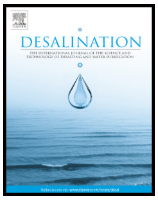
Desalination 397 (2016) 22–29

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal



Magnetic core-hydrophilic shell nanosphere as stability-enhanced draw solute for forward osmosis (FO) application

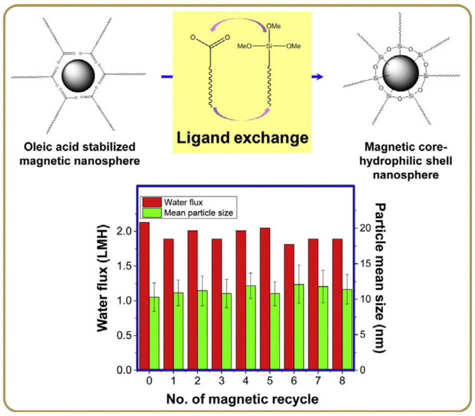
Sung Yong Park [a,1], Hyo-Won Ahn [a,1], Jae Woo Chung [b], Seung-Yeop Kwak [a,*]

[a] Department of Materials Science and Engineering, Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul 151-744, Republic of Korea
[b] Department of Organic Materials and Fiber Engineering, Soongsil University, 369 Sangdo-ro, Dongjak-gu, Seoul 156-743, Republic of Korea

HIGHLIGHTS

- Preparation of magnetic core-hydrophilic shell nanosphere
- Core-shell magnetic nanosphere applies to durable draw solute in FO.
- Magnetic draw solutes generate reasonable osmotic pressures.
- Robustly capped hydrophilic siloxane prevents particle aggregation.
- Osmotic power is maintained during repeated magnetic recovery process.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 March 2016
Received in revised form 13 June 2016
Accepted 17 June 2016
Available online xxxx

Keywords:
Forward osmosis
Draw solute
Magnetic core-hydrophilic shell nanosphere
Core-shell structure
Magnetic recovery

ABSTRACT

We have developed magnetic core-hydrophilic shell nanospheres as a draw solute with enhanced stability for use in forward osmosis (FO) processes, which were prepared via a ligand exchange reaction. The combined results of TEM, DLS, FT-IR, and TGA analysis indicated that spherical magnetic nanospheres with 10 nm in diameter were successfully prepared via a thermal decomposition method. Hydrophilic shell layers were prepared using a ligand exchange reaction, and the hydrophilic siloxane agents were robustly bound to the surfaces of the magnetic nanosphere without inducing morphological changes. The number of hydrophilic agents presented in the magnetic nanospheres increased dramatically as a result of the covalently attached hydrophilic siloxane agents. The magnetic core-hydrophilic shell nanosphere draw solutes generated reasonable osmotic pressures due to their hydrophilic shell layer, rendering them useful for purifying mildly brackish water. As we intended, the osmotic pressure of the magnetic core-hydrophilic shell nanosphere was well maintained during repetitive magnetic recovery processes because the robustly bound the hydrophilic shell layer prevented particle aggregation.

1. Introduction

Fresh water is in short supply due to the worldwide growth in demand for residential, agricultural, and industrial water uses. The fresh water shortage is considered one of the most pressing challenges of the 21st century [1–3]. Water shortage problems may potentially be

---

[*] Corresponding author.
E-mail address: sykwak@snu.ac.kr (S.-Y. Kwak).
[1] Equally contributing co-first author.

http://dx.doi.org/10.1016/j.desal.2016.06.017
0011-9164/

alleviated by implementing membrane processes to purify undrinkable water resources, such as sea water, brine, or contaminated water. Among various membrane processes, forward osmosis (FO) membrane process was recently recognized as promising approaches to water treatment applications [4–7] due to their low energy consumption and low membrane fouling tendency. FO processes have been studied in a variety of research fields, including desalination [8], wastewater treatment [9–11], osmotic pressure generation [12], agricultural fertilizing [13], and food processing [14]. However, FO processes tend to be limited in their applicability to commercial water treatment applications due to their low water permeation performance and poor separation of highly purified water from the permeate. The issues with FO processes must be addressed for the development of a suitable draw solute.

The main requirements for draw solutes are generation of reasonable osmotic pressures and the easy recovery of draw solutes from the permeate to obtain purified water. To satisfy these requirement, a variety of draw solutes have been tried to apply FO process such as inorganic salts [15], thermolytic/volatile solutes [16,17], organic solutes [18,19], polyelectrolytes [20], hydrogels [21,22], or solvents with a switchable polarity [23,24]. These materials can generate osmotic pressures by dissolving or dispersing the permeate, and they can be recovered from the permeate through a variety of treatments, such as chemical precipitation [25], pressure control [26], thermal decomposition/evaporation [27], or membrane filtration [28,29]. However, these attempts have been limited to FO processes due to their low osmotic driving force, difficulties associated with separating the particles from the permeate, the generation of toxic thermolytic products, the high energy requirements of the draw solute recovery process, and the inability to reuse the materials [5,6].

Magnetic nanoparticles were considered as potential draw solutes [30–34] because they can be readily separated from a permeate by an external magnetic field without supply of chemical and thermal energy. The advantage of magnetic draw solute is easy separation from purified water and reuse of draw solute without any post treatments, which can reduce FO operation cost by suppression of supplying disposable draw solute. The osmotic pressure generated by the magnetic nanoparticles are enhanced by a variety of surface functional agents, such as poly acrylic acid (PAA), polyethylene glycol (PEG), or diacid, applied as coatings onto the magnetic nanoparticles [30]. The hydrophilic modified magnetic nanoparticles (hydrophilic-MNs) showed reasonable water fluxes up to 10.4 $\text{Lm}^{-2}\ \text{h}^{-1}$ [32]. However, the hydrophilic-MNs tend to be aggregated under the high strength magnetic field during the draw solute recovery process due to a lack of binding force between the hydrophilic agents and the surface of magnetic nanoparticle [35,36]. Aggregated Hydrophilic-MNs can significantly reduce the total osmotic pressure in an FO process [30], thereby hindering the utility of the Hydrophilic-MN draw solutes.

Here, we describe the synthesis of magnetic core-hydrophilic shell nanospheres prepared by a ligand exchange reaction between carboxylate stabilizers of magnetic nanosphere surface and hydrophilic modified siloxane ligands to form a covalent linkage between magnetic nanosphere core and hydrophilic shell for prevention of particle aggregation. Two hydroxyl-modified siloxane ligands were used: N-(trimethoxysilylpropyl)ethylenediamine triacetic acid, denoted SiCOOH, to introduce carboxylic acid groups into the magnetic nanosphere, 2-[methoxy-(polyethyleneoxy)propyl] trimethoxysilane, denoted SiPEG, to introduce the hydrophilic PEG chain. As we intended, the core-shell magnetic nanospheres preserved their particle size and their ability to generate an osmotic pressure after repetitive magnetic recycling processes due to the covalent bonding of hydrophilic siloxane agents. These efforts indicate the potential of the core-shell magnetic nanospheres as feasible draw solutes that are readily recovered through magnetic forces and offer a consistent FO performance by preventing magnetic nanoparticle aggregation through the presence of robust covalent bondings among the hydrophilic shell layers.

2. Experimental methods

2.1. Materials

Iron(III) acetylacetonate (Fe(acac)_3, 97%), oleic acid (90%), oleylamine (70%), toluene (97%), 1,2-hexadecanediol (90%), benzyl ether (99%), ethanol (99.9% anhydrous), and tetramethylammonium hydroxide (TMAH, 99%) were purchased from Sigma-Aldrich (St Louis, MO, USA). N-(trimethoxysilylpropyl) ethylenediamine triacetic acid (MW: 462.41 g mol^{-1}, SiCOOH) and 2-[methoxy-(polyethyleneoxy)$_{6-9}$propyl] trimethoxysilane (MW: 459–591 g mol^{-1}, SiPEG) were purchased from ABCR GmbH & Co. (Karlsruhe, Germany). The cellulose triacetate (CTA) membranes used in the FO process were purchased from Hydration Technologies Inc. (HTI) (OR, USA). All chemicals were used as received, without further purification. Aqueous solutions were prepared with deionized (DI) water with a resistivity exceeding 18 MΩ cm^{-1}.

2.2. Preparation of magnetic core-hydrophilic shell nanosphere

Magnetic core-hydrophilic shell nanosphere draw solutes were prepared via a ligand exchange reaction, as reported by De Palma et al. [37]. First, magnetic nanosphere (MN) stabilized with oleic acid (O-MN) was synthesized by the thermal decomposition method [38]. 1.5 g iron(III) acetylacetonate, 5 g 1,2-hexadecanediol, 5 mL oleylamine, and 5 mL oleic acid were mixed in 40 mL benzyl ether. The mixture was heated to 200 °C for 2 h, and the temperature was then raised to 300 °C with reflux for 1 h under an Ar environment. Next, the solution was cooled down to room temperature. The oleic acid stabilizer was exchanged with the siloxane agents, by adding 2 mL SiPEG (or SiCOOH) and 0.05 mL TMAH to the O-MN/toluene solution prepared by dispersing 100 mg O-MN in 300 mL toluene. The mixtures were agitated in an orbital shaker for 72 h. The magnetic core-hydrophilic shell nanospheres (black-brown colored precipitates) were obtained by washing the precipitate several times with toluene. Finally, the core-shell MNs were stored in deionized water prior to use. Fig. 1 shows a schematic illustration of the ligand exchange reaction on the NNs. The core-shell MNs were denoted SiPEG-MN and SiCOOH-MN, in reference to the siloxane ligands.

2.3. Characterization of magnetic core-hydrophilic shell nanosphere

The shape and size distribution of the O-MNs and core-shell MNs were observed using energy-filtering transmission electron microscopy (EF-TEM) (Carl Zeiss LIBRA 120) and dynamic light scattering (DLS) (Otsuka Electronics ELSZ-1000) techniques. The samples used for the EF-TEM observations were prepared by dispersing the MNs in n-hexane to prepare O-MN or DI water to prepare the core-shell MNs. The MNs-dispersed solution was then dropped onto carbon TEM grids and dried under vacuum overnight. The particle size and MNs distribution were measured by dispersing 1 mg of the MNs in 5 mL n-hexane to prepare O-MN or 5 mL DI water to prepare core-shell MNs.

The surface modifications of the core-shell MNs were characterized using Fourier transform infrared spectroscopy (FT-IR) (Thermo Scientific Nicolet 6700 IR) and thermogravimetric analysis (TGA) (TA instruments Q500). The FT-IR analysis was conducted by preparing a KBr pellet containing small amounts of MNs. The FT-IR spectral range was 4000 to 400 cm^{-1}, with a 4 cm^{-1} spectral resolution. The TGA analysis was conducted by drying 10 mg of each sample in a vacuum overnight at room temperature. The samples were heated from 25 °C to 800 °C at a 20 °C/min heat rate under a N_2 atmosphere. The ligand/particle ratio from the combined results of the TGA and DLS analyses were calculated using the following equation [30].

$$N = \frac{\varpi N_A \rho \frac{4}{3}\pi R^3 \times 10^{-23}}{MW}, \tag{1}$$