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Surfactant effects on water recovery from produced water via direct-contact membrane distillation

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ABSTRACT

Increasing demand for oil and gas leads to the generation of substantial amount of produced water, bringing about deleterious impacts on the environment. Direct-contact membrane distillation (DCMD) could be a possible option for dewatering oil-in-water (O/W) emulsions because of many benefits brought by the DCMD process. However, these low surface tension solutions pose some difficult issues such as membrane fouling and pore wetting. The mechanisms involved are not fully understood due to the lack of study of the interaction between the emulsions and the membrane surface in the DCMD domain. To address the challenges, this study aims at developing a fundamental understanding of the relationship between surfactant-stabilized O/W emulsions and polyvinylidene fluoride (PVDF) membrane surface in DCMD operations. Effects of surfactant types (Span 20, Tween 20, and sodium dodecyl sulfate), oil concentration, and oil types (petroleum and vacuum pump oil) were systematically studied to better understand the fouling and wetting mechanisms involved. The results reveal that surfactant concentration and hydrophobicity had an influence on the membrane fouling and wetting behaviors. Surfactants with a lower hydrophilic-lipophilic balance (HLB) value could make the PVDF membrane surface less hydrophobic and cause less severe fouling by restraining the adsorption of oil droplets on the membrane surface. These findings suggest that membrane surface modification is required to achieve anti-fouling and anti-wetting properties to make DCMD an energy-efficient and effective technology for treating produced water.

1. Introduction

Produced water is wastewater co-produced in a producing well along with the oil and/or gas phase(s) [1]. It is commonly known as the largest waste stream from the oil and gas refineries as it contains a variety of pollutants, namely: (i) dissolved and dispersed oils and greases; (ii) production solids; (iii) dissolved gases; (iv) soluble and insoluble organics; (v) production chemicals; (vi) inorganics and (vii) dissolved formation minerals [2]. These constituents of produced water are highly dependent on the geological locations as well as formation processes. As the demand for oil and gas is expected to rise even further in the next couple of decades, the generation of produced water is showing no signs of slowing down [3]. The oil and gas industries are thus facing a grand challenge – huge quantities of wastewater. Therefore, it is of paramount importance to develop effective management strategies for produced water.

Generally, several options are available for produced water management: (i) injection of the produced water into the same formation process or another suitable formation; (ii) discharge back into the environment after treatment; (iii) reuse in oil and gas field operations after treatment; and (iv) beneficial reuse for consumption or agricultural purposes after treatment [4]. Currently, industries are placing more emphasis on the treatment and reuse of produced water mainly due to the stringent environmental regulations, increased pressure on water resources, and the rising cost of wastewater discharge. However, the conventional treatment methods often have several intrinsic disadvantages, including low removal efficiencies of oil droplets with diameters less than 20 μm, low water recovery, high operation costs as well as the possibility of corrosion and recontamination [5]. The rapid development of membrane technologies offers attractive solutions to

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produced water treatment. Over the past few decades, membrane processes such as microfiltration (MF) [6–8], ultrafiltration (UF) [9–11], nanofiltration (NF) [12–14], reverse osmosis (RO) [15,16], and forward osmosis (FO) [17] have been applied for produced water treatment. These membrane technologies have been preferred over the conventional methods due to their high oil removal efficiencies, small footprint, and easy operation and maintenance. While some of these processes can be combined to achieve high removal efficiencies, high operating costs remain a major concern. Another grand challenge is membrane fouling caused by oil droplets and soluble organics.

Membrane distillation (MD), which is an emerging technology that can utilize low-grade waste heat to generate high quality water, offers a possible solution. In MD, water vapor from the higher temperature feed side is transported through a porous hydrophobic membrane and condensed on the lower temperature permeate side, driven by the vapor pressure difference across the membrane caused by the temperature gradient [18]. MD is favored for the dewatering of produced water due to its moderate operating conditions, lower operating hydrostatic pressure, theoretically complete removal of non-volatiles and high recovery amongst other benefits [19]. Its main advantage over other membrane processes is its capability for utilizing low-grade waste heat, which is abundant in oil and gas refineries. This could potentially reduce the energy costs for the MD process. Among four different types of configuration, the direct-contact membrane distillation (DCMD) is widely studied due to its simple operation mode [20].

Over the past decade, numerous studies have been conducted on the application of MD for the treatment of oily wastewater and produced water [4,21–25]. The influences of pretreatment, operation conditions, and novel membrane surface modifications have been intensively studied. In most of these works, different pretreatment techniques were used to remove oil before the MD stage. Therefore, the true potential of MD in the treatment of produced water has not been explored. In particular, very limited amount of work has been reported on the influences of surfactants on membrane fouling and pore wetting. In produced water, oil is typically emulsified by the existence of natural or added surfactants, which can significantly reduce the pore liquid entry pressure (LEP) of MD membranes, leading to the penetration of feed water into the permeate stream, consequently resulting in the failure of the MD operation.

This study aims at developing a fundamental understanding of the relationship between surfactant-stabilized O/W emulsions and polyvinylidene fluoride (PVDF) membrane surface in the DCMD process. A PVDF membrane was selected because it is hydrophobic in nature, which is a fundamental requirement for MD operations. Specifically, a series of bench-scale experiments were conducted to investigate on the roles of different types and concentrations of oil and surfactant on the fouling and wetting behaviors of the PVDF membrane. Membrane autopsy was also conducted using Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy (FE-SEM) to confirm the wetting and fouling phenomena in the DCMD process. It is expected that this study can provide guidance for developing new strategies to facilitate DCMD as an energy-efficient and effective technology for treating produced water.

2. Experimental

2.1. Chemicals

Sodium chloride (NaCl, 99.5%), Span 20, Tween 20, and sodium dodecyl sulfate (SDS) were purchased from Merck Millipore. The reagents were used as received. Petroleum and vacuum pump oil (VPO) were purchased from Sigma-Aldrich and used without any treatment. The properties of oils and surfactants used in this study are presented in Table 1 and Table 2, respectively. Milli-Q water was produced by the Millipore Water Purification System.

Table 1
Properties of oils used in this study.

Oil type	Relative density (g ml^{-1})	Boiling point (K)	Flash point (K)	Components
Petroleum	0.79	453–493	334	~18% aromatics
VPO	0.88	662	523	Solvent-refined heavy paraffinic

2.2. Characteristics of PVDF hollow fiber membrane

PVDF hollow fiber membranes were supplied by a commercial manufacturer. The relevant membrane properties were characterized and summarized in Table 3. Lab-scale modules were prepared by sealing 10 pieces of 18 cm long hollow fiber in Teflon tubing. A new membrane module was used for each experiment. The effective membrane area for each module was 87 cm^2.

2.3. Preparation and characterization of surfactant-stabilized O/W emulsions

8 L of synthetic produced water was formulated using predetermined concentrations of oil, surfactant, and NaCl. Oil and surfactant were mixed at 9:1 mass ratio in Milli-Q water to mimic produced water. It also contained 3.5 wt% NaCl to represent the total dissolved solids (TDS). The surfactant-stabilized O/W emulsions were obtained by mixing the solutions using a heavy-duty blender (Waring® Commercial, USA) at a high speed for at least 3 min. The conductivities of the emulsions were measured to be around 50 mS cm^{-1}.

The oil droplet sizes of the emulsions were measured by a Mastersizer (Hydro 2000SM, Malvern Instruments, UK). The zeta potentials of the emulsions were measured by a Zetasizer (Nano ZS, Malvern Instruments, UK).

2.4. DCMD experiment

The DCMD experimental rig used for the experiments has been illustrated in our previous work [28]. The feed solutions were heated and maintained at 333 K and circulated on the shell side of the hollow fiber membranes. The permeate water was cooled and maintained at 293 K and circulated in the lumen side of the hollow fiber membranes in a countercurrent flow to the feed. The feed and permeate volumetric flow rates were maintained at 0.7 L min^{-1} and 0.25 L min^{-1} respectively, corresponding to Reynolds numbers of 1631 and 609 respectively. A higher flow rate was employed on the feed side to mitigate concentration and temperature polarizations [28]. The permeate overflow was collected into a tank. The permeate flux was measured and recorded every minute after the experimental conditions were stabilized (approx. 1 h). Throughout the entire duration of the MD experiments, the tubes and membrane modules were insulated to minimize heat loss.

2.5. Characterization tests

An in-house-made LEP experimental setup was used for the measurement of LEP_w of the pristine PVDF membrane as described in our previous research [29]. The mechanical properties of the membrane were measured by a Zwick Roell BT1-FR0.5TN.D14 Material Testing Machine at a constant elongation velocity of 50 mm min^{-1} under room temperature. The mean pore size and pore size distribution of the membrane were determined by a capillary flow porometer (CFP 1500A, Porous Material, Inc., USA). The membrane porosity was calculated by dividing the volume of pores by the total volume of the membrane as described in our previous research [29].

The presence of surfactants on the inner surfaces of the membranes