6th International Conference on Water Resources and Arid Environments (ICWRAE 6): 01-06
16-17 December, 2014, Riyadh, Saudi Arabia

Seawater Desalination by Air Gap Membrane Distillation with Hydrophobic Tunisian Clay Membrane

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Abstract: The scarcity of freshwater especially potable water is jeopardizing many region of the world. It is estimated that about three-quarters of the world's population may suffer from high or moderate water shortages, with a focus on North Africa, the Middle East, Latin America and South-east Asia. This paper focuses on current application for seawater desalination in Tunisia by hydrophobic membranes. New kinds of hydrophobic membrane was prepared by grafting 1H,1H,2H,2H-perfluorodecyltriethoxysilane (C8 compound) on the Tunisian clay ceramic membrane with pore diameters of 0.18µm. Air Gap Membrane Distillation (AGMD) experiments was performed for seawater as feed. The water vapor permeability of the proposed membrane was determined. The new membrane seems to be promising in the field of membrane distillation. High salt rejection rates higher than 99% were obtained for modified MF ceramic clay membrane. AGMD is a low cost process very efficient to produce fresh water from seawater.

Key words: Sea Water Desalination · Air gap membrane distillation · Surface modified · Tunisian clay · Ceramic membrane

INTRODUCTION

Today, about three billion people in the world have no access to clean drinking water [1]. According to the World Water Council, by 2020, the world will be about 17% short of the fresh water needed to sustain the world population. Moreover, about 1.76 billion people live in areas already facing a high degree of lacking water. The need for fresh water is at the top of the international agenda of critical problems, at least as firmly as climate change. As a consequence of the growing scarcity of fresh water, the implementation of desalination plants is increasing on a large scale.

The oceans represent the earth's major water reservoir. About 97% of the earth's water is seawater while another 2% is locked in icecaps and glaciers. Available fresh water accounts for less than 0.5% of the earth's total water supply [2]. Vast reserves of fresh water underlie the earth's surface, but much of it is too deep to access in an economically efficient manner. Additionally, seawater is unsuitable for human consumption and for industrial and agricultural uses. By removing salt from the virtually unlimited supply of seawater, desalination has emerged as an important source of fresh water. Today, some countries depend on desalination technologies to satisfy their fresh water requirements.

In 2001, seawater and brackish water accounted for about 60 and 40%, respectively, of all desalinated water sources in the world [3]. At the end of 2002, multistage flash desalination (MSF) and reverse osmosis (RO) accounted for 36.5 and 47.2%, respectively, of the installed brackish and seawater desalination capacity. For seawater desalination MSF accounted for 61.6% whereas RO accounted for 26.7%. It should be noted that MSF holds the lead in all plants producing over 5000 m^3/day units [4]. The current world desalination plant capacity is 40 Million m^3/day and the annual average growth rate for the last five years is 12% [5]. These facts have urged engineers to look for alternative approaches for conventional desalination technologies. Membrane distillation was patented by Bodell [6] as an alternative approach mainly for desalination. Being considered as a branch of membrane contactors, it offers many distinct advantages over conventional desalination technologies.

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The operating temperatures in this process can be maintained as low as 50 °C and the operating pressures are atmospheric [7, 8, 9, 10]. This process has a great potential to be energy efficient and cost effective, especially if combined with low grade or waste energy sources. However, in contrast to its great potentials, this process has not been widely accepted by the industry during the last four decades. One important reason is probably due to its relatively lower flux compared to reverse osmosis process [10]. Therefore, flux enhancement in this process has become of great interest among membrane scientists and researchers. In an MD process, a porous hydrophobic membrane is utilized to perform the separation among water and dissolved minerals. In this process, the liquid feed is heated up to about 50-90 °C and is brought into contact with one side of the hydrophobic membrane.

MD is a relatively new process that can be adapted effectively for water desalination. It requires moderate temperatures to produce the driving force across the membrane, the difference between the partial vapor pressures at both sides of the membrane. Compared to RO, Walton *et al*. [11] reported that, when fully developed, MD should be significantly lower in capital and operational expenses for remote areas. Also, the operational behavior of the MD process is easier to that of RO systems, especially for remote areas regarding to:

- The absence of high pressure flows allows thinner piping and fewer problems with leaks and pump failure than RO systems.
- Requirement of intensive pre-treatment which is not needed under MD process [12]. Recent studies confirm that pretreatment may has an influence on MD performances [13]. Thus, Gryta [14] reported a detailed study of fouling and scaling and their influence on the long term runs with and without pretreatment.
- The ability to treat high concentrated brines.

In MD processes, one side of the membrane is in contact with liquid feed. However, regarding to permeate side configuration, four MD processes have been identified: Direct Contact Membrane Distillation (DCMD), Air Gap Membrane Distillation (AGMD), Vacuum Membrane Distillation (VMD) and Sweep Gas Membrane Distillation (SGMD) [15]. For the purpose of desalination, the AGMD configuration was employed in this paper because it is simple to perform in the laboratory scale and generally produce a high water permeate flux.

The aim of this research is to use hydrophobic modified clay MF membrane elaborated in our laboratory in order to water desalination under AGMD process. It is shown that fresh water with totally free salt can be produced from seawater.

Membrane Distillation

Principle: Membrane distillation (MD) is a thermally driven membrane process in which a hydrophobic microporous membrane separates a hot and cold stream of water [16, 17]. The hydrophobic nature of the membrane prevents the passage of liquid water through the pores while allowing the passage of water vapor. The temperature difference produces a vapor pressure gradient which causes water vapor to pass through the membrane and condenses on the colder surface. The result is a distillate of very high purity which, unlike in conventional distillation, does not suffer from the entrainment of species which are nonvolatile. For desalination processes, the salt solution passes on the one side of the membrane at an elevated temperature, about 80°C. At the other side of the membrane, a lower temperature obtained by cooling the condenser, creates a water vapor partial pressure difference between the two sides of the membrane and allows the evaporation through the membrane. The water vapor condenses on the low-temperature side and distillated water is formed. MD may be carried out in various modes differing particularly in a way of permeate collection [18]. Various types of MD have been known for several years: direct contact, air gap, sweeping gas and vacuum.

Air Gap MD: In AGMD (Fig. 1) only the feed solution is in direct contact with the membrane.

The permeate is condensed on a cold surface. There is an air gap situated between the membrane and the cold surface to reduce energy loss by heat conduction through the membrane. The main drawback of the air gap is that it is also an additional resistance to mass transfer. AGMD is also suitable to separate volatile substances, e.g. alcohols from an aqueous solution [19, 20]. This is not possible in direct contact MD, because those substances are likely to wet the membrane at permeate side due to lower surface tension and/or smaller contact angle with the membrane. Since in AGMD, the permeate is not in direct contact with the membrane, there is no danger of membrane wetting at the permeate side in this case.

Experimental

Materials: Tunisian clay microfiltration (MF) membranes (15 cm-long, with an internal diameter of 7mm and an outer

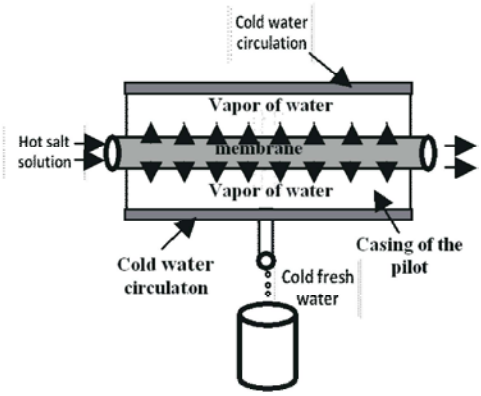

Fig. 1: Schematic presentation of AGMD in counter current flow configuration.

one of 10 mm), with pore diameters of 0.18 µm were used. This type of membrane is elaborate in our laboratory from the support to the finest layer as described earlier [21, 22]. Prior to chemical modification, the membrane was cleaned in an ultrasonic bath in presence of ethanol and acetone successively for 5min and dried in an oven at 100°C. The triethoxy-1H,1H,2H,2H perfluorodecylsilane $C_8F_{17}(CH_2)_2Si(OC_2H_5)_3$ (97%) from Sigma was used. Analytical grade ethanol (99%) was purchased from Riedel-de-Haën.

Preparation and Characterizations of Hydrophobic Membranes: Hydrophobic membranes were prepared by grafting the triethoxy-1H,1H,2H,2H perfluorodecylsilane $C_8F_{17}(CH_2)_2Si(OC_2H_5)_3$ onto Tunisian clay ceramic membranes. Grafting occurs with a succession of condensation reactions between the OH groups found in the membrane and the Si-O-alkyl groups of the silane. To realize grafting, solution of C8 was prepared in ethanol at a concentration of 10^{-2} mol l^{-1}. Samples, planar membranes as well as tubular membranes, are completely immersed in solutions for 15 min at room temperature. The grafted membranes were then rinsed in ethanol and acetone successively and placed in an oven at 100°C for 1 h.

The FTIR spectroscopy using a Perkin-Elmer BX II spectrophotometer under transmission mode was used to confirm the existence of the perfluorinated groups on the membrane surface. The spectra were collected for each measurement in the spectral range 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. The measurements of contact angles were performed at room temperature (20°C) using a OCA 15 from Dataphysics, equipped with a CCD camera, with a resolution of 752-582 square pixels, working at an acquisition rate of 4 images per second. Collected data were processed using OCA software. Distilled water was used for measurements and planar membranes realized with clay were grafted. The drop image was recorded by video camera and digitalized. Each contact angle is the average value of 20 measurements.

Membrane Distillation Experiments: In our work seawater treated is collected from SIDI MANSOUR Sea, located at Sfax (Tunisia). The experimental set-up presented in Fig. 1 was used for the performances of the triethoxy-1H,1H,2H,2H perfluorodecylsilane grafted membranes in the AGMD configuration process. The air-gap width was 10 mm. The used water was heated in a feed tank and it was circulating through the membrane module. During experiments, permeate vapors were condensed at a cooled stainless steel surface close to the membrane (Fig. 1). The permeate water flux through the membranes was determined by measuring permeate volume as a function of time.

In each experiment, two liters of water were used and was circulated through the membrane module by using a variable flow peristaltic pump. The feed pressure was measured with a manometer at the inlet of the feed cell frame. The feed flow rate was measured with a digital flowmeter at the outlet of the feed cell frame and it was kept constant during the experimental run by adjusting the pump speed. The feed and cooling plate temperatures were kept constant by using controlled heating and cooling thermostats, respectively.

The fine control of the feed temperature was achieved by using an auxiliary heat exchanger between the feed reservoir and the pump. The temperatures were measured with two thermometers located at the feed cell frame and at the cooling plates, respectively. The obtained distillate was collected directly in a calibrated graduated cylinder. The distillate flow through the membrane was determined from the temporal evolution of the liquid level in the cylinder. The temperature difference is defined as $T = T_2 - T_1$ where T_2 is the feed solution temperature and T_1 is the cooling water temperature. Salt concentration both in feed and permeate solutions were determined through conductivity measurement. The separation factor, R was calculated using the following expression:

$$R = \left(1 - \frac{C_p}{C_F}\right) \times 100$$

Where Cp and Cf are the salt concentration in the permeate and in the bulk feed solution, respectively.

Fig. 2: Picture of the water droplet on the membrane surface grafted with the fluoroalkylsilane.

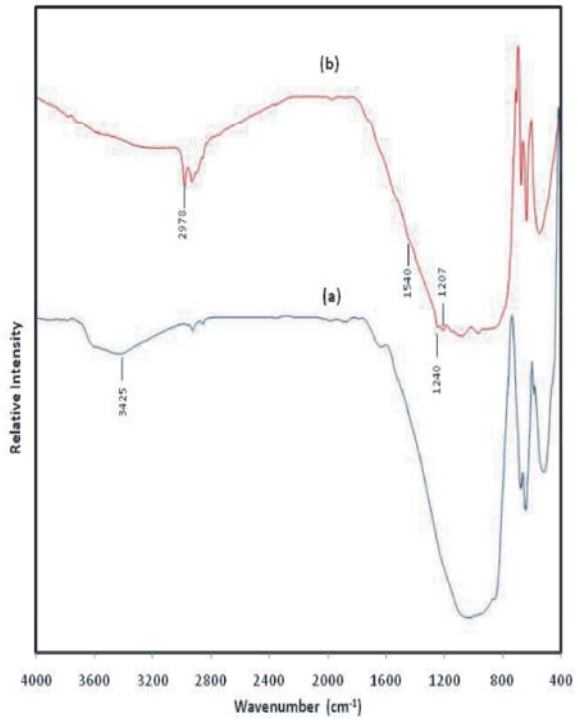

Fig. 3: Infrared spectra of (a) ngrafted membrane, (b) microfiltration grafed membrane.

RESULTS AND DISCUSSION

Characterization of Grafted Membranes: The hydrophobicity of the grafting of MF membrane was proven by measuring their contact angles. With a grafting time of 15 min, we obtained a non-wetting material and a high hydrophobicity is noticed. As shown in Fig. 2, a water drop deposited on the grafted flat microfiltration membrane surface forms an angle of 179°, which is characteristic of super-hydrophobic materials.

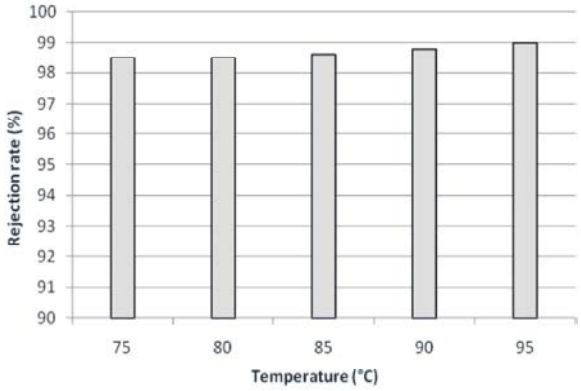

Fig. 4: Salt rejection rate as a function of temperature in desalination by AGMD using MF clay membrane.

Infrared spectra on each grafted or ungrafted membrane were measured. The infrared spectra of the ungrafted clay membrane were shown in Fig. 3a. It could be confirmed that there are hydroxyl groups in ungrafted clay membrane from the band at 3100–3500 cm^{-1}. The peak at 3425 cm^{-1} corresponds to the –OH stretching vibration of the adsorbed water. In Fig. 3b, a new weak band at 2978 cm^{-1} attributed to antisymmetric stretching of $–CH_2$ group of C8 was observed, indicating the presence of silane in the grafted products (Fig. 2). Similarly, the bands at 1540 cm^{-1}, 1240 cm^{-1} and 1207 cm^{-1} corresponding respectively to the stretching vibration of C-C, C_xF_{2x+1} group and Si-CH2CH2C_xF_{2x+1} group of the grafted C8.

Desalination of Seawater by AGMD: Seawater desalination aims to obtain fresh water with free salt adequate for drinking. In our work seawater treated is collected from SIDI MANSOUR Sea, located at Sfax (Tunisia). Measurements of permeate flux and rejection rates were carried out by AGMD as a function of the temperature. The feed side temperature was thus varied from 75 to 95 °C, while keeping the cooling system temperature constant at 5 °C. As it was shown in Fig. 4 the rejection rate of salt is about 100% for MF membrane. It can be seen that the salt retention in AGMD process with grafted ceramic membranes is close to 100%. These results proved that in the case of AGMD with aqueous solutions containing non-volatile compounds like salt, only water vapor is transported through the membrane.

Effects of Temperature in AGMD: Effects of mean temperature on permeate flux and a rejection rate in AGMD for seawater was studied using MF clay

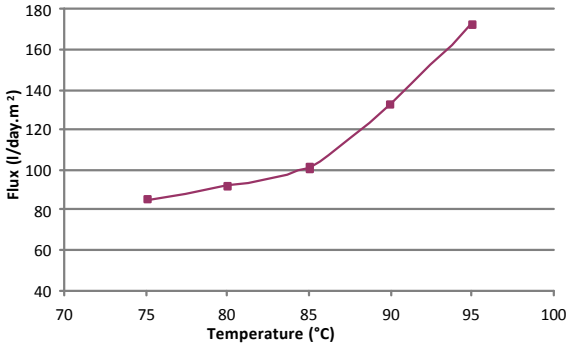

Fig. 5: Variation of the permeate flux as a function of the temperature in desalination by AGMD using MF clay membrane.

membrane at a feed velocity of 2.6 m/s. The feed side temperature was thus varied from 75 to 95°C, while keeping the cooling system temperature constant at 5°C. Fig. 5 shows the permeate flux variations of seawater tested at different temperature of the feed side. Increasing the temperature of the source solution from 75 to 95°C led to an increase of permeate flux from 85 to 173 L/day.m^2 for modified MF membrane, because the vapor pressure differences, increases with the increasing of the temperature. Thus, the flux values through the membrane in the membrane distillation process depend strongly on temperature differences.

This result have been observed by other authors [23, 24, 25] who showed that the fluxes of the grafted MF and UF membranes exhibit an exponential dependence on temperature due to the exponential increase of vapor pressure with temperature.

CONCLUSIONS

Membrane distillation is an emerging technology for desalination. Membrane distillation differs from other membrane technologies in that the driving force for desalination is the difference in vapor pressure of water across the membrane, rather than total pressure.

In our study, interesting results were obtained for the membrane distillation experiment conducted using MF modified clay membrane, validating the ability of this modified ceramic membrane to act as membrane contactors for desalination. An important influence of the feed temperature on the permeate flux was observed. In the same time, high salt rejection rates were obtained in AGMD process with grafted clay ceramic membranes.

The membranes for MD are hydrophobic, which allows water vapor (not liquid water) to pass. The vapor pressure gradient is created by heating the source water, there by elevating its vapor pressure. The major energy requirement is for low-grade thermal energy. It is expected that the total costs for drinking water with membrane distillation, depending on the source of the thermal energy required for the evaporation of water through the membrane. Solar energy could very much help this process in our countries which are very sunny resulting in a reduction of energy costs. Thus, membrane distillation could become competitive relative to other processes.

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