

Assessing the Performance and Fouling of Polytetrafluorethylene Hydrophobic Membrane for the Treatment of Oil-Polluted Seawater Using AGMD



A. E. Mansi, Y. Elhenawy, Maggie Gad, Noran Ashraf, Ahmed Eteba, and M. Bassyouni

1 Introduction

Bilgewater is a chronic source of oil pollution that is being increasingly discharged to the marine ecosystem. Bilgewater is complex shipboard wastewater comprising mainly seawater in addition to various ship pollutants (e.g., fuels, lubrication oils, solid particulates, etc.) [1]. The environmental and ecological impacts of ship fluids discharge into the ocean are very far-reaching. Coastal plants are very vulnerable to the hydrocarbon residues in the bilgewater. The heavy residues can accumulate in the

A. E. Mansi · M. Gad · N. Ashraf · M. Bassyouni (✉)
Department of Chemical Engineering, Faculty of Engineering, Port Said University, Port Said 42526, Egypt
e-mail: m.bassyouni@eng.psu.edu.eg

A. E. Mansi · M. Bassyouni
Center of Excellence in Membrane-Based Water Desalination Technology for Testing and Characterization, Port Said 42526, Egypt

Y. Elhenawy
School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg 2000, South Africa

Department of Mechanical Power Engineering, Faculty of Engineering, Port Said University, Port Said 42526, Egypt

Y. Elhenawy
e-mail: dr_yasser@eng.psu.edu.eg

A. Eteba
Civil Engineering Department, Higher Future Institute of Engineering and Technology, El Mansoura, Egypt

M. Bassyouni
East Port Said University of Technology, Saini, Port Said 45632, Egypt

soil and adversely affect its permeability. Marine mammals are as well threatened by the bilgewater pollutants, they are susceptible to accidental consumption of tar residuals and physical contact with oils all of which cause severe health conditions. Therefore, the treatment of bilgewater is mandatory for sustaining the ecosystem and for potential reutilization for the irrigation of coastal plants [2]. Minimization or elimination of ship fluids discharge to the ecosystem adheres to the Sustainable Development Goals (SDGs) by sustaining the marine life, the coastal plants, and the water ways (Goals No. 14, 15, and 6 respectively).

Various treatment technologies have been proposed for the treatment of oil-contaminated seawater including electro dialysis, adsorption, coagulation and floatation, photodegradation, and chemical oxidation [3, 4]. Among the proposed processes, membrane technologies exhibited outstanding performance in terms of effluent quality and process cost [5–7]. Pressure-driven membrane technologies such as ultrafiltration and reverse osmosis have been reported widely in the literature for the treatment of oil-polluted wastewater [8–11]. However, the presence of oil in water causes severe fouling and subsequent deterioration of the membrane performance [12–15]. Previous studies tested ultrafiltration units for the treatment of bilgewater. Crossflow pilot ultrafiltration experiments were conducted for the treatment of oily bilgewater containing 6100 Total dissolved solids (TDS) and 27.2 ppm oil. The oil content in the obtained permeates was reduced by 80% however, no considerable removal of salts was observed [16–18].

Membrane distillation processes are generally utilized for the elimination of salts from oily-saline wastewater. Membrane distillation is a thermally driven membrane process that can utilize waste energy or renewable energy to desalinate water [19, 20]. Capillary polypropylene commercial membrane (Accurel PP V8/2 HF) was tested in direct contact membrane distillation (DCMD) for the treatment of bilgewater from a port in the Baltic Sea (TDS ~ 6500 ppm, average oil = 40 ppm). Excellent separation efficiency was achieved, and the obtained distillate was practically freshwater [21, 22]. Treatment of high-oil content bilgewater can foul MD membranes and cause severe wetting. A recent study investigated the treatment of bilgewater containing 360 ppm oil and TDS of 3700 ppm using a capillary polypropylene membrane in DCMD configuration. Oil rejection was virtually 100% however, salt rejection was only ~ 10% indicating severe membrane wetting. The authors included an ultrafiltration pretreatment step to minimize the oil load on the MD module from 360 to 10 ppm. The permeate quality was enhanced greatly and freshwater was obtained [23, 24].

In this work, hydrophobic polytetrafluoroethylene membrane is—tested for the treatment of bilgewater from a ship berth in the Suez Canal using air gap membrane distillation (AGMD). Membrane characterization is carried out to assess the fouling behavior and separation efficiency of the membrane. To our knowledge, no previous study tested the treatment of bilgewater in AGMD configuration using polytetrafluoroethylene and investigated the fouling behavior on the membrane surface.

2 Materials and Methods

Polytetrafluoroethylene (PTFE) membrane was obtained from STERLITECH USA, the membrane characteristics are shown in Table 1. Bilgewater was collected from a ship berth in the city of Port Said, Egypt.

Membrane characterization was carried out to assess the fouling behavior of the membrane-bilgewater system. Surface morphology was analyzed by scanning electron microscopy (TESCAN MIRA). The samples were fixed on pieces of conductive carbon tape and coated with 10 nm of silver using argon plasma sputtering. Surface composition was detected before and after experimental bilgewater treatment by using energy dispersive X-ray (OXFORD Xplore) using a landing energy of 15 keV and a beam current of 100 picoamps. The active functional groups and organic fouling bonding to the membrane were detected by Fourier transform infrared spectroscopy (FTIR) (BRUKER ALPHA II equipped with ATR crystal). The surface roughness of the membrane was determined by atomic force microscopy (Nanosurf FlexAFM).

Membrane performance was tested using a pilot-scale AGMD system. A graphical illustration of the system is shown in Fig. 1 and a photograph of the actual system is shown in Fig. 2. The system comprises four main sections:

1. Hot feed cycle.
2. Cooling fluid cycle.
3. The membrane unit
4. Monitoring and control.

The separation efficiency of the PTFE membrane was tested in the system described. The membrane used was 10 cm × 10 cm. The feed temperature is 70 °C and the cooling temperature was fixed at 20 °C. The feed flow rate was 2 l/min.

The purification efficiency was determined by measuring the TDS, TSS, Turbidity, and chemical oxygen demand (COD) of the bilgewater before and after treatment. TDS and TSS were measured by conductivity measurement and gravimetric method respectively. The COD was measured by the dichromate method using spectrophotometry. The error in COD measurements due to the presence of a high concentration of chloride ion in bilgewater was compensated by diluting the sample and using a COD kit that contains mercuric (II) sulfate. The flux, J (l/m^2 h) was calculated using the following equation (Eq. 1):

Table 1 Characteristics of the membrane utilized in this study

| | |
|------------------------|-------------------------|
| Membrane material | Polytetrafluoroethylene |
| Support layer material | Polypropylene |
| Average pore size | 0.45 μ m |
| Membrane porosity | 65% |
| Membrane thickness | 127 μ m |
| Water contact angle | 127° |
| Liquid entry pressure | 0.76 bar |

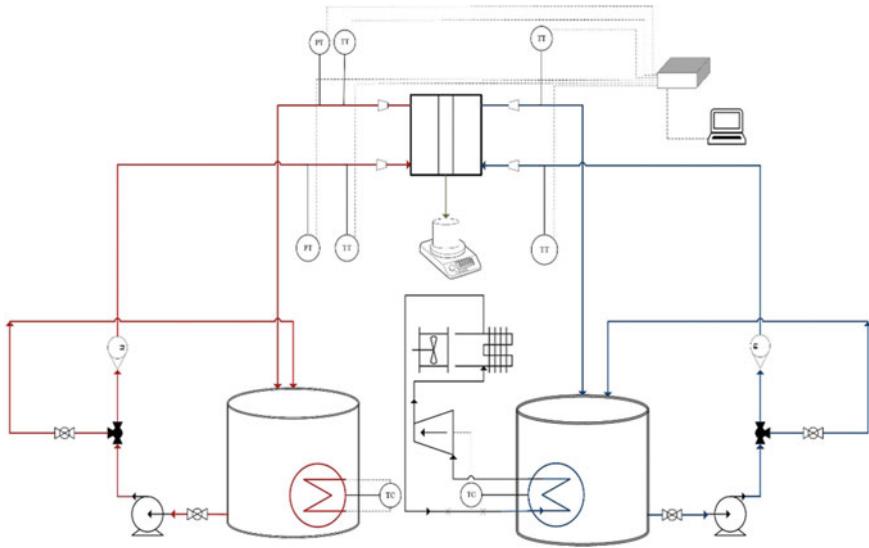


Fig. 1 Illustration of the pilot MD module utilized in this work. The red lines represent the hot fluid cycle, the blue lines represent the cold fluid cycle, and the dashed lines represent the electrical connections. The abbreviations “PT”, “TT”, “TC”, and “FI” are “pressure transmitter”, “temperature transmitter”, “temperature control”, and “rotameter”, respectively

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

where (W) is the permeate mass, (ρ) is the density (A) is the area of the membrane, and (Δt) is the experiment time.

3 Results and Discussion

3.1 Surface Morphology and Surface Composition

Scanning electron microscope images of the PTFE membrane before and after the treatment of bilgewater are shown in Fig. 3. In MD operation, the surface hydrophobicity of the membrane is crucial to prevent the deposition of salts and membrane wetting. In addition to the presence of the hydrophobic C-F function group, the presence of a rough surface at the Cassie-Baxter state may capture micro air bubbles and minimize wetting (Fig. 3). However, higher roughness may induce the deposition of inorganic scales. The morphology of the PTFE membrane (Fig. 4, left) indicated the presence of surface roughness. Deposition of salts is obvious (Fig. 4 right) after the treatment of bilgewater. The size of the deposits is variable, coarse salt particles



Fig. 2 The actual experimental system utilized in this study; 1—synthetic PW tank, 2—feed pump, 3—rotameter, 4—thermocouples, 5—pressure transmitters, 6—membrane module, 7—cooling water pump, 8—cooling water tank, 9—refrigeration cycle, 10—data logger, 11—electricity panel

are observed at magnifications of 1 kx and 5 kx. At a magnification of 45 kx, the attachment of particles to the membrane surface is evident.

Energy dispersive X-ray analyses were performed to assess the nature of the deposited particles. EDS analyses of the PTFE membrane before and after treatment are given in Table 2. Elemental mapping of the membrane after treatment is shown in Fig. 5.

The Elemental analysis revealed the presence of a wide variety of salts and minerals in the bilgewater. Sodium and calcium are the most abundant cations while chloride is the most abundant anion. The presence of oxygen may be attributed to the presence of Silicates, iron oxides, or carbonate ions in the bilgewater. The elemental mapping illustrates that sodium ions (which represent the formation of NaCl scales) are distributed uniformly over the membrane surface. However, Calcium ions tend to be present in large deposits or particle aggregates, these observations suggest

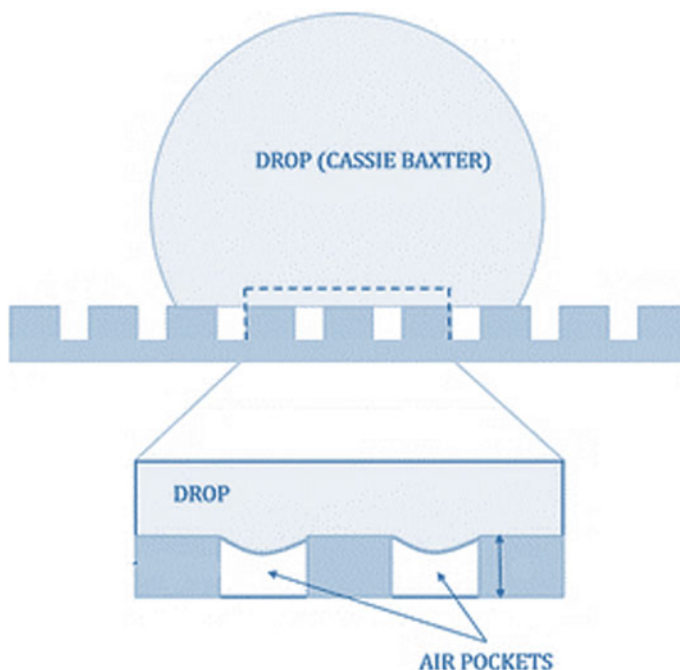


Fig. 3 Illustration of the underwater Cassie-Baxter state

two different scaling mechanisms. Sodium chloride precipitates due to the effect of concentration polarization, while calcium salts normally precipitate from water at higher temperatures and form salt clusters.

3.2 Chemical Structure

The FTIR spectrum was captured within the wave number region of $400\text{--}4000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . The IR absorption spectrum for the PTFE membrane is shown in Fig. 6. The CF_2 characteristic peaks of the symmetric and asymmetric stretching of C–F are observed at 1204 cm^{-1} and 1148 cm^{-1} respectively. Lower wave number CF_2 characteristic peaks of the deformation and rocking modes are observed at 550 cm^{-1} and 640 cm^{-1} respectively. The C–H bending peak at 755 cm^{-1} and the strong C–H stretching peaks at 2850 and 2930 cm^{-1} represent the polypropylene support. The presence of noise in the FTIR chart is due to the trapping of air molecules between the very thin membrane coupon and the ATR crystal.

3.3 Membrane Surface Roughness

Numerous studies have established the relationship between surface roughness and the liquid-repel ability of the membrane surface. Surface roughness was determined by obtaining height images from atomic force microscopy. The membrane was imaged in dynamic force mode using a gold-coated silicone tip with an average resonance frequency of 191 kHz and height of 13 μm . The height color map and 3D height map for a sample area of 225 μm^2 are shown in Fig. 7.

The average line roughness parameter R_a and area roughness parameter S_a were 0.7 μm and 0.73 μm respectively. The height fluctuation ranged from -0.9 to 2.8 μm .

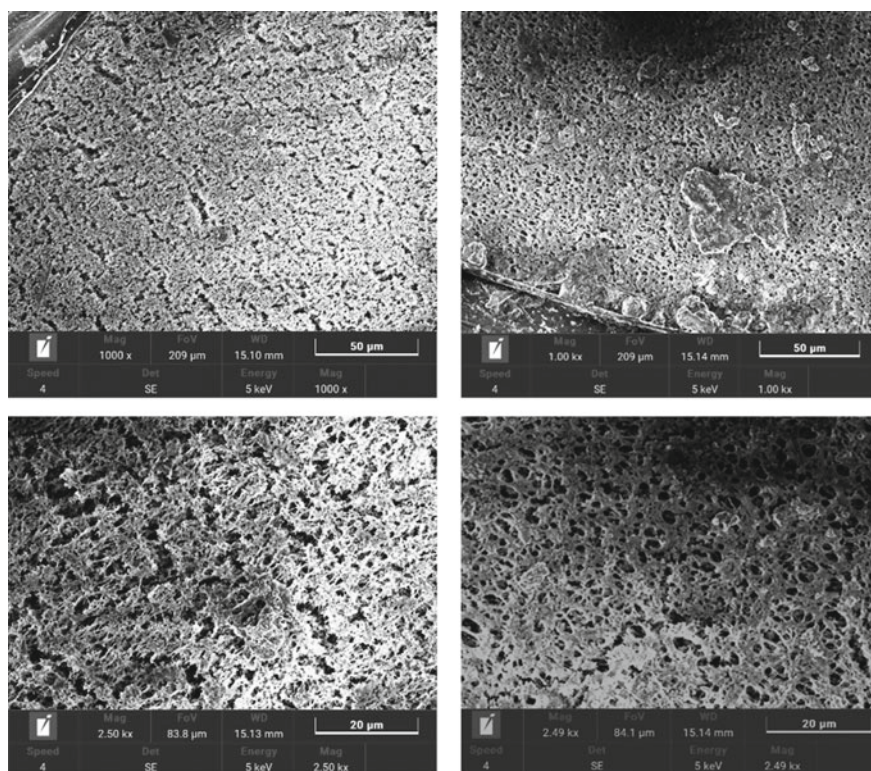


Fig. 4 Field-emission scanning electron microscope images of the pristine PTFE membrane (left) and images of the PTFE membrane after treatment of the bilgewater (right)

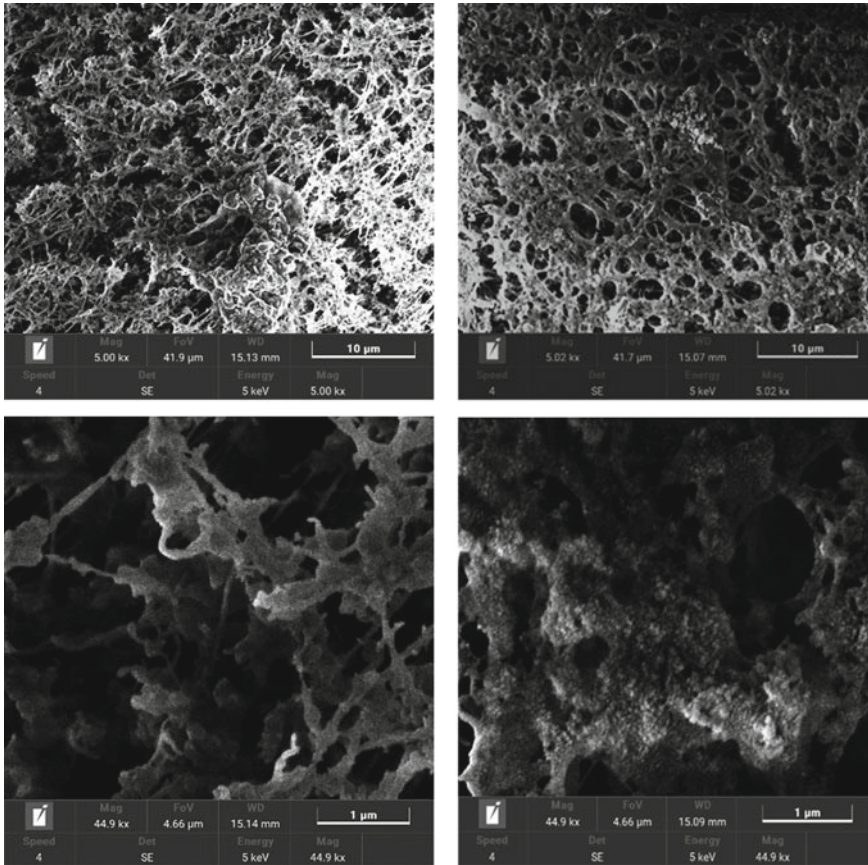


Fig. 4 (continued)

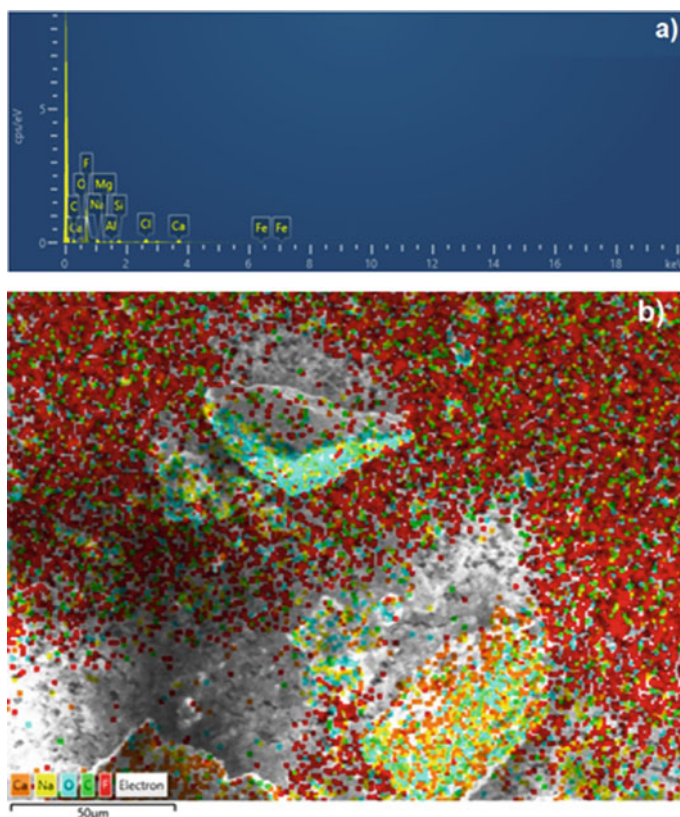
3.4 Membrane Testing Experiment

The membrane flux was approximately stable during the experiment with little fluctuations. The membrane flux and salt rejection percentage are plotted as a function of time and the results are presented in Fig. 8. The initial water flux was $4 \text{ l/m}^2 \text{ h}$. The flux remained stable at $3.4 \text{ l/m}^2 \text{ h}$ during the first hour then deteriorated to $2.6 \text{ l/m}^2 \text{ h}$ and finally increased again to $3.3 \text{ l/m}^2 \text{ h}$ and remained stable. The initial deterioration in flux is attributed to the initial deposition of foulants on the membrane surface. However, the membrane flux increased again and stabilized due to the widening of pores which is obvious in the SEM images after treatment (Fig. 4, right). The increase in pore size is due to the simultaneous effect of the elevating membrane temperature and the passage of hot water vapor.

Salt rejection was always above 99%. The COD of the permeate was 70% less than that of the feed. The feed and permeate water qualities are given in Table 3.

Table 2 Elemental analysis of the PTFE membrane before and after treatment of bilgewater

| Element | PTFE membrane before bilgewater treatment | | PTFE membrane after bilgewater treatment | |
|---------|---|----------|--|----------|
| | wt% | Atomic % | wt% | Atomic % |
| C | 22.80 | 31.84 | 16.25 | 23.87 |
| F | 77.20 | 68.16 | 63.33 | 58.80 |
| O | NA | NA | 10.40 | 11.47 |
| Na | NA | NA | 3.05 | 2.34 |
| Mg | NA | NA | 0.38 | 0.28 |
| Al | NA | NA | 0.63 | 0.41 |
| Si | NA | NA | 0.99 | 0.62 |
| Cl | NA | NA | 2.03 | 1.01 |
| Ca | NA | NA | 2.27 | 1.00 |
| Fe | NA | NA | 0.68 | 0.21 |

**Fig. 5** Elemental distribution data of the PTFE membrane after bilgewater treatment. **a** The EDS intensity chart and **b** elemental mapping of the membrane surface

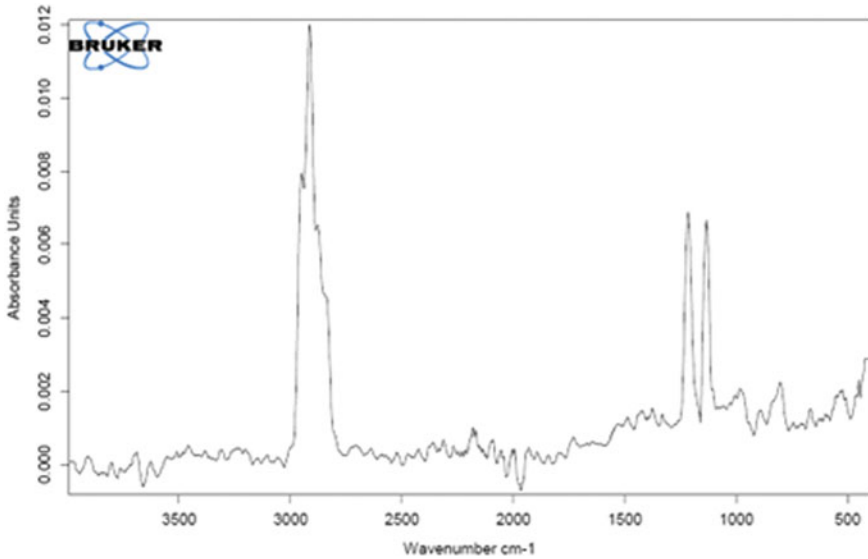


Fig. 6 FTIR absorbance spectrum of the polytetrafluoroethylene membrane

4 Conclusion

An experimental study was carried out to assess the effectiveness of using AGMD for treating saline oil-polluted seawater. Various membrane characteristics were measured and their influence on the membrane performance and fouling tendency were investigated. The membrane morphology was uniform with an equal distribution of pores. Elemental analysis revealed the deposition of inorganic monovalent and divalent salts in addition to a few metal oxides. Sodium and calcium were the most abundant cations and chlorine was the most abundant anion. Calcium formed large aggregates which on long-term operation will clog the pores and damage the membrane and is, therefore, recommend being removed in a pretreatment step. Surface topography showed high variation in features height which enhanced the roughness. The average linear roughness parameter was $0.7 \mu\text{m}$. AGMD process using PTFE membrane showed an excellent solids rejection above 99% and COD minimization up to 70%. The membrane flux increased on increasing the membrane pore size and salt rejection was not affected considerably. The initial water flux was $4 \text{ l/m}^2 \text{ h}$ and the flux stabilized after 3 h at $3.3 \text{ l/m}^2 \text{ h}$. The membrane distillation process is not energy intensive and can be driven by waste heat or renewable energy sources which renders the process applicable in ships, ports, or coastal treatment facilities. The process showed promising results in handling such a challenging feed and further elaboration of the process parameters and membrane materials is recommended.

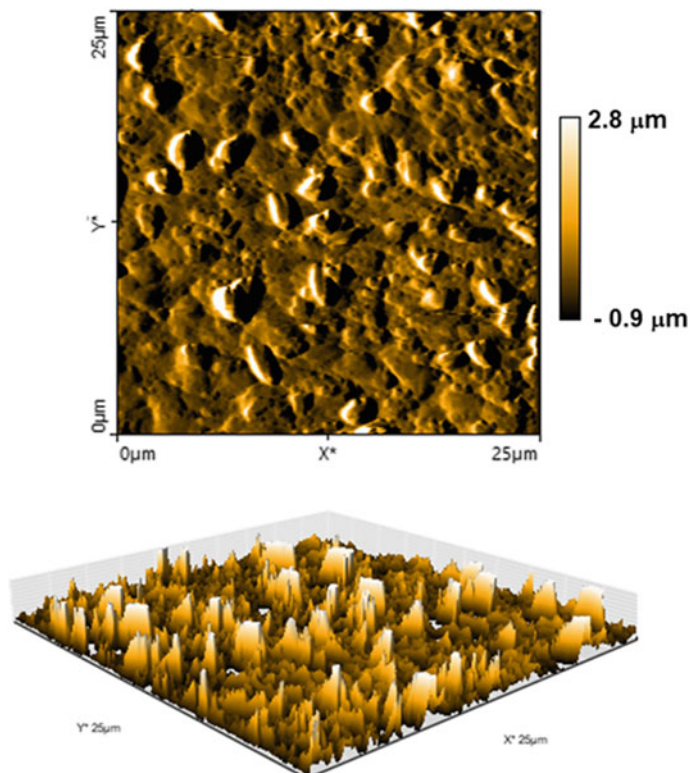


Fig. 7 Atomic force microscopy height images featuring the topography of the membrane surface

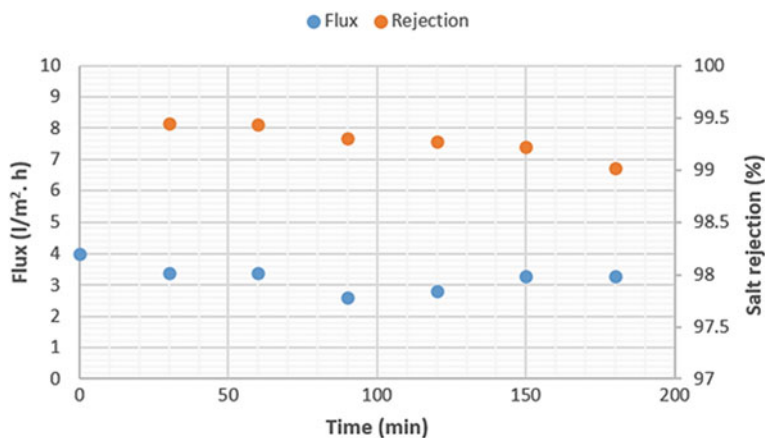


Fig. 8 AGMD performance of the PTFE membrane against the oily-saline bilgewater. The feed and cold temperatures were 70 ± 0.5 °C and 20 ± 0.5 °C respectively. The cross flow velocity of the feed was 0.167 m/s

Table 3 Water quality of the feed and the permeate

| Parameter | Bilgewater | Permeate |
|--------------|-------------|----------------|
| TDS | 16,046 ppm | 130 ppm |
| TSS | 1305.9 ppm | Not detected |
| Conductivity | 15.73 ms/cm | 115 μ s/cm |
| Turbidity | 4.4 NTU | 0.8 NTU |
| COD | 537 ppm | 161 ppm |

5 Recommendations

Membrane distillation is a recent technology that is still at its early stages. It is therefore recommended to test the AGMD system at different operating conditions (temperature, flow rate, etc.). Different membrane materials can yield distinctive results; PTFE membrane showed outstanding results however, modification to the intrinsic membrane characteristics (e.g. porosity, hydrophobicity, etc.) can improve the process sustainability. The AGMD system offers low thermal conduction losses, yet this comes at the expense of reducing the water flux. The air gap configuration should be compared with other configurations such as direct contact or vacuum membrane distillation to assess the most efficient configuration. The behaviour of the system varies greatly with the wastewater to be treated. Collecting different samples of bilge water from different locations and perform a comparative study should provide insights into the effect of feed characteristics on the process effectiveness.

Acknowledgements The researchers would like to acknowledge the assistance provided by the Science and Technology Development Fund (STDF) for funding the project, No. 41902 (Center of Excellence in Membrane-based Water Desalination Technology for Testing and Characterization

References

- Özkaynak ÖH, İçemer GT (2021) Determining the bilge water waste risk and management in the Gulf of Antalya by the Monte Carlo method. *J Air Waste Manag Assoc* 71(12):1545–1554
- Fletcher LM, Zaiko A, Atalah J, Richter I, Dufour CM, Pochon X, Wood SA, Hopkins GA (2017) Bilge water as a vector for the spread of marine pests: a morphological, metabarcoding and experimental assessment. *Biol Invasions* 19(10):2851–2867
- Eteba A, Bassyouni M, Saleh M (2022) Modified coal fly ash for textile dye removal from industrial wastewater. *Energy Environ.* 0958305X221130536
- Fouad K, Alalm MG, Bassyouni M, Saleh MY (2020) A novel photocatalytic reactor for the extended reuse of W-TiO₂ in the degradation of sulfamethazine. *Chemosphere* 257(14):127270
- Mansi AE, El-Marsafy SM, Elhenawy Y, Bassyouni M (2022) Assessing the potential and limitations of membrane-based technologies for the treatment of oilfield produced water. *Alex Eng J* 68(50):787–815
- Elhady S, Bassyouni M, Mansour RA, Elzahar MH, Abdel-Hamid S, Elhenawy Y, Saleh MY (2020) Oily wastewater treatment using polyamide thin film composite membrane technology. *Membranes* 10(5):84

7. El-Mehalmey WA, Safwat Y, Bassyouni M, Alkordi MH (2020) Strong interplay between polymer surface charge and MOF cage chemistry in mixed-matrix membrane for water treatment applications. *ACS Appl Mater Interfaces* 12(24):27625–27631
8. Sandid AM, Bassyouni M, Nehari D, Elhenawy Y (2021) Experimental and simulation study of multichannel air gap membrane distillation process with two types of solar collectors. *Energy Convers Manag* 243(14):114431
9. Maddah HA, Alzhrani AS, Bassyouni M, Abdel-Aziz MH, Zoromba M, Almalki AM (2018) Evaluation of various membrane filtration modules for the treatment of seawater. *Appl Water Sci* 8(6):1–13
10. Elhenawy Y, Moustafa GH, Attia AM, Mansi AE, Majozi T, Bassyouni M (2022) Performance enhancement of a hybrid multi effect evaporation/membrane distillation system driven by solar energy for desalination. *J Environ Chem Eng* 10(6):108855
11. Ali I, Bamaga OA, Gzara L, Bassyouni M, Abdel-Aziz MH, Soliman MF, Drioli E, Albeirutty M (2018) Assessment of blend PVDF membranes, and the effect of polymer concentration and blend composition. *Membranes* 8(1):13
12. Elrasheedy A, Rabie M, El-Shazly A, Bassyouni M, Abdel-Hamid SMS (2021) El Kady, MF Numerical investigation of fabricated MWCNTs/polystyrene nanofibrous membrane for DCMD. *Polymers* 13(1):160
13. Alhathal Alanezi A, Bassyouni M, Abdel-Hamid SM, Ahmed HS, Abdel-Aziz MH, Zoromba MS, Elhenawy Y (2021) Theoretical investigation of vapor transport mechanism using tubular membrane distillation module. *Membranes* 11(8):560
14. Soliman MF, Abdel-Aziz MH, Bamaga OA, Gzara L, Sharaf F, Al-Sharif M, Bassyouni Z, Ahmad R (2017) Performance evaluation of blended PVDF membranes for desalination of seawater RO brine using direct contact membrane distillation. *Desalin Water Treat* 63(6):6–14
15. Tomczak W, Gryta M (2021) Application of ultrafiltration ceramic membrane for separation of oily wastewater generated by maritime transportation. *Sep Purif Technol* 261(9):118259
16. Gryta M (2020) Bilge water separation by membrane distillation. *Sep Purif Technol* 237(38):116332
17. Kalla S (2021) Use of membrane distillation for oily wastewater treatment—a review. *J Environ Chem Eng* 9(1):104641
18. Magnusson K, Jalkanen JP, Johansson L, Smailys V, Telemo P, Winnes H (2018) Risk assessment of bilge water discharges in two Baltic shipping lanes. *Mar Pollut Bull* 126(34):575–584
19. Bilgili MS, Ince M, Tari GT, Adar E, Balahorli V, Yildiz S (2016) Batch and continuous treatability of oily wastewaters from port waste reception facilities: a pilot scale study. *J Electroanal Chem* 760(1):119–126
20. Lu D, Liu Q, Zhao Y, Liu H, Ma J (2018) Treatment and energy utilization of oily water via integrated ultrafiltration-forward osmosis–membrane distillation (UF-FO-MD) system. *J Membr Sci* 548(32):275–287
21. Ahmad NA, Goh PS, Abdul Karim Z, Ismail AF (2018) Thin film composite membrane for oily waste water treatment: recent advances and challenges. *Membranes* 8(4):86
22. Andrés-Mañas JA, Ruiz-Aguirre A, Ación FG, Zaragoza G (2018) Assessment of a pilot system for seawater desalination based on vacuum multi-effect membrane distillation with enhanced heat recovery. *Desalination* 443(12):110–121
23. Couto CF, Lange LC, Amaral MCS (2018) A critical review on membrane separation processes applied to remove pharmaceutically active compounds from water and wastewater. *J Water Process Eng* 26(19):156–175
24. Damtie MM, Kim B, Woo YC, Choi JS (2018) Membrane distillation for industrial wastewater treatment: studying the effects of membrane parameters on the wetting performance. *Chemosphere* 206(33):793–801