Desalination 393 (2016) 39–51

Contents lists available at ScienceDirect

Desalination

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

Desalination and concentration of saline aqueous solutions up to supersaturation by air gap membrane distillation and crystallization fouling

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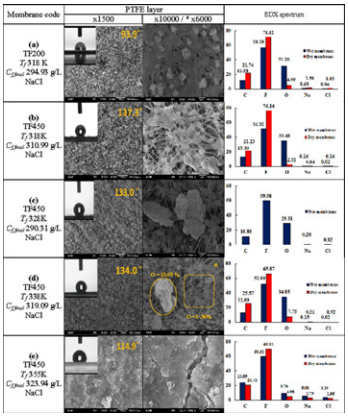
HIGHLIGHTS

- Desalination of saline solutions by air gap membrane distillation (AGMD)
- Treatment of supersaturated salt aqueous solutions by AGMD
- Study of crystallization fouling of porous hydrophobic membranes by AGMD
- Crystallization fouling reduces both the permeate flux and thermal efficiency of AGMD
- Change of the initial membrane characteristics by crystallization fouling

GRAPHICAL ABSTRACT



Salt deposition on the surface of the PTFE membrane top layer (at different magnifications) and water contact angles of the membranes TF200 and TF450 used in air gap membrane distillation (AGMD).

ARTICLE INFO

Article history:
Received 9 December 2015
Received in revised form 11 March 2016
Accepted 12 March 2016
Available online 23 March 2016

Keywords:
Air gap membrane distillation
Fouling
Crystallization
Desalination
Supersaturated solutions
Thermal efficiency

ABSTRACT

The possibility to concentrate synthetic brines (65 g/L of NaCl) above the saturation concentration of NaCl at different feed inlet temperatures up to 355 K is studied, using the AGMD configuration and two different polytetrafluoroethylene (PTFE) membranes, TF200 and TF450. A good quality distillate (<0.5 g/L NaCl) and high salt rejection factors (>99.89%) were achieved when treating high saline aqueous solutions. When applying the highest feed inlet temperature, 355 K, better AGMD results were observed, permeate flux of 23.84 ± 0.09 kg/m^2 h and 46.50 ± 0.21 kg/m^2 h with a thermal efficiency of 80.97% and 96.06%, for the membranes TF200 and TF450, respectively. Once the saturation limit of NaCl was overpassed, crystallization fouling occurs by blocking or wetting the membrane pores due to the continued deposition and growth of salt crystals on the membrane surface and inside the membrane pores. Membrane properties changed with crystallization fouling and reduced the thermal efficiency of the AGMD process. When using NaCl aqueous solutions, a simple washing with water is enough to partially recover the initial properties of the membrane.

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http://dx.doi.org/10.1016/j.desal.2016.03.010
0011-9164/

1. Introduction

Desalination of seawater and brackish water is considered nowadays an important solution to the problem of potable water shortage especially in coastal zones. At the present time, thermal and membrane processes are the two major used desalination processes. Thermal technology, like multi-stage flash distillation (MSF) or multi-effect distillation (MED) processes, dominates the desalination market in warm countries of the Middle East [1]. In the rest of the world, membrane processes especially reverse osmosis (RO) is well recognized as the most convenient desalination technology. It heads the membrane desalination processes with 2/3 of the contracted capacity [2]. The economic sustainability of desalination processes depends mainly on the reduction of energy consumption costs, the increase of the water recovery factor and the management of the generated wastes or brines. In general, brines have been always associated with the rejection of the desalination processes and discharged in seas. High saline content and additives of brine, with a concentration of total dissolved solids (TDS) vover 70 g/L have direct effects over the marine environment due to the salt composition of brines, which is approximately the double of that of seawater [3]. As a result, the major effects of brine discharge are eutrophication, pH changes and heavy metal accumulation, among others [4,5]. Therefore, new options to improve the management of concentrates from desalination plants are a current demand. Recent strategic research lines for brine management are focused on the accomplishment of the zero liquid discharge (ZLD) concept [6,7] and recovery of valuable byproducts such as salts through the combination of different individual technologies (i.e. hybrid systems), trying to make the desalination process environmentally more sustainable.

Among the proposed technologies, the non-isothermal process membrane distillation (MD) has emerged as an important process for desalination of high saline aqueous solutions and treatment of brines [8–15]. One of the main advantages of MD over other membrane processes in the field of desalination is its capability to operate under high salt concentrations (i.e. >65 g/L of sodium chloride (NaCl), equivalent to the salt concentration of RO brines), producing relatively high permeate fluxes with high salt rejection factors. The most used MD configuration to achieve this purpose is direct contact membrane distillation (DCMD). Tun et al. [14] by using a flat sheet polyvinylidene fluoride (PVDF) membrane with a mean pore size of 0.22 μm, achieved permeate fluxes up to 20 kg/m^2 h for a temperature difference of 40 °C and a feed aqueous solution of 260 g/L NaCl. Alkhudhiri et al. [10] used an air gap membrane distillation (AGMD) system with a polytetrafluoroethylene (PTFE) flat-sheet commercial membrane with a pore size of 0.2 μm. A permeate flux of 24.48 kg/m^2 h and a NaCl rejection factor of 99.98% were obtained. An aqueous solution of 84.4 g/L NaCl was used as feed, at a temperature difference between feed and permeate membrane sides of 343 K and a feed flow rate of 90 L/h. Compared to DCMD and AGMD, vacuum membrane distillation (VMD) is less studied due to the need of external condenser(s) and a vacuum pump. Safavi and Mohammadi [15] tested VMD for desalination of 100, 200 and 300 g/L NaCl feed aqueous solutions using PP commercial hollow fiber membranes of 0.2 μm mean pore size with a feed temperature of 55 °C and a vacuum pressure of 40 mbar. In this study, the NaCl feed concentration was kept nearly constant during the experiments. The reported permeate fluxes were 14.2, 13.1 and 11 kg/m^2 h for the NaCl feed solutions 100, 200 and 300 g/L, respectively, with salt rejection factor of 99.99%.

Since MD can be applied for the treatment of high saline aqueous solutions, including those with concentrations above their saturation point, (i.e. supersaturated salt solutions), and due to its feasibility to be combined with other separation processes and crystallization systems [11,13,14,16], this technology is suitable to achieve the above said ZLD [17]. However, the concentration and temperature polarization effects diminish the driving force of the process (i.e. transmembrane vapor pressure) and then facilitate the nucleation of inorganic salts with positive solubility coefficients, such as NaCl, near the membrane surface [14]. When supersaturated saline solutions are treated by MD, the formation and growth of salt crystals above the membrane surface and inside the pores is more pronounced [18], reducing the permeate flux [19] and the membrane hydrophobicity, limiting the operating conditions in MD systems and consequently decreasing the salt rejection performance [19] and the lifetime of the membranes. This phenomenon is defined as crystallization fouling.

The present study is intended to use AGMD configuration for desalination and the concentration of a feed saline aqueous solution having an initial NaCl concentration of 65 g/L, which is approximately the concentration of brine rejected by RO desalination plants, to values above the saturation concentration, using different feed inlet temperatures. It should be mentioned that there are only few published studies on MD separation using saline aqueous solutions with concentrations above the salt concentration saturation point. In this paper, systematic experiments were carried out with two commercial membranes having different pore sizes. Besides the concentration experiments, complementary experiments of membrane control (to check the reproducibility of different membrane samples) and membrane characterization (to check the membrane performance) were conducted in order to study the effects of supersaturation salt concentration on membrane fouling. The membranes were characterized before and after the concentration experiments. Inorganic fouling by crystallization of NaCl and its influence on the membrane parameters and on the thermal efficiency of the MD process were investigated.

2. Experimental

2.1. Membranes and characterization techniques

Two commercial polytetrafluoroethylene (PTFE) flat sheet membranes (TF200 and TF450, Pall Corporation) supported by a PP net were used. Their characteristics as supplied by the manufacturer are summarized in Table 1.

Both membranes were characterized before and after desalination tests by means of different techniques to determine the thickness (δ), pore size (d_p) and its distribution, void volume fraction (ε) (i.e. porosity), water contact angle (θ) and liquid entry pressure of water (LEP_w). The obtained initial characteristics of the membranes together with those given by the manufacturer are reported in Table 1.

The thickness was measured by an electronic micrometer Schut (Schut Geometrical Metrology) on different points of each membrane sample. At least 50 values were obtained and the average values together with their standard deviations were reported.

The mean pore size was measured by a flow porometer (POROLUX™ 100 Porometer) that considers the pressure scan method within a pressure range of 0–0.7 MPa at a room temperature. The gas used was compressed air and the effective membrane area was 2.7 10^{-4} m^2. POREFIL® was used as a wetting liquid agent due to its low surface tension (16 mN/m). The applied method was reported elsewhere [20].

The void volume fraction of the membranes was determined at room temperature by measuring the density of each membrane sample using isopropyl alcohol (IPA, ACS reagent supplied by Sigma-Aldrich), which penetrates inside the membrane pores, and distilled water, which does not go into the pores as described elsewhere [21].

The water contact angle of the membrane surface was measured at room temperature by a computerized optical system CAM200, equipped with CCD frame grabber camera and image analysis software. Distilled water drops of about 3 μL were deposited on the membrane surface employing a tight syringe. The contact angles were performed at both left and right sides of each drop and were automatically calculated by fitting the captured drop shape to Young–Laplace equation. Five drops and five readings per drop were obtained for each sample and