Chapter 1

Introductory Chapter: Osmotically Driven Membrane Processes

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Additional information is available at the end of the chapter

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1. Forward osmosis fundamentals

Global climate patterns and urban growth are two of the many factors that have affected the world's water resources. During the twentieth century, the population of the world tripled, and it is predicted to increase by another 15–20% in the next 50 years [1, 2]. The demand for fresh potable water correlates with the increase in the world's population, thus access to safe and sufficient drinking water is now an international aim. Sadly, over 1 billion people across the world currently have limited to no access to drinking water [3]. In particular, the demand for water drastically outweighs the availability of water in some Middle Eastern countries and even within the United States, in states such as California that has recently experienced droughts [4]. Further, urbanization throughout the world has also impacted groundwater resources [5], and this controversy has led to surging interest in the efficiency and practicality of ocean water desalination [6].

Desalination is the process of obtaining drinking water by removing salt ions, minerals, and other undesired contaminants from seawater [7], and currently, there is an increasing interest in using FO in desalination. In arid regions of the world, such as the Mediterranean and the Middle East, desalination research has made great strides over the past 30 years [8]. In fact, there are approximately 14,000 desalination plants in 150 countries with a production of millions of gallons per day [8]. In countries, such as Saudi Arabia and the United Arab Emirates, 70% of water supplies are dependent on desalination. Hence, energy production is concurrently linked to the production of freshwater, as desalination of seawater requires more energy than transportation of water from a lake or river [9]. It is also important to note that nuclear plants and other energy sources (coal or oil) require 20–50 K gallons of water per megawatt-hour of electricity produced [10]. Furthermore, gasoline vehicles, plug-in vehicles, ethanol-running vehicles and hydrogen-fuel cell vehicles all consume gallons of water to operate. Thus, the demand for water is intrinsically tied to energy and sustainable practices and processes must be used. Discovering energetically efficient methods to produce and reuse water is pertinent in providing strategies to combat the energy consumption demands. Additionally, industrial plants consume a drastic amount of water for their industrial processes, and 70% of fresh water is utilized in agricultural processes [11]. Therefore, water shortages will hinder many areas of human daily activity and existence.

Most water-related technologies are based on advanced materials, advanced manufacturing technologies, biotechnology, and integrated filtration systems. Therefore, research and development of new materials with tailored properties and nanomaterials are necessary to meet the water demands and provide connections between eco-efficiency, performance, processing, recyclability, costs, and water reuse. Although the development of membrane technology for producing clean water in wastewater treatment and desalination is vital, there are challenges that must be further addressed in all water filtration processes [12, 13]. Water-selective membranes have gained vast interest for their advantages like high energy efficiency, reasonable cost, and environmental sustainability. The ideal water-selective membranes are fabricated to have high water permeability, selectivity, as well as stability [14]. However, major constraints include operational fouling, waste residue disposal, cost, and acceptance by utility organizations and the public.

The current and most widely used water purification is reverse osmosis (RO)—a membrane-based separation process that removes salts, microbial constituents, both organic and inorganic compounds from water and has been used extensively in a variety of fields including desalination of seawater, ultrapure water production, and wastewater treatment [15, 16]. RO goes against the laws of nature and uses pressure to force a solvent through the membrane, which retains the solute on one side and allows the pure solvent to pass to the other side. Since its discovery, RO has become a very useful process when it comes to removing salt ions from a solution.

There has been an increased focus on membrane technology research because of the high efficiency and low-cost solutions for water purification. Currently, forward osmosis (FO) systems are seen as favorable alternatives to RO systems, as they have been also utilized in electricity generation, food processing [11], industrial wastewater, and add produced water treatment [17–19]. In nature, when two solutions are separated by a semipermeable membrane, the solvent molecules will tend to move through the membrane into the region of higher solute concentration until equilibrium is reached. FO separates two solutions with different concentrations using the natural osmotic pressure difference. The osmotic gradient is the driving force instead of externally applied pressure.

Even though RO systems have dominated the water purification arena for decades, FO systems offer an advantage of rejecting a wide range of contaminants. FO systems experience less fouling than RO systems; therefore, a membrane with anti-fouling properties could be efficient and beneficial. Within the RO process, the saline water, which has a high salt concentration, is forced through a membrane to a region of low solute concentrate by applying pressure in excess of osmotic pressure [20, 21], where the osmotic pressure is the minimum pressure needed to prevent the water molecules from moving back to the feed side from the permeate side. This occurs when the hydrostatic pressure differential resulting from the concentration changes on both sides of the semipermeable membrane is equal to the osmotic pressure of the solute [21]. The semipermeable membrane allows the passage of water but not salt ions. The feed water must pass through a very narrow passage as a result of the way the membrane is packaged. This causes for an initial treatment phase, where fine particulates or suspended solids must be removed to prevent fouling. In contrast, the FO system will have higher productivity and be considered an energy saving device since no external pressure is required. However, a major and unresolved challenge in FO remains an efficient draw solution that could result in high flux and reconstituted using a low-energy separation process which will be discussed later.

Two key factors in FO utilization are selecting the membrane and appropriate draw solute (DS). The DS should be non-toxic, generate high osmotic pressure, and be easily regenerated [22]. Continuous reconcentration is required to sustain the FO driving force to purify water. NaCl, $MgCl_2$, $CaCl_2$, and $MgSO_4$ are commonly used DSs; however, they are energy intensive and consequently costly [22, 23]. Alternatively, the DS can be treated wastewater effluent brine or seawater; the diluted DS will lower the energy demand [22]. Other limitations are the diffusion of the DS into the feed solution, low water flux compared to RO, membrane fouling, and concentration polarization. Therefore, many researchers are investigating alternative DSs.

1.1. Wastewater and water recycling

Wastewater sources include municipal and industrial plants and consume a drastic amount of water for their industrial processes. Some plants also produce oily wastewater end products. The industries that account for oil in water emulsions are petroleum, pharmaceutical, polymer, leather, polish, cosmetic, food, polymer, textile, agriculture, prints, and paper [24]. Helen Wake reports that oil refineries in European and Middle Eastern countries alone produce over 2 billion tons of wastewater [25]. This strikes as a major ecological problem, due to the discharge of oily wastewater into the ecosystem [25]. Furthermore, a principal fraction of oil/water emulsions' treatment technologies is often ineffective and expensive [24].

Produced water (PW) is generated during oil and gas production and is the biggest waste stream in the energy industries [26, 27]. Therefore, PW is contaminated with oils and salts of organic and inorganic compounds [27]. Releasing PW onto nature has an environmental impact and is a noteworthy issue of ecological concern. Ordinarily, PW is treated through various physical, chemical, and biological strategies. In offshore stages, as a result of space imperatives, minimal physical and substance frameworks are utilized. Unfortunately, current advances cannot dislodge these minute suspended oil particles. In addition, natural pretreatment of wastewater can be financially expensive. As high salt fixation and varieties of influent qualities have an impact on PW, it is suitable to fuse a physical treatment (e.g., film) to refine the material. Hence, future research endeavors are concentrating on the streamlining of flow innovations, utilization of consolidated methodology, organic treatment of delivered water, and review of reuse and release limits.

Agricultural wastewater, which comes from all animal farms and food processing, requires unique treatment before disposal or reuse [28]. Untreated agricultural wastewater results in pollution of groundwater, rivers, and lakes, thereby disrupting ecosystems and resulting in a chain of negative effects. However, with proper treatment and filtration, this wastewater can become a valuable resource. Primary treatment involves separating solids from the liquids and producing "sludge." The secondary treatment removes contaminants and dissolved solids from the effluent. Ultraviolet light, specialized enzymes, and microbes are often used for further treatment [29, 30]. After which, the "safe" water is returned to a waterway (ocean or river) or reused in agriculture [31]. Thus, treated wastewater can be reused in a sustainable fashion.

Where efficient irrigation methods and collection of run-off are in place, there is little wastewater [tailwater] to be treated for reuse. However, when bountiful tailwater is available, it often contains large amounts of salt and nutrients which makes it non-permissible for irrigation [31]. Innovative effluent treatment permits water reuse for irrigation and animal needs, making the "sludge" and subsequent effluent suddenly valuable. Additionally, collecting and reusing tailwater can benefit a farm through fertilization, and it can protect the environment by avoiding salt and nutrient discharge. Thus, utilizing tailwater and food processing wastewater could be profitable for farmers and positive for our environment.

1.2. Membrane fouling

Most membrane technologies experience reduction in performance as a result of various types of fouling. Therefore, designing and investigating membranes to combat fouling is imperative in creating proficient systems. Membrane fouling is the accumulation of unwanted matter such as colloids, salts, and microorganisms during the water purification process. Foulants accumulating on the surface reduces the water flow either temporarily or possibly permanently. Unfortunately, this is a common problem, and these foulants deteriorate and increase the ineffectiveness of the system.

During mass transport, various aspects lead to adsorption of particles within and onto the membrane surface, causing membrane fouling [22]. Contaminated feed water results in compounds and unwanted material adhering to the membrane, resulting in fouling, which is a major problem for most membrane-based systems and often results in a decline in flux [23]. Therefore, minimizing fouling is the key to optimal membrane operation and keeping costs down. Depending upon the polymer utilized for membrane fabrication, additional characteristics can be optimized to prevent fouling. Regardless of the membrane system, biofouling is a long-term problem [32]. All types of fouling (biofouling, organic, colloidal, and scaling) can be damaging [32]. It has been noted that FO is less likely to foul and less complicated than pressure-driven membrane processes like RO [23, 32]. This is because applied hydraulic pressure causes compact foulant layers, which diminish the effectiveness of cleaning the membranes.

Biofouling is considered to be the most difficult and detrimental to water filtration processes and decreases the durability of membranes. Therefore, membranes that are resistant to the accumulation of microorganisms are a necessity for water purification. Ultimately, biofouling causes higher than necessary energy consumption, deterioration of system performance, and water production. Due to the aforementioned issues, it is technologically essential to find efficient methods to minimize membrane biofouling. Studies have shown that FO membranes are more effective in preventing foulant permeation into the draw solute and reducing fouling in the downstream RO membrane [23].

Organic foulants are dominant and precursors to biofouling when using membrane bioreactor (MBR) for wastewater treatment [22, 33]. Therefore, biofouling can be prevented by controlling the organic matter. Hydrophobic and hydrophilic polysaccharides and transphilic organic macromolecules are all found in the feed water and may lead to organic fouling. Of these examples, polysaccharides are three times more likely than other humic acid contaminants to cause fouling [33].

1.3. Membrane selection

Material selection for membrane fabrication is significant in developing a system with optimal flux, as flux decline is directly connected to membrane fouling. Regardless of the polymeric material, asymmetric membranes are preferred during liquid separation due to their thin top layer on top of a porous support layer. FO asymmetric membranes consist of a dense active layer and a loosely bound support layer. The dense top layer is selective and the large pores in the support layer reduce hydraulic resistance [34]. Thin-film composite (TFC) and polysulfone are currently the most widely used materials for membrane fabrication due to their stability and high-pressure tolerance. However, Poly [vinyl alcohol] (PVA) hydrogels have been shown to be a suitable membrane used for water treatment, and PVA is an excellent surface modifier. Their hydrophilicity, water permeability, and anti-fouling potential make them ideal candidates in the further development of composite membranes [35, 36]. Research continues to investigate ways to optimize PVA hydrogel membranes based on their degree of polymerization and incorporation of nanoparticles [37]. Furthermore, studies have proven that ideal membranes should have high water permeability, selectivity, and stability [14].

1.4. Concentration polarization

As many are investigating FO for wastewater treatment and desalination, one of the major weaknesses of FO is internal concentration polarization (ICP). The configuration of the membrane contributes to the aforementioned fouling possibility and other complications such as ICP which minimized flux efficiency [33]. Traditionally, the support layer faces the feed in normal mode and faces the active layer in the reverse mode. The inability of the salt to pass easily through the active layer results in a concentration increase within the support layer. Amid the process, fouling such as scaling contributes to concentrative ICP [22, 33]. In the normal mode, the support layer diminishes water transport hydraulic resistance, and the solute freely enters, leading to minimum ICP [38]. Just as fouling leads to lower water flux, ICP within asymmetric thin-film composite (TFC) FO membranes does the same. Contrarily, in reverse mode, the active layer faces the feed solution contributing to ICP. The concentration is increased in the support as the active layer prevents the passage of salt. Thus, ICP greatly reduces the driving force for transport. However, a thin low porosity support minimizes ICP [33] and surface modifications, such as coating with another polymer, has been one of the most effective methods [21]. Studies have been conducted to improve membrane design for new-generation FO membranes and mitigate the ICP effect. Researchers have explored membrane structures to prevent salt leakage and minimize ICP in FO [39]. Altering phase inversion fabrication protocol by examining different casting substrate, consequently, results in an open structure with increased porosity in the middle support layer. During desalination, the FO system showed decreased salt leakage with mitigated ICP [21]. The ICP and ECP (external concentration polarization) structural value of the double dense-layer membrane is much smaller than those reported in the literature [21]. Moreover, lower CP values were seen after an intermediate solvent/water immersion was performed before complete immersion in water [39]. Additionally, Tang et al. [33] investigated ICP and fouling during humic acid filtration. They reported that despite initial ICP, the active facing orientation resulted in stable flux in contrast to flux diminution when facing foulant humic acid feed water.

2. Pressure retarded osmosis

Most water purification processes are known to consume energy. However, using the salinity differences between two bodies of water, pressure retarded osmosis (PRO) generates power. PRO is based on membrane technology similar to FO but results in sustainable osmotic power energy. During PRO, additional back pressure is applied to the draw solute, creating chemical potential between seawater and fresh water. As a result, electricity is produced from the conversion of flux into mechanical energy [22], and the net flux is similar to FO in the direction of the DS [40]. Unfortunately, membrane fouling consequently reduces the permeate flux and osmotic power generation, thus increasing overall cost similar to other membrane technologies. Research has been conducted on different quality feed waters to identify the main foulants on the surface in the PRO processes, and silica has been shown to cause severe scaling [41]. Again, structural parameters, material choice, pH of FS and/or DS played a critical role in mitigating IC of silica scaling [41]. Furthermore, organic and inorganic salt water was used to investigate cleaning methods to resolve fouling issues [32]. Using salt water as the DS, iron, aluminum, calcium, sodium, and silica were the inorganic foulants discovered [32]. Also, humic substances, polysaccharides, and proteins were the organic foulants identified [32]. Sequential acidic and basic cleaners were proven to be successful with a flux recovery above 95% [32]. PRO processes and consequently osmotic power generation can be enhanced by decreasing membrane fouling via chemical cleaning [32].

3. Summary

In summary, many researchers have compared FO, PRO, and RO as shown in **Figure 1** [22]. The most noted comparisons are the necessary pressure difference, fouling tendencies, and application. All three systems have advantages but require necessary improvements for expansion of utilization in various applications. Although fouling is a challenge for membrane technologies, research has demonstrated various ways to diminish its effects on flux [22, 32, 41]. With the increasing water demands, FO is certainly a viable option to meet the water and energy challenges of a growing global population as PRO has the potential to be widely used for sustainable energy. With polymer chemistry and membrane innovations, FO will advance for continuous use in producing safe water for irrigation, pharmaceuticals, and human

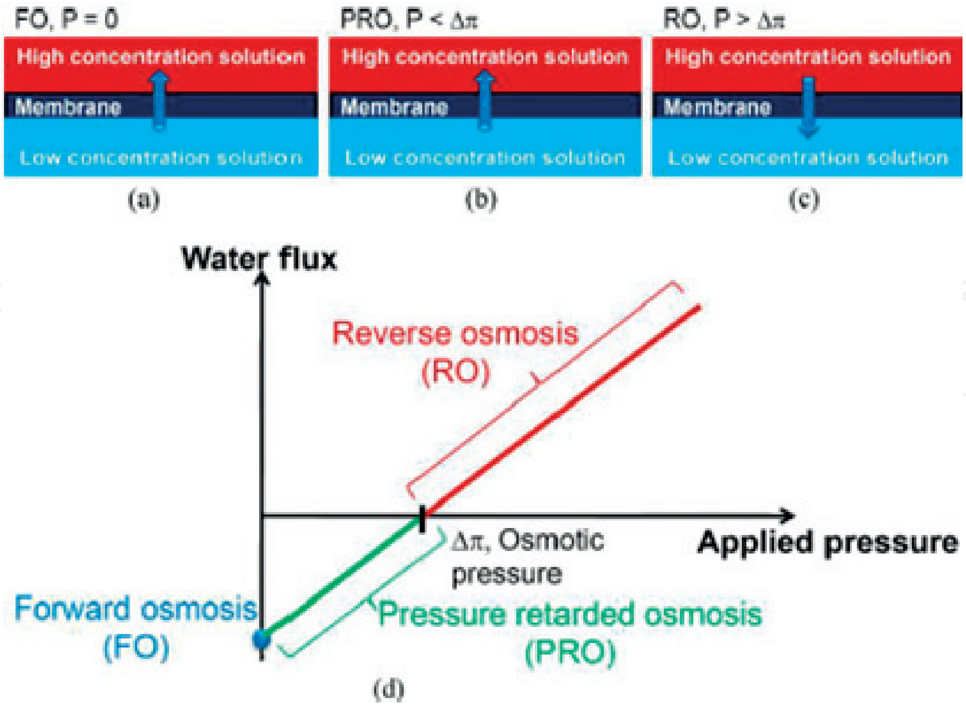

Figure 1. Illustration of FO, PRO, and RO processes [22].

consumption. This book will further discuss the headway in osmotically driven membrane processes (ODMP) research, findings, and contributions to membrane processes.

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