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Johnson, D., Suwaileh, W., Mohammed, A. & Hilal, N. (2017). Osmotic's potential: An overview of draw solutes for forward osmosis. *Desalination*

<http://dx.doi.org/10.1016/j.desal.2017.09.017>

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# Osmotic's Potential: An Overview of Draw Solutes for Forward Osmosis

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## **Abstract**

Forward osmosis (FO) is a membrane separation process using a highly concentrated draw solution with high osmotic potential to draw water across a semi-permeable membrane from a feed source. This feed source may be seawater, wastewater or other natural or contaminated water sources. Unlike other membrane driven purification processes, the product is not clean water, but a diluted draw solution. As a result a second step is often needed to produce a pure water product. A major advantage of FO is that the low hydrodynamic pressure involved leads to lowered fouling of membranes and greater flux recovery after cleaning, as well as often providing a low energy process which can recover clean water from difficult or highly fouling sources. Selection of an appropriate and effective draw solution is essential for the practical operation of an FO process. This review will give an overview of the theoretical underpinnings of draw solution performance and a comprehensive summary of the current literature regarding the different types of draw solutions which have been investigated and their respective benefits and detriments.

## Highlights

- Literature on draw solutions used in forward osmosis processes reviewed including the state-of-the-art
- Overview of theoretical underpinning of draw solution performance
- Up to date developments of draw solutes
- Comparison of draw solute recovery methods

## Keywords

Forward osmosis, draw solution, membrane separation, desalination, water treatment

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### List of abbreviations

Abbreviation	
BSA	bovine serum albumin
CA	citric acid
CQD	carbonised quantum dot
DI	de-ionised
DME	dimethyl ether
ECP	external concentration polarization
EDTA	ethylene diamine tetra-acetic acid
Fe(acac) <sub>3</sub>	ferric triacetylacetonate
FO	forward osmosis
HA	hyaluronic acid
ICP	internal concentration polarization
LCST	lower critical solution temperature
MD	membrane distillation

MED	multi-effect distillation
MFC	magnetic field control
MSF	multi-stage flash
NF	nanofiltration
P <sub>4444</sub> DMBS	tetra butyl phosphonium 2,4 dimethyl benexene sulfonate
P <sub>4444</sub> TMBS	tetra butyl phosphonium mesitylene sulfonate
P <sub>4448</sub> Br	tri butyl octyl phosphonium bromide
PAA	poly acrylic acid
PAM	poly(acrylamide)
PDMAEMA	poly(2-(dimethylamino) ethyl methactylate)
PEG	poly(ethylene glycol)
PNIPAM	poy( <i>N</i> -isopropylacrylamide)
PRO	pressure retarded osmosis
PSA	poly (sodium acrylate)
PSA-NIPAM	poly(sodium acrylate)- <i>co</i> -poly( <i>N</i> -isopropyl acrylamide)
PSS	poly (sodium-4-syrenesulfonate)
PSSS-PNIPAM	poly(sodium styrene-4-sulfonate- <i>co</i> - <i>N</i> -isopropylacrylamide)
PVA	poly (vinyl alcohol)
RO	reverse osmosis
SPS	switchable polarity solvents
TEM	transmission electron microscopy
TMA	tri-methylamine
TREG	tri-ethylene glycol
UF	ultrafiltration

### List of symbols

Symbol	
$A$	water permeability coefficient
$B$	solute permeability coefficient within membrane
$B_2, B_3, B_4...$	virial coefficients
$B^A$	solute permeability coefficient for the active layer
$c$	mass concentration of solutes
$C_D$	draw solute concentration
$C_F$	feed solute concentration
$D$	solute diffusion coefficient
$D^A$	draw solute diffusion coefficient through active layer
$D_{eff}$	effective solute diffusion coefficient
$d_h$	hydraulic side of flow channel
$d_p$	pore diameter
$d_s$	solute molecular diameter
$H$	partition coefficient
$J_s$	solute flux
$J_{specific}$	specific reverse solute flux
$J_w$	water flux
$K$	solute resistivity to flow through prous membrane
$k_d$	mass transfer coefficient for draw solution side

$k_f$	mass transfer coefficient for feed solution side
$k_m$	mass transfer coefficient for membrane support layer
$M$	molar concentration
$n$	number of ions produced by draw solute dissolution
$N_p$	number of ions
$R$	fractional salt rejection
$R_g$	ideal gas constant
$S$	membrane structural parameter
$Sh$	Sherwood number
$T$	absolute temperature (K)
$t_A$	membrane active layer thickness
$t_s$	membrane support layer thickness
$V$	solution volume
$\delta$	membrane constrictivity parameter
$\Delta C$	concentration gradient of solute across active layer
$\epsilon_{eff}$	effective porosity
$\pi$	osmotic pressure
$\pi_{D,b}$	bulk osmotic pressure of draw solution
$\pi_{D,i}$	osmotic pressure within support layer adjacent to active layer
$\pi_{D,m}$	osmotic pressure close to membrane (draw side)
$\pi_{F,b}$	bulk osmotic pressure of feed solution
$\pi_{F,m}$	osmotic pressure at membrane active layer (feed side)
$\sigma$	reflection coefficient
$\tau$	membrane tortuosity
$\phi$	osmotic pressure coefficient

## 1 Introduction

Amongst the several membrane based technologies currently being developed, the process of forward osmosis (FO), also known as manipulated osmosis, is showing great promise, particularly for treatment of hypersaline, high fouling or otherwise challenging feed waters [1-8]. Unlike pressure driven membrane processes, such as reverse osmosis (RO), instead of pumping the feed water at a pressure sufficient to overcome the osmotic pressure difference between the feed and permeate, with FO it is the difference in osmotic pressure between the feed water and a more concentrated draw solution which drives the filtration process. As a result, the initial filtration step requires less applied energy and suffers from lower fouling and scaling, with greater fouling reversibility observed subsequent to cleaning measures [9]. However, unlike other membrane processes, the end product

of FO is not purified water, but rather a diluted draw solution. As a result, unless the diluted draw solution is of use of itself or the process is purely being run to dewater the feed rather than produce a useful product water, then a second separation step is necessary to both re-concentrate the draw solution for reuse and to produce a purified water product. The regeneration step requires additional energy, which in some cases may push the total energy costs above that of alternatives, such as RO or membrane distillation (MD). Shaffer et al [3] analysed the energy efficiency of the FO process in light of this necessary regeneration step from a thermodynamic perspective, particularly in comparison with RO processes. They pointed out that the energy needed to run an FO process with draw solute regeneration cannot be less than the minimum energy of separation, a minimum which is already close to the operating parameters of recent RO designs [10]. Furthermore, they point out that if using a regeneration process such as ultrafiltration (UF), which typically has higher water flux and would be suitable for regeneration of larger sized solutes, the energy required to re-concentrate the draw solution to its original osmotic potential would require the same energy as for using RO, as the amount of energy needed is based on the osmotic pressure difference between the concentrated and diluted draw solutions, not on the process itself [3]. In addition Field and Wu [11] studied mass transfer limitations when scaling up FO processes and found them to be more severe for FO than for other membrane applications as module size is increased, making FO less favourable at large scale than RO for seawater desalination.

However, FO still has much potential for treating hypersaline streams too concentrated for RO [12], dewatering wastewater [4, 8, 13, 14], concentrating foods [15, 16] or niche applications where draw solute does not need regeneration, such as using fertiliser as the draw solute which can then be utilized for fertigation applications [14, 17-19]. In addition much research has been applied to the energy generating process of pressure retarded osmosis (PRO) [20-22], where the difference in osmotic potential between the feed and draw solutions is harnessed to produce electrical energy, for example from the difference in osmotic pressure between freshwater and saline [23] or concentrated brines [24, 25].

This paper summarises the operating principles of FO processes and provides a comprehensive state of the art review of draw solutions used in FO water treatment processes. Particular attention is paid to recent developments of novel draw solutes and their potential applications and regeneration methods.

## 2 Basic Principles of Forward Osmosis

### 2.1 Solution Osmotic Pressure

The basis for separation using FO is the difference in osmotic pressure between two different solutions separated by a semi-permeable membrane which allows free passage of the solvent, but restricts flow of solutes. As a result, the osmotic pressures which can be achieved are of great importance when selecting a draw solute. For very dilute solutions the osmotic pressure of a simple solution containing a non-electrolyte solute is described by the Van't Hoff equation, which is analogous to the ideal gas equation [26, 27]:

$$\pi = \frac{xR_gT}{V} = MRT \quad (1)$$

where  $\pi$  is the osmotic pressure,  $V$  is the solution volume (assuming solution is sufficiently dilute that the solute and solution volume are essentially identical),  $M$  is the molar concentration ( $\text{mol L}^{-1}$ ),  $R_g$  is the ideal gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ), and  $T$  is the absolute temperature in Kelvin. For a weak solution containing a strongly dissociated electrolyte it becomes:

$$\pi = \frac{mxR_gT}{V} = iMR_gT \quad (2)$$

Where  $m$  is the number of ions and  $x$  the mole fraction of the solute,  $i$  is the number of ionic species each solute molecule will dissociate into if solute is an electrolyte. This relationship only holds true when the solute is so dilute that it behaves as an ideal solution (i.e. in effect is infinitely dilute), which is not the case during FO operation where highly concentrated feed and draw solutions may



be employed. For more concentrated solutions an osmotic pressure coefficient,  $\varphi$ , can be added as a correction factor [28]:

$$\pi = \varphi MR_g T \quad (3)$$

More specifically, the osmotic pressure of high salinity solutions can be derived by a virial expansion to a power series [3, 27, 29, 30]:

$$\pi = cRT \left( \frac{1}{M} + B_2 c + B_3 c^2 + B_4 c^3 \dots \right) \quad (4)$$

where  $c$  is the mass concentration of the solute and  $B_2, B_3, B_4$  etc. are the experimentally determined virial coefficients. Theoretically this relationship contains an infinite series, but in practice empirical determination of  $B_2$  and  $B_3$  is sufficient. The osmotic pressure of a solution can be directly determined experimentally using a membrane based osmometer [31, 32], use of a freezing point depression osmometer [33, 34] or from measurement of the solution vapour pressure [35]. The latter two techniques are used more commonly than direct measurement due to practical convenience, as direct membrane osmometers can take some time to equilibrate. In addition, the osmotic pressure is often calculated using specialised software, where it is determined from the known thermodynamic properties of the solution, such as with the OLI Stream analyser (OLI Systems, USA) [36]. However, techniques used for estimating osmotic pressure have a number of idiosyncratic limitations: for instance vapour pressure measurements are inaccurate when studying solutions with dissolved volatile components, whereas freezing point depression measurements are not reliable if solutions with particulate matter are being investigated due to their particles acting as nucleation sites for freezing [37].

## 2.2 Water Flux During FO

Water flux across a semi-permeable membrane due to differences in osmotic potential alone is generally described by the following equation [5, 36]:

$$J_w = A(\pi_{D,b} - \pi_{F,b}) \quad (5)$$

where  $J_w$  is the water flux,  $A$  is the water permeability constant of the membrane, and  $\pi_{D,b}$  and  $\pi_{F,b}$  are the bulk osmotic pressure of the draw and feed solutions respectively. This is assuming that there is no difference in the applied hydraulic pressure at each side of the membrane. The water flux may be rephrased in terms of the resistivity of the solute to flow through a porous structure,  $K$  [38]:

$$J_w = \frac{1}{K} \ln \left( \frac{\pi_{D,b}}{\pi_{F,b}} \right) \quad (6)$$

where  $K$  is related to the structural properties of the membrane and solute diffusion coefficient,  $D$  [39]:

$$K = \frac{S}{D} = \frac{t_s \tau}{D \epsilon_{eff}} \quad (7)$$

where  $t_s$ ,  $\tau$  and  $\epsilon_{eff}$  are the thickness, tortuosity and effective porosity of the support layer respectively. These last three measures can be combined to comprise the structural parameter,  $S$ . The effective porosity differs from the simple porosity by disregarding dead-ended pores which do not contribute to a path through the membrane [29].

Whilst conventionally an effective diffusion coefficient,  $D_{eff}$  is defined in terms of the  $D$ ,  $\epsilon_{eff}$ , and  $\tau$ , Zhou and Zhang introduced an extra constrictivity parameter,  $\delta$  [40]:

$$D_{eff} = \frac{D \epsilon_{eff} \delta}{\tau} \quad (8)$$

where the constrictivity factor is related to the ratio of solute molecular diameter,  $d_s$ , to the pore diameter,  $d_p$ :

$$\delta = \left( 1 - \frac{d_s}{d_p} \right)^4 \quad (9)$$

Inclusion of the constrictivity parameter or effective diffusion constant also allows the inclusion of an improved value for the solute resistivity:

$$K = \frac{t_s \tau}{D \epsilon_{eff} \delta} = \frac{t_s}{D_{eff}} \quad (10)$$

As shown by Field and Wu [11] the maximum possible water flux is proportional to the natural log of the ratios of the osmotic pressure of the feed and draw solutions:

$$J_w \cong \frac{k_m k_f k_d}{k_m k_f + k_m k_d + k_f k_d} \ln \left( \frac{\pi_D}{\pi_F} \right) \quad (11)$$

where  $k_m$ ,  $k_f$  and  $k_d$  are the mass transfer coefficients for the membrane support layer, feed solution side and draw side respectively. This relationship holds for cases where the FO membrane is close to ideal, that is when  $A$  and  $k_m$  are large. Generally speaking, the mass transfer coefficient can be related to the Sherwood number (the ratio of convective to diffusive mass transfer), which are in turn related to the Reynolds and Schmidt numbers, by the following relationship:

$$k = \frac{Sh D}{d_h} \quad (12)$$

where  $Sh$  is the Sherwood number and  $d_h$  is the hydraulic diameter of the flow channel.

### 2.3 Concentration Polarization

The above relationships all assume that the osmotic pressure of the solutions in proximity with, and internal to, the membrane are essentially the same as in the bulk solutions. However, in most practical cases this is not the case due to one or more of several types of concentration polarization occurring. Concentration polarization may be concentrative or dilutive and may be internal or external to the membrane, depending on the orientation of the membrane if an asymmetric membrane is used, i.e. consisting of a dense active layer and porous support layer [41]. Most commonly in the literature 'internal' is defined as on the support layer side, whilst 'external' is defined as on the active layer side. Whether internal or external correspond with the feed side or draw side depends on the orientation of the membrane. There is a tendency in the literature to label configurations with the active layer facing the feed solution as FO mode, with configurations with the active layer facing the draw solution as PRO mode. This terminology is not entirely universal, but

we use it here as it appears to be by far the most common. In figure 1, asymmetric membranes in FO and PRO configurations are shown with factors relevant to water and salt flux and concentration polarization illustrated.

Concentration polarization leads in all cases to deviation of the water flux from ideal as described by equation 4, with the terms for bulk osmotic pressure replaced by the osmotic pressure of the parts of the feed and draw solutions immediately adjacent to the membrane, which will generally lead to a significantly attenuated osmotic pressure difference across the membrane active layer [41-45]. This is in effect due to an increase in the concentration of the feed solution and decrease in the concentration of the draw solution close to the membrane, leading to a reduction of water flux.

### 2.3.1 External Concentration Polarization (ECP)

ECP occurs on the active side of an asymmetric membrane which may be oriented to the feed side (FO mode) or draw side (PRO mode). ECP may be concentrative or dilutive depending upon whether an increase in the concentration of solute or solvent occurs in the vicinity of the active layer.

If the membrane is in the FO mode, that is permeate flows from the active side of an asymmetric membrane to the support side, then as solute is rejected the solute concentration will increase in the vicinity of the active layer leading to concentrative ECP to occur. A modulus can be defined for the concentrative ECP, which is a ratio of the membrane to bulk osmotic pressures [44]:

$$\frac{\pi_{F,m}}{\pi_{F,b}} = \exp\left(\frac{J_w}{k_f}\right) \quad (13)$$

where  $\pi_{F,m}$  is the osmotic pressure at the membrane active layer. In the case of concentrative ECP then  $\pi_{F,m} > \pi_{F,b}$ .

When the membrane is in the PRO configuration then convective flow of fluid through the membrane will lead to a decrease in draw solution concentration resulting in dilutive ECP close to the active layer. Here:

$$\frac{\pi_{D,m}}{\pi_{D,b}} = \exp\left(-\frac{J_w}{k_d}\right) \quad (14)$$

where  $\pi_{D,m}$  is the osmotic pressure close to the membrane on the draw side. For dilutive ECP then  $\pi_{D,m} < \pi_{D,b}$ . ECP can be mitigated by increasing cross-flow velocity or by improving mixing by increasing turbulence of the cross-flow, such as by improved design of feed spacers [46]. As the water flux increases, effects of ECP have to be taken into account. A version of equation 4 including these terms was given by McCutcheon and Elimelech [44]:

$$J_w = A \left[ \pi_{D,b} \exp\left(-\frac{J_w}{k}\right) - \pi_{F,b} \exp\left(\frac{J_w}{k}\right) \right] \quad (15)$$

However, the lack of applied hydraulic pressure means that build-up of solutes on the active layer of the membrane is much less severe for FO than pressure driven membrane filtration techniques such as RO.

### 2.3.2 Internal concentration polarization (ICP)

ICP occurs within the support layer of the membrane. As such the diffusion rate of ions to or from the active layer are hampered by the material of the support layer leading to ICP being much more dependent on the diffusion rate of the solutes. Like ECP, ICP can be both concentrative or dilutive.

Concentrative ICP occurs when the support layer of an asymmetric membrane is adjacent to the feed solution, as in the PRO mode. As a result feed solute molecules build up within the support layer, reducing osmotic pressure difference across the membrane.

Of major concern for FO applications is dilutive ICP. This is a reduction of draw solute concentration within the support layer due to convective flow of water through the active layer. Unlike ECP, this

issue cannot be solved though increasing cross flow velocity or flow turbulence due to support layer restriction. Repopulation of solute close to the membrane is therefore dependent on diffusion rate. As a result this has led to specialist FO membranes with greatly reduced support layer thickness [3]. This also makes choice of a suitable draw solute with low diffusion rate necessary where dilutive ICP is a major issue. However, recent work by Heikkinen et al [47] used ultrasound applied to the porous support layer of a membrane to partially alleviate ICP. An increase of flux of 75% was noted when using ultrasound with a TFC membrane. However, ultrasound was ineffective with a CTA membrane. In the case of dilutive ICP a modulus may also be defined as before [44]:

$$\frac{\pi_{D,i}}{\pi_{D,b}} = \exp(-J_w K) \quad (16)$$

where  $\pi_{D,i}$  is the osmotic pressure of solution within the support layer adjacent to the active layer. Loeb et al [38] derived the following equation for the solute flow resistivity within the porous support of an asymmetric membrane in the case of dilutive ICP:

$$K = \left(\frac{1}{J_w}\right) \ln \frac{B + A\pi_{D,m} - J_w}{B + A\pi_{F,b}} \quad (17)$$

where  $B$  is the solute permeability coefficient of the support layer.  $B$  can be further related to both the fractional salt rejection,  $R$ , and water permeability by [20, 38]:

$$B = \frac{(1 - R)J_w}{R} \quad (18)$$

Again, equation 4 can be modified to include effects of both concentrative ECP and dilutive ICP [44]:

$$J_w = A \left[ \pi_{D,b} \exp(-J_w K) - \pi_{F,b} \exp\left(\frac{J_w}{k}\right) \right] \quad (19)$$

A more sophisticated model based on film theory relating the water flux to the water permeability, the salt permeability,  $B$ , diffusion coefficient and the film side mass transfer coefficient  $k_f$ , and taking into account concentrative ECP and dilutive ICP was reported by Tiraferri et al [48, 49]:

$$J_w = A \left\{ \frac{\pi_D \exp\left(-\frac{J_w S}{D}\right) - \pi_F \exp\left(\frac{J_w}{k}\right)}{1 + \frac{B}{J_w} \left[ \exp\left(\frac{J_w}{k}\right) - \exp\left(-\frac{J_w S}{D}\right) \right]} \right\} \quad (20)$$

Here the concentrative ECP and dilutive ICP are accounted for by the terms  $\exp(J_w/k)$  and  $\exp(-J_w S/D)$  respectively. This allows determination of  $S$  from experimentally derived values for the water flux, and water and solute permeability coefficients. However, here only a single mass transfer coefficient for the boundary layer is used, whereas we know from eq (10) that there are several distinct mass transfer coefficients at play. In seeking to improve the accuracy of predictions of the structural parameter, Bui et al [50] derived an alternative flux model which includes terms for the mass transfer coefficients at both feed and draw sides:

$$J_w = A \left\{ \frac{\pi_{D,b} \exp\left[-J_w \left(\frac{1}{k_d} + \frac{S}{D_d}\right)\right] - \pi_{F,b} \exp\left(\frac{J_w}{k_f}\right)}{1 + \frac{B}{J_w} \left\{ \exp\left(\frac{J_w}{k_f}\right) - \exp\left[-J_w \left(\frac{1}{k_d} + \frac{S}{D_d}\right)\right] \right\}} \right\} \quad (21)$$

where  $D_d$  is the solute diffusion coefficient in the bulk draw solution. It should be noted that these flux equations all assume that the Van't Hoff relationship is valid, that is a linear proportionality is preserved between the osmotic potential and the solute concentration in the vicinity of the membrane.

Work by Nagy generated an alternative equation for water flux for FO which also accounts for concentrative and dilutive concentration polarization [51]. For membranes aligned in the FO mode:

$$J_w = A \left[ \pi_{D,b} \left( \frac{C_{D,i}}{C_{D,b}} - \frac{C_{F,m}}{C_{D,b}} \right) - \Delta P \right] \quad (22)$$

where  $C_{D,i}$ ,  $C_{D,b}$  and  $C_{F,m}$  are the draw solute concentrations at the membrane active/support layer interface, at the bulk draw side and at the feed side active layer surface respectively.

It is generally agreed that the various structural parameters of the membranes contribute to ICP. However, there has been some past disagreement about the role of the diffusion coefficient of the draw solution. In the work of McCutcheon and Elimelech [44] it was concluded that both the

solution diffusion coefficient and the support characteristics of the membrane contribute to ICP. However, later work by Tan and Ng [52] suggested that the membrane support layer properties alone affected ICP. It is worth noting that both studies looked exclusively at NaCl as a draw solute. Later work by Yasukawa et al [53] compared NaCl with polyethylene glycol (PEG) molecules of various molecular weights. The authors found a clear correspondence between the PEG molecular weight, and hence diffusion rate, and the severity of ICP.

#### *2.4 Reverse Solute Flux*

Another major issue affecting FO membrane processes is the reverse flux of solute across the membrane. An ideal FO membrane should allow easy passage of solvent across the membrane, whilst rejecting practically all solute molecules. However, in practice this is not necessarily the case and can be a major problem for FO processes [14, 54-59], by increasing membrane fouling [59, 60], reducing the concentration gradient between the feed and draw solutions and by contaminating the feed water [36]. This reverse solute flux is a result of the concentration gradient necessary for the FO process to function [1]. Reverse diffusion through the membrane must be distinguished from back diffusion, which is a result of concentrative ECP effects at the feed side [38]. Solute flow across the membrane follows Fick's law, which relates it to the solute permeability and the concentration gradient across the active layer,  $\Delta C$  [46]:

$$J_s = B \Delta C \quad (23)$$

where  $J_s$  is the solute flux. It should be noted that in the case of FO, unlike RO, solute diffusion occurs in both directions, with reverse solute diffusion specifically referring to flow from the draw side into the feed water. This means that small molecules with high diffusion constants tend to have a greater reverse solute flux. As a result, in situations where reverse solute flux is a particular problem, larger solutes with higher diffusion constants may be preferable. It is worth noting however, that as shown above, high diffusion constants tend to reduce dilutive ICP by diffusion



quickly through the support layer. In choosing a suitable draw solution therefore, a decision may need to be made as to whether reverse salt flux or ICP is the more pressing problem.

For an asymmetric membrane the reverse solute flux can be separated into that across both the active layer and the support layer. According to Phillip et al [58] the solute flux through the support layer can be described by the following relationship:

$$J_s^S = \frac{J_w \left[ \frac{J_w t_s \tau}{D\varepsilon} \right] C_{D,i}^S - C_{D,b}}{\exp\left(\frac{J_w t_s \tau}{D\varepsilon}\right) - 1} \quad (24)$$

where  $J_s^S$  is the solute flux through the support,  $C_{D,i}^S$  is the draw solute concentration at the support layer side of the active layer-support layer interface (which is not experimentally accessible),  $C_{D,b}$  is the bulk draw solute concentration and  $t_s$  is the thickness of the support layer. Within the active layer however, solute flux is [58]:

$$J_s^A = -\frac{D^A}{t_A} (C_{D,i}^A - 0) \quad (25)$$

where  $J_s^A$  is solute flux through the active layer,  $D^A$  is the draw solute diffusion coefficient through the active layer,  $C_{D,i}^A$  is the draw solute concentration on the active layer side of the active layer-support interface and  $t_A$  is the active layer thickness. A combined equation for a complete asymmetric membrane which removes the experimentally inaccessible  $C_{D,i}^S$  and  $C_{D,i}^A$  is [58]:

$$J_s = \frac{J_w C_{D,b}}{1 - \left(1 + \frac{J_w t_A}{D^A H}\right) \exp\left(\frac{J_w t_s \tau}{D\varepsilon}\right)} = \frac{J_w C_{D,b}}{1 - \left(1 + \frac{J_w}{B^A}\right) \exp\left(\frac{J_w S}{D}\right)} \quad (26)$$

where,  $H$  is the partition coefficient and  $B^A$  is the solute permeability coefficient for the active layer:

$$B^A = \frac{D^A H}{t_A} \quad (27)$$

Another property of interest in FO processes is the specific reverse solute flux [61]:

$$J_{specific} = \frac{J_s}{J_w} \quad (28)$$

This is an important parameter when selecting a FO membrane, as it gives an indication of the membrane selectivity and is directly related to the efficiency of an FO process [1, 61]. Furthermore, this value is unaffected by the concentration of the draw solution [58]. Knowledge of both the water and solute flux can be used to calculate solute resistivity [62]:

$$K = \frac{1}{J_w} \ln \left( \frac{J_s + J_w C_{D,b}}{J_s + J_w C_{D,i}} \right) \quad (29)$$

A more accurate model for the reverse salt flux was proposed by Suh and Lee, when modelling reverse solute flux during FO with the effects of concentration polarization on both sides of an asymmetric membrane considered [63]:

$$J_s = B \left( \frac{C_{D,b} + \frac{J_s}{J_w}}{\exp(J_w K) \exp\left(\frac{J_w}{k_d}\right)} - \left( C_{F,b} + \frac{J_s}{J_w} \right) \exp\left(\frac{J_w}{k_f}\right) \right) \quad (30)$$

This equation takes account of ICP and ECP as well as reverse solute draw flux, unlike eq. 23 which considers only the bulk properties of the feed and draw solutions.

The reverse fluxes of three neutral draw solutes (urea, glucose and ethylene glycol) across an asymmetric membrane were investigated by Yong et al [64]. The urea and ethylene glycol permeated at a much faster rate than glucose, and for these two solutes an extra resistance to mass transfer was observed. Whilst this rapid permeation caused ECP to occur on the feed side of the membrane, this was insufficient to account for the low water permeation observed. The authors ascribed this observation to be due to a coupling occurring between the water and salt fluxes within the membrane active layer, which needed to be accounted for by the inclusion of a reflection coefficient,  $\sigma$ :

$$J_s = \frac{B}{J_w A n R T \sigma} \quad (31)$$

Where  $n$  is the number of ions produced by dissolution of the draw solute. The reflection coefficient is necessary for membranes which are imperfectly selective and has a value between zero, when no

solute rejection occurs, and unity when solute rejection is total [65]. This rejection coefficient was defined by Bui et al [50] as:

$$\sigma = \frac{1/B}{1/B + 1/k_f + 1/k_d} \quad (32)$$

### 3 Draw Solutes and Solutions

#### 3.1 Selection of Suitable Draw Solutes

As the function of the draw solution is central to the FO process in determining both the water flux through the membrane as well as the regeneration costs, then selection of a suitable draw solute is of paramount importance. In choosing an effective draw solution a number of criteria will need to be satisfied: i) it must be able to generate a high enough osmotic pressure to allow an effective driving force for the FO process; ii) it should have a low viscosity to allow easy pumping around the system and improved water fluxes; iii) low reverse solute flux; iv) a high diffusion coefficient to reduce ICP; v) be available in large amounts at low cost; vi) must be easy to re-concentrate at a competitive cost; vii) if there is risk of contamination of the finished product water any toxicity of the draw solute will be a major concern. However, there may be some contradictions between or exceptions to some of these criteria. For example, solutes of small size, such as NaCl, tend to have high diffusion coefficients which reduces ICP, but their size also leads to relatively high reverse solute fluxes. In addition, several groups have examined the use of polymer hydrogels as draw agents, which have a high viscosity [66]. But in these instances the draw agent does not necessarily need to be pumped and is regenerated *in situ*, making viscosity irrelevant [67].

Achili et al [36, 68] proposed a protocol for the selection of inorganic draw solutes. This process began with a desktop screening process consisting of a series of questions, followed by evaluation of water flux and reverse salt flux from FO experiments and finally an analysis of reconcentration costs of the draw solutes using commercial RO system design software. Over 500 compounds were initially

considered, with 14 selected for lab tests. However, only RO was considered as a regeneration step. Kim et al [69] also proposed a systematic approach for selection of optimal draw solute. Draw solute selection was considered as part of a holistic approach to FO system design. OLI and ASPEN chemical databases were used to narrow 4058 candidate compounds down to 7. Optimal regeneration systems were designed for each short-listed compound and the economies of each approach used to select the best candidate.

Research into draw solutes can be categorised in several ways: by the physico-chemical properties of the draw solute; by the regeneration methods used; by the type of feed-water to be used and whether the intended product is a cleaned permeate or a de-watered feed. As all draw solutes can be categorised easily by the first approach that will be the primary approach here. However subsequent sections will deal with the different recovery approaches available. Table 1 shows a summary of the main types of draw solution, categorized by their properties, with data including osmotic pressure reported in the literature, costs of the solutes or precursor materials, advantages and disadvantages and recovery methods.

### *3.2 Gases and Volatile compounds*

The earliest draw solutes used were dissolved gases, such as ammonia and carbon dioxide, as described by Neff in a 1964 patent describing a solvent extractor using a semi-permeable membrane to produce potable water from sea water [70]. Here, the dissolved gases exist in the draw side as ammonium bicarbonate ions, with applied heat used to evolve ammonia and carbon dioxide gases leaving behind the purified water. More recently, McCutcheon et al revived ammonia-carbon dioxide based FO [6, 7]. The researchers found they could generate high water fluxes due to the very high osmotic pressures available with the bicarbonate solutions, although fluxes were lower than initially expected due to the presence of ICP. Another issue is that the relatively high diffusion constant of ammonia dissolved in aqueous solution ( $1.64 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  [71]) will promote reverse

solute flux. Whilst this is an issue for any small molecule or ionic species, in the case of ammonia there is the additional problem of ammonia being a nutrient, which can thus promote increased biofouling on the feed side of the membrane [72]. However, as many potential feed water streams, such as municipal wastewater and water from natural sources, may contain quantities of nutrients, it is unclear what the scale of the effect of additional nutrients from reverse ammonia diffusion will be during prolonged processing of such contaminated waters.

A tri-methylamine- $\text{CO}_2$  (TMA- $\text{CO}_2$ ) system as a draw agent was investigated by Boo et al [54] and its performance compared with  $\text{NH}_3$ - $\text{CO}_2$  and NaCl draw solutes. The osmotic pressure for the TMA- $\text{CO}_2$  system was comparable with the NaCl solution for both at 1.0 M concentrations and was higher than for the  $\text{NH}_2$ - $\text{CO}_2$  solution. Experiments were carried out with two different membranes and in the FO and PRO orientations. Water flux was comparable for all draw solutes, but the reverse solute flux was slightly lower for the TMA- $\text{CO}_2$ . The main advantage for the TMA- $\text{CO}_2$  system over the  $\text{NH}_3$ - $\text{CO}_2$  was that it had a lower energy requirement for regeneration calculated using a simulated distillation column, due to it having a high Henry's law constant and low enthalpy of vapourization. However, the low volatility also meant that TMA has a low odour threshold, which makes its undesirable fishy smell detectable at very low concentrations (< 0.6 ppb).

The use of sulfur dioxide was also proposed as a draw solute in two early patents. Glew [73] proposed an aqueous  $\text{SO}_2$  solution, or a solution consisting of  $\text{SO}_2$  and aliphatic alcohols, as a draw solution, whereas Batchelder [74] proposed using a salt solution with dissolved  $\text{SO}_2$  as a draw solution. In both cases the  $\text{SO}_2$  was recovered by thermal processes. However,  $\text{SO}_2$  is not ideal due to its corrosive nature and the potential bad odours it may impart to the recovered permeate.

Aqueous alcohol solutions have also been considered as possible draw solutions. McCormick et al [75] examined the diffusion of ethanol through an unoptimised membrane. It was found that for the membranes studied selectivity was very variable and ethanol loss to the feed through reverse

diffusion was probably too high to make ethanol a commercially acceptable draw solute using conventional membranes.

Sato et al [76] investigated the use of dimethyl ether (DME) as a draw solute. They were able to recover permeate from a 0.5 %wt feed solution with a 19 %wt DME solution used as the draw solution, which was made by dissolving DME gas under pressure into ion-exchanged water. Permeate water was allowed to recover from the diluted draw solution by simply allowing the dissolved gas to volatilize at room temperature. Figure 3 shows the osmotic pressure of DME solutions compared with inorganic salts. Note how widely the measured osmotic pressure varies from that calculated by the Van't Hoff equation, especially at higher concentrations.

### *3.3 Inorganic Draw Solutes*

The most common draw solutes are monovalent salts, particularly NaCl, with recent research still investigating their use [1, 45, 55, 56, 77, 78]. These have a number of advantages – they are cheap and available in large quantities, can produce relatively high osmotic pressures and resultant water fluxes and their high diffusion coefficients are helpful in retarding concentrative ICP and their solutions are low viscosity. However, their small size tends to lead to large reverse salt fluxes. This can have a negative effect on the fouling at the feed side. She et al [79] examined the effect of reverse salt diffusion of inorganic draw solutes on organic fouling during PRO operation. It was found that divalent cations promoted significant amounts of fouling by the anionic polysaccharide alginate, a common constituent of bacterial cell walls. Furthermore, increased draw solute concentration dramatically increased fouling due to synergistic effects due to increased water flux and increased reverse solute diffusion occurring at higher concentrations.

Multivalent salts, such as  $MgCl_2$  and  $CaCl_2$  have several advantages over monovalent salts . Their larger radii of hydration leads to reduced reverse salt fluxes compared with NaCl [36, 68, 78], and it

is possible to achieve higher osmotic pressures with the same molar concentrations, due to the greater number of ionic species formed on dissociation [3]. Zho et al [80] studied the use of divalent draw solutes ( $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$ ) in a FO-nanofiltration (NF) process. For the FO process the flux reversal point, i.e. the point at which draw and feed solutions became equalised, was at a concentration of 0.6M, which was then used as the concentration as the feed for a NF recovery process. Comparison of their hybrid FO-NF process with conventional RO showed that the hybrid process required lower hydraulic pressure, had a lowered flux decline due to fouling and an increased flux recovery after cleaning compared with RO. Achilli et al [36] studied a great number of mono- and divalent ions as draw solutes, at various concentrations designed to give the same bulk osmotic pressure. Water fluxes varied from  $10.9 \text{ L m}^{-2} \text{ h}^{-1}$  for KCl to  $5.5 \text{ L m}^{-2} \text{ h}^{-1}$  for  $\text{MgSO}_4$  at undiluted draw solution osmotic pressures of 2.8 MPa. These differences were attributed solely to ICP, as draw solution osmotic pressures had all been set at the same level. In addition the authors carried out a comparison of replenishment costs for all of the solutes, using combined FO and RO process costs. It was found that costs were highest for KBr ( $\$0.7 \text{ L}^{-1}$ ) and lowest for  $\text{Na}_2\text{SO}_4$  ( $\$0.004 \text{ L}^{-1}$ ), progressing from highest to lowest:  $\text{KBr} > \text{NH}_4\text{HCO}_3 > \text{Ca}(\text{NO}_3)_2 > \text{KCl} > (\text{NH}_4)_2\text{SO}_4 > \text{CaCl}_2 > \text{K}_2\text{SO}_4 > \text{NH}_4\text{Cl} > \text{MgCl}_2 > \text{MgSO}_4 > \text{KHCO}_3 > \text{NaCl} > \text{NaHCO}_3 > \text{Na}_2\text{SO}_4$ . Several of these draw solutions cause problems with scaling, so have been suggested to only be used in situations concentration of feeds is intended, without secondary steps to reconcentrate the draw solution [1].

Ansari et al [81] used seawater directly as a draw solution for the recovery of phosphorus from digested sludge concentrate. A large draw solution / feed solution volume ratio was used to minimise draw solution dilution, with 80% recovery achieved after 3 days processing. Sea water is an ideal draw solution to use for dewatering applications, as diluted sea water can be discharged into the sea without need for further treatment, assuming no contamination has occurred.

The use of  $\text{CuSO}_4$  solution as a draw agent for brackish water desalination was investigated by Alnaizy et al [82]. The maximum solubility of  $\text{CuSO}_4$  gives a maximum possible osmotic pressure of

2.99 MPa, which is insufficient for desalination of sea water or RO brines. However, it was attractive for brackish or lower salinity water purification due to simple reconcentration by precipitation by reaction with  $\text{BaSO}_4$ . The resultant  $\text{CuO}$  precipitate can then be regenerated with reaction with  $\text{H}_2\text{SO}_4$ .

One group of largely inorganic compounds of interest as draw solutes is the use of fertilizers [18, 83]. The major advantage of using concentrated fertilizer solutions as draw agents is that they can be directly re-used for fertigation, without the need for reconcentration for re-use and the corresponding energy costs. Phuntsho et al examined a range of fertilizer components as draw agents [19, 84]. Urea was found to perform poorly, when using seawater as a feed, due to low osmotic pressure, hydrophobicity and agglomeration. The highest performance ratio was found for  $\text{NH}_4\text{NO}_3 > \text{KCl} > \text{NH}_4\text{Cl}$ . Blended fertilizers demonstrated lower osmotic pressures than that of individual components. Zhou and He [14] examined the use of commercially available fast release fertilizers as draw solutes for wastewater release applications. Like Phuntsho et al, it was found that the low urea content fertilizer blend had a better performance than blends with higher urea contents. Significant reverse salt flux was observed to occur during the first 24 hours of operation. In addition, some loss of nutrients were observed, which was ascribed to volatilization of urea at the feed side of the membrane after reverse solute flux had occurred. Potassium and phosphate content both decreased by 9 and 8% respectively due to precipitation or salting out on the sides of glassware. A later study by Chekli et al [17] examined 9 different inorganic chemicals used in fertilisers as draw solutes with a polyamide membrane, with the aim of simultaneously de-watering waste water and production of nutrient solutions suitable for hydroponics applications. Unexpectedly, although the solute with the highest bulk osmotic pressure was  $\text{Ca}(\text{NO}_3)_2$  (16.63 MPa)  $\text{NH}_4\text{Cl}$  and  $\text{KCl}$ , with much lower osmotic pressures (5.42 and 7.56 MPa respectively) had the highest water fluxes. It was also found that the diluted draw solutions were still much too concentrated to be directly applied as plant feed and had to be diluted on the order of 100 times before they were rendered useable.



Sodium phosphate has been used as a draw solute to dewater a simulated high-nutrient feed [85, 86] with MD regeneration. Performance was found to be connected to the draw solution pH value (see figure 4). Water flux was greatest ( $12.5 \text{ L m}^{-2} \text{ h}^{-1}$ ) at pH 9, with a coincident lowest value reverse salt flux. The specific reverse salt flux was found to be lower than for a NaCl solution of similar concentration (both 0.1M concentration). This was attributed to higher complexation between  $\text{Na}^+$  ions and  $\text{HPO}_4^{2-}$  at pH 9 leading to a reduced number for free  $\text{Na}^+$  ions. Regeneration was by MD with one membrane found to have a 100% salt rejection with a flux of  $10.3 \text{ L m}^{-2} \text{ h}^{-1}$ .

### *3.4 Organic Draw Solutes*

#### *3.4.1 Simple Organics*

Due to their easy availability and non-toxicity sugar compounds have been investigated as potential draw solutes. Their larger size, compared to monovalent salts, is an advantage when one considers reverse salt flux. However, solutions of sugar are unable to achieve the high osmotic pressures achievable with monovalent and divalent salts. The simple monosaccharides fructose and glucose were investigated as potential draw solutes for seawater desalination using a cellulose acetate membrane in an early FO paper [87], with an intended use in emergency packs on lifeboats. Osmotic pressures were found for the 2.0 M hypertonic sugar solutions of about 5.6 MPa, easily enough to recover water from seawater sources [1]. Later studies with the disaccharide sucrose [15] found a similar osmotic pressure, sufficient for the effective concentration of tomato juice. As for other molecules which act as nutrients, sugars are potential promoters of biofouling if mixing with the feed side occurs.

Another category of solutes which have been investigated as possible draw solutes are ionic liquids. A recent study investigated the use of several amphiphilic organic ionic liquids [88]: tetra butylphosphonium 2,4 dimethyl benzene sulfonate ( $\text{P}_{4444}$  DMBS); tetra butyl phosphonium mesitylene sulfonate ( $\text{P}_{4444}$  TMBS); and tributyl-octyl- phosphonium bromide ( $\text{P}_{4448}\text{Br}$ ) . A non-linear correlation was observed between the osmolality and molality, which was attributed to hydrophobic

association between molecules occurring at high concentrations. These liquids were capable of drawing water from feed water with a saline content approximately three times that of seawater. Regeneration was brought about by increasing the temperature to above the lower critical solution temperature (LCST) (between 30-50 °C for the substances studied), causing the diluted draw solution to undergo a phase separation. The majority of the draw agent could be recovered by sedimentation, with the remainder of the draw agent recovered from the supernatant by NF. The energy requirement for the FO process plus regeneration was estimated to be significantly lower than for a similar separation performed using RO. Zhong et al [89] used a thermally responsive ionic liquid as a draw agent. The 3.2 M solution of protonated betaine bis(trifluoromethylsulfonyl)imide was capable of drawing water from 3.0 M saline water, with the temperature maintained at a constant 56 °C. The diluted draw solution was then allowed to cool to below the upper critical solution temperature causing phase separation to spontaneously occur forming an ionic liquid rich phase and a water rich phase (process scheme shown in figure 5). The ionic liquid rich phase could then be reused as draw solution without further concentration needed.

Switchable polarity solvents (SPS) based on tertiary amines are of recent interest [33]. This class of molecules change their miscibility with water depending upon the concentration of dissolved CO<sub>2</sub>. Protonation of N,N-dimethylcyclohexamine (N(Me)<sub>2</sub>Cy) brought about by an increase in dissolved CO<sub>2</sub> concentration leads to it becoming readily dissolved in water. The draw solute can be returned to the immiscible state by using heat from a low grade source and purging with N<sub>2</sub> gas (see figure 6 for process outline). This allows the majority of the N(Me)<sub>2</sub>Cy to be mechanically recovered, with the remaining trace amounts removed using RO. High osmotic pressures were found for the draw solutions tested, which produced high fluxes when treating saline solutions. Computer models of this system have shown it to be competitive in terms of the energy needed to treat water produced by gas and oil drilling operations [90]. However, care should be taken with choice of membranes, as it was found that conventional cellulose tri-acetate membranes were damaged by N(Me)<sub>2</sub>Cy, leading to reverse solute leakage, whilst polyamide membranes appeared to be unaffected [33]. The SPS 1-

cyclohexylpiperidine (CHP) was used as a thermolytic draw agent [91]. This substance demonstrated comparable performance with the  $N(\text{Me})_2\text{Cy}$  but had an improved compatibility with polyamide membranes, which was demonstrated by long term filtration testing.

Organic ionic salts have been examined as potential draw agents. For instance Bowden et al [68] investigated the use of several in an osmotic membrane bioreactor. The amino poly-carboxylic acid ethylene diaminetetraacetic acid (EDTA) has been examined by several researchers as a draw solute. Hau et al [92] used EDTA to dewater a high nutrient sludge. Optimal operating pH was determined to be pH 8, where it outperformed NaCl draw solutions with the same molar concentration in terms of high water flux and low reverse solute flux. This was due to most of the EDTA taking the form of  $\text{H}(\text{EDTA})^{3-}$ , with each molecule coordinating with 3  $\text{Na}^+$  ions, leading to an advantage in the number of osmoles formed over NaCl. However, at concentrations of over 1M solution viscosity increased and EDTA- Na dissociation decreased leading to loss of flux. Another study examined the use of EDTA complexed with a variety of metal ions (Zn, Mn, Ca and Mg) as draw solutes [93]. When the membrane was oriented in the FO mode (i.e. active layer facing the feed solution) flux values were similar to, but slightly lower than, NaCl, but were superior to NaCl when membranes were oriented in the PRO mode configuration. When using a NF process for draw solute regeneration recovery of > 96% was achieved when the diluted draw had a concentration of 0.25 M, with recovery decreasing for more dilute solutions. Nguyen et al [94] investigated the use of direct contact membrane distillation for recovery of the disodium form of EDTA. This process required lower operating pressures than pressure driven membrane processes and was capable of salt rejection values as high as 99.99%, with the flux not greatly affected by solution osmolality. It was concluded that this would be an effective process for EDTA recovery, which had previously been problematic, especially when low grade waste heat from other processes is available.

Hexavalent phosphazene salts were synthesized for use as draw solutes by Stone et al [95]. FO tests were carried out with pure water feed solutions, although the measured osmotic potential of both

salts at the concentrations investigated were considered to be high enough for seawater desalination. Li salts had a higher dissociation than Na salts, and hence a higher osmolality. This resulted in higher initial fluxes for the Li salts. One drawback was that some hydrolysis of the cellulose acetate membranes used occurred at pH 8.

Compounds based on 2-methylimidazole have also been studied as potential draw solutes. These compounds were found to have good solubility and were either charged or uncharged in aqueous solution. Charged compounds demonstrated higher water fluxes, due to their greater ionic strengths. The two charged species exhibited similar water fluxes, despite one being monovalent and the other being divalent, which was designed to have a greater osmolality based on the Van't Hoff equation. This was due to a greater ICP cancelling out the benefits of the higher charge.

A major drawback to using organic draw solutes compared with simple inorganics is that their larger sizes leads to decreased diffusion coefficients. As can be seen from equations 5 and 6 this affects the resistivity of the membrane to solute flow both through the membrane and the porous support layer. Whilst the attenuation of reverse solute flux is desirable, the slow diffusion through the porous support on the draw side of the active layer also leads to enhanced ICP, as can be seen for both equations 20 and 21, leading to reduced effective osmotic pressure differences across the membrane.

#### *3.4.2 Polyelectrolyte Draw Solutes*

The use of polyelectrolytes as draw agents has been an attractive area of research, due to the high osmolality of charged polymer solutions and the high molecular weight leading to potentially lowered reverse salt flux and easier recovery if using pressure driven membrane processes. One investigation examined poly acrylic acid sodium salts (PAA-Na) based draw solutions [96]. In terms of water flux the performance was found to be comparable with a model seawater solution, but showed a greatly reduced reverse solute flux. It was noted that while the bulk draw osmotic pressure increased with concentration, this relationship was not linear, which was attributed to a

decrease in dissociation at high concentrations. Duan et al [97] examined sodium lignin sulfonate (NaLS) as a draw agent. Lignin is a naturally occurring structural component of wood fibres and is available in large amounts cheaply as a waste product of wood pulp manufacture. A solution with a concentration of  $60 \text{ g kg}^{-1} \text{ H}_2\text{O}$  demonstrated an osmotic pressure of 7.8 MPa, sufficient for desalination of seawater. Laohaopranon et al [98] also investigated the use of natural polyelectrolytes as draw agents. Their approach was to graft 2,3 epoxy propyl trimethylammonium chloride onto corn starch. A 30 %wt. solution had an osmotic pressure of 1.21MPa, insufficient for seawater desalination, but capable of dewatering brackish or waste water. The intended application was in the purification of proteins without protein denaturation. The draw solution was regenerated using UF with a rejection rate > 99%.

Poly (aspartic acid sodium salts) (PAspNa) has also been investigated as a potential draw solute [99] and were observed to show water fluxes comparable with NaCl and  $\text{MgCl}_2$  solutions, but markedly lower reverse solute fluxes, leading to much lower  $J_{\text{specific}}$  values. The specific costs of these three draw solutions were considered, based upon the cost of materials and amount needed to produce a litre of draw solution, finding a much lower operating cost ( $\$0.002 \text{ L}^{-1}$  for PAspNa compared with 0.011 and  $0.016 \text{ \$ L}^{-1}$  for NaCl and  $\text{MgCl}_2$  respectively). However, this comparison did not take into account costs involved with draw solution reconcentration and permeate recovery. As PAspNa is often used commercially as an anti-scalant, the effects of its reverse flux on mineral scaling was investigated. Whilst conducting FO tests using a synthetic wastewater feed containing only inorganic ions with either PAspNa and NaCl draw solutions, flux decline was much lower for the PAspNa draw solution tests. In later measurements [100], draw solutes of NaCl blended with either PAspNa or the anti-scalant sodium hexametaphosphate (SHMP) were found to reduce scaling by a gypsum feed solution compared with NaCl draw solution alone.

Another research team used a dendrimer based draw solute for desalination of seawater consisting of poly(amidoamine) terminated with sodium carboxylate groups (PAMAM-COONa) [57]. Using a

33.3 %wt. solution of PAMAM-COONa water fluxes were achieved of  $9 \text{ L M}^{-2} \text{ h}^{-1}$ , with a lower reverse solute flux than for NaCl draw solutions. The dendrimer solution was found to have a lower viscosity than for solutions of other polymers of equal molecular weight. It was also found that the generation number (i.e. the amount of branching) affected a number of parameters: viscosity; osmolality and water flux. For each generation the ratio between the number of terminal groups and molecular weight decreases along with the  $\text{Na}^+$  dissociation rate, leading to lower solution osmotic pressures. Recovery of the draw agent was by MD. The use of another polyelectrolyte, poly (sodium-4-syrenesulfonate) (PSS), was investigated at three different molecular weights [101]. PSS is highly water soluble and has a high degree of disassociation. Water flux measurements using a DI feed water were over  $12 \text{ L m}^{-2} \text{ h}^{-1}$ . PSS was recovered from diluted draw solution using an UF process. However, decreasing performance of the recycled draw solution suggested that not all PSS was recovered for each cycle.

#### 3.4.3 Environmentally Responsive Polymer Solutions

Cai et al [102] investigated the use of switchable pH-responsive polymers as draw agents. Poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) is a low molecular weight polymer which becomes a polyelectrolyte at low pH. This pH lowering was achieved by purging solutions with  $\text{CO}_2$  gas to create a solution with a high osmotic potential, with the osmolality increasing by a factor of 4 after  $\text{CO}_2$  purging. Draw solutions were regenerated, as for the switchable polarity solvents mentioned previously, by purging with an inert gas at temperatures above their LCST, causing precipitation to occur. Osmotic pressures for the protonated PDMAEMA were high enough for seawater desalination to become a possibility. As for the SPSs, if there is a low grade heat source available to heat spent draw solutions to above the critical temperature of  $40^\circ\text{C}$ , then this can become a very cost effective process. Reverse solute flux was monitored and found to increase with concentration and decrease with compound molecular weight. Interestingly the specific flux was maintained at a constant value, regardless of concentration or molecular weight: 30 mg of PDMAEMA was found to leak for each

litre of desalinated water. Thermo-responsive copolymer based systems have also been utilised, with one study examining the use of poly(sodiumstyrene-4-sulfonate-co-*N*-isopropylacrylamide) (PSSS-PNIPAM) as a draw solute [32]. PSSS is a strong electrolyte, which when PSSS-PNIPAM is dissolved in aqueous solution, creates a large osmotic potential. When using a 33.3 %wt. draw solution with a simulated seawater feed (0.6 M NaCl) fluxes of  $4 \text{ L m}^{-2} \text{ h}^{-1}$  were achieved. The solution was regenerated using MD.

#### 3.4.4 Hydro-acid complexes

The use of hydro-acids complexed with metal ions is an interesting approach to the problems of draw solutes [103, 104]. These compounds are very water soluble, are large enough to have negligible reverse solute fluxes and easy recovery and the abundance of ionic groups leads to high osmotic pressures. A 2013 study used ferric and cobaltous complexes with citric acid (CA) which readily dissociated to produce multiple-charged anions and Na cations [105]. When using a 2M ferrous-citric acid (Fe-CA) draw solution, water permeation rates of  $17.4 \text{ L m}^{-2} \text{ h}^{-1}$  when using a simulated seawater feed containing 3.5 %wt. NaCl. Furthermore, these solutes are easily re-concentrated using NF processes (see figure 7 for an experimental schematic). A later study compared two cobalt hydroacid complexes with the ferric complex, but found that the earlier iron based complex generated superior osmotic pressures, which was attributed to the greater number of ionic species each complex could dissociate into (i.e.  $\pi D \propto n$ ).

Further research used oxalic acid complexed with ferric and chromium (III) ions, with  $\text{Na}^+$  as a counter ion. Again, negligible reverse solute flux was observed, with a specific reverse solute flux of zero. It was noted that having the membranes in the PRO mode consistently outperformed the FO mode for both draw solutions and with both membranes tested. The researchers successfully used these draw solutes for concentration of bovine serum albumin (BSA) without producing conformational changes to the BSA, which was a problem when using NaCl as the draw solute. To

further extend the range of applications of these complexes, removal of As(III) using oxalic complexes as draw solutes was demonstrated in a later study [106].

#### *3.4.5 Stimuli Responsive Hydrogels*

Stimuli responsive hydrogels are hydrogels, often polymers, which undergo a volume change or gel to solution phase change according to some external stimulus, such as temperature, pH, solvent composition change, pressure, light, magnetic field or applied electrical charge, taking up or releasing water as they transition between hydrophilic or hydrophobic character. There have been a number of recent studies to exploit this behaviour to use responsive hydrogels as draw agents in FO processes. For instance, Li et al [66] synthesised four different polymer based hydrogels (see figure 8 for FO process with hydrogel draw agent): two ionic, poly(sodium acrylate)(PSA) and poly(sodium acrylate)-*co*-poly(*N*-isopropyl acrylamide (PSA-NIPAM); and two non-ionic, poly(acrylamide) (PAM) and poly(*N*-isopropylacrylamide) (PNIPAM) with the intention of investigating their charge density on their ability to draw water through the membrane, and also the effect of applied temperature on the dewatering process. Their results were the first to demonstrate the applicability of polymer hydrogels to the FO process, with dewatering of the hydrogel achieved by a thermal process. These hydrogels demonstrated a high water uptake capacity, creating a high osmotic pressure with the ionic hydrogels showing superior performance to the non-ionic hydrogels. Other thermo-responsive hydrogels which have been investigated include PNIPAM with sodium acrylate [107, 108]. Cai et al [109] studied hydrogels based on PNIPAM with polyvinyl alcohol (PVA) and PSA to create hydrogels with a semi-interpenetrating network structure (semi-IPN). Interpenetrating polymer networks consist of two or more polymers which are partly interlaced at the chemical level but not covalently bonded and require breaking of chemical bonds to separate them [110, 111]. The semi-IPN hydrogels released almost 100% of the adsorbed water at a temperature of 40°C. The high viscosity of the hydrogels makes pumping of the swollen hydrogels impractical. As a result the authors



proposed a quasi-continuous FO desalination procedure (see figure 9) with repeated heating and cooling cycles used to draw water through the membrane before release [109]. Such a system only requires temperature variation of 15°C, which could be easily supplied by waste heat from other processes, such as power generation. In addition to this the only process energy required is for pumping. The authors compared the process to more conventional FO using  $(\text{NH}_4)_2\text{CO}_3$  and found that whilst water flux was lower for the hydrogel process, regeneration was much easier.

Electrically responsive polymer hydrogels have also been studied. Zhang et al used hydrogels prepared from mixtures of hyaluronic acid (HA) and PVA [67]. The flux was heavily dependent upon the voltage applied across the filtration cell – see figure 10 for a schematic of their experimental set-up. Water flux was measured at 17.27, 20.95, 25.49, and 26.47  $\text{L m}^{-2}$  for voltages of 0, 3, 6 and 9V respectively, with initial flux values of 1.2, 1.24, 1.52 and 1.82  $\text{L m}^{-2} \text{h}^{-1}$  over 24 hours collection using a pure water feed. These values were lower when using NaCl as the feed, with the flux also dependent upon the feed concentration. Although water flux occurred when no electrical potential was applied, it was calculated by the authors that when taking into account the pumping energy, over a 24hr period the application of 6V lead to a reduced energy demand per unit amount of water than when no electrical potential was applied.

Carbon nanoparticles have been combined, as fillers, with poly(sodium acrylate) based hydrogels. When used as a draw agent the nanoparticles demonstrated improved water flux and rejection due to greater swelling ratios than pure hydrogel alone [112]. However loading of the carbon filler beyond a certain point lead to decreased fluxes, due to the reduction in direct contact between hydrogel particles and the membrane. Magnetic nanoparticles have also been integrated into hydrogels [113]. This allowed for the rapid dewatering of swollen hydrogels due to magnetic field induced heating. The use of the magnetic nanoparticles dispersed throughout the gel matrix allowed an even application of heat, although this was accompanied by a loss of water capacity and a lower osmotic pressure compared with pure hydrogel.

### *3.5 Functionalised Nanoparticles*

The use of nanoparticles functionalised with hydrophilic groups has been investigated by several researchers in recent years. In particular, nanoparticles made of magnetic materials have been of particular interest as they make possible draw solution regeneration by passing through magnetic separators [114, 115]. The large size of magnetic nanoparticles means that reverse solute flux is effectively eliminated and selection of suitable ligands combined with the nanoparticle's high surface area to volume ratio can allow creation of nanoparticle-based solutes with a high osmotic potential.

#### *3.5.1 Nanoparticles Functionalised with Simple Polymers*

The earliest use of functionalised nanoparticles as draw agents was reported by Ling et al [116] who studied magnetic nanoparticles capped with three different types of hydrophilic surface functional groups: 2-pyrrolidone; triethylene glycol (TREG) and PAA. The nanoparticles were fabricated from the iron precursor ferric triacetylacetonate ( $\text{Fe}(\text{acac})_3$ ) using a thermal decomposition method (see figure 11 for the reaction scheme). For all functional groups the solutions showed a much greater osmolality for the functionalised nanoparticles than for the end groups alone across a range of concentrations (see figure 12). This was reflected in improved water fluxes for the functionalised nanoparticles over surface functionalising groups alone. At low concentrations ( $0.05 \text{ mol L}^{-1}$ ) PAA showed the higher flux, followed by TREG and then 2-pyrrolidone. Calculation of the chemical potential energy of surface capping groups showed that the gap in potential energy between the functionalising group and water, which is responsible for the osmotic potential of the surface functionalised nanoparticles, showed the same trend. Nanoparticle recovery was achieved using a

commercially available benchtop magnetic separator. Whilst recovery was efficient, flux dropped after regeneration of the draw solution, which was ascribed to nanoparticle aggregation.

Ge et al [114] coated magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles with PEG diacid ( $\text{PEG}-(\text{COOH})_2$ ), which were synthesised by a previously reported one-pot reaction using  $\text{Fe}(\text{acac})_3$  and TREG [117]. Transmission electron microscopy (TEM) imaging showed the particles to be approximately spherical with the mean size depending upon the ratio of  $\text{PEG}-(\text{COOH})_2$  to  $\text{Fe}(\text{acac})_3$ , with mean diameters of between 4.2 and 11.5 nm [114]. A schematic of the reaction process alongside a TEM image of the nanoparticles is shown in figure 13. Higher flux values were observed when the membrane was in the PRO configuration rather than the FO configuration when using a pure water feed, which was attributed to lower concentration polarization. The water flux decreased as the molecular weight of the PEG ligands increased, with fluxes at 13.5, 13.0 and 11.5  $\text{L m}^{-2} \text{h}^{-1}$  for PEG molecular weights of 250, 600 and 4000 respectively. This was likely due to the smaller particles created with lower molecular weight PEG having a greater cumulative surface area leading to a greater osmotic pressure. However, this change in flux was not linear, due to the effects of concentration polarization.

It was found that particle sizes below 20 nm were superparamagnetic, meaning that they exhibited magnetic properties whilst under a magnetic field, losing their magnetism when the field was turned off. This led to a straightforward recovery technique based upon magnetic separation. A magnetic separator was constructed consisting of a plastic column filled with iron gauze (figure 14) surrounded by an electromagnet. The diluted suspension of magnetic nanoparticles was passed through this column, with nanoparticles adhering to the gauze when the magnet was on and being quickly released when turned off. The magnetic nanoparticles were found to still maintain activity after 9 recycling runs with a decrease in water flux with a pure water feed of less than 5% per pass, decreasing by 21% after 9 passes, attributed to particle aggregation after the recycling step. Treatment of a 50 ml batch of diluted draw took less than 30 min. Mishra et al [118] compared

magnetic nanoparticles coated with either PEG or PAA when used as draw agents. Nanoparticle sizes were similar and both achieved water fluxes in excess of  $13 \text{ L m}^{-2} \text{ h}^{-1}$ .

The problem of particle aggregation during magnetic recovery of nanoparticles in the above investigations is a potential issue when one considers that to be economic nanoparticles must go through very many such recovery cycles if they are to be used practically outside of the laboratory. Ling and Chung investigated the use of ultrasonication, which effectively reduced the size of nanoparticle agglomerates [119]. However, magnetic properties were also seen to be weakened, hampering recovery by magnetic separation methods over several cycles.

### *3.5.2 Nanoparticles Functionalised with Natural Macromolecules*

There are a number of naturally occurring macromolecules which are non-toxic and show high water solubility. As such several have been investigated as ligands for nanoparticle based draw agents. For instance, the polysaccharide molecule dextran has been utilized as a ligand on magnetite nanoparticles [120]. The dextran coated nanoparticles were used as draw agents in FO tests using both pure water and  $2 \text{ g L}^{-1} \text{ MgSO}_4$  as feed (see figure 15) and an initial nanoparticle concentration of  $0.5 \text{ M}$ . Water flux values were higher for smaller nanoparticles containing a greater proportion of dextran (78.03% wt.) than for the smaller nanoparticles with a lower dextran content (64.44 %wt.), due to the greater aggregated surface area with hydrophilic groups.

Citrate is another common biological molecule which has been utilised as a magnetic nanoparticle ligand. Synthesis by co-precipitation of citrate onto magnetite nanoparticles [121] and thermolytic techniques [122] have been reported. Na et al demonstrated that citrate coated nanoparticles have a high negative surface charge and high surface charge density [121]. Using DI water as a feed solution, high initial water fluxes of  $17.3 \text{ L m}^{-2} \text{ h}^{-1}$  were achieved using a  $20 \text{ mg L}^{-1}$  citrate nanoparticle concentration. The flux declined rapidly due to interactions between the citrate coating

and the cellulose triacetate membrane used. To remedy this a magnetic field control (MFC) module was used to limit interaction between citrate and the membrane. This resulted in a lower initial water flux ( $13.7 \text{ L m}^{-2} \text{ h}^{-1}$ ), but was more stable than without the MFC module.

$\text{Na}^+$  functionalised carbonised quantum dots (CQDs), created by heating of CA powder in air followed by dispersion in water with the pH adjusted using NaOH, have been tested as potential draw agents for FO [123]. Solutions using these CQDs generated very high osmotic pressures, with a  $0.5 \text{ g L}^{-1}$  solution demonstrating an osmotic pressure of 5.7 MPa, much more than sufficient for overcoming the osmotic pressure of seawater. This high osmotic pressure was attributed to the small size of the CQDs (mean diameter = 3.5 nm) combined with the ionic richness of their surfaces. When used for FO desalination of seawater initial fluxes of  $10.4 \text{ L m}^{-2} \text{ h}^{-1}$  were obtained, which only reduced slightly after 5 test cycles.

Magnetic nanospheres with a siloxane based hydrophilic surface layer were investigated as draw solutes by Park et al [124]. Siloxane was capped with either PEG (Si-PEG) or carboxyl groups (Si-COOH). Osmotic pressures were measured for  $50 \text{ g L}^{-1}$  solutions of 0.77 MPa and 0.64 MPa for the Si-PEG and Si-COOH respectively, which is insufficient for desalination of seawater using FO, but could be used to purify low salt content brackish water. Water flux values of  $2.13 \text{ L m}^{-2} \text{ h}^{-1}$  were obtained for a pure water feed, dropping to  $0.87 \text{ L m}^{-2} \text{ h}^{-1}$  when 5000 ppm methylene blue was used as feed solution. However, the particles were relatively stable and agglomeration only was observed to be significant after the fourth draw solution regeneration cycle.

### *3.5.3 Stimulus Responsive Nanoparticles*

As stimulus responsive polymer systems have been previously investigated for use as FO draw agents (see section 3.4.2), so they have also been investigated to provide functionality for magnetic nanoparticles for use as draw agents. For example, the thermo-responsive polymer PNIPAM has

been utilized as a ligand with magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles to overcome the regeneration problems of aggregation seen with other nanoparticle systems, and also the low osmotic pressure seen with naked thermo-responsive polymers [125]. Functionalisation of nanoparticles leads to a concentration of the ligand due to the high specific surface area of nanoparticles, which increases with decreasing nanoparticle size. However, small particles are less easily trapped by magnetic fields. The thermally responsive aggregation and de-aggregation of PNIPAM was thus utilized to aggregate the nanoparticles for improved recovery and de-aggregate them after recovery for improved draw performance, with aggregates forming at, and dissociating below, the LCST of  $\sim 35^\circ\text{C}$ . After 5 cycles flux was maintained, showing that the aggregation problem had been successfully overcome, but the flux when using a pure water feed was much lower than seen for many other systems ( $< 2 \text{ L m}^{-2} \text{ h}^{-1}$ ). PAA-PNIPAM copolymer functionalised nanoparticles were found to perform less well than nanoparticles functionalised with PAA alone [126].

A later study used PNIPAM conjoined to the polyelectrolyte poly(sodium styrene-4-sulfonate) PSSS, to create a PSSS-PNIPAM copolymer ligand on magnetite nanoparticles. This setup was capable of achieving a flux of  $2.7 \text{ L m}^{-2} \text{ h}^{-1}$  when using a simulated seawater feed solution, with fluxes maintained above  $2 \text{ L m}^{-2} \text{ h}^{-1}$  after repeated cycles [115, 127]. Magnetic thermally responsive nanogels were formed by Zhou et al [128] by incorporating the copolymer poly(*N*-isopropylacrylamide-*co*-sodium 2-acrylamido-2-methylpropane sulfonate) (PNIPAM-*co*-AMPS) on the surface of magnetite nanoparticles. Their results suggested a 2.4 times increase in water flux compared with PAA-PNIPAM.

As well as examining thermal responsive functionalities, some research efforts have been directed to light-responsive ligands incorporated onto nanoparticles. Whilst use of heat as a stimulus may not require large amounts of energy on a lab scale, on an industrial scale in the absence of a convenient source of low grade waste heat, repeat heating cycles could cumulatively lead to substantial energy costs. Use of light responsive materials on the other hand are potentially cheaper as this allows

sunlight to be used as a stimulus. For instance, Han et al [129] combined magnetic nanoparticles functionalised with PNIPAM with plasmonic Ag nanoparticles, also functionalised with PNIPAM, to create photo-responsive heterodimers (see figure 16). This is due to localised heating of the Ag nanoparticles when absorbing sunlight being sufficient to raise the attached PNIPAM molecules on the Ag and Fe<sub>3</sub>O<sub>4</sub> above their LCST leading to structural collapse of the polymer, followed by disaggregation of adjacent heterodimers. However, as seen previously, the osmotic pressure of PNIPAM coated nanoparticles can be low, so future use of thermally responsive polymer systems with higher osmolality, such as by incorporating polyelectrolytes, may be the way forward.

Another class of stimulus responsive nanoparticles for use as draw agents are ones with functionalities sensitive to CO<sub>2</sub> concentrations. Chen et al [130] functionalised magnetite nanoparticles with 1,8 diamino-octane. This molecule contains two primary amine groups – one to bind to the nanoparticle and one free to interact with other molecules. In aqueous solution the hydrophobicity of these chains leads to aggregation of the nanoparticles. After the solution is purged with CO<sub>2</sub> gas, the primary amines react with CO<sub>2</sub> to form alkylammonium ions, which are hydrophilic groups, allowing the nanoparticles to successfully disperse in aqueous solution. Removal of dissolved CO<sub>2</sub> by purging with N<sub>2</sub> gas return the nanoparticles to their aggregate form. Whilst the authors did not investigate their utility as FO draw solutes, it is conceivable that a system such as this could be used as a draw agent, as the use of switchable polarity solvents, as described above, has shown.

#### **4 Draw Solution Regeneration**

As FO does not directly produce pure water, a second draw solute recovery step is essential where a purified product is the aim. As a potentially energy hungry process, the recovery of draw solutes and the cost of doing so are important when it comes to designing and FO process and deciding on the appropriate draw solution. In this section we will broadly cover the main draw solute recovery

processes described in the literature, as well as discussing advantages and disadvantages where appropriate.

#### *4.1 No draw solution regeneration*

Whilst FO has been put forward as a low energy alternative to pressure driven membrane processes such as RO, the need for a second step to recover draw solutes and produce clean water is a major determinant of the energy costs of the system. As a result, situations where no draw regeneration is needed are likely to be the least energy demanding. An early example is the use of glucose draw solutions in emergency packs, where the diluted draw solution is drinkable [87]. Other situations where no regeneration of the draw solute include the use of concentrated fertiliser solutions [14, 17-19], with the diluted draw used for fertigation. However, the spent draw solution is generally still too concentrated for direct application to crops, needing as much as a 100 times dilution before it is suitable [17]. In addition, the use of seawater as a draw solution itself, for instance, to dewater wastewater, would lead to a solution safe to discharge into the sea [81], providing toxic compounds can be prevented from passing the membrane. Another interesting use of FO which does not require draw solution regeneration is the use of Na-lignin as the draw agent. This system was proposed by Duan et al [97] where the diluted draw solution was to be used for the regeneration of desert areas, by providing irrigation simultaneously with the application of lignin as a soil stabiliser and medium for plant growth.

#### *4.2 Temperature driven systems*

As noted previously, early applications of FO used volatile draw solutes, allowing recovery due to heating. This can include the application of heating to cause draw solutes to decompose into gaseous forms, such as for ammonium bicarbonate [6, 131] or sulfur dioxide based systems [73, 74],



in the form of switchable polarity solvents which change their physico-chemical nature when heat is applied to remove dissolved CO<sub>2</sub> from the system [33, 90], or in the use of thermally responsive polymers which precipitate at temperatures above a critical limit [32], allowing collection via a filtration method. We have also seen that use of the same polymers, such as PNIPAM, can be integrated with nanoparticles to disperse nanoparticle systems after recovery by other methods [127, 128].

Many of these approaches aim to find simple and, more importantly, low energy recovery methods for recycling diluted draw solutions. McGinnis and Elimelech [132] investigated the energy usage when using an ammonia-carbon dioxide based system with a thermal recovery process. They simulated distillation of diluted draw solutions. It was concluded that an FO system combined with a low pressure vapour distillation system could deliver energy savings over other existing desalination technologies, including multi-stage flash (MSF), multi-effect-distillation (MED) and RO, with projected energy savings of between 75-82% on an equivalent-work basis.

Membrane distillation has been used as a reconcentration method by several researchers. For instance, Yen et al [133] investigated the use of an integrated FO-MD system for the use and recovery of 2-methylimidazole based organic compounds used as draw agents. Membrane distillation is a process whereby a temperature gradient, and hence difference in vapour pressure, is created across a hydrophobic membrane, which only allows water to pass in vapour form whilst retaining solute molecules [134].

#### *4.3 Pressure-driven Filtration Processes*

A number of researchers have considered RO, NF and UF for the re-concentration of draw solutions. Whilst it may seem counter-intuitive to select these processes downstream of FO when considering that FO has been in large part proposed as a low energy cost alternative. However, due to the low

propensity to scaling and other fouling, FO can be used as a front end filtration technology [59, 135], with downstream RO membranes exposed to a simple draw solution with little associated fouling potential. Bamaga et al [136] carried out a preliminary investigation of osmotic energy recovery in a hybrid FO-RO system when seawater and RO brine are used as draw solutions. They concluded that due to the low water flux of the FO membranes, hybrid FO-RO systems are only suitable for pre-treatment prior to RO desalination of feed water with a high fouling or scaling risk. However, considering the high salt rejection rate and low molecular weight cut-offs RO is an attractive option for draw solute reconcentration when using monovalent salts as draw solutes.

Yangali-Quintanilla et al [137] used low pressure RO as a draw solute regeneration step when using FO to desalinate seawater. They found that the energy consumption for the hybrid FO-RO process was 50% of that used when desalinating the same feed water using a conventional high pressure RO process. A cost analysis showed that FO-RO systems have the potential to be more cost effective than sweeter RO, but only when flux rates above  $5.5 \text{ L m}^{-2} \text{ h}^{-1}$  can be achieved, with flux rates needing to be as high as  $10.5 \text{ L m}^{-2} \text{ h}^{-1}$  to compete on cost effectiveness with a combined UF – low pressure RO desalination process. This highlights the need to choose suitable draw solutions with high osmotic potential that can achieve these high flux rates.

Cath et al [138] used an innovative combination of a wastewater feed with seawater as a draw solution, with the used draw solution then providing a brackish water source for further conventional RO, a process the authors referred to as osmotic dilution. This allowed the wastewater source to be concentrated, whilst reducing the required energy for seawater RO by pre-diluting the RO feed. This process allowed the production of high quality drinking water and was concluded to provide a favourable economic return with recovery of water from impaired sources of 63%.

NF and UF have also been explored as draw solute recovery steps. As they are looser membranes with higher molecular weight cut-offs, they can achieve higher flow rates than RO for a given pressure, but are only viable when using large molecules or nanoparticles as draw agents. NF is

typically tight enough for removal of multivalent ions and organics by size exclusion [139], with divalent salt rejection of 99% [140]. Tan and Ng [141] investigated NF as a draw recovery process for a number of draw agents:  $\text{MgCl}_2$ ,  $\text{MgSO}_4$ ,  $\text{Na}_2\text{SO}_4$  and ethanol. Flux rates as high as  $10 \text{ L m}^{-2} \text{ h}^{-1}$  are achievable for both FO and NF, with NF rejection rates observed to be as high as 97.4 %. From their findings they recommended using a two-pass NF treatment process to recover water which meets total dissolved solid content of  $500 \text{ mg L}^{-1}$  as recommended for drinking water by the world health organisation. Zhao et al [142] used a hybrid FO-NF system for desalination of brackish water with  $\text{NaSO}_4$  and  $\text{MgSO}_4$  as draw solutes. When compared with conventional RO, there was lower membrane fouling with a consequent lower flux decline, lower hydraulic pressure needed and higher flux recovery after cleaning.

Ultrafiltration has a high flux and lower energy cost than RO or NF [142, 143] and as such is suitable where the draw solute is sufficiently large to be retained by UF membranes. Ling et al [125] investigated the use of UF for recovery of super-hydrophilic nanoparticle draw agents. They found that UF was superior for collection of magnetic nanoparticles than magnetic separation due to a lack of particle agglomeration, hence the osmotic pressure of the re-concentrated draw solution was retained after 5 regeneration cycles. Ge et al [96] also used UF to re-concentrate draw solution, this time when using PAA as a draw agent, at a pressure of 1 MPa, achieving a rejection of 98.5 to >99%, depending on the molecular weight of polymer. After 9 regeneration cycles the water flux of the membrane dropped by 3% due to losses of draw solute.

Shaffer et al [3] expressed scepticism that UF regeneration is necessarily an improvement over RO on the basis that to regenerate the draw solution back to the original osmotic pressure the same hydraulic pressure will be needed for UF as for RO, therefore the minimum energy requirements for the two processes are the same. In the case that energy costs are the same for FO or UF it would be sensible to use RO due to the superior rejection rates for RO membranes.

#### *4.4 Magnetic Recovery*

As mentioned in section 3.4.5, much work with nanoparticles as draw solutes involves functionalisation of magnetite with hydrophilic species to create superparamagnetic nanoparticles, to enable easy recovery by magnetic separation, using commercial magnetic separators [114]. However, there are problems with using such a system. Primarily, aggregation of particles occurs, increasing suspended particle size and decreasing specific surface area, leading to a drop in solution osmotic pressure and hence FO performance. Several approaches have been used to counteract this, including the use of ultrasonication to disperse aggregates, but with the loss of some magnetic properties [119] or by use of responsive polymer ligands allowing changes in environmental stimuli, such as a temperature [125, 126, 128] or sunlight [129], to cause dispersion of aggregates after collection.

In addition, Razmjou [113] incorporated magnetic nanoparticles into hydrogels to allow release of water through magnetically induced heating. It was observed that magnetic induced heating was rapid and more even than other forms of heating. It was found that magnetic heating could release as much as 53% of bound water, compared with only 7% when using convective heating.

#### *4.5 Electrolytic Recovery*

When studying PAA-PNIPAM copolymer functionalised nanoparticles it was found that they showed a weakened magnetic response, making recovery by applied magnetic field impractical [126]. However, the nanoparticles also exhibited increased electrical conductivity, so the authors investigated a novel recovery method using electrical fields generated by electrodes placed into the draw solution tank, with nanoparticles accumulating on the anode plate, allowing easy recovery. This left behind an alkaline solution of metal ions which were recovered using NF. The concentrated metal solution was then used to dissolve and disperse the precipitated nanoparticles. Repeated

regeneration cycles did not reduce the water flux and the nanoparticle sizes were unchanged, demonstrating the effectiveness of the regeneration process.

Zou and He [144] investigated the use of electrodialysis as a method to recover diammonium phosphate (DAP) draw solute which had contaminated feedwater through reverse salt flux in a hybrid forward osmosis – electrodialysis (FO-ED) system. DAP recovery from the feed was approximately 96.6%, with the FO-ED system operating at  $0.72 \text{ kWh m}^{-3}$ . However, when treated wastewater was used as the feed, fouling occurred requiring repeated cleaning.

#### *4.6 Precipitation of Draw Solute*

Another technique for recovering and re-concentrating draw solutes is by the use of precipitation reactions. The first reported use of this was in a patent describing the recovery of water from an  $\text{Al}_2(\text{SO}_4)_3$  draw solution [145], using calcium hydroxide as a precipitant. Other investigators using  $\text{MgSO}_4$  [146] or  $\text{CuSO}_4$  [82] draw agents have used similar precipitation reactions to remove draw solutes from the diluted draw solution. Metathesis reactions with a stoichiometric amount of  $\text{Ba}(\text{OH})_2$  produced  $\text{Mg}(\text{OH})_2$  or  $\text{Cu}(\text{OH})_2$  and  $\text{BaSO}_4$  precipitants. The precipitate can then be recovered by filtration or sedimentation.

### **5 Economic Aspects**

This review covers the scientific literature to date regarding development of draw solutions for RO processes. As much of this literature consists of basic research and FO is not a mature or widely adopted technology at an industrial scale, there is little information on the real world economic aspects of it. However, as the end point to all FO research is to provide a commercially viable technology for water purification or resource concentration then some consideration to economic aspects needs to be given. When considering draw solutes specifically, there are two major costs to

be considered – the cost of the draw solutes themselves and the energy cost associated with solute recovery / reconcentration, as well as how effective the recovery process is (a low energy recovery process that only recovers some of an expensive solute is unlikely to be cost effective). In table 1 is summarised a number of example chemicals which have been investigated as potential draw solutes. Table 1 shows the prices of commercially available solutes, with common inorganic salts being much cheaper than many of the complex organics. Prices for functionalised nano[particles are not available, but any large scale manufacturing costs could be expected to be quite substantial, due to the complexity of the manufacturing process and in some cases expensive precursor molecules.

Another major consideration is the energy costs of regeneration of the draw solute. For applications where the draw solution does not require regeneration, such as where the diluted draw solution is to be applied to the land as nutrient, regeneration costs are minimal, consisting of pumping, storage and other miscellaneous costs depending on the particular requirements. In this case the energy cost FO alone for seawater desalination has been calculated as approximately  $0.59 \text{ kWh m}^{-3}$  [132], consisting of mainly energy needed for pumping. This compares favourably with the desalination costs for the rival technology of RO which has a practical minimum energy of  $1.5 \text{ kWh m}^{-3}$  [10], with a suggestion that other technologies need energy requirements of below  $4 \text{ kWh m}^{-3}$  to compete [147].

However, in most cases, particularly with expensive draw solutes, the draw solution needs regenerating. The most commonly used methods reported in the literature are RO or thermal methods, including MD. As would be expected, and as has already been pointed out [3], an FO-RO hybrid process cannot have a lower energy consumption than an RO process alone. However, in this case a lower propensity for fouling due to the lower hydraulic pressure does still make FO-RO an attractive process for feed waters with a high fouling propensity. Where the solute molecules or particles are sufficiently large UF can be substituted for RO, allowing higher flux rates and lower

energy costs [142, 143], whilst acknowledging the previously mentioned reservations of other researchers on this point [3].

As mentioned above, a number of researchers have investigated MD regeneration of diluted draw solutions. Zhao et al [32] considered the energy consumption of a hybrid FO-MD system for regenerating PSSS-PNIPAM thermo-responsive copolymer draw solute. They calculated that 29 kWh m<sup>-3</sup> was needed to reach a temperature of 50°C necessary for MD. This puts the energy costs for a FO-MD system much higher than for a FO-RO or RO system. However, as they point out, this energy could be provided by waste heat from another process if available, although doing so could potentially preclude the use of waste heat from another source.

Finally, much recent research has been on the use of functionalised magnetic nanoparticles. The major advantage being the use of a magnetic separator to quickly and cheaply reconcentrate the nanoparticle solutes [114, 116, 118-120]. However, this process does not always achieve as high a recovery as desired, with some researchers needing to add a UF process to make the product water fit for consumption [119, 148]. As the manufacture of large quantities of functionalised nanoparticles is likely to be expensive a high recovery is essential for their use to be cost effective.

## **6 Conclusions**

Whilst FO processes for the production of potable water have been proposed since the mid 1960's, it is only within the last decade and a half that there has been real momentum in the research to improve water recovery. If the FO process is to compete with other more established membrane processes in desalination and water treatment then high flux rates will be needed. This will require the use of draw solutes capable of producing high osmotic pressures to drive the membrane flux. Another problem with FO is the need in many cases for a second step to recover pure water from the diluted draw solution and to simultaneously reconcentrate the draw solute. This second step

needs to have a low energy consumption and be capable of high output. Selection of an appropriate draw solution is key to the efficient and cost effective operation of FO. An effective draw solute must be abundant, be capable of generating a high osmotic potential, have low reverse solute flux, be non-toxic and non-corrosive, be inexpensive and be easy and cheap to regenerate. Small ionic species are capable of producing high osmotic pressures, have high diffusion coefficients which limit concentration polarisation and can be easy to reconcentrate with RO, but on the other hand have a relatively high reverse solute diffusion. Many innovative draw solutes have been used including polyelectrolytes, hydrogels, stimuli responsive polymers and nanoparticles coated with hydrophilic groups. Whilst these larger molecules and nanoparticles have low reverse salt diffusion and innovative recovery pathways, they often struggle to match the osmotic pressures exhibited by small molecules.

A substantial body of research into draw solutions for FO water treatment currently exists and is ever expanding as we collectively seek to produce better draw agents capable of higher fluxes and lower operating costs. It is unlikely that there is any single perfect draw agent to be discovered – rather the solution to problems of water treatment with FO is in the selection of and development of the best draw solutions for the needs of specific situations. Currently FO outperforms other membrane based water treatment systems when it comes to treating problematic feed waters. Whether the ability of FO will expand in the future to displace those more conventional technologies will depend on future improvements in both draw solution and membrane technologies.

### **Acknowledgements**

The authors would like to thank the Royal Society for funding this work through Royal Society International Collaboration Award (IC160133).



## Figure Captions

Figure 1: Illustration of asymmetric membranes: a) in 'FO' mode with active layer facing feed solution and b) 'PRO' mode with active layer facing draw solution. For an ideal situation water flux will be dependent on pressure difference between  $\pi_{D,b}-\pi_{F,b}$ , but the concentration polarization effects lead to a reduced osmotic pressure difference between the fluid layers immediately adjacent to the active layer.

Figure 2: a) Reverse solute fluxes and b) water permeability for urea, ethylene glycol and NaCl, plotted versus molar concentration, measured with DI water as a feed solution. Reproduced with permission from [64]. Copyright 2012 Elsevier.

Figure 3: Effect of concentration on DME solution osmotic pressure compared with dissolved  $MgCl_2$  and fructose. Reproduced with permission from [76]. Copyright 2014 Elsevier.

Figure 4: Effect of pH of draw solution on a) water flux and reverse salt flux; b) specific reverse salt flux and solution osmolality. Reproduced with permission from [85]. Copyright 2016 Elsevier

Figure 5: a) Schematic of process used by Zhong et al [89] for FO using temperature responsive liquid; b) phase separation of diluted draw solution into ionic liquid and water rich phases. Adapted with permission from Zhong et al [89]. Copyright American Chemical Society 2016.

Figure 6: Scheme used by Stone et al for FO using a switchable polarity solvent. Reproduced with permission from [33]. Copyright 2013 Elsevier.

Figure 7: FO filtration system with NF regeneration step for recovery of water from seawater using hydro-acid drawing agents. Reproduced with permission from [105]. Copyright 2014 Elsevier.

Figure 8: Schematic showing a responsive hydrogel driven FO process. Water is drawn through the membrane by the swelling of the hydrogel. Stimulus is applied to the hydrogel causing de-watering, allowing the process to be repeated. Reproduced from [66] with permission from The Royal Society of Chemistry.

Figure 9: Semi-IPN hydrogel driven FO using a quasi-continuous process as proposed by Cai et al [109]. Reproduced with permission from [109]. Copyright 2013 Elsevier.

Figure 10: Experimental outline for electrically responsive HA-PVA hydrogel driven forward osmosis. Reproduced with permission from [67]. Copyright 2015 Elsevier.

Figure 11: Synthesis of surface functionalised magnetic nanoparticles. Reproduced with permission from Ling et al [116]. Copyright 2010 American Chemical Society.

Figure 12: Osmolality of magnetic nanoparticles functionalised with 2-pyrrolidone, triethylene glycol and polyacrylic acid. Reproduced with permission from Ling et al [116]. Copyright 2010 American Chemical Society.

Figure 13: Schematic of PEG functionalised magnetite nanoparticles (left) and TEM images with size distributions of various formulations (right). Figure adapted with permission from [114]. Copyright 2011 American Chemical Society.

Figure 14: Diagram of magnetic separator assembly used to re-concentrate PEG functionalised magnetite nanoparticles as used by Ge et al. Figure reproduced with permission from [114]. Copyright 2011 American Chemical Society.

Figure 15: Water flux using dextran coated magnetite nanoparticles using a) DI water and b)  $2 \text{ g L}^{-1}$   $\text{MgSO}_4$  as feed solutions. Adapted with permission from [120]. Copyright 2011 Elsevier.

Figure 16: Ag-magnetite heterodimers functionalised with PNIPAM to make photoresponsive nanoparticles: a) expanded polymer chains at temperatures below LCST lead to dispersion within the polymer; b) localised heating of Ag nanoparticles due to photothermal effects when exposed to light leads to aggregation of nanoparticles. Reproduced with permission from [129]. Copyright 2013 Royal Society of Chemistry.

Figures

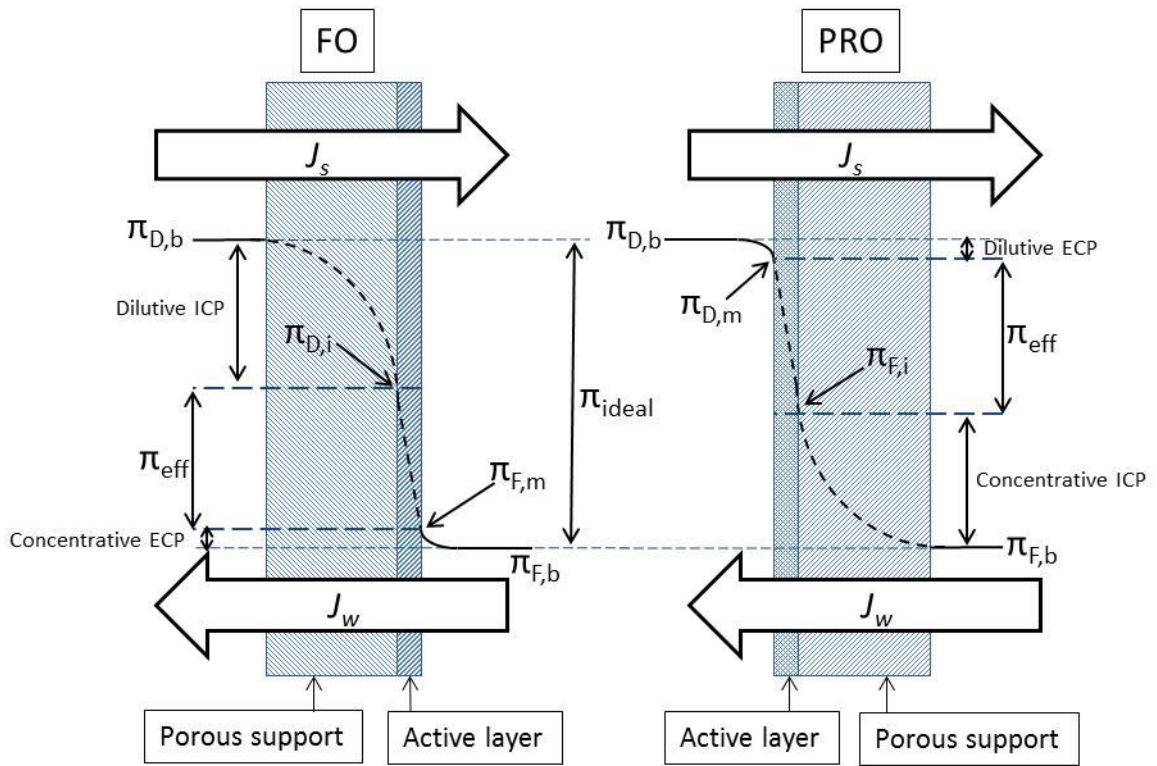


Figure 1

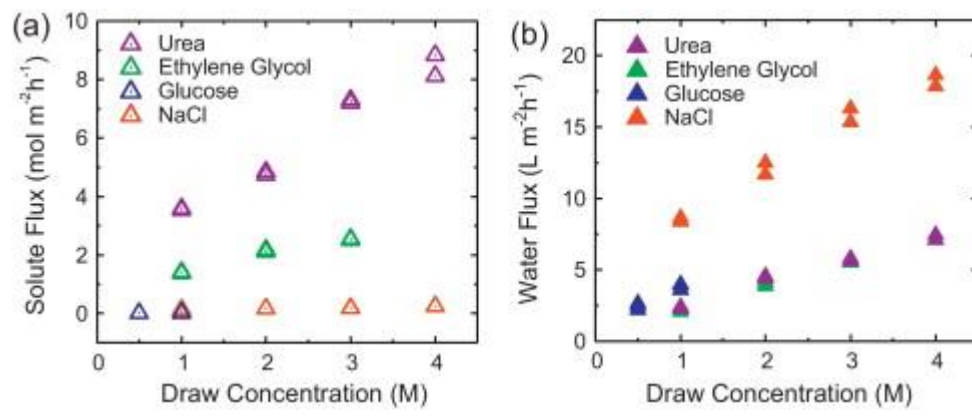


Figure 2

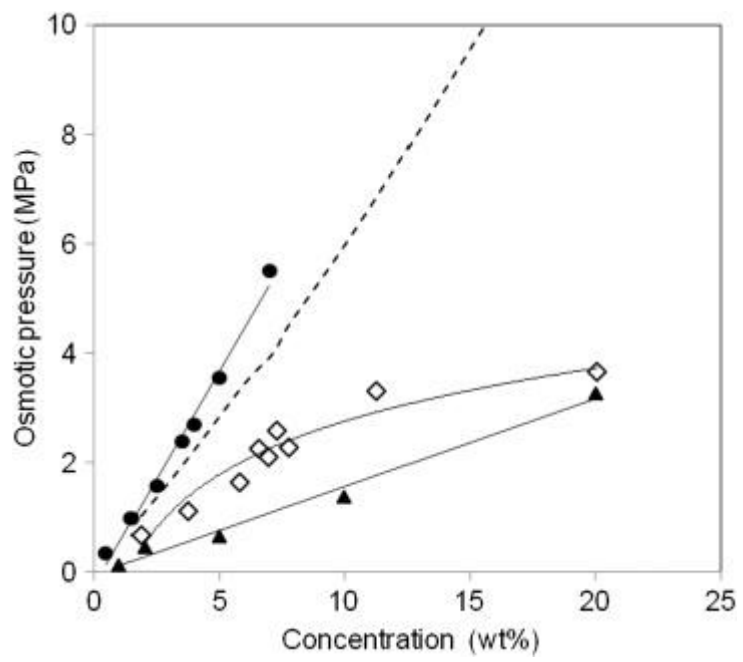


Figure 3.

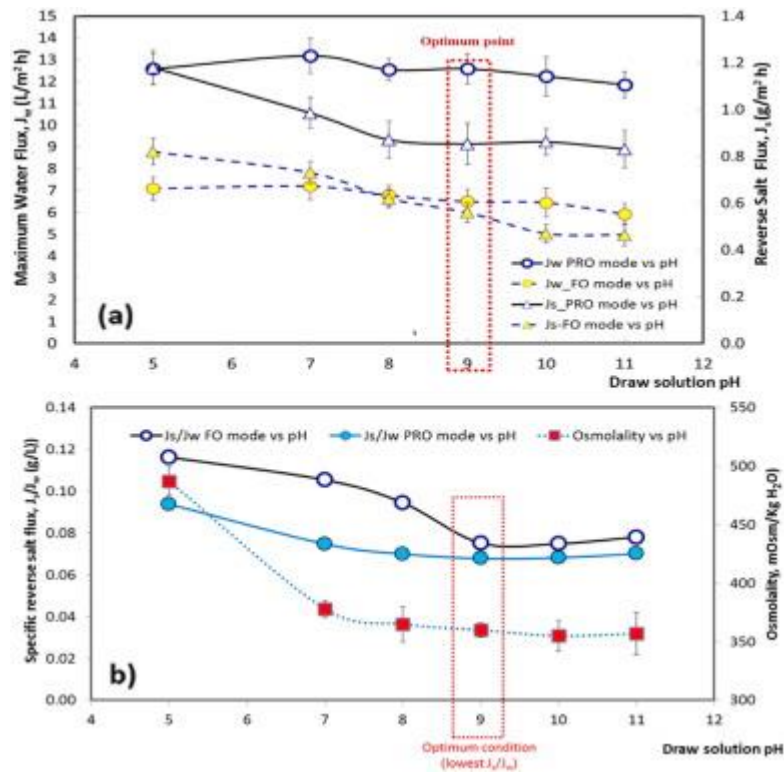


Figure 4.

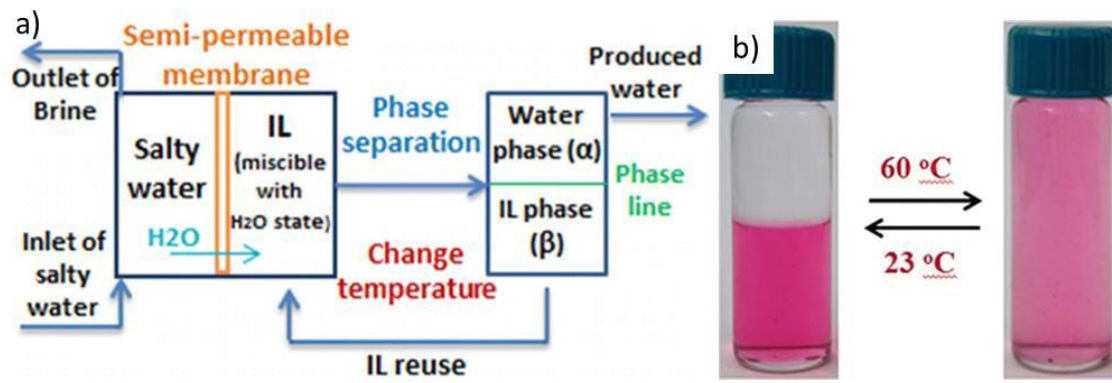


Figure 5

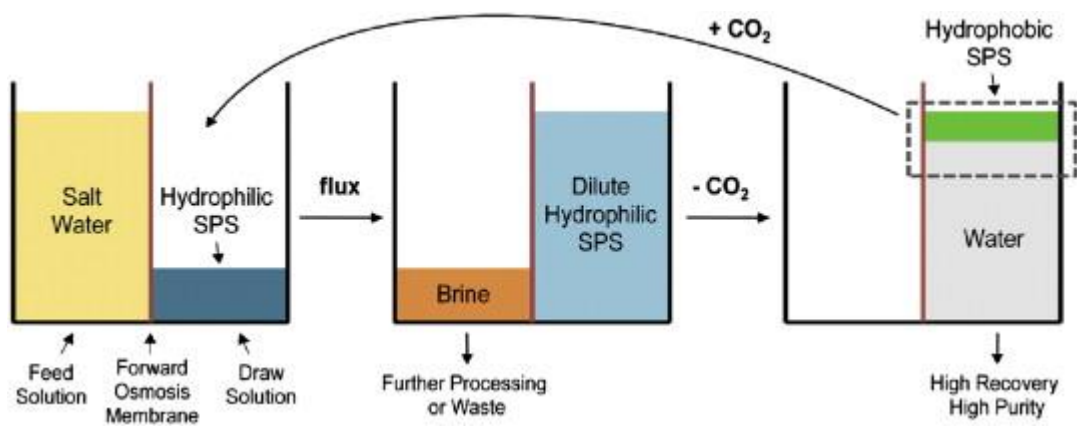


Figure 6



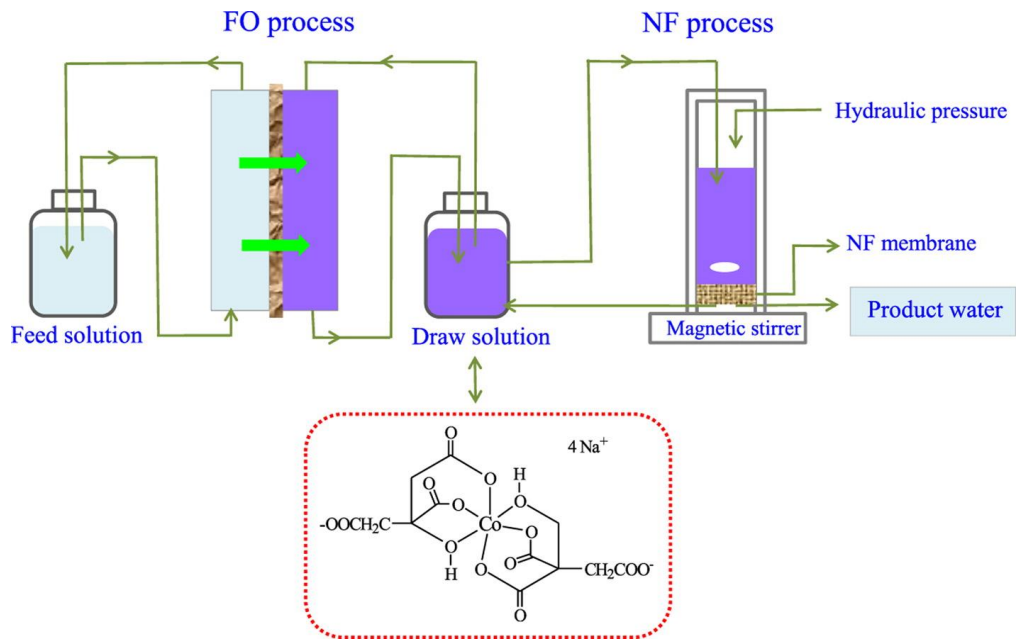


Figure 7

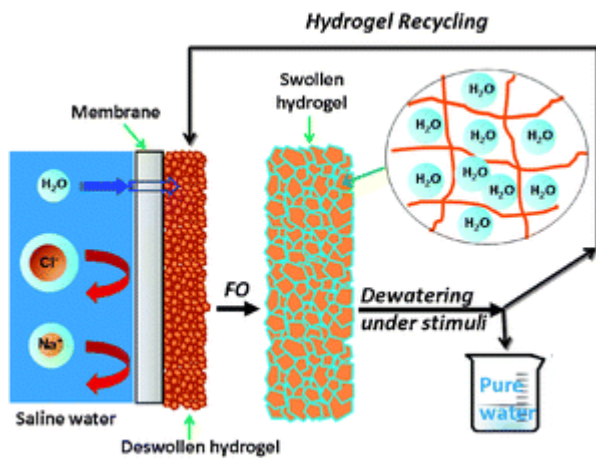


Figure 8

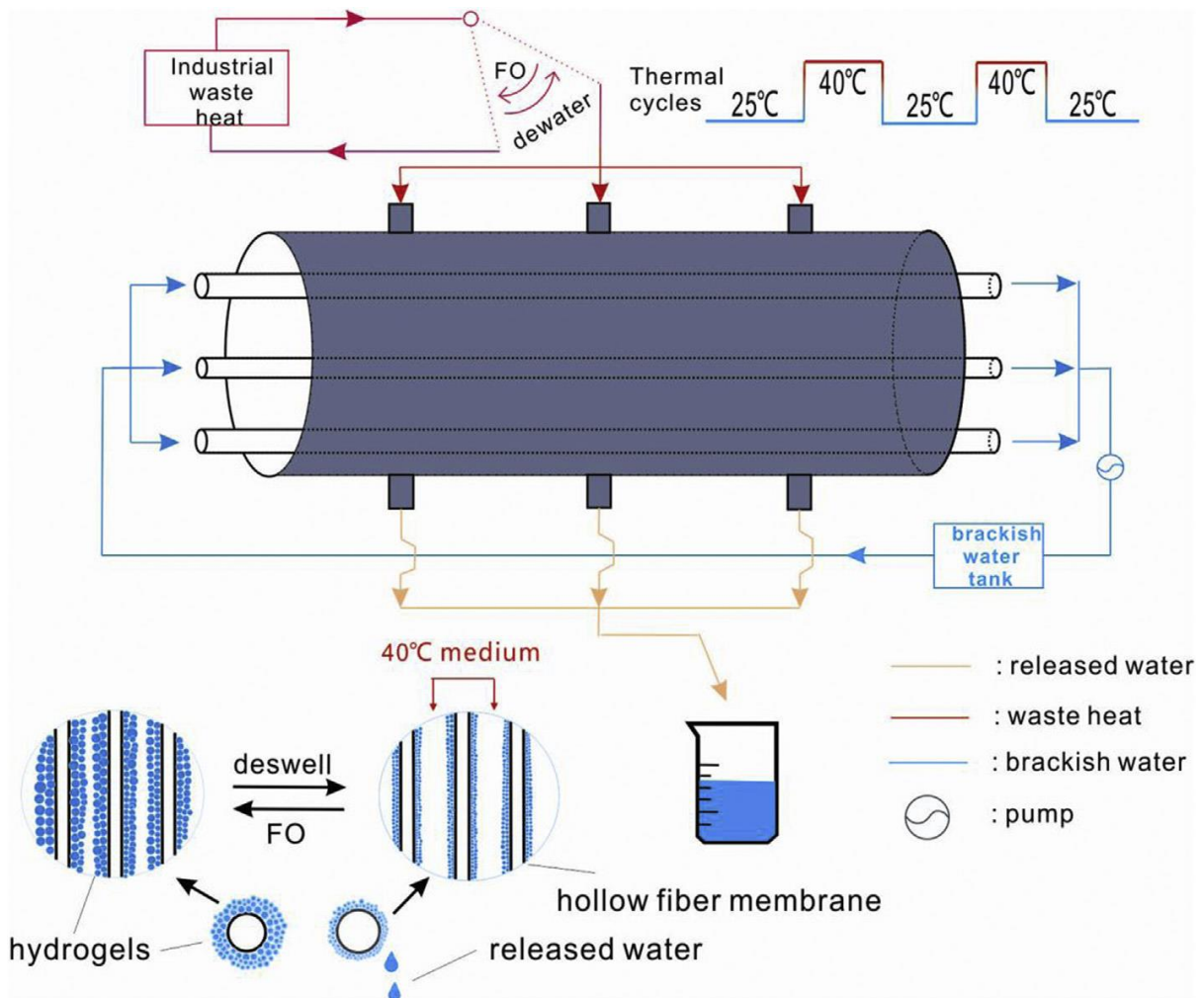


Figure 9

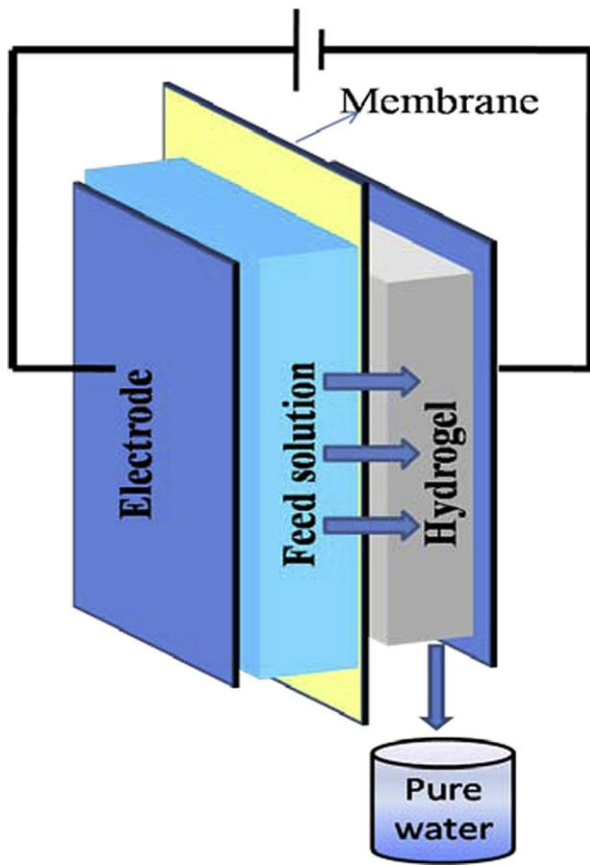


Figure 10

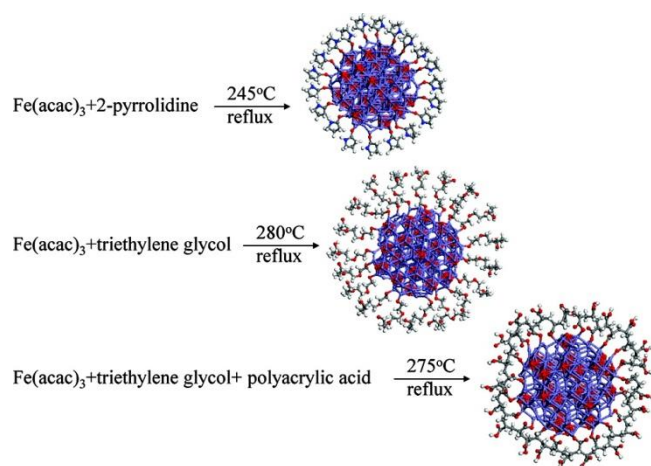


Figure 11

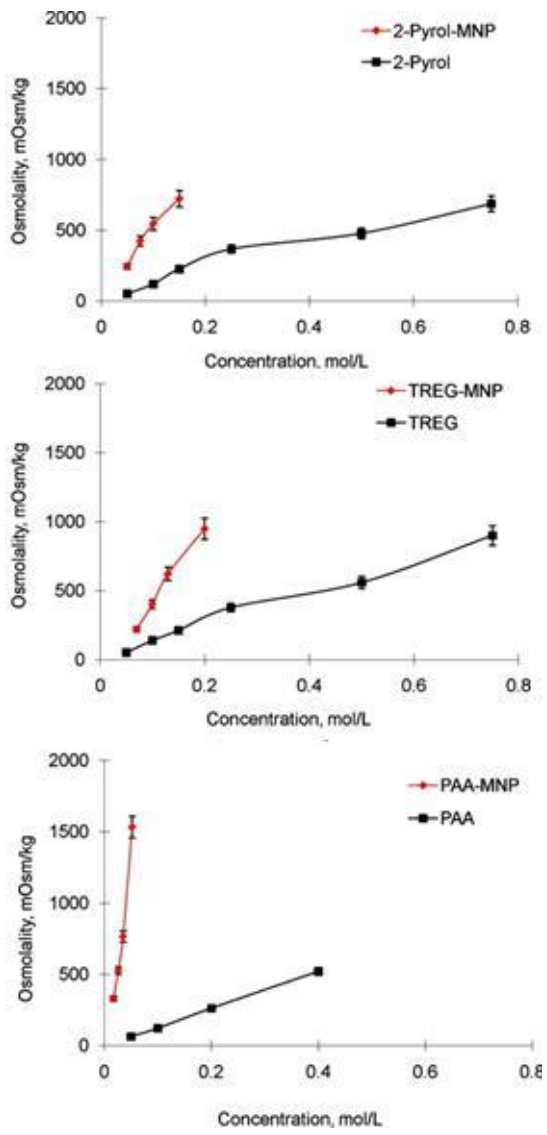


Figure 12

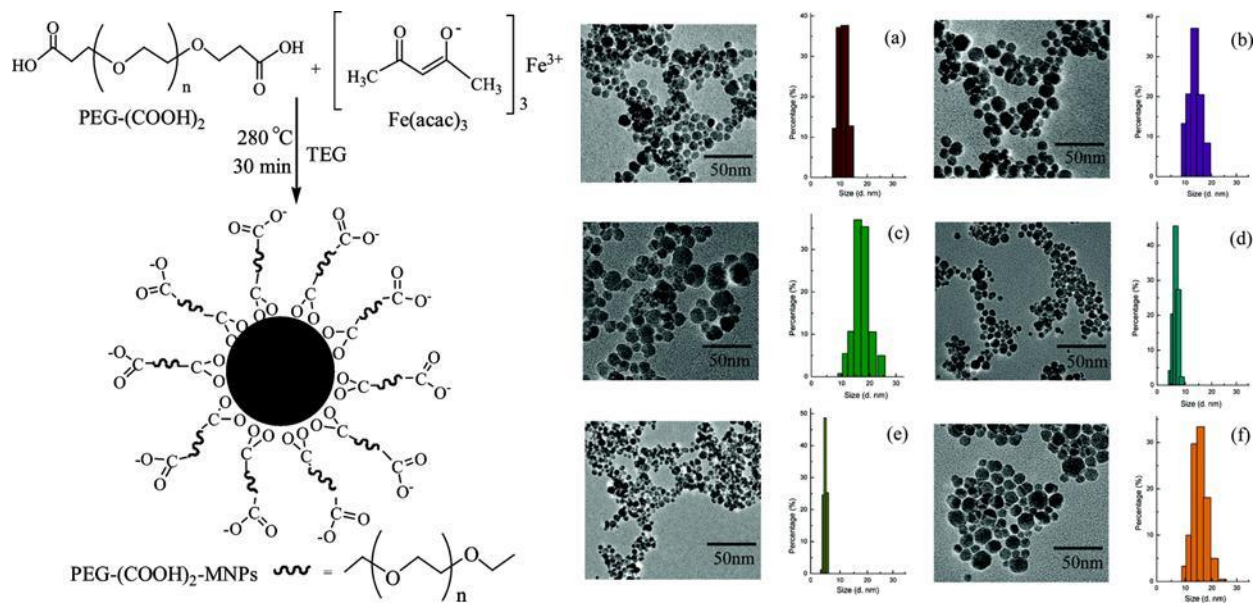


Figure 13

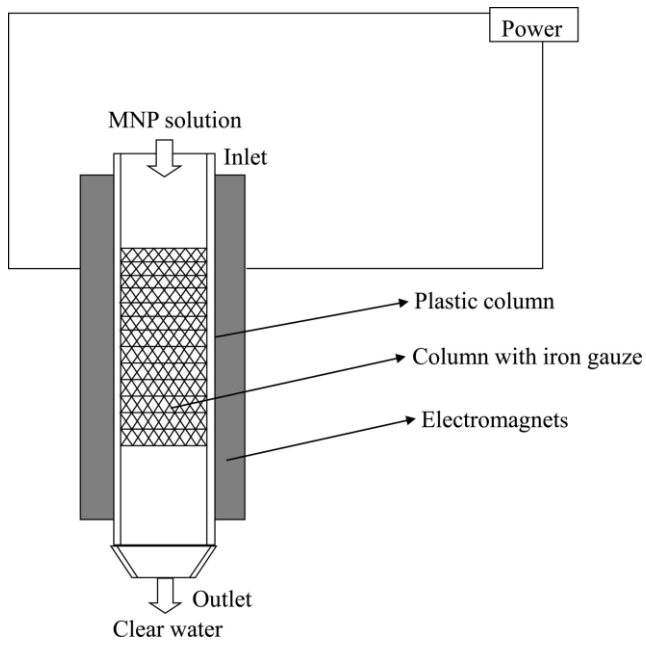


Figure 14



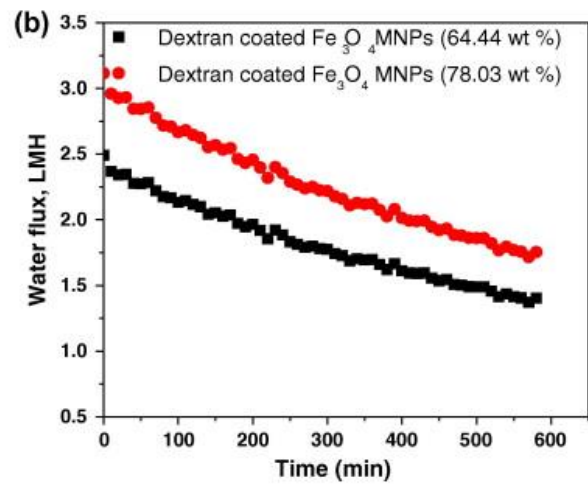
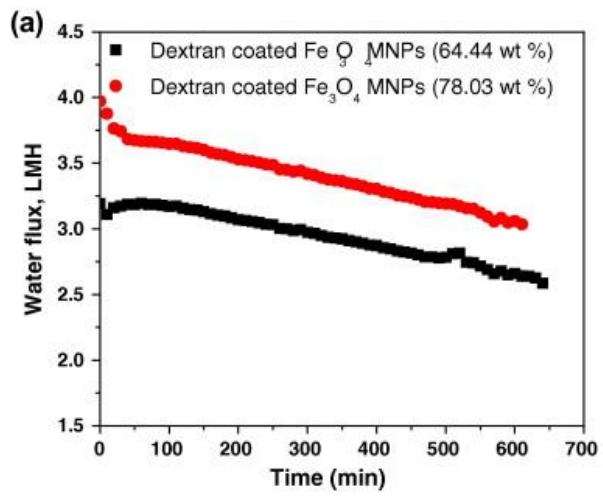


Figure 15

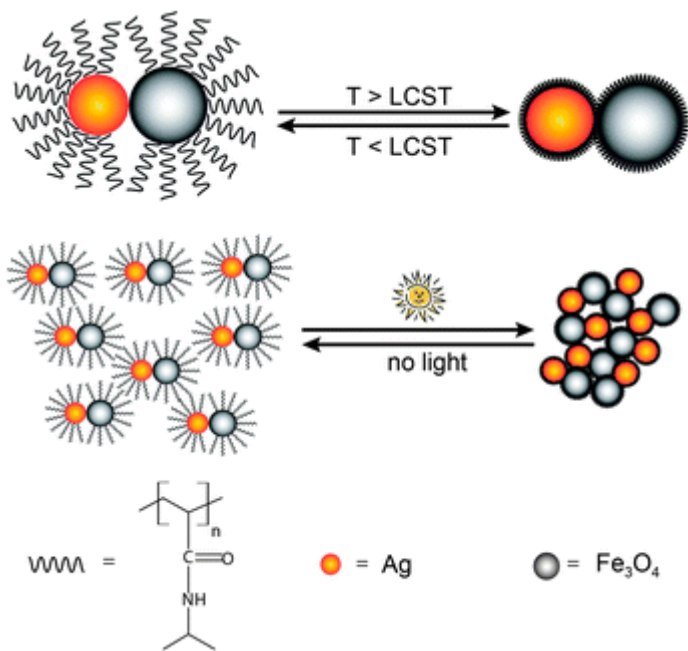


Figure 16

## Tables

Table 1: Summary of draw solutes described in the scientific literature for FO tests. An exhaustive list of all potential draw solutes would be extensive, so only example solutes from each major category have been included. Osmotic pressure values, where available, were taken from indicated references. Prices for solutes have been indicated where possible. Price data was obtained from the VWR International website, with largest available quantity prices scaled down to price per kilogramme, except where otherwise indicated. Prices not available from VWR International were taken from Sigma Aldrich, marked with \*.

Solute Category	Example Solute	Osmotic Pressure / Concentration	Cost of solute (\$/kg)	Advantages	Disadvantages
Gas and Volatile Compounds	NH <sub>4</sub> HCO <sub>3</sub>	4.80 MPa / 1.1M [7]	8.75	High osmotic pressure capable of desalinating seawater	Volatile flux high biofouling affected
	Tri-methylamine	4.88 MPa / 1.0M [54]	32.93 / L (40% sol.)		
Inorganic Solutes	NaCl	4.8 MPa / 1.0M	10.61	Low viscosity, low cost, high osmotic pressures achievable	High diffusivity
	KCl	4.46 MPa / 1.0M [17]	18.88		
	MgCl <sub>2</sub>	7.3 MPa / 1.0M	20.41		
Inorganic solutes (fertilizers)	Ca(NO <sub>3</sub> ) <sub>2</sub>	4.94 MPa / 1.0M [17]	86.82	Diluted draw solute can be re-used for fertigation, therefore recovery not required	Reverse flux may be high concentration considered economic
	KH <sub>2</sub> PO <sub>4</sub>	3.70 MPa / 1.0M [17]	34.28		
	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	5.13 MPa / 1.0M [17]	61.00		
	K <sub>2</sub> SO <sub>4</sub>	2.8 MPa / 0.58M [36]	93.13		
	NH <sub>4</sub> Cl	4.41 MPa / 1.0M [17]	46.84		
	NaNO <sub>3</sub>	8.22 MPa / 2.0 M [149]	43.95		
	KNO <sub>3</sub>	3.77 MPa / 1.0M [17]	48.86		
	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	4.67 MPa / 1.0M [17]	42.57		
	NH <sub>4</sub> NO <sub>3</sub>	3.41 MPa / 1.0M [17]	13.48		
Simple Organics	Sucrose, glucose, fructose	2.4 MPa / 1.0M	14.39	High solubility,	Lower than may mixing occur
Amphiphilic organic ionic liquids	P <sub>4444</sub> DMBS	1.34 Osmol/kg 30 % wt.	322.22	Low regeneration costs	Expensive
Switchable Polarity Solvents	N,N-dimethylcyclohexamine	32.93 MPa / 59 % wt.	74.6 / L	High osmotic pressures achievable for concentrated solutions	Sophisticated requirements of chemical further RO or drink
Organic ionic salts	EDTA	3.60 Osmol kg <sup>-1</sup> / 1.0M [115]	192.98	Low energy consumption	Expensive
Polyelectrolyte draw solutes	PAA-Na	~2.0 MPa / 2.5 g L <sup>-1</sup> [96]	58.3	High water flux; low reverse solute flux	Expensive
	PSS	-	1439		
pH Responsive Polymers	PDMAEMA	1.208 Osmol kg <sup>-1</sup> / g g <sup>-1</sup> [102]	-	High osmotic pressure, easy recovery	Complex preparation

Thermo-responsive copolymer	PSSS-PNIPAM	2.87 MPa / 33 % wt. [32]	1439 (PSS) 1985* (PNIPAM)	High osmotic pressure, easy recovery	precu Comp prepa precu
Hydro-Acid Complexes	Oxalic Acid complexes with Fe/Cr/Na	8.1 / 2.0M [105]	158.16 (oxalic acid)	High solubility; high osmotic pressures; high water flux; minimal reverse solute diffusion; easily recovered	Meta acid p
Stimuli-responsive Hydrogels	PNIPAM + PVA/PSA	-	1985* (PNIPAM)	Low reverse solute flux, high water flux, high solubility below LCST	High expe
Magnetic Nanoparticles Functionalized with simple polymers	Ferrite + PEG-(COOH) <sub>2</sub>	5.57-7.4 MPa / 0.065M [114]	-	Easy magnetic recovery of magnetic NPs	Aggre low c after water durin to UF prod
	Ferrite + PAA	7.1 MPa/ - [119]	-		
	Ferrite NPs + Dextran	-	-		
	Ferrite + Siloxane	0.64-0.77 MPa / 50 g L <sup>-1</sup> [124]	-		
Quantum dots	Carbonised quantum dots	5.7 MPa / 0.5g L <sup>-1</sup> [123]	46.20 (citric acid precursor)	High osmotic pressures, cheap precursor compounds	
Stimuli Responsive Nanoparticles	Ferrite NPs + PNIPAM	-	-	Lower aggregation due to dispersal by environmental stimuli	Expe and s
	Ferrite NPs + PSSS- PNIPAM	4.13-5.57 MPa / 33 % wt. [127]	-		
	Ferrite NPs + PNIPAM- co-AMPS	-	-		
	Ferrite + Ag + PNIPAM	-	-		

**Table 1**

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