The sweet spot of forward osmosis: Treatment of produced water, drilling wastewater, and other complex and difficult liquid streams

Bryan D. Coday [a], Pei Xu [b], Edward G. Beaudry [c], Jack Herron [c], Keith Lampi [c], Nathan T. Hancock [d], Tzahi Y. Cath [a],*

[a] Colorado School of Mines, Golden, CO, USA
[b] New Mexico State University, Las Cruces, NM, USA
[c] Hydration Technology Innovations, Albany, OR, USA
[d] Oasys Water, Boston, MA, USA

HIGHLIGHTS

- Highly impaired liquid streams can be sustainably treated by forward osmosis.
- Forward osmosis treatment of drilling mud and produced water was evaluated.
- Water recovery >70% was achieved in pilot and demonstration scales.

GRAPHICAL ABSTRACT
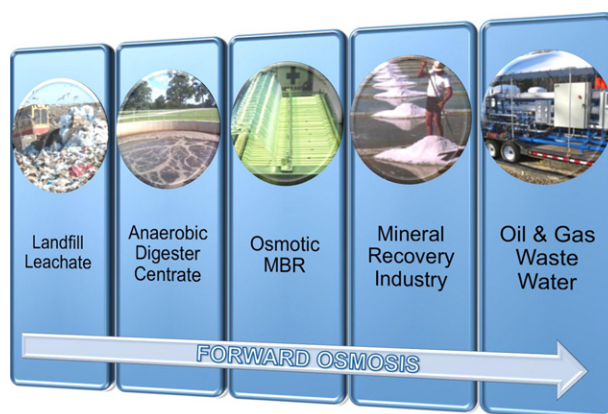
ARTICLE INFO

ABSTRACT

Global water scarcity and substantial challenges associated with treatment of complex and impaired liquid streams have advanced the development of forward osmosis (FO), which can successfully treat and recover water for beneficial reuse. Surging research and advancements in FO, a technology once unable to compete with conventional wastewater treatment processes, have identified its sweet spot: treatment and desalination of complex industrial streams, and especially oil and gas (O&G) exploration and production wastewaters. High salt concentrations, decentralized and transient operations, the presence of free and emulsified hydrocarbons, silts and clays leached from producing formations, and process additives common in O&G drilling wastewater and produced water render many common treatment technologies ineffective. Treatment and reuse of O&G wastewater, and other complex industrial streams, in a cost effective and environmentally sound manner is critical for sustainable industrial development and to meet increasingly stringent regulations. This review focuses on the successful development and demonstration of FO membrane treatment systems, supported by a review of bench-scale, pilot, and demonstration studies on treatment of O&G waste streams, landfill leachates, centrate from anaerobic digesters, activated sludge in membrane bioreactors, and liquid foods and beverages. Recent developments in membrane fabrication, system configurations, and draw solutions are briefly reviewed.

* Corresponding author. Tel.: +1 303 273 3402; fax: +1 303 273 3413.
  E-mail address: tcath@mines.edu (T.Y. Cath).

1. Introduction

The United States and many countries around the world are rapidly expanding exploration and development of unconventional gas resources, including shale gas, coalbed methane, and tight sands [1–5]. With recent advancements in horizontal well drilling and hydraulic fracturing, unconventional gas is expected to account for nearly 45% of the natural gas produced in the U.S. by 2035 [6,7]. As production increases and new formations become economically viable, water demands for well development and the volume of wastewater generated during exploration and production (E&P) (e.g., drilling muds, hydraulic fracturing flowback water, produced waters) will increase significantly.

Drilling mud is an integral part of well development, providing lubrication to drilling equipment, stabilization to well walls, pressure control within the borehole, and flushing of debris from the well. Up to one million gallons (3800 m^3 or 24,000 bbl) of fresh water can be consumed during drilling of a single well, producing grit-laden streams contaminated with drilling additives and containing high concentrations of chemical oxygen demand (COD), total dissolved solids (TDS), and organic and inorganic constituents [8–11]. When borehole drilling is completed, the drilling mud is usually stored on-site in lined ponds/pits. In some locations, closed-loop drilling is required in which no pits are used. In most drilling operations, these fluids receive minimal treatment and are trucked off-site for deep well injection. Occasionally, the waste fluids may be land applied if a proper permit is obtained [9].

After drilling, well productivity can be enhanced with hydraulic fracturing. Between one and four million gallons (3800–15,000 m^3 or 24,000–95,000 bbl) of water-based slurry are injected into the well bore under high pressure, forming fractures in the target formation [9,12,13]. Hydraulic fracturing facilitates free flow of oil and gas; thus, increasing recovery from formations previously considered economically unfavorable. A portion of the fracturing fluids that were injected is recovered from the well over a span of several weeks, generating a waste stream of water, sand, and chemical additives [7,13]. Depending on the formation, the flowback wastewater can also have high concentrations of TDS attributed to leaching of earth minerals from the subsurface. Similar to drilling muds, fracturing flowback is recovered and stored on-site. Historically, most flowback water received minimal treatment before being disposed into deep wells [7,9,13]; however, Class II injection wells are not available in all locations. Wastewater treatment is possible, and the treated water can supplement or replace the fresh water necessary for drilling and fracturing of additional wells; yet, highly saline waste streams and some hydraulic fracturing chemical additives are difficult to treat with conventional processes.

The wastewater stream flowing with the gas after most of the fracturing water is recovered, is considered produced water [13,14]. This stream can represent nearly 70% of the total wastewater generated during the lifetime of a well, producing volumes several times greater than the volume of oil and/or gas recovered [15]. The quantity of produced water is highly dependent on well location, and its quality just as variable. These streams typically contain a wide range of TDS concentration, free and emulsified hydrocarbons, and silt and clay leached from the formation [8,16]. Depending on the quality and composition of produced water, a broad range of technologies can be utilized for its treatment; however, the complexity and total cost of treatment is dependent on its salinity and ultimate use [9].

As the development of unconventional oil and gas (O&G) continues in the U.S. and abroad, maximizing water resources while minimizing the volumes of E&P waste will become increasingly important. Several O&G exploration regions are considered at high risk for water resource depletion [8], providing an excellent opportunity for beneficial reuse of reclaimed waste streams. Properly applied management techniques and emerging water treatment processes can drastically reduce industrial water demands, promoting closed loop water recycling and minimizing environmental exposure associated with E&P of unconventional O&G resources.

Many other industrial streams are difficult to manage, similar to O&G E&P wastewaters, and require special technologies to provide sufficient treatment. For example, landfill leachates are heavily contaminated waste streams that often require advanced treatment processes to provide adequate contaminant rejection prior to discharge or reuse. Water recovery from domestic wastewater sludge and anaerobic digester centrate has also gained attention as a result of surging interest in direct and indirect potable water reuse in the United States. The nexus between food production and water recovery has also grown in complexity as the food industry strives to increase liquid food and beverage quality, while simultaneously concentrating these streams. Though each stream is unique and complex, O&G wastewater and other industrial streams can be treated by a small group of advanced processes.

2. Processes for treatment of O&G E&P wastewaters

Chemical, biological, and physical processes have been previously investigated and implemented for treatment of O&G E&P wastewaters; however, high salinity, prohibitive capital cost, extreme chemical demand, large installation footprint, residual (brines and solids) management challenges, and limited removal of emerging contaminants are some of the hurdles to successful implementation of many technologies. Desalination processes such as distillation and membrane separation processes, have demonstrated the ability to achieve adequate treatment of these streams; yet, further improvements to these technologies to reduce the high costs and operational challenges, and development of more effective pretreatment are needed before they are broadly adopted and implemented [10,11,15–18].

2.1. Commercial desalination processes

2.1.1. Distillation

In distillation a feed stream is heated and sometimes also placed under partial vacuum to increase its vapor pressure and form water vapor that can be condensed and recovered as high quality water. Vapor extraction can be repeated several times in the process to enhance evaporation while further concentrating the feed stream. Common commercial distillation methods include multi-effect distillation (MEF), multi-stage flash (MSF), and vapor compression (VC) distillation [19]. Desalination by distillation can minimize physical and chemical treatment and the amount of de-oiling equipment necessary for treatment of O&G wastewater. This eliminates capital costs and minimizes secondary chemical waste sludge [17]. Additionally, distillation can treat highly saline feed streams because it is not affected by the high osmotic pressure of saline and hypersaline streams; however, corrosion and scaling can occur during distillation and incur high operating and maintenance (O&M) costs [14,19]. If volatile organic compounds are present in the feed stream, they may be poorly removed because they will volatilize and condense in the distillate stream. Energy demand is also a limiting factor in distillation, accounting for more than 95% of the total operating costs in a recent review of commercial scale processes [17].

2.1.2. Membrane separation

Membrane separation technologies are commonly pressure driven separation processes that rely on diffusive- or convective-based mass transfer phenomena to separate dissolved and suspended constituents from aqueous solutions. Traditional pressure driven membrane technologies include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Membrane permeability and the size of constituents rejected by each process decrease in the order presented (MF > UF > NF > RO); while MF sieves suspended particles, RO can effectively reject monovalent ions, including sodium, chloride, and low molecular weight organic compounds [17]. Membrane processes, and especially NF and RO, can successfully reject a broad range of contaminants and TDS present in impaired feed streams.

RO and NF are very effective desalination processes; however, they are highly susceptible to inorganic scaling and to particulate, biological, and organic fouling [20]. These foulants can become compacted and difficult to clean, leading to low water permeability, increased pressure loss, and considerable chemical consumption for cleaning. Additionally, polymeric membranes can be sensitive to feed stream chemical and oil contaminants and natural polymers such as guar (used in the hydraulic fracturing process), which can compromise membrane performance and surface chemistry. Hydraulically driven membrane processes must also overcome the osmotic pressure of the feed stream, limiting the variety of streams (e.g., TDS concentration lower than 70,000 mg/L) that can be treated.

2.1.3. Desalination pretreatment

Distillation systems, and to a larger extent desalination membranes, must be protected with appropriate pretreatment processes. NF and RO membranes are susceptible to scaling, particulate/colloidal fouling, organic fouling, extreme pH, oils and fats, insoluble liquids, and microbial biofilms [17,20,21]. Pretreatment will promote system/membrane longevity and minimizes capital and O&M costs associated with chemical cleaning and energy consumption [22]. Common pre-treatment strategies may include coagulation/flocculation/sedimentation, pH control, softening, filtration (granular/MF/UF), dissolved air floatation, advanced oxidation, and disinfection [17,20,21]. Other traditional and new processes, including biological processes, are also utilized.

These pretreatment processes, coupled with desalination, can treat highly contaminated waste streams generated in the O&G field. Yet, some of the streams, and specifically fracturing flowback water, pose unique challenges to conventional and advanced treatment technologies. Furthermore, the fast expansion (and sometimes contraction) of the O&G E&P industry also requires the development of more modular, on-site water treatment systems. New technologies that employ different driving forces and have the capacity to separate a broad range of contaminants are needed for both the O&G industry and other waste treatment industries.

2.2. Engineered osmosis: forward osmosis

Engineered osmosis, and specifically forward osmosis (FO), is an emerging desalination and treatment technology that can provide robust and modular treatment, reject contaminants found in O&G waste streams, and avoid the drawbacks of pressure driven membrane processes. Engineered osmosis is a promising alternative for difficult to treat waste streams such as produced water [14], hydraulic fracturing flowback water, and drilling mud. In some cases, FO can be used as a standalone desalination process, or it can be considered an advanced pretreatment process for RO or NF. The following sections provide details on the principles of FO and showcase its successful treatment of complex industrial wastewater streams.

2.2.1. Principal of forward osmosis

Osmosis is the net transfer of water across a semi-permeable membrane resulting from an osmotic pressure difference across a semipermeable membrane. In FO (Fig. 1a), a synthetic polymeric membrane separates a feed stream and a concentrated draw solution, and the osmotic pressure difference across the membrane facilitates diffusion of water through the membrane from the low osmotic pressure feed to the high osmotic pressure draw solution while rejecting almost all dissolved and suspended constituents [23,24]. Commonly, the FO process is completed in two separate steps: 1) recovery of water from a feed stream and dilution of the draw solution, and 2) production of high quality product water using RO or distillation while reconcentrating the draw solution (Fig. 1b) [18,25–32]. The reconcentrated draw solution is then reused in the FO process; however, several industrial applications such as O&G well fracturing are able to beneficially use the dilute draw solution, eliminating the need for the reconcentration step.

FO has many advantages over other membrane technologies. High rejection of almost all solutes and suspended solids while operating at very low hydraulic pressures and ambient temperature are the greatest benefits of FO. These significantly reduce energy consumption and capital costs associated with pumping and system design and construction. They also allow for the development of highly modular systems that can be operated in harsh conditions with minimal access to electric power and supplies. FO experiences less membrane fouling compared to pressure driven membrane processes such as UF, NF, and RO [33–35]. This is due to minimal cake layer formation and lower compaction of foulants on the membrane active layer. Fouling deposits on FO membranes are easily removed with osmotic backwashing [36–40] or turbulent flow at the feed-membrane interface. During osmotic backwashing, the draw solution is replaced with deionized or fresh water. This develops an osmotic pressure gradient in the opposite direction across the FO membrane and water permeates from the draw solution channel into the feed channels. The permeation of water back into the feed channels helps to dissolve and detach foulants from the membrane surface. Unlike pressure driven membrane processes, FO can be used to treat highly saline feed streams because it does not require high hydraulic pressures to overcome high osmotic pressures.

2.2.2. Draw solutions

Draw solution selection is important for maintaining a sustainable and efficient FO process. There are several factors that dictate what constitutes an appropriate draw solution, which are defined by the type of FO application. If the draw solution requires reconcentration, the chosen solutes should be highly soluble to avoid scaling during RO
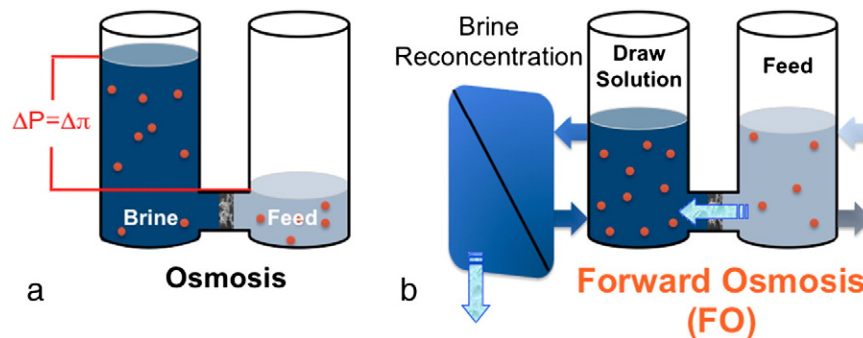
Fig. 1. A synthetic polymeric membrane separates a feed stream and a concentrated draw solution, and the osmotic pressure difference across the membrane facilitates diffusion of water through the membrane: (a) the osmosis process and (b) FO process when the osmosis process is coupled with a brine reconcentration system, producing high quality product water, while reconcentrating the FO draw solution to maintain constant osmotic pressure.

or distillation reconcentration. Draw solutions must also be suitable for industrial applications and inexpensive. Several laboratory studies have investigated suitable draw solutions for their osmotic pressure, recoverability, and mass transfer through the membrane [23,25,28,41–47]. These include mono and divalent salts, dissolved gasses, sugars, engineered nanoparticles, or fertilizers. A review of promising draw solutions was recently published [48], and the osmotic pressures of potential inorganic draw solutions as a function of their molar concentration are presented in Fig. 2 [23].

2.2.3. FO membranes

FO membranes have unique properties that enable efficient diffusion of water through the polymer. These include very thin active and support layers and very porous support layer with pores having low tortuosity. Despite being a relatively new process, several manufacturers are developing and commercializing suitable FO membranes (Table 1). The most common commercially available membranes are cellulose triacetate (CTA) and polyamide thin-film composite (TFC) membranes manufactured by Hydration Technology Innovations (HTI, Albany, OR) and Oasys Water (Boston, MA) [48]. Between these companies, different FO membrane packaging configurations have been developed, including plate-and frame, spiral wound, and tubular (e.g., hollow fibers) [23]. Spiral wound FO elements are similar to commercial RO membrane elements; however, they are modified to allow forced-flow inside the membrane envelopes (Fig. 10) [23]. Plate and frame configurations use flat sheet membranes separated by spacers, providing lower surface area to volume ratio in cassette packages. Tubular and hollow fiber FO membranes are commonly potted in large bundles, significantly increasing the packing density of a membrane element.

3. Forward osmosis for treatment of complex streams

Through extensive research and development in recent years, FO has been demonstrated as a promising technology for treatment of challenging liquid streams. Successful applications include desalination of seawater and brackish water, concentration of landfill leachates, treatment of wastewater (including in osmotic membrane bioreactor configurations), and processing of foods and beverages [23,25,41]. FO has been investigated at almost all scales as a hybrid pretreatment process for production of high quality water, and as a standalone process where the diluted draw solution is beneficially used. In the following section we summarize various applications where FO was successfully tested for treatment of complex streams, starting with the treatment of waste streams in the O&G industry.
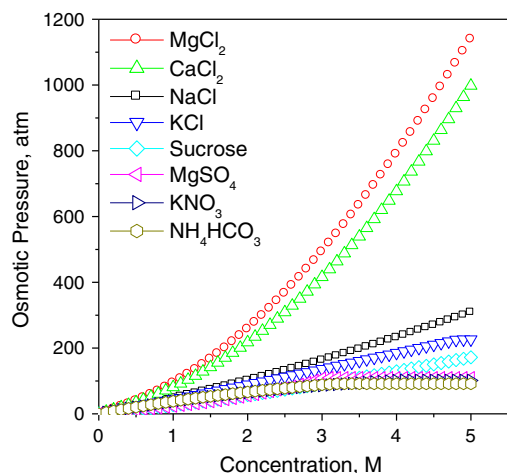

Fig. 2. Osmotic pressure as a function of draw solution concentration for potential draw solutions. Adopted from [23].

Table 1
Current FO membrane manufacturers and commercial status. Adapted from [48].

Firm/ manufacturer	Membrane type	System supply[a]	Primary current application	Commercial status
Aquaporin A/S	Aquaporin	No	FO, OC[e]	Pre-commercial
Fuji	NA	No	NA[b]	Development
GKSS	Polymeric	No	NA[b]	Development
GreenCentre Canada	NA[b]	No	SWFO[c]	Development
HTI	CA, TFC	Yes	Various	Commercial
Idaho National Lab	NA[b]	No	NA[b]	Development
IDE Technologies	NA[b]	Yes	PRO[d]	Pre-commercial
Modern Water	Undefined	Yes	SWFO[c]	Commercial
Oasys Water	TFC	Yes	Brine concentration	Commercial
Porifera	TFC	Yes	Various	Pre-commercial
Samsung	NA[b]	No	NA[b]	Development
Trevi Systems	NA[b]	Yes	SWFO[c]	Development

[a] Demonstration-scale FO membrane treatment systems available (yes/no).
[b] Not available.
[c] Seawater forward osmosis.
[d] Pressure retarded osmosis.
[e] Osmotic concentration.

### 3.1. FO treatment of O&G E&P wastewater

3.1.1. The green machine

The three dominant waste streams generated during E&P contain chemicals and polymers that assist in drilling and hydraulic fracturing, minerals leached from the formations, and organic and inorganic constituents. Research conducted by Hutchings et al. [11] investigated the performance of FO for treatment of O&G waste streams for beneficial, intra-basin reuse using the Green Machine concept.

The Green Machine is a mobile and scalable FO treatment process operated at the well site, thus limiting water and wastewater trucking and providing a local, reusable water source. Operational success was measured by the system's ability to minimize fresh water demand through reuse, preventing secondary waste generation, reducing O&G wastewater volumes for disposal, and utilizing readily available and on-site chemical energy to generate a predetermined osmotic pressure driving force. Carbon footprint reduction, resulting from efficient FO operation and minimized trucking demands, was also of high importance.

Since 2010, two distinct models of the Green Machine have been manufactured and pilot tested by HTI and Emerald Surf Sciences (Shreveport, LA) (previously Bear Creek Services). The first generation Green Machine (Fig. 3) utilized 20 to 280 vertically oriented, 8-inch (0.2 m) diameter by 40-inch (1.0 m) long spiral wound FO membrane elements to treat stream flows of 8 to 170 gal/min (30–640 L/min; 275-5800 bbl/d). The system operated in an osmotic dilution mode, where a 26% w/w NaCl draw solution recirculates inside the membrane envelope while drilling wastewater (2.5% w/w TDS) flows by gravity on the active side side of the membrane. The highly concentrated NaCl draw solution is diluted to less than 7% w/w (~70,000 mg/L) NaCl while concentrating the E&P wastewater by more than 3.5 times (greater than 70% water recovery). Testing results [49] showed that this system was able to reclaim more than 125,000 gallons (473 m³ or 3000 bbl) of O&G wastewater using less than twenty gallons (75 L) of diesel fuel. This same volume would have required over 25 truckloads for disposal at an off-site deep well injection facility. The first generation system could ultimately save nearly a million gallons (3800 m³ or 24,000 bbl) of water per well application and account for up to 20% of the saline completion fluid needed at each drilling location. These savings translate into approximately 150 saved truckloads, both in fresh water and fuel consumption.

However, in a recent study [10], results have shown that the first generation Green Machine FO treatment could be further optimized.
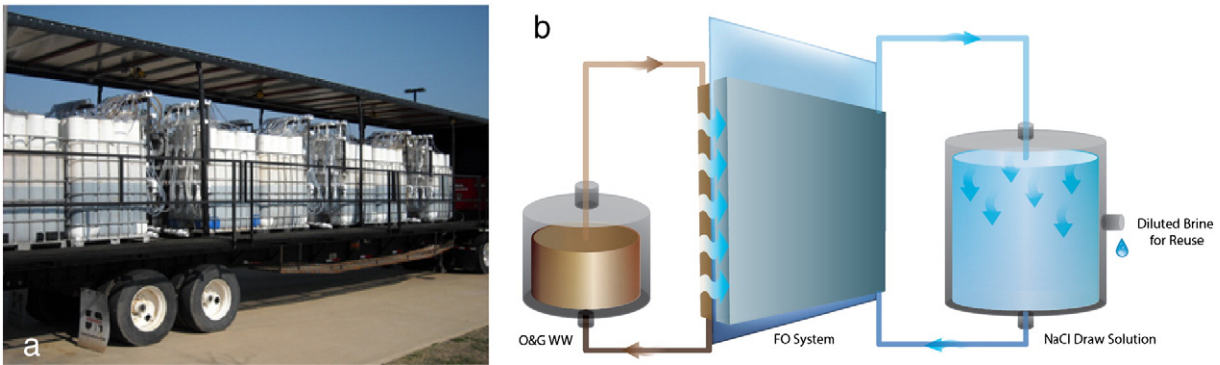
Fig. 3. (a) The HTI's first generation Green Machine mobile system. (b) The FO treatment system operated under osmotic dilution using 20–280 vertically oriented spiral wound FO elements. The membrane elements were grouped into several pods and were installed on a trailer (b) that was operated at O&G drilling locations in the field.

Using a custom made FO membrane test cell with a CTA membrane and a 26% w/w (~320,000 mg/L) NaCl draw solution, osmotic dilution experiments were performed during which at least 50% of the O&G drilling waste feed volume was recovered. Results from the study suggest that while FO can concentrate O&G drilling waste streams by up to three times, increased feed stream velocities can decrease membrane fouling and concentration polarization [50], minimize feed channel clogging, and leads to higher water flux. Minimal irreversible fouling was also observed, demonstrating the effectiveness of osmotic backwashing of FO membranes [36–40]. Additionally, high rejection of inorganic and organic constituents during pilot testing was confirmed by the bench-scale study.

In 2012 the second generation Green Machine (Fig. 4) was developed, optimizing system performance as a result of previous experimental work and pilot testing. The second generation FO system utilizes 24 horizontally oriented, 8-inch diameter by 40-inch long spiral wound FO membrane elements housed in pressure vessels on a mobile membrane skid. The system operates under forced feed flow through the membrane elements (~40 to 60 PSI hydraulic transmembrane pressure) and is coupled with an RO system for reconcentration of the NaCl draw solution.

Recent pilot testing was conducted where 6% w/w (~60,000 mg/L) NaCl draw solution was diluted to 4.5% w/w (~45,000 mg/L) after a once through pass in the FO system. The diluted draw solution was then reconcentrated by the RO system, producing a high quality permeate stream. During a weeklong field test in the Haynesville shale gas play, the system recovered 85% of O&G drilling wastewater (6.8 mS/cm or ~3500 mg/L TDS) while concentrating it by five times (32.5 mS/cm or ~16,000 mg/L TDS) and producing highly purified water for reuse. The system operated with raw drilling wastewater without membrane cleaning and experienced a mere 18% flux decline (versus 50% flux decline during less than half the equivalent testing period using the first generation Green Machine). Flux decline was

attributed to limited membrane fouling and mainly due to the decline in the osmotic pressure driving force that resulted from increased osmotic pressure of the concentrated feed. Unlike the first generation Green Machine, where the diluted draw solution was suitable for use as completion fluid at future drilling applications, the second generation Green Machine produces a high quality RO permeate suitable for a wide range of reuse applications. However, this comes at the price of increased operating and pumping costs. The second generation Green Machine is also limited to a maximum 7% w/w NaCl draw solution if RO reconcentration is used.
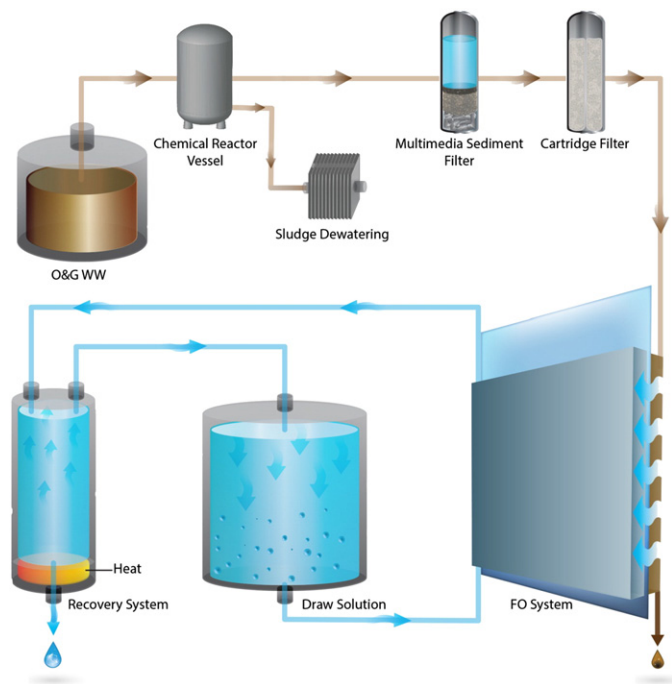
3.1.2. The FO membrane brine concentrator (MBC)

Oasys Water has developed the first Membrane Brine Concentrator (MBC) (Fig. 5) employing a patented ammonia/carbon dioxide based draw solution to treat high salinity brine steams and O&G wastewater. A fully integrated, mobile, demonstration scale Oasys MBC system was constructed and field-tested treating high salinity, pretreated produced water. The mobile treatment system consists of three components: pretreatment, MBC platform, and product water/brine polishing. Raw produced water is first pretreated in a chemical reactor where chemical oxidizer, caustic soda, and soda ash are added to form mineral precipitates and organic flocs. The precipitate suspension is pumped through a filter press to separate the sludge from the treated raw water. The pretreated produced water is then filtered through a greensand media filter for additional iron and particulate removal and then through a cartridge filter. Pretreated feed water flows into the FO membrane and is concentrated by the MBC to between 150,000 and 250,000 mg/L TDS, depending on subsystem operating conditions [18].

The proprietary draw solution is a mixture of ammonium bicarbonate and ammonium hydroxide dissolved in water. The resulting draw solution is highly soluble and produces a high osmotic pressure driving force that facilitates permeation of water through the TFC membrane even when the salinity of the feed stream exceeds 200,000 mg/L TDS.
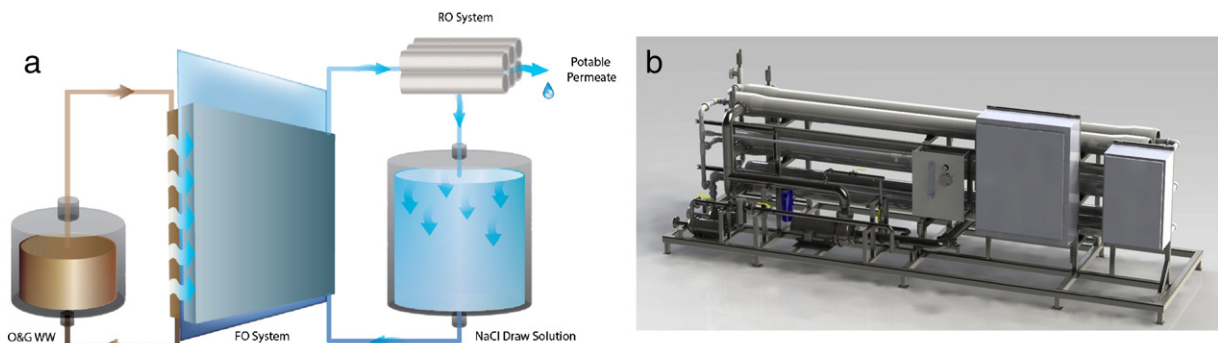
Fig. 4. HTI's second generation Green Machine. (a) The FO treatment system operates under constant influent draw solution concentration using an RO membrane reconcentration system. (b) 8-inch spiral wound FO elements are housed in membrane pressure vessels and are installed on a trailer tested at O&G drilling locations in the field.

Fig. 5. Oasys Water's Membrane Brine Concentrator. The FO treatment system operates under constant influent draw solution concentration using a thermolytic reconcentration system. Several pretreatment technologies are used prior to FO membrane treatment to reduce oil emulsions and elevated hardness concentrations in O&G wastewaters.

The diluted draw solution is then heated to evaporate the thermolytic draw solution solutes, which have lower vapor pressure than water. This recovery method requires less energy than would be required to overcome the enthalpy of vaporization of water during conventional distillation [51]. The ammonia and carbon dioxide gasses are then condensed, and a reconcentrated draw solution is generated for reuse in the FO system. During piloting of the MBC process the system retained more than 99.75% of its nitrogen containing species during 100 h of operation [18]. Product water stripped of dissolved ammonia and carbon dioxide exits the system as a purified water stream.

In two separate commercial demonstrations (Fig. 6), the MBC process demonstrated to provide water treatment and waste volume minimization of fracturing flowback and produced water from the Marcellus Shale and Permian Basin. During the Marcellus Shale trial, approximately 60,000 gallons (230 m³ or 1430 bbl) of produced water were treated during 800 h of operation. Pilot operations were sustained for a six-month period, and included seven weeks of continuous (5 days a week/24 h a day) operation. Average daily steady-state water flux was between 2 and 3 L/m² h (LMH) depending on operating conditions of the system (i.e., draw solution and feed temperature, draw solution concentration, and solution flow rates). It is important to note that water flux under these conditions (feed TDS concentration between effectively 6.5% and 7.5% w/w NaCl) with hydraulically driven membrane based processes would be negligible, if not negative, due to operating limits and material constraints of these systems [52]. System water recovery averaged 64%.

During system operations in the Permian Basin, approximately 40,000 gallons (150 m³ or 950 bbl) of produced were treated during 400 h of operation. Average MBC feed salinity in the Permian Basin was 103,000 ± 7,000 mg/L and contained a high concentration of TOC, boron, and heavy metals. Although TDS and hardness were relatively constant, organic and heavy metal constituents and their concentration were observed to vary substantially between wastewater batches. The average TDS concentration of treated water from the MBC in the Permian Basin trial was 737 ± 284 mg/L and the concentrated brine concentration averaged 241,000 ± 35,000 mg/L TDS. System water flux averaged 3 L/m² h, and average system recovery was 60% [18]. The higher water flux and percent recovery despite the higher salinity of the feed stream compared to the Marcellus Shale demonstration are attributable to improvements in the Oasys membrane, membrane element, and other subsystem refinements.
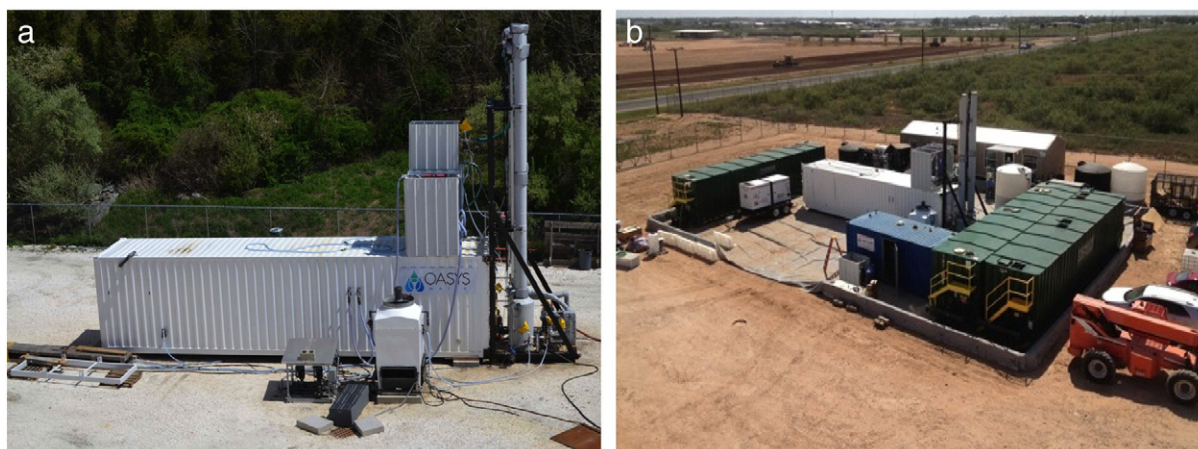
In both the Marcellus Shale and the Permian Basin demonstrations, it is evident that the MBC system is capable of achieving substantial water recovery from highly saline brines, thereby minimizing brine disposal volumes and generating a high quality, tunable product water quality suitable for numerous beneficial use applications.

The use of FO has shown many advantages in the treatment of E&P wastewater: low hydraulic pressure operation, reduced fouling propensity compared to pressure-driven processes (RO), and substantial rejection of known contaminants found in oil and gas waste streams. While these pilot and bench scale-testing studies are promising, little is known about the long term (>1 year) fouling propensity and its effects on FO process efficiency when treating oil and gas saline E&P wastewater. Future testing will require such investigations while attempting to broaden the application to other basins outside of the Haynesville, Marcellus, and Permian O&G fields.

3.2. Other applications of FO for difficult waste streams

3.2.1. FO treatment of landfill leachate

Most landfills produce leachate, which originates from decomposition of stored wastes or from precipitation that percolates through the piled solid waste. Typical contaminants of concern in landfill leachates include TDS, dissolved metals, organic matter, and organic/inorganic

Fig. 6. Oasys Water's Membrane Brine Concentrator shown during pilot-testing in (a) the Marcellus Shale basin and (b) Permian Basin.

nitrogen. The volume and concentrations of leachate constituents can be highly variable and they depend on the location of the landfill and corresponding local climate. Leachates are commonly sent to conventional wastewater treatment facilities; however, TDS present in leachates is not efficiently removed by conventional wastewater treatment processes and it can negatively impact biological processes and effluent quality [23].

An FO pilot study was conducted at the Coffin Butte Landfill in Corvallis, Oregon in 1998, attempting to provide advanced treatment of leachate [53]. The landfill is located in the Pacific Northwest and receives enough precipitation to produce 20,000–40,000 m^3 of leachate annually (annual average of 15,000–30,000 gal/day). In this particular case, the leachate had to be treated for surface discharge with effluent TDS concentration of less than 100 mg/L.

Cellulose triacetate membranes from Osmotek (now HTI) were utilized for the three-month pilot study. Using NaCl draw solution, the pilot system was operated at 94–96% water recovery, while providing high contaminant rejection and minimal irreversible membrane fouling [23]. As a result of successful piloting, a full-scale FO/RO system was built [53]. At full-scale operation (Fig. 7), landfill leachate was collected and pretreated using hydrochloric acid to prevent inorganic scaling. The system consisted of four treatment trains, each with six FO plate-and-frame membrane stacks in series. While the leachate became concentrated, diluted draw solution was treated and reconcentrated using an RO system, producing high-quality permeate meeting discharge regulations [53].

After approximately one year of operation, the full-scale system treated 18,500 m^3 (~5 million gallons) of landfill leachate at greater than 91% water recovery. The FO/RO process also continually produced permeate having less than 100 mg/L TDS. Contaminants of concern, including cadmium, chromium, copper, lead, zinc, and ammonia were consistently more than 99% rejected, with effluent biochemical oxygen demand (BOD) concentrations below 5 mg/L. The FO/RO application successfully provided effluent contaminant concentrations lower than the National Pollutant Discharge Elimination System (NPDES) total maximum daily loads (TMDL) [23,53].

3.2.2. FO treatment of centrate from anaerobic digesters

Municipal wastewater treatment facilities typically treat primary and secondary biosolids in aerobic or more commonly anaerobic digesters. Solids digestion promotes degradation of organic constituents and BOD, producing stabilized biomass and biogas. After digestion the sludge is dewatered, producing a concentrated liquid waste stream (i.e., centrate) and dewatered biosolids. While the biosolids are typically land applied or trucked for off-site disposal, the liquid waste stream is commonly returned to the facility headworks. This practice increases facility loading because the liquid contains high nutrient concentrations (e.g., organic nitrogen, orthophosphate, ammonia), dissolved metals, TDS, total suspended solids (TSS), and organic carbon [23,54,55]. By removing this return stream, treatment facilities can reduce total waste loadings, operating costs, and effluent nitrogen and phosphorous concentrations. Concentrated centrate can also be sold as a product and used as a fertilizer.

An FO treatment study [54] was conducted at the Truckee Meadows Water Reclamation Facility in Reno, Nevada in 2006 as a method to treat and reduce the volume of centrate produced at the facility. The purpose of the study was to evaluate FO performance for concentrating raw and filtered centrate as an alternative to their common practices. During the bench-scale investigation centrate was filtered through a 150-mesh sieve prior to the FO process. Water was then extracted from the filtered centrate across a CTA FO membrane operating in osmotic dilution mode [27]. FO provided sustainable water flux and high rejection of contaminants of concern while successfully concentrating raw and filtered anaerobic digester centrate. While water flux decline was noticed between each test cycle due to fouling, membrane cleaning restored water flux to its original level. Even though increased flux decline was

Fig. 7. Full-scale plate-and-frame FO treatment system operated at Coffin Butte Landfill by HTI (previously Osmotek) for treatment of landfill leachate.

observed when testing raw centrate, the ability to recover most permeate flux indicated that minimal irreversible fouling occurred during the FO process.

Constituents of concern included ammonia, total Kjeldahl nitrogen (TKN), and ortho-phosphate with average feed concentrations of 1300, 1400, and 240 mg/L, respectively. FO provided 87% ammonia rejection, 92% TKN rejection, and greater than 99% rejection of phosphorous, color, and odor compounds. Results from the study suggest that combining the FO process with RO could successfully produce 35,000 gal/day (130 m^3/day) of purified water from a 50,000 gal/day (190 m^3/day) stream of centrate [54].

3.2.3. FO treatment of domestic wastewater and osmotic membrane bioreactors (OMBR)

Stringent wastewater treatment regulations and advancements towards indirect and direct potable water reuse require implementation of improved treatment processes to produce high quality reclaimed water. Membrane bioreactors (MBR) have demonstrated the ability to provide advanced treatment, producing effluent suitable for irrigation, industrial processes, and even potable water when provided proper effluent polishing [56]. MBRs replace the combined biological, clarification, and filtration processes in conventional, municipal wastewater treatment facilities. Using MF or UF membranes, MBRs reject nearly all suspended solids and maintain high biomass concentration, providing consistent effluent quality in a significantly smaller footprint than tradional treatment processes (i.e., sequencing batch reactors, extended aeration facilities, lagoons) [56].

Yet, due to limited rejection of TDS, low molecular weight contaminants, and trace organic compounds (TOrCs), and because of membrane properties and fouling propensity associated with the operation of conventional MBRs, FO has been investigated as a potential alternative for advanced wastewater treatment [56–66]. Independent studies conducted since 2008 have aimed at developing an efficient osmotic membrane bioreactor (OMBR). For example, Achilli et al. [56] investigated membrane fouling, water flux, reverse solute diffusion, and nutrient rejection at the bench scale. Three flat-sheet CTA membranes were employed in a plate and frame cell configuration and results concluded that membrane fouling in the OMBRs was lower than in MF/UF MBRs. Water flux was restored to within 10% of the original flux using membrane relaxation (when no filtration takes place) and osmotic backwashing, showing minimal irreversible fouling. Flux was easily sustained throughout the duration of the experiments, and decline in the driving force was associated with easily cleaned fouling layers. The FO membranes rejected 99% of influent TOC and 98% of influent ammonia. This is significantly better rejection than that of porous MBR membranes,

which can range between 28 and 87% of soluble organic matter, depending on the extent of membrane fouling.

Another important study by Alturki et al. [57] was recently published, evaluating FO rejection of TOrCs that pass through MBR processes. A thorough literature review revealed that conventional wastewater treatment processes do not provide effective removal of TOrCs. MBRs provide slight enhancement of pollutant removal through biological degradation due to increased solids retention times and biomass concentration. However, due to the porous nature of MBR MF and UF membranes, low molecular weight TOrCs can easily flow through the treatment process. Only those pollutants readily biodegradable and hydrophobic are removed. Flat sheet cellulose acetate membranes were employed in a plate and frame test cell and 50 TOrCs, each with an average concentration of 750 ng/L, were investigated. Experimental results show that the OMBR provided high rejection (permeate concentration below analytical detection limits) of many TOrCs with molecular weights greater than 266 g/mol. This high rejection promoted biological degradation of the pollutants within the bioreactor. Rejection of pollutants smaller than 266 g/mol was highly variable, ranging from minimal rejection to removal below analytical detection limits.

Long-term pilot-scale tests have since been conducted using a novel FO plate and frame membrane module (Fig. 8) [67]. The objective of the long-term pilot scale evaluation was to determine the sustainability and permeate water quality of a coupled FO and RO process. High quality permeate was consistently produced through the coupled FO–RO system; however, excessive FO membrane fouling was observed after four months of system operation. Fouling was attributed to insufficient membrane air scouring and gas lift between the membrane plates. Additionally, the salinity in the bioreactors steadily increased due to ion rejection of the FO membranes coupled with reverse salt flux from the concentrated draw solution through the FO membrane into the activated sludge. The increase in bioreactor salinity resulted in reduced osmotic driving force and negatively impacted biological activity in the activated sludge.

In a second, long-term evaluation, a UF membrane was operated in parallel with the FO membrane (UFO-MBR) to maintain constant bioreactor salinity. This mitigated the negative effects of salt accumulation in the activated sludge and produced a treated water stream fit for phosphorus recovery and non-potable reuse applications [68,69]. High quality RO permeate and phosphorus rich UF permeate were continuously produced for an additional four months of system operation and the salinity in the activated sludge was sustained at a low concentration because ions were continuously extracted from the bioreactor through the UF membrane. Furthermore, the addition of coarse bubble aeration (previously fine bubble) used to air-scour the FO membranes and provide gas lift through the plate and frame cassette resulted in

dramatically reduced membrane fouling (Fig. 9). This is exemplified by constant water flux that was maintained for 125 days of operation without membrane cleaning.

3.2.4. FO for concentration of foods and beverages

The concentration of liquid foods and beverages is an important and equally sensitive process in industrial food production. Traditionally, foodstuffs are concentrated using multi-stage vacuum evaporation or even RO. However, these processes can reduce the quality of the final concentrated product. Heat generation and vapor losses can negatively impact food color, taste, and potentially the nutritional value of the final concentrate [70], and RO operation is limited by osmotic pressures at high feed concentrations. Jiao et al. [71] and Petrotos and Lazarides [70] have published thorough summaries of membrane application in the food industry, including results from FO studies. The first attempt to use modern applications of FO was by Popper et al. in 1966 [72]. First generation RO membrane made of cellulose acetate was used in both flat sheet and tubular configurations. Using a highly concentrated NaCl draw solution, the membranes produced 2.5 L/m^2 h and were able to increase grape juice concentration by 44° Brix (the measure of sugar content of an aqueous solution). However, reverse solute diffusion of salt [73,74] into the grape juice concentrate demonstrated the need for different, more appropriate draw solutions. Improving upon the concept, Beaudry and Lampi [75] investigated a 72° Brix sugar draw solution employed in a newly developed plate-and-frame membrane element, housing a thin film composite (TFC) membrane coupon. These improvements increased water flux to 5–6 L/m^2 h, while providing greater than 99.9% rejection of orange juice acids and red raspberry juice color sensory. In 1993, Wrolstad et al. [76] compared Osmotek's FO treatment of red raspberry juice to traditional vacuum concentration. Using a high fructose corn syrup draw solution, the resulting FO concentrate was analyzed and found to be of equal or higher quality than that produced by vacuum evaporation.

Two studies conducted by Petrotos et al. [72,77,78] further investigated these findings when applying FO to tomato juice concentrate. This is a very challenging application because tomato juice is considered one of the most concentrated vegetable juices in the industry. Experimental results suggest that draw solution viscosity directly impacts overall water flux (e.g., low viscosity draw solutions provide improved water flux). Additionally, it was concluded that decreasing membrane thickness provided an exponential increase in water flux. When the tomato juice feed stream was also pretreated with a filtration process FO performance improved, providing a 39% increase in water flux in comparison to no pretreatment. Over ten years later, FO is still being investigated for treatment of liquid foodstuff, where Garcia-Castelloa et al. [79] concentrated orange peel press liquor using FO. This research
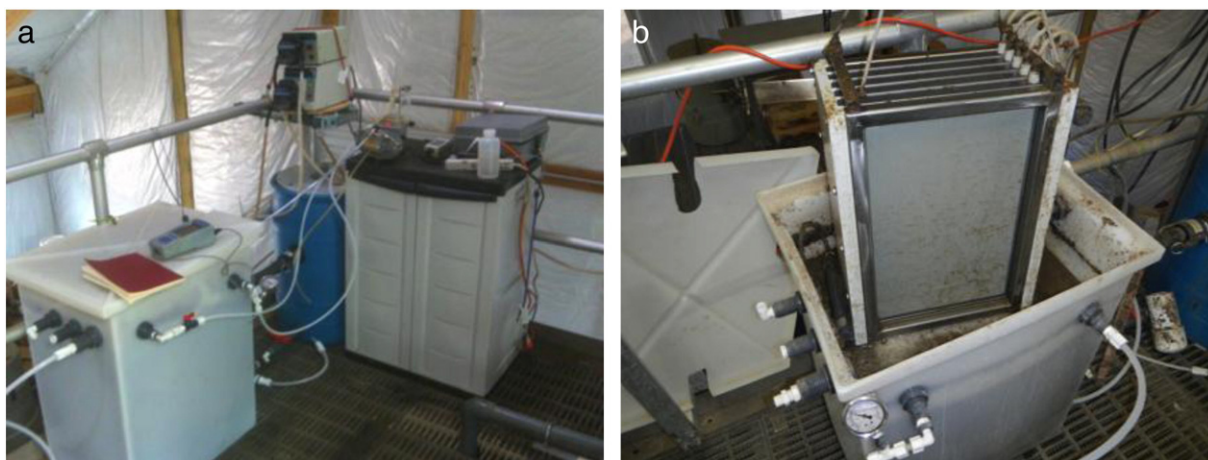

Fig. 8. Pilot-scale plate-and-frame FO treatment system operated and at the Colorado School of Mines AQWATEC laboratory.

Fig. 9. FO CTA membrane fouling from long-term pilot-scale testing (a) before and (b) after introducing a parallel UF membrane operation and course air bubble aeration between plate-and-frame cassettes.

showed that FO is a promising alternative to traditional dewatering processes and also concluded that minimal pretreatment prior to FO may help limit declining permeate flux due to membrane fouling.

Based on tested membrane performance, FO can be a well-suited treatment alternative for use in the food processing industry and competitive with traditional vacuum evaporation and RO. Under optimized membrane design and proper choice of osmotic draw solution, sustainable water flux can be generated at low temperatures and low pressures that are desired in these types of applications.

4. Technological progress to enable better utilization in the O&G and other industries

FO treatment has shown great applicability and competitiveness in challenging industrial applications. Two commercialized FO membrane processes have proven successful in treatment of O&G wastewater for beneficial water reuse. Nonetheless, to better apply the treatment strategies and optimize system performance, substantial improvements can still be made in FO. Three independent reviews [23,25,48] presented several shortcomings of FO that need to be addressed by future research and development. Membrane manufacturing and module design are being continually improved, including increasing membrane robustness, permeability, chemical stability and range and rejection of contaminants of concern. New FO membranes for O&G must minimize internal concentration polarization [50,74,80–85] in order to reduce the loss of osmotic driving force across the membrane as waste streams become concentrated. Improvements should also be made to draw solutions, maximizing osmotic pressure while minimizing reverse solute diffusion, regeneration and recovery costs, toxicity, and reactivity with the membrane active layer.

4.1. New membranes

First generation FO membranes were produced by HTI using cellulose triacetate. This polymer is cast with an embedded polyester mesh for membrane support while forming a dense semi-permeable active layer. The goal was to minimize the active layer thickness of the asymmetric membrane, theoretically increasing membrane water permeability without compromising contaminant rejection or membrane integrity. These CTA membranes for FO are still under development and are the workhorse of the Green Machine; however, studies and recent field tests in regional gas plays have shown that while these first generation membranes are very robust, they do not have the desired water permeability and salt rejection, and they can only operate in a

narrow pH range [86,87]. Recently developed TFC FO membranes by HTI and Oasys for this same application were tested by Coday et al. [88]. The TFC membranes exhibited better water flux than CTA membranes; however, the reverse salt flux of TFC membranes was higher and more affected by the transmembrane pressure common in the latest O&G FO treatment membrane modules. Rejection of organic molecules was comparable between the TFC and CTA membranes, at approximately 96%. The study demonstrated that new membrane materials and structure, coupled with operating conditions, might influence the preferential reverse diffusion and rejection of charged ions. This phenomenon is important and can impact specific process applications and requires further investigation.

Looking to the future, Wang et al. [86] suggest that the most effective FO membranes must have a very thin active layer supported by a thin support whose structure is highly porous to minimize internal concentration polarization. The membrane surface composition should be hydrophilic, which may help minimize O&G foulant deposition on the membrane surface and increase water permeability when treating viscous fracturing flowback fluids. Furthermore, the membrane chemistry must tolerate large shifts in pH and maintenance with various aggressive chemicals to maintain efficient and uninterrupted operation at the well site.

Several academic studies have focused on the advanced development of these FO membranes [82,83,85–87,89–96]. For example, Wang et al. [86] investigated the production of thin-film composite FO hollow fibers with an ultra-thin active layer. This active layer, very similar to an RO selective layer, can be cast on either the inside or outside of the hollow fiber membrane wall. Results from the experiments suggest that it is possible to easily tailor this process and the membrane active layer to meet specified requirements. The use of hollow fiber membranes could increase membrane-packing density and avoid the severe pressure drop of spiral wound membrane modules when they become fouled/clogged. Qiu et al. [87] produced a positively charged flat sheet membrane using polyamide-imide (PAI) substrate with a polyelectrolyte post-treatment. This produced an asymmetric, micro-porous membrane with an active layer similar to that of a NF membrane. Unfortunately, membranes for O&G wastewater treatment should be negatively charged, which would decrease the affinity of negatively charged organic molecules to adhere to the membrane surface. Setiawan et al. [89] built upon this same research to develop a PAI membrane with a less positively charged active layer to help mitigate the attraction of negatively charged organic molecules. In general, both casting techniques and membrane substrate selection have allowed polymer scientists to produce better FO membranes, tailored for specific

applications and different feed water compositions, with the goal of satisfying the criteria established above. For O&G wastewater recovery, membrane manufacturers are challenged with balancing several requirements; membrane robustness, support layer porosity, and rejection should be maximized, while the thickness of the membrane active layer and tortuosity of the membrane's support layer should be minimized.

4.2. New membrane configurations

Several different membrane configurations have been developed and investigated in attempts to provide the best overall rejection, water flux, and operating efficiency, given certain feed water composition and characteristics. Well-developed configurations include plate-and-frame, spiral wound, hollow fiber, and tubular. FO membranes have been tested at the pilot-scale using traditional spiral wound and plate-and-frame configurations. Spiral wound modules are very similar to those used in traditional RO applications but with specific design modifications [23]. Typical RO spiral wound modules only accept one stream flow (e.g., feed stream) while FO modules must accept two streams simultaneously (Fig. 10). To do this, the membrane envelope and center collection tube in spiral wound FO modules are modified. The center tube (now the draw solution conduit) is plugged half way and the envelope is partially glued down the centerline [23]. This forces the draw solution to enter one half of the membrane envelope, flow across the membrane surface, and be collected in the other half of the plugged center tube. The feed solution flows through the module over the modified membrane envelopes, similar to the feed flow in RO spiral wound modules. Using spiral wound modules, feed channel clogging has been observed in previous O&G tests in the field; this is especially true when no pretreatment is applied before the FO process as practiced in the operation of the Green Machine.

In plate-and-frame modules, flat membrane sheets are held in place on frames and support systems. This system is typically submerged in a tank containing the feed stream (e.g., OMBR applications) while draw solution flows between the sealed membranes and plate support. This configuration can also be applied to O&G wastewater recovery; however, the footprint of the setup would likely increase in comparison to a spiral wound configuration. A custom tank may also be necessary that is capable of providing air scouring between the membrane plates, similar to an OMBR application.

Tubular and hollow fiber membranes (Fig. 11) are similar to MF and UF designs commonly employed in MBR applications. These configurations are durable and self-supported, with an active layer that can be produced on either the inner or outer sides of the tube/fiber. It is important to note that in hollow fiber membranes and other configurations, the orientation of the FO membrane (e.g., active layer facing feed or draw solution) can have significant impacts on system performance and fouling tendency.

For O&G wastewater treatment, one of the main technological challenges is the need to improve process hydraulics to avoid clogging of flow channels in the membrane elements and optimize the manufacturing and operation of membranes. Dissolved and suspended constituents in drilling and frac flowback wastewater and produced water are major membrane foulants, and upon concentration during the treatment process they can clog the membrane elements. Membrane fouling results in high operating and maintenance costs, prolonged system shutdowns, and ultimately permanent membrane damage. Although typical FO membranes are hydrophilic, and thus reduce fouling propensity of the membrane, precipitation of solids in the feed flow channels inside the membrane elements may retard the performance of the process. Novel membrane feed spacers, new membrane configurations (such as capillary membranes), optimized membrane manufacturing and incorporation of applicable pretreatment processes should be further investigated.
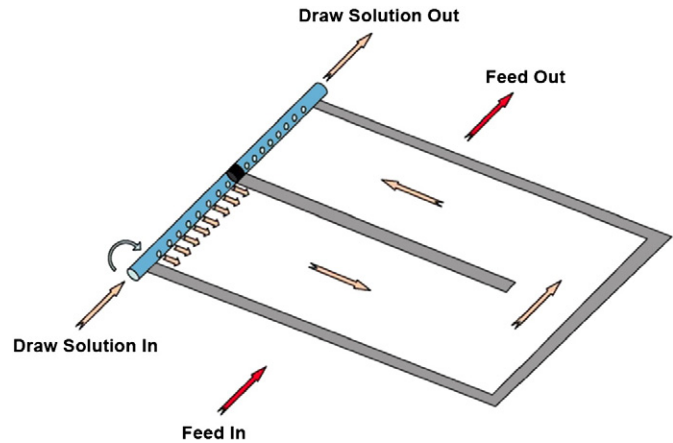
Fig. 10. In spiral wound FO modules, the membrane envelope and center collection tube are modified. The center tube (the draw solution conduit) is plugged half way and the envelope is partially glued down the centerline. This forces draw solution to enter one half of the membrane envelope, flow across the membrane surface, and be collected in the other half of the plugged center tube. The feed solution flows through the module over the modified membrane envelopes, similar to the feed flow in RO spiral wound modules. Adapted from [23].

4.3. New draw solutions

Another important aspect to successful FO is the selection of a suitable draw solution that is well matched to the process (e.g., toxic or saline solutions are inadequate for beverage concentration). NaCl is used in the Green Machine because it is readily available on site, highly soluble, non-toxic, inexpensive, and easily reconcentrated while providing high osmotic pressures. However, there are more than 500 inorganic compounds that can be potentially used as draw solutions; 14 were chosen and investigated in a recent study by Achilli et al. [42]. Other investigations have studied the applicability of dissolved gasses such as sulfur dioxide and ammonium bicarbonate, or even nanoparticles such as magnetoferritin as suitable draw solutions in tailored FO applications [18,42–47]. A summary of FO draw solutions is provided in Table 2. Due to the highly saline nature of O&G produced water, which effectively lowers the osmotic pressure driving force, innovative draw solutions with exceptionally high osmotic pressure are required. Solutions that are also compatible with O&G reuse options such as hydraulic fracturing or well drilling must also be considered.
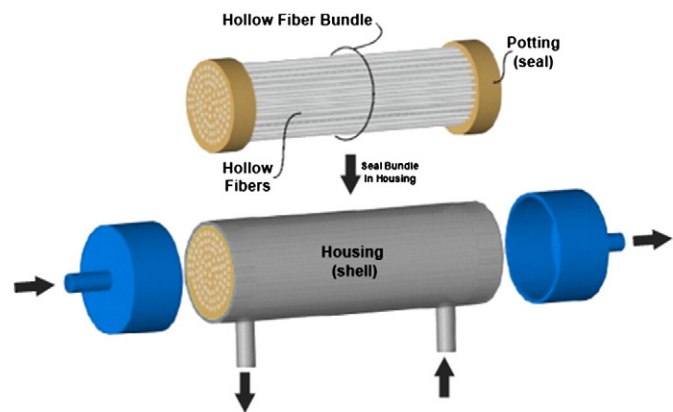
Fig. 11. Hollow fiber FO membranes are group in bundles of varying size and potted at each end. The potted membrane bundle is then installed into a membrane housing or shell where, depending on the membrane orientation, the draw solution can either flow on the inside or outside of the hollow fiber.

4.4. Pretreatment before FO

Similar to pressure driven membrane processes, FO can be appreciably enhanced if appropriate pretreatment processes are implemented upstream of the FO process. While the Green Machine operates with no pretreatment, the MBC relies on adequate feed stream pretreatment to protect the FO membranes. The following is a list of suitable pretreatment processes, each with a short description:

- Coagulation/flocculation aids in the removal of suspended and colloidal particulates to reduce premature membrane fouling. It can make the fouling cake layer more porous and permeable when treating highly fouling feed streams, such as O&G frac flowback and concentrated domestic wastewater sludge and digester centrate.
- Acid/base pH control aids in precipitation of dissolved metals and protects the chemistry of the membrane active layer. This is especially important when using a CTA FO membrane, where the feed stream pH should be between 5 and 7.
- Scale mitigation/softening aids in precipitation or exchange of scale forming compounds to limit premature membrane scaling. Scale mitigation can be used prior to FO when treating high salinity produced waters (>70,000 ppm) having elevated concentrations of sparingly soluble salts.
- Filtration (granular media/MF/UF) aids in the removal of suspended and precipitated particulates to reduce premature membrane fouling and flow channel blocking/clogging. Filtration can be used when treating grit laden drilling mud and frac flowback wastewaters. Filtration may be especially used to protect TFC FO membranes because the active layer of these membranes is more delicate than that of the CTA FO membrane.
- Dissolved air floatation aids in the removal of oil, fats, and insoluble organics to reduce premature membrane fouling and damage to the membrane active layer. Dissolved air floatation can be used to remove elevated concentrations of emulsified hydrocarbons from produced waters, which may sorb to the membrane active layer and irreversibly foul the membrane.
- Advanced oxidation aids in the destruction of oils and fats and oxidizes reduced inorganic metal species for subsequent removal. Advanced oxidation can be especially important when treating frac flowback wastewater by further degrading any remaining polymers or guars remaining from the hydraulic fracturing process.
- Disinfection minimizes the potential for biological fouling and degradation of the membrane active layer.

5. Conclusions

Forward osmosis is a suitable and effective process for treatment of difficult waste streams, and it was demonstrated at all scales of research and development, including bench scale, pilot scale, and commercial demonstration. Specifically in O&G exploration and production, FO is a promising technology that enables exploration companies to utilize effective wastewater treatment and promote beneficial water reuse in decentralized and remote locations. Currently, there are several different approaches and methods for implementing the technology; however, it is unclear which approach is most suitable, leaving significant room for more research. Ultimately, O&G exploration companies will choose the water management option that (a) is physically practical for on-site operation with their waste stream, (b) accepted by state and federal regulators, and (c) sustainable over extended periods of operation.

Compared to traditional disposal methods, both the HTI Green Machine and the Oasys Water Membrane Brine Concentrator FO systems demonstrated net cost advantages of more than 45% and 60%, respectively, in recent demonstration scale tests; however, a direct cost comparison between these two FO technologies is difficult to conduct at this time. The Green Machine is suitable for treating O&G waste streams with minimal or no pretreatment, but is currently more suitable for treating wastewaters with less than 70,000 ppm TDS. The Membrane Brine Concentrator system uses two pretreatment steps prior to FO membrane treatment, but can target feed stream salinities in excess of 70,000 ppm TDS.

FO has shown great versatility by successfully treating a wide range of feed stream salinities and producing equally wide ranges of product water quality — from diluted saline solution to RO permeate suitable for potable and non-potable reuse. Ultimately, other industries that produce complex liquid streams can benefit from the experiences of FO treatment of O&G E&P wastewater. The limitations of FO need further investigation, as new generations of TFC membranes and novel draw solutions are being developed. Further research is needed to test these membranes and draw solutions in conjunction with true wastewater streams to determine if they can further enhance the FO process for these difficult applications.

Table 2
Overview of draw solutes/solution used in FO investigations and their recovery methods. Adapted from [25,28].

Year	Draw solute/solution	Recovery method	Research group
1964	NH$_3$ and CO$_2$	Heating	Neff [97]
1965	Volatile solutes (e.g. SO$_2$)	Heating or air stripping	Batchelder [98]
1965	Mixture of water and another gas (SO$_2$) or liquid (aliphatic alcohols)	Distillation	Glew [99]
1970	Organic acids and inorganic salts	Temperature variation/chemical reaction	Hough [97]
1972	Al$_2$SO$_4$	Precipitation by doping Ca(OH)$_2$	Frank [100]
1975	Glucose	None	Kravath & Davis [101]
1976	Nutrient Solution	None	Kessler & Moody [102]
1989	Fructose	None	Stache [103]
1992	Sugar	RO	Yaeli [104]
1997	MgCl$_2$	None	Loeb [105]
2002	KNO$_3$ and SO$_2$	SO$_2$ is recycled through standard means	McGinnis [106]
2005–07	NH$_3$ and CO$_2$ (NH$_4$HCO$_3$)	Moderate heating (~60 °C)	Elimelech [44,107,108]
2007	Magnetic nanoparticles	Captured by a canister separator	Adham [109]
2007	Dendrimers	Adjusting pH or UF	Adham [109]
2007	Albumin	Denatured and solidified by heating	Adham [109]
2008	Salt, ethanol	Pervaporation	McCormick [110]
2010	2-Methylimidazole-based solutes	FO–MD	Chung [47]
2010–11	Magnetic nanoparticles	Recycled by a magnetic field	Chung [111,112]
2011	Stimuli-responsive polymer hydrogels	Deswelling the polymer hydrogels	Wang [113]
2011	Fertilizers	Unnecessary	Shon [114,115]
2011	Hydrophilic nanoparticles	UF	Chung [115]
2011	Fatty acid-polyethylene glycol	Thermal method	Lyer & Linda [116]
2012	Sucrose	NF	Su [117]
2012	Thermo-sensitive solute (derivatives of Acyl-TAEA)	None	Noh [118]
2012	Urea, ethylene glycol, and glucose	None	Yong [119]
2012	Polyglycol copolymers	NF	Carmignani [120]
2012	Hexavalent phosphazene salutes	Chemical	Stone [121]
2012	Organic ionic salts (e.g. Mg(CH$_3$COO)$_2$)	RO	Childress [43]
2012	Polyelectrolytes	UF	Chung [45]

Acknowledgements

References

[1] Y. Chang, X. Liu, P. Christie, Emerging shale gas revolution in China, Environ. Sci. Technol. 46 (2012) 12281–12282.

[2] R. Weijermars, Economic appraisal of shale gas plays in Continental Europe, Appl. Energy 106 (2013) 100–115.

[3] Z. Xingang, K. Jiaoli, L. Bei, Focus on the development of shale gas in China—based on SWOT analysis, Renew. Sust. Energ. Rev. 21 (2013) 603–613.

[4] B. Lin, T. Wang, Forecasting natural gas supply in China: production peak and import trends, Energy Policy 49 (2012) 225–233.

[5] R.F. Aguilera, R.D. Ripple, Technological progress and the availability of European oil and gas resources, Appl. Energy 96 (2012) 387–392.

[6] D. Rahm, Regulating hydraulic fracturing in shale gas plays: the case of Texas, Energy Policy 39 (2011) 2974–2981.

[7] B.G. Rahm, S.J. Riha, Toward strategic management of shale gas development: regional, collective impacts on water resources, Environ. Sci. Pol. 17 (2012) 12–23.

[8] P. Xu, J.E. Drewes, D. Heil, Beneficial use of co-produced water through membrane treatment: technical–economic assessment, Desalination 225 (2008) 139–155.

[9] T. Cath, Novel engineered osmosis technology: a comprehensive approach to the treatment and reuse of produced water and drilling wastewater, Colorado School of Mines, Research Partnership to Secure Energy for America, 2010.

[10] K.L. Hickenbottom, N.T. Hancock, N.R. Hutchings, E.W. Appleton, E.G. Beaudry, P. Xu, T.Y. Cath, Forward osmosis treatment of drilling mud and fracturing wastewater from oil and gas operations, Desalination 312 (2013) 60–66.

[11] N.R. Hutchings, E.W. Appleton, R.A. McGinnis, Making high quality frac water out of oilfield waste, The International Society of Petroleum Engineers 2010 Annual Technical Conference and Exhibition, Florence, Italy, September 19–22, 2010, September 19–22, 2010.

[12] R. McIlvaine, A. James, The potential of gas shale, World Pumps 2010 (2010) 16–18.

[13] A.D. Horn, N.E. Mid-Continent, Breakthrough mobile water treatment converts 75% of fracturing flowback fluid to fresh water and lowers CO2 emissions, Proceedings of the SPE Americas E&P Environmental and Saftey Conference, San Antonio, Texas, 23–25 March 2009, March 23–25 2009.

[14] D.L. Shaffer, L.H. Arias Chavez, M. Ben-Sasson, S. Romero-Vargas Castrillon, N.Y. Yip, M. Elimelech, Desalination and reuse of high-salinity shale gas produced water: drivers, technologies, and future directions, Environ. Sci. Technol. 47 (2013) 9569–9583.

[15] M. Cakmakce, N. Kayaalp, I. Koyuncu, Desalination of produced water from oil production fields by membrane processes, Desalination 222 (2008) 176–186.

[16] M. Ebrahimi, K.S. Ashaghi, L. Engel, D. Willershausen, P. Mund, P. Bolduan, P. Czermak, Characterization and application of different ceramic membranes for the oil-field produced water treatment, Desalination 245 (2009) 533–540.

[17] A. Fakhru'l-Razi, A. Pendashteh, L.C. Abdullah, D.R.A. Biak, S.S. Madaeni, Z.Z. Abidin, Review of technologies for oil and gas produced water treatment, J. Hazard. Mater. 170 (2009) 530–551.

[18] N.T. Hancock, M.S. Nowosielski-Slepowron, L.S. Marchewka, Application of forward osmosis based membrane brine concentrators for produced water treatment, IDA World Congress, Tianjin, China, October 20–25, 2013, October 20–25, 2013.

[19] B. Van der Bruggen, C. Vandecasteele, Distillation vs. membrane filtration: overview of process evolutions in seawater desalination, Desalination 143 (2002) 207–218.

[20] I. Sutzkover-Gutman, D. Hasson, Feed water pretreatment for desalination plants, Desalination 264 (2010) 289–296.

[21] N. Prihasto, Q.-F. Liu, S.-H. Kim, Pre-treatment strategies for seawater desalination by reverse osmosis system, Desalination 249 (2009) 308–316.

[22] E.-S. Kim, Y. Liu, M. Gamal El-Din, The effects of pretreatment on nanofiltration and reverse osmosis membrane filtration for desalination of oil sands process-affected water, Sep. Purif. Technol. 81 (2011) 418–428.

[23] T.Y. Cath, A.E. Childress, M. Elimelech, Forward osmosis: principles, applications, and recent developments, J. Membr. Sci. 281 (2006) 70–87.

[24] R.J. Salter, Forward osmosis, Water Cond. Purif. 48 (2005) 36–38.

[25] S. Zhao, L. Zou, C.Y. Tang, D. Mulcahy, Recent developments in forward osmosis: opportunities and challenges, J. Membr. Sci. 396 (2012) 1–21.

[26] T.Y. Cath, J.E. Drewes, C.D. Lundin, N.T. Hancock, Forward osmosis–reverse osmosis process offers a novel hybrid solution for water purification and reuse, Int. Desalin. Assoc. 2 (2010) 16–20.

[27] T.Y. Cath, N.T. Hancock, C.D. Lundin, C. Hoppe-Jones, J.E. Drewes, A multi-barrier osmotic dilution process for simultaneous desalination and purification of impaired water, J. Membr. Sci. 362 (2010) 417–426.

[28] Q. Ge, M. Ling, T.-S. Chung, Draw solutions for forward osmosis processes: developments, challenges, and prospects for the future, J. Membr. Sci. 442 (2013) 225–237.

[29] N.T. Hancock, P. Xu, D.M. Heil, C. Bellona, T.Y. Cath, Comprehensive bench- and pilot-scale investigation of trace organic compounds rejection by forward osmosis, Environ. Sci. Technol. 45 (2011) 8483–8490.

[30] T.-S. Chung, X. Li, R.C. Ong, Q. Ge, H. Wang, G. Han, Emerging forward osmosis (FO) technologies and challenges ahead for clean water and clean energy applications, Curr. Opin. Chem. Eng. 1 (2012) 246–257.

[31] D.L. Shaffer, N.Y. Yip, J. Gilron, M. Elimelech, Seawater desalination for agriculture by integrated forward and reverse osmosis: improved product water quality for potentially less energy, J. Membr. Sci. 415–416 (2012) 1–8.

[32] N.T. Hancock, P. Xu, M.J. Roby, J.D. Gomez, T.Y. Cath, Towards direct potable reuse with forward osmosis: technical assessment of long-term process performance at the pilot scale, J. Membr. Sci. 445 (2013) 34–46.

[33] B. Mi, M. Elimelech, Gypsum scaling and cleaning in forward osmosis: measurements and mechanisms, Environ. Sci. Technol. 44 (2010) 2022–2028.

[34] B. Mi, M. Elimelech, Organic fouling of forward osmosis membranes: fouling reversibility and cleaning without chemical reagents, J. Membr. Sci. 348 (2010) 337–345.

[35] S. Lee, C. Boo, M. Elimelech, S. Hong, Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO), J. Membr. Sci. 365 (2010) 34–39.

[36] K.S. Spiegler, J.H. Macleish, Molecular (osmotic and electro-osmotic) backwash of cellulose acetate hyperfiltration membranes, J. Membr. Sci. 8 (1981) 173–192.

[37] N. Avraham, C. Dosoretz, R. Semiat, Osmotic backwash process in RO membranes, Desalination 199 (2006) 387–389.

[38] A. Sagiv, N. Avraham, C.G. Dosoretz, R. Semiat, Osmotic backwash mechanism of reverse osmosis membranes, J. Membr. Sci. 322 (2008) 225–233.

[39] L.A. Hoover, W.A. Phillip, A. Tiraferri, N.Y. Yip, M. Elimelech, Forward with osmosis: emerging applications for greater sustainability, Environ. Sci. Technol. 45 (2011) 9824–9830.

[40] A. Sagiv, R. Semiat, Backwash of RO spiral wound membranes, Desalination 179 (2005) 1–9.

[41] T.-S. Chung, S. Zhang, K.Y. Wang, J. Su, M.M. Ling, Forward osmosis processes: yesterday, today and tomorrow, Desalination 287 (2012) 78–81.

[42] A. Achilli, T.Y. Cath, A.E. Childress, Selection of inorganic-based draw solutions for forward osmosis systems, J. Membr. Sci. 364 (2010) 233–241.

[43] K.S. Bowden, A. Achilli, A.E. Childress, Organic ionic salt draw solutions for osmotic membrane bioreactors, Bioresour. Technol. 122 (2012) 207–216.

[44] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, A novel ammonia–carbon dioxide forward (direct) osmosis desalination process, Desalination 174 (2005) 1–11.

[45] Q. Ge, J. Su, G.L. Amy, T.-S. Chung, Exploration of polyelectrolytes as draw solutes in forward osmosis processes, Water Res. 46 (2012) 1318–1326.

[46] S. Phuntsho, H.K. Shon, S. Hong, S. Lee, S. Vigneswaran, A novel low energy fertilizer driven forward osmosis desalination for direct fertigation: evaluating the performance of fertilizer draw solutions, J. Membr. Sci. 375 (2011) 172–181.

[47] S.K. Yen, F. Mehnas Haja N, M. Su, K.Y. Wang, T.-S. Chung, Study of draw solutes using 2-methylimidazole-based compounds in forward osmosis, J. Membr. Sci. 364 (2010) 242–252.

[48] C. Klaysom, T.Y. Cath, T. Depuydt, I.F.J. Vankelecom, Forward and pressure retarded osmosis: potential solutions for global challenges in energy and water supply, Chem. Soc. Rev. 42 (2013) 6959–6989.

[49] HBC system launches revolutionary 'Green Machine', http://www.htiwater.com/google/hti_search.php?concept=hti2010.

[50] J.R. McCutcheon, M. Elimelech, Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis, J. Membr. Sci. 284 (2006) 237–247.

[51] R.L. McGinnis, N.T. Hancock, M.S. Nowosielski-Slepowron, G.D. McGurgan, Pilot demonstration of the NH3/CO2 forward osmosis desalination process on high salinity brines, Desalination 312 (2013) 67–74.

[52] M. Mulder, Basic principles of membrane technology, 2nd ed. Kluwer Academic Publishers, Dordrecht, The Netherlands, 1997.

[53] R.J. York, R.S. Thiel, E.G. Beaudry, Full scale experience of direct osmosis concentration applied to leachate management, Proceedings of the Seventh International Waste Management and Landfill Symposium, S. Margherita di Pula, Cagliari, Italy, 4–8 October 1999, October 4–8 1999.

[54] R.W. Holloway, A.E. Childress, K.E. Dennett, T.Y. Cath, Forward osmosis for concentration of anaerobic digester centrate, Water Res. 41 (2007) 4005–4014.

[55] Stahlbush Island Farms—turning waste into revenue, http://www.htiwater.com/divisions/industrial_waste/forward_osmosis_systems/lead_story.html2013.

[56] A. Achilli, T.Y. Cath, E.A. Marchand, A.E. Childress, The forward osmosis membrane bioreactor: a low fouling alternative to MBR processes, Desalination 239 (2009) 10–21.

[57] A. Alturki, J. McDonald, S.J. Khan, F.I. Hai, W.E. Price, L.D. Nghiem, Performance of a novel osmotic membrane bioreactor (OMBR) system: flux stability and removal of trace organics, Bioresour. Technol. 113 (2012) 201–206.

[58] J. Zhang, W.L.C. Loong, S. Chou, C. Tang, R. Wang, A.G. Fane, Membrane biofouling and scaling in forward osmosis membrane bioreactor, J. Membr. Sci. 403–404 (2012) 8–14.

[59] H. Zhang, Y. Ma, T. Jiang, G. Zhang, F. Yang, Influence of activated sludge properties on flux behavior in osmosis membrane bioreactor (OMBR), J. Membr. Sci. 390–391 (2012) 270–276.

[60] E.R. Cornelissen, D. Harmsen, E. Beerendonk, J.-J. Qin, H. Oo, K.F. de Korte, J. Kappelhof, The innovative osmotic membrane bioreactor (OMBR) for reuse of wastewater, Water Sci. Technol. 63 (2011) 1157–1565.

[61] E.R. Cornelissen, D. Harmsen, K.F. de Korte, C.J. Ruiken, J.-J. Qin, H. Oo, L.P. Wessels, Membrane fouling and process performance of forward osmosis membranes on activated sludge, J. Membr. Sci. 319 (2008) 158–168.

[62] D. Xiao, C.Y. Tang, J. Zhang, W.C.L. Lay, R. Wang, A.G. Fane, Modeling salt accumulation in osmotic membrane bioreactors: implications for FO membrane selection and system operation, J. Membr. Sci. 366 (2011) 314–324.

[63] J.-J. Qin, K. Kekre, H. Oo, G. Tao, W.C.L. Lay, C. Lew, E.R. Cornelissen, C.J. Ruiken, Preliminary study of osmotic membrane bioreactor: effects of draw solution on water flux and air scouring on fouling, Water Sci. Technol. 61 (2010) 927–936.

[64] R. Valladares Linares, V. Yangali-Quintanilla, Z. Li, G. Amy, Rejection of micropollutants by clean and fouled forward osmosis membrane, Water Res. 45 (2011) 6737–6744.

[65] W. Yap, J. Zhang, W.C.L. Lay, B. Cao, A.G. Fane, Y. Liu, State of the art osmotic membrane bioreactors for water reclamation, Bioresour. Technol. 122 (2012) 217–222.

[66] W.C.L. Lay, Q. Zhang, J. Zhang, D. McDougald, C. Tang, R. Wang, Y. Liu, A.G. Fane, Study of integration of forward osmosis and biological process: membrane performance under elevated salt environment, Desalination 283 (2011) 123–130.

[67] A.S. Wait, Towards potable reuse: assessment of the first filot-scale hybrid osmotic membrane bioreactor and denitrification system, Colorado School of Mines, Golden, CO, 2012.

[68] T.Y. Cath, R.W. Holloway, J.R. Herron, K. Lampi, M.S. Pravin, Water reuse system and method, United States patent application 61/751,195, 2013.

[69] R.W. Holloway, A. Wait, T.Y. Cath, J. Herron, K. Lampi, UFO MBR-A novel potable reuse and nutrient recovery system, 23rd Annual North American Membrane Society Conference, Boise, ID, June (8–12) (2013).

[70] K.B. Petrotos, H.N. Lazarides, Osmotic concentration of liquid foods, J. Food Eng. 49 (2001) 201–206.

[71] B. Jiao, A. Cassano, E. Drioli, Recent advances on membrane processes for the concentration of fruit juices: a review, J. Food Eng. 63 (2004) 303–324.

[72] K. Popper, W.M. Camirand, F. Nury, W.L. Stanley, Dialyzer concentrates beverages, J. Food Eng. 38 (1966) 102–104.

[73] N.T. Hancock, T.Y. Cath, Solute coupled diffusion in osmotically driven membrane processes, Environ. Sci. Technol. 43 (2009) 6769–6775.

[74] N.T. Hancock, W.A. Phillip, M. Elimelech, T.Y. Cath, Bidirectional permeation of electrolytes in osmotically driven membrane processes, Environ. Sci. Technol. 45 (2011) 10642–10651.

[75] E.G. Beaudry, K.A. Lampi, Membrane technology for direct osmosis concentration of fruit juices, Food Technol. 44 (1990) 121.

[76] R.E. Wrolstad, M.R. McDaniel, R.W. Durst, N. Micheals, K.A. Lampi, E.G. Beaudry, Composition and sensory characterization of red raspberry juice concentrated by direct-osmosis or evaporation, J. Food Sci. 58 (1993) 633–637.

[77] K.B. Petrotos, P.C. Quantick, H. Petropakis, Direct osmotic concentration of tomato juice in tubular membrane–module configuration. II. The effect of using clarified tomato juice on the process performance, J. Membr. Sci. 160 (1999) 171–177.

[78] K.B. Petrotos, P. Quantick, H. Petropakis, A study of the direct osmotic concentration of tomato juice in tubular membrane–module configuration. I. The effect of certain basic process parameters on the process performance, J. Membr. Sci. 150 (1998) 99–110.

[79] E.M. Garcia-Castello, J.R. McCutcheon, Dewatering press liquor derived from orange production by forward osmosis, J. Membr. Sci. 372 (2011) 97–101.

[80] G.T. Gray, J.R. McCutcheon, M. Elimelech, Internal concentration polarization in forward osmosis: role of membrane orientation, Desalination 197 (2006) 1–8.

[81] C.Y. Tang, Q. She, W.C.L. Lay, R. Wang, A.G. Fane, Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration, J. Membr. Sci. 354 (2010) 123–133.

[82] S. Zhang, K.Y. Wang, T.-S. Chung, H. Chen, Y.C. Jean, G. Amy, Well-constructed cellulose acetate membranes for forward osmosis: minimized internal concentration polarization with an ultra-thin selective layer, J. Membr. Sci. 360 (2010) 522–535.

[83] K.Y. Wang, R.C. Ong, T.-S. Chung, Double-skinned forward osmosis membranes for reducing internal concentration polarization within the porous sublayer, Ind. Eng. Chem. Res. 49 (2010) 4824–4831.

[84] S. Zhao, L. Zou, Relating solution physicochemical properties to internal concentration polarization in forward osmosis, J. Membr. Sci. 379 (2011) 459–467.

[85] X. Song, Z. Liu, D.D. Sun, Nano gives the answer: breaking the bottleneck of internal concentration polarization with a nanofiber composite forward osmosis membrane for a high water production rate, Adv. Mater. 23 (2011) 3256–3260.

[86] R. Wang, L. Shi, C.Y. Tang, S. Chou, C. Qiu, A.G. Fane, Characterization of novel forward osmosis hollow fiber membranes, J. Membr. Sci. 355 (2010) 158–167.

[87] C. Qiu, L. Setiawan, R. Wang, C.Y. Tang, A.G. Fane, High performance flat sheet forward osmosis membrane with an NF-like selective layer on a woven fabric embedded substrate, Desalination 287 (2012) 266–270.

[88] B.D. Coday, D.M. Heil, P. Xu, T.Y. Cath, Effects of transmembrane hydraulic pressure on performance of forward osmosis membranes, Environ. Sci. Technol. 47 (2013) 2386–2393.

[89] L. Setiawan, R. Wang, K. Li, A.G. Fane, Fabrication and characterization of forward osmosis hollow fiber membranes with antifouling NF-like selective layer, J. Membr. Sci. 394–395 (2012) 80–88.

[90] A. Tiraferri, Y. Kang, E.P. Giannelis, M. Elimelech, Superhydrophilic thin-film composite forward osmosis membranes for organic fouling control: fouling behavior and antifouling mechanisms, Environ. Sci. Technol. 46 (2012) 11135–11144.

[91] W. Fang, R. Wang, S. Chou, L. Setiawan, A.G. Fane, Composite forward osmosis hollow fiber membranes: integration of RO- and NF-like selective layers to enhance membrane properties of anti-scaling and anti-internal concentration polarization, J. Membr. Sci. 394–395 (2012) 140–150.

[92] G. Li, X.-M. Li, T. He, B. Jiang, C. Gao, Cellulose triacetate forward osmosis membranes: preparation and characterization, Desalin. Water Treat. 51 (2013) 2656–2665.

[93] M. Amini, M. Jahanshahi, A. Rahimpour, Synthesis of novel thin film nanocomposite (TFN) forward osmosis membranes using functionalized multi-walled carbon nanotubes, J. Membr. Sci. 435 (2013) 233–241.

[94] X. Li, K.Y. Wang, B. Helmer, T.-S. Chung, Thin-film composite membranes and formation mechanism of thin-film layers on hydrophilic cellulose acetate propionate substrates for forward osmosis processes, Ind. Eng. Chem. Res. 51 (2012) 10039–10050.

[95] T.P.N. Nguyen, E.-T. Yun, I.-C. Kim, Y.-N. Kwon, Preparation of cellulose triacetate/cellulose acetate (CTA/CA)-based membranes for forward osmosis, J. Membr. Sci. 433 (2013) 49–59.

[96] G. Han, T.-S. Chung, M. Toriida, S. Tamai, Thin-film composite forward osmosis membranes with novel hydrophilic supports for desalination, J. Membr. Sci. 423–424 (2012) 543–555.

[97] R.A. Neff, Solvent extractor, United States patent 3130156, 1964.

[98] G.W. Batchelder, Process for the demineralization of water, United States patent 3171799, 1965.

[99] D.N. Glew, Process for liquid recovery and solution concentration, United States patent 3216930, 1965.

[100] B.S. Frank, Desalination of Sea Water, United States patent 3670897, 1972.

[101] R.E. Kravath, J.A. Davis, Desalination of sea water by direct osmosis, Desalination 16 (1975) 151–155.

[102] J.O. Kessler, C.D. Moody, Drinking water from sea water by forward osmosis, Desalination 18 (1976) 297–306.

[103] K. Stache, Apparatus for transforming sea water, brackish water, polluted water or the like into a nutrious drink by means of osmosis, United States patent 4879030 A, 1989.

[104] J. Yaeli, Method and apparatus for processing liquid solutions of suspensions particularly useful in the desalination of saline water, United States patent 5098575 A, 1992.

[105] S. Loeb, L. Titelman, E. Korngold, J. Freiman, Effect of porous support fabric on osmosis through a Loeb–Sourirajan type asymmetric membrane, J. Membr. Sci. 129 (1997) 243–249.

[106] R.L. McGinnis, Osmotic desalination process, United States patent 8002989 B2, 2011.

[107] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, Desalination by ammonia–carbon dioxide forward osmosis: influence of draw and feed solution concentrations on process performance, J. Membr. Sci. 278 (2006) 114–123.

[108] R.L. McGinnis, M. Elimelech, Energy requirements of ammonia-carbon dioxide forward osmosis desalination, Desalination 207 (2007) 370–382.

[109] S. Adam, J. Oppenheimer, L. Liu, M. Kumar, Dewatering reverse osmosis concentrate from water reuse applications using forward osmosis, WateReuse Foundation Research Report, 2007, (Report number 05-009-1).

[110] P. McCormick, J. Pellegrino, F. Mantovani, G. Sarti, Water, salt, and ethanol diffusion through membranes for water recovery by forward (direct) osmosis processes, J. Membr. Sci. 325 (2008) 467–478.

[111] M.M. Ling, K.Y. Wang, T.-S. Chung, Highly water-soluble magnetic nanoparticles as novel draw solutes in forward osmosis for water reuse, Ind. Eng. Chem. Res. 49 (2010) 5869–5876.

[112] Q. Ge, J. Su, T.-S. Chung, G. Amy, Hydrophilic superparamagnetic nanoparticles: synthesis, characterization, and performance in forward osmosis processes, Ind. Eng. Chem. Res. 50 (2010) 382–388.

[113] D. Li, X. Zhang, J. Yao, G.P. Simon, H. Wang, Stimuli-responsive polymer hydrogels as a new class of draw agent for forward osmosis desalination, Chem. Commun. 47 (2011) 1710–1712.

[114] L. Liu, Dewatering reverse osmosis concentrate from water reuse applications using direct osmosis, Proceedings of the 2007 AWWA Membrane Technology Conference and Exposition, Tampa, FL, March 18–21, 2007.

[115] M.M. Ling, T.-S. Chung, Desalination process using super hydrophilic nanoparticles via forward osmosis integrated with ultrafiltration regeneration, Desalination 278 (2011) 194–202.

[116] S. Iyer, Systems and methods for forward osmosis fluid purification using cloud point extraction, United States patent 8021553, 2011.

[117] J. Su, T.-S. Chung, B.J. Helmer, J.S. de Wit, Enhanced double-skinned FO membranes with inner dense layer for wastewater treatment and macro-molecule recycle using Sucrose as draw solute, J. Membr. Sci. 396 (2012) 92–100.

[118] M. Noh, Y. Mok, S. Lee, H. Kim, S.H. Lee, G.-w. Jin, J.-H. Seo, H. Koo, T.H. Park, Y. Lee, Novel lower critical solution temperature phase transition materials effectively control osmosis by mild temperature changes, Chem. Commun. 48 (2012) 3845–3847.

[119] J.S. Yong, W.A. Phillip, M. Elimelech, Coupled reverse draw solute permeation and water flux in forward osmosis with neutral draw solutes, J. Membr. Sci. 392–393 (2012) 9–17.

[120] G. Carmignani, S. Sitkiewitz, J.W. Webley, Recovery of of retrograde soluble solute for forward osmosis water treatment, United States patent application 13/454,062, 2012.

[121] M.L. Stone, A.D. Wilson, M.K. Harrup, F.F. Stewart, An initial study of hexavalent phosphazene salts as draw solutes in forward osmosis, Desalination 312 (2013) 130–136.