



Original Research Paper

Functional magnetic particles providing osmotic pressure as reusable draw solutes in forward osmosis membrane process



Yasushi Mino, Daichi Ogawa, Hideto Matsuyama*

Center for Membrane and Film Technology, Department of Chemical Science and Engineering, Kobe University, 1-1, Rokkodai, Nada, Kobe 657-8501, Japan

ARTICLE INFO

Article history:

Received 23 May 2016

Received in revised form 30 July 2016

Accepted 1 August 2016

Available online 11 August 2016

Keywords:

Magnetic core/shell particle
 Forward osmosis (FO) membrane process
 Draw solution
 Surface-initiated atom transfer radical polymerization (SI-ATRP)

ABSTRACT

The forward osmosis (FO) membrane separation process is one of the emerging membrane technologies that can meet the increasing global demand for clean water. We synthesize the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ core/shell particles functionalized with sodium polyacrylate (PNaAA) as a draw solute, which generates the driving force to transport water through an FO membrane in this process. The Fe_3O_4 core enables the recovery and dispersion of the particles using a magnetic field, while the grafted PNaAA provides the high osmotic pressure required to transport water. Preparing an SiO_2 shell over the Fe_3O_4 core of the particles enables the chemical immobilization of the PNaAA on the particle surface and increases their stability as a draw solute. Here, Fe_3O_4 core particles with a controlled size of the submicron-meter order are prepared by a solvothermal method, followed by the formation of the SiO_2 shell. Subsequently, the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ core/shell particles are modified with PNaAA using surface-initiated atom transfer radical polymerization (SI-ATRP). The effects of the amount of grafted PNaAA and the particle size on the performance as a draw solute are investigated by conducting osmolality measurements and recovery tests. The synthesized particles are able to maintain a stable dispersion even after ten cycles of assembling/dispersing operations.

© 2016 The Society of Powder Technology Japan. Published by Elsevier B.V. and The Society of Powder Technology Japan. All rights reserved.

1. Introduction

Magnetic particles (MPs) allow us to control their motion simply and cost-effectively with a magnetic field. Because of this advantage, suitably-functionalized MPs are used in many applications such as in colloidal separation [1–4], cell treatment [5,6], and drug carriers [7], where functional group modifications of the MPs allow target substances to be captured. In recent years MPs have attracted much attention as materials for generating the driving force to transport water in a forward osmosis (FO) membrane separation process [8,9], one of the emerging membrane technologies that can meet the increasing global demand for clean water.

Fig. 1 shows a schematic illustration of an FO membrane process. In this process, the osmotic pressure difference between two solutions separated by an FO membrane provides the driving force for spontaneous water transport. Water is drawn from a feed solution into a solution with higher osmotic pressure, which is usually called a draw solution. Compared to conventional pressure-driven membrane processes, this spontaneous process

can essentially reduce the energy consumption and the membrane fouling [10], which shortens the life of the membrane and increases the cleaning cost. The FO process is thus potentially applicable to a wide range of applications, including water reuse [11,12], osmotic power generation [13], and food processing [14,15]. However, since the water transported through the membrane is miscible with the draw solution, an additional step of separating the water from the mixture is required to obtain clean water. From an economic and environmental perspective, the separated draw solution must be reusable.

To create a draw solution that addresses these needs, we have focused on functionalized MPs, the basic concept being as follows. While the MPs can be recovered and recycled by a magnetic field, the particles themselves do not exert a high osmotic pressure. By modifying the MPs with polyelectrolytes, the larger number of counter ions of the polyelectrolytes generate a higher osmotic pressure. This draw solution potentially provides the FO membrane processes with a lower energy cost than other draw solutions (e.g., ammonium-carbon dioxide complex [16,17], stimuli-responsive hydrogel [18], polyelectrolyte [19], and stimuli-responsive polymers [20,21]). Several other groups have successfully generated draw solutions utilizing a similar concept. Ling et al. [22] synthesized magnetic nanoparticles (MNPs) grafted poly-

* Corresponding author.

E-mail address: matuyama@kobe-u.ac.jp (H. Matsuyama).

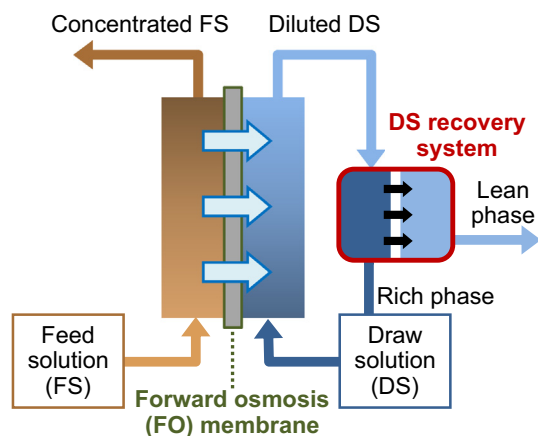


Fig. 1. Schematic illustration of a forward osmosis (FO) membrane separation process.

acrylic acid and demonstrated the applicability of water-soluble MPs to a draw solute for the first time. Ge et al. [23] prepared the poly(ethylene glycol)diacid-coated (PEG-(COOH)₂-coated) MNPs and characterized their physical properties. The PEG-(COOH)₂-coated MNPs were easily recovered from draw solutions with a magnetic field, demonstrating the feasibility of PEG-(COOH)₂-coated MNPs as draw solutes. Zhao et al. [24] synthesized MNPs grafted with poly(sodium styrene-4-sulfonate)-co-poly(N-isopropylacrylamide) (PSSS-PNIPAM) to develop thermoresponsive magnetic draw solutes. The MNPs functionalized with PSSS-PNIPAM successfully drew pure water from seawater, and this draw solution was recovered by magnetic separation assisted by heating. However, as shown by Ling et al. [22] and Ge et al. [23], it is generally difficult to use MP draw solutions repeatedly. The polyelectrolytes physically immobilized on the MPs are gradually detached from their surfaces through the repeated assembly/dispersion operations. Furthermore, the MPs, especially those with a size of less than several tens of nanometers, are likely to aggregate.

In this study, we synthesized MPs that can be used as stable and reusable draw solutes. The key feature of our MP-based draw solutes is the SiO₂ shell coating the MPs, which enables the chemical immobilization of the polyelectrolytes on the particle surfaces, and also increases the stability of the MPs. Polyelectrolyte-grafted Fe₃O₄/SiO₂ core/shell particles were synthesized as shown in Fig. 2. MPs (core) with controlled sizes of the submicron-meter order were synthesized via a solvothermal reaction. In this, MPs were coated with SiO₂ shells, on which we immobilized the silane coupling agent providing a starting point for surface-initiated atom

transfer radical polymerization (SI-ATRP). Subsequently, the Fe₃O₄/SiO₂ particles were modified with varying amounts of sodium polyacrylate (PNaAA). To evaluate the performance of the synthesized particles as a draw solute, we measured their osmolality and conducted the recovery and recycling tests.

2. Experimental

2.1. Materials

Iron(III) chloride hexahydrate (FeCl₃·6H₂O, 99.0%), ethylene glycol (99.5%), sodium acetate (NaAc, 98.5%), polyethylene glycol (PEG, M_w = 3000, 20,000, 500,000), sodium citrate dihydrate (99.0%), aqueous ammonia (NH₃ aq., 25.0–27.9%), methanol (99.8%), ethanol (99.5%), *i*-propanol (99.7%), and triethylamine (TEA, 99.0%) were purchased from Wako Pure Chemical Ind., Ltd. (Japan). Tetraethyl orthosilicate (TEOS, 96.0%), 3-aminopropyltrimethoxysilane (APTS, 96.0%), 2-bromoisobutyryl bromide (BIBB, 98.0%), tetrahydrofuran (THF, 99.5%), N, N, N', N'', N''-pentamethyldiethylenetriamine (PMDETA, 98.0%), and L-ascorbic acid (99.0%) were purchased from Tokyo Chemical Ind. Co., Ltd., (Japan). Sodium acrylate (NaAA, 97%) was purchased from Sigma-Aldrich Co. LLC. (Japan). Copper(II) bromide (CuBr₂) (98%) was purchased from Nacalai Tesque, Inc. (Japan). All chemicals were used as received. High purity (Milli-Q) water with a resistivity >18 MΩ cm was obtained from a Millipore water purification system.

2.2. Magnetic particle preparation

MPs were synthesized by a solvothermal method with two types of stabilizing agents, PEG [25] and sodium citrate [26,27].

PEG stabilization. FeCl₃·6H₂O (1.35 g, 5 mmol) was dissolved in ethylene glycol (40 mL). PEG (1.0 g) was added to this solution along with NaAc (3.6 g, 44 mmol) and vigorously stirred for 30 min. The resulting solution was reacted at 220 °C and 1500 rpm for 5 h in a stainless steel container. The synthesized particles were washed twice with ethanol and twice with Milli-Q water.

Sodium citrate stabilization. FeCl₃·6H₂O (1.35 g, 5 mmol) was dissolved in ethylene glycol (40 mL). Sodium citrate dihydrate (0.394 g) was added to this solution with NaAc (3.6 g, 44 mmol) and vigorously stirred for 30 min. The resulting solution was reacted at 220 °C and 1500 rpm for 5 h in the stainless steel container. The synthesized particles were washed three times with Milli-Q water.

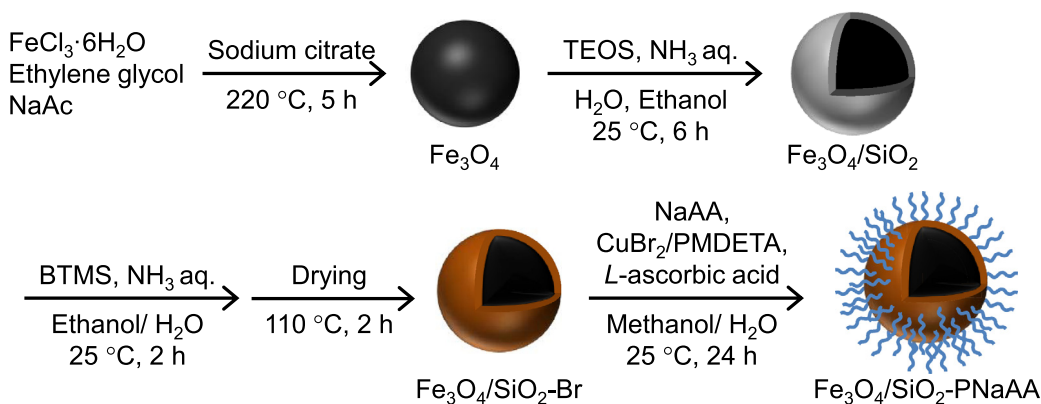


Fig. 2. Schematic of the synthesis procedure.

Download English Version:

<https://daneshyari.com/en/article/6464754>

Download Persian Version:

<https://daneshyari.com/article/6464754>

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