AN OVERVIEW ON THE USE OF ELECTROLYTE SOLUTION AS A STRONG OSMOTIC AGENT IN FORWARD OSMOSIS

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Abstract

Forward osmosis (FO) has gained attention of people in recent decades due to its magnificent properties and less energy requirements. This paper aims to discuss various characteristics of draw solutes which are differentiated due to their performance and show exceptional results as osmotic agents in FO. Different types of membranes are being selected for different applications according to needs and requirements. Among them, CTA (Cellulose Triacetate Membrane) and TFC (Thin-film composite membrane) membranes are widely used and show higher flux as compared to others. Responsive draw solute causes remarkable change in osmotic pressure of the diluted solution when exposed to external factors such as pH and temperature. Responsive and Non-responsive draw solutes have advantages and disadvantages on their usage in FO. Comparative study has been done which shows that as compared to the different techniques for purification, FO stands tallest in terms of economic analysis and also results shown by FO are phenomenal. This review targets recent progress, challenges and opportunities concerning the development of appropriate and efficient osmotic agents with low-cost energy recovery to achieve largescale application of FO and its future development.

Introduction:

Membranes are the thin sheet of material forming a barrier or lining, which allows material separation based on the particle size. Membranes can be selectively permeable, semi-permeable, freely permeable, or impermeable to the material being processed. It is selectively permeable when the membrane allows only certain molecules to pass through it. For example, cell membranes allow only selected materials to pass like water, CO₂, O₂, etc. Semi-permeable ones are those which allow only solvent molecules to pass and retain all the solute particles. Such membranes are widely used in many processes like Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF), Reverse Osmosis (RO), etc. No such selectivity exists in the case of freely permeable membranes. Membranes like cell walls are freely permeable as their structure allows all the materials like water, proteins, CO₂, O₂ to pass through. Impermeable membranes are rarely used in purification and separation technologies as they don't permit any transfer through them.

The membrane process plays a very important role in many industries including water, textile, chemicals, pharmaceuticals, foods, etc. Membrane handling is very simple and is easily replaceable [1]. External hydraulic pressure is a driving force for most of the membrane systems[2]. The advantages of using membrane processes...
includes its simplicity in design, retention of colour, odour and volatile matter in the system and economically viable nature[3]. Forward Osmosis (FO) operates on an osmotic pressure gradient and operates at low energy in terms of electrical energy [4].

Membrane processes are categorized based on pore sizes which may occur in the range of nanometre (nm) to micrometre (mm). Also, pore size affects the performance of the membrane significantly. For example, it was found that in both, Pressure Retarded Osmosis (PRO) and Forward Osmosis (FO) mode, the water flux first gradually increased with increasing support layer pore size until pore size reaches 0.2 μm, and then dramatically dropped when the pore size was increased to 0.45 μm[5].

![Membrane pore size compared with the particle size of foreign matter](image)

The membranes used in FO are not so different from the ones used in RO. They are available in different configurations, shapes and sizes. Currently, many researchers are actively involved in various areas of membrane research to find the most durable and economically feasible processes to bring about promising results. Most of the membranes have a bilayered structure. Bilayered membranes comprise a selective active thin layer and a porous support layer to provide mechanical strength [7], [8]. They are mostly categorized based on the arrangement of sublayers. Some of the sublayers are Carbon nanotube layers [9], hydrophilic crosslinked PVA nanofibers sublayers [10], crosslinked chitosan sublayer [11], polydopamine sublayer [12].
Membranes are categorized according to their material used like organic membranes and inorganic membranes. Organic membranes are mostly polymeric membranes. Inorganic membranes are divided into zeolite membranes and ceramic membranes of metal oxides. Materials with low adsorption, strong cohesive forces, low thermal conductivity and inert nature are preferred. Due to adsorption, fouling and blocking can occur in a membrane which may lead to lower flux or replacement of the membrane. A high-pressure gradient can be sustained if the cohesive forces are strong. The inert nature of membrane material facilitates optimum pH and temperature range [14].

The pore size of the zeolite membrane can be adjusted in the range of 0.3-1nm [15]. Some frequently used zeolite membranes are MFI(silicalite-1, ZSM-5) and CHA(SAPO-34), etc.[16]. Ceramic materials are often used to separate radioactive material and strong solute at high temperatures. Some common examples are SiO$_2$, TiO$_2$, ZrO$_2$, etc.[17]. The polymeric membranes have low thermal stability compared to inorganic membranes. Polymeric membranes are used due to their ability to change pore size and adjustable membrane thickness. Some commonly used polymeric membranes are cellulose acetate(CA), Polyether ketone(PEK), Poly(tetrafluoroethylene), Polyacrylonitrile(PAN), etc.[18].

Various kind of membranes are used, for instance, cellulose triacetate (CTA), nanofiltration membrane, flat sheet membrane, hollow fibre membrane (HF), thin-film composite membrane (TFC), etc.[7]. CTA membranes have remarkably high mechanical strength, high porosity, wide availability and good resistance to degradation by chemicals including chlorine and other oxidants. They can be operated under a pH range of 2-10 and at 35°C[19]. CTA membrane has high reverse flux than TFC membrane; which causes fouling of membrane, decrease in osmotic pressure gradient and contamination of feed solution. TFC membrane is preferred for high water flux with the less effective area and due to its thin gauge. Due to their low cost and better stability, TFC membranes are used regardless of the type of feed and its composition.

Water purification can be done by several methods such as: (1) Physical processes- filtration, sedimentation, or distillation; (2) Biological processes- sand filters, active carbon; (3) Chemical processes- flocculation, chlorination, the use of ultraviolet light[20]. Osmosis is one of such processes which can be used. Osmosis is not a new process as nature itself uses osmosis for transportation of fluids and food materials, for example, the phloem and xylem bundles present in plants transport essential materials through the osmosis process.
The process in which solvent flows from higher osmotic potential to lower osmotic potential and movement of solute particles is obstructed by a semi-permeable membrane is called forward osmosis. Without any external hydraulic pressure and through the regeneration of draw solute, the overall energy consumed and the cost of FO is much lesser than RO[4]. This makes it suitable for large-scale production and purification. In RO, the displacement of solvent takes place through a semi-permeable membrane, which is driven by external force requiring membrane to be high pressure-bearing hence, it may cause fouling of the membrane. So, it need to be replaced in a short interval of time whereas in case of FO there is no external pressure applied, reducing the probability of membrane fouling. In the current era of separation and purification technologies, FO finds many applications such as water purification, seawater desalination, food processing and drug delivery. As in food processing industry, it is used in the concentration of fruit juices [22], whey concentration [23], etc.

As compared to other membrane processes, which depend on external hydraulic pressure like RO and basic filtration processes, whereas in FO, the driving force is concentration gradient which makes it economically feasible over other processes. FO is a spontaneous process and nowadays it is a major focus research areas in the membrane separation processes. FO system can be used in recirculating and continuous single-pass mode [24]. RO cannot be used above 50000 ppm concentration, above this concentration evaporation and FO can be used. This is because the RO membrane can’t resist externally applied pressure above this limit whereas we do not require external pressure in FO so it can be used[25].

Membrane fouling is affected by factors like feed composition, membrane property and hydrodynamic environment. The autopsy of a membrane in both FO as well as RO showed that the deposit of foulant in the FO membrane was greater than in the RO membrane[26]. FO is used widely in food processing, water, textiles and chemical industry. Owing to the reduced energy requirement, easy regeneration of draw solute and lesser probability of membrane fouling and its wide applications, it has become a major focus for research. This will lead to a longer shelf life of membranes.

In FO, the solution used to draw out solvent from the feed solution is called draw solution. There are lots of varieties of draw solutions used in the FO system including nanoparticles, polymers and organic solutions, inorganic solutions, ionic liquids and many more. Draw solution must have high osmotic potential which will be the driving force to make the process thermodynamically feasible. The high osmotic pressure can be achieved by increasing the effective number of particles as osmotic pressure is a colligative property. Here, solubility, association and dissociation properties of solute particles play a vital role. Therefore, as compared to others, inorganic draw solutes
generate more particles because of their instant solubility and generation of high osmotic pressure. An caution when using an electrolyte as a draw solute in FO is to maintain a certain temperature so that the diffusion of the draw should be as minimal as possible which can cause contamination, fouling of membrane and a decrease in osmotic pressure which ultimately reduces flux. To overcome this issue modified draw solutes were made, for example, Fe₃O₄ nanoparticles were coated with silica and sodium alginate sulphate, which reduced the reverse salt flux and increased the water flux. Due to this modification, size of solute particle increased which prohibited the particles to pass through the membrane. Also, the draw could be easily regenerated using an external magnetic field [27]. We should select a draw solute such that it is easily available, economical and readily regenerated. Most of the draw solutions studied to date proved to be satisfactory but still, we are a long way from achieving optimal efficiency.

**Draw Solutes:**
The driving force for FO is an osmotic pressure gradient, such that a draw solution of high concentration is used to induce a net flow of water from feed solution to draw solution through the membrane. This separates the feed water from its solutes. Ideally, a draw solute should have high osmotic pressure and reduce the reverse solute flux. Hence, identifying a suitable draw solute becomes one of the key challenges in FO. Until now, a wide range of new draw solutes have been developed and evaluated to maximize the efficiency of the FO and PRO processes, but none of them have been successfully commercialized [28].

**Categorization Of Draw Solutes:**
Electrolyte draw solutes can be classified into two types 1) Strong electrolytes 2) Weak electrolytes [29]. Strong electrolytes such as sodium chloride (NaCl), magnesium sulphate (MgSO₄), ammonium nitrate (NH₄NO₃), calcium chloride (CaCl₂), have high osmotic pressure gradient and higher dissociation constant so they are used in industries where some contamination is accepted and do not have many harmful effects. Whereas, acetic acid (CH₃COOH), carbonic acid (H₂CO₃), ammonia (NH₃), and H₃PO₄ phosphoric acid (H₃PO₄) are all examples of weak electrolytes. Weak electrolytes are preferred in food and pharmaceutical industries as weak electrolytes have small dissociation constant and are less likely to contaminate the feed which can cause an immense effect on the consumers [29].

**Responsive Draw Solute**
In the FO process, a major issue is energy consumption in regeneration of the draw solute. Regeneration of draw solute becomes easier if we use responsive draw solute. Responsive draw solute is a type of draw solute that can cause a remarkable change in osmotic pressure of dilute solution when exposed to external factors like temperature, pH, electric field, etc. [30].

**Nanoparticles**
These are the particles with size between 1-100 nm. Energy consumption for regeneration of draw solute can be effectively reduced by using magnetic core hydrophilic shell nanoparticles owing to their ability to get regenerated on the application of an external magnetic field. Applying hydrophilic coating on the magnetic core increases its diameter which restricts the mobility of particles resulting in low reverse flux. Usually, hydrophilic surface coatings are applied which enhance the solubility and hence the osmotic pressure. For example, magnetic nanoparticles of Fe₃O₄ are immobilized by coating sodium alginate sulphate (SAS) which also increases the osmotic pressure due to the hydrophilic interaction of carboxylic and hydroxyl groups. Electromagnets or neodymium magnets are used to recover synthesized magnetic nanoparticles [19].

**Thermoresponsive:**
Thermoresponsive draw solutes are recovered by controlling the temperature. Lower critical solution temperature (LCST) and upper critical solution temperature (UCST) are the temperatures between which the solution is not completely miscible for all compositions. By changing the temperature, we can alter the solubility which makes separation easier. In recent times, scientists and researchers have studied different thermoresponsive draw solutes with LCST and UCST properties for FO some of which are homopolymers, copolymers, oligomers, hydrogels and ionic liquids [31].

**Gas Responsive:**
Since thermo-responsive bulk hydrogels and micro-hydrogels require variation in temperature for recovery, in an attempt to avoid the costly dewatering process gas-responsive microgels are novel draw solutes used in the FO process. For an instance, CO₂ is purged and the microgel gets protonated by the CO₂ molecule and makes the hydrogel hydrophilic. Hence the protonated hydrogel can absorb water even at low pH. For the recovery of water,
N\textsubscript{2} should be purged at the isoelectric point. In contrast to the application of moderate heating and cooling, CO and N\textsubscript{2} were purged as a stimulus for water absorption and water recovery. Similarly, in O\textsubscript{2}/N\textsubscript{2}- responsive microgels, O\textsubscript{2} is being purged for reversible activation to draw water and N\textsubscript{2} is purged for water recovery which can be used as a draw solute. Such gas responsive draw solutes are capable of eliminating internal concentration polarization (ICP), resolve back diffusion issues and also yield high water flux. It has been observed that the functional O\textsubscript{2}/N\textsubscript{2} gas-responsive microgels that were synthesized using fluorine monomers of trifluoroethyl methacrylate (FM) or pentfluorostyrene (FS) and water-soluble monomers of diethylamino ethyl methacrylate (DEAEMA), dimethylamino ethyl methacrylate (DMAEMA), hydroxyethyl methacrylate (HEMA) and N-isopropyl acrylamide (NIPAM) provide a high water flux up to 29 LMH for a 2000 ppm NaCl feed at room temperature, while the NIPAM-FM microgels show the best water recovery of 56% [32].

pH
By changing the pH of the responsive draw solution, we can alter the effective charge on the draw solute. The charged solutes are repelled by the FO membrane depending upon the orientation of the membrane (mode of operation). This property helps to retard the reverse flux of draw solute and recover draw solute. This effect is observed in cyclohexanecarboxylic acid, 1-adamantaneacetic acid (AAA) [33].

Electro-Responsive Hydrogels
These kinds of stimuli-responsive draw agents extricate water molecules via osmotic pressure from the feed solution. Electro-responsive polymer hydrogels are more advantageous for application and control. Usually, electro-sensitive hydrogels are made up of polyelectrolytes. By applying an electric field, electro-responsive hydrogels undergo shrinking and swelling. Hydrogel causes anisotropic shrinking at the anode while water seepage at the cathode induced by electric osmosis in hydrogels deriving from water electrolysis [34]. In the field such as micro-mechanics, flexible actuators and artificial muscle tissues, electro-responsive hydrogels have shown excellence on comparing with other rigid materials [35].

Non-Responsive Draw Solutes, Inorganic Salts, Polymers and Organic Molecules
Non-Responsive Draw Solutes:
Draw solutes that do not have a particular special change in water affinity in response to terms such as temperature, pH, electro-magnetic field or light are termed as non-responsive draw solutes. However, responsive draw solutes have exposure to stimuli factors [30]. Solute-solvent intermolecular forces in non-responsive draw solutes are not affected by external factors [36]. Non-responsive draw solutes include non-functionalized polymers, inorganic salts, seawater and RO brine. There are several analyzed classes of non-responsive draw solutes with some elaborate molecular designs. Non-responsive draw solutes have application in indirect desalination where regeneration is not involved and diluted draw solution can be directly used for irrigation purposes [37], desert restoration etc.[38].

Table 1:- Advantages and Disadvantages of non-responsive draw solutes[39].

| Draw solute                  | Examples                                                                 | Advantages                                                  | Disadvantages                                                      |
|------------------------------|--------------------------------------------------------------------------|--------------------------------------------------------------|--------------------------------------------------------------------|
| Inorganic salts (e.g., NaCl, MgCl\textsubscript{2}, Na\textsubscript{2}SO\textsubscript{4}, (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, Ca(NO\textsubscript{3})\textsubscript{2}) | High solubility, Low cost, High osmotic pressure potential    | Sensitive to scaling/clogging, Higher reverse draw solute flux with small draw solutes, Difficult to recover in the reconcentration system |
| Polymers/macro-organic molecules (e.g., poly-sodium-acrylate, glycine) | Reduce reverse diffusion, High water flux                                | Aggravate Concentrate Polarization, Difficulties in regeneration process and circulation, Limited storage time due to biodegradation |
Inorganic salts:
They are economical, easily available, easy to handle and have a greater osmotic gradient which makes them suitable to use in FO/RO/NF system. In studies, it is found that no single solute has come up to increase the performance. The highest water flux was produced by KCl whereas MgSO$_4$ had the highest retention rate during regeneration. Problems associated with FO like mass transport and concentration polarization are easily understood by the study of inorganic draw solutes [30]. As seawater contains inorganic salts like NaCl, MgCl$_2$, etc., it can be used as a draw solute. The benefit of using seawater is that diluted seawater can be discharged directly without any further treatment. Despite having high osmotic pressure, Ca(NO$_3$)$_2$ has lower flux as compared to KCl and NH$_4$Cl [40]. It was found that costs were highest for KBr and lowest for Na$_2$SO$_4$, from highest to lowest cost: KBr > NH$_4$HCO$_3$ > Ca(NO$_3$)$_2$ > KCl > (NH$_4$)$_2$SO$_4$ > CaCl$_2$ > K$_2$SO$_4$ > NH$_4$Cl > MgCl$_2$ > MgSO$_4$ > KHCO$_3$ > NaCl > NaHCO$_3$ > Na$_2$SO$_4$. CuSO$_4$ gives osmotic pressure of 2.99 MPa, Ca(NO$_3$)$_2$ gives 16.63 MPa, NH$_4$Cl gives 5.42 MPa and KCl gives 7.56 MPa osmotic pressure but unexpected results were depicted by KCl and NH$_4$Cl solution as they have higher water flux than Ca(NO$_3$)$_2$ and CuSO$_4$[41]. At pH of 9, sodium phosphate solution showed the highest water flux of 12.5 LMH (litres per square meter hour)[42].

Polymeric and organic molecules:
In addition to inorganic draw salts, there are many polymeric and organic compounds which are soluble in water and are also categorized under non-responsive draw solutes. Compared to inorganic draw solutes, polymeric compounds are advantageous due to their high molecular weight which reduces the reverse diffusion. However, polymeric compounds have high viscosity which can create problems in recirculation and regeneration [43]. By changing the linking between polyelectrolyte chains, we can change the reverse flux. The inter-conversion between the straight-chain polymers to branched change/dendritic chain polymer decreases the reverse flux rate. Organic draw solutes

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**Fig. 4**: Mechanism of forward osmosis[30].
like sugar, carotenoids possess low toxicity but they have intrinsic problem, that is bio-fouling. These bio-molecular solutions exhibit growth of microorganism which lead to bio-fouling [44].

**Limitations Of Non-Responsive Draw Solute:**
A major limitation of non-responsive draw solutes is that they cannot be regenerated. The solution flux decreases with time and causes an increase in the net pressure of the membrane. Non-responsive copolymers with non-ionic monomers produce even lower water flux and have high viscosity with limited application than the copolymers with ionic monomers [30].

**Temperature Effects on Membranes:**
There is a huge impact of temperature on the osmotic pressure of the solution and thermodynamic properties such as diffusion coefficient, viscosity, etc. On increasing the temperature, the viscosity of solute decreases and simultaneously there is an increase in the diffusion coefficient of solute and water molecules. From studies, we can see a drastic change in flux of draw and feed solution under isothermal conditions. For a remarkable change in water flux, we do not require to change the temperature of both draw as well as feed solution, creating a temperature difference between a draw and feed effectively increases FO efficiency [45]. Increasing the temperature of draw solute to 50°C increases the flux rate of FO membrane to 3.1 LMH, which is approximately equal to 10 times as that of at 3°C[46]. On increasing every degree there is an increase of 1.2% on water flux in a range from 25°C to 35°C whereas when we increase the temperature in the range of 25°C to 45°C there is an increase of 2.3% in flux rate [47].

**High-Efficiency FO and Its pH, Temperature:**
As osmotic pressure is directly dependent on temperature, if we increase the temperature flux will increase. An increase in temperature decreases the density and viscosity of feed solution whereas, this change will increase solubility and diffusivity [6]. At higher temperature, membrane is less prone to bio-fouling which is seen by experimentation [48].

The fouling tendency of fatty acid was investigated at various pH values from 4 to 9 during the operation of the osmotically driven membrane process in the presence of the octanoic acid as a model fatty acid. It was observed that pH has a significant effect on fatty acid fouling. Initially permeate flux sharply decreased, then as the fatty acid layer developed, the flux decreased moderately throughout the pH range [49], [46].

**Reverse Salt Flux:**
The passage of salt from the draw solution to the feed solution through the membrane is called reverse salt flux. Reverse salt flux causes contamination of feed solution which can lead to an increase in the cost of retrieval of draw solute. This also reduces the osmotic pressure gradient which eventually leads to decreases in flux. To overcome this problem, recently some experiments were done which came up with remarkable results. Tegretol NP7 and NP9 with a long straight carbon chain and low critical micelle concentration (CMC) were integrated with highly charged ethylenediaminetetraacetic acid (EDTA) as a draw solution to minimize reverse salt diffusion in FO. EDTA along with nonylphenol ethoxylates surfactant can minimize the reverse salt flux up to 3 times lower compared to EDTA-2Na. This happens due to the interaction of nonylphenol ethoxylates tail with membrane surface which decreases the pore size. Using NF-TS80 membrane recovery of draw solute can be increased up to 95% [50].

The below Table - 2 shows different applications of Thin Film Composite membranes to variety of draw solutes.

| Sr. No. | Feed | Draw | Osmotic Pressure Difference | Membrane | Flux | Draw Regeneration | Reference |
|--------|------|------|-----------------------------|----------|------|------------------|----------|
| 1.     | Wastewater | Magnesium acetate, Sodium formate, Sodium acetate | (CH$_3$COO)$_2$Mg-10.3 MPa HCOONa-31.4MPa CH$_3$COONa-27.0 MPa | SW30 Polyamide TFC membrane | At 2.8 MPa flux value ranges from 2.60-106 m/s for sodium formate to | No | [51] |
The Cellulose-tri-acetate (CTA) membranes are the most common and widely used membranes due to their properties. Some of its applications are reviewed in the below table - 3.

Table 3: Performance of CTA membrane for various feed and draw solutes.

| Sr. No | Feed | Draw | Osmotic Pressure Difference | Membrane | Flux | Draw Regenerate | Reference |
|--------|------|------|----------------------------|----------|------|----------------|-----------|
| 1.     | Treated Sewage Effluent | 4 M NaCl | - | CTA FO membrane | Highest Flux of 5.5 LMH at flow rate 1.2 | No | [57] |

| 2.     | Raw Juices | Potassium sorbate solution, NaCl | 46 bar, 93 bar | TFC polyamide | 5 LMH | No | [22] |
| 3.     | DI water | Poly (4-styrenesulfonic acid-co-maleic acid) Sodium salt and 3 solution (0.25 g/mL) | 32.8 bar [For P (SSA-co-MA)-Na-1] 25.12 bar [For P (SSA-co-MA)-Na-3] | TFC Membrane (18.9 cm²) | 15 LMH [For P (SSA-co-MA)-Na-1] 16 LMH [For P (SSA-co-MA)-Na-3] | Yes | [52] |
| 4.     | Distilled Water | Zwitterionichomopolymer polysulfobetaine (PBET) | 194 mOsmol/kg for 5% by wt. PBET solution 898 mOsmol/kg for 20% by wt. PBET solution | TFC membrane (ALFS mode) | 0.92 LMH for 5% by wt. solution, 3.22 LMH for 20% by wt. solution | Yes | [53] |
| 5.     | DI water, salt solution (2 g/L NaCl) | Corn starch powder NaCl solution (0.5 M) | 11.91 atm | Flat sheet PAN UF membrane, TFC membrane | DI water 4.1 LMH and NaCl 2.2 LMH | Yes | [54] |
| 6.     | DI water and NaCl | Ethanol | 46.7 bar and 65 bar | TFC (Porifera membrane) | Selectivity 0.08 bar⁻¹ Flux-3 LMH Selectivity 0.63 bar⁻¹ Flux-20 LMH | Yes | [55] |
| 7.     | DI water | NaCl | 26 bar | TFC-FO membrane | 9–10 LMH | No | [56] |
| t (TSE) | Seawater, Brine, Wastewater, Ionic liquids (IL) and deep eutectic solvents (DES) | DES such as Ethaline ($\pi \sim 365$ atm), Glycine ($\pi \sim 317$ atm), IL such as P4444DMBS ($\pi \sim 5.4$ osmol/kg), P4444TMBS ($\pi \sim 3.6$ osmol/kg) reported high osmotic potential | CTA FO membranes | LPM. IL like nBuTAEE, nBu-PHEL, Glycol ethers and [Hbet][T2N] had flux (<1 LMH), IL like P4444D MBS generated water flux of ~4LMH with 1.6 M NaCl feed solution | Yes | [58] |
|---|---|---|---|---|---|---|
| 2. | Seawater, Brine, Wastewater, Ionic liquids (IL) and deep eutectic solvents (DES) | DES such as Ethaline ($\pi \sim 365$ atm), Glycine ($\pi \sim 317$ atm), IL such as P4444DMBS ($\pi \sim 5.4$ osmol/kg), P4444TMBS ($\pi \sim 3.6$ osmol/kg) reported high osmotic potential | CTA FO membranes | LPM. IL like nBuTAEE, nBu-PHEL, Glycol ethers and [Hbet][T2N] had flux (<1 LMH), IL like P4444D MBS generated water flux of ~4LMH with 1.6 M NaCl feed solution | Yes | [58] |
| 3. | The liquid remaining after curd formation in cheese making. | Sodium chloride (NaCl) | 74 bar Flat-sheet CTA Membrane | 7.2 LMH | No | [59] |
| 4. | DI water | Poly(N-isopropylacrylamide) (PNIPAM) | Cellulose triacetate (CTA) | The highest flux was 1.99 LMH by PNIPAM/γ-PGA/PEG hydrogel. | No | [60] |
| 5. | Distilled water, Brine, and Brackish water | Fe$_3$O$_4$ nanoparticles coated by sulfonated sodium alginate | Fe$_3$O$_4$@SiO$_2$(CH$_3$)$_2$Cl: SAS. At 1:1 Osmotic pressure is 111.3 atm | CTA membrane | 12.8, 12.4, and 12.0 LMH for the first, second and third run respectively. | Yes | [19] |
| 6. | Brackish groundwater, Seawater | SodiumLignin Sulphonate (NaLS) | 78 bar FO-CTA-1 FO-CTA-2 | 15 LMH with FO-CTA-1 and 10 LMH with FO-CTA-2 membrane both with AL-DS mode | No | [61] |
| 7. | Skim milk and Dairy Whey | Standard Brine Solution (48-57g/L) | 30.1 - 35.7 bar OsmoF2OFO-CTA 8040-45 SDS (12m$^2$) | Started at 5 LMH and diminished to 0.5 LMH | No | [23] |
| 8. | Distilled Water | PolyDADMAC and DADMAC solutions each with 0.035, 0.085, 0.12 0.0, 0.155 g/mL of H$_2$O were used. | 26.41 atm for DADMAC and 7.95 atm for PolyDADMAC both at 0.085 g/mL | CTA membrane | 10.50 LMH for PolyDADMAC and 20 LMH for DADMAC | Yes (NF90) | [62] |
| 9. | Brackish water (NaCl 5050 ppm) | CuSO$_4$*5H$_2$O solution (200000 ppm) | 29.94 bar Flat Sheet CTA Membrane | 3.57 LMH (AL-FS mode) | Yes | [63] |
| 10. | Rainwater (TDS of 4.5 mg/L) | Cooling water from Steam Plant | CA Membrane (20 cm$^2$) | 1.75 LMH at 23°C and 3.1 LMH at 50°C | No | [46] |
| 11. | Fruit juices and DI Water | Gluconate Salt Solution (2M) | CTA TFC (18.9 cm$^2$) | 17.98 LMH CTA membrane and 23.17 LMH TFC membrane PRO mode | Yes | [64] |
Various modifications in membranes are possible so as to get higher flux, low fouling and higher salt rejection. Some of such modified membranes are listed and compared in the table - 4.

Table 4: Application based performance of various modified membranes.

| Sr. No. | Feed | Draw | Osmotic Pressure Difference | Membrane | Flux | Draw Regenerate | Reference |
|---------|------|------|-----------------------------|----------|------|----------------|-----------|
| 1.      | Wastewater and Slug | NaCl | 7.14 to 23.1 bar when using ES membrane, and 7.91 to 25.1 bar when TFC membrane | ESMade up of CTA and TFC made up of Polyamide | $1.48 \times 10^8$ to $5.56 \times 10^6$ m/s for the ES membrane | $3.37 \times 10^8$ to $8.90 \times 10^6$ m/s for TFC membrane | No | [69] |

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2. 100 mg of ACS grade NaCl (33 mg/L). Single salts (NaCl, MgCl₂(H₂O)_{6}, MgSO₄(H₂O)₂, CH₃COONa·3H₂O and trisodium citrate dihydrate) 23 bar CTA or TFC Membrane The average water flux for mixed salts DSs (Draw solution) flux was similar to NaCl only DS 10% MgSO₄ has a slightly lower flux than that of the other tested DSs. No [70]

3. Greywater containing Sodium Alginate, Organic Fouulant, CaCl₂ and Sodium Dodecyl Sulfate (20 mg/L) NaCl solution (2.0 M) - Biomimetic Membrane (ABBM) 28 cm² - No [71]

4. Model Brackish Groundwater [NaCl Solution (5 g/L)] Sulphur Based Seed Solution, {ammonium sulphate and ammonium sulphitemonohydrate in DI water (1 M)} 46.24 bar TFC Membrane CTAMembrane 19 LMH for TFC membrane for 0.8 MSOA and 0.2 M SIOA No [72]

5. Seawater Ethyleneoxidepropyleneoxide copolymer - 10-inch HollowFibre Membrane (336 m²) 6.8 to 16.7 kWh/m³ of freshwater Yes [73]

6. DI water and simulated seawater (0.5 M NaCl) EDTA-MgNa₂, EDTA-CaNa₂, EDTA-MnNa₂, EDTA-ZnNa₂, and NaCl 3600 mOsm/kg NF membrane 0.07 M EDTA sodium salt as NF feed solution, the specific water flux and rejection rate were between 0.7 and 1.0 LMH/bar, and 80 and 93%, respectively. Yes [74]

6. 2000 ppm NaCl solution P (AMPS-co AM) hydrogel - FO membrane (22.05 cm²) 2.76 LMH Yes [34]

7. Dilute draw solution (DDS) TMA-CO₂-H₂O 0.6-1.01 bar - 6.8 to 16.7 kWh/m³ of freshwater Yes [75]

8. DI water DI water and - CTA membrane - No [76]
Techno-Economic Aspect-
The operating cost contains three parts, counting the cost of draw solutes and FO membrane, FO process, and the regeneration of draw solutes. A large part of the energy consumed in the FO process is taken up for regeneration of draw solute especially when there is non-responsive draw solute [18].

Due to the growing demand for potable water, there is an increase in the need for robust, efficient, and economic techniques for the treatment of water. Various membrane processes like RO, RO coupled with ultraviolet treatment (RO-UV), nanofiltration, etc. are gaining popularity. However, for the feasibility of these technologies, they should be economic and efficient. Factors like capital expenditure (CAPEX), operational cost (OPEX), quality of water generated, reflux ratio, etc. are crucial for the practical application of these membrane technologies [79].

Recently, fertilizer drawn forward osmosis processes are gaining worldwide attention. In this process, fertilizer solution is used as draw solute and low saline water is used as feed solution which are separated by a selectively permeable membrane; wherein, the freshwater will flow from feed solution to draw solution due to difference in osmotic pressure. This will result in a diluted fertilizer-containing solution that can be utilized for direct irrigation in fields. However, the concentration after dilution should be compatible for direct application. More than often, the diluted draw solution after the FO process is either treated back to concentrate them or suitable utilized for the suitable purpose. However, finding the right application to diluted draw solution or regenerating draw solution using NF, RO, UV, etc might not be economically feasible. Post-treatment processes like RO and NF are used for draw solution recovery and water purification [80].

In a recent study, it was found that the limitation of only FO can be overcome by the pressurization of feed solution. It was observed that FO coupled with pressurization of feed solution is cost-efficient and also the diluted draw solution obtained can be safely used as a water-fertilizer solution.

**Economic analysis:**
CAPEX and OPEX parameters are analyzed for different processes and in different scenarios. This study will help in broadening the understanding of the economic feasibility of the process in different conditions. During such studies, it was observed that the life of the FO membrane was more than that of the RO membrane. This is because FO membranes, unlike RO membranes are not prone to membrane fouling while in operation. It was observed that the membrane cost for both FO and RO membrane is almost the same 700 $, but RO membrane has an average life of 3 years and an average life of FO membrane is 7 years. Moreover, the energy cost required for draw solute regeneration is also an important aspect and hence while estimating the cost of draw solute both the cost of draw solute themselves as well as the cost of regeneration is considered and how effective is the regeneration [41].
To estimate CAPEX and OPEX per year following empirical formula is used

\[
\text{CAPEX (annualized)} = \text{Total CAPEX cost} \times \left\{ \frac{[i(1+i)/(1+i)^n -1]}{n} \right\}
\]

where, \(i\) = interest rate,
\(n\) = plant lifetime

Other empirical formulae were derived to estimate CAPEX required for pumps and pressure exchanger

\[
\text{CAPEX} = 52 \times \text{Total summation of (Pout} \times F) \]

Where, \(Pout\) = discharge pressure and \(F\) = volumetric flowrate in \(m^3/h\).

The membrane CAPEX was estimated using the following formula

\[
\text{CAPEX}_m = C_m \times A_m
\]

Where, \(A_m\) is the membrane area in \(m^2\) and \(C_m\) is the specific membrane cost per square meter [81].

OPEX cost per year will include the energy consumption, maintenance of plant, chemical and raw material required, etc.

In a comparative study of the desalination process using UV, RO, and MBR it was found that the OPEX of RO (0.321 $/m^3) followed by MBR and UV, $0.277/m^3 and $0.167/m^3 respectively. For CAPEX, the MBR cost ($0.302/m^3) was highest and followed by RO and UV disinfection units ($0.242/m^3 and $0.130/m^3 respectively) and FO on the application of 2 bar is $0.364/m3 while that of 6 bar is $0.395/m3 (7.9% increase). As expected, the major factors responsible for such a high OPEX cost of the plant are the energy consumption of the RO and UV units [79].

Another study compared the economic aspect of the two-stage RO process vs FO-RO hybrid process for desalination of seawater. In this study, it was found that the total OPEX for two-stage RO was 687.3 million $ and for the hybrid FO-RO process, it was 733.4 million $. Whereas, the total CAPEX for two-staged RO is 122.4 million $ and for FO-RO it is 170.6 million $. However, it was hypothesized that if FO element cost is reduced by 50% and the life of the membrane is extended then the hybrid FO-RO process is more economic than the two-stage RO process [80].

In another case study where stand-alone RO and FO system were discussed in cost sensitivity, it was revealed that approximately 0.2 US$/m^3 was required for the FO process; whereas in the case of the stand-alone RO process minimum of 0.85 US$/m^3 was required. Moreover, the study also revealed that the cost rises if recovery of draw solute is also considered and both the processes become expensive in case of high saline water [81].

**Advantages of Forward Osmosis (FO) over reverse osmosis (RO)**

Since there is no external pressure application in FO, the fouling of the FO membrane is very negligible and can be easily maintained by mechanical or chemical cleaning. FO is a spontaneous process that does not require high temperature or high pressure for operation. For the desalination using FO, mere energy of 0.84kWh/m^3 is required. It can be made more economic by draw solute recovery or by utilizing diluted draw solute for other suitable purposes.

**Table 5**: Comparison of RO and FO.

| Parameters                      | RO          | FO                                    |
|---------------------------------|-------------|---------------------------------------|
| Electric energy consumption, kWh/m^3 potable water | 2.5-7       | 3-68 and additional 0.25 for circulation pumps |
| Water recovery                  | 30-50%      | Up to 50%, although rarely in stand-alone FO technology |
| Water desalination cost, $/m^3  | 0.5-3       | 0.8-2                                 |
| Ease of pre-treatment           | Chemical cleaning, pre-treatment for mitigating the fouling of the membrane | Fouling is reversible, can be treated mechanically |
| Operating pressure and temperature | 50-70 bar, ambient temperature | Atmospheric pressure, ambient temperature |

FO-RO hybrid process cannot be economically viable as compared to only RO system [41].

| TYPE                      | ENERGY CONSUMPTION (kWh/m³) | WATER RECOVERY % | COST (OPEX) $/m³ |
|--------------------------|-----------------------------|------------------|-----------------|
| Stand alone FO           | 0.59                        | Upto 50%         | 0.8-2           |
| Stand alone RO           | 1.5                         | 30-50%           | 0.5-3           |
| FO-RO                    | 1.5                         | 2                | Water desalination cost: 0.91 |
| RO-MD                    | 4.8                         | 84.6             | Water desalination cost: 0.63 |
| RO-CD-UF-MD              | 4.8                         | 66.9             | Water desalination cost 1.05 |
| RO-NF-MD                 | 4.8                         | 73.4             | Water desalination cost 0.70 |
| RO-MD-PRO                | 2.68                        | 30% of RO brine  | OPEX 1.04       |
| RO-MD-MDC                | 3+ RO stand alone           | 99.8             | -               |
| RO-CDI                   | 3.17                        | -                | -               |
| RO-MCDI                  | 0.15-0.21+ standalone RO    | -                | -               |
| RO- FCDI                 | 1.3+ stand alone RO         | 45               | -               |

1) CD- Chemical deposition
2) CDI- Capacitive deionisation
3) FCDI- flow electrode capacitive deionisation
4) FO- forward Osmosis
5) MCDI- Membrane capacitive deionisation
6) MD- Membrane distillation
7) MDC- Membrane Crystallisation
8) NF- Nano filtration
9) PRO- Pressure retarded osmosis
10) RO- Reverse osmosis
11) UF- Ultra filtration

**Conclusion:**
Forward Osmosis has been known to us for a long time but, the research of this topic has gathered momentum in the last two decades. In FO, selection of the appropriate draw solute is necessary to generate enough osmotic pressure gradient to make the process efficient. The other membrane separations like RO, Nanofiltration, Ultrafiltration etc. also have a lot of applications. But since these processes cannot be used at very high concentrations, FO can emerge as a cost-effective choice. For the desalination using FO, mere energy of 0.84 kWh/m³ is required. Regeneration of the draw solutes is the major problem in FO, but use of responsive solutes makes it affordable. This gives the responsive solutions an advantage over the non-responsive draw solutes. The responsive draw solutes are then further classified under the classes as Nanoparticles, Thermostressive, Gas Responsive, pH Responsive and Electro-responsive depending on the external factor to which they respond. Even though inorganic salts are non-responsive draw solutes, they are still a popular choice as they are economical, easily available, easy to handle and have a greater osmotic gradient. KCl gives the highest water flux whereas MgSO₄ carries out the retention rate during regeneration. Reverse salt flux is another major problem with membrane separation processes but large complexes like EDTA along with nonylphenol ethoxylates surfactant can minimize the reverse salt flux up to 3 times lower compared to EDTA-2Na.

Of all the different types of membranes used for membrane separations, TFC and CTA membranes are the most popular choices. The salts of weak acids including Magnesium acetate, sodium formate showed maximum osmotic pressure of 10.3 MPa and 31.4 MPa respectively and ethanol as a draw could achieve flux upto 20 LMH with TFC membrane. With CTA membranes, Fe₃O₄ nanoparticle coated SAS solution as a draw and distilled water as feed exhibited remarkable flux of 85 LMH in FO mode with osmotic pressure gradient of 112.7 atm. On the other hand, ionic liquids and deep eutectic solvents as draw showed maximum osmotic pressure of 365-317 atm but very low flux (upto 4 LMH). The membrane cost for FO and RO is almost equal (700 $), but RO membrane has an average
life of 3 years and that of FO membrane is 7 years. In the long run the FO-RO conjugated process is more economical as revealed by the economic analysis.

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