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

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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
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 reason- able 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 inorgan- ic 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 precipita- tion [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 mate- rials [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 Lm−2 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 nanoparticle surface and hydrophilic modified siloxane ligands to form a covalent linkage between magnetic nano- sphere 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 nano- sphere, 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) acetylacetone (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 (TMAB, 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)propyl]trimethoxysilane (MW: 459–591 g mol⁻¹, SiPEG) were pur- chased 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 nanospheres were prepared using 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) acetylacetone, 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 re- flux 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 TMAB 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 MNs. 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 Scientif- ic Nicolet 6700 IR) and thermogravimetric analysis (TGA) (TA instru- ments 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 oven at room temperature. The samples were heated from 25 °C to 800 °C at a 20 °C/min heat rate under a N₂ atmosphere. The ligand/particle ratio from the combined results of the TGA and DLS analyses were cal- culated using the following equation [30].

\[
N = \frac{\sigma N_\mu}{\frac{4}{3} \pi R^3} \times 10^{-23} \frac{1}{MW}
\]
where \( N \) is the number of ligands on each particle (ligand/particle ratio), \( \omega \) is the percent weight loss, \( N_A \) is Avogadro’s number, \( \rho \) is the density of the nanospheres, approximated as 5.1 g/cm\(^3\) [39], \( R \) is the mean radius calculated from the DLS analysis (cm), and \( MW \) is the molecular weight of the ligand molecules (g mol\(^{-1}\)).

The osmotic pressure generated by the core-shell MNs was measured via freezing point depression osmometry (KNAUSER Semi-micro osmometer K-7400). The osmotic pressure generated by the core-shell MNs was calculated based on a rearranged expression of the van’t Hoff equation.

\[
\Pi = iMRT
\]

where \( \Pi \) is the osmotic pressure, \( i \) is the van’t Hoff factor, \( M \) is the molarity (mol L\(^{-1}\)), \( R \) is the gas constant (0.08206 L atm K\(^{-1}\)·mol\(^{-1}\)), and \( T \) is the thermodynamic temperature (K).

2.4. Evaluation of the water permeability during the FO process

The core-shell MNs were used as draw solutes in a simple FO process. A wetted FO membrane (HTI flat sheet CTA membrane, effective area: 2.54 cm\(^2\)) was placed between equal volumes (120 mL) of the DI water feed solution and the core-shell MN aqueous draw solution. The active layer of CTA membrane was oriented toward the feed solution. The concentration of the core-shell MN draw solution was varied between 20 g L\(^{-1}\) and 50 g L\(^{-1}\). During the 90 min FO process, the draw solution volume increase was recorded at 30 min intervals at room temperature.

To evaluate water flux under mild brackish conditions, we prepared feed solution by dissolving methylene blue into DI water with various concentrations (500, 1000, and 5000 ppm) of which the osmotic pressure was under 1 atm. In case of use inorganic salt for preparation of feed solution, some of ions were penetrated over membrane, resulting in influenced osmotic gradient between feed and permeate solutions. Methylene blue does not penetrate over the TCA membrane due to its molecular weight (M.W.: 379.8 g mol\(^{-1}\)). The pH condition for methylene blue feed solution and core-shell MN draw solutions were recorded as 6.8 for methylene blue feed solution, 6.3 for SiPEG-MN draw solution, and 11.3 for SiCOOH-MN draw solution, respectively.

The water flux in the FO process was calculated according to the equation:

\[
J_v = \frac{\Delta V}{A \Delta t}
\]
where \( J_w \) is the water flux. The units of the water flux were \( \text{L m}^{-2} \text{h}^{-1} \), abbreviated LMH. \( \Delta V \) is the volume change in the draw solution, \( \Delta t \) is the predetermined time for permeation, and \( A \) is the effective membrane surface area.

**2.5. Evaluation of the particle stability during the magnetic recycling process**

The stability of the magnetic draw solutes were determined using a repetitive magnetic recycling test carried out using a 50 g L\(^{-1}\) core-shell MNs dispersed aqueous solution. The particle stability was evaluated by varying the pure water flux and the mean particle diameter after each magnetic recycling process. The water flux was recorded during the FO process, and the core-shell MNs were separated from the permeate using a permanent magnet with a magnetic field strength exceeding 13,000 G for 15–20 min. The magnetic recovery efficiency was almost 100% for both core-shell MN draw solutions. The particles were then dried under vacuum at room temperature overnight. The dried core-shell MNs were re-dispersed in DI water and adjusted to a 50 g L\(^{-1}\) concentration. The magnetic recycling process was repeated 5–8 times. Fig. 2 shows the schematic illustration for FO filtration and magnetic recycle processes. After each recovery process, the recovered core-shell MNs were used in an FO process to measure the water flux, and the mean particle size was analyzed by EF-TEM and DLS to determine the variation in the particle size distribution during magnetic separation.

![Image](image.png)

Fig. 3. (left) EF-TEM images (inset images: schematic illustration for MN with difference stabilizes) and (right) particle size distribution evaluated by DLS analysis of (a) O-MN, (b) SiCOOH-MN, and (c) SiPEG-MN.
Similarly, the C=O stretch, and at 3600 cm$^{-1}$, corresponding to the OH stretch. Simultaneously, the C=O stretch (1040–1120 cm$^{-1}$) and OH stretch (3600–3300 cm$^{-1}$) were observed in the FT-IR spectra of SiPEG-MN upon exchange of the surface stabilizers, replacing the oleic acid with PEG-siloxane. The FT-IR spectra demonstrated that the hydrophilic surface modification reactions proceeded successfully, and hydrophilic siloxane ligands thoroughly covered the surfaces of the core-shell MNs.

The assembly of the surface siloxane agents on the MNs was confirmed by quantitatively analyzing method using TGA. As shown in Fig. 5, the TGA analysis results revealed that the weight loss in the MNs from room temperature to 800 °C resulted from the decomposition of the ligand molecules. The ligand molecule weight loss was measured based on the percent difference between the weights measured before and after the primary weight loss peaks. As the ligand exchange proceeded, the weight loss in the core-shell MNs samples increased. The O-MN sample (Fig. 5(a)) lost about 20% of its weight whereas the SiCOOH-MN (Fig. 5(b)) and SiPEG-MN (Fig. 5(c)) samples lost 42.5% and 57.2% of their weights, respectively.

The TGA and DLS results were used to calculate the ligand/particle ratio according to Eq. (1). The mean radii of the MNs were 5.1 nm (O-MN), 6.3 nm (SiCOOH-MN), and 6.8 nm (SiPEG-MN) based on the DLS analysis. The calculated ligand/particle ratios of the O-MN, SiCOOH-MN, and SiPEG-MN samples were 1269, 4261, and 5250, respectively. These results indicated that greater amounts of hydrophilic siloxane agents were bound to the surfaces of the MNs through the ligand exchange reaction than that for the O-MN. The difference between the quantities of surface hydrophilic siloxane agents bound to the surfaces of the core-shell MNs might be related to the packing structure of the hydrophilic agents. The SiCOOH molecules form multi-branched structures composed of three of carboxylic functional groups, which can introduce steric hindrance and electronic repulsion. These effects could disrupt the efficient packing of the SiCOOH ligands on the particle surface. By contrast, SiPEG consists of polyethylene glycol chains that can effectively pack onto the MN surfaces.

The results obtained from HR-TEM, DLS, FT-IR, and TGA analysis indicated that modifying the surfaces of the magnetic nanoparticles with the hydrophilic siloxanes provided robust interfacial bondings for the hydrophilic surface functional groups without introducing morphological changes.

### 3. Results and discussion

#### 3.1. Magnetic core-hydrophilic shell nanospheres

Magnetic nanoparticles were used in the FO process as a draw solute to facilitate their separation from the permeate during repetitive recycling processes through the application of an external magnetic field [30]. The typical magnetic draw solute tended to form aggregates, however, during the later magnetic separation cycles due to loss of hydrophilic stabilizer from the surface of magnetic nanomaterial. In this study, the magnetic nanospheres (MNs) were robustly bound to the hydrophilic capping agents via a ligand exchange reaction under basic condition. The magnetic core-hydrophilic shell nanospheres (core-shell MNs) were synthesized by replacing the oleic acid stabilizer on the MN with hydrophilic siloxane. The FT-IR spectra of core-shell MNs preserved their original spherical shape and size during the ligand exchange reaction without undergoing significant deformations. The particle size increased slightly from 10.3 ± 2.0 nm to 12.7 ± 2.5 (SiCOOH-MN) and 13.6 ± 2.4 nm (SiPEG-MN), respectively.

The chemical composition of the core-shell MNs was analyzed by FT-IR spectroscopy, as shown in Fig. 4, the major FT-IR bands corresponding to the oleic acid groups in the O-MN, e.g., C=C stretch disappeared after the ligand exchange reaction had gone to completion. The siloxane IR bands were observed near 1030 cm$^{-1}$ (for Si-O-Fe) and 1250 cm$^{-1}$ (for Si-C) in the FT-IR spectra of core-shell MNs. As the carboxylated siloxane bound to the MNs, the IR bands corresponding to the carboxylic acid groups appeared at 1620 cm$^{-1}$, corresponding to the carbonyl stretch, and at 3600–2700 cm$^{-1}$, corresponding to the OH stretch. Similarly, the C–O stretch (1040–1120 cm$^{-1}$) and OH stretch (3600–3300 cm$^{-1}$) were observed in the FT-IR spectra of SiPEG-MN upon exchange of the surface stabilizers, replacing the oleic acid with PEG-siloxane. The FT-IR spectra demonstrated that the hydrophilic surface modification reactions proceeded successfully, and hydrophilic siloxane ligands thoroughly covered the surfaces of the core-shell MNs.

3.2. Osmotic pressure

The osmotic pressure generated by the core-shell MNs aqueous solution indicated that the hydrophilic shells on the MN surface were the major components driving the osmotic pressure of the draw solution. The osmotic pressure due to the core-shell MNs was measured based on freezing point depression osmometry techniques using a variety of concentrated core-shell MN solutions (10 g L$^{-1}$–50 g L$^{-1}$, see Fig. 6). Beyond a magnetic core-shell MN solution concentration of 50 g L$^{-1}$, the MNs aggregated and precipitated in an aqueous solution. The osmotic pressure of O-MN could not be measured because it did not disperse in water. Fig. 6 shows that the osmotic pressures of both core-shell MN solutions increased linearly with the solution concentration. The maximum osmotic pressures of SiPEG-MN and SiCOOH-MN were 7.6 and 6.3 atm, at 50 g L$^{-1}$ concentrations.

These results revealed that a 50 g L$^{-1}$ core-shell MN draw solution could be used in an FO process applied to mild brackish water with...
ion concentration below 5000 ppm because their osmotic pressures were under 4 atm. In particular, the SiPEG-MN solution generated a larger osmotic pressure than the SiCOOH-MN solution at comparable concentrations. It seemed that generation of osmotic pressure was more influenced by number of surface hydrophilic agents than the number of ionic groups. The SiCOOH-MN had more ionic groups i.e., three carboxylates, and less surface ligand ratio than that for the SiPEG-MN. In this study, the osmotic pressure of SiPEG-MN at 50 g L\(^{-1}\) concentration was 20.6% more than that of the SiCOOH-MN at the same concentration. It was well consistence the ligand/particle ratio of core-shell MNs. As mentioned in the previous section, the SiPEG-MN incorporated 23% more hydrophilic surface agents than that for the SiCOOH-MN. The osmotic pressure measurements indicated that the MN hydrophilic siloxane surface modifications generated an osmotic pressure sufficient to generate a driving force in an FO process.

### 3.3. The water flux in the FO process, and particle stability of the magnetic core-hydrophilic shell nanosphere draw solute during the magnetic recycling process

The pure water permeability in an FO process conducted using the core-shell MN draw solution was measured using 20 g L\(^{-1}\) and 50 g L\(^{-1}\) concentrated draw solutions. Fig. 7 plots the water flux in an FO process over 90 min. As the concentration of the core-shell MN draw solution increased, the pure water flux increased. The pure water flux through the 20 g L\(^{-1}\) SiCOOH-MN and SiPEG-MN aqueous solutions was 1.22 and 1.1 LMH, respectively. SiPEG-MN and SiCOOH-MN draw solutions containing 50 g L\(^{-1}\) core-shell MN yielded water fluxes of 2.13 and 1.81 LMH. The 20 g L\(^{-1}\) draw solution yielded a lower flux than the 50 g L\(^{-1}\) draw solution. Higher draw solution concentrations were maintained during the water permeation processes, whereas low draw solution concentrations easily decreased further upon dilution. The osmotic pressure measurements obtained from the core-shell MN draw solutions revealed that SiPEG-MN yielded a greater osmotic pressure than the SiCOOH-MN solution. The pure water flux through the SiPEG-MN draw solute was more 10% greater than that obtained from the SiCOOH-MN draw solution.

The stability of the core-shell MNs was measured during repetitive magnetic recycling process. Fig. 8 shows the changes in the core-shell MN draw solutes, in terms of the water flux and particle size, measured after each magnetic recycling step. The concentrations of the core-shell MN aqueous solutions were maintained at 50 g L\(^{-1}\). The water fluxes through both of the core-shell MN solutions were preserved during 3 repetitive recycling processes. The water fluxes through the SiPEG-MN (Fig. 8(a)) and SiCOOH-MN (Fig. 8(b)) solutions were 2.01 ± 0.12 LMH and 1.69 ± 0.11 LMH, respectively. The mean particle sizes for both core-shell MNs were also preserved, and no particle aggregation was observed during 3 repetitive magnetic recycling. However, the aggregation of SiCOOH-MN draw solute was observed after 4th magnetic recycling due to occurrence of particle aggregation. The fluxes were also rapidly declined by loss of particle stability of SiCOOH-MN. The SiCOOH-MN has three carboxylate groups which can form hydrogen bonding with other carboxylate groups in neighborhood SiCOOH-MNs under strong magnetic recycling and drying process.

By contrast, the SiPEG-MN draw solution maintained water flux, 2.13 LMH for initial flux-1.89 LMH over 8 repetitive magnetic recycling processes because the SiPEG-MN did not undergo particle aggregation. Its particle diameter was changed within 10% from 10.3 nm to 11.4 nm. This strong stability was derived from covalent linkage of hydrophilic surface layer and steric hindrance effect without ionic interaction between magnetic particles.

These results indicated that the SiPEG-MN were sufficiently stable to prevent particle core aggregation during the magnetic separation steps. Previous reported recycling test results obtained from non-covalently modified hydrophilic MN solutes [30] revealed that the water flux tended to decrease and the mean particle size increased continually.
MN surfaces were robust, endowing the particles with sufficient stability for use in magnetically driven recyclable FO processes.

The draw solute stabilities and the pure water permeabilities led us to select the SiPEG-MN as a feasible draw solute with high osmotic pressure generation and superior stability during the recycling processes associated with FO processes applied to brackish water. Fig. 9 shows the water fluxes measured using 50 g L\(^{-1}\) SiPEG-MN draw solutions and a brackish feed solution composed of 500, 1000, or 5000 ppm methylene blue aqueous solution use as brackish feed water. The water fluxes of the low brackish water were maintained at 500 ppm or 1000 ppm methylene blue aqueous solution. Even the highly concentrated brackish water, 5000 ppm methylene blue aqueous solution, yielded a water flux that was around 40% of the value obtained from pure water. These results indicated that the SiPEG-MN draw solutes could be used in an FO water treatment process applied to mildly brackish water.

4. Conclusions

We demonstrated the use of magnetic core-hydrophilic shell nanoparticles as magnetic recyclable draw solutes in an FO process. The core-shell MNs were synthesized through a ligand exchange reaction between the carboxylate groups of oleic acid-stabilized MN and hydrophilic siloxane ligands to prevent aggregation during the magnetic recovery process. The combined results of TEM, DLS, FT-IR, and TGA analysis revealed that spherical magnetic nanoparticles with 10 nm in diameter were successfully prepared, and the hydrophilic siloxane agents robustly bound to the surfaces of the MN without inducing morphological changes during the ligand exchange reaction. The core-shell MN draw solutes generated a reasonable osmotic pressure that can be applied to purify mildly brackish water. As intended in this work, the covalently bound surface hydrophilic agents ensured a high level of particle stability during the repetitive magnetic recovery processes. The SiPEG-MN generated a larger osmotic pressure and provided higher particle stability during the magnetic recycling processes compared to the values obtained from the SiCOOH-MN due to differences in the molecular structures of siloxane ligands. Our approach provides a repetitive recyclable draw solute performed well due to the covalent attachment of hydrophilic agents to the nanoparticle surfaces.

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