

## LESS COMMONLY USED MEMBRANE DESALINATION TECHNOLOGIES

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**Abstract:** The literature on membrane distillation and forward osmosis for treating natural and recovered wastewaters is reviewed. There is renewed interest in these membrane technologies as alternatives to pressure driven processes such as reverse osmosis, which are expensive in both capital and energy, and generally require pre-treatment of the feed water. Membrane distillation with hydrophobic microfiltration membranes can make use of low-grade heat energy, and give higher yields of product water from concentrated feed waters. Forward osmosis uses hydrophilic membranes akin to reverse osmosis, and needs a draw solution that is appropriate in the product water, or must be recovered and reused in large-scale operation. Although they show great promise as simple low energy systems, no large-scale installation of either process exists as yet. Membrane distillation has considerable potential for desalination to produce drinking water, whereas FO is currently confined to small-scale systems, especially as a source of energy drinks in emergency situations.

**Keywords:** Membrane distillation, forward osmosis, desalination, draw solutions, solar energy.

### INTRODUCTION

There are many desalination plants installed around the world, one estimate being 15,000 in 2004, of which about half are membrane plants [46]. A huge research effort has been put into desalination by the pressure-driven process of reverse osmosis (RO), where a pressure is applied to overcome osmotic forces to push water through a semipermeable membrane that rejects salts and larger species. It is a costly procedure, both in capital and energy, and requires pre-treatment of the feed water to minimise the scaling and fouling that reduce productivity and shorten membrane life. RO cannot treat high salinity waters economically and is seen as lacking in efficiency as regards the yield of desalted seawater. A number of processes that require no or little applied pressure exist. Two of these options are membrane distillation and forward or direct osmosis.

### MEMBRANE DISTILLATION

Membrane distillation (MD) involves the transport of water vapour through the pores of a membrane that separates two solutions [2, 7, 14, 31]. A hydrophobic membrane is used that rejects the liquid phase of water, but on heating vapour is created that can readily pass through the membrane. Condensation takes place on the other, cooler side of the membrane. The driving force is the temperature difference, and hence vapour pressure difference, between the warm and cool surfaces. The general scheme is shown in Figure 1. Low-grade energy sources can be utilised, the energy requirement being significantly less than thermal distillation.

The process in effect combines the advantages of RO but has higher yields of desalted water and the possibility of using cheap waste heat energy. The differential in vapour pressure of the water rather than the total pressure is the driving force.

The process has been explored in various configurations:

- direct contact membrane distillation has the condensing fluid in direct contact with the membrane
- air gap membrane distillation, where an air gap separates the condensing surface from the membrane
- sweep gas membrane distillation, which is similar but utilises air and steam in the gap
- vacuum membrane distillation, which is similar to pervaporation but differs in that the separation is determined by vapour-liquid equilibria rather than selectivity imparted by the membrane.

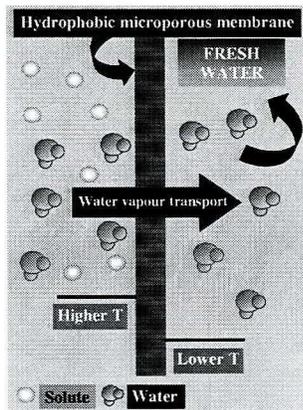


Fig. 1. Schematic representation of MD principle.

### ***Direct Contact Membrane Distillation***

Direct contact MD is best suited to systems where the major component is water, as in desalination or the concentration of an aqueous medium such as wastewater, orange juice or blood. It requires the least equipment and is the simplest to operate. Fluxes as high as  $79 \text{ L/m}^2\text{h}$  have been obtained [47] which are competitive with RO, and salt rejections of nearly 100%, which cannot be achieved with RO at high fluxes [33]. One of the problems with direct contact MD is the relatively low efficiency of heat utilisation, as large amount of the heat is lost by conduction through the membrane. One answer is to increase the conductive heat transfer resistance by placing an air gap between the permeate side of the membrane and the condensing surface.

### ***Air Gap Membrane Distillation***

Air gap MD substantially reduces the conductive heat loss through the membrane, but in doing this the mass transfer resistance also increases unless the system is de-aerated.

Air gap MD fluxes are therefore lower than for other MD configurations, a recent study using low-grade thermal energy (between  $13$  and  $75^\circ\text{C}$ ) from a salt-gradient solar pond reporting fluxes up to  $6 \text{ L/m}^2\text{h}$  [51]. The flux was heat transfer limited, and only weakly responsive to vapour pressure

gradients between the feed and the cooling waters. The method has been applied successfully to pure water production and the concentration of various non-volatile solutes. The configuration is the most general and can be used for many applications. A recent paper claims that the air gap mode is the most efficient way of carrying out MD as it gives an almost ideal counter-current flow process [42].

### ***Sweep Gas Membrane Distillation***

Air or steam stripping with a membrane as in sweep gas MD combines the low conductive heat loss of air gap MD with the reduced mass transfer resistance of direct contact MD. Instead of a stagnant layer of air separating the membrane and the condensing surface, air is blown over the membrane surface and permeate is condensed in an external condenser. However, the condenser must do a lot more work in this configuration as a small volume of permeate is vaporised in a large volume of sweep gas. It has been shown that the flux is independent of the temperature of the sweep gas. As the gas velocity increases to a maximum, the flux increases, but then starts to decrease because the pressure of the sweep gas also increases so that the resistance in the boundary layer increases. There is hence an optimum in the flux versus gas velocity graph. The approach is especially useful for the removal of volatile compounds.

### ***Vacuum Membrane Distillation***

With vacuum MD the conductive heat loss through the membrane is negligible. It is most often used to remove volatile components from dilute aqueous solutions, but special care must be taken to prevent membrane wetting, as  $\Delta P_{\text{interface}}$  is typically higher than for other MD configurations. A flux of 70 L/m<sup>2</sup>h has been obtained with brine at 85°C, higher than for the same test module in direct contact MD mode, which yielded a flux of 54 L/m<sup>2</sup>h [47]. The approach is useful for volatile compound removal from aqueous solutions. With hollow fibre systems having a variety of plasma-polymerised microporous silicone fluoropolymer coatings, those with the more open coating, more porous membrane wall and larger pore size, lead to greater water vapour permeation [32].

### ***Membrane Materials***

The commercially available membranes that have been used for MD include polypropylene (PP), polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE) and silicone rubber [31]. The membrane

- must be porous with a narrow size distribution of pores, with an overall porosity of 30-80% [7], so that it has a high permeability
- have a low thermal conductivity
- should not be wetted
- should not allow capillary condensation to occur inside the pores
- not alter the vapour-liquid equilibrium of the components in the feed
- must have at least one side in direct contact with the feed water
- should be as thin as possible, to minimise membrane area requirements.

The polymers that have been used for MD membranes are hydrophobic as measured by their low surface energy [2]: PTFE, 9.1; PP, 30.0; PVDF, 30.3 and polyethylene, 33.2 kN/m surface energy. The pore size needs to be small enough to minimise liquid water penetration, yet large enough to give the desired flux. In practice it ranges from 0.02 to 1 µm, optimally 0.2-0.6 µm, and the membrane is generally 25 to 150 µm thick. Hollow fibre PP membranes of 200-330 µm internal diameter and wall thickness 50-150 µm have been employed recently [43]. Other workers indicate that the preferred characteristics for a PVDF membrane for vacuum MD are mesoporous structures in a hollow fibre format with pore sizes of 0.05 to 0.2 µm and a high permeability [8].

### **Membrane Wetting**

There have been some serious problems with membrane wetting causing MD to slow down and, in the worst cases, being brought to a halt [45]. The pores of the membrane may become clogged with water during prolonged use, leading to a decrease in the flux of water vapour [28]. Hydrophilically modified membranes have since been explored. A composite MD membrane has been made by using a PVDF membrane of 0.2  $\mu\text{m}$  pore size as a substrate, pretreating it with a potassium dichromate/sulphuric acid solution and casting a poly(vinyl alcohol), MW 2 kDa/ poly(ethylene glycol), MW 10 kDa solution, then crosslinking with a dialdehyde, to produce a membrane that has a hydrophilic coating on one surface [44]. In treating 3.5% NaCl at 70°C, the hydrophilic layer was placed in contact with the salt solution. The lower the cooling temperature, which varied from 12-25°C, the higher the flux obtained, over a range of 26-23.5 L/m<sup>2</sup>h. The wetting problem facing traditional MD with a purely hydrophobic PVDF membrane was avoided because of the hydrophilic surface layer.

An analogous approach had been taken using a composite membrane having a hydrophilic layer (cellulose acetate, polysulphone or polyallylamine) located between the salt water and the hydrophobic membrane (PTFE or PVDF), with the pores of the hydrophobic membrane preventing intrusion of water and stopping the salt precipitation at the hydrophobic surface which would otherwise allow water logging to occur [12]. The fresh water production rate was increased by almost 50% relative to a membrane that had no hydrophilic layer.

The reverse type of composite porous hydrophobic/hydrophilic membrane has been proposed also, using a polyetherimide as a hydrophilic base polymer to which was added fluorinated surface-modifying macromolecules of MW ~10 kDa [22, 24, 26, 27]. The membranes were prepared in one casting step, using a phase inversion method with a solution containing the hydrophilic host polymer and the fluorinated additive. The fluorinated macromolecules migrate to the surface and the fluorine end groups orient themselves towards the air-polymer interface, reducing the surface energy of the hydrophilic base polymer to values close to that of PTFE. Because only small amounts of the added polymer are required, the bulk properties of the base polymer remain relatively unchanged. The exposed external surface of the membrane was thus significantly more hydrophobic than the bulk membrane phase. The mean pore size was smaller than that of the unmodified membrane, but there was a lower conductive heat loss through the membrane because of the thick hydrophilic sub-layer that was filled with water. The permeate flux for one product was higher than that of commercial PTFE membranes, because the composite membranes had a thinner hydrophobic porous top layer responsible for water vapour transport. This layer (<8  $\mu\text{m}$ ) was thinner by an order of magnitude over that of commercial membranes, resulting in a lower resistance to mass transport because of the shorter length for water vapour passage. Such a structure could provide an ideal arrangement, with the pores being hydrophilic, facilitating condensate draining, and the membrane surfaces hydrophobic.

### **Membrane Fouling**

Direct contact MD has been observed to give less fouling than pressure-driven membrane processes in the treatment of waters containing 30 mg/L of soil-derived humic acids, using PVDF and PTFE membranes [25]. The membranes showed insignificant fouling at elevated salt concentrations, in contrast with nanofiltration, suggesting that MD is a better process for separating humic acids than pressure driven processes [23].

Experiments with a flat sheet PVDF membrane in direct contact mode showed a negligible (< 6%) decline in flux with feed waters containing 20 mM NaCl and up to 100 mg/L of soil-derived humic acid [49]. The presence of calcium reduced the flux considerably when the Ca<sup>2+</sup> concentration exceeded the critical coagulation concentration of 0.5-1 mM. Raising the feed water temperature from 50 to 70°C was also detrimental, increasing the amount of humic acid precipitated from 61 to 68%. Performance could be easily controlled as the fouling was physical, the loosely packed deposit being easily removed with 0.1 M NaOH, giving a 100% flux recovery.

Microbial growth on polypropylene MD membranes has been examined when the feed was untreated tap water, to reveal little bacterial accumulation on the hot water side of the membrane [17]. Several species of diatoms were observed, plus inorganic deposits containing Fe, Ca, Si, Zn, Al, Cl and F. Pretreatment with nanofiltration revealed no microbial presence after 1400 h of operation. Biofouling was significantly less than that seen in other membrane processes, and was less the higher the feed temperature and salinity. However, with a PTFE membrane treating seawater pretreated by microfiltration there was a 25% increase in flux for direct contact MD, compared to that for the raw seawater [19]. The permeate flux for a 3% NaCl solution was twice that for raw seawater. It was concluded that for seawater feed pretreatment was a significant positive factor.

### **Costs**

Capital costs are difficult to estimate as a large-scale MD plant has yet to be built, but capital and operating costs should be significantly less than for RO [51]. The process performs best at very low pressures, so thinner piping is employed and fewer problems arise with leaks and pump failures. A comparison of vacuum MD with RO has shown that it can compete energetically with RO, but the flux is lower so that a higher membrane area would need to be installed [8]. Membranes that are very thin and are very porous could give a 100-fold greater permeability, and have been shown, in theory, to be competitive at 25°C on energy consumption and with the same level of permeate flux. If operated at high temperature and coupled with solar energy the flux could be increased from 5-15 to 40-85 L/m<sup>2</sup>h, reducing the amount of membrane surface needed, and vacuum MD then would clearly be very competitive with RO. MD can only be competitive when low cost heat energy is available and/or the source water is too difficult for RO treatment.

Total water costs for seawater desalination for air gap MD have been predicted from small pilot plant studies to be as low as US\$ 0.26/kL for large-scale operation (105 ML/d) in the year 2020, far lower than that for RO, where they are currently at least US\$ 0.45/kL [41]. The estimate for air gap MD in 2005 was also US\$ 0.45/kL.

### **Solar Powered MD**

The feasibility of solar power in desalination by direct contact MD was first contemplated some time ago [18]. A plant was designed and constructed from a computer simulation of the process. Heat recovery was carried out with a conventional heat exchanger. For a domestic sized plant delivering 50 L/d the optimum component sizes were 3 m<sup>2</sup> for a solar collector, 1.8 m<sup>2</sup> for the membrane area and 0.7 m<sup>2</sup> for the total heat exchange area. The process is claimed to be cost competitive in isolated locations that can use solar energy, such as in remote localities with poor infrastructure [6]. A spiral wound direct contact unit was employed that utilised a PTFE membrane. This eliminated the need for thermal insulation and mechanical support. A prototype has been tested on the island of Ibiza in Spain. A direct contact module with a PP membrane has been integrated with a solar still, using the hot brine from the still as feed [3]. The system gave a flux of ~1 L/m<sup>2</sup> when the feed temperature was 50°C and the feed corresponded to 3.5% salt. The solar still contributed only some 20% of the total water yield of the dual system.

Small-scale air gap MD units powered by solar energy have been proposed in Germany for sea water desalination [29]. A polytetrafluoroethylene (PTFE) membrane that had a mean pore size of 0.2 µm was used. It had an area of 8 m<sup>2</sup> and an output of 20-30 L/h. Solar collectors had to be designed with an emphasis on corrosion resistance. Tests when the solar insolation was 700 W/m<sup>2</sup> and the feed flow was 225 L/h gave an input temperature of 90°C and a distillate production of 15 L/h, to give a total yield for the day of 81 L. The best result was 130 L/d for summer operation in central Europe. Simulation results showed that with a collector area of <6 m<sup>2</sup> and no heat storage a yield of 120-160 L/d should be attained in hotter climes. Four compact systems of capacity ~100 L/d have been installed in Egypt, Jordan, Morocco and the Canary Islands, and a larger two-loop system of 1000 L/d in Jordan [45]. The solar collector used had areas of 5.7 to 7.2 m<sup>2</sup> and were directly integrated into the salt water loop instead of using a heat exchanger. In the larger unit a

thermal storage unit of size 3 kL was incorporated to extend the operation time for some hours after sunset. The solar collector area was 80 m<sup>2</sup> and four of the MD modules used in the compact systems were employed. So far the technical results and operating experiences have been very promising, indicating that systems of this type with internal heat recovery should be feasible for capacities of up to 20 kL/d.

### FORWARD OSMOSIS

Forward or direct osmosis (FO) relies on osmosis, the natural diffusion of water through a semipermeable membrane from a low concentration solution to a solution having a higher concentration of dissolved material. Figure 2 illustrates the principles of RO and FO. FO has been explored as an alternative to RO, and is the subject of a recent review [11].

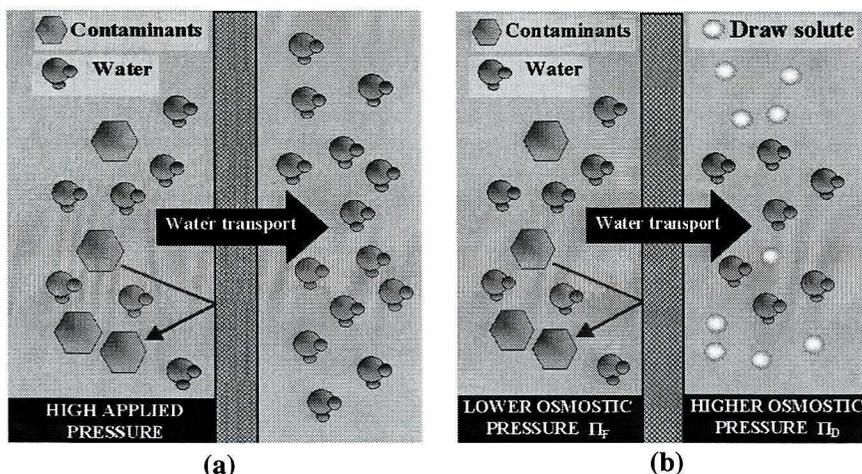


Fig. 2. Schematic illustration of the principles of RO (a) and FO (b)

The osmotic pressure is related to the molar concentration of the concentrated draw solution. It is the pressure that must be applied to a solution to prevent transfer of water into the solution through a semipermeable membrane. These forces can be significantly greater than the hydraulic forces used in RO, leading to the possibility of higher water flux rates and recoveries [39]. The osmotic pressure for some compounds is given in Table 1 [19]. It depends on the molar concentration of the dissolved species, so low molecular weight compounds are preferred.

FO has been applied to contaminated waters, converting them on the small scale to purified fluids containing sugars and critical electrolytes that are appropriate as energy drinks. The first suggestion for practical use seems to have been to use glucose as the draw solute with seawater as the feed, and a membrane made of cellulose acetate [30].

Table 1. Osmotic pressure of aqueous solutions [20]

Compound	MW, Da	Concentration, %	Osmotic Pressure, kPa
Sea water salt	58.5	3.5	2800
Brackish water salt	58.5	0.16	140
Fructose	180	15	2800
Fructose	180	6	900
Sucrose	342	6	540

Formulations have been developed as water and nutrient sources, suitable in emergency situations and for military and nature walking purposes. Personal packs capable of delivering a litre of product water in an hour have been developed, with 4,000 donated to victims of the tsunami disaster in Southern Asia, and 25,000 as a response to the United States Gulf Coast hurricane disaster [21]. The contaminated feed can be urine, as in space travel situations. FO is also used to concentrate fruit juices [5] and to hydrate dry ration foods and beverages [48]. Large-scale desalination systems that have a recyclable draw solution have been proposed [37].

### Membranes

The membrane employed is a cellulose ester with the same selectivity as RO membranes. However, RO membranes are not ideal for FO because of their low water flux [39]. The pore size is 0.3-0.5 nm, much smaller than bacteria (200-50,000 nm) or virus (5-100 nm). Since it is a diffusion process, water transfer through the membrane is slow, so FO membranes need to be very thin (10  $\mu\text{m}$ ) and supported on the surface of a porous microfiltration membrane [20]. The filters are claimed to be tolerant to very muddy water, up to 1000 nephelometric turbidity units. Because there is no high pressure, particles are not forced into the membrane pores, so the performance in muddy water being essentially the same as that for clear water. This is in contrast with pressure driven MF, which does not protect against viruses or toxins, and may plug up rapidly when the feed is of high turbidity.

It has been shown that RO membranes of the polyamide and cellulose acetate type, both having thick fabric backing layers to provide mechanical support, are not suitable for FO because of low fluxes, despite their having similar water permeability to cellulose triacetate FO membranes [38]. This has been attributed to severe internal concentration polarisation in the porous support and fabric layers of the RO membranes. The FO membrane, on the other hand, is made up of two layers, between which is embedded a polyester mesh to give reinforcement, eliminating the need for a thick polymer support layer and a thick fabric layer.

The application of FO as a pretreatment for RO in wastewater reclamation in space, using a draw solution of 1.7 M NaCl, two cellulose diacetate/triacetate and two thin film polyamide composite RO membranes give fluxes of 1.90, 1.97, 0.54 and 0.66 L/m<sup>2</sup>h respectively, versus 17.4 L/m<sup>2</sup>h for a cellulose triacetate FO membrane [9]. The low flux of the RO membranes was again ascribed to internal concentration polarisation [34]. As a pretreatment module FO could efficiently recover more than 90% of the wastewater and was highly effective in rejecting salt and organic compounds as well as providing a high flux. However, trace amounts of surfactants were found to diffuse through the system, so tighter semipermeable membranes are to be tested. All membranes performed very badly in rejecting urea. Complete urea rejection can be achieved by a dual FO/MD process which can successfully treat a complex feed not addressable by the separate processes [10].

### Large-Scale Operation

Finding draw solutions that are readily recoverable is the main challenge in large-scale operation. The ideal draw solution must have high water solubility and a low molecular weight in order to generate a high osmotic pressure, and should not be consumed in the process. It must be non-toxic

and palatable. Compatibility with the membrane is essential. As the product water is not primarily used as a nutrient provider, there must be a simple and economical method of recovering and recycling the solute. A number of early patents quoted in a recent article [38] describe systems that use volatile solutes such as sulphur dioxide or aliphatic alcohols that are recyclable. Another specifies a salt such as aluminium sulphate that can be precipitated, when after the transfer stage it is treated with calcium hydroxide to produce  $\text{Al}(\text{OH})_3$  and  $\text{CaSO}_4$ .

Ammonia and carbon dioxide also fulfil the requirements, so a novel desalting system based on FO has been proposed that utilises a concentrated ammonium bicarbonate solution as the draw solution to extract water from a saline source [38]. Separation of fresh water from the FO product is simply achieved by moderate heating ( $\sim 60^\circ\text{C}$ ), when the ammonium bicarbonate decomposes into ammonia and carbon dioxide. The gases can be removed by low-pressure distillation with a relatively low energy requirement. Laboratory-scale experiments employed a feed of 0.5 M NaCl (seawater concentration) and a draw solution of 6 M  $\text{NH}_4\text{HCO}_3$  at  $50^\circ\text{C}$ . A high water flux with very little salt passage resulted ( $> 95\%$  rejection). However, fluxes were considered to be too low and a salt concentration of 1 M was desirable for economic and operational reasons.

Later workers found that they could achieve less than half this flux at  $50^\circ\text{C}$  with 0.5 M NaCl and 4 M  $\text{NH}_4\text{HCO}_3$  [43]. The flux difference was attributed to different membrane and experimental conditions. Fluxes were always higher at  $50^\circ\text{C}$  than at  $30^\circ\text{C}$ . Two flat sheet RO membranes, one an asymmetric cellulose acetate membrane, the other a polyamide composite membrane, were studied, together with an FO membrane made of cellulose ester supported on an MF membrane. Decomposition was evident with 6 M  $\text{NH}_4\text{HCO}_3$  even at  $35^\circ\text{C}$ . When glucose or fructose was tested, the flux for 0.5 M NaCl and 4 M fructose was consistently higher, by some 50%, than that for 1 M NaCl and 4 M glucose. Fructose is more soluble but creates the same osmotic pressure at the same molar concentration. Salt rejections of  $> 97\%$  were achieved.

Further studies of the system made use of different mole ratios of ammonia and carbon dioxide, with higher ratios needed for more concentrated solutions, varying from 1.2 for a 1.1 M draw solution to 1.4 for a 6 M solution [39]. The higher ratios favour formation of ammonium carbamate,  $\text{NH}_2\text{CO}_2\text{NH}_4$ , which is very soluble in water. The membrane was made from a hydrophilic cellulosic polymer. It had a thickness of less than  $50\ \mu\text{m}$  and was quite different to RO membranes in that it lacked any porous polymer or fabric support layer, just an embedded polyester mesh to provide mechanical support. The feed, 0.05 to 2 M NaCl, and draw liquors were held at  $50^\circ\text{C}$ . Results showed that increasing the draw solution concentration led to less utilisation of the osmotic driving force, because of an increase in concentration polarisation (CP), as had been found in earlier studies of osmosis [34]. CP can be of two types: external and internal. External CP is a build up of solute at the active membrane layer surface on the feed side, arising from convective permeate flow. A reduced permeate flux results because of an increased osmotic pressure and possible osmotic de-swelling of the membrane. They were shown to have negligible effects on performance. In internal CP the draw solution within the porous backing substructure becomes diluted as water permeates the active layer, resulting in a significant decrease in the net driving force and water flux. Figure 3 is a schematic representation of the effect of internal CP on the effective osmotic pressure across the dense layer. Draw solutions of higher concentration increase the severity of the internal CP. In the case of the hydrophilic cellulosic membrane without a fabric support layer, salt rejection was good and feed concentrations were high, simulating high water recovery. The less than optimal performance was ascribed to the membrane not being designed for desalination of this type; the design of better salt rejection systems having minimal internal CP was anticipated. The coupled effects of internal and external CP have been discussed recently [37].

Other draw solutions that have been proposed include albumin, magnetic nanoparticles and dendrimers [1]. As the osmotic driving force is a function of the molar concentration of solute, these high molecular weight materials are unlike to provide practical operating fluxes. Magnetic nanoparticles in the form of ferritin-encapsulated iron oxides for use in FO have been patented [34]. Ferritin is a globular protein complex of 24 proteins that stores iron. The extreme MW of 10,000 Da or so indicates a low driving force, but a very practical separation system is achievable.

Dendrimers have a biomedical and drug delivery history. The same high MW approach has been made with poly(propylene glycol), an additive that can be recovered by a thermally induced phase separation [51]. The draw solutions that have been looked at so far are listed in Table 2.

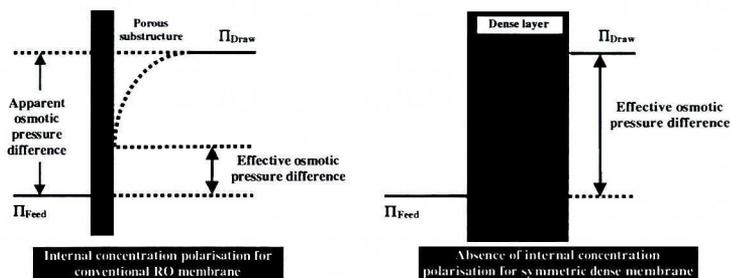


Fig. 3. Schematic representation of the effect of internal CP on the effective osmotic pressure difference across the dense layer

Table 2. Draw solutions for FO treatment of saline water

Compound	FO Product	Recycling of Draw Solute	Reference
Glucose	Energy drink	No; seawater as solvent for glucose	[30]
Glucose	Energy drink	No	[20]
Fructose	Energy drink	No, variation of glucose work	[50]
Sulphur dioxide, aliphatic alcohols	Drinking water	Heating or air stripping	[4, 16]
Aluminium sulphate	Drinking water	Ca(OH) <sub>2</sub> precipitates Al(OH) <sub>3</sub> & CaSO <sub>4</sub>	[15]
Sucrose (NB: low osmotic pressure)	Drinking water	Loose RO to remove sucrose	[52]
Potassium nitrate, hot; SO <sub>2</sub> in step 2	Drinking water	Cooling precipitates some KNO <sub>3</sub> in step 1	[40]
Ammonium bicarbonate	Drinking water	Heating to ~60°C forms NH <sub>3</sub> & CO <sub>2</sub>	[38, 39]
Ammonium bicarbonate, sugars	Drinking water	Regenerable by heating	[43]
Albumin, dendrimers	Drinking water	Ultrafiltration to separate	[1]
Magnetic protein nanoparticles	Drinking water	Magnetic separation	[35]

## SUMMARY AND CONCLUSIONS

The major advantages of MD over RO are [31, 33, 51]:

- greater simplicity, such as gravity flow through the membrane module
- use of very low grade heat as the energy source, down to 30°C, but typically 60 to 90°C
- the ability to treat highly concentrated wastes
- low operating pressures, from zero to a few hundred kPa
- lower operating temperature than conventional distillation

- recovery rates of up to 87%, versus 40% for RO [13]
- better process safety
- feed water does not require extensive pretreatment
- reduced chemical interaction between the membrane and feed components
- less demanding membrane mechanical properties
- complete or very high rejection of salt, colloids, cells and other impurities
- better suited to wastewater reclamation than RO.

The process is claimed to be cost competitive in several areas

- isolated locations using solar energy [3, 6, 18, 29, 45]
- waste heat applications, as from electrical generation power plants
- geothermal waters
- mobile military applications
- treatment of RO concentrate [36].

Its disadvantages are [14]:

- relatively low permeate flux compared to RO
- flux decay arising from concentration and temperature polarisation
- membrane and module design for MD
- high thermal energy consumption
- uncertain energy and economic costs for each MD mode.

The unknown long-term performance as regards flux and uncertain economic cost have long been emphasised [31]. Flux decay can arise from biofouling, scaling, or the presence of colloidal material in the feed water. Membrane wetting is another hurdle that apparently can be overcome by a hydrophobic composite membrane that has an appropriate hydrophilic surface. Because the flux is lower than that for RO a higher membrane area is required. Modelling has shown that MD membranes that are very thin and are very porous could give a 100-fold faster flux [8]. This would make them competitive at 25°C with RO on energy consumption and with the same level of permeate flux. If operated at high temperature and coupled with solar energy the flux could be further increased, so that MD would then clearly be very competitive with RO.

As regards FO, it needs only a low operating pressure (< 170 kPa), so

- membrane support
- compaction of the membrane and
- pressure-driven fouling

are not significant problems. FO removes the water and leaves the salt and impurities untouched. It has the major benefit of low energy requirements. Practical and economic draw compounds are yet to be found. At the very least, FO is a good candidate for pre-treatment of feed water to an RO plant, in that all particulate and dissolved organic matter are removed. The draw solution is recovered in the RO operation.

It can be seen that MD has considerable potential for large-scale desalination, whereas FO is currently confined in its immediate applications to small-scale systems, especially as a source of energy drinks in emergency situations.

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