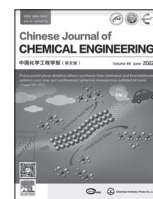




Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

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

Full Length Article

Preparation of novel magnetic nanoparticles as draw solutes in forward osmosis desalination

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ARTICLE INFO

Article history:

Received 28 March 2021

Received in revised form 15 July 2021

Accepted 20 July 2021

Available online 28 July 2021

Keywords:

Magnetic nanoparticles

Forward osmosis

Draw solute

 Fe_3O_4 $\text{PEG}-(\text{COOH})_2$

ABSTRACT

Novel magnetic nanoparticles (MNPs), $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ and $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{PEG}-(\text{COOH})_2$, were prepared by loading different amounts of SiO_2 or/and $\text{PEG}-(\text{COOH})_2$ onto Fe_3O_4 nanoparticles, and their feasibility to be used as forward osmosis (FO) draw solutes was investigated. The characterization of the materials showed that, compared to normal Fe_3O_4 nanoparticles, the modified MNPs exhibited enhanced dispersity and high osmotic pressure in aqueous solution. The FO experiment indicated that the synthesized draw solutes could obtain a water flux as high as $10 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ with an aquaporin FO membrane. The optimal concentration of the added tetraethyl orthosilicate was 30% during the synthesis. The novel MNPs could be easily recovered from draw solutions by magnetic field, and the recovery rate of $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ and $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{PEG}-(\text{COOH})_2$ was 83.95% and 63.37%, respectively. Moreover, after 5 recycles of reuse, the water flux of $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ and $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{PEG}-(\text{COOH})_2$ as draw solutes still remained 64.36% and 85.26%, respectively. The experimental results demonstrated that the synthesized core-shell magnetic nanoparticles are promising draw solutes, and the $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{PEG}-(\text{COOH})_2$ was more suitable to be used as draw solute in FO process.

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1. Introduction

Nowadays, membrane separation has been widely used in sea-water desalination, sewage reclamation, and industrial wastewater treatment [1]. Among all membrane technologies, forward osmosis (FO) has been considered to be one of the most promising processes for water/wastewater treatment. Compared with distillation technology or reverse osmosis, FO has the advantages of low energy consumption, light membrane fouling, and simple operation [1,2]. However, the recovery of FO solutes from draw solution was the primary issue that determines whether FO could be widely used in water/wastewater treatment [3,4]. Therefore, it is of great importance to develop new and efficient draw solutes in order to solve the crucial problem impeding the application of FO technology.

The core function of draw solutes is to generate high osmotic pressure in water solutions, and requires easily recovery from draw solution with low energy consumption [5]. In order to meet these requirements, various attempts have been made in developing new draw solutes, such as inorganic salts, volatile solutes,

organic solutes, polyelectrolytes, hydrogels, aerogels, light-responsive materials, solvents with switchable polarity, and so on [6–14]. These substances could be dissolved or dispersed in water solutions to generate osmotic pressure and be recovered by various methods such as chemical precipitation, thermal decomposition/evaporation, membrane filtration, reverse osmosis, etc. [6,7,15]. However, the application of these solutes was also limited by their low osmotic pressure, high energy consumption for separation from solutions, generation of toxic by-products, or their unrecyclable properties, therefore, which makes the forward osmosis process uneconomic [15–17].

Unlike other solutes, magnetic nanoparticles are considered to be good draw solutes for forward osmotic process [18–20], to be widely used in medicine, biology, and other fields [21–25]. Magnetic nanomaterials can be easily separated from draw solutions by external magnetic fields, and require no chemical reaction or high energy consumption. Therefore, the cost of forward osmosis could be greatly reduced by repeated use of these magnetic solutes. Previous studies have investigated the application of magnetic nanoparticles which were functionalized with natural macromolecules (such as polysaccharide molecule dextran), stimulus responsive (such as PAA-PNIPAM and PSSS-PNIPAM) or polymers

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(such as PAA and TREG) in the treatment of different concentrations of simulated saline water [26].

However, magnetic nanoparticles tend to aggregate in aqueous solutions, which would greatly reduce the osmotic pressure and thereby limit their utility as FO solutes [19]. Therefore, in order to increase the stability in water, the magnetic nanoparticles need to be further modified, which was usually carried out by loading hydrophilic functional groups as shell structures on the surface of the nanoparticles, and the modified magnetic nanoparticles could exhibit enhanced osmotic pressure and higher FO water flux [27–30]. The type of solute and its functional groups affected the efficiency of FO greatly, besides inorganic and organic draw solutes, functional nanoparticles have been given more and more attentions by researchers in recent years. When polyethylene glycol dicarboxylic acid (PEG-(COOH)₂) hydrophilic group was loaded on magnetic nanoparticles, the size of the particles increased, the van der Waals force between the draw solutes and the solvent was also enhanced, as well as the hydrophilicity of the solute itself. In the process of FO, the stretched solute was more likely to diffuse to the boundary of the membrane, reducing the external concentration polarization [14]. Several researchers have proved the feasibility of loading hydrophilic groups on magnetic nanoparticles for using as FO solutes [28]. But there are still some defects in these materials, such as unsatisfactory recovery rate, release of loaded agents, decrease of stability, etc., since the single modification in existing studies may be unstable or ineffective in a complex environment. For example, dehydroascorbic acid-coated Fe₃O₄ nanoparticles were reported as draw solutes, but the two adjacent enol-type hydroxyl groups in the molecule were easily dissociated to release H⁺ in water [28]. Therefore, choosing a suitable draw solute helps to increase the water flux, improve the efficiency of purifying salt water, and is conducive to solving the problem of concentration polarization.

In this study, the novel magnetic-nuclear-hydrophilic shelled magnetic nanoparticles Fe₃O₄@SiO₂@PEG-(COOH)₂ were synthesized to be used as FO draw solute. Firstly, siloxane was loaded on the surface of Fe₃O₄ nanoparticles and then the organic polymer PEG-(COOH)₂ was introduced to the modified magnetic nanoparticles in order to improve the osmotic pressure as FO solutes. Besides the characterization of the synthesized nanoparticles was illustrated and application as FO solutes was investigated under various experimental conditions. Finally, the recovery and reuse performance was tested in water treatment.

2. Material and Methods

2.1. Chemicals

Iron acetylacetonate, oleic acid, and oleylamine in this study were provided by Beijing Chemicals Co. Ltd., China. Benzyl ether, 1,2-hexadecanediol, anhydrous ethanol and tetraethyl orthosilicate (TEOs) were purchased from Xilong Scientific Co. Ltd., China. Fe₃O₄ nanoparticles were obtained from Chaowei Nano Scientific Co. Ltd., China. Triethylene glycol, NaCl, NH₃·H₂O, and ethyl acetate were provided by Macklin, China. Polyethylene glycol dicarboxylic acid (PEG-(COOH)₂, *M_n* = 600) was obtained from Aladdin Co. Ltd., China. Forward osmosis membrane (AQP membrane) was purchased from Aquaporin Company, Denmark. All of the water utilized in the experiment was deionized water stored at room temperature.

2.2. Preparation of Fe₃O₄ nanoparticles

Magnetic nanoparticles were prepared by coordination exchange reaction as suggested in literature [31]. Firstly, 5 g of 1,2-hexadecanediol and 1.5 g of iron acetylacetonate were dis-

solved in a mixture of 5 ml oleylamine and 5 ml oleic acid in a 250 ml three-neck flask. Then, the solution was heated to 200 °C, and was uniformly stirred (IKA RW20, Germany) under a nitrogen atmosphere for 2 h. After that, the solution was subjected to condensation reflux at 300 °C for 1 h, and then cooled to room temperature. The obtained suspension was centrifuged at 12,000 r·min⁻¹ with a high-speed centrifuger (Xiangyi H1650-W, China) and the pellets were washed six times with deionized water. Magnetic separation was used to isolate magnetic Fe₃O₄ nanoparticles, which were dried in vacuum oven (Yiheng DHP-9602, China) at 50 °C for further use.

2.3. Preparation of Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂@PEG-(COOH)₂ nanoparticles

Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂@PEG-(COOH)₂ nanoparticles were synthesized by one-pot method [32]. The reaction was conducted in a 250 ml flask, and 0.3 g of Fe₃O₄ nanoparticles were dispersed in 50 ml ethanol–water solution (ethanol–water 5:1, v/v), and then ultrasonically dispersed for 10 min (Kunshan Ultrasonic KQ-5200, China). Subsequently, 10 ml aqueous ammonia and 30 ml TEOs were successively added into the dispersion, and the reaction continuously went on at 45–50 °C for 3 h. Then, the reaction was stopped by adding 5 ml ethanol, and the obtained Fe₃O₄@SiO₂ nanoparticles were thoroughly washed with anhydrous ethanol and deionized water and dried in vacuum at 50 °C for further use.

The ligand exchange reaction was illustrated in Fig. 1, showing how to synthesize Fe₃O₄@SiO₂@PEG-(COOH)₂ nanoparticles [27]. A portion of 2 g of the synthesized Fe₃O₄@SiO₂, 100 ml triethylene glycol, and 0.75 g of PEG-(COOH)₂ were mixed in a 250 ml flask. The solution was purged with nitrogen for 30 min to remove the dissolved oxygen, and then was heated to 100 °C in water bath and vigorously stirred for 30 min to initiate the reaction. Next, the mixture was cooled to room temperature and 100 ml ethyl acetate was added. The solution was stirred for 5 min, then the reaction was completed. After centrifugation, the obtained Fe₃O₄@SiO₂@PEG-(COOH)₂ nanoparticles were washed three times with water/ethyl acetate solution (1:3, v/v) and dried in vacuum for use.

2.4. Nanoparticles characterization

Fourier transform infrared spectroscopy (FTIR) spectra were collected for all nanoparticles using an FTIR spectrometer (6700,

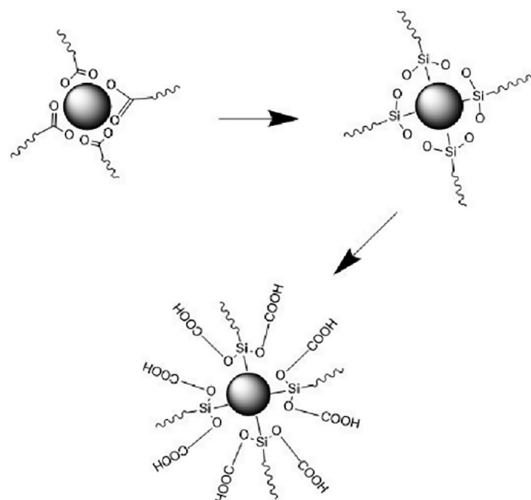


Fig. 1. Schematic illustration of ligand exchange reaction for the synthesis of Fe₃O₄@SiO₂@PEG-(COOH)₂ nanoparticles.

Nicolet, USA). Spectra were recorded from 349 to 4000 cm^{-1} , and all samples were blended with KBr and pressed into tablets before measurement. X-ray powder diffraction (XRD) patterns of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ were prepared using an X-ray diffractometer (D/Max2500VB2+/PC, Rigaku, Japan) equipped with Cu radiation at a wavelength of 0.154 nm. Measurements were obtained at room temperature with a scanning rate of 0.02 ($^\circ$) $\cdot\text{s}^{-1}$ and a diffraction angle range of 5 $^\circ$ –90 $^\circ$ (2θ range). Transmission electron microscope (TEM) images of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ were obtained using a Hitachi TEM system (HT7700, Hitachi, Japan). The test was kept at room temperature and the voltage was set at 100.0 kV. The magnetic behavior of the particles was evaluated through a vibrating sample magnetometer (VSM, MPMS XL-7, Quantum Design, USA) from –30 to 30 kOe at room temperature. The saturation magnetization values were normalized to the mass of nanoparticles to yield the specific magnetization, moment/mass ($\text{emu}\cdot\text{g}^{-1}$). The mass loss of MNPs was characterized by thermogravimetric analysis (TGA) with a thermogravimetric analyzer (TGA/DSC 3+, Mettler Toledo, Switzerland) during thermal oxidation. The measurement was conducted under N_2 from 40 to 830 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C}\cdot\text{min}^{-1}$.

2.5. FO experiment

A lab-scale FO experimental device was established to test the performance of the synthesized MNPs as FO solutes, and a commercial Aquaporin FO membrane was employed and NaCl solution was used as feeding solution. The cross-flow permeation cell was designed as a frame structure with rectangular channels on both sides of the membrane (10.9 cm length, 5.6 cm width, and 2.1 cm height). During the FO experiment, different surface flow rates were tested and the water temperature was maintained at (22 ± 0.5) $^\circ\text{C}$. Water permeation flux ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$), abbreviated as LMH) was calculated using the following Eq. (1).

$$Q = \frac{\Delta V}{t \cdot S} \quad (1)$$

Where, Q is the water flux ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$), ΔV is the filtered volume of the feeding solution (L), t is the time (h), S is the effective membrane area (m^2).

2.6. Recycling of MNPs from draw solution

After the FO experiment, the draw solution was circulated to a beaker, and the magnetic field was imposed on the solution to recover the solutes. After dried in vacuum, the weights of the recycled solutes were determined and the recovery rate was calculated. Then, repeated use was conducted to examine the performance in FO process.

3. Results and Discussion

3.1. Characterization of the MNPs

The crystal structure of the Fe_3O_4 nanoparticles and SiO_2 modified Fe_3O_4 nanoparticles was confirmed by XRD, as shown in Fig. 2 (a). The seven diffraction peaks corresponded to the (110), (211), (202), (220), (024), (301), and (224) planes of Fe_3O_4 , respectively. The average particle size of Fe_3O_4 is about 100 nm (Fig. 2(c)). In this study, the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell structure was formed by loading SiO_2 on Fe_3O_4 nanoparticles. The magnetic core was Fe_3O_4 , while the shell was SiO_2 . The loading amount of SiO_2 was regulated by the concentration of the added TEOs. It could be seen that $\text{Fe}_3\text{O}_4@\text{SiO}_2$ exhibited a broad diffraction peak near $2\theta = 23^\circ$, which denoted the amorphous SiO_2 , indicating that SiO_2 was successfully wrapped on the magnetic material. Moreover, the peak height of

SiO_2 increased with the increasing amount of SiO_2 , which also reduced the peak height of Fe_3O_4 around $2\theta = 35^\circ$. The reason was that, when more SiO_2 was loaded onto the surface of Fe_3O_4 nanoparticles, the thickness of shell increased correspondingly, so did the signal intensity of SiO_2 , however, the diffraction signal of Fe_3O_4 was decreased.

Fig. 2(b) and (c) showed the TEM images of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles, respectively. It could be seen that pure Fe_3O_4 nanoparticles were uniform and distributed tightly, but tended to aggregate. While, the silica-loaded Fe_3O_4 was surrounded by a silica layer on the outer contour of the sphere, therefore the shells are not prone to aggregate and the nanoparticles were well dispersed (Fig. 2(c)). The FTIR spectrum of the synthesized core-shell MNPs was shown in Fig. 2(d). The infrared absorption bands of Fe_3O_4 denoted the presence of C–H, C=C, and $-\text{CH}_2-$ bonds, which mainly came from the residual organics that used in the synthesis of Fe_3O_4 nanoparticles. After the modification of SiO_2 and PEG-(COOH) $_2$, the additional functional groups could be clearly observed in the FTIR spectra, i.e., the Si–O and Si–O and Si–O–Fe bonds was for $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and the C=O and O–H bonds for the loaded PEG-(COOH) $_2$. It should be pointed out that the Si–O–Fe bond illustrated that the combination between Fe_3O_4 and SiO_2 was relatively stable, which was favor of the steadiness of the MNPs as FO draw solutes. The FTIR spectroscopy indicated that the surface modification was successful and the hydrophilic silica and carboxyl groups have been loaded onto the Fe_3O_4 nanoparticles. Fig. 2(e) showed the VSM analysis of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PEG}-(\text{COOH})_2$ and TGA analysis of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PEG}-(\text{COOH})_2$. The VSM curves appeared nonlinear and reversible characteristics with no hysteresis (zero coercivity and no remanence), exhibiting superparamagnetic behavior. The reduction in saturation magnetization of the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PEG}-(\text{COOH})_2$ compared to the Fe_3O_4 nanoparticles could be due to the presence of coated materials on the surface of Fe_3O_4 nanoparticles, which reduced the magnetic attraction between particles. Moreover, Fig. 2(e) also showed the TGA thermogram of the modified $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PEG}-(\text{COOH})_2$, the first mass loss in the temperature range 40–200 $^\circ\text{C}$ was due to the release of both physisorbed and chemisorbed water on the surface of the polymer shell. In the second phase of mass loss at 200–800 $^\circ\text{C}$, the organic compounds of nanoparticles were decomposed, and the mass loss after 200 $^\circ\text{C}$ might be due to the loss of structure water within amorphous SiO_2 . The remaining part attributed to the nano- Fe_3O_4 and SiO_2 layers was about 90.62%, which proved that the prepared MNPs had an acceptable percentage of functional groups.

3.2. Contact angle

In order to quantify the hydrophobicity of the material, the contact angle meter (JC2000C1, Testo, Germany) was used to measure the contact angle. The sample was prepared by infrared tablet press. After the tablet was successfully pressed, it was placed on a horizontal workbench, and the liquid drops were dropped onto the sample surface using a microsyringe and a camera was used to determine the contact angles between the material and the drops. The contact angle of the Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PEG}-(\text{COOH})_2$ nanoparticles was measured to evaluate their hydrophilicity, and the results were shown in Fig. 3. The contact angle of Fe_3O_4 was about 90 $^\circ$, while the contact angle of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PEG}-(\text{COOH})_2$ was 50 $^\circ$ and 20 $^\circ$, respectively. Therefore, it could be concluded that the hydrophilicity of the $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PEG}-(\text{COOH})_2$ nanoparticles was higher than that of $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and much higher than that of Fe_3O_4 nanoparticles, indicating that the addition of PEG-(COOH) $_2$ has a decisive influence on the hydrophilicity, followed by the addition of SiO_2 . The hydrophilicity was positively related to the osmotic pressure [1],

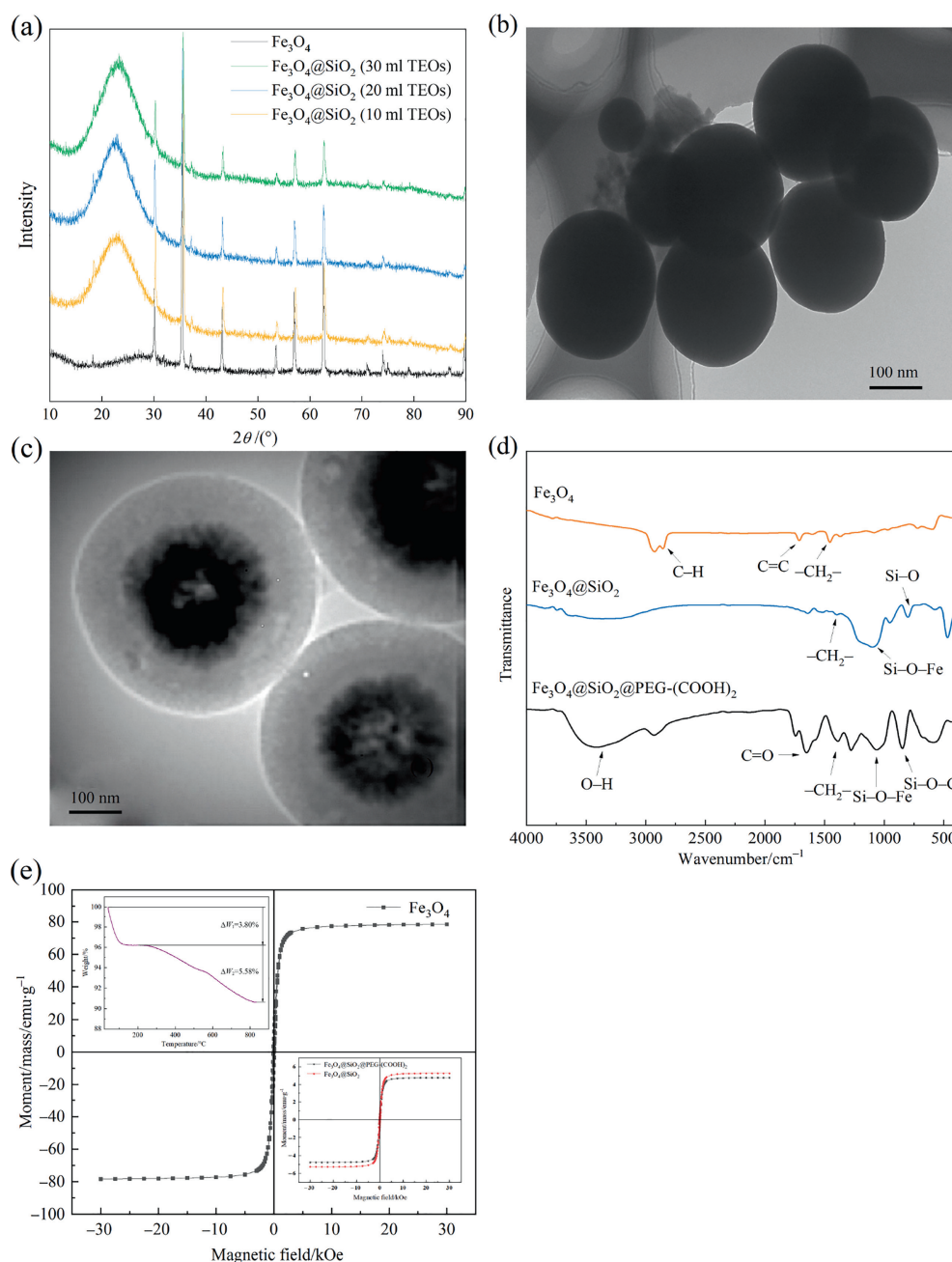


Fig. 2. Characterization of the synthesized magnetic nanoparticles: (a) XRD patterns of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2$; (b) TEM image of Fe_3O_4 ; (c) TEM image of $\text{Fe}_3\text{O}_4@\text{SiO}_2$; (d) FTIR spectra of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PEG}-(\text{COOH})_2$; (e) VSM analysis of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PEG}-(\text{COOH})_2$ and TGA analysis of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PEG}-(\text{COOH})_2$.

so the results suggested that $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PEG}-(\text{COOH})_2$ may have excellent FO performance, which should be confirmed by the following FO experiment.

3.3. Performance of MNPs as FO draw solutes

3.3.1. Effect of surface flow rate

According to the theory of concentration polarization during membrane filtration process, the higher the surface flow rate, the larger the water flux be achieved [33]. In this study, $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PEG}-(\text{COOH})_2$ were selected as draw solutes, both of which have 30% TEOS added in the synthesis reaction, to conduct FO experiment under different surface flow rates, and the results were shown in Fig. 4. Fig. 4 showed that the water flux generally increased with the increasing of surface flow rate. This is because,

with the increased of the water flow velocity on the membrane surface, the concentration polarization near the membrane decreases, which makes the water flux increase accordingly [33]. Moreover, it could also be clearly seen that, under the same flow rate, the water flux of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PEG}-(\text{COOH})_2$ nanoparticles as solute was much higher than that of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ as solute. Actually, the results indicated that the water flux $\text{Fe}_3\text{O}_4@\text{SiO}_2$ decreased to near zero after 70 min, while the number for $\text{PEG}-(\text{COOH})_2$ loaded $\text{Fe}_3\text{O}_4@\text{SiO}_2$ remained around $4 \text{ m}^3\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. It could be attributed to that the introduction of carboxyl groups greatly enhanced the hydrophilicity of the $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PEG}-(\text{COOH})_2$ nanoparticles, hence the solute exhibited good dispersity and relatively higher osmotic pressure in aqueous solutions. On the contrary, the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles cannot be dispersed stably enough and thus the draw performance was not limited.

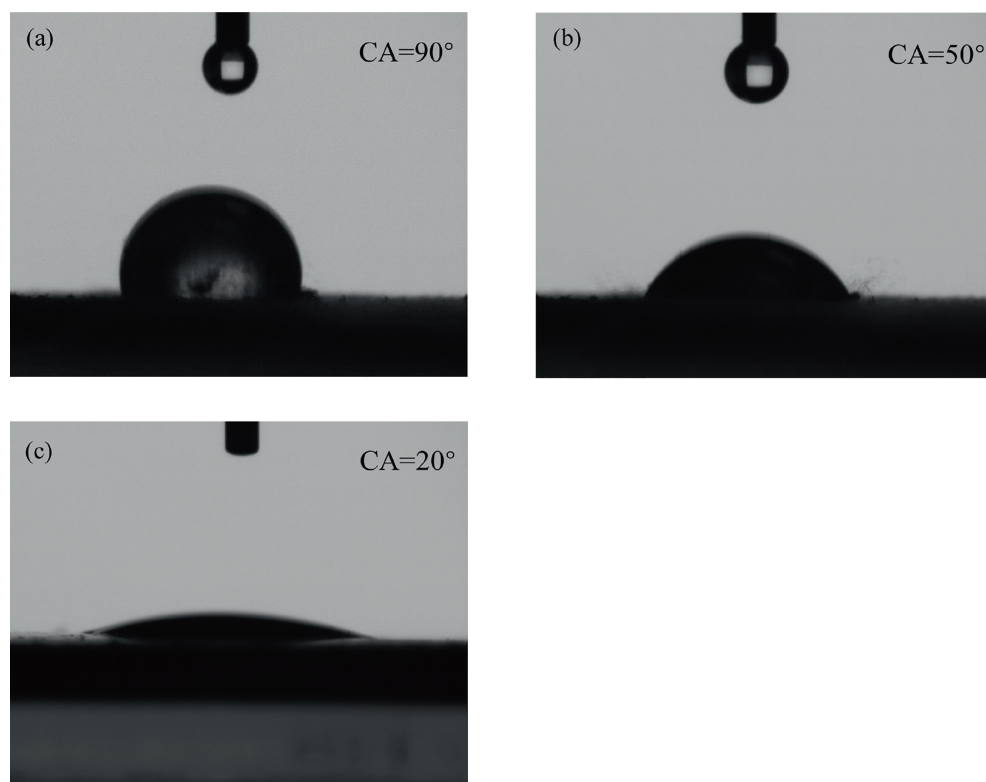


Fig. 3. Contact angles (CA) of (a) Fe_3O_4 , (b) $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and (c) $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PEG}-(\text{COOH})_2$. The concentration of the added TEOs was 30% during the loading of SiO_2 .

The results also showed that the water flux fluctuated along the experiment time. This is because the FO is a dynamic process, and the concentration polarization naturally occurs on the surface of the membrane. However, the surface disturbance also offsets part of the effect of concentration polarization [3]. Therefore, the osmotic pressure was dynamic, followed by a varying water flux. Overall, in the first 10 min, the osmotic pressure was relatively large and the water flux remained high in a short time, but after reaching a balance, it began to decrease to a steady level.

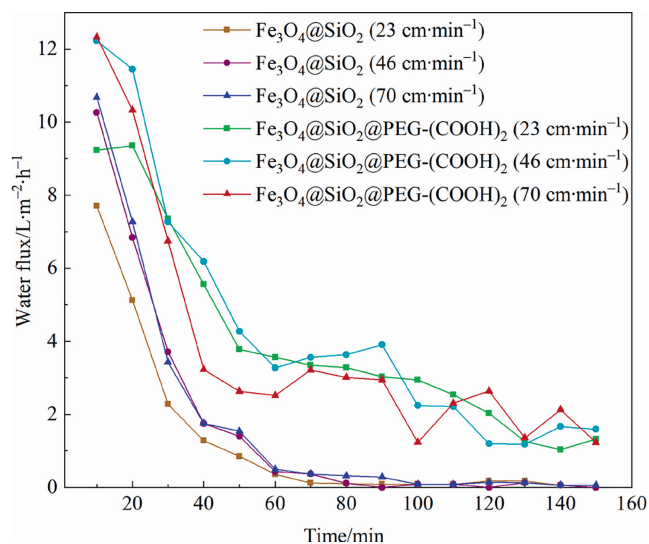


Fig. 4. FO performances of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{PEG}-(\text{COOH})_2$ nanoparticles at different surface flowrate. Conditions: feeding solution: $40 \text{ mg}\cdot\text{L}^{-1}$ NaCl solution; draw solution: $8 \text{ g}\cdot\text{L}^{-1}$ MNPs; initial volume of both solutions: 250 ml; pH = 7.

3.3.2. Effect of SiO_2 loading amount

During the synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2$, the SiO_2 loading amount as well as the size of the nanoparticles were controlled by adding different concentrations of TEOs. Since the loaded SiO_2 are critical to the dispersity and hydrophilicity of the nanoparticles, it is important to illustrate the influence of SiO_2 loading amount on the FO performance. The experimental results were shown in Fig. 5.

Fig. 5(a) illustrated that the SiO_2 shell played an important role in the FO process, and the water flux increased significantly after the modification of Fe_3O_4 by SiO_2 . In fact, SiO_2 plays a positive role in preventing the redox reaction of Fe_3O_4 , and SiO_2 itself has no demagnetization effect. In addition, SiO_2 is also hydrophilic and has active sites for surface doping, providing a basis for further modification [27,34]. This study introduced oleic acid into the synthesis of Fe_3O_4 nanoparticles, which makes them hydrophilic and well dispersed in water. In ideal status, all Fe_3O_4 nanoparticles could be uniformly dispersed in water, however, in actual situation, Fe_3O_4 nanoparticles are not stable and easy to agglomerate, thus not all Fe_3O_4 are involved in the FO process. Therefore, the actual water flux will be much lower than the ideal value.

The results in Fig. 5(a) also showed that the TEOs dosage affected the water flux significantly. For example, when the TEOs increased from 13% to 30%, the initial water flux increased from 9 to $11 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, and the downtrend of water flux became slower during the experimental period. It could be concluded that the thicker the SiO_2 shell that is encapsulated on the surface of the nano Fe_3O_4 , the better the dispersity of the nanoparticles, and the higher water flux that would be obtained. Subsequently, after further modification of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ with $\text{PEG}-(\text{COOH})_2$, a higher water flux was achieved and the decline rate of water flux also slowed down. It should be due to the fact that the shell of $\text{PEG}-(\text{COOH})_2$ is rich in carboxyl groups, which makes the dispersion of the magnetic nanomaterials increased and the hydrophilicity also improved [18]. The results indicated that the nanoparticles

modified by PEG-(COOH)₂ had better FO performance in either the initial water flux or the maximum water flux.

3.3.3. Effect of feeding concentration

In the FO experiment, the influence of the concentration of raw solution on water flux was studied, using Fe₃O₄, Fe₃O₄@SiO₂, and Fe₃O₄@SiO₂@PEG-(COOH)₂ as draw solution, respectively. The feeding solution was 40, 80, and 120 mg·L⁻¹ NaCl solution, and the results were shown in Fig. 6.

It could be seen that, for all draw solutes, the maximum water flux shows a decreasing trend with the increase of the concentration of the raw solution. This result was in accordance with the principle of FO, which utilized the osmotic pressure difference between two sides of the aquaporin membrane as driving force to drive the water flow from the lower osmotic pressure side to the higher side. Therefore, the greater osmotic pressure difference guaranteed a higher water flux. According to this principle, another method is to enhance the hydrophilicity of the material so as to

increase the osmotic pressure difference across the membrane. That is the main purpose to modify the Fe₃O₄@SiO₂ nanoparticles with PEG-(COOH)₂.

3.4. Recovery and reuse

In previous research, polyelectrolytes and inorganic salts are widely used as draw solutes in the FO process to generate large osmotic pressure difference across the membrane in order to obtain high water flux. Traditionally, these solutes were recovered through evaporation or reverse osmosis (RO) and simultaneously recycled treated water. However, these processes consumed so much energy that the overall economical efficiency was not ideally better than RO or membrane distillation or other traditional processes [1,15]. Therefore, the employment of magnetic materials as draw solutes was taken for granted, because they could be recovered by the low-energy-consuming magnetic field.

In this study, the recovery and reuse of the synthesized MNPs were investigated to the application potential on FO process. The results in Table 1 indicated that Fe₃O₄ nanoparticles had the best recovery rate, and more than 90% of the material could be recovery by magnetic field. The loading of SiO₂ negatively affected the MNPs' recovery rate, which decreased gradually with the increasing of loading amount of SiO₂. As shown in the table, Fe₃O₄@SiO₂@PEG-(COOH)₂ with 30% TEOS added, which held the highest water flux, had a lowest recovery rate, it could also be seen that with the introduction of modification of PEG-(COOH)₂, the overall magnetic properties of nanoparticles were weakened, which led to the decrease of recovery rate, because these nanoparticles had the relatively lowest Fe₃O₄ composition. So, it could be deduced that the magnetic property of the draw solutes was of great importance, and thus the strong magnetic field was necessary to recover the Fe₃O₄@SiO₂@PEG-(COOH)₂ nanoparticles as more as possible.

The experimental solutes were recovered through magnetic field and dried in vacuum, and FO performance of the recovered solutes was shown in Fig. 7. The results indicated that, after 5 times' reuse, the performance of Fe₃O₄@SiO₂ was inevitably affected and the initial water flux decreased from 10.9 to 7.1 L·m⁻²·h⁻¹ (Fig. 7(a)). For Fe₃O₄@SiO₂@PEG-(COOH)₂, the value

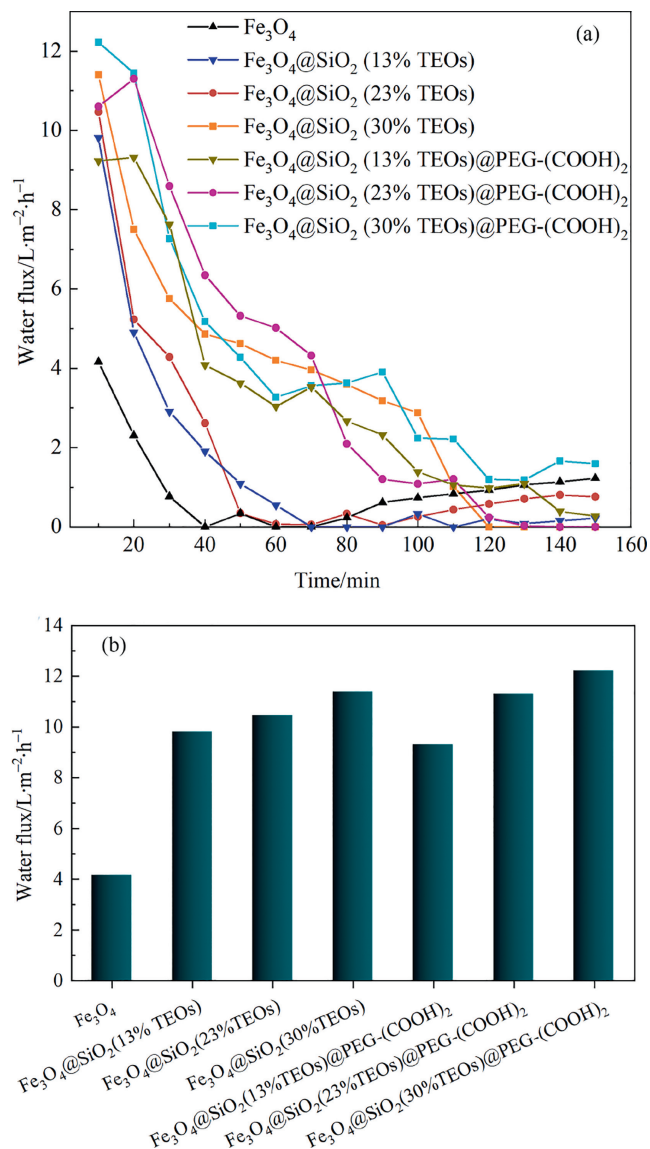


Fig. 5. Effects of SiO₂ loading amount on FO performance: (a) variation of FO water flux along experiment time; (b) the maximum water flux with different draw solutes. Conditions: feeding solution: 40 mg·L⁻¹ NaCl solution; draw solution: 8 g·L⁻¹ MNPs; initial volume of both solutions: 250 ml; surface flow rate: 46 cm·min⁻¹; pH = 7.

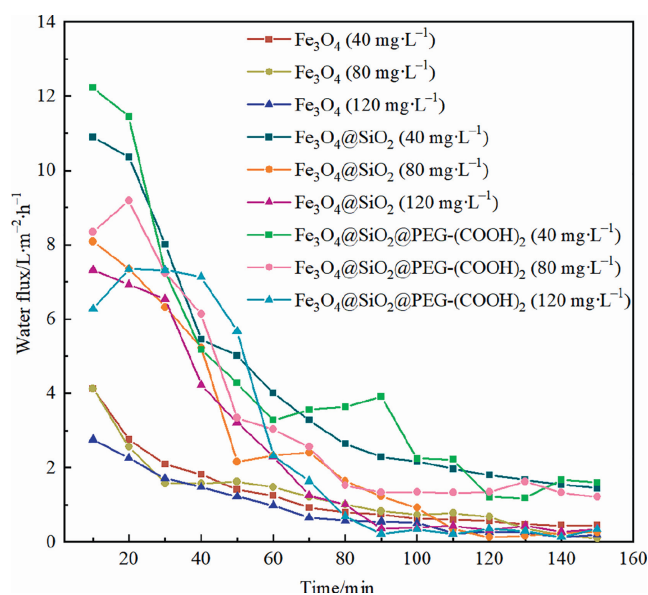


Fig. 6. Effects of the concentration of feeding solutions on FO performance. Conditions: feeding solution: 40 mg·L⁻¹ NaCl solution; draw solution: 8 g·L⁻¹ MNPs; initial volume of both solutions: 250 ml; surface flow rate: 46 cm·min⁻¹; pH = 7.

Table 1
Recovery rate of magnetic nanoparticles from FO draw solution by magnetic field

Material	Recovery rate/%			Average/%
	Test 1	Test 2	Test 3	
Fe ₃ O ₄	96.1	92.6	93.7	94.2
Fe ₃ O ₄ @SiO ₂ (13% TEOs)	89.7	88.1	88.7	88.8
Fe ₃ O ₄ @SiO ₂ (23% TEOs)	88.3	87.1	84.4	86.6
Fe ₃ O ₄ @SiO ₂ (30% TEOs)	83.1	84.0	84.7	83.9
Fe ₃ O ₄ @SiO ₂ (13% TEOs)@PEG-(COOH) ₂	71.8	78.2	75.6	75.2
Fe ₃ O ₄ @SiO ₂ (23% TEOs)@PEG-(COOH) ₂	71.2	72.3	71.6	71.7
Fe ₃ O ₄ @SiO ₂ (30% TEOs)@PEG-(COOH) ₂	69.0	68.2	64.9	67.4

decreased from 12.2 to 10.4 L·m⁻²·h⁻¹ (Fig. 7(b)). The variation trend of the water flux along experiment time was consistent for each reused cycle. This demonstrated that the synthesized nanoparticles could be effectively recovered and be stored under dry conditions, which could be due to the hydrophilic group of silicon oxide in the outer shell. Previous studies have proved that magnetic nanoparticles as FO draw solutes could facilitate their

separation from the draw solution, however, due to the loss of hydrophilicity on the surface, magnetic nanomaterials tended to form aggregates during separation procedures [27]. The tri-layer magnetic nanoparticle, suggested in this study, is strongly bound to the hydrophilic stabilizer through ligand exchange reaction, and therefore the magnetic core-hydrophilic shell structure was formed in the Fe₃O₄@SiO₂@PEG-(COOH)₂ particles.

The experimental results indicated that this novel magnetic nanoparticle had great potential to be an effective FO draw solute.

4. Conclusions

In this study, the novel magnetic nuclear-hydrophilic shell nanoparticles as FO solutes were synthesized by ligand exchange reaction, in which the hydrophilic carboxylic acid and siloxane groups were introduced to nano-Fe₃O₄ to prevent the aggregation of the magnetic nanoparticles. The results indicated that magnetic nanoparticles possessed suitable hydrophilicity, size, magnetism and osmotic pressure, which were be used as FO draw solute. Compared with traditional FO solutes, the synthesized MNPs are superior in the convenience for recycling, and the Fe₃O₄@SiO₂@PEG-(COOH)₂ nanoparticles performed the best in the FO experiment because of the presence of a large amount of carboxyl groups. In addition, the loading of SiO₂ is critical to the dispersity and hydrophilicity of the nanoparticles. However, the modification with covalent surface hydrophilic agents inevitable weakened the magnetic properties of the nanoparticles, which was reflected by the decrease of recovery rate, but this effect could be compensated by exerting an enhanced magnetic field. Even though, the Fe₃O₄@SiO₂@PEG-(COOH)₂ nanoparticles were good FO draw solutes and could be easily recovered from water.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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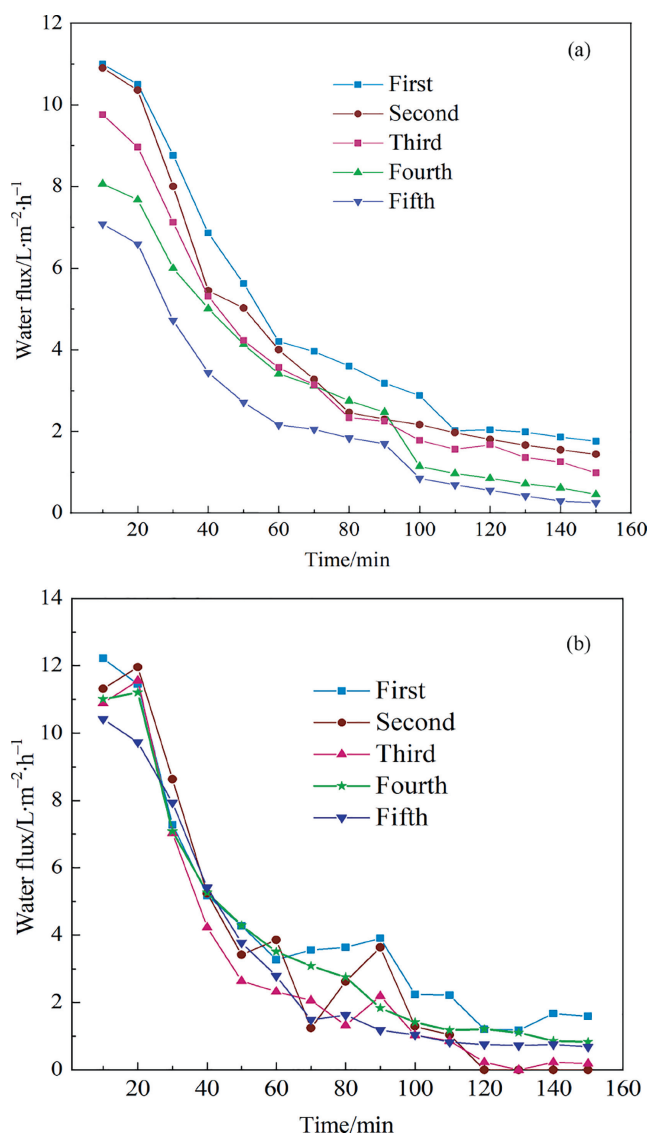


Fig. 7. Water fluxes of recovered MNPs as FO draw solutes at each reused cycle: (a) Fe₃O₄@SiO₂, (b) Fe₃O₄@SiO₂@PEG-(COOH)₂. Conditions: MNPs prepared with 30% TEOs added.

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