angle and water ratio. It was found that the hydrophilicity of hybrid membranes was significantly superior to bare PES membranes, which corresponded to the results of pure water flux and thus may enhance fouling resistance to a certain extent. The ion-exchange capacity (IEC) value could be up to 0.07 mmol/g when the HNTs-poly (NASS) content was only 3 wt%. Meanwhile, the pure water flux of the hybrid membranes increased with increasing the HNTs-poly (NASS) content. The permeation ratio for saline solution increased significantly, such as $P_{(MgCl_2)}$ from 77% to 96.5%. From the analysis above, these prepared hybrid membranes have a potential application in desalination of textile industry and wastewater treatment.

1. Introduction

Nanofiltration (NF) has gained tremendous attention for application in water treatment, textile, pharmaceutical, chemical and other industries [1–4] due to their lower operating pressure and higher permeation flux than reverse osmosis (RO) with a wide range of molecular weight cutoffs (100–1000 Da) [5,6]. NF membranes are mainly used for separation of low-molecular-weight (LMW) organics and saline solution such as desalination and purification because of their high retention of natural organic matter (NOM) and relatively low monovalent ions [7]. Moreover, charged NF membranes exhibit better permeation, purification and fouling-resistant properties than neutral bare NF membranes. The high selectivity of charged NF membranes are based on both surface charge (Donnan effects) and size exclusion (sieving effects), which allow NF membranes to be effective for separation of mixtures composed of NOM and saline solution [6,8–10]. Polyethersulfone (PES), a common membrane material which possesses excellent chemical and thermal stability as well as pressure and heat resistance, is one of the commonly used matrix NF membranes [11–13]. However, the hydrophobicity of PES restrict its commercial potential application in desalination and water treatment due to low flux, membrane fouling and short service life [14,15]. Therefore, synthesis of new-type material or modification of membrane material is indispensable and significant to broaden NF membrane potential application in various fields.

Organic–inorganic hybrid materials have attracted great attention for membrane preparation owing to their unique opportunity to combine their both advantages such as physical, chemical, thermal and mechanical properties [16–19]. Herein, inorganic materials used as carriers of charged material endow the membranes with better hydrophilic characteristics and charge properties. Halloysite nanotubes (HNTs) are a promising inorganic material owing to the following properties: nano-tubular structure, regular open-ending pores, a great deal of hydroxyls on their

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* Corresponding authors. Tel./fax: +86 371 67781734.
E-mail addresses: zhangyatao@zzu.edu.cn (Y. Zhang), liujindun@zzu.edu.cn (J. Liu).

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surfaces and these combination accelerate their widely potential application in versatile fields [20–22].

Nowadays, one of the prevalent "living"/controlled polymerization, atom transfer radical polymerization (ATRP) has attracted considerable attention in view of many excellent properties, such as well-controlled molecular weight, relatively narrow molecular weight distribution, and tunable decorations [20,21,23,24]. SI-ATRP, also known as grafting-from, is a popular technique to generate polymer brush grafted onto inorganic or organic surfaces. Therefore, more and more researchers have been giving attention to the method of SI-ATRP [25–27].

With respect to membrane preparation, numerous modification methods have been employed to enhance hydrophilicity and charge capacity of membranes surface, including blending [12,28–31], surface graft polymerization [32–37], interfacial polymerization [38–40] and coating [41,42]. Among these various techniques, the blending of composites into membrane matrix has the advantages of easy preparation by phase inversion, enhancing homogeneous dispersion as well as strengthening the filler–polymer interaction [28,30].

In this study, HNTs-poly (NASS) were synthesized via surface-initial ATRP and used as the hydrophilic and negatively charged additive, then negatively charged PES hybrid membranes were fabricated via phase inversion method by blending with HNTs-poly (NASS) composites. The effects of composites on the membrane surface hydrophilicity, microstructure and charged capacity were investigated in detail.

2. Experimental

2.1. Materials

Polyethersulfone (PES, Mw=58,000 Da) was supplied by BASF Company. Halloysite nanotubes (HNTs) were refined from clay minerals in Henan province, China. N-dimethylacetamide (DMAc) and polyvinylpyrrolidone (PVP, Mw=24,000 Da) were purchased from Kewei Chemical Reagent Co. (Tianjin, China). Sodium 4-styrenesulfonate, 2-bromoisobutyryl bromide, γ-aminopropyl triethoxysilane (APTES), and 2, 2′-Bipyridine (bpy) were purchased from Aldrich Chemical Co. and used as received. Reactive Red 49 (Mw=576.49 Da) and Reactive Black 5 (Mw=991.82 Da) were purchased from Sunwell Chemicals Co. Ltd., China, and the structural formulas are presented in Fig. 1. All the other chemicals (analytical grade) were obtained from Tianjin Kermel Chemical Reagent Co., Ltd., China and were used without further purification. The used water is deionized water.

2.2. Synthesis of HNTs-poly (NASS)

2.2.1. Synthesis of HNTs-APTES

Modified HNTs grafted with poly (NASS) were prepared via a three-step synthesis route which is shown in Fig. 2. Firstly, HNTs (2.0 g) were dispersed into the mixture of ethanol (200 mL), water (10 mL) and aqueous solution of ammonia (15 mL) under stirring at room temperature for 24 h. APTES (2 mL) was added to the resultant mixture and stirred for 32 h. Afterwards, the products were collected by three cycles of centrifugation followed by drying in a vacuum oven at 50 °C.

2.2.2. Anchoring of initiator on the HNTs-APTES

Briefly, HNTs-APTES (2.0 g) and triethylamine (TEA) (0.1 mL) were dispersed in THF (80 mL) in a dried three-necked flask, then 2-bromoisobutyryl bromide (BIBB, 0.5 mL) was added to the mixture dropwise. The reaction was carried out under N_2 atmosphere in an ice-water bath for 3 h, and then heated to 25 °C for 12 h. Afterwards, the products (HNTs-Br) were purified by centrifugation with washing by methanol and water orderly for 3 times and then dried in a vacuum oven at 40 °C till constant weight.

2.2.3. Polymerization of sodium 4-styrenesulfonate onto HNTs-Br

A mixture of HNTs-Br (0.5 g), sodium 4-styrenesulfonate (0.5 g), and DMF (300 mL) were introduced into a four-necked flask. Then BIBB (0.0032 g) dissolved in DMF (5 mL) was added into the mixture. The flask was sealed and the mixture was degassed via three freeze–pump–thaw cycles. Subsequently, 2, 2′-bipyridyl (0.11 g, 0.72 mmol), copper (I) bromide (0.05 g, 0.30 mmol) dispersed in DMF (20 mL) were added into the mixture and being stirred in an oil bath at 130 °C under nitrogen for a period of time. The samples (3 mL) were removed with a purged syringe at each two hours for GPC measurement. Here, BIBB as a non-fixed initiator was not merely to control the polymerization, but produce an unbound polymer, which was an ingenious measure for molecular weight and distribution of the graft polymer brushes [43]. Then HNTs-poly (NASS) composites were obtained by centrifugation with washing by acetone and then dried in a vacuum oven at 30 °C.

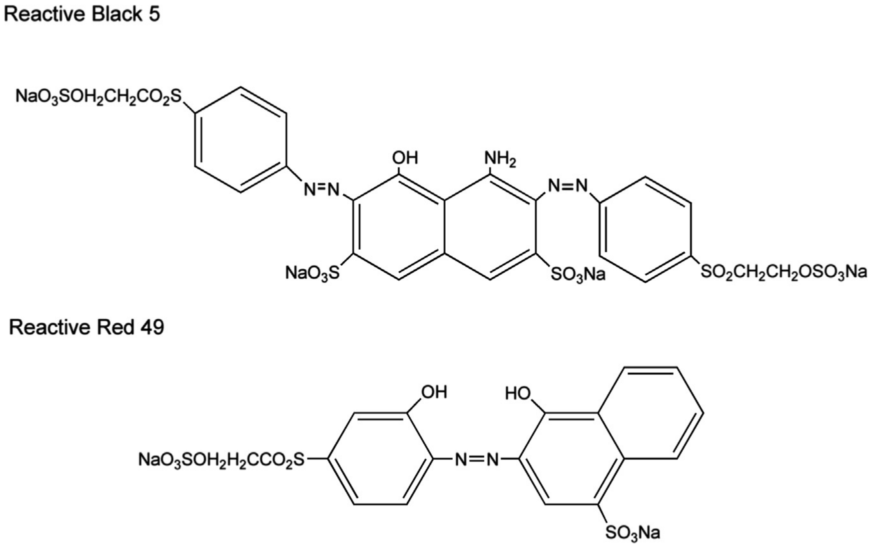

Fig. 1. Structural formulas of Reactive Red 49 and Reactive Black 5.