



Fouling-resistant microfiltration membrane modified with magnetite nanoparticles by reversible conjunction

Seung Taek Woo¹, Taeseon Yun¹, Seung-Yeop Kwak*

Department of Materials Science and Engineering, Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul 151-744, Republic of Korea



ARTICLE INFO

Keywords:
Diels–Alder cycloaddition
Magnetite nanoparticle
Membrane fouling
Microfiltration membrane

ABSTRACT

We developed a stimuli-responsive poly(tetrafluoroethylene) (PTFE) microfiltration (MF) membrane by reversible conjunction of magnetite nanoparticles. We modified the magnetic particles with maleimide functional groups and attached them to a furan-modified PTFE membrane via a Diels–Alder (DA) cycloaddition reaction to prepare an anti-fouling membrane that responds to magnetism and temperature. The combined results of Fourier-transform infrared spectroscopy, X-ray diffractometry, vibrating sample magnetometry, X-ray photoelectron spectroscopy, and field-emission scanning electron microscopy investigations clearly showed that the maleimide-modified magnetic nanoparticles were successfully synthesized and coupled with the furan-modified PTFE MF membrane by the DA reaction. The modified membrane produced a micro-vortex under a rotating magnetic field, and showed a high resistance to fouling with a water flux higher than 50% of initial flux even after 30 min in the fouling test, whereas the neat membrane had a water flux falling below 20% of initial flux in 30 min. Moreover, the magnetite nanoparticles were readily and repeatedly regenerated on the MF membrane surface using a thermally driven peel-and-stick process; 75% of the water flux was recovered, even after three fouling cycles.

1. Introduction

Over the past few decades, lack of clean water has become a serious global problem [1]. Various techniques for securing safe and clean water, such as distillation [2], chemical treatment [3], adsorption [4], and membrane filtration [5], have been investigated. Membrane filtration is regarded as an eco-friendly water purification method because it has advantages such as low energy consumption, time efficiency, and a small footprint. However, membrane filtration systems suffer from fouling, in which foulants in the feed solution are adsorbed on the membrane surface during water permeation and interfere with water permeation. This phenomenon results in increased operating costs because of membrane lifetime reduction, increased energy consumption, and the need for additional cleaning processes [6].

Many approaches to solving the problem of membrane fouling have been investigated, such as introduction of hydrophilic polymers [7–10] or biocidal materials [8–13]. A hydrophilic polymer grafted on the membrane surface can interfere with foulant adsorption on the membrane and enables easy contaminant removal using a simple cleaning process. However, hydrophilic polymers alone do not have sufficient fouling-inhibiting ability, and the use of antibacterial materials such as

silver nanoparticles and titanium dioxide has been investigated to further improve fouling resistance [8–13]. However, these antimicrobial substances are only effective for biofouling and have no effect on fouling by inorganic particles.

As a new solution for reducing various types of fouling, the stimuli-responsive materials emerged. Stimuli-responsive materials respond to external stimuli such as solution pH [14,19] temperature [15], ionic strength [16], magnetic field [17], and light [18], and are widely used in various fields [20–33]. Membranes modified with stimuli-responsive materials have excellent and general anti-fouling properties, and various types of foulant can be physically detached from the membrane surface. Because of these advantages, stimuli-responsive membranes are considered to be a novel next-generation water purification technique [34,35], and removal of fouled layer using stimuli-responsive materials has been examined through introduction of various materials such as thermo-responsive polymers [36–38], dynamic polymer brushes in response to salt concentration [31], and magnetically activated micromixers [39]. However, for membranes that respond to stimuli such as ionic strength and pH, stimulation requires the contents of the feed solution to be changed, which is time consuming and expensive. On the other hand, unlike other stimuli-responsive membranes, membranes

* Corresponding author.

E-mail address: sykwak@snu.ac.kr (S.-Y. Kwak).

¹ Equally contributing co-first author.

based on magneto-responsive materials have advantages such as easy stimulus control without changing the feed properties, a rapid effect, and low energy consumption. Furthermore, the magnetic particles on the membrane surface continuously interfere with foulant attachment through micro-motions induced by the magnetic field [39]. However, although such magneto-responsive anti-fouling membranes effectively retard membrane fouling, they do not completely prevent fouling, and that results in a steady accumulation of foulants. Therefore, we tried to solve this problem by introducing to a membrane two stimuli-response characteristics which are effective for fouling delay and recovery respectively.

In this study, we developed a fouling-resistant microfiltration (MF) membrane by thermo-reversible attachment of magnetite nanoparticles to the membrane. This was achieved by forming thermoreversible covalent bonds between maleimide-modified magnetite nanoparticles and a furan-modified poly(tetrafluoroethylene) (PTFE) membrane. The magnetite nanoparticles produced a micro-vortex on the membrane surface under a changing magnetic field, and were detached from, and reattached to, the membrane surface by a thermally driven process. The resulting membrane had excellent anti-fouling properties under a rotating magnetic field. Moreover, the magnetite-nanoparticle-coupled PTFE membrane showed a high flux recovery after a peel-and-stick process.

2. Experimental

2.1. Materials

A porous PTFE flat sheet membrane with a 47 mm diameter and 0.1 μm average pore size was purchased from Advantec-MFS, Inc. (Tokyo, Japan). Iron(II) chloride tetrahydrate (97%), iron(III) chloride hexahydrate (97%), poly(ethylene glycol) methyl ether maleimide (PEG-Mal; M_n 2000), furfuryl glycidyl ether (96%), hydrazine monohydrate (98%), and LUDOX SM-30 (30 wt% silica suspension, average particle size 7 nm) were purchased from Sigma-Aldrich (St Louis MO, USA). Toluene (99.8%) and tetrahydrofuran (THF, 99.0%) were purchased from Daejung Chemical & Metals (Gyeonggi-do, Korea). Aqueous solutions were prepared with deionized (DI) water.

2.2. Synthesis of maleimide-terminated magnetite (MG@PEG-Mal)

A schematic diagram of the overall synthesis is shown in Fig. 1. Maleimide-terminated magnetite nanoparticles were synthesized by coprecipitation of magnetite nanoparticles and PEG-Mal. Iron(II) chloride tetrahydrate (290 mg), iron(III) chloride hexahydrate (720 mg), and PEG-Mal (1 g) were dissolved in DI water (5 mL). Then 25 wt% aqueous ammonium hydroxide solution was slowly added to the orange solution under nitrogen, and the mixture was stirred for 3 h. The magnetite nanoparticle were separated by magnetic decanting using a neodymium–boron permanent magnet, and washed with DI water and ethanol. The final product was suspended in THF.

2.3. Synthesis of furan-modified PTFE membrane

The modification of PTFE membrane was conducted according to a previously reported method [40]. Sodium hydroxide beads (15 g) were added to hydrazine monohydrate (20 mL) to obtain dehydrated hydrazine. The PTFE flat sheet membrane was placed in a quartz cell. The cell was filled with nitrogen gas and exposed to hydrazine vapor under ultraviolet (UV) light ($\lambda_{\text{max}} = 254 \text{ nm}$, 100 W) for 72 h. After the reaction, the surface-aminated PTFE membrane was washed with THF and dried under vacuum oven overnight. Furfuryl glycidyl ether (1.4 mL) was added to the surface-aminated PTFE membrane and the membrane was kept in an oven at 60 °C overnight. The furan-modified PTFE membrane was rinsed several times with THF, ethanol, and DI water to remove unreacted chemicals.

2.4. Fabrication of magnetite-coupled PTFE membrane (MG-PTFE)

The furan-modified PTFE membrane was wetted with THF. The magnetite nanoparticle–THF suspension (1.4 mL) was added to the membrane, and the membrane was shaken in a 60 °C oven for 24 h. After the DA reaction, the membrane was rinsed with THF, ethanol, and DI water to remove unreacted chemicals, and treated ultrasonically to remove loosely attached magnetite nanoparticles. The final product was dried in a vacuum oven overnight at room temperature.

2.5. Peel-and stick process for MG@PEG-Mal

The MG@PEG-Mal layer was freely removed and reattached by thermo-responsive covalent bonding. DA cycloaddition at 60 °C was used to attach MG@PEG-Mal to the PTFE membrane. Retro DA (rDA) cycloaddition was used to remove MG@PEG-Mal from the surface of the furan-modified PTFE membrane. The MG-PTFE membrane was immersed in toluene (100 mL), and the solution was heated under reflux at 150 °C for 24 h. After the rDA reaction, the membrane was rinsed with THF, ethanol, and DI water, with ultrasonic treatment. The rinsed furan-modified PTFE membrane was dried under vacuum oven overnight at room temperature.

2.6. Characterization

The chemical structure of MG@PEG-Mal was determined using Fourier-transform infrared (FT-IR) spectroscopy (Thermo Scientific Nicolet iS1). The mass of PEG-Mal polymer introduced onto the surfaces of the magnetite nanoparticles was determined using thermogravimetric analysis (TGA; Q-5000IR). The crystal structures of the magnetite samples were examined using X-ray diffraction (XRD; New D8 Advance). The average crystallite size was calculated using the Scherrer equation:

$$d = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where d is the magnetite crystal grain size, K is a dimensionless shape factor, with a typical value close to 0.9, λ is the X-ray wavelength, and β is the line broadening at half the maximum intensity after subtracting the instrumental line broadening in radians. The magnetization of MG@PEG-Mal was determined using vibrating sample magnetometry (VSM; EV9-380V).

The neat, aminated, furan-modified, and magnetite-coupled PTFE membranes were examined using attenuated total reflectance (ATR) FT-IR spectroscopy (Thermo Scientific Nicolet iS5) and X-ray photoelectron spectroscopy (XPS; Kratos AXIS-His, monochromatic Mg K α X-ray source). The surface morphologies of the membranes were examined using field-emission scanning electron microscopy (FE-SEM; SUPRA 55VP) and energy-dispersive X-ray spectroscopy (EDS). The motion of the magnetite nanoparticles in response to an external rotating magnetic field was indirectly observed using particle image velocimetry (PIV; MGL10000) [39]. The membrane was placed in a petri dish, and water containing dispersed silica particles was added. The average diameter of silica nanoparticle was 10 μm , and it was dispersed to the pure water. A monochromatic green laser with a wavelength of 527 nm was projected in a direction perpendicular to the camera lens and illuminating the membrane surface to induce scattering of silica nanoparticle. The observation area was 400 \times 400 μm^2 , and the observation was performed with an exposure time of 11,000 μs and a pixel size of 0.135 μm . The change of the magnetic field was generated by rotating the neodymium-iron permanent magnet around the membrane. A schematic diagram of this system is shown in Fig. S1. Changes in the membrane surface hydrophilicity were evaluated using room-temperature static pure water contact angle measurements (Biolinscientific, Attention® THETA LITE).

Download English Version:

<https://daneshyari.com/en/article/7043744>

Download Persian Version:

<https://daneshyari.com/article/7043744>

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