Separation and Purification Technology 126 (2014) 69–81

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Direct contact membrane distillation for treatment of oilfield produced water

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ARTICLE INFO

Article history:
Received 23 October 2013
Received in revised form 6 February 2014
Accepted 8 February 2014
Available online 20 February 2014

Keywords:
Produced water
Polymeric membrane
Membrane distillation
Water quality
Cost analysis

ABSTRACT

Direct contact membrane distillation (DCMD) process was investigated to treat oil produced water. Polymeric membranes were used in this investigation. The tested polymeric membranes included lab made polyvinylidene fluoride (PVDF) membranes produced under different processing conditions and dope compositions and having different characteristics (PVDF1 and PVDF2). In addition, two commercial polypropylene (PP) based membranes (PP1 and PP2) were also tested. The experimentation was carried out under various hydrodynamic and thermal conditions. In all the performed experimentation, the polymeric membranes showed reliable and stable performance. Analysis of the collected permeates indicates that the membrane distillation (MD) process is an interesting solution for the treatment of produced water, with the overall salt rejection factor greater than 99% and total carbon rejection higher than 90%. An economical evaluation was carried out to assess the feasibility of the process. Data from cost analysis indicate that for MD operating at 50 °C and with a recovery of 70%, water cost is 0.72 $\$/m^3$ when the temperature of the produced water fed to the plant is 50 °C and 1.28 $\$/m^3$ if 20 °C is the temperature of the produced water fed to the plant.

1. Introduction

The importance of the oil and gas industry in today's world is well acknowledged. However, similar to many other production activities, these industries produce large quantities of waste and polluted water. The waste water produced by the oil and gas industry is referred as oilfield produced water or simply *produced water*. The source of this water is (i) primarily from water injected into the reservoir to enhance the oil recovery or (ii) it can be the flow back water from hydraulic fracturing activities or (iii) a mixture of both [1,2]. The produced water contains various organic and inorganic fractions including dissolved and dispersed oil compounds, dissolved minerals, production chemical compounds, production solids and dissolved gases [3]. Such waters can cause pollution of surface and ground waters and pose serious environmental threats; therefore many countries have applied different but very stringent environmental rules and regulations on the discharge and disposal of produced water in the environment [4–7]. On the other hand, it is also the matter of the fact that the production of large volumes of produced water is generally associated with the water–stressed countries. Therefore to meet the environmental standards and to reduce the shortage of water, recently a lot of research activities have been focused to treat this type of water [3,8,9,14–16,27–44].

The daily global production of produced water is 250 million barrels which is three times that of the produced oil and this factor goes up with the maturity of the oil fields [3]. Besides the organics, produced water is enriched with different minerals. Its composition depends upon several factors, a summary of the oilfield related parameters and composition can be found in [10,11].

Various physical, chemical and biological methods and their combinations have been used to treat the produced water. The main physical methods comprise the use of different chemicals including activated carbon, organo-clay [27,28], copolymers [29] and zeolite [27] to adsorb carbon, the use of sand filters to remove the metals from the produced water, the use of cyclones [30] to separate water/oil/gas phases by using the centrifugal force, gas

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http://dx.doi.org/10.1016/j.seppur.2014.02.004
1383-5866/

floatation, evaporation [31,32] and dissolved air precipitation [33]. The major tested chemical methods include chemical precipitation to remove suspended and colloidal particles [34–37], chemical oxidation [38], electrochemical processes [39], photocatalytic treatment [40,41] and treatment with ozone [42]. For biological treatment, different aerobic and anaerobic microorganism treatment techniques have been tried [3].

Due to the problems associated with all the above mentioned methods (i.e., high cost, use of hazardous chemicals, large footprint, etc.), the membrane based operations have been declared as the 21st century pretreatment methods for produced water [12]. The membrane based operations tested so far include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Moreover, the combination of membrane based processes has been investigated as a successful tool to treat the produced water in order to meet the quality standards of potable and irrigation water [8,13,14]. However, the performance of the membrane based methods tested so far is limited either at high solute concentration (RO) or due to their inability to remove hydrocarbons and all the suspended and dissolved solids (MF,UF).

Membrane distillation (MD) is an innovative membrane based process with the capability to treat the highly concentrated solutions and can be suitable to be used for produced water [15,16,43,44]. The process provides the theoretically 100% rejection of all non-volatiles. It can be operated at atmospheric pressure and at temperatures much lower than the boiling point of water and, therefore, provides the opportunity to use waste heat or low grade energy [17]. These unique benefits associated with MD make it a promising membrane based operation capable of removing dissolved solids from produced water. MD has been intensively studied for desalination and to tackle the problem of brine disposal for desalination capacities. Xu et al. have pointed out that MD can be a novel technology to treat the produced water [18]. In a recent review, Camacho et al. [15] have acknowledged that MD can be used to treat the produced water with relatively less temperature (<70 °C) where other thermal processes are not feasible. Moreover, the small footprint associated with MD unit can overcome the drawback of large sized conventional offshore produced water treatment plants [3].

MD is conventionally a temperature gradient driven process in which two phases with different partial pressure are separated through a hydrophobic microporous membrane. The vapors from the side with the highest partial pressure diffuse through the hydrophobic membrane and condense on the distillate or permeate side. The partial vapor pressure difference across the membrane, which serves as the driving force for the process, is strongly temperature dependent and weakly depends upon the concentration of the solution being treated [19]. Different membrane configurations can be used in this process. Four well known configurations utilized in membrane distillation include direct contact membrane distillation (DCMD), vacuum membrane distillation (VMD), sweeping gas membrane distillation (SGMD) and air gap membrane distillation (AGMD). DCMD is the best suited for applications where water is the permeating flux because it does not need an external condenser. Moreover, DCMD requires the least equipment and is the simplest to operate [20].

The current investigation was carried out with the objective to determine the potentiality of membrane distillation for desalting and reuse of oilfield produced water of high salinity; typically about 25% concentration. DCMD configuration was applied. Different membranes with various characteristics and materials of construction were prepared and used. The effect of feed temperature and hydrodynamic conditions on the attained separation was investigated. Finally, an economical evaluation was carried out to assess the feasibility of the MD process in desalting produced water.

2. Experimental

2.1. Basic characterization

Produced water samples for the investigation were collected from an oilfield. The water samples were initially pretreated by microfiltration and activated carbon filtration for oil separation, removal of suspended solids and removal of H_2S. The water was then characterized in term of total suspended solids, total dissolved solids, ionic composition, carbon content, conductivity and pH.

Total carbon (TC), total organic carbon (TOC) and total inorganic carbon (TIC) measurements were carried out using a TOC-V CSN analyzer (Shimadzu). This instrument utilizes the 680 °C combustion catalytic oxidation method to efficiently analyze all organic compounds.

For determination of total solids, a water sample (1 ml) was dried by a thermo-balance (OHAUS MB 45) at a temperature of 105 °C until a constant weight was achieved.

Total dissolved solids were determined via the filtration of a water sample through a filter of 0.45 μm. Then 1 ml of the filtrate was dried by a thermo-balance at a temperature of 105 °C to obtain a constant weight. Total suspended solids were assessed from the difference between total solids and total dissolved solids.

The identification of the different substances within the water sample was carried out by using a GC–MS (Shimadzu QP 2010S), equipped with a capillary column Equity 5 (10 m × 0.1 mm) from Supelco and using helium as carrier gas. The analysis was carried out using the solid phase micro-extraction (SPME) technique that involves the use of a fiber coated with an extracting phase which extracts different analytes (including both volatile and nonvolatile) from different kinds of media, which can be in liquid or gas phase. In particular, in the present work a Carboxen/PDMS coated fiber (thickness = 75 μm) from Supelco was used.

^{1}H NMR spectra were recorded on a Brucker WH-300 spectrometer in $CDCl_3$ with TMS as internal standard. ^{1}H NMR measurements, after extraction of produced water samples with n-Hexane (HPLC grade), were carried out to confirm the GC–MS analyses.

2.2. Membrane used

Polyvinyledene fluoride (PVDF) and polypropylene (PP) based hollow fiber membranes were used in the experimentation. Different PVDF membranes were prepared in the laboratory and were assembled into glass module. Two different PP membrane modules were utilized: one was purchased from Microdyn-Nadir (MD020CP2N) in the form of an already assembled module whereas a second module was assembled in lab using polypropylene fibers provided by Membrana (PP Accurel® S6/2). The detailed characteristics of the membranes used in the experimentation are provided in Table 1.

2.3. MD experimentation

The experimentation was performed with feed temperature ranging from 50 to 70 °C with an interval of 10 °C each. Feed flow rates were varied from 7.4 L/h to 11.4 L/h with an interval of 1.8 L/h each. The permeate flow rate and temperature were kept constant at 6 L/h and 25 °C, respectively. For the commercial PP hollow fiber module, hydrodynamic conditions were varied from feed flow rates of 50 L/h to 150 L/h with an interval of 50 L/h keeping the feed and permeate temperatures at 50 °C and 25 °C, respectively. A detailed investigation of thermal effects on trans-membrane flux was also carried out. In this case, feed flow rate was kept constant at 50 L/h, permeate temperature constant at 25 °C, whereas feed