



## Evaluation of citrate-coated magnetic nanoparticles as draw solute for forward osmosis



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### HIGHLIGHTS

- Citrate-coated magnetic nanoparticles (cit-MNPs) are superhydrophilic as draw solute.
- Cit-MNPs show highly negative surface charge and high surface charge density.
- Cit-MNPs provide high initial FO performance (17.3 LMH).
- A magnetic field control (MFC) FO module optimizes the use of the cit-MNPs.

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### ABSTRACT

Forward osmosis (FO) is a low-energy membrane technology of great interest for water reuse and desalination. A critical step for making FO practical is selection of proper draw solutes. We synthesized superhydrophilic, citrate-coated magnetic nanoparticles (cit-MNPs) through a co-precipitation method, and then systemically investigated their osmotic potential as draw solutes for FO. The adaptability of cit-MNPs as draw solutes was ensured by their special characteristics (highly negative surface charge and high surface charge density).

The initial FO performance was a pure water flux of 17.3 LMH with 20 mg/L MNP in FO mode, however a rapid decline in the water flux occurred due to an interaction between the cellulose triacetate (CTA) membrane and cit-MNPs. A magnetic field control (MFC) FO module was introduced to optimize the use of the cit-MNPs. Magnet field drives the magnetic particle away from the CTA membrane. In MFC FO module, a stable FO initial water flux of 13 LMH resulted with 20 mg/L MNP in FO mode. Our experimental results demonstrated that cit-MNPs can be suitable draw solutes for the FO process and the proposed MFC FO module is believed to be the first device for increasing water flux using magnetic nanoparticles as draw solutes.

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### 1. Introduction

The increasing scarcity of usable water is a major challenge for global society now, and is expected to get much worse in the near future [1]. To alleviate stress from lack of water, and to satisfy the need for high quality potable water, many cutting-edge technologies based on membranes have been developed for seawater desalination and water reuse [2]. Among these technologies, reverse osmosis (RO) is the most mature. RO, however, is relatively expensive and energy intensive because of the pressure required to push the water through the membrane. Two other factors have also made the use of RO problematic: the limited portion of treated water that can be recovered, and the

environmental impact from the toxic concentrate left behind after water treatment [3]. Therefore, other, less expensive technologies with higher recovery rates are needed to optimize water reuse.

Forward osmosis (FO) is a promising alternative to current technologies. In this process, water molecules of a relatively dilute solution with relatively low osmotic pressure, are drawn across a semipermeable membrane toward a more concentrated solution having higher osmotic pressure [4,5]. Major advantages of FO (compared to RO) are high proportion of water recovery, much lower energy consumption, less tendency for membrane fouling and excellent fouling control without deterioration of the membrane [2,6]. Some potential applications of the FO process include desalination, wastewater reclamation, power generation, osmotic engines in drug release, and food and beverage processing. Even with this potential, there are a lot of technical impediments to industrial application. The major critical challenges are high

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salt-rejecting membranes with low internal concentration polarizations (ICP) and high chemical potential draw solution with easy separation. Since Loeb and Sourirajan tested an asymmetric cellulose acetate membrane in 1963 [7], noticeable development of new FO membranes has occurred.

In contrast to the attention focused on membranes, much less attention has been given to draw solutes for use in FO. They are problematic in that ideal draw solutes have antithetic properties: they should exert sufficient osmotic effect to draw water from the feed solution, but should have no reverse salt diffusion. Another essential consideration when designing draw solutes for water reuse is the separation of the drawn solution into pure water and draw solutes in the stage of regeneration of draw solute. The details of this process will certainly involve a number of economic, ecological and environmental issues, so there is a pressing need for strategic considerations when engineering draw solutes. Since the mid-1960s, the use of inorganic salts (e.g., sulfur dioxide [8] and aluminum sulfate [9]) opened a window to draw-solute design. By using ammonium bicarbonate ( $\text{NH}_4\text{HCO}_3$ ) mixtures for desalination, the Elimelech group triggered a new round of study on draw solutes in the mid-2000s [10]. Achilli et al. developed a protocol for the selection of inorganic-based draw solutions for FO [11].

Recently, magnetic nanoparticles (MNPs) have drawn great attention as potential draw solutes for FO [12–15]. A number of unusual properties (i.e., superparamagnetism, high surface area to volume ratios, versatile surface modification, low toxicity and biocompatibility) have caused engineered MNPs to be widely studied for applications in magnetic resonance imaging, immunomagnetic separation, catalysis and drug delivery agents [16]. Such characteristics match well with the critical roles required of draw solutes. Especially, MNPs exhibit the phenomenon of ‘superparamagnetic property’, i.e., on application of an external magnetic field, MNPs become magnetized up to their own saturation magnetization, and on removal of the external magnetic field, MNPs no longer have any residual magnetic interaction. This unique property is size-dependent and exerts when the size of nanoparticles is as small as 10–20 nm. Adham was the first to test engineered MNPs as draw solutes for use in FO [12]. Although the osmotic pressure of MNPs (25 psi at 45 wt.%) was too low to draw water from the feed solution, the results of this research hinted at the possibility of magnetic separation via external magnetic field as a regeneration step, and to the applicability of water-soluble, inorganic–organic, hybrid nanoparticles. Ling et al. reported that 2-pyrol-MNP, TREG-MNP, and PAA-MNP, surface functionalized using the thermal decomposition method, and use of a high-gradient magnetic separator (HGMS) to establish magnetic separation efficiency, were not satisfactory owing both to the weak magnetic property of the polymer-coated MNPs and to nanoparticle aggregation induced by the HGMS [13]. Ge et al. attempted to coat the MNPs with poly(ethylene glycol) diacid (PEG-(COOH)<sub>2</sub>) by means of the same thermal decomposition method above [14]. As the molecular weight of the polymer became larger, the solubility in water, of the polymer-coated MNPs, got lower. Bai et al. introduced dextran-MNPs as draw solute [15].

In this work, superhydrophilic, magnetic nanoparticles coated with  $\text{Na}_3\text{Cit}$  as surface ligands were synthesized. Magnetic nanoparticles can be synthesized through the co-precipitation of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  aqueous solutions by addition of a base [17]. Control of the size and shape of the nanoparticles strongly depends on the molar ratio of  $\text{Fe}^{3+}/\text{Fe}^{2+}$ , type of salts (e.g., nitrates, sulfates, chlorides), pH and ionic strength of the media [18]. Citrate is one of the products from the tricarboxylic acid cycle (TAC), a normal metabolic process in the human body. TA is a natural preservative and also, is recognized as safe for use in food and drugs by all major national and international food regulatory agencies. Citrate with three hydrophilic-COOH groups can easily bind to iron oxide through chemisorption [19], acts as a surfactant to form a stable dispersion of MNPs in aqueous solution, and simultaneously endows the particle surfaces with carboxylate functional groups [20]. Systematic analyses using zeta potential and surface-charge density were performed to verify

the hydrophilic nature of the new citrate-coated MNPs. Water flux experiments were carried out using standard and magnetic field control (MFC) FO modules with cit-MNPs as draw solutes. This discussion leads to the critical question of what qualities of the cit-MNP draw solute most affected water flux performance in the FO process.

## 2. Materials and methods

### 2.1. Materials

Iron(III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 98%), iron(II) chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , 98%) and sodium citrate tribasic dihydrate ( $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ , 99%) were purchased from Sigma-Aldrich Chemical Company (USA). Hydrochloric acid (HCl, 37%) and sodium hydroxide (NaOH, 98%) were purchased from Samchun Chemical Co., Ltd. (Korea). All chemicals are of analytical grade and used as received. The deionized (DI) water used in all experiments was produced with a Milli-Q unit (Millipore).

### 2.2. Preparation of citrate-coated magnetic nanoparticles

#### 2.2.1. Magnetic nanoparticle synthesis

Superparamagnetic iron oxide nanoparticles were synthesized by the coprecipitation of ferric and ferrous ions in alkaline solution according to the literature, the details of which can be found elsewhere [21]. Briefly, magnetic nanoparticles ( $\text{Fe}_3\text{O}_4$ ) were made as follows: 50 mL of 6.36 g  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 17.3 g  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  solution were added using a dropping funnel to 500 mL of 1 M NaOH solution in a three-necked flask heated to 80 °C to hydrolyze the iron chlorides. The contents of the flask were stirred vigorously (315 rpm) for 60 min with a mechanical stirrer while being purged with nitrogen gas. The resulting black, gel-like precipitate was collected on a 0.5 T magnet and washed several times with  $\text{H}_2\text{O}$  (until pH neutral). The remainder was dispersed in 200 mL of distilled water with a pH value of 7. The magnetic nanoparticles with no coating agent are labeled bare-MNP.

#### 2.2.2. Citrate-coated magnetic nanoparticle synthesis

Sodium citrate was used to stabilize the magnetic nanoparticles and to provide hydrophilic functional groups as shown in Fig. 1. In this experiment, 4.85 g of trisodium citrate in 10 mL water was added to a prepared solution of bare MNP while stirring vigorously and continuously for 60 min (cit-MNP1). For cit-MNP2, all the conditions were the same as above except that it was heated to 95 °C for 60 min while mixing with bare MNP and citrate. To remove uncoordinated species and the reaction solvent, the resulting black suspension was ultracentrifuged at 10,000 rpm for 30 min before the supernatant was discarded, and the sediment was re-dispersed in 200 mL of distilled water by sonication in a water-bath sonicator for 20 min.

### 2.3. Characterization of citrate-coated magnetic nanoparticles

Fourier transform infrared measurements were performed using an Infinity Gold FT-IR spectrometer (Thermo Mattson, USA) to confirm that the MNPs were coated with citrate. The scan range was from 4000 to 600  $\text{cm}^{-1}$ . The samples were dried overnight under vacuum at 105 °C air temperature. The spectra were obtained by the solid KBr method. The weight loss of the cit-MNPs was characterized by thermogravimetric analysis (TGA) with a TGA 2050 thermogravimetric analyzer (TA Instruments, USA) during thermal oxidation. The measurement was conducted under argon from 50 to 800 °C at a heating rate of 10 °C/min. X-ray diffraction (XRD) studies were performed on a small-angle X-ray spectroscopy (D/MAX 2500, Rigaku, Japan) operated at 8 kW (40 kV and 200 mA). The scan range was from 10 to 80 °C and the measurement speed 2 °C/min. The osmotic pressures of the draw solutions prepared from MNPs were measured using an Osmomat 030 osmometer (Gonotec, Germany). This device uses the technique of

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