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Polyoxadiazole hollow fibers for produced water treatment by direct contact membrane distillation

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ABSTRACT

Treatment of produced water in the petroleum industry has been a challenge worldwide. In this study, we evaluated the use of direct contact membrane distillation (DCMD) for this purpose, removing oil and dissolved elements and supplying clean water from waste. We synthesized fluorinated polyoxadiazole, a highly hydrophobic polymer, to fabricate hollow fiber membranes, which were optimized and tested for simulated produced water and real produced water treatment. The process performance was investigated under different operating parameters, such as feed temperature, feed flow velocity and length of the membrane module for 4 days. The results indicate that by increasing feed temperature and feed flow rate the vapor flux increases. The flux decreased with increasing the length of the module due to the decrease of the driving force along the module. The fouling behavior, which corresponds to flux decline and cleaning efficiency of the membrane, was studied. The performance of the fabricated hollow fiber membranes was demonstrated for the treatment of produced water, complying with the industrial reuse and discharge limits.

1. Introduction

The regular operations of gas and oil industry involve large amount of injected water to facilitate the petroleum recovery. This water is brought to the surface along with hydrocarbons (oil and gas), salt and other solutes, and is commonly known as “produced water”. The composition depends on onsite natural geological information, containing various soluble mineral ions and being often acidic in nature. Fresh water is also used for desalting crude oil, sweetening of gas and other refinery processes. The liquid waste stream produced by the petroleum industry is estimated to be around 250 million barrels per day (water to oil ratio of at least 3:1) [1]. The water reuse or recycling has become mandatory, especially in water stressed countries. Many countries have implemented more stringent regulatory standards for the permitted oil and grease (O&G) limits for discharging produced water, which range from 10 mg/L, according to the China Environmental Ministry, to the maximum limit of 42 mg/L, regulated by United States Environmental Protection Agency (USEPA) [2]. This can be seen as an opportunity for produced water treatment to provide a viable source of water for beneficial use in many applications, for which drinking water quality is not required. New regulations have been promoting the development of environmentally friendly and economical disposal methods [3] to prevent serious environmental damage. As a consequence, physical, chemical and biological methods have been proposed to treat produced water. A single technology can hardly meet the requirements for a clean effluent and two or more treatment systems might be used in series operation [2].

Membrane distillation (MD) was considered in this work as a potential technology for produced water treatment. MD is based on thermal gradient transport of vapor through hydrophobic porous membranes, the driving force being the vapor pressure difference between the two sides of the membrane pore [4]. MD combines the advantages of conventional distillation and membrane technologies: high selectivity for non-volatile compounds, meaning 100% retention of ions, macromolecules, colloids *etc.* It consumes less energy, operates at low temperatures (compared to conventional non-membrane

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processes), is a low hydrostatic pressure process (in comparison to pressure driven membrane process like reverse osmosis (RO)), is compact (for offshore deployment), simple, and is claimed to be less susceptible to fouling than other membrane processes [5-7]. Most of the published MD works focus on seawater desalination. Only few groups have explored it for the treatment of produced water by MD [8–12]. Whether desalination or treatment of produced water/wastewater, the membranes for MD should be highly porous and hydrophobic to prevent the feed solution from entering into the pores (high liquid entry pressure). Commonly used membranes for MD are polytetrafluorethylene (PTFE), polypropylene (PP) and polyvinylidene fluoride (PVDF) with typical pore sizes varying from 0.1 μm to 1 μm [5,9,13–22]. The MD membrane performance can be enhanced by different means, such as incorporation of nanoparticles [23–33], graphene oxide [34] or use of alternative solvents such as triethyl phosphate (TEP) [35] for the membrane manufacture. Few efforts have been dedicated to development of new polymers, tailor-made for the needs of MD [36–37]. Our group has previously reported polyazole-based membranes for water desalination by MD [38–40]. Polyoxadiazole could be an excellent material comparable to ceramic membrane due to its high thermal and oxidative stability and good mechanical strength [41].

In this study, fluorinated polyoxadiazole hollow fiber membranes have been fabricated, characterized and optimized for produced water treatment. Synthetic and real produced water samples were investigated. Various parameters influencing the permeate flux and rejection factors for salts and organic compounds have been investigated in DCMD operation. The performance of polyoxadiazole hollow fiber membranes, as well as their fouling susceptibility, have been investigated in long-term separation/operation stability tests.

2. Materials and methods

2.1. Materials and chemicals

Fluorinated polyoxadiazole (f-POD) was synthesized according to previously reported procedure [40]. *N*-methyl-2-pyrrolidinone (NMP, ≥ 99.5%, Merck) was used as solvent to prepare hollow fiber spinning dope solution. Methanol (HPLC grade, Fischer scientific) and glycerol (≥ 99%, Sigma Aldrich) were used in the process hollow fiber fabrication and long periods of storage. Produced water was supplied by Saudi Aramco, from one of the drilling locations in Saudi Arabia.

2.2. Fiber spinning

The synthesized polyoxadiazole was washed with methanol to remove any moisture and dried in vacuum oven at 80 °C overnight, before using it to prepare dope solution. The dried polymer flakes were added to NMP in small portions to avoid lump formation and stirred at 600 rpm for 24 h at 70 °C, using overhead mechanical stirrer and hot oil bath. The prepared dope solution was loaded into the high-pressure syringe holder of the spinning machine and degassed to remove any air bubbles entrapped within the solution.

A set-up was built to spin hollow fibers from the laboratory-synthesized polymers, with capacity for 20 to 30 g polymer. The dope solution was loaded in a stainless steel syringe and extruded through the spinneret using a high-pressure syringe pump (neMESYS high pressure syringe pumps, Cetoni GmbH). The extruded polymer solution was immersed in a water tank to form the hollow fibers by phase inversion. The bore liquid was pumped through the needle of the spinneret to form the lumen of the hollow fiber, using HPLC dual head gear pump (Lab Alliance ™).

The hollow fibers were washed by replenishing fresh water (purified by RO) for at least 10 h (at room temperature and a few trials at 50 °C) and stored in RO water for three days (exchanging the water every day) to remove any residual solvent. Finally, the hollow fibers were kept in 25:75 (vol%) glycerol/water solution overnight, slowly air dried and stored in dry environment. Before use, the fibers were extensively washed with water to remove the glycerol.

2.3. Membrane characterization

2.3.1. Hollow fiber membrane morphology

The membrane morphology was investigated by field emission scanning electron microscopy (SEM) (FEI Quanta 600 FE or Nova Nano SEM microscopes) at accelerating voltage of 5 kV. The fibers were dried overnight and were carefully fractured in liquid nitrogen for cross sectional SEM analysis. The fibers were sputter coated with Iridium (~ 3 nm-thick, Quorum Q150T ES) to make the polymer surface conductive for surface analysis.

2.3.2. Pore size distribution and membrane liquid entry pressure (LEP)

The membrane pore size distribution was estimated by using Porolux™ 1000 (Porometer.com, Belgium), at the pressure range from 0 up to 34.5 bar and using perfluoroether (Porefil) with a surface tension of 16 dynes cm^{-1} as pore filler. The same analysis supplied the liquid entry point (LEP), which is the minimum pressure required for liquid to pass through the membrane.

2.4. DCMD experimental set-up

The schematic of the experimental setup for cross-flow DCMD is shown in Fig. 1.

All the experiments were carried out in modules containing 3 to 4 hollow fibers, using 6 mm polyethylene tube housings, which were approximately 15 cm long. The fibers were carefully inserted into the polyethylene tube and sealed with epoxy glue (Devcon, 2 components flow mixture, 5 min epoxy, 1500 psi strength). Fig. 2 shows the hollow fiber modules. At the beginning and end of the housing, T-junctions were placed to circulate cold water in the shell side to condense the permeating water vapor. Before measuring the vapor flux, the fibers were completely dried to regain their intrinsic hydrophobicity. The vapor flux (J_V) through the membrane was measured by pumping (peristatic pumps, Cole Parmer) hot feed (produced water) through the lumen of the hollow fiber and cold RO water (countercurrent flow) through the shell side of the module. The change in weight of the permeate reservoir over time (10 min interval) at steady state was recorded, using the data acquisition software on to a computer. Simultaneously temperatures, pressures and flowrates were recorded. The data presented in this work is an average of at least 3 hollow fiber modules prepared from different sections of the total fiber spun.

The salt rejection (*SR*) and permeate vapor flux (*Jv*) were calculated, using the following equations:

$$SR\% = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (1)$$

$$J_V = \frac{m_p}{At} \quad (2)$$

where C_p and C_f are the salt concentration of permeate and feed solutions, respectively, and m_p is the mass of collected permeate, A is the effective membrane area, and t is the running time.

2.5. Produced water analysis

The total organic content was analyzed by Dohrmann Series Apollo 9000 TOC analyzer. Total dissolved solids (TDS) was analyzed, using an OAKTON conductivity/TDS meter.

2.6. Treatment of produced water by DCMD

Real produced water supplied by Saudi Aramco was used as feed