

Engineering of size-controlled magnetic nanoparticles for use as a draw solution in a forward osmosis process

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ABSTRACT

Forward osmosis (FO), an osmotically driven process, is a promising technique for nutrients and organic matter recovery from urine and wastewater. Its efficiency is highly dependent on the differential osmotic pressure between feed and draw solutions. Therefore, the choice of draw solution is of great significance for successful operation of FO units. While inorganic salts solutions generate high osmotic pressure, their recovery is difficult and energy intensive. An easy to recover draw solution is therefore needed. Recently, few researchers reported that an easy to recover draw solution made of coated magnetic nanoparticles (MNPs) could be engineered. However, synthesis of coated MNPs for use as draw solution is not yet well mastered and not well understood. It is assumed that the size, dispersion, coating ratio and properties of coated MNPs are crucial important factors affecting the performance of the draw solution. In this study, we investigate the effect of several parameters exemplified by synthesis temperature, introduction of MNPs sonication, and timing of coating material addition (separate or simultaneous co-precipitation and coating) as well as initial MNP to coating agent ratio on the size and coating ratio and properties of coated MNPs. Chemical precipitation was adopted for the synthesis of MNPs. The coated nanoparticles were characterized using SEM, coating ratio and osmotic pressure and flux generation. Findings show that by heating at 80°C during the coating process, an increase in the particle size distribution and coating ratio was confirmed. Moreover, by separating the co-precipitation process and the coating process, the coating ratio increased and the particle size distribution became uniform with a small particle size. By introducing ultrasonic treatment after washing the magnetite particles, it was confirmed that the coating ratio increased and the particle diameter decreased. However, introducing sonication after coating stage will lead to smaller particle size, but lower coating ratio as the kinetic energy of sonication will peel off the coating agent from MNPs. With respect to initial MNP to coating agent ratio, coating ratio will increase with increasing the initial ratio. It is worth mentioning that FO tests revealed that the osmotic pressure shows a linear relationship with the coating ratio. Moreover, at similar amounts the generated osmotic pressure is larger in the MNP coated than in the bare sodium poly-acrylate.

Keywords: Forward osmosis; Magnetic nanoparticles; Draw solution; Coating

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1. Introduction

Forward osmosis (FO) is an osmotic process during which solvents move through a semi-permeable membrane from a “feed” solution of low concentration towards a “draw” solution of higher concentration. The osmotic pressure gradient between the two solutions is the driving force of solutes movement. This natural phenomenon emerged as an attractive approach in many applications to separate water from diluted feeds. Applications examples include desalination, power generation, cooling, wastewater treatment, beverage industry, nutrients recovery from urine, among others [1–3]. Unlike reverse osmosis, FO is attractive for being less prone to fouling and less energy demanding [4]. However, the choice of draw solution is very crucial for the successful operation of FO process [5]. Indeed, the performance and efficiency is dependent on several factors and draw solution is one of these factors. Therefore, the choice of the draw solution plays a central role and its selection is a crucial step. An effective draw solution solute should feature high water solubility, high osmotic pressure, low interaction with the membrane, high diffusion coefficient, being readily available at low cost, and easy recoverability. Despite, several draw solutions are available, each has some disadvantages. For instance, inorganic salts such as NaCl, KCl, and Na_2SO_4 are readily available, highly soluble and capable of generating high osmotic pressure, but in the other side they show a high reverse diffusion and they are costly to recover [6]. Organic salts draw solution such as glycine show low reverse diffusion but they are costly. Draw solution made of other organic compounds such as sucrose and fructose present the disadvantage of high viscosity inducing high internal concentration polarization as well as a low osmotic pressure. Volatile compounds exemplified by ammonia carbonate offers the advantage of high osmotic pressure and relatively low cost recovery, but present the disadvantage of high reverse diffusion and high ammonium content in product water. Therefore, novel draw solutions are required to overcome all the above-mentioned disadvantages. The novel draw solution should, therefore, feature high osmotic pressure and easy recoverability. It is obvious that the osmotic pressure required depends heavily on the feed solution being treated and the osmotic pressure difference between draw and feed solution should be maintained at approximately 1–1.5 MPa to achieve appreciable flux. For instance, for economic storage and transport of fertilizers recovered from urine, it is highly recommended to concentrate urine five times [7]. A fivefold concentrated human urine features an osmotic pressure exceeding 10 MPa [8,9]. Hence, draw solution should feature higher than 10 MPa osmotic pressure. Moreover, for wastewater concentration to recover organic matter, experiments conducted by Guizani et al. [10] in their study revealed that a 10 MPa draw solution is preferred for higher and efficient organic matter recovery. It is worth mentioning that sea water of an average salt concentration of 35 g L^{-1} has an osmotic pressure in the order of 2.6 MPa only. A high osmotic pressure can be obtained by synthesizing polyelectrolyte solutions [11,12]. However, it is obvious that a huge energy will be required for their recovery. To address the need of easily recoverable high osmotic pressure draw solution, several researchers focused

on functionalized magnetic nanoparticles (MNPs) [13–17]. Indeed, in many applications (e.g., biomedical), functionalized MNPs were used, their recovery was easily achieved by magnetic field application. As for the engineering of MNPs to serve as draw solution, it is worth mentioning that due to their large size compared with the electrolytes, MNPs are not expected to generate osmotic pressure [13]. Interestingly, they can be coated with osmotic pressure generating polymeric agents. Several coating materials were tested and proved that the synthesis of a novel draw solution featuring high osmotic pressure and easy to recover is an attractive option [13,18–20]. Although the synthesis of functionalized MNPs for use as draw solution for FO process was reported, it is still not well understood how it works and what parameters affects the quality of draw solution. In this paper, we investigate the effect of different synthesis conditions on the properties of novel draw solution. These properties include particle size of the coated MNPs and the coating ratio as well as their ability to generate osmotic pressure. Synthesis temperature is among the factors that may affect these properties. However, researchers have focused on the temperature during the synthesis of the MNPs, but for some reasons the temperature during the addition of coating agents was ignored. Hence, the effect of temperature during coating stage will be addressed. In addition, the timing of coating agent addition will be evaluated. In the other side, treatment of the draw solution with ultrasound is believed to affect the size and coating ratio and hence it will be addressed in this paper. Another important factor related to the initial coating agent to MNP ratio will be subject to evaluation as it may impact the size, coating ratio and the osmotic pressure generation. It is worth mentioning that magnetic properties of the synthesized particles will be evaluated using magnetic hysteresis loops, and insights on their recovery will be gained. In this study sodium poly-acrylate (SPA) will be used as a coating agent.

2. Materials and methods

2.1. Reagents

Chemicals used in this study were of analytical grade. Ferrous chloride (II) tetra-hydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ferric (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium hydroxide solution (NaOH) were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Coating agents (tri-sodium citrate dehydrate $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ with average molecular weight of 294.1 g mol^{-1} and sodium poly-acrylate ($\text{C}_3\text{H}_3\text{NaO}_2$)_n with an average molecular weight of 94.04 g mol^{-1} (SPA) were purchased from Sigma-Aldrich (Japan).

2.2. Magnetic nanoparticle synthesis procedure and conditions

Magnetite nanoparticles (Fe_3O_4) were prepared by co-precipitation method. Ferrous chloride (II) tetra-hydrate and ferric chloride (III) hexa-hydrate were dissolved at 1:2 ratio in a conical beaker under nitrogen gas. Mixture was heated at 80°C under continuous stirring for 60 min. Next, sodium hydroxide (NaOH) was added by syringe to adjust the pH to 11. A black precipitate was formed, and it was confirmed by XRD (data not shown) that it is a magnetite

(Fe₃O₄). During coating stage, different synthesis conditions were tested as illustrated in Table 1.

2.3. Effect of synthesis temperature

The temperature has a great effect on the size and properties of magnetite nanoparticles. Early studies as exemplified by the works of Ling et al. [21] carefully examined the effect of temperature on the size of MNP. A synthesis temperature of 80°C was adopted in many works to synthesize small particles in the order of 5–20 nm. However, due to aggregation and micelles formation around the magnetite during coating, the coating process produces larger particle sizes. While effect of temperature during synthesis was

well covered in the literature, the temperature during coating step is not well documented. In this study, we studied the effect of temperature during the addition of coating material. As shown in Table 1, the coating process was performed at two different temperatures 25°C (case 1) and 80°C (case 2). Synthesis procedure and coating of these two cases is shown in Fig. 1. After addition of coating material, the mixture was stirred for 1 h, while maintaining the temperature at 25°C (case 1) or 80°C (case 2).

2.4. Ultrasonic treatment

As shown in Fig. 1, the synthesized MNPs were washed four times with Milli-Q water before coating agent

Table 1
Summary of synthesis conditions

Cases	Temperature (°C)	Timing of coating material addition	With/without sonication before coating	With/without sonication after coating
Case 1	25	Separation between co-precipitation and coating	Without	Without
Case 2	80	Separation between co-precipitation and coating	Without	Without
Case 3	80	Separation between co-precipitation and coating	With	Without
Case 4	80	Separation between co-precipitation and coating	With	With
Case 5	80	Separation between co-precipitation and coating	Without	With
Case 6	80	Simultaneous co-precipitation and coating	Not applicable	With

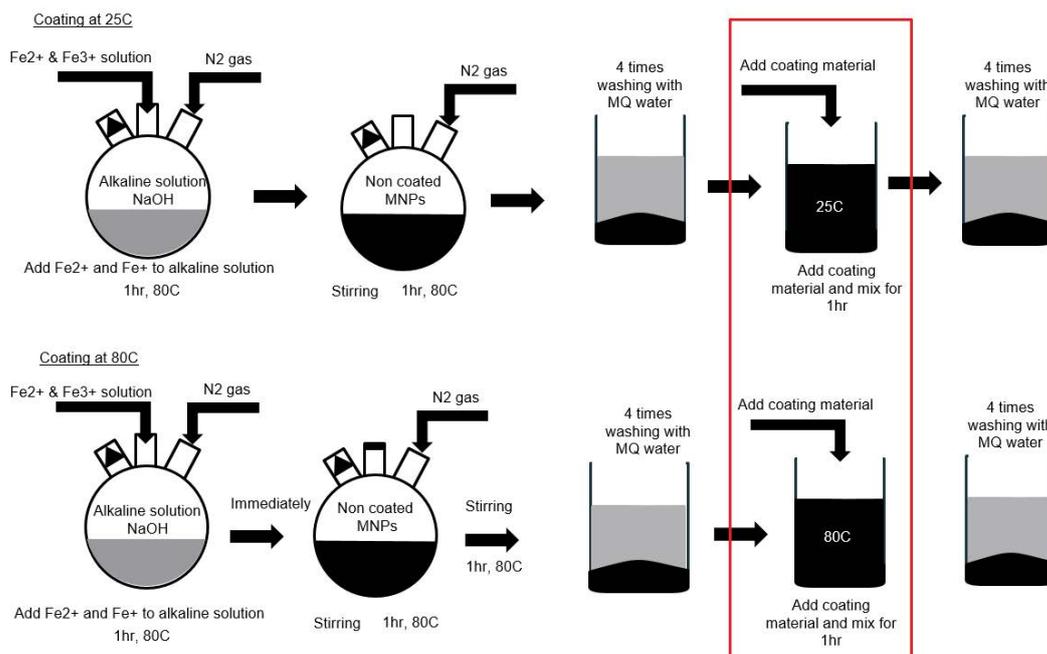


Fig. 1. Experimental procedure for synthesis and coating for temperature effect evaluation.

addition. During washing step, MNPs were separated using centrifugation or recovered by a magnet. During these separation techniques agglomeration of particles is likely to happen. Therefore, ultrasonication was introduced after washing step to disperse the magnetite and break agglomerates and aggregated particles into smaller particles. A 20 kHz, 50 Watt probe-type ultrasonic homogenizer (UH 50, SMT) was used for 30 min. Sonication was applied before coating step (case 3) and compared with the case where no sonication was applied (case 2). Case 4, consisted of case 3 followed by a second sonication after coating agent were added. Finally, case 5 consisted of a single sonication after coating agent addition. Fig. 2 summarizes synthesis cases involving sonication.

2.5. Timing of coating material addition

Furthermore, we evaluated the proper timing of dropping coating solution into the magnetite (coating temperature is 80°C). In the first run (corresponding to case 5), right after the formation of MNPs, coating material is dropped. We wanted to coat the MNPs, while they are still not in agglomerated form. In the second run (corresponding to case 6), we allowed the Fe^{2+} and Fe^{3+} to react with the alkaline solution for 1 h, after 1 h of continuous mixing at 80°C, the coating material is added. Then it is allowed for another 1 h under continuous

mixing conditions. It should be noticed that after coating we used sonication for 30 min in both cases. Fig. 3 illustrates the experimental procedure adopted to evaluate the effect of coating material addition timing.

2.6. Magnetic nanoparticle characterization

Magnetic nanoparticles characterization followed the method used by Guizani et al. [13]. A small portion of synthesized MNPs were dried at 105°C for further characterization and analysis. Coating efficiency was evaluated by a thermal gravimetric analysis. First coated MNPs were dried at 105°C to free up all the contained water. Then, the particles were further heated up to 800°C and the weight loss is measured. It is known that coating material will decompose at temperatures ranging from 300°C to 600°C, while the residual weight is relative to magnetite. The ratio of weight loss to initial weight defines the coating efficiency ratio.

The particle size is an extremely important parameter for MNPs based draw solution. Smaller size leads to higher coated surface area to volume ratio which plays an important role in generating higher osmotic pressure and affecting FO performances. The particle size distribution was analyzed using laser particle size distribution analyzer (Delsa Nano HC, Beckman Coulter). MNPs were first dissolved in deionized water and then run through the analyzer. Furthermore,

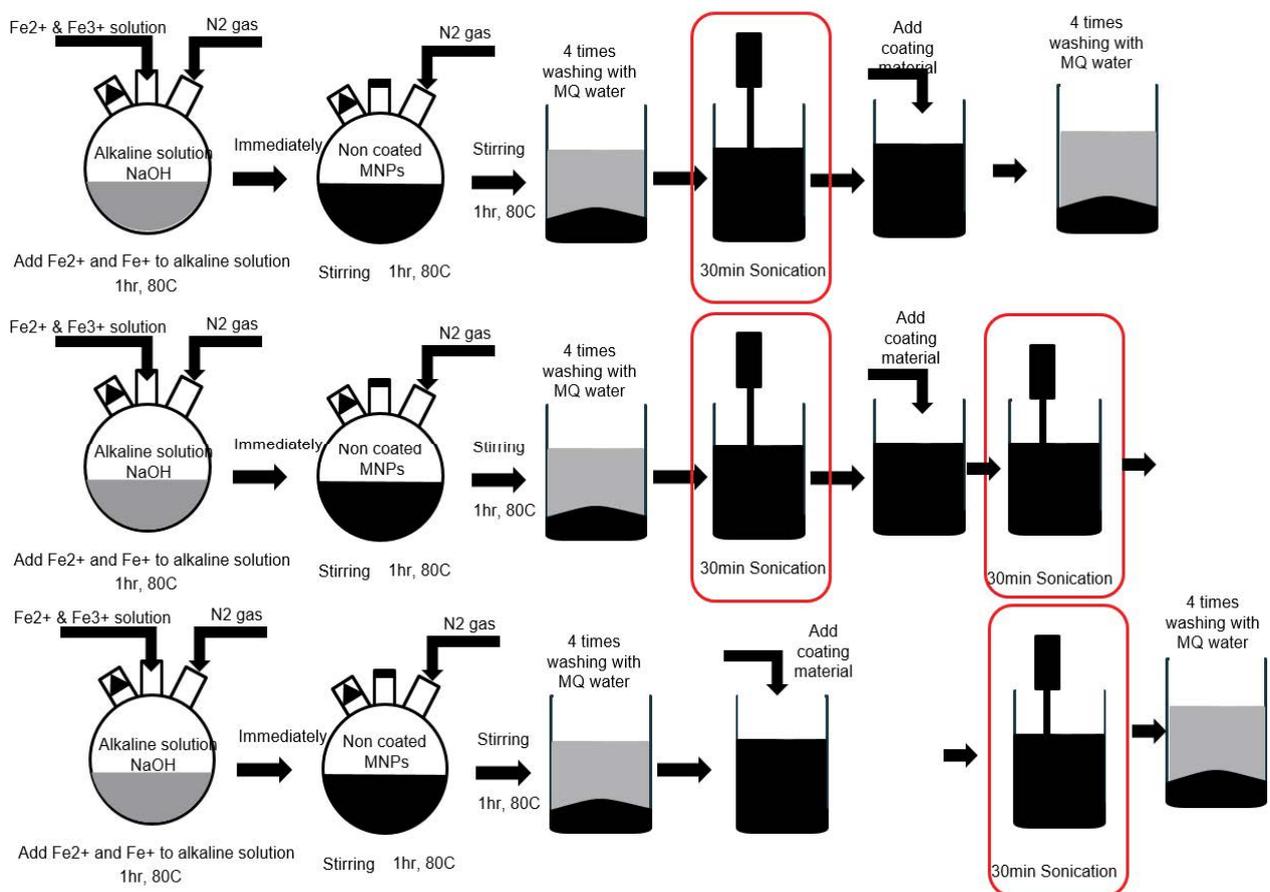


Fig. 2. Experimental procedure for studying the effect of sonication prior to coating.

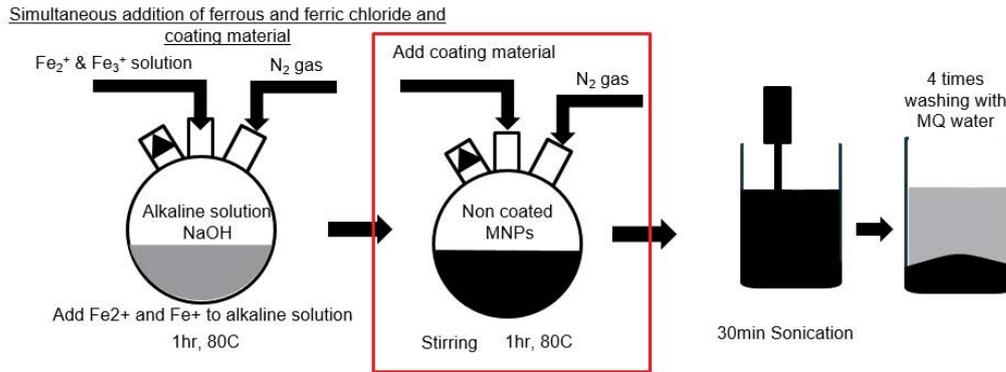


Fig. 3. Experimental procedure for studying the effect of timing of coating material addition.

the shape and size of the particles were observed with a scanning electron microscope (SEM, S4800, Hitachi Ltd., Tokyo, Japan).

The recoverability of the draw solution is a significant factor to judge the usefulness of this draw solution. In this paper, the SPA-coated MNP will be characterized using magnetic hysteresis loop. Therefore, recoverability will be discussed with respect to the super paramagnetic properties of the particles.

2.7. FO tests

The synthesized MNPs were used as draw solution of an FO experiment where distilled water was used as feed solution to assess their possible use as draw solution. FO tests were carried out using a bench-scale laboratory set-up. Fig. 4 illustrates the experimental set-up for FO tests. A flat sheet cellulose triacetate membrane from (Albany, OR, USA) was assembled in a lab-made rectangular membrane cell with a serpentine channel an active membrane area of 98 cm². Before use, the membrane was immersed in de-ionized water for 30 min before use. In feed solution we used de-ionized water, and in draw solution we used coated MNPs solution (1 wt.%). Feed and draw solutions with an equal volume were circulated co-currently by two peristaltic pumps, at the same flow rates of 0.2 m s⁻¹. Weight change in feed solution was recorded using an electronic balance and from flux movement the equivalent osmotic pressure was calculated. Table 2 shows the experimental operating conditions. Osmotic pressure was obtained from water flux using following equation:

$$\Delta\pi = \frac{J_w}{K} \tag{1}$$

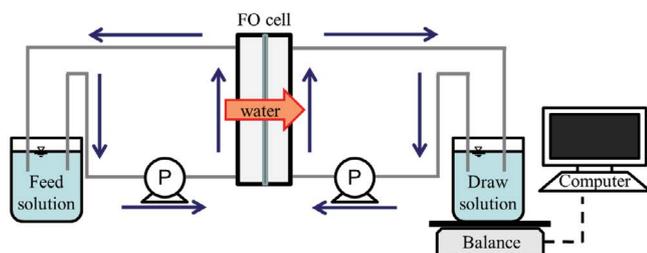


Fig. 4. FO experimental setup.

Table 2
FO experimental operating conditions

Flow rate	0.20 m s ⁻¹
Flow direction	Co-current
Membrane	Cellulose triacetate
Effective membrane area	98 cm ²

where $\Delta\pi$ (MPa) is the differential osmotic pressure between draw and feed solution; J_w is the measured water flux; and K is the membrane permeability.

3. Results and discussion

3.1. Effect of synthesis temperature

Particle size and coating ratios results are summarized in Fig. 5. By comparing case 1 (coating at 25°C) and case 2 (coating at 80°C), we can clearly see the change in size and coating ratio with respect to the synthesis temperature conditions. The particle size of MNPs measurement shows that particles sizes decreased slightly from an average of 166 to 154 nm, respectively, for coating at 25°C and 80°C, respectively. In the other side, coating ratio increased from 4.9% to 6.6% for coating at 25°C and 80°C, respectively. Hence, coating at 80°C favors smaller particle size and better coating ratio. Although the synthesis at 80°C reduced particle sizes and improved coating ratio, it is worth mentioning that further reduction of the particle size and increase of coating ratio are required to produce an efficient MNP for draw solution. Indeed, we assume that smaller size leads to higher coating ratio and this will increase osmotic pressure of the draw solution. Therefore, an improvement of the synthesis conditions is required.

3.2. Effect of sonication

In case 3, we introduced sonication before the addition of coating agent. By comparison between case 2 (no sonication) and case 3 (with sonication), it is revealed that ultrasonic treatment after washing the magnetite particles reduced particle size from 154 to 77 nm and increased coating ratio from 6.6% to 11% (Fig. 5). Data suggest that the kinetic

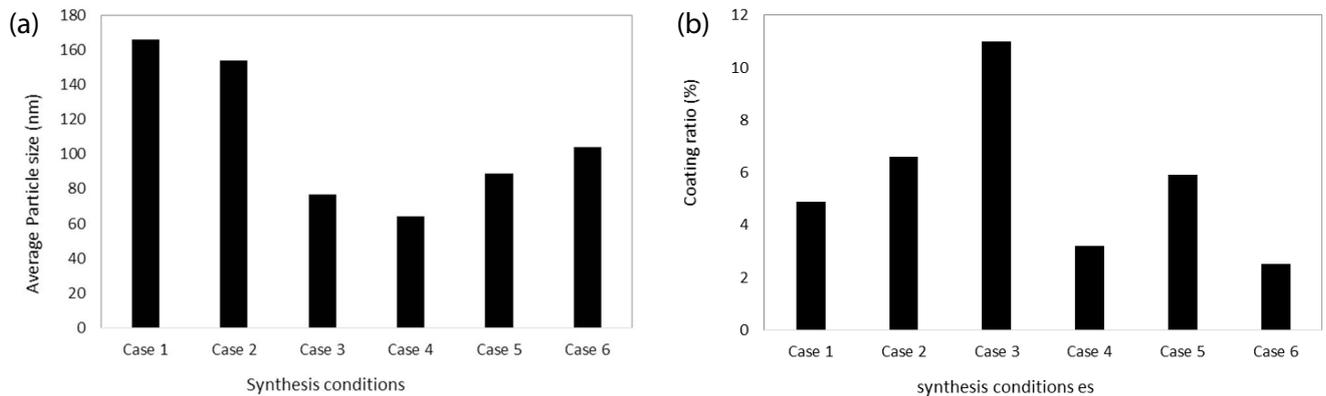


Fig. 5. Average particle size (a) and coating ratio (b) depending on synthesis conditions.

energy from sonication break the MNPs to smaller particles and exposes larger surface area for coating. Indeed, it was reported that kinetic energy can reduce the molecular weight of Fe_3O_4 and break the agglomeration so the particle become small fragments [16,22]. SEM images (Fig. 6) show that with no sonication agglomerates are formed. Samples treated with sonication show primary particles in the order of 10 to 15 nm. Without sonication, agglomerates were formed as illustrated in SEM images (Fig. 6).

Since sonication, lead to a reduction in particle size and an improvement of coating ratio, another stage of sonication was proposed after coating agent addition (case 4). Results reveal that the particle size was further reduced from 77 to 64 nm. However, coating ratio dropped significantly from 11% to 3.2%. This observation suggests that the kinetic energy supplied by sonication break the nanoparticles to smaller ones, but at the same time lead to peel off the coating material from the particles leading to a decrease in coating ratio.

In another trial (case 5), no sonication before addition of coating material was used, and only sonication was used after addition of coating material. Data show that coating ratio improved slightly in comparison with case 4, but particle size has increased. These data suggest that sonication is best to be applied before addition of coating material. According to Hong et al. [17] and Rahmawati et al. [22], the sonication process in specific frequency especially in high frequency (several hundred kHz) will

form agglomeration of particles due to the high energy which caused the forming of bubbles and cavitation. So, finding an optimum condition is crucial. It is also worth mentioning that in a separate experiment, we confirmed that after sonication, particles were well dispersed in the solution and it became difficult to collect them with a neodymium magnet. Data, from hysteresis loop, confirm that they still show a super paramagnetic property. This indicates that for their recovery stronger magnetic field will be required, and therefore more energy is required for their recovery (data not shown).

3.3. Effect of timing to add coating agent

In the last case (case 6), we assumed that if coating agent is added during co-precipitation stage, it would coat the particles without giving them time to agglomerate. Surprisingly, results do not support this assumption (Fig. 5). Indeed, compared with case 5 where coating and co-precipitation were separated, the case 6 led to larger particle size (104 nm) and lower coating ratio (2.5%). The average size dropped to 74 nm and the coating ratio increased to 5.6% when coating material was added after washing step. SEM images show that primary particles were in the order of 10 nm. By separating the co-precipitation process and the coating process of magnetite and synthesizing the coated MNPs, the coating ratio increased and the particle size distribution became uniform with a small particle size.

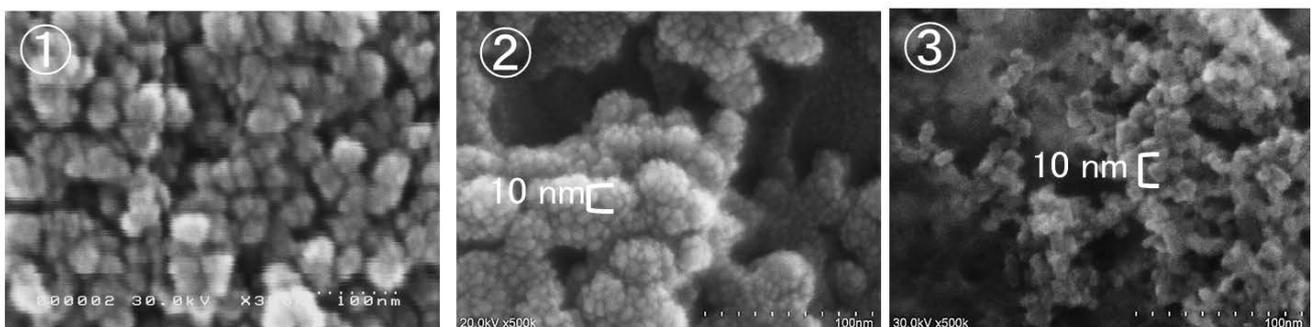


Fig. 6. Effect of sonication on particle size: without sonication (1), with sonication (2 and 3).

3.4. Effect of initial amount of coating agent

In all the above experiment, we used a prefixed amount of coating agent. To assess the effect of initial amount of coating agent on the coating ratio, we synthesized MNPs following the procedure of case 4 where coating was performed by separation between co-precipitation and coating at 80°C with ultrasonication. Before the addition of coating agent, in this experiment no sonication was performed. Coating agent used in this experiment consisted of a sodium poly-acrylate (SPA).

As illustrated in SEM images (Fig. 7) and in Fig. 8a, particle size did not change significantly. More interestingly, increasing initial amount led to a significant improvement of coating ratio (Fig. 8b). At a ratio of initial amount of MNP to coating agent of 1:1, the coating ratio was only 3% by weight. However, if the initial SPA to MNP ratio increased, the coating ratio increased until it reached more than 13% at an SPA to MNP ratio of 45.

3.5. Magnetic hysteresis loop

In order to quantitatively study the magnetic properties of the synthesized coated MNPs, hysteresis loops of the synthesized particles were conducted. Fig. 9 shows magnetic hysteresis loops of uncoated and coated MNPs. All particles show super paramagnetic properties, with a slight decrease of residual magnetism for the same coercive force when the coating ratio increases. As the SPA-coated MNP show super paramagnetic properties, they can be easily collected by a magnet.

3.6. FO tests

The SPA-coated MNPs synthesized at 80°C with separation of co-precipitation and coating steps were used as a draw solution for an FO test experiment. The draw solution consisted of 1 wt.% solution of SPA-coated MNPs. Various

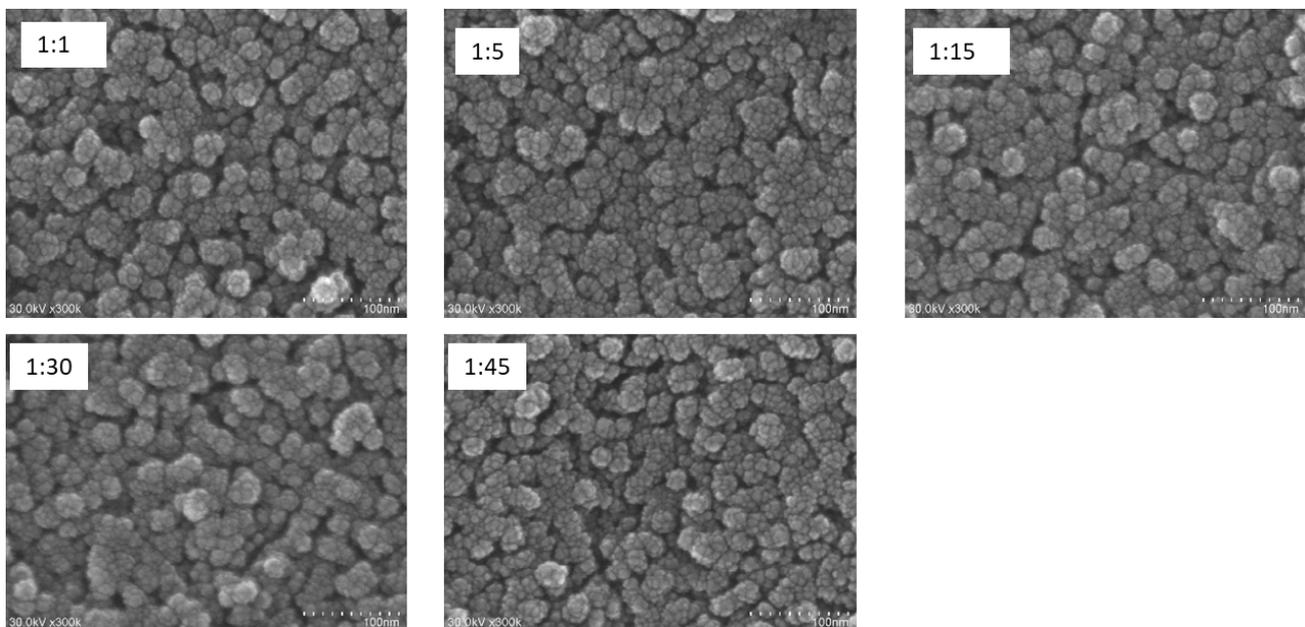


Fig. 7. SEM images of MNP coated with SPA.

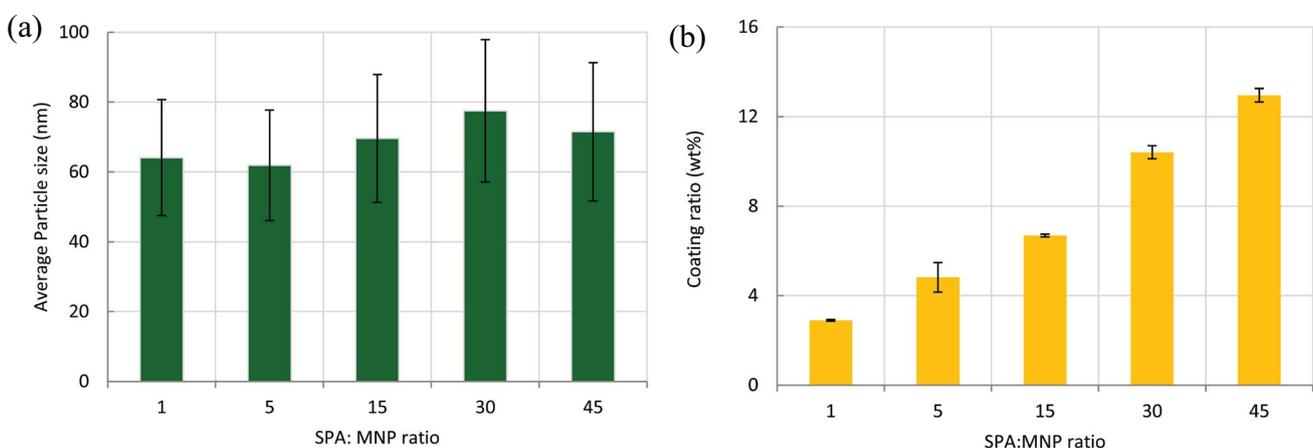


Fig. 8. Average particle size (a) and coating ratio (b) of the synthesized MNPs.

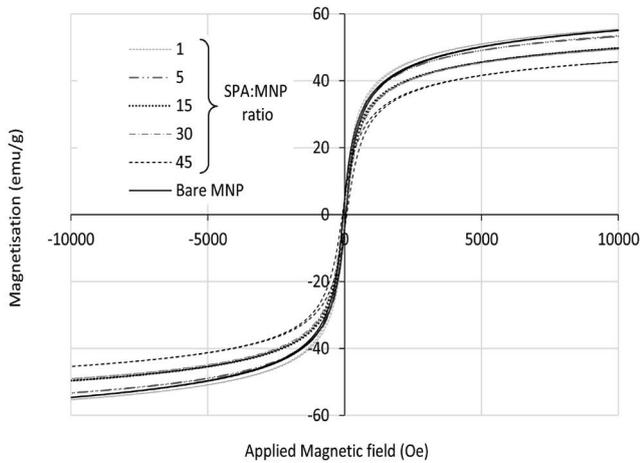


Fig. 9. Magnetic hysteresis loop for uncoated and SPA-coated MNPs.

FO tests were conducted using different initial SPA to MNP ratios. Total amount of SPA present in draw solution can be calculated from coating ratio and solution weight percentage. One of the FO tests was conducted using 0.13 wt.% of SPA solution (without MNP) as draw solution. From this experiment, water flux was obtained and the driving osmotic pressure was calculated. As shown in Fig. 10a, osmotic pressure increases with the increase of SPA amount. Furthermore, Fig. 10b shows a linear relationship correlation between osmotic pressure and coating ratio of per unit surface area. Moreover, it is worth mentioning that at an MNP to SPA ratio of 1:45, the coating ratio is about 13%. Hence, the amount of SPA in this draw solution is equivalent to 0.13 wt.%. However, in a draw solution containing 0.13 wt.% of SPA a much higher osmotic pressure was generated when SPA-coated MNP was compared with a bare SPA of the same amount. So even though, no osmotic pressure can be generated from MNPs alone, and moderate osmotic

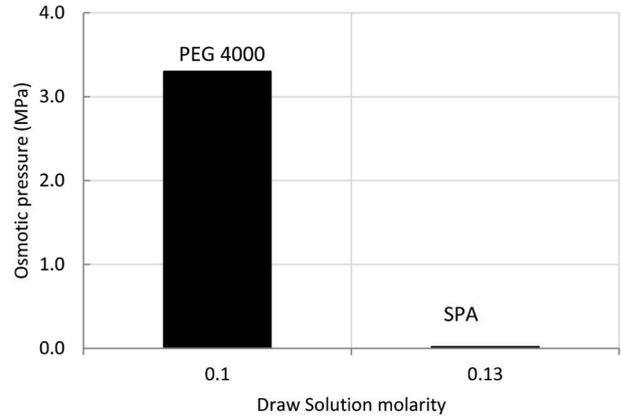


Fig. 11. Osmotic pressure of solution of PEG 4000 and SPA.

pressure is generated using SPA, the composite solution containing the same amount of SPA generates a much higher osmotic pressure.

As shown in Fig. 10a, the highest osmotic pressure generated is in the order of 0.13 MPa. Other researchers as exemplified by the works of Zuiffia Rivas et al. [23], an osmotic pressure in the order of 1.1 MPa was reported. In their case, the SPA represents 60% of the solution, while in our case SPA is only 1 wt.%. So, at higher ratio, a more significant osmotic pressure can be generated. It is worth mentioning that coating ratio is relatively low. Further improvement of synthesis conditions would improve coating ratio and therefore the osmotic pressure which can be generated. However, higher coating ratio may lead to deterioration of super paramagnetic properties. Hence, it is also important to mention that choice of coating agent may affect the osmotic pressure which can be generated. As shown in Fig. 11, a polyethylene glycol (PEG 4000) solution (molarity 0.1%) generates a much higher osmotic pressure than a solution of SPA (molarity 0.1%). Osmotic pressure of PEG solution is compiled from Money [24].

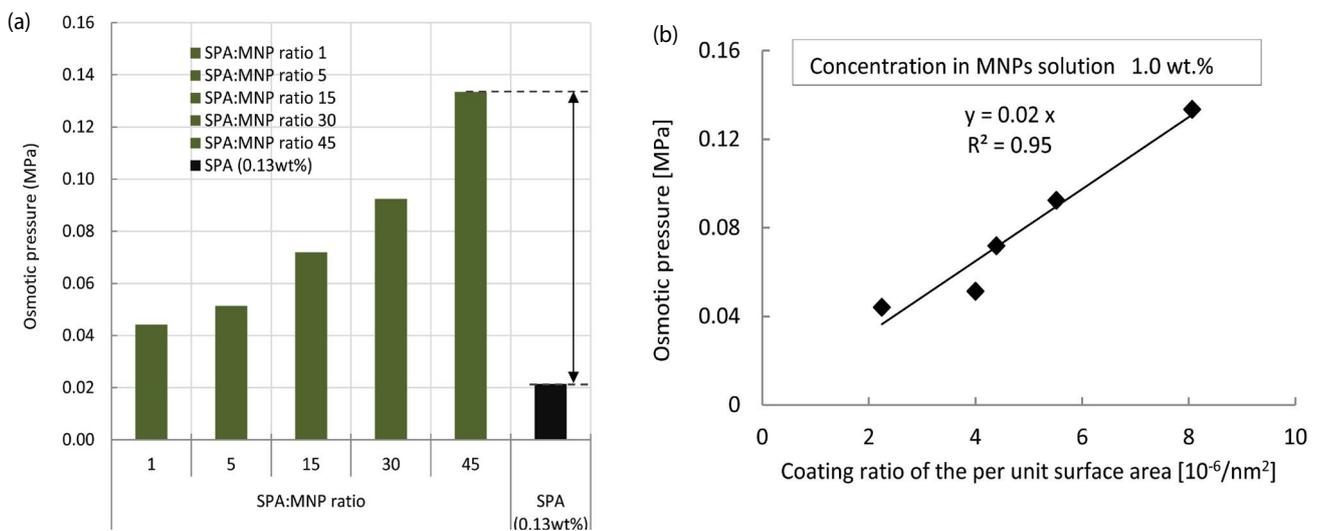


Fig. 10. Relationship between (a) coating ratio per surface area and (b) osmotic pressure.

4. Conclusions

We successfully prepared a novel draw solution made of coated MNP. We confirmed that synthesis conditions affect the size and coating ratio of MNPs. A temperature of 80°C is more favorable for coating than coating at ambient temperature. Indeed, an increase of the coating ratio increased from 4.9% when coating was performed at 25°C to 6.6% for a coating at 80°C. Furthermore, separation between co-precipitation and coating, along with an introduction of sonication before addition of coating material, leads to reduction of particle size from 154 to 77 nm and an improvement of coating ratio from 6.6% to 11%. However, the adoption of ultrasonication after coating is likely to peel of the coating agents, leading to a drop in coating ratio from 11% to 3.2%. In the other side, the initial SPA to MNP ratio was shown to be an important factor. Indeed, the coating ratio increased linearly from 2.9% to 13% with the increase of SPA to MNP ratio from 1% to 45%. The osmotic pressure of draw solution made of 1 wt.% solution of SPA-coated MNPs increased as well from 0.04 to 0.13 MPa, with the increase of SPA to MNP ratio from 1 to 45. The SPA-coated MNP showed super paramagnetic properties, which reflects the possibility for its easy recovery with a magnet.

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