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(2015)

Magnetic nanoparticles boosting the osmotic efficiency of a polymeric FO draw agent: Effect of polymer conformation.
Desalination, 373, pp. 79-85.

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<https://doi.org/10.1016/j.desal.2015.07.010>

Magnetic nanoparticles boosting the osmotic efficiency of a polymeric FO draw agent: Effect of polymer conformation

Priyanka Dey^a and Emad L. Izake^{a}*

^a Discipline of Nanotechnology and Molecular Sciences, Faculty of Science and Engineering, Queensland University of Technology, 2 George Street, Brisbane, QLD 4001, Australia.

*Corresponding author:

E-mail address: e.kiriakous@qut.edu.au (E. L. Izake) Tel.: +61 7 3138 2501; Fax: +61 7 3138 1804

Abstract

Poly sodium acrylate (PSA)-coated Magnetic Nanoparticles (PSA-MNPs) were synthesized as smart osmotic draw agent (SMDA) for water desalination by forward osmosis (FO) process. The PSA-coated MNPs demonstrated significantly higher osmotic pressure (~30 fold) as well as high FO water flux (~2-3 fold) when compared to their polymer (polyelectrolyte) counterpart, even at a very low concentration of ~0.13 wt.% in the draw solution. The PSA polymer chain conformation—coiled to extended—demonstrates a significant impact on the availability of the polymer hydrophilic groups in solution which is the driving force to attain higher osmotic pressure and water flux. When an optimum concentration of the polymer was anchored to a NP surface, the polymer chains assume an extended open conformation making the functional hydrophilic groups available to attract water molecules. This in turn boosts the osmotic pressure and FO water flux of the PSA-MNP draw agents. The low concentration of the PSA-MNP osmotic agent and the associated high water flux enhances the cost-effectiveness of our proposed SMDA system. In addition, easier magnetic separation and regeneration of the SMDA also improves its usability making it efficient, cost-effective and environment-friendly.

Keywords: Smart magnetic osmotic draw agent, forward osmosis, cost effective water desalination, magnetic regeneration, Poly sodium acrylate-coated magnetic nanoparticles.

1. Introduction

One of the most crucial challenges in the 21st century is securing cheap potable water supplies for the ever-increasing population growth.[1] It is estimated that more than one-third of the world's population live in water-stressed countries and this may rise to nearly two-thirds by 2025. With the significant climate change and the related frequent drought and unpredictable rainfall events in many parts of the world, the demand for fresh water supplies is now a topical issue on the national and international agenda.[2] This has been the driving force for researchers and industries to come up with more efficient strategies that could lead to the production of freshwater from various sources of available water. Extraction of drinkable freshwater from seawater, brackish groundwater or wastewater is therefore being increasingly practised. Though science and technology have contributed to water desalination processes to some extent, smarter, efficient, cost-effective technologies are indeed required. The two major established technologies include distillation and Reverse Osmosis (RO). While the distillation processes are energy intensive, RO processes suffer from membrane fouling, requirement of higher pressure to assist the process while recovering only 35-50% of freshwater from seawater.[3] Recently, forward osmosis (FO) has been recognised as one of the most promising low energy processes for water desalination and treatment of difficult liquid discharge streams with high water recovery of ~50-70%.[4-9] The drive towards FO is the lower membrane fouling propensity and higher fouling reversibility with respect to RO and the lower energy consumption than distillation.

The FO process uses concentration gradient driven osmotic pressure instead of hydraulic pressure as in reverse osmosis (RO). Therefore, FO requires significantly lower energy when compared with RO.[6, 10-12] In FO process, a concentrated draw solution (DS) that contains an osmotic agent extracts fresh water from saline water using specialized semi-permeable membranes having high salt rejection properties. Since no mechanical force is used to drive the water across the membrane, membrane fouling in FO process is greatly reduced when compared to RO process, thus reducing a major maintenance problem. In addition, FO requires low capital input while producing high quality water.[13] Reviews emphasize the ability of FO in potential applications like irrigation, protein and pharmaceutical concentration, water reuse and desalination. However, it is still facing many challenges. In a recent critical review Shaffer and co-workers[14] discuss the current state of FO technology. They believe that the concept of FO being a low energy process is misleading. Based on thermodynamic calculations, they pointed out that FO system does not reduce energy as there is always an additional minimum energy required for separation of the draw solution and product water. Thus, they comment that FO would be excellent where the applications of RO are limited, namely, with high osmotic pressure feeds, treating potentially high fouling feed and

specific contaminated feeds. Break-throughs on molecular designs of high performance FO membranes and appropriate draw solutions are urgently needed. A lot of work has gone into building efficient membranes where the focus was to minimize the structural parameter of the support (to increase water flux) and maximize the reverse solute flux selectivity of the active layer (for limiting draw solute loss). Some of the industrial leaders in FO membrane technology who are in pre-commercial stages include Hydration Technologies Innovation (HTI), OASYS Water, Modern Water, Porifera, and Fuji Film.

However, the lack of a suitable osmotic agent makes the application of FO desalination for potable water challenging. The ideal draw agent should be non-toxic, stable, inexpensive, limit reverse draw solute flux, and reduce internal concentration polarization (ICP), in addition to, providing high osmotic pressure and being easily regenerable. To obtain freshwater as the product, the separation of osmotic draw agent from diluted draw solution requires an amount of energy that depends on the nature of the osmotic agent. In order to become economically viable when compared to RO, separation and regeneration of the osmotic agent in FO process should be both easy and cost-effective. This can be done by utilizing the waste heat from an industrial process and/or by applying magnetic field.[15, 16] Shaffer and co-workers[14] points out that novel draw solution regeneration technologies can provide gains in energy efficiency with high osmotic pressure feeds which cannot be handled with RO.

Researchers have investigated various materials as osmotic agents to achieve high flux from saline or waste water feed.[3, 9, 17-23] Materials that have found use as osmotic draw agents include gas molecules like ammonia–carbon dioxide, chemical fertilizers, sugar or inorganic salts, organic salts and polyelectrolytes.[9, 24-27] Small molecules benefit from their ability to generate high osmotic pressure at low solution viscosities, as well as, mitigate ICP due to their high diffusivities. There is always a trade-off between the small molecules to limit ICP and the larger ones to limit reverse draw solute flux, when choosing the ideal draw agent. Polymer and nanoparticle based systems have gained importance as they eliminate the possibility of reverse draw solute flux. Polyelectrolytes like PSA (poly sodium acrylate)[22] and PSS (poly sodium 4-styrenesulfonate)[28] have been utilized as the osmotic draw agent, where they reported high osmotic pressure but at a very high draw solute concentration of $\sim 0.5\text{--}0.75\text{ g}\cdot\text{mL}^{-1}$ PSA and $0.24\text{ g}\cdot\text{mL}^{-1}$ PSS (70 kDa) resulting in high viscosity during the FO process. The high chemical concentration also makes the product water unfit for drinking purposes, increasing its separation and production cost. Although the primary requirement of the ideal osmotic agent i.e., high osmotic pressure was demonstrated by most of the above draw agents; poor recovery of freshwater and regeneration of the draw agent has been the major hurdle for commercialization of such agents. To

overcome these problems, magnetic nanoparticles with polymer coatings were proposed as “smart materials” that could provide high osmotic pressure by virtue of the polymer and also allow for facile and cost effective recovery of the osmotic agent.[20, 29] The terminology “smart” have been frequently linked to stimuli-responsiveness like temperature or magnetic-field responsive materials. Polymer hydrogels have been recently demonstrated as thermo-sensitive agents that can be recycled by changing the temperature of the draw solution above the critical point of the polymer.[20, 30-32] However, the osmotic pressure of these materials was not high enough to drive a cost effective FO process.

Recently, polymer-coated iron oxide nanoparticles were proposed as smart magnetic draw agents (SMDA) that can be recycled under the influence of an external magnetic field.[3, 19, 33] SMDAs were used to enhance the treatment of industrial effluents and reduction of environmental waste load.[33] They were also employed for desalination of brackish and sea water streams.[26, 34] Though magnetic osmotic agents have magnetic properties that facilitate their separation with low energy consumption, they generally do not possess high osmotic pressure. But this could be achieved by grafting polymers of high osmolality to MNP surface. Thus we aim to develop SMDAs with a hydrophilic polymer coating on MNP surface that can provide high osmotic pressure and water flux for an efficient FO process. Several polymers feature high hydrophilicity and hence higher osmotic pressure. Among them PSA (or PAA-Na) has been reported as an efficient osmotic draw agent, with high osmotic pressure but low regeneration capability.[30, 32, 33] To leverage from the high osmotic pressure property of PSA and improve its regeneration in FO desalination, our approach was to prepare PSA-coated MNPs (PSA-MNP), where PSA acted as the high hydrophilic polymer contributing to SMDAs high osmotic pressure for FO process and the magnetic iron oxide core being responsible for easy regeneration of the SMDA. Figure 1 depicts the cartoon representation of the proposed PSA-MNP SMDA. Following that, we also carried out comparative study between our tailored SMDA (PSA-MNP) and the PSA polyelectrolyte to gain in-depth understanding of the role of polymer chain conformation on the osmotic properties of the draw agent.

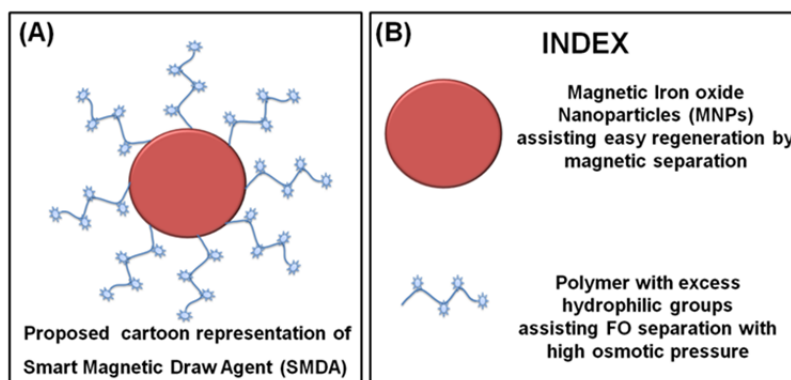


Figure 1. Cartoon representation of the proposed Smart Magnetic Draw Agent (SMDAs).

2. Materials and Methods

2.1 Materials.

Iron (III) acetylacetonate, poly (sodium acrylate) PSA M_w of 2100 Da were bought from Sigma Aldrich and used as received. Triethylene glycol (TEG) was also bought from Sigma Aldrich and used as the solvent.

2.2 Synthesis of PSA-MNPs.

The synthesis of polymer coated MNPs was carried out using one-pot thermal decomposition method,[29] where an organic iron salt act as precursor. The iron (III) acetylacetonate salt $\text{Fe}(\text{acac})_3$ was used as the salt precursor. The polymer used as the ligand was a highly hydrophilic polymer poly (sodium acrylate) PSA. The iron precursor to polymer ligand mole ratio was optimized to 2:1, which provided good polymer coverage as well as the desirable MNP size. 8.4 g of PSA was added to 30 mL of TEG and stirred vigorously. This was followed by the addition of 2.8 g of $\text{Fe}(\text{acac})_3$ with stirring under a stream of N_2 at atmospheric pressure. This mixture was heated to 290 °C and maintained at this temperature for 30 min under reflux. The initial orange-ish mixture turned to a black coloured solution. The final product was precipitated in ethyl acetate, separated by magnetic field and further washed 3 times with ethyl acetate-water mixture (1:1 v/v). The product was then re-dispersed in water and used for characterization and FO studies.[19, 29] The prepared SMDA was characterized by XRD, ATR-FTIR, TEM, TGA, DLS particle size and zeta potential.

2.3 Instruments.

2.3.1 Transmission Electron Microscopy. A JEOL 1400 transmission electron microscope (TEM) at 100 kV was used to study the nanoparticle colloid dispersions. 50 μL of a dilute colloid

was dropped on a 200 mesh holey C-coated copper grid and air-dried. The median sizes were determined using ImageJ software by measuring ~100 individual nanoparticles.

2.3.2. Dynamic Light Scattering (DLS) and zeta potential. DLS measurements were performed using Malvern Zetasizer Nano Series running DTS software and a 4 mW He–Ne laser at 633 nm. Analysis was performed at an angle of 90° and a constant temperature of 25 °C. Dilute NP concentrations were used to ensure that multiple scattering and particle–particle interactions could be considered to be negligible. The zeta potential was measured using a zeta potential cell.

2.3.3. Infrared Spectroscopy. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra with 256 scans and a resolution of 4 cm⁻¹ were obtained on a Nicolet Nexus 5700 FTIR spectrometer equipped with a Nicolet Smart Orbit single bounce containing a diamond ATR accessory (Thermo Electron Corp., Waltham, MA). 25 µL of the colloid was dropped on the ATR diamond and air-dried. The sample spectrum was then collected which was further corrected by a baseline spectra collected after removing the sample with isopropanol.

2.3.4. X-ray Diffraction (XRD). X-Ray diffraction patterns were collected using a Philips X'pert wide angle XRay diffractometer, operating in step scan mode, with Cu Kα radiation (1.54052 Å). Patterns were collected in the range 3 to 90° 2θ with a step size of 0.02° and a rate of 30s per step. Dried powder samples were used for analysis.

2.3.5. Thermogravimetric Analysis (TGA). 1 mL of the colloid was oven-dried at 80°C and a dried powder form of PSA-MNP was obtained. Thermo-gravimetric analysis was carried out on this dried powder sample (5 mg) with a heating rate of 5 °C/min using a Perkin-Elmer TGA 7 thermogravimetric analyzer in a N₂ atmosphere up to 1000 °C. The weight loss % was attributed to the polymer concentration in the PSA-MNPs and thus related to the polymer coverage on the MNPs.

2.4 Forward Osmosis laboratory set-up. The FO water flux against DI water was determined using a laboratory FO set-up, as shown in figure 2. A specialized carbon nanotube FO membrane was obtained from Porifera and utilized in a Sterlitech lab FO unit. The Sterlitech FO unit had an active membrane area of 42 cm² and the Porifera membrane was used with skin side facing the draw solution. The FO unit was set-up using DI water as the Feed solution and poly (sodium acrylate) PSA or the PSA-MNP as the draw solution. Identical flow rates were used for both the feed and draw. Each FO experiment was carried out for a total of 4 h, with the initial 30 min used to equilibrate the system against flow rate fluctuations.

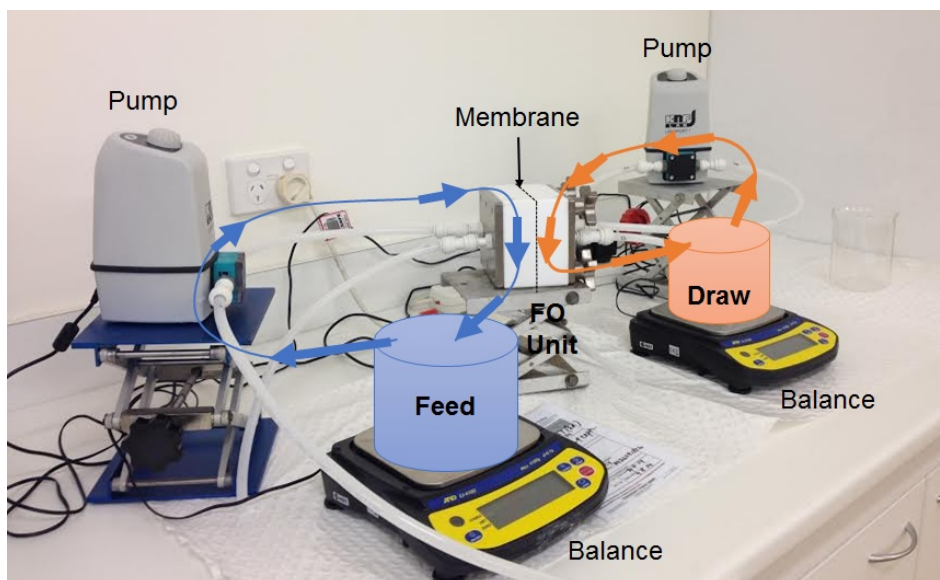


Figure 2. Experimental FO set-up with a Sterlitech laboratory FO unit fitted with a Porifera membrane.

The water flux was obtained experimentally by the difference in weight of draw and feed after regular time intervals. The osmotic pressure was calculated from the experimental FO water flux, using the following equation.

$$\text{Water Flux (LMH)} J_v = A \cdot \pi$$

Where, A = constant, π = osmotic pressure (atm).

3. Results and Discussion

3.1. Synthesis of PSA coated MNP SMDAs (PSA-MNPs).

As the major objective was to achieve high water flux and high osmotic pressure, we choose a low molecular weight (M_w) PSA polymer. It is well established that the osmotic pressure is inversely proportional to the molecular weight. On the other hand, a higher M_w i.e., a longer polymeric chain—which is not fully ionisable—would provide higher number of hydrophilic groups that can ionize improving the osmotic pressure. Previously dendrimers[35] with multiple hydrophilic end groups have been reported to overcome this problem. Zhao and co-workers[35] had observed a decrease in water flux with increase in the dendrimer generation i.e., with increase in number of hydrophilic end groups as well as increase in M_w . They reported the highest water flux of ~31.87 LMH with the lowest dendrimer generation (or lowest M_w) for a very high draw solute concentration of 33.3 wt. %. Thus, we used a PSA with M_w of 2100 Da which is on the lower side

to strike a balance between number of hydrophilic ionisable groups and thus osmotic pressure, as well as, demonstrate a low viscosity under FO process. The reverse draw solute flux and ICP problems were also expected to be lower with the particular PSA chosen. The one-pot synthesis provided an easy and feasible way to anchor the polymer onto the MNP surface as well as control the NP size. Particularly, the $-\text{COOH}$ group of the carboxyl terminated PSA is expected to bind to the iron oxide NP surface,[36] thereby anchoring the COOH -functionalized PSA to the MNPs. In our case, the COOH -PSA served as the ligand influencing the MNP size, polymer functionality on MNP surface as well as hindering MNP aggregation due to the steric stabilization imparted by the polymer ligand. We attempted a NP size in the range of 5-15 nm as it would then provide the optimum blend of magnetic property, dispersion stability and aid in easy magnetic separation. Hence, we optimized the iron salt precursor to polymer molar ratio in the synthesis reaction gaining control over the polymer coverage on the NP surface. A higher polymer coverage would mean more hydrophilic groups translating into higher osmotic pressure, as well as, causing a steric hindrance and reducing chances of aggregation even after regeneration– a problem that has been reported.[29] The steric hindrance due to the polymer helps maintaining the MNPs in suspension and hinders agglomeration. [37, 38]. Even after the magnet-assisted separation, the agglomeration formed was easily broken and the MNPs can be re-dispersed in a short time. The high polymer coverage resulting in higher steric stabilization of the MNPs aids the re-dispersion of the MNPs. We believe that in an industrial set-up, the combination of an industrial ultrasonic homogenizer along with high speed pumps, used in the FO operation, would be capable of keeping the MNPs in dispersion.

3.2. Characterization of PSA-MNPs.

Magnetization data for poly acrylic acid (sodium salt)-coated $\gamma\text{Fe}_2\text{O}_3$ nanoparticles have been previously reported in the literature. [38] Our experimental measurements were in agreement of the reported value of $3.5 \times 10^5 \text{Am}^{-1}$. The PSA-MNPs were characterized by XRD, ATR-FTIR and TEM as shown in figure 3. The XRD graph indicates that the PSA-MNPs assume a cubic maghemite $\gamma\text{-Fe}_2\text{O}_3$ phase which is super-paramagnetic in nature[39] and hence will facilitate easier magnetic separation. On further characterization with ATR-FTIR (figure 3B), presence of PSA polymer on the MNPs was confirmed. The signature peaks of a carboxylic acid salt (here, Na salt of polyacrylic acid i.e., PSA) – peaks at 1403 cm^{-1} , 1455 cm^{-1} (COO^- symmetric stretch) and 1556 cm^{-1} (COO^- asymmetric stretch), are observed in both the PSA polymer and PSA-MNPs. This confirms that the MNPs have been successfully coated with PSA. The synthesized MNPs demonstrated a mean TEM MNP core diameter of $9 \pm 2 \text{ nm}$ as shown in figure 3C. The MNPs with the PSA ligand in the extended configuration (core MNP + ligand shell) demonstrates a median hydrodynamic size

of 26 ± 7 nm, which though higher than expected is explainable. DLS being a scattering technique is skewed towards the higher size intensity data, thus reporting a higher NP size.

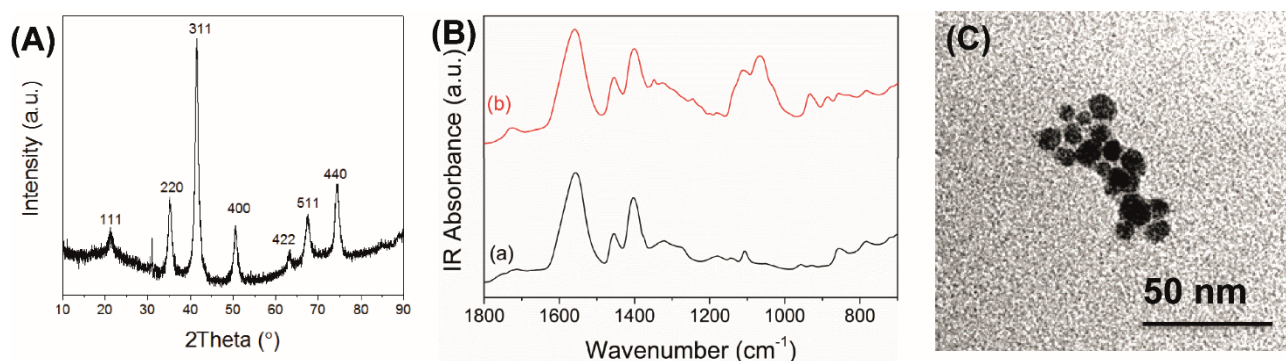


Figure 3. Physical characterizations of synthesized PSA coated MNPs (PSA-MNPs); (A) XRD spectrum of PSA-MNP, (B) ATR-FTIR spectra of (a) PSA polymer and (b) PSA-MNP, and (C) TEM micrographs of PSA-MNPs.

In terms of quality and stability of the polymer coating, the PSA-coated MNPs had undergone purification including several washing, centrifuging, sonication, magnetic separation and re-dispersion steps. The zeta potential (details in the later paragraphs), ATR-FTIR and TGA data reported are of the purified sample which confirms the presence of polymer on MNP surface. Since the purification steps did not affect or strip-off the polymer from the MNP surface, we can safely comment that the polymer adhesion was both stable and of good quality. In addition, Fresnais *et. al.* [38] have also demonstrated that poly acrylic acid-coated $\gamma\text{Fe}_2\text{O}_3$ nanoparticles remained stable from pH 10 down to pH 3.5 and did not agglomerate.

As the dispersion of the PSA-MNP draw agent was very dilute, we also evaporated a fixed volume of the sample and obtained the % solid content of the draw agent. Our SMDA draw solution constituted of 0.13 wt.% of draw solute. TGA was carried out to estimate the polymer coverage on the MNPs which was calculated by the total weight loss of the PSA-MNP sample between 100-1000 °C. The TGA reveals the SMDA polymer content to be approximately 60%. Thus the PSA polymer content in our SMDA system is 0.078 wt.%, which is approximately 6 times diluter than the PSA solution.

To provide for an understanding of how the hydrophilic groups get ionized in the aqueous state, we carried out some initial characterizations of the zeta potential and conductivity of PSA and PSA-

MNP draw agents. The zeta potential of PSA-MNP was recorded as $-24.6 (\pm 2.4)$ mV and conductivity of $0.0115 \text{ mS.cm}^{-1}$, whereas, PSA polymer solution of 5 g/L demonstrated $-43 (\pm 5)$ mV and 1.91 mS.cm^{-1} . Strong electrolytes dissociate completely and demonstrate high electrolytic conductivity. The conductivity is also affected by the concentration. At a significantly high concentration the ions have a higher tendency to form ion-pairs and hence result in lowering the conductivity. The PSA solution was prepared at a very low concentration of 5 g/L (or 0.5 wt.%) as to be able to assess the higher limit of ionization of the polyelectrolyte by itself. In comparison to the PSA polymer, our SMDAs were very low in concentration thus having low hydrophilic group density in the dispersion, resulting in lower conductivity of the PSA-MNPs. On optimizing our reaction parameters we were able to obtain SMDAs with high polymer coverage, an essential requirement to influence the osmotic pressure and FO water flux.

3.3. Osmotic Pressure and FO water flux of PSA and PSA-MNPs.

As a 0.5 wt.% of the PSA solution was not efficient as a draw solute, hence we employed a draw solute concentration of 3.5 wt.% against DI feed water, which was still lower than that mostly reported in the literature. As explained earlier, our PSA-MNP SMDA system consisted of a draw solute concentration of 0.13 wt.% with a net PSA concentration of 0.078 wt.%. At an acidic pH, PSA is reported to acquire a closed polymer conformation where the hydrophilic groups might not be accessible and such a low pH is also unsuitable for the osmosis membranes. The 3.5 wt.% PSA draw solution exhibited a pH of 8 and hence would develop an open extended polymer chain conformation, thereby, presenting the draw solution with higher number of available and ionisable hydrophilic groups. Whereas, the as-prepared PSA-MNP draw solution demonstrated a pH of 6 which also would not have a detrimental effect on the osmosis membranes as well as assume an extended polymer chain conformation. No pH adjustment was thus required, thereby further reducing production costs and boosting FO membrane working life.

In order to gain in-depth understanding of the osmotic properties of the draw agents (PSA polyelectrolyte and PSA-MNPs), three parameters were studied– water flux variation with time, average water flux, and osmotic pressure (calculated from the water flux with previously mentioned equation). Figure 4A shows that the PSA-MNP provides a significantly higher (almost 3-fold) initial water flux than the PSA polymer itself. An average water flux of 5.32 LMH was obtained when using PSA-MNP, in contrast to, 1.72 LMH when using PSA as the osmotic draw agent (figure 4B). The FO water flux (figure 4A) remained stable for 3 h and thereafter decreased slowly due to dilution of the draw solution by the transported water mass from the feed compartment. The

stability in water flux over 3 h indicates the ability of the PSA-MNP agent to maintain strong osmotic pressure and, hence the FO driving force over prolonged time. Similar water flux against DI feed water has been reported by Ling and Chung [3, 19, 20] for hydrophilic MNPs with draw solute concentrations of 100-200 g/L i.e., 10-20 wt.%, as compared to a concentration of 0.13 wt.% in our case. This implies that our SMDA system is far more efficient and economically viable than those previously reported in the literature.

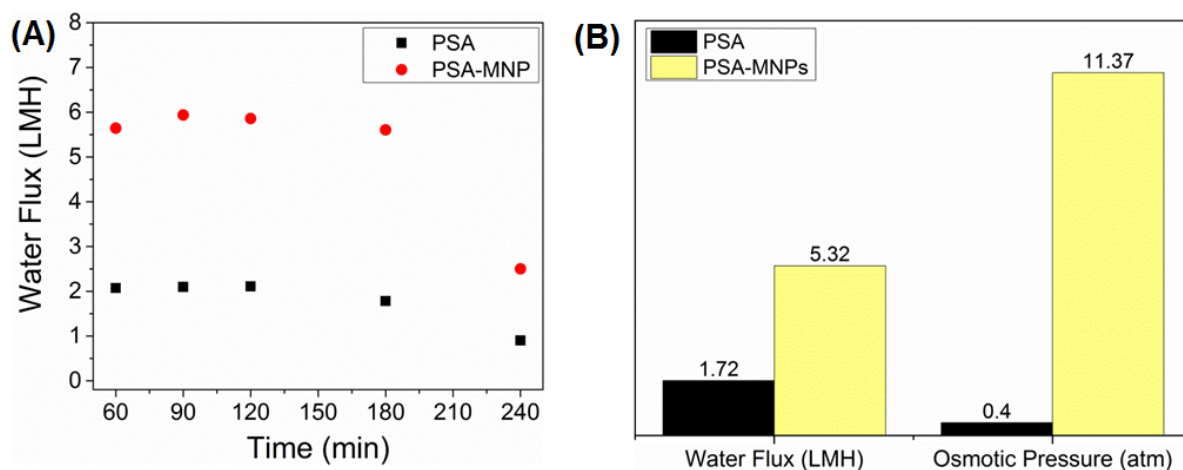


Figure 4. (A) Plot of FO water flux with time, and (B) Comparison of average water flux and osmotic pressure of PSA and PSA-MNPs.

Figure 4B depicts significantly improved osmotic pressure of the PSA-MNPs (11.37 atm) than the equivalent PSA polyelectrolyte (0.4 atm). It is worth noting that the required net PSA concentration (in the form of PSA-MNP draw agent) to generate osmotic pressure of 11.37 atm, was only 0.078 wt.%. Ge and co-workers[22] reported an osmotic pressure of ~11-12 atm with a concentration of ~15 wt.% with PSA (M_n 1800) as the draw solute. Others [3, 9, 22] report the use of 24-48 wt.% PSA draw solute (in the form of free polyelectrolyte osmotic agent) to generate the similar osmotic pressures that we achieved. This thus justifies that the MNPs play an important role in improving the osmotic properties of PSA.

The higher water flux and osmotic pressure of the PSA-MNPs can be attributed to the different PSA conformations—coiled and extended. The extended open conformation of PSA in PSA-MNPs is most likely due to the higher tendency of the polymer chains to uncoil when anchored to a surface (here a NP surface) at a certain optimized polymer concentration, thereby significantly increasing the number of hydrophilic groups available to attract water molecules.[34, 39, 40, 41] Thus, the MNPs boost the osmotic properties of PSA by forcing it to assume an open extended configuration.

Also the MNPs assist in easy regeneration of the PSA. Hence we believe that the catalytic effect of the MNPs in the PSA-MNP SMDAs is the key to understanding and further improving their osmotic properties. Such MNP based SMDAs need to be researched in greater detail so that the industry benefits from the combined improved functionalities.

The stability and resilience of the poly acrylic acid coating has been previously indicated by Fresnais et al [38]. In their work, the authors demonstrated that poly acrylic acid (in its sodium salt form), constitute a resilient adlayer onto the surface of γ -Fe₂O₃ nanoparticles which make them suitable for water treatment applications such as for applications in pollutant removal. As we were concerned about the working of the industrial FO units, we measured the viscosity of the draw agent during FO operation which was similar to that of water as the draw solute concentration was very low. Hence, we do not apprehend significant mechanical hindrance during the industrial FO working condition. Low solution viscosity resulting from low solute concentration is strongly desired to minimize hydraulic pressure losses across the membrane channel. Hence, our system not only combines the advantage of the magnetic separation, but also incorporates benefits of near-neutral pH, low viscosity during the FO process as well as low production cost owing to the low draw solute concentration. This makes our SMDA more industry-friendly reducing the production cost of clean water.

3.4 Regeneration of PSA-MNP draw agent.

The facile separation and regeneration of the osmotic draw agent is of prime importance for a cost effective FO process. The separation of PSA-MNPs osmotic agent and recovery of fresh water product was achieved by applying an external magnetic field for ~5 min. For comparison, we also studied the regeneration of both PSA and PSA-MNP under conductive (or evaporative) heating and magnetic forces. Both draw solutes could be recovered when they were exposed to conductive heating at ~90 °C overnight, but only PSA-MNPs could be recovered under a low magnetic field. Figure 5 demonstrates the ease of separation and regeneration of the PSA-MNPs under a low magnetic field, making the FO process cost-effective. In addition, our developed SMDA (PSA-MNP) is bio-compatible and environment-friendly as it can be recycled without releasing chemicals as by-products in water or air (as in the case of ammonium bicarbonate osmotic agent where the CO₂ may escape to air).[6]

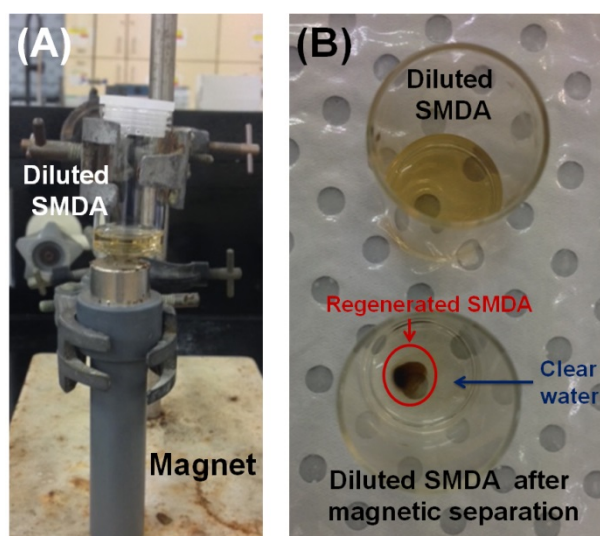


Figure 5. Magnetic separation of SMDA and release of clean water product.

4. Conclusion

We demonstrated that the synthesized ~ 9 nm PSA-coated MNPs have significantly higher osmotic pressure (~ 30 fold) and FO water flux (~ 2 -3 fold) when compared to their polymer (polyelectrolyte) counterpart, even at a low concentration of ~ 0.13 wt.% (literature reports use of significantly higher concentrations of draw solute). The change in polymer conformation (coiled up or extended) with its concentration and anchorage to a surface determine the availability of the polymer hydrophilic groups in solution. Therefore the PSA conformation significantly affects the osmotic pressure and water flux generated by the PSA-MNP and PSA osmotic draw agents. At an optimum concentration of the polymer, the polymer chains when anchored onto a NP surface assumes a brush like conformation thereby making higher number of functional hydrophilic groups available for boosting the osmotic pressure and FO water flux. The significantly low concentration of the PSA-MNP osmotic agent and associated high water flux (5.32 LMH) enhances the cost-effectiveness of our SMDA system. In addition, easier magnetic separation and regeneration of the PSA-MNP draw solution also improves its usability making our improved SMDA efficient, cost-effective and environment-friendly. This improvised process can provide for chemical-free drinking water, as well as, treated wastewater that can be reused in the industrial processes.

Acknowledgements

We also acknowledge the support from Porifera for providing us with their specialized membranes and Prof. Graeme Miller (QUT, Australia) for his support and help with the lab FO experiments.

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