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Synthesis of catalytic polypropylene membranes enabling visible-light-driven photocatalytic degradation of dyes in water

Sanni Ma, Jianqiang Meng*, Jinghua Li, Yufeng Zhang, Lei Ni

State Key Laboratory of Hollow Fiber Membrane Materials and Processes, Tianjin Polytechnic University, Tianjin 300387, PR China

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ABSTRACT

A novel catalytic membrane was synthesized by grafting a poly(ionic liquid) (PIL) onto polypropylene (PP) membrane followed by complexing with polyoxometalate (POM). The membrane was successfully used for degradation of dyes in water under visible light. PP nonwoven fabric membrane (PP NWF) was firstly modified by photoinduced grafting of poly(1-(4-vinylbenzyl)-3-methylimidazolium chloride) (PVBMC) and then anchored with POM $H_3PMo_{12}O_{40}$. The modified membranes PP-g-PVBMC and PP-g-PVBMC-POM were characterized by FT-IR, FESEM and XPS. The results indicate that the PIL–POM composites were successfully immobilized on the membrane surface. By optimizing the synthetic conditions, a PVBMC grafting degree of 370 μg/cm^2 and a POM loading of 312 μg/cm^2 can be achieved. Acid orange 7 (AO7) was used as a model dye molecule to evaluate the photocatalytic performance of the membrane. By static soaking the membrane in solution, the catalytic membrane was demonstrated to be able to degrade 95% of AO7 in 0.02 g/L of solution in 120 min with the irradiation of two 55 W fluorescent lamps. By cycled filtration of the solution, a membrane disc of 47 mm diameter can degrade 70% of the AO7 in 250 mL of 0.02 g/L solution in only 10 min. High pH and the presence of inorganic salts can deteriorate the photocatalytic activity of the membrane. The cycled use and the long-term stability test indicate that the membrane has good reusability and stability as a catalytic membrane.

1. Introduction

Water is essential to human life, agricultural and industrial activities. However, more and more areas suffer from water scarcity because of the increasing demand of fresh water due to the world-wide population booming and industrialization and the decreasing of available fresh water resources due to pollution. As one of the major sources of water pollution, textile effluents contain a large group of organic dye compounds that can bring environmental pollution owing to their non-biodegradability, toxicity and potential carcinogenic risk [1–4]. So it is essential to develop economic and effective methods for dye wastewater treatment.

Adsorption and microbiological discoloration are two major traditional methods for the removal of synthetic dyes from wastewater [5–9]. But both of them have prominent limitations. Although various inexpensive and efficient adsorbents have been developed for dye adsorption, the secondary pollution from regeneration of the adsorbents is inevitable [5,6]. As far as the microbiological methods are concerned, because synthetic dyes are very stable to chemical and microbial attack, the efficiency of these methods are far from enough. On the other hand, because of the high efficiency and complete minimization of the environmental hazard, the photocatalytic degradation method has attracted increasing attention in recent years [10–13].

Membrane technology has been widely used in a variety of sectors of industry including water desalination, waste water treatment, food, pharmaceutical, biological, chemical and petrochemical process and many others. It has the advantages of low energy consumption, low maintenance cost, stable effluent quality, easy operation and easy scale up. The research on catalytic reactors incorporating membranes is about two decades old. The development of these membrane catalytic reactors has been mostly targeting at chemical and petrochemical process such as selective hydrogenations [14,15], reduction of nitrous oxide [16], MTBE decomposition [17,18], dimerization of isobutene as well as catalytic oxidations [19–21]. As developed in parallel, photocatalytic membrane reactors (PMRs) have also been exploited for wastewater treatment. The photocatalysts were suspended in the solution filtrated by the membrane or immobilized on/in the membrane. Among the photocatalysts incorporated into PMRs, TiO_2 is mostly widely used [22–28]. However, it is only responsive to ultraviolet (UV) irradiation due to its large band gap and low quantum yield. This basically excludes the use of polymeric membrane as the membrane material. The membrane materials typically are inorganic membranes which are expensive and fragile. Therefore significant efforts have been devoted to exploring photocatalysts responsive to visible light.

Researches have shown that polyoxometalates (heteropolyacids and their salts, abbreviated herein as POM) and their transition-metal

* Corresponding author. Tel.: +86 22 83955078; fax: +86 22 83955055.
E-mail address: jianqiang.meng@hotmail.com (J. Meng).

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substituted derivatives have the ability of undergoing reversible one or multi-electron transfer while retaining their original structure, which has rendered these compounds attractive acid and redox catalysts in a variety of industrial catalytic applications [29,30]. As one of the most important visible light photocatalysts, POM-based materials have been actively studied for degradation of synthetic dyes [31,32]. Apparently, POM itself is soluble in water and is not recyclable. Therefore, it was used to assemble with poly(ionic liquid)s (PILs) forming water-insoluble and green photocatalysts. In this work, we report a novel catalytic membrane by anchoring the POM–PILs composites on the surface of porous membrane (see Scheme 1). Polypropylene nonwoven fabric membrane (NWF) was selected as the base due to its well-controlled porosity, good chemical stability and low cost [33,34]. The photocatalytic membrane was prepared through UV-initiated grafting polymerization of an ionic liquid monomer 1-(4-vinylbenzyl)-3-methylimidazolium chloride (VBMC) followed by assembly with the phosphomolybdic acid ($H_3PMo_{12}O_{40}\cdot nH_2O$) catalyst. The resulted membrane can be used in a membrane reactor to treat dye wastewater under visible light. Acid orange II (AO7) was selected as a model contaminant to evaluate the photocatalytic performance of the membrane. In addition, the chemical composition and surface morphologies of the catalytic membrane were investigated and the effects of operational parameters on photocatalytic degradation of the dye molecules were also studied.

2. Experimental

2.1. Materials

The substrate used for synthesis of the catalytic membrane is commercial polypropylene non-woven fabric flat sheet membrane (PP NWF, Shanghai XinBu Co., China) with a diameter of 47 mm and average pore diameter of 0.22 μm. Keggin-type structure phosphomolybdic acid ($H_3PMo_{12}O_{40}\cdot nH_2O$), benzophenone (BP, 98%) and methanol (HPLC grade) were purchased from Kermel company (China). Orange II sodium salt, hydrochloric acid, 1-methylimidazole (99%) and 4-vinylbenzylchloride (> 90%) were purchased from J&K Chemical Co. (China). All ultrapure water was obtained from a Millipore Milli-Q Advantage A10 water purification system (18.2 MΩ cm at 250°C, 1.2 μg/L TOC) (Billerica, MA, USA).

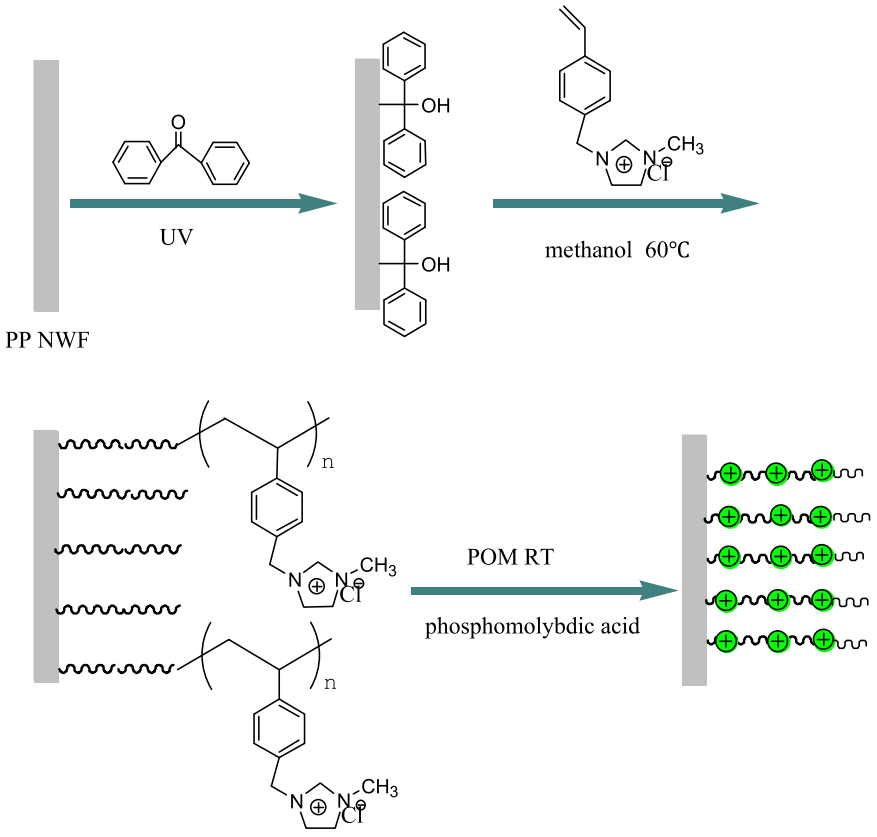
2.2. Synthesis of 1-(4-vinylbenzyl)-3-methylimidazolium chloride (VBMC)

Synthesis of the IL monomer VBMC was conducted according to a procedure modified from that reported in literature [32]. 4-Vinylbenzylchloride (17.2 mL, 0.11 mol) and N-methylimidazole (7.9 mL, 0.10 mol) were mixed via vigorous stirring at 0 °C. The reaction mixture was then stirred at 45 °C under nitrogen for 1 h. The obtained viscous solution was diluted with the mixed solvent of ethyl acetate and ethanol (2:1, v/v). The product was precipitated in ethyl ether, rinsed with ethyl ether for three times and then dried in vacuum at room temperature. The product was obtained as a pale yellow viscous liquid in a yield of 90%.

^{1}H NMR assignments ($CDCl_3$, 300 MHz):10.60 (1H, s, –N–CH–N–), 7.45–7.26 (6 H, m, –N–CH–CH–N–, Ph and $CDCl_3$), 6.71–6.64 (1H, dd, CH_2═CH–), 5.78 (1H, s, CH_2═CH–), 5.73 (1H, s, CH_2═CH–), 5.56 (2H, s, Ph–CH_2–N–), 4.07 (3H, s, –N–CH_3).

2.3. Synthesis of the PP-g-PVBMC membrane

The PP NWF membrane sample was washed with methanol for 24 h to remove the additives and impurities adsorbed on the



Scheme 1. Schematic representation for the synthesis of the catalytic membrane. (For interpretation of the references to color in this scheme, the reader is referred to the web version of this article.)