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Gas field produced/process water treatment using forward osmosis hollow fiber membrane: Membrane fouling and chemical cleaning

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HIGHLIGHTS

- Gas field produced/process water (PPW) was treated using FO hollow fiber membranes.
- The efficiencies of various cleaning agents were evaluated.
- The water flux decreased by 24.8% after fouling, and SDS cleaning recovers the flux.
- The FO membrane can reduce PPW volume by 50% at a water flux of 15.6 $L \cdot m^{-2} \cdot h^{-1}$.
- This study demonstrates the great potential of FO technology for PPW treatment.

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ABSTRACT

This study investigated the fouling behavior and chemical cleaning of forward osmosis (FO) membranes for treating produced/process water (PPW) from a real gas field using thin-film composite FO hollow fiber membranes. Experiments revealed that membrane fouling occurred during the PPW treatment, which hindered the water and solute transport through the membrane. The water permeability and FO reference water flux of the membrane decreased by 22.9% and 24.8%, respectively, after fouling. Membrane surface characterization was carried out, and the results indicated the deposition and entrapment of organic species on the membrane after the PPW treatment. The efficiencies of various cleaning agents, including sodium dodecyl sulfate (SDS), ethylenediaminetetraacetic (EDTA) and NaOH, were evaluated. It was found that cleaning with SDS for 15 min is the most effective method for restoring water flux, and very stable FO performance can be obtained during batch treatment of PPW. The FO membrane can reduce the PPW volume by 50% at a relatively high average water flux of 15.6 $L \cdot m^{-2} \cdot h^{-1}$ in the active layer facing feed solution orientation using 1 M NaCl as draw solution (equivalent to the draw solution available in the field). This study demonstrates the great potential of FO technology for produced/process water treatment.

1. Introduction

Oil and natural gas play a significant role in modern civilization [1]. It is anticipated that by 2040 the global energy demand will increase by 37%, and oil, coal, and natural gas will still be major energy sources [2]. However, large volumes of wastewater, called "produced water" (PW), estimated to be over 437 million barrels per day, are generated in the petroleum industry with oil and gas exploration and production. The amount would likely continue to rise due to increase in energy demand [3,4]. The PW characteristics vary significantly depending on the source, operational conditions and chemical additives used in the process facilities. Generally, PW contains dispersed and dissolved organic compounds (e.g. oil and grease, aliphatic and aromatic hydrocarbons, fatty acids), dissolved mineral salts, and production chemicals (e.g. biocides, scale and corrosion inhibitors), etc. [5,6].

The management of PW has become a key issue for the sustainable development of oil and gas fields [7]. Although many attempts have been made to explore innovative methods for PW recycle and/or reuse, the injection of PW into disposal wells still remains the primary management method [8,9]. However, there are several limitations of current PW injection operation. For example, the availability of injection well with large capacity is a restrictive factor for ongoing oil and gas exploration and production [10]. Also, the expense for the development and maintenance of the disposal well is relative high. An estimated capital cost of US$400,000–3,000,000 is required for installing a well and the reinjection costs US$0.40–1.75 per barrel [11]. Furthermore, there

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are increasing environmental concerns about the long-term adverse effects of the underground injection. Therefore, reducing the volumes of PW for disposal is considered to be crucial to make the deep-well injection a cost-effective option and to minimize its potential environmental impacts. A specific target of 50% volume reduction was set in Qatar to ensure the long term sustainability development [12].

Forward osmosis (FO) is an emerging membrane technology for water treatment driven by osmotic pressure gradient across the membrane [13]. Compared to pressure driven processes, FO exhibits a number of advantages such as low capital and operational costs as it involves atmospheric pressure operation, has potentially low membrane fouling propensity, less stringent pretreatment requirements and high rejection to salts and many contaminants [14–16]. With the rapid development of flat sheet and hollow fiber FO membranes in the last five years [17–20], the FO process has become available for a wide range of potential applications, among those, its application for PW treatment has gained increasing momentum recently. Several studies have reported the treatment of drilling and fracturing flowback wastewater from shale gas and coal bed methane exploration using commercial flat sheet cellulose triacetate (CTA) and thin film composite (TFC) FO membranes from Hydration Technology Innovations (HTI) [10,21–23]. However, a recent study showed that FO membrane fouling would be exacerbated due to the presence of feed spacers in the spiral wound modules when treating the complex feed streams, which would increase the energy demand of the FO system [10]. In contrast, the hollow fiber membrane would be a promising alternative since no spacer is needed in the module [24]. Therefore, the feasibility of the FO process for treating PW from conventional gas fields and the fouling behavior of the TFC FO hollow fiber membrane in this application warrants to be further investigated since the feed constituents vary significantly depending on the different feed sources.

Similar to other membrane processes, fouling inevitably occurs in the FO process. Individual or combined organic fouling, inorganic fouling or scaling, biofouling as well as colloidal fouling negatively affect membrane performance [25–29]. The foulants can deposit on the membrane surface or be trapped in membrane pores or microstructure. The former (surface fouling) would apply to FO in the active layer facing feed solution (AL-FS) orientation and the latter in the active layer facing draw solution (AL-DS) orientation. Once a membrane is fouled, appropriate periodical cleaning is mandatory to maintain the long-term stability of its performance. A variety of chemical cleaning agents including alkaline solutions, metal chelating agents and surfactants have been used to clean nanofiltration (NF) and reverse osmosis (RO) membranes fouled by organics [30–32]. For example, the cleaning efficiencies of NaOH, ethylenediaminetetraacetate (EDTA) and sodium dodecyl sulfate (SDS) have been examined for NF/RO membranes fouled by the PW from a petroleum refinery, and the results showed that SDS was the most effective cleaning agent for recovering membrane flux [33]. So far, only a handful of studies can be found in the literatures regarding the cleaning of PW-fouled FO membranes [10,21,34]. Hickenbottom et al. studied the cleaning efficiency of water flushing and osmotic backwash on the CTA FO membrane after treating the drilling mud and fracturing wastewater. Both methods removed the deposited solid and restored the water flux [21]. In addition, Coday et al. investigated the efficiency of chemically enhanced osmotic backwashing on the CTA and TFC membranes using cleaning agents KL7330 and EDTA. The EDTA solution with high pH was found to be more effective for restoring flux due to its ability to address the divalent-organic compound complexations and scaling at the membrane surface [10]. However, the concentrations of the cleaning agents used in their study are relative high (11,000 mg/L), which might not be cost-effective for long-term operation. Meanwhile, the cleaning protocol was not optimized. It is suggested a systematic comparison of the cleaning efficiencies of various chemical cleaning agents is needed in order to provide an optimized cleaning protocol for potential long-term operation of FO processes for PW treatment.

The objectives of this study are (1) to evaluate the fouling of thin-film composite (TFC) FO hollow fiber membranes used to treat real gas field produced/process water (PPW) for disposal, and (2) to systematically study chemical cleaning methods for water flux recovery of the PPW-fouled FO membranes. It should be noted that large quantities of process water are typically generated during gas treatment/conditioning and thus, this research is focusing on PPW rather than PW. Specifically, the fouling behavior of the membrane during PPW treatment was first monitored, followed by characterization of the virgin and fouled membrane surface using a series of characterization tools. Finally, the cleaning efficiencies of several chemical cleaning agents including SDS, EDTA and NaOH were systematically investigated to identify the most effective cleaning protocol. This paper complements our previous study that assessed the feasibility of FO for PPW volume reduction using an available thermal desalination brine as draw solute [12].

2. Experimental

2.1. Constituents of gas field PPW

The PPW used in this study is a mixture of gas field produced water extracted from the offshore gas well and process water from onshore operations with an approximate blending ratio of 1:5 in Qatar [12]. The concentrations of the major constituents in the water are summarized in Table 1. In brief, the PPW contains total organic carbon (TOC) of 132 mg/L and total dissolved solids (TDS) of 1526 mg/L. Although the TOC content is lower than the values reported in some literature [10,23,34], the fouling behavior of the FO membrane is still worthy to be investigated during the treatment of this conventional gas field PPW, since the quality of PW is temporally and spatially dependent. The particle size and zeta potential of the foulants presented in the PPW were determined using a Zeta Sizer Nano Series (Malvern Instruments Ltd). The average particle size of the foulants was 0.24 μm and the effective zeta potential of the foulants was −8.28 mV (pH = 8.0), indicating the foulants are negatively charged.

2.2. FO hollow fiber membrane and its intrinsic separation properties

The TFC FO hollow fiber membrane was developed in our previous work [13], and was fabricated by forming an RO-like skin layer on the lumen side of a polyethersulfone (PES) hollow fiber substrate using interfacial polymerization [18]. Membrane modules used for the PPW treatment were made by sealing 15 fibers in a teflon tube with a diameter of 0.95 cm and an effective length of 24 cm.

The intrinsic separation properties of the membrane were evaluated in the RO mode using a bench-scale cross-flow filtration system. The water permeability and salt rejection were tested with deionized (DI) water and 500 ppm NaCl as feed under 1 bar, respectively. The membrane was stabilized at 1 bar with a flow velocity of 0.44 m/s in the lumen side for 1 h prior to each measurement. The water permeability coefficient (A value) was calculated using Eq. (1), the salt rejection (R_s) was calculated based on the conductivity measurement of

Table 1
Water quality analysis of the gas field PPW [12].

Parameter	Units	Concentration	Parameter	Units	Concentration
Total dissolved solids (TDS)	mg/L	1526	Sodium	mg/L	329
Total organic carbon (TOC)	mg/L	132	Potassium	mg/L	4.7
Inorganic carbon	mg/L	33	Magnesium	mg/L	8.7
Conductivity	μs/cm	1810	Calcium	mg/L	38
Alkalinity	mg/L	223	Bromide	mg/L	5.6
Turbidity	NTU	32	Chloride	mg/L	286
pH		8.0	Sulfate	mg/L	349
			Ammonium	mg/L	8.5