



Gravity-driven catalytic nanofibrous membranes prepared using a green template



Jianqiang Wang, Hao Guo, Zhe Yang, Ying Mei, Chuyang Y. Tang*

Department of Civil Engineering, The University of Hong Kong, Hong Kong, PR China

ARTICLE INFO

Keywords:

Gravity-driven
Catalytic membrane
Polydopamine
Nanofibrous membrane
Water treatment

ABSTRACT

An efficient gravity-driven catalytic membrane was developed in the current study. By taking advantage of its great surface area and high porosity, we prepared MnO₂ nano-catalysts onto a polydopamine-coated nanofibrous substrate to achieve the combination of high catalyst loading (up to 9.7 wt%) and high water permeability ($6155 \pm 448 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$). In this approach, polydopamine was used as a green template for the spontaneous immobilization of MnO₂ from a potassium permanganate solution, which resulted in uniformly-dispersed nano-catalysts without the need of strong reducing agent. Gravity-driven catalytic filtration results showed efficient removal (>95%) of the model pollutant methyl blue. This gravity-driven catalytic filtration process may open new opportunities for contaminant removal with high efficiency and low energy consumption.

1. Introduction

Metal/metal oxide nanoparticles have attracted considerable attentions and been widely used for environmental remediation due to their large specific surface area and high activities [1,2]. Nanoparticles of gold, silver, palladium, titanium oxide, zinc oxide, ferric oxide, aluminum oxide, manganese oxide and magnesium oxide have been proven to be effective catalysts and adsorbents for their unique physical and chemical properties [3–6]. However, a critical issue for their applications in water treatment is the agglomeration problem: nanoparticles, with high specific surface area and thus high surface energy, tend to stick to each other as a result of their inter-particle interactions such as Van der Waals forces [7]. In addition, separation of the suspended nanoparticles from the treated water can be challenging and energy intensive [8].

Various supports for the nano-catalysts have been developed, such as silica [9], graphene [10], polymer microspheres [11], and polymeric membranes [12–14]. Among these, membranes were considered as good supports for nanoparticles since the need for particle recovery is eliminated. The combined filtration and catalysis also overcome the mass transfer limitations often encountered in diffusive mode operation [15]. Examples of environmental applications include catalysis and dechlorination of polychlorinated biphenyls [16–18]. The key issues for catalytic membrane process are the loading of catalyst (amount and uniformity) and the energy consumption. Highly porous membranes with great specific surface area and high porosity are

expected to further enhance membrane permeability as well as catalyst loading and thus improve process efficiency.

In recent years, electrospun nanofibrous membranes have been increasingly used in water treatment applications due to their great surface area and highly porous structure [19–23]. The possibility to introduce various functional groups onto its surface [20,24] makes the nanofiber a versatile platform for further immobilization of metal nanoparticles. In addition, the highly porous structure of the nanofibrous membrane ensures a high permeability (usually orders of magnitude higher than the membranes prepared from the phase inversion method [25,26]), which can greatly reduce the energy consumption or even allow gravity-driven membrane filtration. To the best knowledge of the authors, catalytic nanofibrous membranes operated under gravity have not been reported in the literature.

In this study, gravity-driven catalytic nanofibrous membranes were prepared and used for highly efficient removal of organic pollutants. A bio-inspired polymer, polydopamine, was used as a green template for the spontaneous immobilization of MnO₂ nanoparticles *in situ* by taking advantage of its reducing catechol functional groups. This gravity-driven catalytic filtration process with high efficiency and low energy consumption may open many new opportunities for water treatment.

* Corresponding author.

E-mail address: tangc@hku.hk (C.Y. Tang).

<http://dx.doi.org/10.1016/j.memsci.2016.12.003>

Received 18 July 2016; Received in revised form 28 November 2016; Accepted 4 December 2016

Available online 09 December 2016

0376-7388/ © 2016 Elsevier B.V. All rights reserved.

2. Materials and methods

2.1. Chemicals

Polyacrylonitrile (PAN, $M_w=150,000$) and Methyl blue (MB) were purchased from Sigma-Aldrich. Dimethylformamide (DMF) and H_2O_2 (30 wt%) were purchased from VWR PROLABO® Chemicals. Tris (hydroxymethyl) aminomethane (99+%) was purchased from ACROS Organics. Dopamine hydrochloride (99%) was purchased from Alfa Aesar. Potassium permanganate ($KMnO_4$, analytical reagent) was purchased from Beijing Chemical Reagent Co. Ltd. All chemicals were used as received.

2.2. Nanofibrous membrane preparation

PAN nanofibrous membranes were prepared by electrospinning (SS-3556H, Ucalery, China). A 4 wt% homogeneous PAN solution was prepared by dissolving the polymer in DMF and stirring the mixture at 60 °C overnight. Electrospinning of the PAN solution was performed at a feed rate of 1.2 mL/h, an air gap between the spinneret and the collector of 10 cm, and a spinning voltage of 21 kV (+18.0 kV for the spinneret and -3.0 kV for the collector). The nanofibers were collected by an aluminum foil mounted to a rotating drum (diameter=10 cm and the rotating speed =80 rpm). A stepping motor was used to control the translational movement of the spinneret to ensure uniform thickness of the resulting nanofibrous membranes. Before further use, the membranes were heat treated at 140 °C for 2 h to enhance their mechanical stability [27–29]. Heat treatment is commonly applied to electrospun nanofibrous, and the FTIR results before and after treatment showed no obvious differences (Fig. S1).

The schematic for catalytic membrane preparation is shown in Fig. 1. The PAN nanofibrous membranes were immersed into a dopamine solution (2.0 g/L dopamine in 10 mM Tris-HCl at pH 8.5) and were shaken for 12 h in a thermostatic shaker at 25 °C to allow the coating of polydopamine onto the PAN membranes. The coated PAN membranes (cPAN) were washed using deionized water for several times to move any labile polydopamine. Coating of PDA on membranes have been reported by many groups [30–32]. According to Lee et al. [33], the polymerization of dopamine results in a sticky layer that can uniformly coat onto a wide variety of substrates, including oxides, polymers and ceramics. According to existing literature, polydopamine coating layer is quite stable even under ultrasonic treatment [34] or over long time of exposure [35].

MnO_2 nanoparticles were loaded onto cPAN membranes through the *in situ* reduction of manganese. Briefly, cPAN membranes were immersed into a $KMnO_4$ solution (0.001, 0.01 or 0.1 M) for 12 h. This step used polydopamine as a green template: its catechol groups were used to reduce MnO_4^- to MnO_2 without the need of additional reducing agents. The *in situ* reduction method is environmentally benign by eliminating the use of strong reducing chemicals for the preparation of MnO_2 catalysts. The MnO_2 loaded nanofibrous membranes (cPAN- MnO_2) were washed by deionized water for several times before further use.

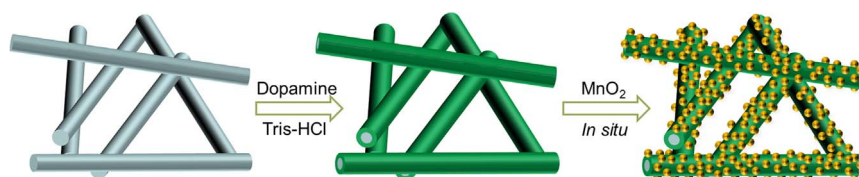


Fig. 1. Schematic diagram of the preparation of catalytic nanofibrous membranes. The pristine PAN membrane was first soaked in a dopamine/Tris-HCl solution to prepare the polydopamine coating. The polydopamine-coated cPAN membrane was then immersed in a $KMnO_4$ solution to allow the spontaneous formation of MnO_2 nano-catalysts on the nanofiber support.

2.3. Membrane characterization

Membrane morphology and chemical composition were examined using a LEO 1530 FEG scanning electron microscope (SEM, Germany) equipped with an energy-dispersive X-ray spectroscopy (EDX) unit. A thin layer of gold was sputter coated onto the samples before SEM analysis. Thermo-gravimetric analysis (PerkinElmer Pyris, USA) was used to determine the MnO_2 loading amount. The measurements were performed over 25–900 °C with a heating rate of 10 °C/min and an air flow of 50.0 mL/min. Brunauer-Emmett-Teller (BET) surface area was measured using SA 3100 surface area analyzer (Beckman Coulter™, USA). Pore size was tested using capillary flow porometry (Porolux 1000, Germany) using pressures ranging from 0 to 4.8 bar. Porosity (ϵ) of the nanofibrous membranes were also determined based on measurements of the dry mass (m_{dry}) and wet mass (m_{wet}) of membrane samples [36]:

$$\epsilon = \frac{(m_{wet} - m_{dry})/\rho_w}{\left(\frac{m_{wet} - m_{dry}}{\rho_w}\right) + (m_{dry}/\rho_p)} \times 100\% \quad (1)$$

where ρ_w and ρ_p are density of wetting solvent ($\rho_w=1.00$ g/mL for deionized water in the current study) and that of the polymer ($\rho_p=1.18$ g/mL for polyacrylonitrile), respectively.

2.4. Catalytic membrane performance

Adsorption experiments were conducted by immersing 50 mg nanofibrous membrane into a 100 mL methyl blue test solution (50 mg/L). The test solution was sampled at predetermined time intervals to measure the remaining methyl blue concentration using a UV-Vis spectrophotometer (Biochrom 6040, UK) with a resolution of 1 nm. At each sampling time step, 1 mL solution was taken and diluted three times with deionized water before UV-Vis analysis. Catalytic removal of methyl blue was performed in a similar manner, except that a 0.3 wt% H_2O_2 (1 mL of 30 wt% H_2O_2 per 100 mL of 50 mg/L methyl blue) was also included in the test solution to allow its reaction with methyl blue.

Catalytic membrane filtration experiments were performed under gravity-driven conditions (Fig. 2). A piece of catalytic nanofibrous membrane (cPAN- MnO_2 obtained at 10^{-2} M $KMnO_4$) was mounted in a stirred cell (Model 8400, Millipore, USA) with an effective membrane area of 41.6 cm². A 50 mg/L methyl blue (with no or 0.3 wt% H_2O_2) solution was filtrated through the membrane at a constant water head of 8 cm. The permeate was sampled at predetermined time intervals for the determination of membrane permeate flux and methyl blue concentration.

3. Results and discussion

3.1. Morphology and chemical composition of catalytic nanofibrous membranes

Morphologies of nanofibers with and without polydopamine coating are shown in Fig. 3a and b, respectively. The mean diameter of PAN nanofibers was approximately 120 nm. The pristine PAN nanofiber had a smooth surface (Fig. 3a). There was no major change in morphology

Download English Version:

<https://daneshyari.com/en/article/4989415>

Download Persian Version:

<https://daneshyari.com/article/4989415>

[Daneshyari.com](https://daneshyari.com)