Osmotically and thermally driven membrane processes for enhancement of water recovery in desalination processes

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ABSTRACT

Osmotically-driven membrane processes, including forward osmosis (FO) and pressure retarded osmosis (PRO), are emerging technologies that have come under renewed interest and subjected to numerous investigations in recent years. In FO, water is extracted from a feed solution utilizing the high osmotic pressure of a concentrated draw solution (DS) that flows on the opposite side of an FO membrane; RO or a distillation process can be utilized to reconcentrate the DS for reuse in the FO process and to produce purified water. The main advantages of FO include operation at very low hydraulic pressures, high rejection of a broad range of contaminants, and lower membrane fouling propensity than in pressure-driven membrane processes. Existing and potential applications of the osmosis phenomenon extend from water treatment and food processing to power generation and novel methods for controlled drug release. While FO relies on osmotic pressure driving force to separate water from a feed streams, thermally driven membrane processes, such as membrane distillation (MD), rely on vapor pressure difference across a microporous hydrophobic membranes to facilitate separation of volatile solvent (water from salt solution) or volatile solutes from impaired feed streams. The vapor pressure gradient is usually achieved by maintaining temperature difference between a warm feed solution and a colder distillate that flow on the opposite side of the membrane. In thermally-driven membrane processes, desalination and production of highly-purified water can be achieved in one step compared to osmotically-driven membrane processes, at much lower temperatures compared to distillation processes, and at much lower pressures compared to pressure-driven membrane processes. It can be most effectively and beneficially used when low-grade heat is readily available. Furthermore, compared to other membrane processes, in MD the salinity of the feed stream minimally affects the driving force for mass transport through the membrane; salts, even at high concentrations, only slightly reduce the partial vapor pressure of such feed streams. Thus, MD can be beneficially used to enhance water recovery in many desalination processes. In this paper, a brief review of the principles of FO and MD is provided. Special aspects of mass transport as well as the membranes used in the processes are discussed, and relevant results from recent studies are presented. Strengths and limitations of the FO and MD processes in a broad spectrum of applications are reviewed and discussed.

Keywords: Forward osmosis; Membrane distillation; Desalination; Pretreatment; Water recovery
1. Introduction

Increasing water demands and diminishing water supplies due to over allocation and contamination are major drivers for exploration of sustainable ways of developing and enhancing existing and new water resources [1,2]. Advanced processes are sought that can enhance water recovery, reduce energy demand, and improve sustainability without the limitations associated with current desalination and water purification processes.

Recent studies have demonstrated that osmotically driven and thermally driven membrane contactor processes, including forward osmosis (FO) and membrane distillation (MD), have many advantages over traditional pressure-driven membrane processes such as reverse osmosis (RO) and nanofiltration (NF). These include high water recovery and salt rejection, operation at low hydraulic pressures, lower sensitivity to membrane fouling and scaling, and above all, potential utilization of renewable energy resources to drive the processes.

FO is an osmotically driven membrane separation process that involves the diffusion of solvent (water) through as semipermeable membrane and rejection of most solute and all suspended particles. Water spontaneously diffuses through the FO membrane from a feed stream of low osmotic pressure (high water activity) to a highly concentrated draw solution stream of high osmotic pressure (low water activity) [3]. Recent studies have demonstrated that FO can effectively concentrate a variety of feed streams, including sea and brackish water, municipal and industrial wastewater, landfill leachate, and beverages [4]. Because in many applications FO cannot operate as a stand-alone process due to dilution of the draw solution, it can be viewed in many instances as an enhanced pretreatment process for other separation processes.

While FO is a very attractive separation process for treatment of difficult to treat streams, several obstacles still exist and must be overcome for FO to become a mainstream separation/desalination technology. These include high energy-demand for regeneration/reconcentration of draw solutions, low water flux despite high driving forces of currently used draw solutions and membranes, and low rejection (compared to RO) of salts in both directions of the membrane. Yet, the many advantages of the process can lead to its near future implementation in unique applications.

MD is a thermally driven membrane separation process that involves evaporation of volatile constituents through a hydrophobic, microporous membrane. The driving force for mass transfer is the vapor pressure difference (induced mainly by temperature difference) across the membrane, rather than hydraulic pressure difference used in RO and NF. Four basic process configurations exist in MD to facilitate evaporative mass transport across the membrane. These include direct contact MD (DCMD), vacuum MD (VMD), air-gap MD (AGMD), and sweep-gas MD (SGMD) [5]. A recent new configuration that synergistically combines elements of DCMD and VMD (termed vacuum enhanced DCMD (VEDCMD)) demonstrated that water flux could be almost doubled compared to DCMD operated at similar temperatures and flowrates [6,7]. Similar to distillation processes, phase change during the MD separation process results in a very pure product water compared to other membrane desalination processes in which solutes also diffuse through the membrane (yet at slower pace). Considering that the salinity of a solution only minimally affects the vapor pressure of the water, MD can be used to treat very saline feed streams without loss of driving force due to high osmotic pressure.

Although high water fluxes can be achieved with a feed temperature of 40°C, and even lower, MD is not without limitations. Non-optimal/non-ideal membranes for MD and conductive heat losses through the membrane are some of the major drawbacks that impede commercial development of the process. In this paper, a review of results from recent studies will illustrate the many advantages and some of the limitations of DCMD and VEDCMD for various applications.

2. Novel membrane technologies and the water–energy nexus

Water and energy are intertwined; it takes energy to extract, clean, and distribute water, and after use it takes more energy to treat water before reuse or discharge to the environment. Water is also used in energy production: as steam that spins turbines, as a cooling medium in power plants, or in hydroelectric power generation. In many publications, Prof. Sidney Loeb promoted another source of renewable energy that stems from water: the pressure retarded osmosis (PRO) process [8–10]. Being part of the group of osmotically driven membrane processes, PRO has many process requirements that are similar to those of FO; and therefore, the future advancement of the two processes is tightly connected.

But FO itself can also be utilized, in conjunction with other desalination processes, for energy recovery or saving during desalination of sea or brackish water. In a recent invention [11,12], natural saline water (e.g., seawater or concentrated brackish water) is the draw solution used in recovery of water from an impaired water stream; water from the impaired stream diffuses through an FO membrane into the seawater draw solution, the seawater is diluted, and the diluted seawater is subsequently processed through a seawater RO desalination system (Fig. 1). This approach provides at least four major benefits related to water and energy resources; these include dilution of seawater before desalination, which result in
lower energy and high recovery seawater desalination, multi-barrier protection of drinking water, reduced membrane fouling, and beneficial reuse of impaired water [13].

MD also plays an important role in the water–energy nexus. Recent studies [6,14,15] have demonstrated that MD can be used for desalination of even highly saline water with throughputs exceeding those of common seawater RO membranes — operating at temperatures that are far below those used in desalination by distillation processes (e.g., MED, MSF, VCD). Furthermore, using the new VEDCMD configurations [7], MD can be operated at very high water fluxes and high solute rejection with renewable sources of energy (e.g., geothermal water [15], low grade heat from industry, solar ponds [16]).

This paper provides a summary of results from recent studies that demonstrate the advantages/benefits and current limitations of osmotically and thermally driven membrane processes and outlines the research gaps and needs for successful commercialization of the technologies.

3. Forward osmosis — new frontiers and old obstacles

3.1. Dual-barrier, multi-benefit forward osmotic of impaired water and seawater

In a study that has been funded by the US Water Research Foundation [17], a new FO approach for combined seawater desalination and wastewater reclamation (Fig. 1) was demonstrated on both the bench and pilot scale. The main objective of the investigation was to determine the performance of the process with a current FO membrane [18]. These include water flux, membrane fouling rates when using different feed streams, and rejection of major constituents associated with reclaimed water (e.g., organic and inorganic chemicals, nutrients, and organic micropollutants).

Synthetic seawater draw solution at different concentrations was used to simulate driving forces under different conditions in a hybrid FO–RO system. Draw solution inlet concentration in all experiments was maintained constant by either dosing highly concentrated seawater salt solution into the draw solution stream (bench scale experiments) or by utilizing a pilot scale RO system that regenerated the draw solution and produced purified water from the draw solution (pilot scale experiments). Feed streams that were investigated include secondary and tertiary treated effluents from Denver Metro and Denver Water Recycling Plant in Denver, Colorado, and impaired water from the South Platte River, collected north of Denver. All feed streams were maintained at constant inlet concentration by either replenishing the feed solution with deionized water to account for water that diffused into the draw solution (bench scale experiments) or using continuous side stream at the water recycling plant (pilot scale experiments).

Short-term average water flux as a function of seawater draw solution concentration is illustrated in Fig. 2 for all feed solutions (i.e., deionized water, secondary and tertiary treated effluents, and river feed water) [13]. Except for deionized water, all feed streams had total dissolved solids (TDS) concentration of approximately 400 mg/l. Error bars represent the standard deviation associated with all feed waters. Results indicated that short-term flux decline was negligible (results not shown) and that process performance in FO is minimally affected by feed water quality (e.g., suspended solids and nutrients concentrations). The non-linearity of water flux with draw solution concentration is an indication of internal concentration polarization, a unique mass transport phenomenon associated with osmotically driven membrane processes that was early on investigated by Loeb et al. [19,20] and later by others [21].

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Pilot-scale experiments conducted with secondary treated effluent feed stream have demonstrated that flux decline is highly dependent on the orientation of the membrane cell, and that water flux declines more rapidly when the feed flows above the flat sheet membrane and suspended solids settle on the membrane (Fig. 3). Physical and mild chemical cleaning were able to almost completely reverse membrane fouling [17].

Water flux as a function of time is illustrated in Fig. 4.
for FO treatment of tertiary treated effluent with sea salt draw solutions at different concentrations. Results demonstrated that long-term fouling of FO membranes is minimal when treating tertiary treated effluent. This can most likely be attributed to the lower concentrations of nutrients and organics in the feed that reduced membrane fouling.

Total rejection of nutrients, organic compounds, and micropollutants by the hybrid FO–RO system was very high. Ammonia was more than 94% rejected, nitrate more than 97%, organic carbon rejection (measured by rejection of UV absorbance) was higher than 99.9%, and organic micropollutants rejection ranged from 93 to 99.9%, with most constituents being more than 99% rejected [17].

One of the most notable advantages of FO is the ability to treat highly contaminated impaired waters with minimal flux decline due to membrane fouling. In one of our early investigations, liquids produced during centrifuge dewatering of anaerobic digester sludge (centrate) were treated and further concentrated with FO [22]. Water flux as a function of time for concentration of centrate is illustrated in Fig. 5 for tests under different operating conditions. Results from comparison of FO and RO membranes in both FO and RO testing modes highlighted two very important advantages of FO. The first is that the fouling tendency of FO membranes under FO conditions is very low, and that the very minimal compaction of the fouling cake layer (organic in nature) may substantially contribute to the low fouling under FO operating mode. The second advantage stems from the hydrophilic nature of the FO membrane, which in conjunction with the minimal compaction of the cake layer is responsible for the negligible irreversible fouling observed after chemical membrane cleaning.

More recently, the performance of FO was tested at the pilot scale level for treatment of heavily contaminated mixed wastewater from cooling towers blowdown and furnace wash waters at a coal-fired power plant in Denver, Colorado (717 MW, Xcel Cherokee Station). Results in Fig. 6 again demonstrate that water flux is minimally affected by the highly contaminated feed water. Temperature-corrected flux and specific flux were also calculated from the data to account for the changes in stream temperatures and draw solution concentration, both of which have high influence on water flux. Specific flux results in Fig. 6
confirm that membrane fouling is almost negligible when pre-treating highly impaired water with FO.

3.2. Mass transfer limitations and current obstacles in forward osmosis

Studies of FO in the past several decades focused mainly on solvent (water) mass transport and its limitations due primarily to internal concentration polarization effects in the porous support structure of the membrane [4]. Very minimal attention was given in the past to solute transport through membranes in osmotically driven membrane processes.

In FO and other osmotically driven membrane processes, feed solutes diffuse with the solvent (water) through the membrane into the draw solution; yet, draw solution solutes diffuse simultaneously into the feed stream due to the very high concentration gradient across the membrane. This bi-directional solute diffusion [23] in osmotically driven membrane processes can adversely affect the process, adjacent separation processes, and the environment.

In a recent study [23] we have shown that membrane characteristics and solution chemistry play major role in the rate and direction of solute diffusion in FO. Results in Table 1 summarize the average specific reverse salt diffusion for experiments conducted with two FO membranes and three draw solutions of interest. Specific reverse salt diffusion is defined as the ratio of solute/salt flux in the reverse direction and water flux in the forward direction through an FO membrane [23], and it is directly related to process efficiency and sustainability. Results indicated that draw solution concentration has minimal effect on specific reverse salt diffusion [23]. Results also revealed that reverse salt diffusion in FO is notably affected by flow velocity on both sides of the membrane, and that in turn affects water flux and specific reverse salt diffusion. Thus, further advancement of FO and other osmotically driven membrane processes will strongly rely on development of new membranes that provide high water flux, high solute rejection, and are chemically and thermally stable. Concurrently, development of draw solutions that will be well rejected and induce high driving force without reacting and degrading the membrane are crucial to the future success and commercialization of osmotically driven membrane processes.

4. Membrane distillation — high recovery desalination of brines

While osmotically driven membrane processes have many benefits and some existing limitations, desalination...
tion of highly saline water, such as seawater and highly brackish water, by FO is restricted due to their very high osmotic pressure. This requires that the draw solution will have substantially higher osmotic pressure, which in turn will require high energy to reconcentrate the draw solution. This is somewhat similar to the main problems of pressure driven membrane processes that require large amount of energy and are often limited to low water recovery.

Taking advantage of the high area-to-volume ratio offered by membranes and the independence of osmotic pressure offered by distillation, MD has the capability to desalinate highly saline streams and achieve high water fluxes and recovery at relatively low feed temperatures of 40°C, and even lower. In recent studies [14,15,24] we have demonstrated that DCMD and VEDCMD can be effectively utilized for desalination and treatment of saline stream under extreme conditions.

Like with osmotically driven membrane processes, membranes for thermally driven membrane processes are not optimal and they are currently not commercially manufactured and sold. Membranes used for investigation of MD are either microporous/microfiltration commercial membranes made of hydrophobic polymers, or new membranes that have been developed and manufactured in research laboratories on a very small scale. These membranes are either thick and have low vapor permeability (and also have low porosity and high tortuosity) or they are composite membrane with very thin (high vapor permeability) but very sensitive and easily damaged active layer. Nevertheless, almost all studies published in the last few decades have demonstrated that regardless of water flux (i.e., vapor permeability), salt rejection in MD is extremely high, even when treating highly saline streams.

4.1. Treatment of concentrate from RO desalination of brackish water

In a recent study we have compared FO and DCMD/VEDCMD for high recovery desalination of RO concentrates [14]. The feed streams to the process were either concentrate stream from an RO system or the RO concentrate that was softened and further concentrated by a second stage RO. In both cases the feed water was close to saturation in respect to sparingly soluble salts such as calcium sulfate and silicate.

Water flux as a function of time is illustrated in Fig. 8 for experiments conducted with the MD–FO hybrid system. Flux was limited by water evaporation in the DCMD process. Results from preliminary experiment with a robust but low permeability MD membrane demonstrated that extremely high water recovery could be achieved without compromising the integrity of the MD membrane. Feed was concentrated from 50 g/L to approximately 200 g/L NaCl during a batch desalination experiment. Flux decline was due to the decrease in partial vapor pressure of water at higher feed temperatures. This was due to higher water flux that induced stronger concentration polarization and therefore faster membrane scaling. Nevertheless, results from the study demonstrated that membrane scaling was almost completely reversible and that very mild cleaning of the membrane left negligible irreversible scaling on the MD membrane.

4.2. High recovery desalination of concentrated salt solutions

In a new approach for treatment of impaired aqueous solutions, DCMD was coupled with MD to form a self balancing water treatment in which the FO membrane provides protection to the MD membrane and the driving force for the entire process is heat for warming up of the draw solution [25]. Water flux as a function of time is illustrated in Fig. 8 for experiments conducted with the MD–FO hybrid system. Flux was limited by water evaporation in the DCMD process. Results from preliminary experiment with a robust but low permeability MD membrane demonstrated that extremely high water recovery could be achieved without compromising the integrity of the MD membrane. Feed was concentrated from 50 g/L to approximately 200 g/L NaCl during a batch desalination experiment. Flux decline was due to the decrease in partial vapor pressure of water at higher feed concentrations and flux was completely recovered after introduction of a new batch of 50 g/L NaCl feed solution (Fig. 8).
In another challenging test, the same membrane (MD-020CP-2N Microdyn-Nadir) was used for desalination of geothermal brine [15]. Three membranes were connected in series and tested with feed water at temperatures exceeding 90°C. Water flux and vapor pressure differential across the membrane as function of time are illustrated in Fig. 9. Flux was declining over time due to lack of cooling capacity during the experiment; this is evident from the parallel decline in vapor pressure difference across the membrane with time. Compared to results in Fig. 8, flux was much higher due to the higher feed and distillate temperatures.

5. Concluding remarks

Both MD and FO are emerging membrane separation technologies that have been successfully tested in different application at the bench and pilot scale. Both can utilize renewable sources of energy to produce purified potable water and each has unique niche of applications for specific waters. Yet, lack of optimized membranes for both technologies is one of the main hurdles for commercialization of the technologies. Better understanding of the mechanisms controlling the two processes will further promote the utilization of the technologies in existing and new applications of water and wastewater treatment.

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