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PAPER

# A low-energy forward osmosis process to produce drinking water†

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Forward osmosis (FO) represents a tremendous and untapped opportunity with the potential to solve the global water crisis. The biggest challenge facing the application of FO technology is the economical separation of drinking water from its draw solution. Using advances in nanotechnology, we herein describe a novel draw solute separation system which mimics a natural "destabilization" phenomenon with the help of superparamagnetic nanoparticles, thus separating drinking water from draw solution without any intensive energy, such as, hydraulic pressure or heat. Also, this process is not afflicted by the commonly observed problem of reverse salt diffusion. All these characteristics of this novel draw solution separation system make FO to be an eco-sustainable process for the production of drinking water from wastewater without any waste.

## Introduction

Drinking water scarcity is one of today's most pressing challenges representing both economical and ecological hazards. Rapidly expanding populations, coupled with increasing standards of living, is straining a natural resource already afflicted by climate change.[1] Wastewater reuse and seawater desalination have become the only viable means of meeting demand in many places.[2] At present the technologies used to produce drinking water require enormous energy inputs which further aggravate greenhouse gas emissions and accelerate climate change.[3]

Reverse osmosis (RO) is a membrane treatment process which offers an efficient footprint and is employed widely across the globe.[4] A high hydraulic pressure is used to force water through a semipermeable membrane against the natural osmotic tendency of water. Primary drawbacks include heavy consumption of electrical power, severe membrane fouling and brine discharge. This process has served well as an interim solution but is neither economically viable in the long run nor environmentally sustainable.

In contrast to the RO process, FO membrane technology utilizes the natural phenomenon of osmosis. Water is drawn across a semipermeable FO membrane from a feed solution into a draw solution with higher solute concentration,[5] as shown in Fig. S1 (supplementary information†). The diffusive flux of water is driven by the osmotic pressure difference between the feed and draw solutions.[6] High quality drinking water can subsequently be separated from the draw solution which is concentrated and reused in near perpetuity. In theory, the FO process requires zero hydraulic pressure and does not consume energy. It drastically reduces the costly problem of membrane fouling associated with pressure-driven membrane processes.[7] Recent developments in FO membrane technology have demonstrated promising results in seawater desalination,[8]

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## Broader context

Scarcity of drinking water is a major problem globally and will continue to get worse in the coming decades as the cost of energy skyrockets in price. Driven by the natural osmotic pressure gradient, the forward osmosis (FO) process exhibits unparalleled advantages of no intensive energy input and low membrane fouling tendency for drinking water production. However, the industry has not fully embraced the FO process because of a major obstacle: the lack of an ideal process for draw solution separation, which can be operated in an energy-efficient way. Here, we, for the first time, mimic a natural destabilization phenomenon to design a novel draw solution separation process to overcome this obstacle. With the introduction of nanotechnology, alum draw solution can be economically separated and reused with a low-cost coagulation process. With this technical breakthrough, FO technology could be expected to make a huge difference in the water and energy industry by radically replacing the current industry technology such as reverse osmosis membrane technology. Hence, this novel FO process is an ideal solution to answer both energy and environmental problems.

wastewater reclamation,[9] food and pharmaceutical processing,[10] and even power generation.[11] Despite its tremendous potential, FO has not been widely embraced because the absence of a low-energy separation method for drinking water from draw solution has presented a major obstacle.[5,6]

Many draw solutions have been tested with an aim to achieve a low energy separation method for clean water production.[6,12] Menachem Elimelech at Yale University made a breakthrough in the FO process with the successful application of a $NH_4HCO_3$ draw solution. The salt solution contains highly concentrated carbon dioxide ($CO_2$) and ammonia ($NH_3$).[13] Clean water is recovered from the draw solution through a thermal process which boils away the $NH_3$ and $CO_2$ at around 58 °C. The $NH_3$ and $CO_2$ are then recombined to form salt and the process is repeated. The process is claimed to require only one-tenth of the energy consumed in conventional desalination systems.[14] However this approach still requires considerable amounts of thermal energy to boil away $NH_3$ and $CO_2$ in the draw solution. This limitation is overcome in areas where exhaust thermal energy is available from sources such as power or incineration plants. Moreover, drinking water standards are stringent and require the removal of $NH_3$ from the water to a residue of <2mg $L^{-1}$.[15] This potential safety drawback represents one of the largest obstacles facing the $NH_4HCO_3$ draw solution that has to date demonstrated the best promise for application.

The challenge presented now is to achieve economical draw solute separation which will produce clean and safe drinking water. As we know, the interaction of oppositely charged fine particles gives rise to a natural "destabilization" effect. This phenomenon has been used for hundreds of years in the production of drinking water from natural waters in the absence of hydraulic or thermal energy.[16] Wherein, positively charged alum ($Al_2(SO_4)_3$) is added to these natural waters to destabilize the negatively charged colloids in a process called coagulation. The initially dispersed solids agglomerate to form larger and heavier flocs which can then be removed through a sedimentation process driven only by gravity. This process still represents the most widely employed solution in drinking water production because of its economy.[17] In 1972 Frank demonstrated that $Al_2(SO_4)_3$ had adequate osmotic pressure in solution to desalinate seawater through a FO process.[18] He also demonstrated the separation of $Al_2(SO_4)_3$ draw solute through a centrifugation method, which is an economically impractical solution.

Present advances in nanotechnology have led to the discovery that nanoparticles typically possess negatively charged surfaces.[19] This led us to attempt the destabilization of positively charged $Al_2(SO_4)_3$ by these nanoparticles. To ensure an economically feasible process, the issue of recovering these relatively costly nanoparticles needed to be addressed. The application of magnetism in the selective recovery of paramagnetic particles in biotechnological and ore refining industries inspired a novel solution to this challenge.[20] The development of a superparamagnetic nanoparticle with a negatively charged surface would facilitate the recovery of $Al_2(SO_4)_3$ draw solute through coagulation. Applying an external magnetic field to the draw solution would enable drinking water recovery with virtually no depletable energy input.

Augmenting the universally embraced "destabilization (coagulation)" process with modern day advances in nanoparticle technologies presents an unexplored and critical opportunity to solve the challenges that have hindered the development and adoption of FO as a viable solution to the looming water crisis. Our novel drinking water production system is described in the in-principle diagram in Fig. 1. In addition, our $Al_2(SO_4)_3$ draw solute provides another advantage of no reverse salt diffusion over the other currently-used draw solutes.

The operation of this novel process for drinking water production does not require any intensive energy, such as hydraulic pressure or heat, due to the innovative design of $Al_2(SO_4)_3$/superparamagnetic nanoparticle draw solute system, which paves the way for FO to become an eco-sustainable solution to answer both water and energy problems globally.

## Results and discussion

### 1) Low-energy process for draw solute separation

Currently it is well known that although the FO process generally consumes much lower energy compared with other pressure-driven membrane processes for drinking water production, the major challenge for FO applications is the economical separation of draw solute from the product water, which accounts for the

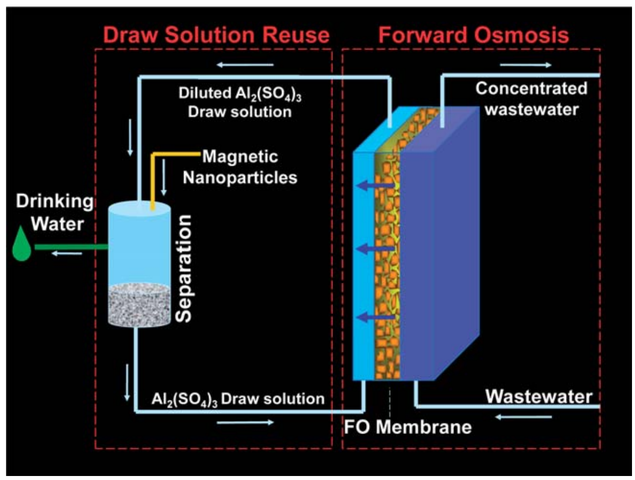


**Fig. 1** In-principle diagram of the low-energy FO process to produce drinking water. With the help of nanotechnology, a low-energy method for draw solution separation was invented, which overcomes the biggest challenge for FO to be an affordable industry process. Wherein, the whole process is illustrated with two parts: forward osmosis and draw solution reuse. In the forward osmosis part, an $Al_2(SO_4)_3$ draw solution is used to draw fresh water from wastewater across a semipermeable FO membrane. Then, in the draw solution reuse part, the diluted $Al_2(SO_4)_3$ draw solution with fresh water is sent to a $Al_2(SO_4)_3$ separation system, which will separate $Al_2(SO_4)_3$ draw solute, meanwhile producing drinking water. A special kind of negatively-charged and magnetic nanoparticles are introduced to the $Al_2(SO_4)_3$ separation system, which mimics a natural "destabilization" phenomenon to economically separate $Al_2(SO_4)_3$ draw solute with low energy consumption. This novel draw solution separation process does not require any intensive energy input, such as hydraulic pressure or heat. The discovery of this low-energy "destabilization" phenomenon for draw solute separation is paving the way for FO process to be an eco-sustainable solution for the global demand of drinking water and energy. The detailed process diagram is shown in Fig. S3 of the supplementary information.†

largest part of energy consumption for current FO processes.[6] Here, we choose $Al_2(SO_4)_3$ as draw solute, which could be economically separated by a natural "destabilization" phenomenon with the help of nanotechnology.

To demonstrate the separation process of $Al_2(SO_4)_3$ draw solute, laboratory experiments were carried out for the proof-of-concept. The bench-top setup for the forward osmosis part is shown in Fig. S2 (supplementary information†). After fresh water naturally diffused through the flat-sheet semipermeable FO membrane from wastewater into the $Al_2(SO_4)_3$ draw solution, the diluted $Al_2(SO_4)_3$ draw solution was sent to a draw solution reuse system to separate $Al_2(SO_4)_3$ and produce drinking water, as shown in Fig. 2 and Fig S3. And the chemical routes for the $Al_2(SO_4)_3$ recycle process are also shown in the supplementary information (Experimental details 4). In the $Al_2(SO_4)_3$ separation process, firstly, the diluted $Al_2(SO_4)_3$ draw solution (Fig. 2a) was added with calcium oxide (CaO) to adjust the pH, leading to the formation of a white and gel-like mixture composing of positively-charged aluminum hydroxide ($Al(OH)_3$)[16] and calcium sulfate ($CaSO_4$), both of which are stably suspended in the solution due to electrostatic repulsion of each other and could not be separated by gravity sedimentation (Fig. 2b).

Then, a cost-effective "destabilization" phenomenon was tried to separate the positively-charged gel-like mixture of $Al(OH)_3$ and $CaSO_4$ from the solution. But currently in the draw solution, due to the lack of negatively-charged fine particles, the positively-charged gel-like mixture can not be destabilized and settled by gravity sedimentation like in conventional water treatment plants. Therefore, we introduced a special kind of negatively-charged $Fe_3O_4@SiO_2$ nanoparticles (Fig. 3), which also are superparamagnetic,[21] into this gel-like mixture. After mechanical mixing, the positively-charged gel-like mixture was destabilized by the negatively-charged $Fe_3O_4@SiO_2$ nanoparticles (black-colored), coagulating to form a large and heavy floc (Fig. 2c). Conventionally, these flocs are settled down by gravity in more than 30 min in water treatment plants.[16]

However, here we used an external magnetic field to accelerate the sedimentation of the floc from the solution, because the floc (Fig. 2c) contains magnetic $Fe_3O_4@SiO_2$ nanoparticles. Under the magnetic field, the floc rapidly settled down towards the magnet (Fig. 2d), and the solution became clear within 5 min.

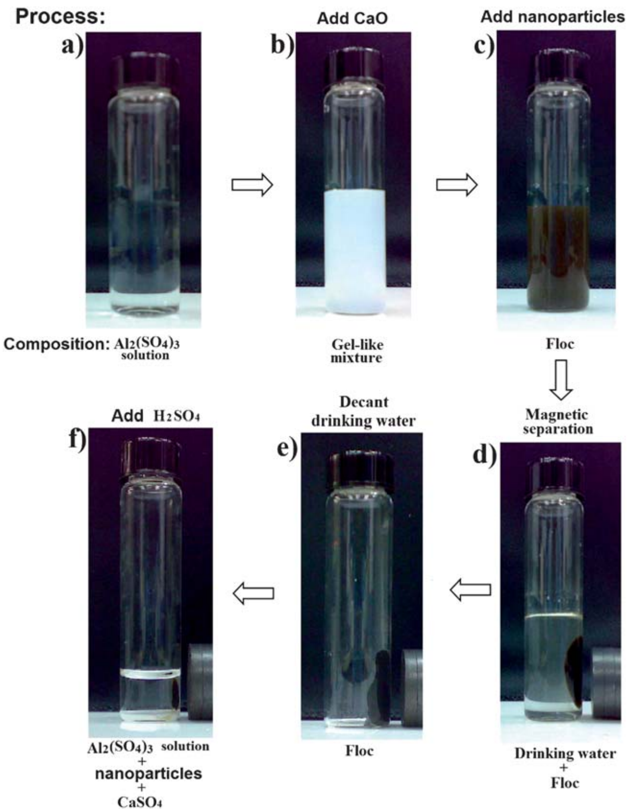


**Fig. 2** Photos of the separation and regeneration process of $Al_2(SO_4)_3$ draw solution. a) Diluted $Al_2(SO_4)_3$ draw solution; b) adding CaO into a) until pH = 6.8, resulting in the formation of a white gel-like mixture composing of $Al(OH)_3$ and $CaSO_4$; c) adding the negatively-charged and superparamagnetic $Fe_3O_4@SiO_2$ nanoparticles (Fig. 3b) into b) to destabilize (or coagulate) the positively-charged gel-like mixture, resulting in the forming of a big floc (brown color) comprising of $Al(OH)_3$, $CaSO_4$ and $Fe_3O_4@SiO_2$ nanoparticles; d) the floc deposited towards a magnet outside the right wall of the vial, leaving clear drinking water in the vial; e) decanting out the drinking water and keeping the floc in the vial; f) adding $H_2SO_4$ solution into the floc to regenerate $Al_2(SO_4)_3$ solution from $Al(OH)_3$, while the white-colored $CaSO_4$ precipitated to the bottom of the vial and the black-colored $Fe_3O_4@SiO_2$ nanoparticles were collected by the magnet outside the right wall of the vial. The regenerated $Al_2(SO_4)_3$ solution and $Fe_3O_4@SiO_2$ nanoparticles can be reused. The detailed process can be referred to in Fig. S3 of the supplementary information.†

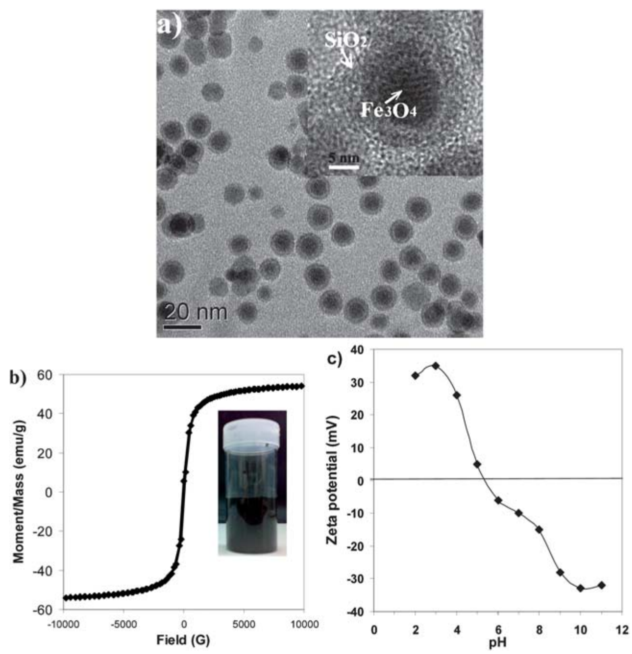


**Fig. 3** $Fe_3O_4@SiO_2$ nanoparticles. a) TEM of the $Fe_3O_4@SiO_2$ nanoparticles with $Fe_3O_4$ core and $SiO_2$ shell, insert is the enlarged TEM of a $Fe_3O_4@SiO_2$ nanoparticle, showing different contrast of the $SiO_2$ shell and the $Fe_3O_4$ core; b) the magnetism curve indicates the strong magnetic property of the $Fe_3O_4@SiO_2$ nanoparticles, insert is the photo of aqueous solution of $Fe_3O_4@SiO_2$ nanoparticles; c) surface charges of $Fe_3O_4@SiO_2$ nanoparticles as the function of solution pH, showing the negative surface charge of the $Fe_3O_4@SiO_2$ nanoparticles when the pH is over 5.3.

This rapid sedimentation under a magnetic field is meaningful for reducing the size of sedimentation tanks in conventional water treatment plants, which in turn can dramatically cut off the capital costs of the land footprint. The clear water in the vial (Fig. 2d) was the product water (conductivity = 581 μs $m^{-1}$, pH = 6.8), which met drinking water standards.

So far, the $Fe_3O_4$@$SiO_2$ nanoparticles have a double function: 1) to destabilize the positively-charged gel-like mixture; and 2) to reduce the sedimentation time of the floc under a magnetic field. Therefore, owing to the introduction of these nanomaterials, $Al_2(SO_4)_3$ draw solute can be economically separated with a low-energy "destabilization" phenomenon. During this process, there was not any intensive energy input, such as hydraulic pressure or heat, just mechanical mixing was needed.

Finally, we need to regenerate the used $Al_2(SO_4)_3$ draw solution and $Fe_3O_4$@$SiO_2$ nanoparticles for reuse. After decanting out the clear water, the floc (Fig. 2e), which comprised of Al $(OH)_3$, $CaSO_4$ and $Fe_3O_4$@$SiO_2$ nanoparticles, was sent to a regeneration system. Firstly, it was dosed with sulfuric acid ($H_2SO_4$) to regenerate the $Al_2(SO_4)_3$ solution from $Al(OH)_3$, wherein the $Fe_3O_4$@$SiO_2$ nanoparticles were collected by an external magnetic field, and the $CaSO_4$ precipitated on the bottom of the vial, respectively (Fig. 2f). Then, the regenerated $Al_2(SO_4)_3$ solution and $Fe_3O_4$@$SiO_2$ nanoparticles were fed back into the FO process, while $CaSO_4$ could be used as a valuable industrial product.[22] In this regeneration process, the super-paramagnetic property of the $Fe_3O_4$@$SiO_2$ nanoparticles is critical for their easy recovery.

It's very obvious that there is no any intensive energy, such as, hydraulic pressure or heat in the separation and regeneration process of the $Al_2(SO_4)_3$ draw solute. The realization of this low-energy process is due to the utiliztion of a natural "destabilization" phenomenon with the help of a special kind of nanomaterial, $Fe_3O_4$@$SiO_2$ nanoparticles, which are concurrently positively-charged and superparamagnetic. These nanoparticles provide triple functions in the whole process: 1) destabilize $Al_2(SO_4)_3$ draw solute; 2) accelerate the separation process; and 3) the used nanoparticles can be easily recovered.

### 2) No reverse diffusion of draw solute

Recently, researchers found that mono- and divalent draw solutes, such as $NH_4HCO_3$, NaCl, and $MgCl_2$, can reversely diffuse from the draw solution into the feed solution through the commercial FO membrane and may jeopardize the FO process.[23,24] Especially, the salt loss of $NH_4HCO_3$ is magnitudes higher than NaCl, which means people can't afford the huge amount of replenishment of $NH_4HCO_3$ in the practical FO applications. In our FO process, the rejection rate of $Al^{3+}$ ion by the FO membrane is 99.99%, indicating almost no reverse diffusion of ions from the $Al_2(SO_4)_3$ draw solution into the wastewater feed solution. This is mainly because the trivalent $Al^{3+}$ ion normally has a much larger hydrate ion size than mono- and divalent ions; and ions with larger sizes are more difficult to diffuse through the FO membrane. This advantage of the $Al_2(SO_4)_3$ draw solution is critically important for FO practical applications, which do not need constant replenishment of draw solutes; therefore our alum/nanoparticle draw solution system possesses this special benefit over mono- or divalent draw solutes.

## Conclusions

Owing to the introduction of nanotechnology, this novel FO process is capable of separating the $Al_2(SO_4)_3$ draw solute from drinking water with a low-energy "destabilization" phenomenon, which makes the FO process an affordable water industrial process. In addition, this $Al_2(SO_4)_3$ draw solute also eliminates the problem of reverse salt diffusion associated with other draw solutes. These advantages could make a huge difference for FO processes in the water and energy industry by radically replacing current industrial technologies, such as RO membrane technology. Therefore, it is an eco-sustainable solution to answer both water and energy problems throughout the world, by meeting the global demand for drinking water production with low energy consumption. The principle of this novel FO process can be applied in both wastewater reclamation and seawater desalination.

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## References

1 P. Aldhous, *Nature*, 2003, **422**, 251.
2 J. B. Zimmerman, J. R. Mihelcic and J. Smith, *Environ. Sci. Technol.*, 2008, **42**, 4247.
3 R. L. McGinnis and M. Elimelech, *Environ. Sci. Technol.*, 2008, **42**, 8625.
4 L. F. Greenlee, D. F. Lawler, B. D. Freeman, B. Marrot and P. Moulin, *Water Res.*, 2009, **43**, 2317.
5 M. A. Shannon, P. W. Bohn, M. Elimelech, J. G. Georgiadis, B. J. Marĩas and A. M. Mayes, *Nature*, 2008, **452**, 301.
6 T. Y. Cath, A. E. Childress and M. Elimelech, *J. Membr. Sci.*, 2006, **281**, 70.
7 E. R. Cornelissen, D. Harmsen, K. F. de Korte, C. J. Ruiken, J.-J. Qin, H. Oo and L. P. Wessels, *J. Membr. Sci.*, 2008, **319**, 158.
8 J. R. McCutcheon, R. L. McGinnis and M. Elimelech, *J. Membr. Sci.*, 2006, **278**, 114.
9 R. W. Holloway, A. E. Childress, K. E. Dennett and T. Y. Cath, *Water Res.*, 2007, **41**, 4005.
10 K. B. Petrotos and H. N. Lazarides, *J. Food Eng.*, 2001, **49**, 201.
11 A. Seppälä and M. J. Lampinen, *J. Membr. Sci.*, 1999, **161**, 115.
12 E. R. Cornelissen, D. Harmsen, K. F. de Korte, C. J. Ruiken, J.-J. Qin, H. Oo and L. P. Wessels, *J. Membr. Sci.*, 2008, **319**, 158.
13 Q. Schiermeier, *Nature*, 2008, **452**, 260.
14 http://www.oasyswater.com/.
15 F. W. Pontius, W. C. Stephen, Chapter 1, Drinking Water Quality Standards, Regulations and Goals. Water Quality and Treatment, Fifth Edition, *American Water Works Association*, Ed. Raymond D. Letterman, McGraw-Hill, Inc., 1999.
16 J. L. Lin, C. Huang, C. J. M. Chin and J. R. Pan, *Water Res.*, 2009, **43**, 4285.
17 R. Fabris, C. W. K. Chowa, M. Drikas and B. Eikebrokk, *Water Res.*, 2008, **42**, 4188.
18 B. S. Frank, Desalination of sea water, *US Patent 3,670,897*, 1972.
19 O. Toikkanen, V. Ruiz, G. Rönnholm, N. Kalkkinen, P. Liljeroth and B. M. Quinn, *J. Am. Chem. Soc.*, 2008, **130**, 11049.
20 G. Reiss and A. Hütten, *Nat. Mater.*, 2005, **4**, 725.
21 Y. Lu, Y. Yin, B. T. Mayers and Y. Xia, *Nano Lett.*, 2002, **2**, 183.
22 R. J. Hand, *British Ceramic Transactions*, 1997, **96**, 116.
23 N. T. Hancock and T. Y. Cath, *Environ. Sci. Technol.*, 2009, **43**, 17.
24 W. A. Phillip, J. S. Yong and M. Elimelech, *Environ. Sci. Technol.*, 2010, **44**, 5170.