



# Development of a molecular separation membrane for efficient separation of low-molecular-weight organics and salts



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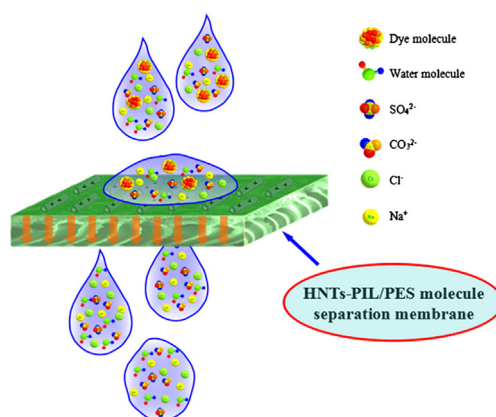
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## HIGHLIGHTS

- HNTs were firstly modified by poly (ionic liquid) brushes via RATRP.
- Molecular separation membranes were fabricated by incorporation of HNTs-PIL.
- These membranes possess high salt passage and organic matter removal.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A positively charged nanomaterial was prepared adopting the graft polymerization of ionic liquid monomers on halloysite nanotubes (HNTs) via reverse atom transfer radical polymerization (RATRP). A novel and facile organic–inorganic hybrid molecular separation membrane was then fabricated by the incorporation of modified HNTs via phase inversion method. This hybrid membrane was investigated in terms of morphology structure, hydrophilicity, thermal, mechanical and electrical properties, and separation performances. The results revealed that the hybrid membranes represented thickened and loosened skin layer, enhanced surface hydrophilicity and water flux, as well as good thermal and mechanical properties. Most importantly, the hybrid membranes showed stabilized rejection for Reactive Black 5 (above 90%) and Reactive Red 49 (80%–90%), whereas the rejection for sorts of salts declined to below 10% indicating a potential molecular separation characteristic for dye desalination.

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## 1. Introduction

In printing and dyeing industry of reactive dyes, a mass of electrolytes (usually  $\text{NaCl}$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{Na}_2\text{SO}_4$ ) is often required in dyeing process to improve the dyeability and remains in wastewater. Such large amount of wastewater with high salinity and chroma will result in serious environmental pollution, waste of resources as well as cost

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increases. If the low-molecular-weight organic substances in the wastewater can be removed and the salts are still remained, the treated wastewater containing salts may be recycled and reused in dyeing industry of reactive dyes. Besides, the quality and stability of dye products will also decrease on account of the presence of salts. Hence, it is in bad need to find outstanding desalting method for dyestuff wastewater treatment or dye purification. Nanofiltration (NF) has gained the public attention since it was first introduced in 1980s for the increased selectivity for mono- and divalent or multivalent ions, low operating pressures, relatively low capital and operating costs. NF membrane has been used in a wide range of water softening [1–3], removal of dyes [4,5], NOM [6], and pesticides [7,8] in drinking water treatment, and removal of heavy metal ions from industrial wastewater before discharging [9]. The nominal molecular weight cut off of a NF membrane is in the range of 100–1000 Da indicating an approximate pore size of 1 nm, which provides possibilities for molecular separation between low-molecular-weight organics and salts. However, common NF membranes have higher rejections for salts which are difficult to realize the molecular separation effect. Therefore, it is of great theoretical and practical significance to study molecular separation membranes with an enhanced salt passage behavior and a stabilized and higher rejection for low-molecular-weight organics. Given the fact that the remained salts in reactive wastewater are mostly sodium salts like  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{SO}_4$ , a positively charged membrane may facilitate the transmission of such bivalent salts to some extent. Meanwhile a small change in the structure of separation layer of NF membrane may produce a great influence in salt passage ability, especially for a NF membrane prepared by a phase inversion method, in which a loose skin layer tends to be formed upon the incorporation of nanoparticles because of the enhanced viscosity of casting solution. Hence, a molecular separation effect for the treatment of reactive dye wastewater is likely to be achieved by the preparation of positively charged loose NF membrane through a “blending-phase inversion method”. Typically, positively charged NF membrane can be fabricated by coating a positively charged separation layer on a supporting membrane, introducing positive charge groups to the membrane surface [10–15]. But the above methods are very complicated, uneconomic, and environmentally hazardous and tend to decrease the membrane pore size and generate a dense skin layer.

Polyethersulfone (PES) has been used extensively in many membrane separation processes with the advantages of good flexibility, toughness, and separation properties [14,16]. However, the limited chemical, mechanical and thermal resistance restricts its application range and scale. Conversely, inorganic nanomaterials have higher chemical, mechanical and thermal resistance. As reported, inorganic mixed polymer membrane could combine the processability of polymers with enhanced performance of inorganics in a single membrane, which may offer specific advantages for the preparation of artificial membranes with excellent separation performances, good thermal and chemical resistance and adaptability to the harsh environments [17,18]. Thus, the fabrication of organic–inorganic membrane has attracted increasing attentions. Previously, many hybrid membranes were prepared via “blending-phase inversion method” [16,19–24] as well as sol–gel method [25–30]. As expected, the hybrid membranes exhibited good permeability and separation properties, suggesting the advantages for hybrid composites to produce molecular separation membranes.

Halloysite nanotubes (HNTs), a kind of aluminosilicate clay, are promising inorganic nanomaterials due to their tubule structure and chemically active external and internal surfaces. The readily obtainable and far less expensive feature makes HNTs a good alternative in a wide application as superior inorganic nanomaterials [31]. In our previous study, pristine HNTs were added to PES casting solution to prepare ultrafiltration membranes which exhibited an enhanced water flux and however a very slight change in rejection for polyethylene glycol (PEG) [32]. Atom transfer radical polymerization (ATRP), allowing for

the polymerization of most vinyl monomers in a controlled/“living” manner, is a promising method to tailor the surface properties of nanoparticles [33]. Numerous kinds of polymer brushes have been successfully grafted onto the surface of inorganic nanomaterials via ATRP method [34–37].

Herein, poly (ionic liquid) brush modified HNTs were fabricated through a reverse ATRP (RATRP) method which is relatively easy to operate than ATRP. Scheme 1 illustrates the differences between ATRP and RATRP. The modified HNTs, endowed with well hydrophilicity and organic compatibility, were then introduced to PES casting solution to prepare hybrid positively charged molecular separation membrane. Fig. 1 shows a brief fabrication process for such membrane, which may open opportunities for treatment of dye wastewater or separation between low-molecular-weight organics and salts.

## 2. Experimental

### 2.1. Materials

Allyl chloride, 2-bromoisobutyryl bromide, triethylamine (TEA),  $\gamma$ -aminopropyl triethoxysilane (APTES), 2, 2'-bipyridine (BPy), azodiisobutyronitrile (AIBN), and polyvinyl pyrrolidone (PVP,  $M_n = 24,000$ ) were purchased from Aldrich Chemical Co. and used as received. Polyethersulfone (PES, Ultrason E6020P with  $M_w = 58$  kDa) was obtained from BASF, Germany. Halloysite clay from Henan Province (China) was milled and sieved to obtain halloysite nanotubes (HNTs). Reactive Red 49 ( $M_w = 576.49$ ) and Reactive Black 5 ( $M_w = 991.82$ ) were purchased from Sunwell Chemicals Co., Ltd., China and used without any treatment. All the other chemicals (analytical grade) were obtained from Tianjin Kermel Chemical Reagent Co., Ltd., China and used without further purification. The used water was deionized water.

### 2.2. Fabrication of poly (ionic liquid) brush modified HNTs

#### 2.2.1. Synthesis of ionic liquid monomer allyl triethylammonium chloride (ATEA-Cl)

Briefly, TEA (10.12 g, 0.1 mol) and allyl chloride (9.18 g, 0.12 mol) were put into a dried flask. The mixture was then stirred at 60 °C under reflux conditions for 7 h and the redundant allyl chloride was removed upon vacuum evaporation. The solid product was cooled to room temperature, followed by washing with anhydrous ether for several times and drying under vacuum at room temperature for 12 h.  $^1\text{H}$  NMR (400 MHz,  $\delta$ , ppm, DMSO): 1.20 (9H, t,  $-\text{CH}_3$ ), 3.21 (6H, q,  $-\text{CH}_2-\text{CH}_3$ ), 3.88 (2H, d,  $-\text{CH}_2-\text{CH}=\text{CH}_2$ ), 5.66 (2H, d,  $-\text{CH}=\text{CH}_2$ ), 6.01 (1H, m,  $-\text{CH}=\text{CH}_2$ ).

#### 2.2.2. Synthesis of 2-bromo-2-methyl-N-(3-(triethoxysilyl) propyl) propanamide (BTPAm)

Briefly, APTES (9 mL, 40 mmol) and TEA (6 mL, 40 mmol) were dissolved to toluene (30 mL) and the mixture was then cooled to 0 °C. Another mixture of toluene (20 mL) with 2-bromoisobutyryl bromide (5 mL, 40 mmol) was added dropwise to the above cold mixture under stirring, followed by reacting for 3 h in an ice-water bath and 10 h at room temperature, respectively. The newly generated solid (TEA·HBr) was removed by vacuum filtration and the final product was then obtained by vacuum evaporation at 60 °C to remove the solvent.  $^1\text{H}$  NMR (400 MHz,  $\delta$ , ppm,  $\text{CDCl}_3$ ): 0.65 (2H, t,  $-\text{CH}_2-\text{Si}$ ), 1.23 (9H, t,  $\text{CH}_3-\text{CH}_2-\text{O}-\text{Si}$ ), 1.66 (2H, m,  $-\text{CH}_2-\text{CH}_2-\text{Si}$ ), 1.96 (6H, s,  $\text{CH}_3-\text{C}-$ ), 3.28 (2H, q,  $-\text{CH}_2-\text{N}$ ), 3.83 (6H, q,  $-\text{CH}_2-\text{O}-\text{Si}$ ), 6.87 (1H, s,  $-\text{NH}$ ).

#### 2.2.3. Synthesis of initiator-coated HNTs (HNTs-Br)

Previously dried HNTs (2 g) were immersed in a 30 mmol/L solution of BTPAm in anhydrous toluene and the mixture was then heated to 120 °C to react for 12 h under reflux condition. After the reaction, the products

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