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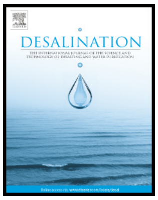

Exploration and optimization of two-stage vacuum membrane distillation process for the treatment of saline wastewater produced by natural gas exploitation

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HIGHLIGHTS

- Wastewater produced by natural gas exploitation has been successfully treated.
- A novel two-stage VMD processing route was developed.
- Membrane fouling occurred and VMD performance can be recovered via cleaning.
- Cleaning intervals were shortened when wastewater became concentrated.
- Total water recovery rate can be up to 88.6%.

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ABSTRACT

Membrane distillation has recently been recognized as the emerging foremost membrane separation technology for applications in industrial wastewater treatment and desalination. By employing polypropylene hollow fiber membrane, this study firstly performed the optimization of the vacuum membrane distillation (VMD) process. Subsequently, the feasibility of the VMD for the treatment of real saline wastewater produced by natural gas exploitation was investigated under optimized operation conditions. An ultrahigh water flux of 30.4 kg/($m^2 \cdot h$) with a salt rejection rate of 99.8% was achieved. Membrane fouling was observed during experiment, which induced a sharp decrease in permeate flux and salt rejection. Thus, membrane was cleaned and the VMD performance was recovered. The membrane cleaning intervals were shortened when wastewater became concentrated. After being treated for 110 h, the wastewater was filtered and then further concentrated for another 20 h through the second-stage VMD. The final conductivity of wastewater feed reached 230,000 μS/cm, indicating a total water recovery rate of 88.6%. This study successfully treated wastewater produced by natural gas exploitation via a newly developed two-stage VMD process, which would provide an insightful guideline for its further industrial applications and may open up alternative options of effective technologies for the treatment of high-saline wastewater.

1. Introduction

Natural gas is a generous gift of nature, and fuels the development of modern society. With extensive natural gas exploitation in recent years, a huge amount of wastewater with high salinity, COD, organics and other complex pollutants has been produced. This wastewater stream cannot be re-injected into an empty gas well without treatment. On the other hand, the direct discharge of wastewater will cause severe pollution of soil and water bodies. To date, wastewater produced from the process of natural gas exploitation is difficult to treat via normally applied chemical methods. Desalting this wastewater through traditional distillation is not energy efficient and the processing cost is quite prohibitive. For these reasons, exploring new and effective approaches for the treatment of this wastewater is highly imperative.

As an emerging technology in desalination and drinkable water production from brackish and saline water, membrane distillation (MD), which is a thermally driven process based on the vapor pressure difference across the hydrophobic membrane surfaces, has risen in importance since the 1980s [1]. Compared to multi-effect evaporation or multi-stage flash processes, MD can be operated at a lower operating temperature, which is below the boiling point of liquid feed. On the other hand, MD is safer and requires a much lower operating pressure

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than pressure-driven membrane processes (e.g., reverse osmosis), which saves energy and equipment costs [2].

Among various MD processes, vacuum membrane distillation (VMD) has several competitive traits compared with other MD configurations: 1. Conductive heat loss across the membrane in DCMD is nearly negligible in VMD; 2. VMD has a higher permeate flux since higher partial pressure gradients can be achieved with the application of vacuum pump; and 3. there are minimal temperature and concentration polarization effects on the permeate side of VMD because of the immediate removal of vapor [3].

VMD has now been widely used in numerous fields, including the removal of organic compounds [4,5] and ammonia [6] from aqueous feed solutions, concentrating the fruit juices [7] and plant crude extracts solution [8,9] in food/agro industries, seawater desalination [10], and treatment of various wastewater [11–13]. When saline water is treated through VMD, a regression in permeate (water) flux is often observed with the increase of salt concentration, which lowers the vapor pressure in feed solution. According to Wirth and Cabassud [14], the VMD water flux decreased less than 30% when the salt concentration was increased from 15 g/L to 300 g/L. Similarly, Safavi and Mohammadi [15] also reported that when the NaCl concentration was changed from 100 g/L to 300 g/L, a 35% decline in permeate flux was found at constant vacuum pressure. Naidu et al. [16] investigated the influences of NaCl concentration on VMD permeate flux through experimental and modeling approaches, and observed that elevating the salinity from 1 to 3 mol/L reduced the permeate flux by 18–20%. These studies mentioned above confirmed the feasibility of applying VMD technique on the treatment of saline water. However, all of them only used artificially prepared NaCl solution as the feed, and hence these results may not be applicable to the treatment of real saline wastewater containing other complex pollutants. Besides salinity, membrane fouling and scaling has been also a key problem that exacerbates the flux decline and permeate quality worsening in VMD, since fouling increases energy consumption, costs on membrane cleaning and replacement, as well as creates permeate contamination from membrane pore wetting [17]. Wastewater constituents vary drastically according to the source, so the fouling types and influences of membrane fouling on VMD performance may be hard to predict.

This bench-scale study is part of a leading pioneer project at SINOPEC Group, which aims to explore the VMD industrial application in the treatment of natural gas exploitation produced wastewater. However, there is quite a fair amount of information available about utilizing VMD to treat this wastewater stream. Therefore, the main objective of this paper was to investigate the feasibility of using the VMD for treating real saline wastewater produced by natural gas exploitation. At first, by using polypropylene (PP) hollow fiber as the membrane and NaCl solution as the feed, the operation conditions of the VMD process were optimized. As the key and interesting part of this study, the real saline wastewater produced in natural gas field without pre-treatment was then semi-continuously treated through VMD under optimized operation conditions. One novel two-stage VMD operating route was developed to achieve a high water recovery rate. Water flux and produced water quality was monitored and the membrane cleaning was conducted when the water flux or salt rejection rate evidently declined. The membrane cleaning intervals were adjusted accordingly during the experiment. The membrane fouling and contaminants, which was a major reason of the significant reduction of water flux and deterioration of produced water quality, were analyzed after the treatment.

2. Materials and methods

2.1. Membrane materials and module fabrication

Polypropylene (PP) hollow fiber membranes provided by Membrana GmbH, Germany, was used as the MD membrane. The PP fibers were fabricated through thermally-induced phase separation (TIPS) method, and the major characteristics of PP hollow fiber membrane and membrane module were tabulated in Table 1. PP hollow fibers were assembled into a glass tube. Two ends of the fiber bundle together with glass tube were sealed with solidified epoxy resin to compose a membrane module. After 24 h, the hollow fibers were cut open at both ends to accommodate shell side feed configuration. The membrane compactness and module length/diameter ratio can be adjusted accordingly.

2.2. VMD apparatus

The schematic diagram of the laboratory scale VMD system used in this study was shown in Fig. 1. The VMD system mainly consisted of two thermostatic cycles: the feed cycle and vacuum cycle. The feed cycle compartment, which was connected to a feed tank together with a thermostatic water bath, was kept at a high temperature. The circulation feed rate was controlled by a liquid flow meter. On the other hand, the vacuum cycle was comprised of a condenser, a vacuum pump, a water collector and the controlling system. The condenser was a heat exchanger, which used tap water as the condensing fluid, remaining a constant temperature of 25 °C. The feed was pumped through the lumen side of the fibers, and the vapor/permeate in the shell side of module was removed by vacuum pump.

2.3. Feed solution and characteristics of wastewater

The feed solution with the conductivity of 20 mS/cm for the VMD optimization test was NaCl solution. It was prepared by NaCl (Sinopharm, China) and ultrapure DI water (Milli-Q® system, Merck Millipore, Germany). The wastewater sample without pre-treatment was collected from a natural gas field located in Sichuan Province, China. The characteristics of the wastewater were analyzed and summarized in Table 2.

2.4. Experimental procedure and equation

During the experiment, the feed was heated up to the pre-set temperature via the thermostatic water bath. Then, the magnetic pump was switched on and the feed was pumped into the lumen side of membrane module. The feed flow rate was adjusted to the pre-set value through liquid flow meter. Waiting until the inlet and outlet temperature of membrane module to be unchanged, the vacuum pump was switched on to provide a vacuum pressure that experiment needed. After the system stably ran for 10 min, the produced water was collected on a regular basis and weighed through an electronic balance. The conductivity and pH of the produced water was measured during the experiment.

The permeate flux J ($\mathrm{kg/(m^2 \cdot h)}$) was calculated by:

$$J = \frac{W}{A \times t} \tag{1}$$

Table 1
Major characteristics of PP hollow fiber membrane and membrane module.

Characteristics	Measurement results
Hollow fiber membrane	
Outer diameter (μm)	2700
Inner diameter (μm)	1800
Porosity (%)	73.9
Average pore size (μm)	0.238
Contact angle of outer surface (°)	147.7
Module	
Length (mm)	230
Diameter (mm)	8
Total membrane surface area (m^2)	0.008
Number of fibers	5
Shell material	glass