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# A Review of Ultrafiltration and Forward Osmosis:application and modification

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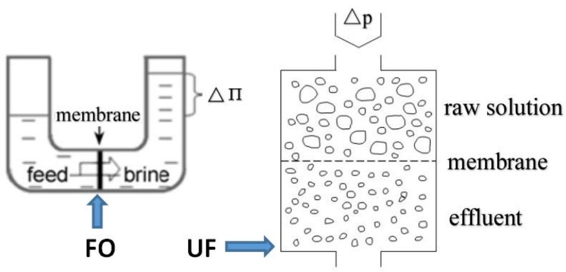
**Abstract.** As a new treatment , membrane filtration is playing a more prominent role in treating many kinds of wastewater. Among all the membrane technologies, ultrafiltration(UF) and forward osmosis(FO) technology has been widely utilized and developed in oil field and refinery produced water. However, the reports about the differences between the two kinds of membrane technology used in oily wastewater are not yet available. In this review, at first we introduce the advantages, shortcomings and applications of UF and FO membranes. Among these , we mainly illustrate the membrane fouling, which now is a big problem because it increases costs and decreases membrane life to limit the industrialization of the membrane, and the different modification methods of membranes are discussed to figure out how these ways can ease the membrane fouling. Next we make a comparison of the two membranes. Finally we illustrate the future research topics.




## 1. Introduction

Water scarcity is a severe problem facing our country these years due to environmental pollution and overpopulation. As many new technologies have emerged to reduce the cost of desalination of seawater, more and more countries turn to membrane technology to solve the water problems[1-4]. So far, many membrane processes have been utilized in the water plant, such as ultra-filtration(UF), micro-filtration(MF), nano-filtration(NF) and reverse osmosis (RO).

Ultrafiltration is a pressurized membrane separation technology, namely under certain pressure, makes the small molecule solute and solvent pass through a certain aperture of a special film, and stops the macromolecular solute from passing, so that the macromolecular material has been partially purified.

As an alternative desalination and water recycle process, forward osmosis (FO) has gained much attention in recent years. Technically, any dense, non-porous, selectively permeable material can be used to make the membrane for FO. In the past, such membranes have been tested (in flat sheet and capillary configurations) for various applications of FO. Early membrane researchers tried with every type of membrane material available, including bladders of pigs, cattle,and fish; collodion (nitrocellulose); rubber; porcelain; and gold beaters' skin. Nowadays the FO membranes can be made of cellulose acetate (CA) and supported by an embedded polyester mesh to enhance its mechanical strength (**Figure 1**).

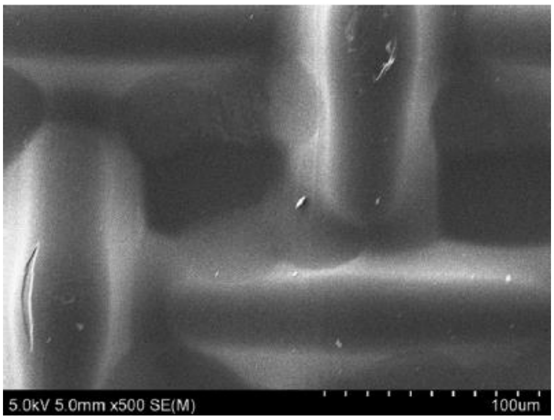



**Figure 1.** A SEM image of the cellulose acetate membrane surface

Now ultrafiltration and forward osmosis technology has played an important role in oil field and refinery produced water and they are very different. Therefore, it is essential to illustrate the differences between UF and FO when they are used in oily wastewater treatment . Unfortunately, to the best of our knowledge, reviews in this area are rather sparse. In this reviews we introduce UF and FO at first, and then compare the characteristics of the two kinds of membrane technology, finally introduce the authors' views of the future research topics.

## 2. Ultrafiltration (UF)

*2.1 The advantages and shortcomings of UF in treating oily wastewater*

More and more oily wastewater has been generated from the development of oil fields, especially from those using water injection technology[5-8]. To purify this water is always necessary in order that it can be reused as water resource again and during the recycling process，it protects the environment. Conventional oily wastewater treatment methods include gravity separation and skimming, dissolved air flotation, de-emulsification, coagulation and flocculation, which have several disadvantages such as low efficiency, high operation costs, corrosion and recontamination problems. Also, the removing of the smaller oil droplets and emulsions can not be achieved by these ineffective methods. All of these disadvantages have resulted into a whole new processes for oily wastewater treatment. Membrane filtration,as a new treatment, is playing a more prominent role in treating oily wastewater with its numerous advantages: no chemical additives to break the emulsion, high COD removal efficiencies, and compact treatment facilities which is fully automated[9].

Among all these membrane technologies, Ultrafiltration technology has been widely utilized in wastewater treatment and reclamation because of its superiority of low energy consumption and high efficiency and with no chemical preparation involved[2].The common membrane materials are PVDF,CA and PTFE. They all have their own physico-chemical properties, while the property of extremely hydrophobicity can leads to membrane fouling, which will limits the industrialization of these UF membranes. Membrane fouling is affected by surface hydrophilicity, i.e., improving hydrophilicity of the membrane can reduce membrane fouling to some extent. The common ways we use to promote its surface hydrophilicity are blending a hydrophilic polymer with a hydrophobic polymer, grafting hydrophilic branches on hydrophobic polymer backbones and the deposition of hydrophilic films on hydrophobic materials. So, the different hydrophilic modification methods of UF membranes will be discussed in following part to figure out how these ways can ease the membrane fouling.

*2.2 Modification methods of UF*

Yu et al.[10] made the Al2O3–PVDF tubular membranes by phase-inversion method. They added nano-sized Al2O3 particles (2%, by weight of PVDF) and other additives (1% sodium hexaphosphate, by weight of PVDF; 3% PVP, by weight of the solution) with dissolved PVDF. Pure water and wastewater experiment were conducted respectively under cross-flow Ultrafiltration. The test turned out that the modified Al2O3–PVDF membranes could reach greater flux and better removal efficiency than the normal PVDF both in two different feed solutions. Moreover, they had membranes washing experiment after using oily wastewater fouling the membranes. In this study, flux recoveries of two membranes were good after backwashing with pure water, and the modified membrane's flux recovery was higher slightly than that of the unmodified one, which indicated the modified membrane had greater anti-fouling property because of the change of its surface hydrophilicity[9]. Another modification experiment of PVDF membrane were couducted by Zuo et,al[11] .They succeeded making a SiO2/PVDF blending membrane and conducted several tests to figure out its surface surface morphology and examine the chemical composition of the fouled membrane surface. The feed used in this experiment simulated the polymer-flooding produced wastewater in Daqing oilfields. And it was found that the SiO2/PVDF membranes exhibited better antifouling capacity than PVDF membranes indicated in the membrane fouling behavior.

PTFE is another membrane material employed in UF treatment. The study Liu et [12]alconducted has pointed out that PTFE membrane had better chemical stability and greater pure water flux than PVDF membrane under the same condition. And the high flux recovery indicated its excellent antifouling property. Though PTFE has great antifouling property,it can't ignore that its surface free energy is rather high compared with those hydrophilic material. So Zhou et al[13] tried to use zwitterionic surfactants to change the membrane's surface property. By adding the aqueous solution of different zwitterionic surfactants respectively, Zhou and his team tested the contact angle of the drop and adhesion tension of both the membrane surface and the solution. The results showed that the calculations of the Gibbs surface excess of the zwitterionic surfactants at the water-air and PTFE-water interfaces were lower than the normal PTFE, which indicated that the adsorption of these surfactants on the membrane did improve the hydrophilicity of PTFE surface and lead to a decrease of the PTFE-liquid interfacial tension.

## 3. Forward Osmosis (FO)

*3.1 The advantages of FO*

The main advantages of the FO are that it can operates at low or no hydraulic pressures, which is different from the traditional membrane process. It also has high rejection of a wide range of contaminants, and due to the low pressure, it may have a lower membrane fouling propensity than pressure-driven membrane processes. And the equipment used is very simple and membrane support is less of a problem[14-16].

The concept of FO had not been proposed until 1970s, although the the osmotic phenomenon was discovered long time ago.The theory of the FO is easily understood. The high concentrated solution(DS) and the low concentrated solution(FS) is separated by a semi-permeable membrane, so water can be drawn automatically from the feed side to the draw side due to the osmotic pressure gradient generated by the concentration difference between the two sides. In the past decade, FO has gained vast popularity in many fields, such as the areas of food processing, pharmaceutical concentration, power generation, portable water reuse, and desalination. For food and pharmaceutical processing, FO has the benefit of concentrating the feed stream without requiring high pressures or temperatures that may be detrimental to the feed solution. For medical applications, FO can assist in the slow and accurate release of drugs that have low oral bio availability due to their limited solubility or permeability.

*3.2 The shortcomings of FO*

Although so many advantages of FO has been reported, some shortcomings restrict its utilization in large scale. The most important problem of the process of osmotic is the concentration polarization(CP). In the osmotic processes, the osmotic pressure difference across the active layer is much lower than the bulk osmotic pressure difference, so the water flux is much lower than expected. The lower-than-expected water flux is often attributed to several membrane-associated transport phenomena. Specifically, two types of concentration polarization phenomena can take place in osmotic-driven membrane processes, they are external CP and internal CP [17].

CP is not just a phenomenon in pressure-driven membrane processes , it also occurs in osmotic-driven membrane processes, on both the feed and permeate sides of the membrane. When the feed solution flows on the active layer of the membrane, solutes get together at the interface of the active layer, which is called concentrative external CP and is similar to CP in pressure-driven membrane processes. Simultaneously, the draw solution in contact with the permeate side of the membrane is being diluted at the permeate–membrane interface by the permeating water. This is called dilutive external CP. Both of the external CP phenomena reduce the effective osmotic driving force, which is caused by the osmotic pressure gradient. There are some means to minimize the adverse effect of external CP on osmotic-driven membrane processes, like increasing flow velocity and turbulence at the membrane surface or manipulating the water flux. However, because water flux in FO is already low, the ability to decrease external CP through reducing flux is limited.

FO membrane often consist of a dense separating layer and a porous support layer, so that two phenomena can occur according to the membrane orientation. If the porous support layer of an asymmetric membrane faces the feed solution, a polarized layer is established along the inside of the dense active layer as water and solute propagate the porous layer. This phenomenon is similar to concentrative external CP, except that it takes place within the porous layer, and cannot be minimized by cross-flow, we called it the concentrative internal CP. In FO applications for water treatment and desalination, the active layer of the membrane faces the feed solution and the porous support layer faces the draw solution. As water permeates the active layer, the draw solution within the porous substructure becomes diluted. This is referred to as dilutive internal CP, dilutive ICP is illustrated in Figure 2(a).

*3.3 Applications of FO*

Forward osmosis has been utilized in a large range of fields. Although the shortcomings still restrict the commercial applications of the FO, it is emerging in the water purification field and in the pharmaceutical industry. And the most meaningful applications are wastewater treatment and water purification, seawater desalination.

Several modern applications of FO in wastewater treatment have been reported already. These include an early study on concentration of dilute industrial wastewater, an investigation on treatment of landfill leachate, a study on direct potable reuse of wastewater in advanced life support systems for space applications, and an investigation on concentration of liquids from anaerobic sludge digestion at a domestic wastewater treatment facility. In most wastewater treatment applications, FO is not the ultimate process, but a high-level pretreatment step before an ultimate wastewater treatment process.

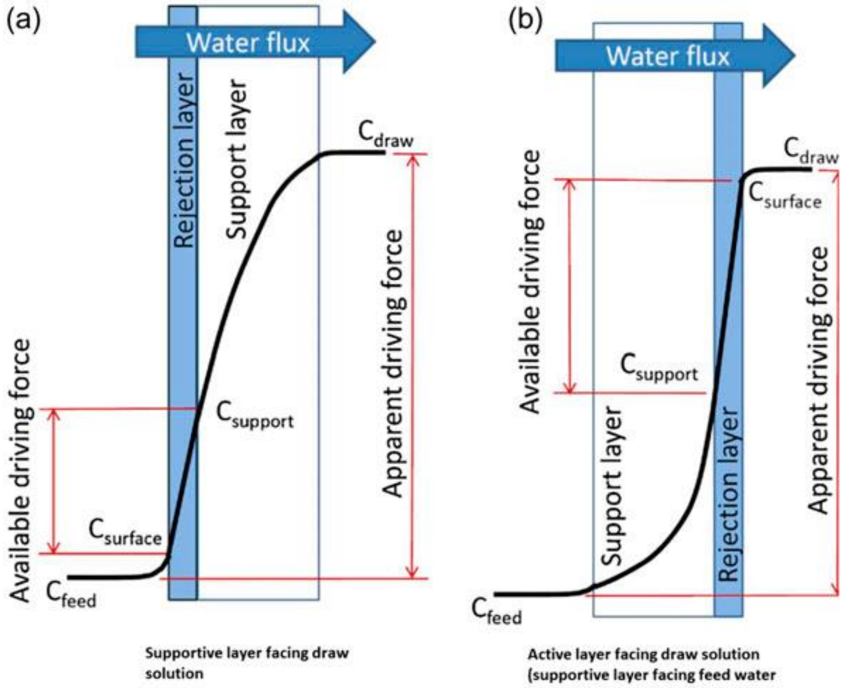



**Figure 2.** Illustration of driving force and concentration polarization for (a) the FO mode and (b) the PRO mode. The ICP in(a) is called dilutive ICP, and in (b) concentrative ICP.

In terms of the desalination, several patents have been awarded for different kind of methods and systems for water desalination by FO ; however, most of the systems have not matured or utilized in factory. Publications on FO desalination could not be easily found. Kravath and Davis investigated desalination of Atlantic Ocean seawater by FO, which used cellulose acetate flat sheet and hollow fiber membranes and glucose solution as a draw solution. Kessler and Moody attempted similar applications of FO for desalination. Their tried to develop a batch desalination process for emergency water supply on lifeboats, not as a continuous process for seawater desalination.

In recent bench-scale studies, it was demonstrated that when using a suitable FO membrane and a strong draw solution, seawater can be efficiently desalinated with FO. The mixing ammonium carbonate and ammonium hydroxide in specific proportions draw solution is used as draw solution. The salt species formed include ammonium bicarbonate, ammonium carbonate, and ammonium carbamate. Analysis of the process has shown that an osmotic pressure driving force as high as 238 bar for a feed water with a salt concentration of 0.05M NaCl, and as high as 127 bar for a feed water with a salt concentration of 2M NaCl, can be achieved with the ammonia/carbon dioxide draw solution[18].

## 4. Comparison between UF and FO

Compared with Ultrafiltration, Forward osmosis (FO) is another membrane technology which is getting more attention recently for the treatment of oil field and refinery produced water. In the UF process, pressure has to be applied to push the feed solutions(oil waste water or PW) and force the water molecule to pass through the membrane. While in the FO, the permeate side contains extremely high osmotic solution as draw solution and the separation occurs spontaneously due to osmotic pressure difference between feed and draw solution. In FO, the draw solution should have more osmotic pressure than the feed and the feed side osmotic pressure (from the PW) should be less compared to the draw solution for the efficient separation. The more osmotic pressure difference between feed and draw solution the more efficient separation occurs. The FO operates at low pressure, normally at ambient condition, therefore the irreversible fouling should be less compared to the UF process. Since the fouling formation likely to be less compact, it was suggested that the removal of fouling layers in the FO processes should be easier than high pressure membranes like UF though using chemical wash can rather efficiently reduce membrane fouling. However, the main problem of FO employed in oil wastewater treatment is the diluted draw solutions can not be so easily separated that the resource in the solution are unable to be recycled and reused. And with water coming through the membrane from the feed side, the huge volume of draw solution cause some other problems like concentration instability. That is the reason why the treatment of oil wastewater by FO remains in experimental stage.

Besides membrane modification methods above-mentioned, it is also important to know molecular mechanisms of UF membrane fouling in polymer-flooding wastewater treatment[19].

And there are two major problems when using the FO as a desalination process—lack of high-performance membranes and the necessity for an easily separable draw solution. Moreover, when considering seawater desalination, and especially when high water recovery is desired, FO can be utilized only if the draw solution can induce a high osmotic pressure.

## 5. Conclusion

There are more advantages of these two membrane technologies than shortcomings they have. UF is widely utilized in wastewater treatment and reclamation because of its superiority of low energy consumption and high efficiency and with no chemical preparation involved. The biggest problem of UF is the severe membrane fouling. However it can be improved by modification which aim at changing the property of membrane such as increasing its surface hydrophilicity. At the same time, FO can operates at low or no hydraulic pressures and has high rejection of a wide range of contaminants. Due to the low pressure, it may have a lower membrane fouling propensity than UF processes. And the equipment used is very simple and available. The biggest problem of FO is concentration polarization(CP)，and it can be reduced by membrane washing as well as membrane modification. Another problem of FO is the low separability of diluted draw solution. However, study has shown that changing the constituents of draw solutions can solve this problem such as using the mixing ammonium carbonate and ammonium hydroxide in specific proportions.

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