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A hybrid dead-end/cross-flow forward osmosis system for evaluating osmotic flux performance at high recovery of produced water

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HIGHLIGHTS

- A new method for testing forward osmosis at high recovery is presented.
- Approach uses dead-end for the feed solution and a crossflow for the draw solution.
- Allows testing at high recovery using membrane coupons rather than elements.
- Up to 94% recovery of produced water was achievable using this system.
- Other dewatering and concentration processes can be tested with this system.

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ABSTRACT

Forward osmosis (FO) has recently been considered as a means of treating or concentrating produced water because of its low fouling propensity at high recoveries. However, while numerous studies have been published on produced water treatment with FO, many benchtop studies use "coupon" type membrane systems that can only operate at limited recovery because of large holdup volumes and small membrane areas. Newly available commercial elements could be used, but working with such dirty waters would be costly as elements would need regular replacement. In this work, we propose a new method for testing the efficacy of forward osmosis that enables high water recovery using coupon based testing systems. Our hybrid dead-end/cross-flow filtration cell operates in a dead-end mode on the feed side and a cross-flow mode on the draw side, maximizing the recovery of the feed while minimizing dilution of the draw. We demonstrate the value of this type of testing apparatus using an unprocessed produced water provided by Chevron Corporation. This water, which contains small quantities of oil and approximately 7500 ppm total dissolved solids (TDS), could be concentrated by up to 20 fold using this approach.

1. Introduction

With the increased demand of petroleum based products, there has been a substantial investment in expanding the hydrocarbon production infrastructure. In the past decade, unconventional production techniques such as fracking and horizontal drilling, have become commonplace as we extract oil and gas from shale formations around the United States [1]. These techniques require the use of large quantities of water along with chemical additives [2]. In fracking, 50–70% of the injected water typically comes back up as flow-back water. In general, these, and other type of water recovered during the production of oil and gas, are known as produced water [3]. Different approaches have been considered for managing produced water. Large evaporation ponds [4], direct well injection, media filtration, adsorption, oxidation, chemical treatment [5], reverse osmosis [6,7], forward osmosis [8–12], membrane distillation [13] etc. are a few examples. Among these, forward osmosis is a relative newcomer. It has been advertised as being a technology with a low fouling propensity [14,15] and the capability of handling high total dissolved solids (TDS) water sources in comparison to other technologies [13,16,17].

The academic community has long been challenged to demonstrate the efficacy of forward osmosis, especially in its ability to recover large percentages of water from feed solutions. Demonstrating high recovery requires substantial membrane area with membranes that exhibit high flux. Only recently have membranes been available to academics that exhibit high flux, either through making such membranes or by purchasing them from a company that manufactures them. The difficulty in making membranes or obtaining enough membrane has long necessitated the conservation of membrane material and has resulted in the preferred use of small coupons in benchtop test rigs. These membrane areas (sometimes reported as being below 20 cm^2) are not large enough

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Nomenclature

J_w	Water flux (L m^{-2} h^{-1})
J_s	Salt Flux (gm m^{-2} h^{-1})
ρ	Density of solution (Kg m^{-3})
C_{Fb}	Bulk feed concentration (mol L^{-1})
C_{Fm}	Interfacial concentration between the active and feed side boundary layer (mol L^{-1})
C_i	Interfacial concentration between the active and support layer (mol L^{-1})
C_{Dm}	Interfacial concentration between the support and draw side boundary layer (mol L^{-1})
C_{Db}	Bulk draw concentration (mol L^{-1})
A_m	Membrane area (m^2)
D_{Fb}	Feed side diffusion coefficient of salt (m^2 s^{-1})
D_{Db}	Draw side diffusion coefficient of salt (m^2 s^{-1})
Ds	Salt diffusion coefficient inside the support layer (m^2 s^{-1})
k_{mtf}	Feed side mass transfer coefficient (m s^{-1})
k_{mtd}	Draw side mass transfer coefficient (m s^{-1})
t_s	thickness of support layer of the membrane (m)
B	Salt permeability (L m^{-2} h^{-1})
S	Structural parameter (m)
τ	Membrane support layer tortuosity (dimensionless)
A	Pure water permeance (L m^{-2} h^{-1} bar^{-1})
R	Ideal gas constant (L atm mol^{-1} K^{-1})
δ_{tf}	Feed side mass transfer boundary layer thickness (m)
δ_{td}	Draw side mass transfer boundary layer thickness (m)
φ_m	Pitzer osmotic coefficient (dimensionless)
z_+	Charge on cation (dimensionless)
z_-	Charge on anion (dimensionless)
f^{φ}	Function of ionic strength (temperature and solvent dependent) expressing the effect of the long-range electrostatic forces (dimensionless)
m	Molality (mol Kg^{-1})
υ_+	Number of cations (dimensionless)
υ_-	Number of anions (dimensionless)
B^{φ}_{MX}	Pairwise ion-interaction parameter of Pitzer's equation for the Gibbs energy (Kg mol^{-1})
C^{φ}_{MX}	Triplet ion-interaction parameter of Pitzer's equation for the Gibbs energy (Kg mol^{-1})
π	Osmotic pressure (atm)
T	Temperature (°C)
M_w	Molecular weight of water (Kg mol^{-1})
υ_{water}	Molar volume of pure water (m^3 mol^{-1})
π_i	Osmotic pressure at the selective and support layer interface (atm)
π_{Fm}	Osmotic pressure at the feed side boundary layer and selective layer interface (atm)

to generate high recoveries in short amount of time with conventional crossflow systems [18]. Recovery is also limited by the amount of the feed solution required to run the system. The pumps must be primed, the heat exchangers must be filled, and the tubes must all contain water free of air, meaning that hold up volumes may approach50% of the total volume of feed solution. Holdup volumes could be reduced by reducing tubing size or heat exchanger area but these changes will increase pressure drop in the system and may limit temperature control capability, respectively.

Many of these problems could be solved by simply testing with full-scale modules. A number of them are now out on the market and have been tested and described in the literature in rare instances [8,19,20]. However, the standard operating procedures for these modules has not yet been established across the spectrum of possible feed and draw solutions. Furthermore, modules are expensive to purchase and therefore researchers are hesitant to use them with high fouling feeds, such as produced waters. If the module fouls, they may be cleaned, but they will likely never work as they did when they were first installed. Coupon testing allows for membranes to simply be disposed of after use, which is especially valuable when conducting tests with high fouling solutions.

However, without the capability of testing FO performance of coupons at high recovery for these fouling solutions, we are forced to *simulate* high recovery by starting with a higher TDS feed solution. This is possible if these solutions can be synthesized. For example FO performance for a seawater feed at 50% recovery can be simulated by using a feed solution containing ~74,000 ppm TDS. However, if a non-synthetic feed that is difficult to replicate is provided, the only way to concentrate it for testing is to evaporate the water to the desired "recovery" level (i.e. evaporating half of the water to simulate 50% recovery). Heating a solution, especially if it contains volatiles or salts with low or retrograde solubility, can change the chemistry substantially during this "pre-concentration" process. Furthermore, if one wishes to study fouling phenomenon as a function of recovery, this approach effectively bypasses the early part of the process. Some have attempted to get around this with coupon test systems by simply running experiments for extended periods of time [8]. However, this can occupy conventional benchtop crossflow systems for days and make tubing and instrumentation on the feed side of the system susceptible to damage from long term exposure to high salinity or solutions that cause fouling. While mathematical modeling of FO could be used to calculate recovery, most of the modeling efforts in the literature have been focused on finding membrane properties and osmotic performance [18–26]. Though these models on membrane performance may be used to predict recovery, many of them are prone to inaccuracy due to assumptions which are only applicable for dilute solutions [27].

Dead-end cell based laboratory testing is commonly used in ultrafiltration and microfiltration applications and sometimes to characterize nanofiltration and reverse osmosis membranes [28]. To the best of our knowledge, dead-end cells have never been used in FO, except for u-tube osmometers, which could be construed as being a dead-end FO system [29]. Here, we propose a new hybrid dead-end/cross-flow cell bench top FO system to study flux performance of any solution at high recovery. A hybrid dead-end/cross-flow FO system is unique as it provides relatively consistent driving force from the draw solution which flows through the cell in a crossflow nature and can be made in relatively large volumes (liters). The feed is kept in a stirred chamber on the opposite side of the membrane, allowing small volumes (half a liter or less) to be rapidly concentrated. Such a method has value in measuring possible recovery levels for various water sources using FO in a reasonable amount of time with coupon based membranes. Such a system also reduces risks to component damage due to scaling and fouling by limiting the feed solution to a dead-end chamber with few additional components. We demonstrate the value of this system using oil field produced water provided by Chevron Corporation. We used our data to develop a mathematical model to understand and predict water flux, feed, and draw concentration changes over a range of recoveries for the hybrid system.

2. Materials and methods

2.1. Materials

Commercial asymmetric cellulose triacetate (CTA) and thin film composite (TFC) forward osmosis (FO) membrane coupons were used for this study. Forward osmosis membranes were provided by HTI (Hydration Technology Innovations, Albany, OR). The membranes were stored in DI water at 5 °C. An 8 cm × 3 cm size membrane coupon was used for each experiment. Sodium chloride was purchased from

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