Use of synthesized hydrophilic magnetic nanoparticles (HMNPs) in forward osmosis for water reuse
Tripti Mishra, Sudipta Ramola, Anil Kumar Shankhwar and R. K. Srivastava

ABSTRACT
Forward osmosis (FO) is attracting worldwide attention as an emerging technology in the fields of power generation, water reuse, desalination, pharmaceuticals and food processing. Still, the critical challenge of finding a suitable draw solute for FO persists. Therefore the current research focuses on synthesizing hydrophilic magnetic nanoparticles (HMNPs) and systematically investigating their potential as draw solutes. HMNPs were synthesized using functional groups polyethylene glycol (PEG 400) and polyacrylic acid (PAA). These functional groups under different ratios with a metal precursor react by one-pot polyol and thermal decomposition methods respectively to give different diameter HMNPs. In addition the effect of different sizes of synthesized HMNPs was investigated for their recovery under an external magnetic field and reusability in FO performance. The physical properties and chemical compositions of the resultant MNPs are fully characterized. Transmission electron microscopy (TEM) analyses show the characteristics as spherical morphology with a narrow size distribution, and a mean size from 9 to 32.5 nm for PEG and 8 to 30 nm for PAA coated HMNPs depending on the ratio of the functional group and metal precursor. The PEG and PAA layer on the MNPs is confirmed by Fourier transform infrared (FTIR) analysis, and thermogravimetric analysis demonstrates a hydrophilic surface composition. The PEG and PAA coated HMNPs generate high osmotic pressures and exhibit good dispersibility in aqueous solutions. Water fluxes of >13 L m⁻² h⁻¹ are achieved across Hydration Technologies Inc. flat sheet membranes at a concentration of 0.05 M of HMNPs using deionized water as the feed solution. The MNPs can be easily recaptured from draw solutions by applying an external magnetic field and recycling them back as draw solute in the FO process. The MNPs remain active after nine runs of recycling but with a total water flux decrease of 5% in PEG and 3% with each successive recycling due to slight aggregation, and reduced surface to volume ratio is observed. Results of the present study have demonstrated that PEG and PAA coated HMNPs can viewed as promising and potential draw solutes in the FO process.

Key words | forward osmosis, hydrophilic magnetic nanoparticle, water reuse

INTRODUCTION
Freshwater shortage is gradually increasing and has attracted the attention of scientists and social activists all round the globe (Mishra et al. 2015). This serious worldwide problem is expected to be made worse by climate change and expanding industrial and agricultural demand for water (Radjenovic et al. 2008; Kim et al. 2012). Therefore there is an urgent research demand for clean water reuse to avert potential disaster. Reverse osmosis (RO) is a well-known technology of water treatment, but due to its energy-intensive nature it faces a major disadvantage. Recovery limitations and environmental impact further disfavor its application in water treatment (Drewesa et al. 2005). Therefore, less expense and higher recovery technologies are urgent demands in the field of water treatment and reuse.
Forward osmosis (FO) is an osmosis-driven membrane process with the advantages of high feed-water recovery, brine discharge minimization, and relatively low energy requirement and cost (Cath et al. 2006). FO can be viewed as a potential alternative to the widely used RO. Although FO technology has shown great potential in desalination and water reuse, research is still needed for development of high flux membranes with minimum internal concentration polarization (ICP), and the exploration of easily separable draw solutes, keeping in view a variety of draw solutes that have been developed and tested over the past 30 years (McCutcheon et al. 2005; Cornelissen et al. 2008). As the osmotic pressure of the draw solute (DS) is the driving force in the FO process, it is crucial to select an appropriate concentrated solution prior to any application (Achilli et al. 2010). Sugars or salt remain extensively used as draw solutions that provide high osmotic pressures and create good water fluxes. Despite progress, the application remains limited due to the need for high external energy to separate the draw solute from the water in order to obtain pure potable water. So far only a few draw solutes have been found that are useful for water reuse, such as NH$_3$-CO$_2$ solution and magnetic nanoparticles. NH$_3$-CO$_2$ can be separated by heating at approximately 60°C, using low-grade heat (McCutcheon et al. 2005, 2006; McGinnis & Elimelech 2007).

Recently efforts have been made to overcome these constraints by using hydrophilic magnetic nanoparticles (HMNPs) as draw solutes. It has been reported that magnetic nanoparticles generate high osmotic pressure and can be separated by a magnetic separation process (Ge et al. 2011). These draw solutes are nontoxic, capable of producing very high osmotic pressure, up to 70 atm (for polyacrylic acid MNPs), which is far higher than seawater osmotic pressure of 26 atm (Ling & Chung 2011). HMNPs can be easily captured and separated from the product water by an external applied magnetic field. HMNPs consist of a magnetic core and polymer shell. The magnetic core contains small magnetic nanoparticles and can be separated from mixtures under an external magnetic field. The polymer shell surrounds the magnetic core to prevent particle aggregation and also provides its hydrophilic character to draw water from the feed solution. The MNPs can be easily separated from the dilute draw solution via an external magnetic field. The recovered MNPs can be dispersed in water to reproduce the draw solution and used again. These characteristics favor MNPs as draw solutes in water reuse via FO processes.

In this work, a series of magnetic nanoparticles using polyethylene glycol (PEG 400) and polyacrylic acid (PAA) as surface ligands have been synthesized by the thermal decomposition approach. The PEG 400 and PAA ligand has the characteristics of nontoxicity, good water solubility, and high boiling point. All these advantages make them a competitive candidate in the design of hydrophilic MNPs for FO purposes. These prepared PEG 400 and PAA coated MNPs have proven to satisfy the criteria of being an ideal draw solute and are separable with recyclable characteristics. Systematic performance experiments were carried out through the FO process by using the resultant MNPs as draw solutes.

**MATERIALS AND METHODS**

Two kinds of water soluble magnetic nanoparticles capped with different surface functional groups such as polyethylene glycol and polyacrylic acid were synthesized by the one-pot polyol and thermal decomposition methods respectively. Synthesis of HMNPs was done in two different batches to get different diameter particle sizes.

**Starting materials for magnetic nanoparticle synthesis**

Iron chloride tetrahydrate (FeCl$_2$·4H$_2$O), iron (III) acetylacetonate (Fe(acac)$_3$), PEG 400, triethylene glycol (TEG), and PAA, ethyl acetate (EtOAc), sodium hydroxide (NaOH) and ethyl alcohol. All chemicals were high purity analytical reagent grade, purchased from S.D. Fine Chemical, India. Deionized (DI) water from a Milli-Q (Millipore) system was used in all experiments.

**Method for synthesis of magnetic nanoparticles coated with polyethylene glycol (PEG 400)**

Synthesis of PEG 400 coated HMNPs was done in two different batches according to the procedure given by Abbas et al. (2013). For sample 1a 4.8 g of FeCl$_2$·4H$_2$O was
dissolved in 80 mL of PEG 400 solution under continuous stirring. PEG 400 serves as a high boiling point solvent which controls the nucleation and growth of iron oxide cores from iron chloride salts. PEG also prevents agglomeration of synthesized particles by creating a steric barrier. The pH of the solutions was adjusted to around 10–11 by adding NaOH. An inert atmosphere was created before heating by purging nitrogen for 30 min in the reacting solution. The solution was then gradually heated up to 300 °C and refluxed for 2 h. Then the solution was naturally cooled down to room temperature, and 100 mL of EtOAc was added to precipitate the resultant MNPs. The precipitate obtained was collected using a magnet and was subsequently washed three times with water/EtOAc.

In another set of experiments referred to as sample 1b reaction parameters were modified to synthesize a different size of HMNPs. Modifications were made in the ratio of the reactant and the heating procedure: 2.4 g of FeCl₂·4H₂O was dissolved in 80 mL of PEG, and before refluxing the solution at 300 °C for 2 h the solution was heated at 200 °C for 30 min.

**Method for synthesis of magnetic nanoparticles coated with PAA**

Synthesis of PAA coated HMNPs was done according to the procedure given by Li et al. (2004) and Cai & Wan (2007). In the first batch of PAA coated HMNPs, referred to as sample 2a, 1 g PAA was dissolved in 25 mL TEG under continuous stirring until the PAA was completely dissolved in the TEG. Nitrogen gas was then piped into the solution from a nitrogen cylinder to make the reaction flask oxygen-free. The gas flow was controlled using a standard regulator. The flow was minimized through the reaction flask to reduce the cooling effect of gas on the reaction solution. Fe(acac)₃ (2.0 M) was later introduced into this oxygen-free flask and the mixture was then slowly heated to 190 °C for 30 min and then quickly heated to reflux at 275 °C for 30 min. By removing the heat source, the black homogeneous colloidal suspension was cooled down to room temperature; 30.0 mL EtOAc was added to the reaction solution and then separated via centrifugation. Centrifuging was performed at a rotational speed of 6,000 rpm for 30 min. The black precipitate was again dissolved in DI water and reprecipitated in EtOAc; this procedure was repeated three times to remove any impurities and residuals thoroughly.

In another set of experiments referred as sample 2b a similar synthesis procedure was followed with a few modifications in the amount of the precursor weight; 1.5 g PAA was dissolved in 25 mL triethylene glycol (TEG). This modification in the heating temperature and ratio of the reacting precursor is expected to bring changes in the particle size, particle size-distribution and in the magnetic behavior of the synthesized magnetite nanoparticles.

**Characterization**

The size and morphology of the synthesized nanoparticles were characterized by a transmission electron microscope (TEM) (LEO435VP) with a field emission system operated at 200 kV. The samples were prepared by drying a dispersion of magnetic nanoparticles on amorphous carbon coated copper grids. Fourier transform infrared (FTIR) spectroscopic data were recorded on a thermo Nicolet FT-IR spectrophotometer in the range of 4,000 to 400 cm⁻¹ to determine the functional group on the nanoparticles. Thermogravimetric analysis (TGA) helps in calculating the mass percent of surface ligands attached to the magnetic cores of the nanoparticles. The samples (10 mg) were heated in alumina pans from 50 to 660 °C at a rate of 10 °C per minute to oxidize all the elements attached to the magnetic cores. The model of TGA instrument used was Exstar TG/DTA 6300 and while samples were being heated, air flow was maintained at 200 mL/min.

**Forward osmosis using magnetic nanoparticles as draw solute**

The performance evaluation was carried out in a custom-made glass chamber having two compartments with the dimensions 7.7 cm long, 2.6 cm wide and 0.3 cm deep to hold feed and draw solutions. This design of the FO cell was inspired by McCutcheon et al. (2005). The compartments were separated by an asymmetrical cellulose triacetate (CTA) membrane supplied by Hydration Technology Innovations. The membrane consists of an active layer formed above a support layer. The active layer of the
membrane faces the feed solution and the support layer of the membrane faces the draw solution. In order to obtain higher water flux and reduce strain on the membrane, the feed and draw solutions were circulated in the cell at a velocity of 21.4 cm/s. The change in volume of draw solution with time is calculated as permeation flux:

\[ J_v = \frac{\Delta V}{A \Delta t} \]

where \( \Delta V \) (L) is the volume change of the feed solution over a predetermined time \( \Delta t \) (h) and \( A \) is the effective membrane surface area (m²).

## RESULTS

The TEM image analysis shows that the synthesized PEG coated nanoparticles are uniformly spherical and crystalline shaped with average mean sizes of 32.3 and 9.2 nm in samples 1a and 1b respectively. This change in the particle size may be due to the difference of FeCl₂·H₂O concentration and the reflux heating temperatures in both the samples. The reduced size of sample 1b may also be attributed to PEG concentration which possess a strong reducing character. PEG stabilizes the nanoparticles by forming a monolayer around the nanoparticles and at extra heating temperature improves nucleation in the reaction chamber thus checking the size growth of the nanoparticles. Similarly to PEG coated magnetic nanoparticles, the concentration of PAA in the reaction mixture effectively controls the PAA-MNP size resulting in particles with average diameters of 30 and 8 nm in samples 2a and 2b respectively with no agglomeration. This property may be due to the bonding of carboxylate groups between PAA and magnetite nanocrystal surfaces.

FTIR spectroscopy confirms PEG-(COOH)₂ attachment in samples 1a and 1b (Figure 1(a)). The OH peaks at 3,400 cm⁻¹ and carboxylate peaks at 1,631 and 1,407 cm⁻¹ confirm the COOH group attached to the MNPs (Zhang et al. 2007), the polyether chains of PEG(COOH) are visible at 2,873 cm⁻¹ (C–H asymmetric stretching) and 1,083 cm⁻¹ (CO–C stretching) (Palma et al. 2007) and finally the strong bands at 542 and 400 cm⁻¹ confirm the lattice absorption of iron oxide (Das et al. 2008). In samples 2a and 2b (Figure 1(b)) the characteristic peaks around 1,630 cm⁻¹ are caused by the vibrating mode of the C–O bond; the O in the C–O bond anchors to Fe on the surface of the magnetic nanoparticles. The bands at 2,950–2,900 cm⁻¹ are typical of C–H stretching. A strong absorption band at 1,736 cm⁻¹ is a characteristic of the C–O stretching mode for carboxylate groups. The peaks at 1,459–1,395 and 1,621 cm⁻¹ of symmetric and asymmetric C–O stretching modes of carboxylate groups further confirm a large amount of polyacrylic acid attached on the surface of the magnetic nanoparticles (Cai & Wan 2007, Ge et al. 2007).

Thermogravimetric analysis (TGA) calculates the mass (or weight) of PEG and PAA attached to the surface of the MNPs. TGA is measured as a function of temperature or time under controlled temperature in a controlled atmosphere (Earnest 1988). The TGA curves of both the samples are broadly characterized by three regions for weight loss in the temperature range (Figure 2). The first region is attributed to the loss of water and ethyl alcohol, the second major weight-loss demarcation is due to the degradation of the organic shell and the weight loss thereafter may be ascribed to the reduction of iron oxide after the loss of the surface coating. In the case of sample 1a with less ratio of PEG to the
precursor, the first weight loss corresponded to the evaporation of adsorbed water and ethanol, and this weight loss is due to the decomposition of the surface adsorbed PEG coating from the HMNPs. The amount of weight loss in this case up to this demarcation is about 2.5% only. In the case of sample 1b with a high ratio of PEG to the precursor, the region of weight loss remains the same as in the case of sample 1a due to the evaporation of adsorbed water and ethanol. But, in the second region a higher rate of weight loss was observed up to the refluxing temperature of the PEG, and beyond this temperature the weight loss was gradual up to 550°C. The total weight loss up to this second demarcation was about 19% and 24.5% for samples 1a and 1b respectively (Figure 2(a)). This higher rate of weight loss has been ascribed not only to the presence of the larger amount of PEG on the particle surface but also to the corresponding higher loss of the same when the temperature moves past the refluxing temperature. However, it can be inferred from the variation of this TGA curve that the larger amount of PEG coated on the surface of the nanoparticles could well lead to them being stabilized in the solution.

In the case of PAA MNPs the average 5% loss of weight in the initial phases of heating corresponded to the evaporation of adsorbed water and ethanol. The long chain length of PAA adding considerable weight to the HMNPs is shown by the decomposition of the polymer shell. Losses of 57% up to 560°C in sample 2a and 87% of the particles’ weight at 460°C in sample 2b were noted (Figure 2(b)), and hence finally the mass of HMNPs needed to pull the desired batch size of water. These data show that the synthesis process was effective in developing hydrophilic nanoparticles.

HMNP performance as draw solute in FO process using DI as feed solution

To investigate the effect of the different surface chemistry of magnetic nanoparticles as draw solutes on water flux, the PEG-HMNPs and PAA-HMNPs were tested in the FO system. The feed solution consisted of DI for performance analysis and different concentrations of 0.02, 0.03, 0.04, 0.05 and 0.08 M of HMNPs as draw solute (Table 1) were used in order to predict the potential of the FO system.

Sample 1a showed a water flux of $4.83 \pm 0.18$ (L m$^{-2}$ h$^{-1}$) at the 0.02 M concentration, the flux increasing with the increase in the concentration of draw solute to $6.43 \pm 0.09$, $6.43 \pm 0.09$, $6.43 \pm 0.09$ and $11.16 \pm 0.39$ (L m$^{-2}$ h$^{-1}$) at 0.03 M, 0.04 M, 0.05 M and 0.08 M respectively. There was
Table 1 | Water flux (L m⁻² h⁻¹) at different concentrations (M) of draw solute using DI as feed solution

<table>
<thead>
<tr>
<th>Samples</th>
<th>1a</th>
<th>1b</th>
<th>2a</th>
<th>2b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc (M)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>4.83 ± 0.18</td>
<td>6.77 ± 0.23</td>
<td>4.73 ± 0.27</td>
<td>6.86 ± 0.19</td>
</tr>
<tr>
<td>0.03</td>
<td>6.43 ± 0.09</td>
<td>7.99 ± 0.27</td>
<td>5.80 ± 0.25</td>
<td>7.93 ± 0.28</td>
</tr>
<tr>
<td>0.04</td>
<td>6.43 ± 0.09</td>
<td>8.13 ± 0.13</td>
<td>6.23 ± 0.06</td>
<td>8.12 ± 0.08</td>
</tr>
<tr>
<td>0.05</td>
<td>6.43 ± 0.09</td>
<td>8.78 ± 0.18</td>
<td>7.27 ± 0.11</td>
<td>8.82 ± 0.33</td>
</tr>
<tr>
<td>0.08</td>
<td>11.16 ± 0.39</td>
<td>11.50 ± 0.30</td>
<td>12.70 ± 0.78</td>
<td>13.85 ± 0.83</td>
</tr>
<tr>
<td>P-value</td>
<td>0.001298</td>
<td>0.00162</td>
<td>0.004421</td>
<td>0.007725</td>
</tr>
<tr>
<td>r value</td>
<td>0.989457</td>
<td>0.987771</td>
<td>0.976095</td>
<td>0.931768</td>
</tr>
</tbody>
</table>

a significant positive correlation between the rise in flux and concentration of sample 1a, where \( r = 0.98, P < 0.05 \). Sample 1b showed a water flux of 6.77 ± 0.23 (L m⁻² h⁻¹) at a concentration of 0.02 M and this flux rose to 7.99 ± 0.27, 8.13 ± 0.13, 8.78 ± 0.18 and 11.30 ± 0.30 (L m⁻² h⁻¹) at concentrations of 0.03 M, 0.04 M, 0.05 M and 0.08 M respectively. Sample 1b too had a significant positive correlation between the rise in flux and concentration where \( r = 0.98 \) and \( P < 0.05 \). Sample 2a had a water flux of 4.73 ± 0.27 (L m⁻² h⁻¹) at 0.02 M and the trend line of water flux shows an increment with the rise of draw solute concentration, i.e. with the increment of DS osmotic pressure. The water flux increased from 5.80 ± 0.25 to 6.23 ± 0.06, 7.27 ± 0.11 and 12.70 ± 0.78 (L m⁻² h⁻¹) at draw solute concentrations of 0.05, 0.04, 0.05 and 0.08 M. The flux was significant and positively correlated with the draw solute concentration having an \( r value = 0.98 \) and a \( P-value < 0.05 \). Sample 2b also followed the same trend line as the others; it gave a water flux of 6.86 ± 0.19, 7.95 ± 0.28, 8.12 ± 0.08, 8.82 ± 0.33 and 13.85 ± 0.83 (L m⁻² h⁻¹) at draw solute concentrations of 0.02, 0.03, 0.04, 0.05 and 0.08 M. The results were significant and positively correlated having \( r = 0.93 \) and \( P-value < 0.05 \).

It was observed that even though samples 1a, 1b and samples 2a, 2b had similar polymer coatings of polyethylene glycol and polyacrylic acid respectively around the magnetic core, still sample 1b and sample 2b had a better water flux than sample 1a and sample 2a at the same draw solute concentration. The increment in flux value may be due to the smaller size of samples 1b and 2b with respect to samples 1a and 2a respectively. In accordance with the findings of Ge et al. (2011), the smaller the size of the particle, the larger is the surface area relative to the volume; this produced higher osmotic pressure to extract water from the same volume of feed solution (DI). Moreover Ling & Chung (2011) reported that the highest driving force is achieved by smaller size MNPs, since more magnetic nanoparticles of smaller diameters can be located per unit volume to provide the higher driving force. The use of smaller size MNPs in FO increased draw solute osmotic pressure but had some drawbacks. The magnetic property became weaker as a result of the higher concentration of hydrophilic polymer wrapping the magnetic cores. In addition, the recovery of smaller diameter HMNPs was found unsatisfactory (Ling & Chung 2011).

The flux also increased with the rise of draw solute concentration, which may be due to the increased effective osmotic pressure as the driving force. Although water fluxes usually have logarithmic correlation with pressure (Seppälä & Lampinen 2004; Hancock & Cath 2009), this experiment exhibited correlation between molar concentration and water fluxes that was found to be non-linear. The increase in the water flux was not in proportion with the increase in the draw solution concentration, which could be due to the effect of ICP in the asymmetric FO membrane (Faibish et al. 1998; Elimelech & Bhattacharjee 1998).

The other possible reasons for the nonlinear rise in water flux may be the strong hydrogen bonding between carboxylate groups along polymer chains (PEG and PAA) and hydroxyl groups of the FO membrane surface. As a result, the HMNPs may closely adhere to the membrane surface and possibly partially block the pores to retard the flux enhancement. Ling & Chung (2011) also observed in his study that the viscosity of polyacrylic acid increases with the rise of polymer concentration in the DS, which also plays an important
role in retarding water flux. Thus, all this water transport resistance in the FO system retards any logarithmic enhancement in water flux, as observed in the results.

**Water flux of HMNPs using saline water as feed solute**

In order to utilize magnetic nanoparticles more effectively for water reuse, the synthetic saline water (NaCl) was tested at different concentrations of 0, 5,000, 10,000, 20,000 and 35,000 mg/l as feed solution. The draw solute was kept at concentrations of 0.05 and 0.08 M in samples 1a, 1b, 2a and 2b. (Table 2) In the present experiment, it was observed that the water flux increased at higher molar concentrations of the DS, but at the same time it decreased with an increase in the concentration of feed solution. The correlation between feed concentration and water flux was found to be non-linear. In fact, a logarithmic correlation was observed between FS concentration and the water flux under the effect of the DS. These studies were in accordance with the studies done by Seppälä & Lampinen (2004), which stated that although the water flux increased with the increase in DS concentrations, at same time it was affected by the feed solute concentration. All the samples showed a negative correlation between the water flux and FS concentration in the FO system.

**Recovery and recycling of MNPs**

To fulfill the application of hydrophilic magnetic nanoparticles in the FO system for water desalination, the drawn water and magnetic nanoparticles on the DS side must be easily separated. Since the nanoparticles used in this study were synthesized with magnetic properties, it was found that the magnetic nanoparticles (PEG HMNPs and PAA HMNPs) were readily captured by an applied electromagnet from the DS side leaving behind the pure water. Moreover these nanoparticles captured by the electromagnet were recyclable, hence each kind of magnetic nanoparticle was then recycled and retested in the FO system as draw solutes.

It was observed that the water flux of the regenerated nanoparticle draw solution tested in the FO system decreased with the consecutive number of recycles. The flux dropped possibly due to the high strength of the electromagnets causing slight aggregation of magnetic nanoparticles after each cycle, when they were captured from the draw solution. The change in size due to aggregation of the MNPs is also reported by Ge et al. (2011), who tested PEG 600 found them active still after nine runs of recycling and with a water flux decrease of <5% after each run of the performance test and, by the end of ninth recycle, the water flux decreasing by 21% of the initial value. Although the recycled magnetic nanoparticles were found to be dispersing in water promptly, this confirmed that the hydrophilic surface functional groups of the polymer were still firmly anchored onto the magnetic cores.

**CONCLUSIONS**

HMNPs with high water hydrophilicity and magnetic behavior have been synthesized by the one pot polyol and thermal decomposition methods. The FO performance of these HMNPs as draw solutes is dependent on their particle size
and concentration in the draw solution. The observed high water flux in the present MNP draw solutions is encouraging. Despite the remaining problem of nanoparticle aggregation, the advantages of easy recovery, reusability, and absence of the draw solute leakage problem still make MNPs attractive as draw solutes. Future studies will be focused on (1) the optimization of surface chemistry and diameter selection of magnetic nanoparticles, (2) the investigation of their performance in FO for seawater desalination, and (3) the investigation of their sustainability in FO processes.

REFERENCES


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