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Influence of operating conditions and membrane fouling on water flux during seawater desalination using air gap membrane distillation

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Abstract

Membrane distillation (MD) has emerged as a promising process for seawater desalination applications to augment fresh water supply in remote coastal areas. Amongst four basic MD configurations, air gap membrane distillation (AGMD) exhibits the highest thermal efficiency, and thus is the most used configuration for small-scale seawater desalination. In this study, the influences of operating conditions and membrane fouling on water flux of a lab-scale AGMD process with actual seawater feed were systematically investigated. The experimental results demonstrated strong impacts of feed temperature, circulation rates, and membrane fouling on the process water flux. Increasing feed temperature exponentially raised water flux but also aggravated polarization effects of the AGMD process. Elevating water circulation rates, particularly of the feed stream, helped alleviate polarization effects, hence improving the process water flux. During the AGMD process of raw seawater feed, the accumulation of organic matters on the membrane reduced its active surface for water evaporation, increased polarization effects, and therefore significantly reduced the process water flux. Pretreatment of the seawater feed by 0.45 μm paper filters removed organic foulants from the feed, and hence helped sustain the water flux of the AGMD process at water recoveries up to 70 %. When the process water recovery exceeded 70 %, water flux rapidly dropped owing to the precipitation of sparingly soluble salts (e.g. $CaSO_4$, $CaCO_3$) on the membrane. Subsequent cleaning the fouled membrane using vinegar removed nearly all foulants from the membrane surface to restore the membrane hydrophobicity, and thus the process water flux. The results reported in this study manifest that seawater AGMD desalination can be a practical process to supply drinking water to small and remote communities in Vietnam.

Keywords. Membrane distillation (MD), air gap membrane distillation (AGMD), seawater desalination, membrane fouling, membrane fouling mitigation.

1. INTRODUCTION

Membrane distillation (MD) has emerged as a promising process for seawater desalination applications to increase fresh water supply in remote coastal areas around the world [1, 2]. MD utilizes a microporous hydrophobic membrane to separate a hot saline water feed from a cold distillate stream. Under the temperature difference across the membrane, water vaporizes from the feed, transfers through the membrane pores, and condenses to distillate on the other side of the membrane. The hydrophobic nature of the membrane retains liquid water and thus all dissolved salts in the feed while allowing only the permeation of water vapor. Therefore, ultrapure water can be obtained directly from seawater using MD [3, 4]. In addition, unlike other pressure-driven membrane desalination processes (e.g. reverse osmosis (RO)), the desalination process using MD does not require high hydraulic pressure pumps and expensive stainless-steel piping; thus, the investment cost of the MD systems is significantly lower than that of RO. Moreover, water flux in MD is negligibly affected by the feed osmotic pressure, allowing the MD process to achieve much higher water recoveries than RO [5, 6]. Finally, seawater MD desalination can be efficiently operated at feed temperature as low as 40 °C, hence facilitating the utilization of low-grade heat sources such as waste heat or solar thermal energy to meet the process energy demand [3].

MD can be operated in four basic configurations. Amongst the basic MD configurations, air gap

membrane distillation (AGMD) is most used for seawater desalination applications because of its high thermal efficiency and process simplicity [3, 7]. However, AGMD offers lower water flux than other configurations [7-9]. Low AGMD water flux stems from the inserted air gap, temperature and concentration polarization effects, and membrane fouling that occurs under certain process operating conditions. The air gap increases the resistance to the water vapor transfer, thus hindering the process water flux. Polarization effects, particularly temperature polarization, render the water vapor pressure at the membrane surface lower than that in the bulk feed stream, and therefore lower the process water flux. Finally, the accumulation of foulants on the membrane during the seawater AGMD process limits the membrane active surface for water evaporation, hence further reducing the process water flux.

This study aimed at investigating the influences of operating conditions and membrane fouling on water flux during the seawater AGMD desalination process. First, the AGMD process with a synthetic sodium chloride solution was conducted to examine the impacts of feed temperature, water circulation rates, and polarization effects on the process water flux. Subsequently, the effects of membrane fouling on the process water flux were elucidated using actual seawater collected from a coastal location in Vietnam. Finally, the efficiency of membrane cleaning using vinegar to recover the water flux of the fouled membrane during the seawater AGMD process was also delineated. The results obtained in this study help to shed light on the feasibility of AGMD for seawater desalination applications in remote coastal areas in Vietnam.

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. The lab-scale AGMD system

A lab-scale AGMD system was used in this study. The system consisted of a plate-and-frame membrane module, hot water feed and coolant water tanks, a controlled heating element, water circulation pumps (i.e. submerged in the water tanks), and a computer for data logging. The membrane module had a hydrophobic flat-sheet PTFE membrane, an air gap (i.e. 3 mm thick), an aluminum condenser foil, and feed and coolant channels with depth, width, and length of 0.3, 9.5, and 14.5 cm, respectively. The flat-sheet PTFE membrane was from Porous Membrane Technology (Ningbo, China), and had thickness, nominal pore size, and porosity of 60 μm, 0.2 μm, and 80 %, respectively.

2.1.2. Feed solutions and cleaning agent

Synthetic sodium chloride (NaCl) solution (i.e. 35 g/L), and actual seawater (i.e. 10 L) were used as feed solutions. Seawater was collected from Vung Ro Bay (Dong Hoa, Phu Yen) and directly used in the AGMD membrane fouling experiments. For the experiments to investigate membrane scaling, seawater was pre-filtered by 0.45 μm filter papers. The pre-filtered seawater had total dissolved solids (TDS) of 34.5 g/L. A commercial rice vinegar (i.e. produced by Tam Duc Fisheries Company, Hanoi) was used as a cleaning agent in the fouled membrane cleaning experiments.

2.2. Analytical methods

Contact Angle Measurement device, CAM 200 (i.e. provided by KSV Instruments Ltd., Helsinki, Finland), was used to determine the hydrophobicity of the virgin membrane, the membrane fouled during the AGMD process with actual seawater feed, and the fouled membrane after cleaning with vinegar. A field emission-scanning electron microscope (FE-SEM) (Hitachi S-4800, Japan) was used to examine the morphology of membrane surfaces. An Orion 4-Star Plus meter (Thermo Scientific, Waltham, Massachusetts, USA) was used to monitor the electrical conductivity of the distillate during all AGMD experiments.

2.3. Experimental protocols

AGMD of the synthetic NaCl solution was conducted to evaluate the influence of operating conditions on water flux and polarization effects of the process. The synthetic solution feed at a temperature from 35 to 75 °C was introduced to the feed channel at flow rate of 0.1, 0.2, and 0.3 L/min (i.e. equivalent to cross flow velocity of 0.6, 1.2, 1.8 cm/s, respectively, inside the channel). Fresh water at 25 °C was circulated through the coolant channel at the same flow rate to the feed. Water flux of the process at each set of operating conditions was measured for 1 hour after the feed and coolant temperatures had been stabilized. The water flux of the process was calculated as:

$$J = \frac{\Delta V_{distillate}}{S \times \Delta t} \quad (1)$$

where J was the water flux (L/m^2.h), $\Delta V_{distillate}$ was the volume of distillate (L) obtained in a time

interval Δt (h), and S was the active membrane surface for water evaporation (m^2).

AGMD experiments with raw seawater feed at the temperature of 60 °C was conducted to examine membrane fouling caused by organic matters in seawater. At the end of the experiments, the fouled membrane was removed from the system for subsequent surface analysis using CAM 200 and FE-SEM. AGMD of pre-filtered seawater was also implemented to demonstrate the process feasibility to desalinate concentrated seawater feed. The scaled membrane at the end of this experiment was cleaned with vinegar. During the cleaning stage, vinegar at room temperature was circulated (i.e. 0.3 L/min) along the membrane inside the feed channel. The scaled membrane was cleaned for 1 hour then removed from the system, rinsed with DI water, air-dried, and proceeded to surface analysis.

2.4. Water flux and polarization effects in AGMD

Water flux through the membrane in AGMD can be expressed as:

$$J = K_m \Delta P \quad (2)$$

where K_m is the mass transfer coefficient ($L/Pa.m^2.h$), and ΔP is the water vapor pressure difference between the feed membrane surface and the condenser (Pa). K_m is a function of membrane properties, air gap thickness, and operating conditions, including feed and coolant temperatures, and water circulation rates, and can be determined using empirical correlations [10, 11] or experimentally measured [4, 9].

The vapor pressure of pure water is calculated using the Antoine equation:

$$P^0 = exp\left(23.1964 - \frac{3816.44}{T - 46.13}\right) \quad (3)$$

where P^0 is in Pa and T is the temperature in K. The water vapor pressure of saline water (P) is calculated as [8]:

$$P = x_{water}\left(1 - 0.5x_{salt} - 10x_{salt}^2\right)P^0 \quad (4)$$

where x_{water} and x_{salt} are the molar fraction of water and salts, respectively.

Temperature and concentration polarization effects are intrinsic problems for the AGMD process with saline solution feeds. Polarization effects render water vapor pressures at the membrane surface and the condenser different from those of the feed and coolant streams; therefore, they negatively affect water flux of the process. In AGMD temperature polarization effect exists in both the feed and coolant streams, whereas concentration polarization effect only occurs in the feed stream with the assumption that the salinity of the coolant stream is negligible.

3. RESULTS AND DISCUSSION

3.1. Influences of operating conditions on AGMD water flux

Feed temperature and circulation rate exerted strong influences on the water flux of the AGMD process. As expressed in Eq. (3), elevating feed temperature led to an exponential increase in the water vapor pressure difference between the feed and distillate streams, thus noticeably increasing the process water flux. Indeed, when the feed temperature was increased from 42 to 68 °C at the feed and coolant circulation rate of 0.1 L/min, the process water flux increased five-fold from 1 to 5 $L/m^2.h$ (Fig. 1A). The water flux-feed temperature relation observed here is consistent with those reported in previous studies using AGMD and other MD configurations [3-5]. The exponential growth of water flux with increased temperature emphasizes the fact that MD is a thermally driven separation process.

Increasing feed circulation rate also favored water flux of the AGMD process (Fig. 1A), but by a different mechanism as compared to feed temperature. Increasing feed circulation rate and hence the cross-flow velocity of the feed stream promoted the fluid turbulence adjacent to the membrane surface, therefore alleviating both temperature and polarization effects. As a result, water flux increased at higher feed circulation rates (Fig. 1A). It is noteworthy that the influence of feed circulation rate on water flux was stronger for the AGMD process at high feed temperatures (Fig. 1A). This is because polarization effects were also affected by feed temperature. Increasing feed temperature raised the process water flux and hence exacerbated polarization effects.

The circulation rate of the feed stream affected water flux more than that of the coolant stream. As shown in Fig. 1B, increasing feed circulation rate from 0.1 to 0.3 L/min while coolant circulation rate was remained at 0.1 L/min raised water flux from 3.7 to 4.7 $L/m^2.h$. On the other hand, increasing coolant circulation rate from 0.1 to 0.3 L/min at feed circulation rate of 0.1 L/min only raised water flux to 4.5 $L/m^2.h$. The difference in the effects of feed and coolant circulation rates on water flux could be attributed to the polarization effects, particularly concentration polarization. The concentration polarization existed only in the feed channel but not in the coolant channel with negligible coolant salinity.

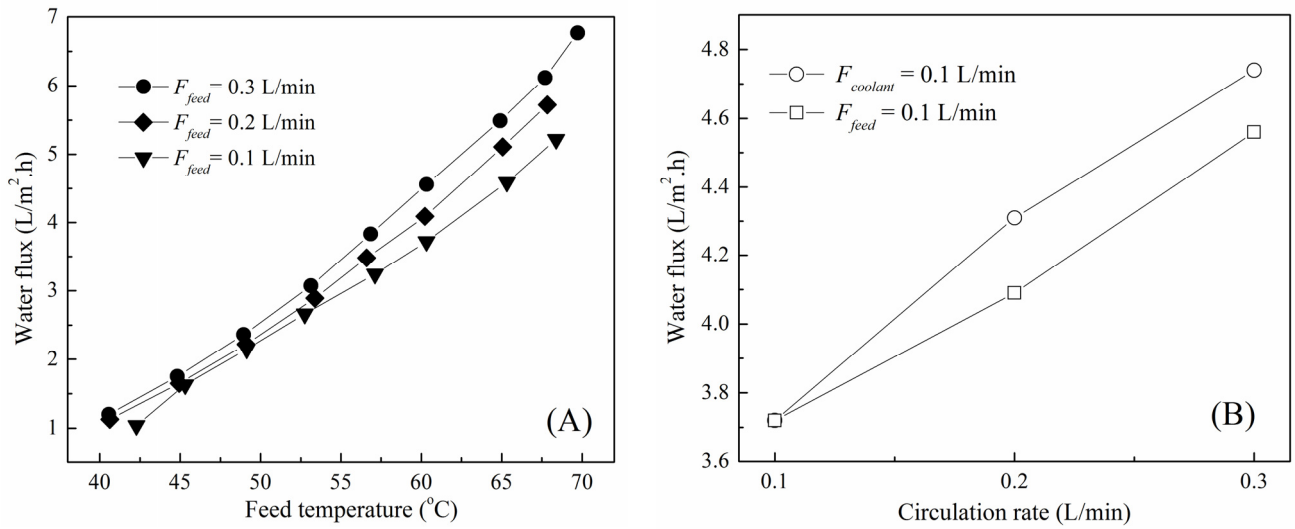

Figure 1: The influences of feed temperature and circulation rates on water flux of the AGMD process with the synthetic NaCl solution at: (A) coolant temperature $T_{coolant}$ = 25 °C, coolant circulation rate $F_{coolant}$ = 0.1 L/min, and (B) feed temperature T_{feed} = 60 °C, coolant temperature $T_{coolant}$ = 25 °C

3.2. Membrane fouling during AGMD with actual seawater feed

The AGMD process with raw seawater feed experienced severe membrane fouling. During the first three hours of the AGMD process with raw seawater feed, the process water flux was stable at 5.5 L/m^2.h (Fig. 2A). Subsequently, the process water flux gradually decreased to 3.5 L/m^2.h after 14 hours of the operation (Fig. 2A). The gradual decline in the process water flux was attributed to the accumulation of organic matters in the raw seawater feed on the membrane surface. Because most organic matters present in seawater (e.g. humic acids and oil) are hydrophobic [12], they are prone to attach to the hydrophobic PTFE membrane used in the AGMD system due to their hydrophobic interaction. Indeed, the SEM images of the membrane at the completion of the process with raw seawater feed also revealed that most of the membrane surface has been covered by amorphous deposition (Fig. 3A&B). When organic matters accumulated on the membrane, they limited the membrane active surface for water evaporation, increased temperature and concentration polarization, and therefore reduced the process water flux.

Pre-filtration of raw seawater with 0.45 μm paper filters helped sustain the water flux of the AGMD process. The AGMD process with pre-filtered seawater feed obtained a stable water flux throughout 14 hours of operation (Fig. 2A). Pre-filtering seawater feed with 0.45 μm paper filters removed all suspended particles with sizes lager than 0.45 μm. The cake layers formed on the paper filters also facilitate the removal of organic matters smaller than the size of the filters. Therefore, during 14-hour AGMD operation with the pre-filtered seawater feed, there was only the influence of feed salinity on the process water flux. After 14 hours, the AGMD process had extracted 1.0 L of distillate from 10 L of pre-filtered seawater feed (i.e. equivalent to a water recovery of 10 %). During an MD process of seawater feed at low water recovery, the influence of increased feed salinity on water flux is unnoticeable [4, 13].

Membrane scaling caused by the precipitation of sparingly soluble salts was a serious challenge to the AGMD process of pre-filtered seawater feed at high water recoveries. As demonstrated in Fig. 2B, at water recoveries below 70 %, increased feed salinity due to the extraction of fresh water from the feed resulted in a slight decrease in the process water flux. Water flux decreased from 5.5 to 4 L/m^2.h as water recovery was increased from zero to 70 %. According to the Eq. 4, increasing feed salinity reduces the water vapor pressure of the feed stream at the membrane surface, thus reducing water flux. It is, however, noteworthy that the influence of increased feed salinity on water flux in MD processes is negligible as compared to that in seawater RO desalination [7, 11]. When water recovery of the AGMD process exceeded 70%, water flux rapidly dropped from 4 L/m^2.h to almost zero. At the water recovery above 70%, the pre-filtered seawater feed was concentrated more than 3.3 times. The sparingly soluble salts in the feed (e.g. $CaSO_4$, $CaCO_3$) might have reached their saturation limits, and precipitated on the membrane. The SEM analysis of the membrane surface at the

end of the experiment showed well-shaped salt crystals on the membrane surface (Fig. 3C). The morphology of salt crystals obtained in this study is consistent with those reported by Nghiem et al. [14] and Duong et al. [9].

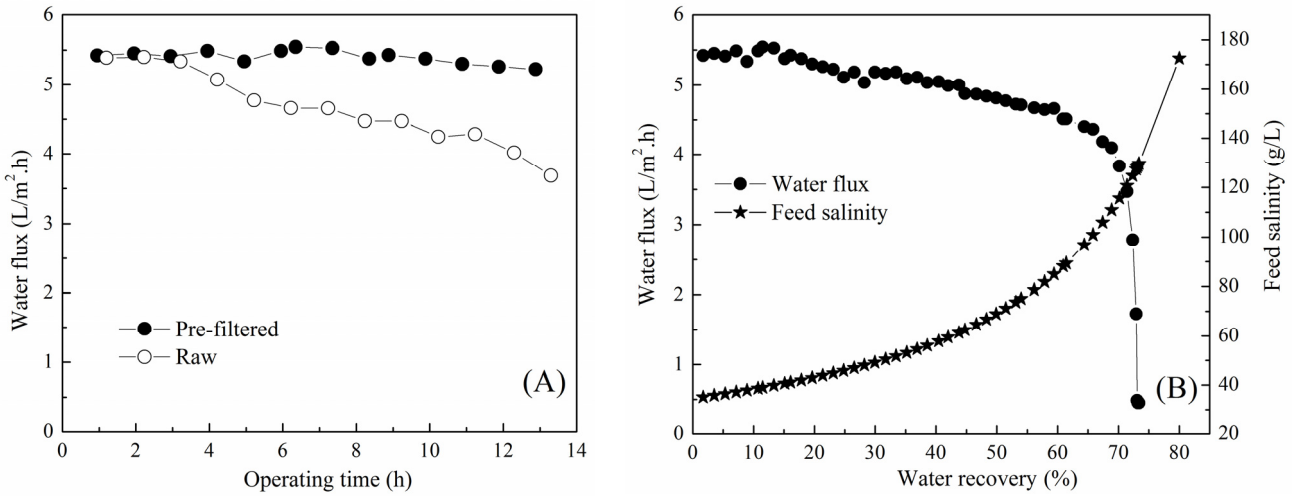

Figure 2: (A) Water flux of the AGMD process with raw and pre-filtered seawater feed, and (B) water flux and feed salinity versus water recovery during the durable AGMD process of pre-filtered seawater feed. Operating conditions: feed temperature T_{feed} = 60 °C, distillate temperature $T_{distillate}$ = 25 °C, water circulation rates F_{feed} = $F_{distillate}$ = 1.0 L/min

The observation of distillate conductivity confirmed that the AGMD process could produce ultrapure water from seawater. During the AGMD process with the pre-filtered seawater feed before the onset of membrane scaling, the distillate conductivity was always below 60 μS/cm. This conductivity was similar to that of deionized (DI) water. Following the scale formation on the membrane surface as water recovery exceeded 70 %, the distillate conductivity started to increase. The salt crystals scale formed on the membrane surface altered the membrane hydrophobicity and thus facilitated the intrusion of liquid seawater into the membrane pores. The intrusion of liquid water into the membrane pores also contributed to the flux decline of the AGMD process at water recoveries above 70 % because it reduced the amount of membrane pores available for water evaporation.

3.3. Fouled membrane cleaning with vinegar

Vinegar proved to be an effective cleaning agent for seawater desalination using the AGMD process. Rinsing the scaled membrane at the end of the AGMD process at water recovery above 70 % with vinegar removed most the scale deposition from the membrane surface. The SEM image of the scaled membrane after vinegar cleaning was similar the that of the virgin membrane (Fig. 3A&D). Contact angle measurements of the membrane surfaces also confirmed the efficiency of vinegar cleaning. The contact angle of the virgin membrane was 147° (Fig. 4A). Scale layers formed on the membrane rendered its surface so hydrophilic that the water droplet could not form on the surface for the contact angle measurement. After vinegar cleaning, the contact angle of the scaled membrane was restored to 132° (Fig. 4B). The slight decrease in contact angle of the cleaned membrane compared to that of the virgin membrane was expected. Indeed, Ge et al. [15] also reported slight decreases in membrane contact angle during an MD process with fresh water. The authors believed that the microstructure of the membrane had been altered by the hot water feed. The membrane mean pore size increased after the long operation, hence resulting in decreased contact angle [15].

The results reported here manifest the great potential of AGMD for drinking water provision in small, remote coastal communities in Vietnam. With a simple pre-filtration, seawater AGMD desalination process can produce fresh water of super quality at stable flux until when nearly 70 % of fresh water has been extracted from seawater. The AGMD process can obtain a water flux of about 5 L/m^2.h at feed temperature of 60 °C. Given this water flux, a small AGMD system with 10 m^2 of membrane surface can produce 400 L of drinking water for a daily 8-hour operation. This amount of drinking water is sufficient to meet the demand of small communities with a population of 200 residents. In addition, the main energy source for AGMD is thermal energy which can be sourced from waste heat (i.e. heat

generated from ship engines) and solar thermal energy, which are widely available in Vietnam. Finally, the seawater AGMD process does not require an intensive membrane cleaning procedure to recover the process performance when membrane fouling has occurred. Cleaning the fouled membrane with vinegar, which is a low cost and domestic cleaning agent, can effectively restore the water flux of the fouled membrane. Thus, seawater desalination using AGMD can be a practical solution to fresh water provision in remote coastal areas in Vietnam.

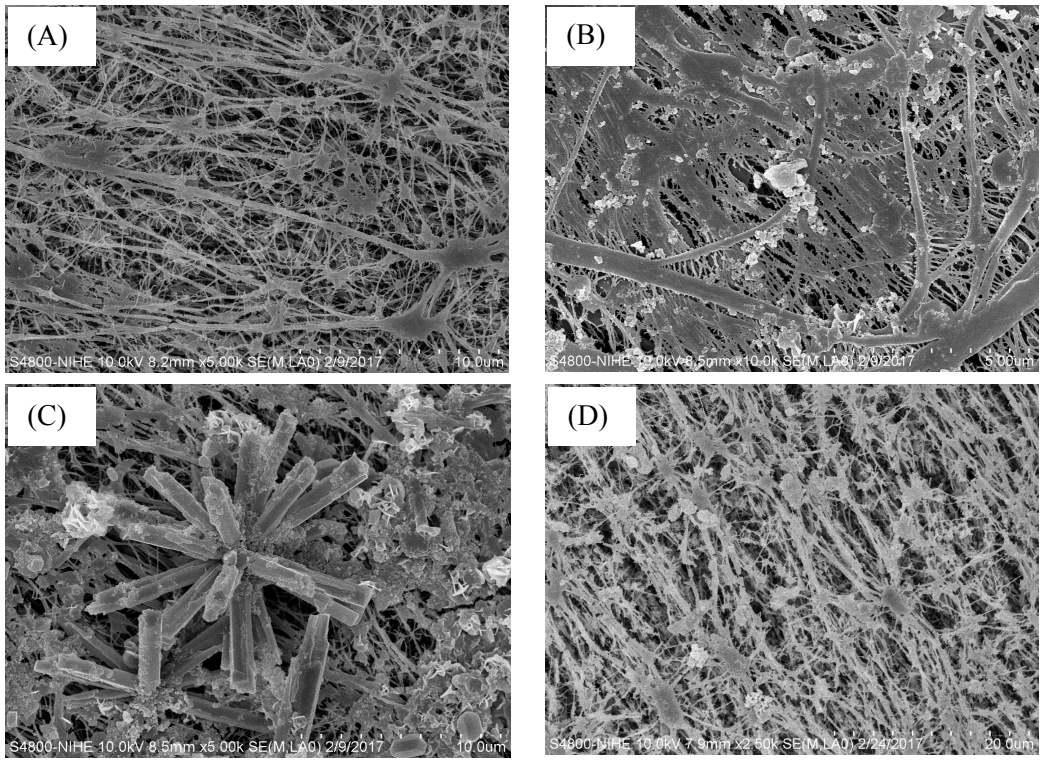

Figure 3: SEM images of: (A) a virgin membrane, (B) membrane fouled with organic matters, (C) membrane scaled with sparingly soluble salts, and (D) the scaled membrane after cleaning with vinegar

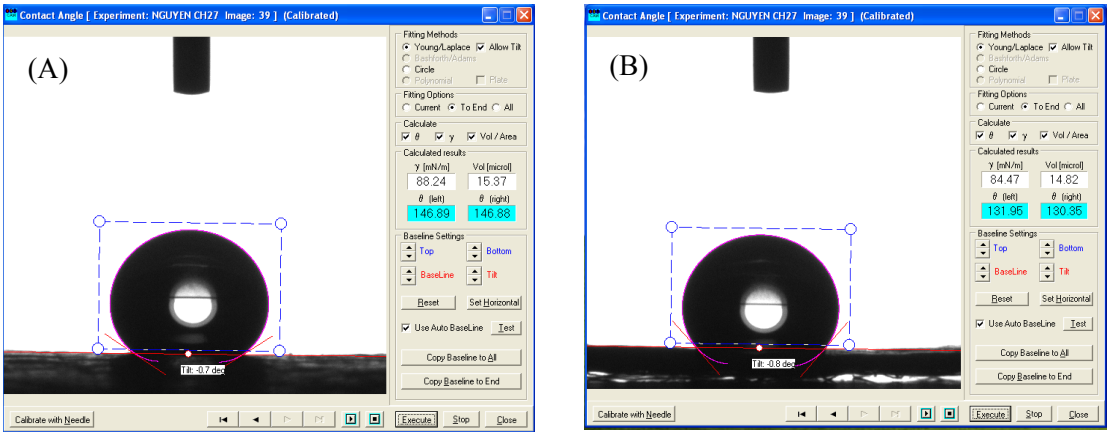

Figure 4: Contact angles of (A) the virgin membrane and (B) the fouled membrane after cleaning with vinegar

4. CONCLUSIONS

Results from this study demonstrate the great viability of seawater AGMD desalination for fresh water provision in remote coastal areas in Vietnam. During the AGMD process of seawater, the operating conditions, particularly feed temperature and circulation rate, strongly affected the process water flux. Operating the process at high feed temperatures and circulation rates was beneficial with respect to water flux. Membrane fouling caused by organic matters in raw seawater feed resulted in a

gradual decrease in the process water flux. Pre-filtration of the seawater feed using paper filters helped eradicate organic matters from the feed, thus sustaining the AGMD process performance. The AGMD process with the pre-filtered seawater feed could achieve a stable water flux at water recoveries up to 70 %. Operating the AGMD process with the pre-filtered seawater feed at water recoveries above 70 % experienced severe membrane scaling due to the precipitation of sparingly soluble salts when the seawater feed was over concentrated. The scale formation significantly reduced the process water flux. Subsequent membrane cleaning with vinegar effectively removed nearly all scale particles from the membrane surface, thus restoring the scaled membrane back to the conditions which are similar those of a virgin membrane.

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