

# Treatment of Brackish-Water Reverse Osmosis Brine Using Only Solar Energy

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# Ibrahim Abdallah

Associate Director of Wastewater Testbeds **Civil & Environmental Engineering NSF-NEWT** Rice University 6100 Main St., MS 6398 Houston, TX 77251-1892 P: 573.466-3837 Email: Ibrahim.A.Abdallah@rice.edu

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The manuscript introduces an experimental work for treating high-salinity brine from reverse osmosis desalination technology at El-Paso, Texas using a nanophotonics solar membrane distillation reactor for the first time. The proposed technology provides low-cot solution using only the solar energy for treating high salinity waters, and is considering a potential solution towards zero/minimum liquid discharge.

1	Treatment of Brackish-Water Reverse Osmosis Brine Using Only Solar
2	Energy
3	Ibrahim A. Said <sup>1,2*</sup> , Naomi Fuentes <sup>1</sup> , Ze He <sup>1,2</sup> , Ruikun Xin <sup>1,2</sup> , Kuichang Zuo <sup>1,2</sup> ,
4	W. Shane Walker <sup>1,3</sup> , and Qilin Li <sup>1, 2*</sup>
5 6	<sup>1</sup> Nanotechnology-Enabled Water Treatment Center (NEWT), Rice University, MS 6398, 6100 Main Street, Houston 77005, United States
7 8	<sup>2</sup> Department of Civil and Environmental Engineering, Rice University, MS 519, 6100 Main Street, Houston 77005, United States
9 10	<sup>3</sup> Department of Civil Engineering, The University of Texas at El Paso, El Paso, TX 79968-0513, United States
11	*Corresponding authors: Said (dr.ibrahim.a.said@gmail.com) & Li (qilin.li@rice.edu)
12	

## 13 Abstract

Posttreatment of brine produced by reverse osmosis (RO) is a great challenge as it often requires 14 high energy input and works at extreme operating conditions. In this study, brine from a RO 15 plant in El Paso, TX USA was successfully treated using pilot-scale nanophotonics enhanced 16 solar membrane distillation (NESMD) system. The novel NESMD reactor has a nanophotonic 17 membrane surface area of 0.2 m<sup>2</sup> and an internal heat recovery system to recover latent heat 18 released during vapor condensation. By utilizing a sweeping gas operational mode under real 19 solar irradiation (585-827 W/m<sup>2</sup>), the NESMD realized successful desalination of RO brine with 20 membrane flux reaching 0.45-0.65 kg m<sup>-2</sup> hr<sup>-1</sup> and total dissolved solids (TDS) removal greater 21 22 than 99.5% without external heat condenser. The decrease in the feed flow rate to the evaporation channel of the NESMD system led to increasing the gained output ratio (GOR) from 23 24 0.35 to 0.62. To the best of our knowledge, this is the largest photothermal reactor utilized for the desalination of real RO brine under practical solar irradiation. Compared with conventional 25 26 brine treatment processes that require high temperature or pressure, the NESMD desalinates RO brine at a near-ambient temperature and pressure with free solar energy, providing a promising 27 approach for water desalination, and RO brine posttreatment. 28

29 Keywords

30 Solar membrane distillation; pilot-scale; solar irradiation; RO brine; water desalination

#### 32 **1. Introduction**

In recent decades, because of the large gap in water demand and supply, water scarcity has been 33 a severe threat to the development of human society. In the latest version of the global risk report 34 by the World Economic Forum, the water crisis is considered one of the top risks in terms of 35 both likelihood of occurring in the next decade and the severity of its impact (1). Unlike other 36 37 vital commodities such as oil or wheat, water has no alternatives in most situations. Moreover, water is crucial for most productions people are relying on, ranging from food, goods, electricity 38 39 to manufactured products [2]. According to the analysis of world water demand and supply by the International Water Management Institute (2), not only North Africa and West Asia (NAWA) 40 41 but also some of the major populated countries, like India and China, are or will be suffering from water deficit. The amount of the affected population is expected to increase continuously. 42 Even in some regions not suffering water scarcity on an annual basis, the affordability of water 43 shows an extreme intra-annual variation due to the seasonal runoff patterns. In a "blue water" 44 45 scarcity map modeled by Mekonnen (3), two-thirds of people face freshwater scarcity at least one month per year. As a result of water scarcity to such an extent, the cost of drinking waters is 46 exaggerated in some regions. For example, the cost of sufficient municipal drinking water can be 47 11% to 112% of the typical household income across sub-Saharan Africa (4). An alternative 48 solution for providing drinking water is desalination (5-7). Desalination technologies (including 49 thermal processes such as multi-effect distillation and multistage evaporation and pressure-50 driven processes such as nanofiltration and reverse osmosis) have been successfully 51 implemented at various scales to purify and desalinate a wide range of source waters (8-10). 52

Reverse osmosis (RO) consumes 1.5 to 2.5 kWh/m<sup>3</sup> to desalinate seawater; it requires pretreatment to control membrane fouling and scaling. In addition, water recovery of RO desalination systems is between 50 and 85% (depending on feed water quality), and for inland plants, disposal of the brine poses a major challenge and may be very costly.

The State of Texas, USA is a pioneer in utilizing brackish groundwater as a municipal water supply. As of 2006, there were 38 inland brackish water desalination plants in Texas in operation with a total design capacity of 52.3 MGD. These plants dispose of their brines by discharging to surface water, municipal sewer, or evaporation ponds, or in rare situations, the brine can be used for land application (11, 12). Considerations with brine disposal include cost and potential negative impacts on the receiving water body, municipal wastewater treatment plant, or soil quality. The 27.5 MGD Kay Bailey Hutchison brackish groundwater RO plant in El Paso, TX USA started operation in 2007 and the 12 MGD San Antonio Water System (SAWS) brackish groundwater RO plant both use deep-well injection for brine disposal, which incur a large capital cost.

Membrane distillation (MD) is a promising thermal-based membrane technology that realizes the 67 separation of two aqueous solutions by allowing vapor passage of the more volatile component 68 through a hydrophobic microporous membrane under a temperature gradient across the 69 membrane. The hydrophobicity of the membrane allows only the vapor transfer of the volatile 70 liquid, whereby a liquid-vapor interface is formed. Membrane distillation can turn any source of 71 water into clean water such as hypersaline water, oil and gas produced waters, surface water, 72 73 groundwater, seawater, RO concentrate brines, irrigation drainage water, and other industrial wastewaters. MD works at lower operating temperatures than those of conventional thermal 74 technologies, has a modular configuration and structure that can be easily scaled up or down in 75 76 treatment capacity, and has relatively low capital costs. Desalinating using a renewable energy 77 source to recover freshwater while minimizing liquid waste disposal at low cost is very attractive for economic, environmental, and regulatory reasons. 78

79 We propose a solar-powered treatment technology for the brine stream of reverse osmosis using nanophotonics enhanced solar membrane distillation (NESMD) (13-15). The proposed process 80 81 efficiently uses sunlight instead of electricity from a power grid or solar photovoltaic panels to drive membrane distillation. It has the benefit of conventional MD processes, i.e., low pressure, 82 low fouling potential, insensitive to total dissolved solids (TDS) concentration, high-recovery, 83 and powered by renewable energy. The susceptibility of the NESMD technology to complex 84 85 aquatic systems like synthetic hypersaline brine, seawater, and oil-produced water was investigated in previous studies (14, 15). In the case of treating oil-produced waters (total 86 dissolved solids (TDS) of 62,000 - 132,000 ppm) (14), the NESMD showed an excellent 87 rejection both of the Dissolved Organic Carbon and dissolved solids; the hydrophilicity of the 88 NESMD membrane was recovered after washing with de-ionized water. Furthermore, the results 89 90 showed that the hydrophilic nanophotonics layer appeared to mitigate the wetting of fouling ions into the hydrophobic PTFE layer of the membrane. In a different study (15), NESMD has been 91 92 employed for treating real seawater from Galveston Bay, Texas, the U.S., and high salinity

simulated feedwaters (TDS of 113 200–200 000 ppm) have been tested for long-term testing under the weather conditions of Houston, Texas. The field testing results and observations showed a stable desalination performance of the NESMD reactor in consecutive 5–8 hour operation cycles without operational problems, with a TDS reduction of  $\geq$ 99.5% in all the field experiments. An average daily membrane flux of  $\geq$ 0.75 L m<sup>-2</sup> h<sup>-1</sup> was achieved at a solar intensity close to 1 kW m<sup>-2</sup> without an external heat exchanger.

In the light of the previous NESMD studies, the NESMD technology is attracting growing commercial interest due to its special advantages, including 1) superb tolerance to high salinity; 2) off-grid and stand-alone desalination technology; 3) operating at low temperature and atmospheric pressure; 4) no need for external condensers, external heaters, and neither solar collection systems; 5) high quality of the permeate water (TDS removal >99.5%). Hence, the authors extended the applications of the NESMD to treating the discharge brine of reverse osmosis plants.

The current study demonstrates the capability of the NESMD technology for increasing 106 desalination water recovery by treating the RO brine from the brackish water RO plant of Kay 107 108 Bailey Hutchison Desalination at El Paso, TX USA. The field experiments have been performed outdoor using real solar irradiance at different solar irradiances and feed velocities. This is 109 110 considered the first time, NESMD was used to treat a discharge real brine from the RO pilot plant. Also, detailed energy balance calculations, for the first time, have been performed to 111 112 quantify the energy losses from the NESMD reactor to the environment and brine. Those kinds of thermal calculations are considered a great step towards efficient operation of the NESMD 113 with higher water production and lower heat losses. The study is unique in terms of providing a 114 unique solution for the brine management associated with the inland brackish RO water as well 115 116 as maximizing the water recovery of the RO plants.

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#### **2.** Materials and Methods

# 119 2.1. Nanophotonics Enhanced Solar Membrane Distillation (NESMD) Reactor: 120 Principles and operational mode

NESMD is a novel solar-thermal technology that uses only solar energy for desalination and wastewater treatment(13, 14). It combines both the membrane distillation and solar-thermal collection in a single module using a nanophotonics microporous membrane that serves both as a solar-thermal collector and a desalination membrane. Figure 1A shows the principles of the

NESMD reactor. The photothermal membrane absorbs sunlight across a wide range of the solar 125 spectrum and converts solar energy to thermal energy. This results in an elevated liquid 126 127 temperature on the feed side of the membrane, and a vapor pressure difference across the membrane, driving vapor transport through the microporous membrane. The condensation of the 128 generated vapor happens on the permeate side of the membrane and generating clean water. The 129 130 operational mode of the NESMD is similar to the conventional MD, while the key difference is the temperature polarization on the feed side. The temperature polarization is reversed in the case 131 of NESMD as the membrane is the source of heating (13, 16, 17). There are four main 132 configurations of MD or NESMD: sweeping gas membrane distillation (SGMD) (18), vacuum 133 membrane distillation (VMD) (19), air gap membrane distillation (AGMD) (20), direct contact 134 membrane distillation (DCMD) (21, 22). All those different MD configurations are distinguished 135 136 by modifications implemented on the permeate side of the microporous membrane. Recently, SGMD is gaining a lot of interest due to its lower mass transfer resistance and higher evaporation 137 efficiency (18). In the case of SGMD, an inert gas stream is used to sweep off the vaporized 138 solution out of the permeate chamber and into an external condenser where the purified solution 139 140 condenses back into a liquid. Hence, in this study, the SGMD using atmospheric air is used in all the NESMD experiments. Implementing SGMD in the current experiments has improved the 141 142 performance of the NESMD. This could be attributed to the that SGMD has a lower level of conductive-membrane heat loss and lower resistance to mass transfer of the created vapor across 143 144 the microporous membrane. A higher airflow rate should be avoided to allow the carried vapor by the air to exchange heat with the bottom channel. Also, a lower airflow rate should be avoided 145 146 to achieve a better mass transfer.

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#### 148 **2.2 Preparation and characteristics of the nanophotonics membranes**

Hydrophobic microporous membranes were acquired from Pall Corp for developing and fabricating the nanophotonic membranes. This pristine membrane is a composite membrane having a thin polytetrafluoroethylene (PTFE) active layer of 34  $\mu$ m thickness on top of polypropylene (PP) support sublayer of 184  $\mu$ m. The porosity and nominal pore size of the membrane are 77% and 0.2  $\mu$ m, respectively.

The Nanophotonics membranes were developed by a relatively thin (25 μm), optically absorbing,
 microporous, and a hydrophilic layer of polyvinyl alcohol (PVA) coating deposited onto the PP

layer. Functionalized carbon black nanoparticles (Cobalt Corporation) with broadband 156 absorption over the entire solar spectrum were dispersed into the PVA solution(17). Following a 157 pretreatment by polydopamine to ensure adhesion. Figure 2 shows scanning electron microscope 158 (SEM) images of the nanophotonics membrane, where the coating is homogenous over the PP 159 layer. More details about the preparation and characterization of the nanophotonics membranes 160 can be found elsewhere(23, 24). Sunlight is converted into thermal heat on the feed side of the 161 membrane through photothermal heating through the light-absorbing nanomaterials embedded in 162 the PP's porous surface layer. The generated temperature gradient across the photothermal 163 membrane results in water evaporation on the feed side and condensation on the permeate side. 164

#### 165

#### 2.3. NESMD Module and Experimental System

NESMD outdoor experiments were conducted using a large-scale plate and frame module with 166 an active membrane surface area of 0.2 m<sup>2</sup>. The NESMD module has external dimensions of 1.1 167 m by 0.38 m with three parallel flow channels (feed/concentrate evaporation, distillate, and feed 168 preheater). Figure 1 (B&C) shows the physical picture of the NESMD module, and Figure 3 169 shows the process flow diagram of the NESMD process. The three flow channels are (1) 170 evaporation of brackish/saline feed (top) channel between the transmittance window and 171 photothermal membrane; (2) distillate condensation and sweeping air (middle) channel between 172 the membrane and heat exchanger foil; (3) heat exchanger (bottom) channel, where the cold 173 feedwater is preheated with latent heat provided by the condensing vapor in the middle channel. 174 The three-channel design facilitates energy recovery and optimization. During the operation of 175 the NESMD module, the cold feedwater flows first to the third chamber (bottom chamber) to be 176 preheated before entering the top feed chamber. The system has two recirculation loops, the top 177 (hot) recirculation loop to recover the sensible heat from effluent hot concentrate from the 178 evaporation channel, while the bottom recirculation loop is compensating the difference in the 179 flowrates between the top and middle channels. The feed flow rate in the bottom channel is 180 181 approximately 5 times higher than the feed flow rate in the evaporation channel. The temperature of the feed over the nanophotonics membrane is increasing with increasing the membrane 182 length(13). Thus, since the water flux increases with increasing module length or hydraulic 183 retention time (13), a baffling design is used in the top and bottom channels to achieve adequate 184 185 channel length while maintaining a reasonable aspect ratio of the module. Both the top and bottom feed-flow channels have been designed and developed with baffles to have a flow cross-186

section of 1.5 mm height by 21.1 mm width and able to achieve a uniform fluid distribution as 187 well as achieving higher heat and mass transfer coefficients in the bottom channel. The plate and 188 frame three-channel module is developed by using two closing plates of high-density 189 polyethylene with UV resistance from ePlastics (thickness 12.7 mm), three high-temperature 190 silicon rubber sheets (thickness 1.58 mm) for sealing between the flow channels, and a Clear 191 Marine Vinyl film from Marine Vinyl Fabric (thickness 0.5 mm) used as condensing surface. 192 193 The middle channel is filled with a Nylon net spacer (1.7 mm thickness and 55% porosity) from McMaster-Carr (9318T41), which is necessary for the mechanical supporting of the membrane 194 and condensing foil but also useful for mixing enhancement. 195



Figure 1. (A). Conceptual illustration of the NESMD reactor. (B) The physical picture of the front view of the NESMD system, including the NESMD reactor and solar panel. (C). The physical picture of the back view of the NESMD reactor, including flow and power control panels.

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Figure 2. SEM surface images of (left) pristine PP of PTFE membrane, (right) photothermal coating of PP layer (100 µm Resolution)



LEGEND			
BV	Ball valve		
СТ	Conductivity transmitter		
FT	Flow transmitter		
HT	Humidity transmitter		
P - 001	Feedwater pump		
P - 002	Recirculating hot feed water pump		
TT	Temperature transmitter		

Figure 3. Process Flow Diagram of NEMD system

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## 203 2.4 Process flow control and monitoring

The process flow diagram of the NESMD system (Figure 3) has two recirculation loops as 204 described in section 2.2. Hence, two magnetic-drive pumps (12 Volts, 100W Pan World 30px) 205 are used - one in the bottom (cold feedwater) loop and one in the top (hot feedwater) loop. A 206 12V DC air compressor (60W RESUN MPQ-904) is used to pump the sweeping air into the 207 middle channel. The measurement system consists of three flow meters for controlling the liquid 208 and airflow rates to the NESMD module, and a series of T-thermocouples (1/16" OD) to track 209 the process temperatures across the three flow channels. All the thermocouples were connected 210 to a data logger with a USB Cable (Onset HOBO UX120-014M). The productivity of the 211 NESMD unit is expressed in terms of water flux, which is defined as the mass 212 of permeate produced per unit membrane area per unit time. Hence, the insulated permeate tank 213 was kept on a weighing balance to monitor the mass of liquid distillate. The increase in the mass 214 215 of distillate was measured at 15 minutes intervals. Furthermore, the total dissolved solids (TDS) and conductivity for the feed and permeate streams were measured using Cole-Palmer Oakton 216 PC2700 Meter probes in all the experiments. 217 A solar power irradiance meter (pyranometer) is connected to a data logger to measure solar 218

- A solar power infadiance meter (pyranometer) is connected to a data togger to measure solar irradiation. The solar meter has an accuracy of  $\pm 10 \text{ w/m}^2$  and is placed in a horizontal plane adjacent to the NESMD reactor. It is worth mentioning that all the environmental parameters, including the ambient temperature, relative humidity, barometric pressure, and ambient wind speed of the air were recorded for every experiment. Table 1 shows the experimental instruments for more details, including the model number, measurement range, application, and accuracy.
- 224
- 225 Table 1. List of experimental instruments

Instrument	Application	Measurement range	Model number	Accuracy
K-type thermocouple	Temperature	-50 to 700 <sup>o</sup> C	TJ36-CASS- 116-12	±0.75%
Water liquid flowmeter	Flowrate	0.003 to 0.3 Liter/min	UXcell - s14070200a m8595	±3% full scale
Air-gas flowmeter	Flowrate	3 to 30	CNBTR51	±3% full scale

		Liter/min		
Solar power irradiance meter	Solar radiation	400 to 1000 nm	TES132	±5% (±10 w/m <sup>2</sup> )
Mass scale	Mass monitoring	0 to 4000 g	CBC8a	±0.1g
Temperature data logger	Temperature	-260 to 1820 °C	Onset HOBO UX120-014M	0.04 <sup>o</sup> C
Humidity meter	Relative humidity (RH)	1% – 99% RH	AcuRite 02067M	±3%RH
Conductivity/TDS meter	TDS and conductivity	Conductivity: 0 - 500 mS/cm TDS: 0.050 ppm (parts per million) to 500 ppt (parts per thousand)	Cole-Palmer Oakton PC2700	Conductivity: ±1% full scale TDS: ±1% full scale
	Ambient Temperature	-30 to 70 <sup>o</sup> C		±0.5 °C
Environmental digital USB data logger	Ambient relative humidity (RH)	0.1 to 99.9% RH	TEKCOPLU S	±3%RH @ 25 <sup>o</sup> C and 10- 99% RH (others ±5%RH)
	barometric pressure	300 to 1100 hpa		±3.5 hpa @ 0 to 65 °C and 10 to 90% RH

## 227 **2.5** Chemical analysis of the RO brine

Two different volume samples of RO brine solutions were used in this study. RO concentrate
solutions were obtained from the Kay Bailey Hutchison (KBH) Desalination Plant (El-Paso TX,
USA). The RO concentrate solutions were used directly in the NESMD module without any
pretreatment. The RO concentrate solutions have a salinity with TDS of 17,440 – 18,550 mg/L
with a conductivity ranging between 18.47 – 19.53 mS/cm.

## 233 **3. Results and discussion**

The main aim of this study is to evaluate the technical feasibility of recovering clean and pure 234 water from the real discharge brine of the RO by implementing NESMD technology. Technical 235 simplicity, high quality permeate water output, standing alone over different solar irradiance and 236 environmental parameters are the essential aims which will enable successful application of the 237 NESMD system on a large scale. The heat flux used as heat source of the process will proceed 238 from an nanophotonics coating membrane with the solar irradiance. Hence, it is really important 239 to capture a whole spectrum of the solar irradiance data (sunny, cloudy, and partially cloudy 240 conditions). Field tests under real environmental conditions are very important for assessing the 241 performance of the NESMD with the discharge brine of the RO. 242

## 243 **3.1 Desalination performance of NESMD reactor under real solar irradiation**

The NESMD experiments have been executed for a typical three days in July of 2019 in the city 244 of Houston, TX, USA (29.7174° N, 95.4018° W). Ambient temperature and solar radiation for a 245 sunny, mostly sunny, and partly cloudy day (07/09/2019, 07/12/2019, and 07/16/2019, 246 respectively) have been reported in the NESMD experiments. The maximum solar irradiance 247 occurred at around 1:00 PM local time. Figure 4 shows the relative humidity of the sweeping air 248 and process temperatures across the three-flow channels of the NESMD reactor. One can remark 249 that the heat exchanger (bottom) channel is getting more latent heat from the generated vapor in 250 the condensation and sweeping (middle) channel, which is very clear in the temperature gained 251 along the bottom channel (T<sub>out,bottom</sub> and T<sub>in,bottom</sub>). Furthermore, a small difference in the values 252 of the relative humidity of the sweeping air across the middle channel is observed for all 253 experiments. Also, in all the experiments, the relative humidity of sweeping air out is a little bit 254 lower than the relative humidity of the sweeping air inlet. This confirms that the majority of 255 generated vapor in the middle channel is condensed within the middle channel as well as the 256 third channel is working as an excellent heat exchanger. It is really important to monitor the 257

temperature of the process lines across the flow channels, including feed water and sweeping air 258 temperatures. The values of the process temperatures have great indication on the thermal 259 260 performance of the NESMD reactor. The intensity of the evaporation, condensation, and heat exchange in the top, middle, bottom channels respectively are directly relating to the process 261 temperatures differences. Figures 5-7 show bar graphs for the average process temperatures 262 263 across the flow channels. It is clear that a small temperature difference is noticed across the top channel for the experiments of 7/12/2019 and 7/16/2019. While the outlet feed temperature is 264 lower than the inlet feed temperature for the experiment of 7/9/2019. These observations could 265 be attributed to the that the heat absorbed by the nanophotonics membrane was used to evaporate 266 the adjacent layer of the liquid at the membrane interface (more evaporation). Also, Figures 5-7 267 confirm that the outlet temperature from the bottom channel is higher than the inlet for all 268 experiments, while the outlet sweeping air temperature is a little bit higher than the inlet 269 sweeping air. That observations confirm that the middle and bottom channels are working 270 efficiently for condensing the generated vapor and recovering the latent heat (condensation and 271 heat exchange). In all the experiments, the temperature of the permeate stream is equal or lower 272 273 than the air outlet temperature.



В





275 Figure 4. Process field temperature and sweeping gas relative humidity distributions as a function of 276 solar irradiance across the three flow chambers: (A) feed TDS of 17,220 ppm with a TDS removal of 277 99.5% - flow rates of top channel 3.8 L/hr (cross-flow velocity of 0.03 m/s), bottom channel 17 L/hr 278 (cross-flow velocity of 0.15 m/s), and air 120 L/hr (cross-flow velocity of 0.087 m/s), (7/9/2019); B. feed 279 TDS of 17,440ppm with a TDS removal of 99.5% - flow rates of top channel 1.8 L/hr (cross-flow velocity 280 of 0.016 m/s), bottom channel 17 L/hr (cross-flow velocity of 0.15 m/s), and air 120 L/hr (cross-flow 281 velocity of 0.087 m/s), (7/12/2019); C. feed TDS of 18,550ppm with a TDS removal of 99.6% - flow rates 282 of top channel 1.8 L/hr (cross-flow velocity of 0.016 m/s), bottom channel 17 L/hr (cross-flow velocity of 283 0.15 m/s), and air 120 L/hr (cross-flow velocity of 0.087 m/s), (7/16/2019). 284



Figure 5. Field temperature of the three flow chambers (TDS of 17,220 ppm with a TDS removal of 99.5% - flow rates of top channel 3.8 L/hr (cross-flow velocity of 0.03 m/s), bottom channel 17 L/hr (cross-flow velocity of 0.016 m/s)) – 7/9/2019.







Figure 7. Field temperature of the three flow chambers (TDS of 18,550ppm with a TDS removal of 99.6%
flow rates of top channel 1.8 L/hr (cross-flow velocity of 0.016 m/s) bottom channel 17 L/hr (cross-flow velocity of 0.15 m/s), and air 120 L/hr(cross-flow velocity of 0.087 m/s)) – 7/16/2019.

The production rate of the NESMD in terms of liquid permeate was normalized using the 286 effective membrane surface area (0.2 m<sup>2</sup>) and illustrated in Tables 2-3 as a function of the solar 287 irradiation (permeate flux expressed as kg/m<sup>2</sup>hr). As shown in Tables 2-3, for a solar irradiance 288 289 range of 784 -827 w/m<sup>2</sup>, the membrane flux was only 0.45 kg/m<sup>2</sup> h<sup>1</sup> at the highest feed flowrate (3.8 L/hr). As the feed flowrate dropped to 1.8 L/hr, the membrane flux increased to 290  $0.65 \text{ kg/m}^2 \text{ h}^1$ . This is attributed to the great increase in the retention time of the feedwater, and 291 consequently higher heat abosprtion and higher vapor pressure at feed side of the top channel 292 293 which drove the mass transport through the NESMD membrane. It can be also observed that the membrane flux, for the same feed flowrate 1.78 L/hr, increased with the solar irradiance. The 294 reason is that the increased solar irradiance intensifies the feedwater temperature at the 295 feedwater-vapor interface, resulting in higher temperature difference between thetop feed and 296 permeate sides, and consequently higher vapor pressure differences. In another study on a 297 NESMD-SGMD system, An increase in flux had been reported with decreasing the feed flowrate 298 299 and increasing the solar irradiance (15). Said et al (15) have optimized the cross flow velocity of the air of in the middle channel of NESMD-SGMD (0.087 m/s). Hence, all the field experiments have 300 been performed using a cross-flow velocity of 0.087 m/s, which is corresponding to higher 301 302 performance stability and higher permeate flux.

In summary, the permeate flux increase with increasing solar irradiance and it also increases with decreasing the feed flow rate to the top channel. The lower the feed flow rate, the higher hydraulic retention time, and consequently higher permeate flux. One more important parameter in membrane distillation technologies is the water recovery ratio (WRR), which indicates the fraction of the feed water that is separated into pure water. The WRR is defined as follows:

308 Water recovery ratio (WRR%) = 
$$\frac{m_p}{m_f} * 100$$
 (1)

Where  $m_f$  is the mass flow rate of the feed water to the top channel, while  $m_p$  is the mass flow rate of the distillate. The values of the WRR are also reported in Tables 2-3. It can be seen from Tables 2-3 that the WRR increases with decreasing the feed flow rates to the top channel. The water recovery of the experiment of the feed flow rate of 1.8 L/h (cross-flow velocity of 0.016 m/s) is ~ 3 times the experiments of 3.8 L/hr (cross-flow velocity of 0.03 m/s). This indicates

- that lower feed flow rates promote more evaporation and consequently higher water recovery.
- Also, Tables 2-3 summarize all the experiments for different operating conditions, including
- average solar irradiance, average permeate flux, and TDS removal. Also, all the experiments
- 317 have a TDS removal of  $\geq$  95%.
- Table 2. A summary of the outdoor lab-scale NESMD experiments (flow rate of the top channel: 3.8 L/hr
- 319 (cross-flow velocity of 0.03 m/s), middle channel: 120 L/hr (cross-flow velocity of 0.087 m/s), and the
- 320 *bottom channel: 17 L/hr)* (cross-flow velocity of 0.15 m/s)).

Feedwater	TDS Feed, ppm	Average Flux, kg/m²hr	Solar irradiance, w/m <sup>2</sup>	TDS removal, %	Water recovery ratio, RR%	GOR
Real feed water, KBH, RO concentrate (2L/min air)	17,220 (7/9/2019)	0.45±0.17	827±251	99.5	2.26	0.35

322 Table 3. A summary of the outdoor lab-scale NESMD experiments (flow rate of the top channel: 1.8 L/h

- 323 (cross-flow velocity of 0.016 m/s), middle channel: 120 L/hr (cross-flow velocity of 0.087 m/s), and the
- 324 *bottom channel: 17 L/hr* (cross-flow velocity of 0.15 m/s)).

Feedwater	TDS Feed, ppm	Average Flux, kg/m²hr	Solar irradiance, w/m <sup>2</sup>	TDS removal, %	Water recovery ratio, RR%	GOR
Real feed water, KBH,	17,440 (7/12/2019)	0.65±0.28	784.40±217	99.5	7	0.54
RO concentrate	18,550 (7/16/2019)	0.59±0.16	585±345	99.6	6.30	0.66

325

326 It is very clear now that the thermal desalination of the RO brine, using NESMD technology,

327 could be an appropriate feed source for NESMD to further increase the overall water recovery

328 and reduce the marine environmental impacts by reducing the volume of the brine discharge and

329 its process temperature. However, more improvements are required to maximize the water

recovery and membrane productivity. One of the key improvement strategies is to recover the

latent heat of the vapor using the concept of the multi-effect as well as concentrating the

332 sunlight.

#### **3.2 Energy analysis of the NESMD system** 334

#### 3.2.1. Solar energy and NESMD 335

The sun is the source of the majority of energy found on earth. The earth receives about 336  $1.74 \times 10^{26}$  W of the incoming solar irradiance (25). However, 70% is only absorbed by the earth 337 while 30% is reflected. The spectrum of electromagnetic sunlight divides into 5% ultraviolet 338 339 (UV), 40% visible light, and 55% near-infrared and infrared (NIR and IR). Table 4 summarizes the components of sunlight in terms of wavelength and frequency. 340

- It is worth mentioning that the amount of solar energy received by the NESMD system depends 341 on many parameters, including hour, day, location, season, and an inclination angle as well as 342 weather factors. Some of these factors are shown and discussed in section 3.2 and Figure 4. 343 344 Cloud is one of the weather factors which has the most significant impact on the solar energy absorbed by the NESMD reactor. The drop in the solar irradiance can reach up to 90% during a 345 thick cloudy condition, while it reaches 10% for a clear day (26). One can remark, in Figure 4, a 346 drop in the readings of solar irradiance in the experiment of July 9th, 2019 at 2:45 PM (CT), and 347 348 in the experiment of July 16<sup>th</sup>, 2019 over different time frames of 9:30 AM-10:00 AM (CT), 10:30 AM-10:45 AM (CT), and 1:00 PM-1:45 PM (CT). All that drops in the values of the solar 349 350 irradiance have a negative impact on the thermal performance of the NESMD system, and consequently the membrane flux. In the next section, a detailed energy balance analysis is 351 352 performed to quantify the solar energy absorption and losses.
- 353

Table 4. Electromagnetic	c components of the sun	light	
Electromagnetic	% of the total	Wavelength nm	Frequency, THz
components	sunlight	wavelength, him	(terahertz)
Ultraviolet (UV)	Less than 5	200-390	790-30,000
Visible light	40	390-780	430-790

55

780-1,400

1,400-1,000,000

214-400

0.3-214

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355

#### 356 **3.2.2 Heat losses calculations**

Near Infrared (NIR)

Infrared (IR)

Generally, the heat transfer process in the NESMD system divides into two groups, gained heat 357 transfer and losses heat transfer. The gained heat transfer is responsible for heating the feedwater 358 and generating product water vapor at the liquid-membrane interface. The heat transfer losses 359 360 include any other forms of heat loss such as heat losses by convection and radiation from the NESMD into the environment as well as heat losses by scattering and reflection. Both the two 361

- 362 heat transfer processes are briefly described in this section. Figure 8 illustrates the whole process
- in the NESMD process in terms of heat losses and heat gained.



Figure 8. Schematic of energy flux in NESMD reactor (top and middle channels)

The thermal energy losses from the transmittance window of the NESMD reactor to the ambient are represented by free convection and radiation heat transfer modes that are independent of one another. The convective heat transfer losses,  $Q_c$ , can be expressed as follows:

$$Q_c = h_c A \left( T_s - T_a \right) \tag{1}$$

369 where,  $T_s$  and  $T_a$  are the surface temperature of the transmittance window and the ambient

temperature, respectively, while A is the active membrane surface area. The convective heat

transfer coefficient,  $h_c$ , is expressed as a function of the relative speed between the transmittance window and the ambient air (v, m/s) as follows (27):

373 
$$h_c = 3v + 2.8$$
 (2)

The heat loss by radiation,  $Q_r$ , from the outer surface of the Plexiglas transmittance window to the atmosphere is estimated by:

$$376 \quad Q_c = h_r \operatorname{A} \left( T_s - T_a \right) \tag{3}$$

In the above equation, the radiative heat transfer coefficient,  $h_r$ , is calculated by (27):

378 
$$h_r = \sigma \xi \left[ \frac{(T_s + 273)^4 - (T_{sky} + 273)^4}{T_s - T_a} \right]$$
(4)

where  $\sigma$  and  $\xi$  are the Steven Boltzman constant and emissivity, respectively, while  $T_{sky}$  is approximated as follows:

381 
$$T_{sky} = T_a - 6$$
 (5)

382 One more source of the energy losses in the NESMD system is the sunlight scattering and reflection by the water layer of the feedwater on the top of the NESMD membrane. The density 383 384 of the water is ~800 times denser than the ambient air. As the sunlight enters the water, it interacts with the molecules of the water and salt to cause losses in solar energy. The amount of 385 386 sunlight reflected depends strongly on the inclination angle of the NESMD reactor, which is 35<sup>o</sup>. According to (28, 29) with a reference to the NESMD with an inclination angle of 35<sup>0</sup>, 8% of the 387 incident light is scattered and reflected by the water layer (Q<sub>rw</sub>). Furthermore, there is one more 388 source of energy losses from the NESMD system, which is the sunlight reflected by the 389 transmittance window of the Plexiglas. The light reflected by the Plexiglas sheet depends on the 390 window thickness, angle of incidence, and reflective index. Actual measurement shows that the 391 used transparent Plexiglas sheet with a thickness of up to 6 mm transmits 92% of the incident 392 light striking it at the perpendicular  $(Q_m)$  (30). 393 On the other hand, the rest of solar energy is used to heat the feedwater and consequently 394

generating vapor at the water-membrane interface. The heat of evaporation (Q<sub>e</sub>) is calculated as
 follows:

$$397 \qquad Q_e = J A \Delta H_v \tag{6}$$

Where J is the membrane flux (kg/m<sup>2</sup> hr), A is the active membrane surface area (m<sup>2</sup>), and  $\Delta H_v$ is the latent heat of vaporization (kJ/kg). Furthermore, the sensible heat gained by the feedwater (Q<sub>s</sub>) depends on the temperature difference of the feed across the top channel, heat capacity of the feedwater (C<sub>p</sub>), and mass flow rate of the feed (m·). The Q<sub>s</sub> is calculated by:

402 
$$Q_s = m \cdot C_p \left( T_{F,effluent} - T_{F,influent} \right)$$
 (7)

- 403 Thermal losses efficiency,  $\eta$ , of the NESMD reactor is one of the key parameters used to assess
- 404 the performance of the solar thermal desalination process. The  $\eta$  can be calculated as follows: 405  $\eta = \left[\frac{Q_c + Q_r + Q_{rw} + Q_{rp}}{IA}\right] * 100$  (8)

The results showed that heat losses compose up to 64% of the overall solar heat amount. In other
solarthermal desalination technologies such as solar stills, the heat losses compose 70-80%

- 408 409
- 410

# 411 3.2.3 Gained-Output Ratio of the NESMD

towards overall solar heat input (26).

The energy efficiency of the NESMD system was evaluated using gained output ratio (GOR) which is the most important performance parameter in thermal desalination technologies to gauge the energy efficiency of MD. GOR is defined as the latent heat required to evaporate all the mass flow rate of clean water produced compared with the external energy added to the NESMD system. A higher GOR can be attained by recovering the latent heat from the permeate vapor to preheating the feed solution. The GOR is defined as follows:

418 
$$GOR = \frac{\Delta H_{v} \cdot m_{v}}{Q_{solar} A_{m}}$$
(2)

where  $\Delta H_{\mu}$  (kJ/kg) is the latent heat of vaporization of water,  $\dot{m}_{\mu}$  (kg/s) is the mass flow rate of 419 clean water produced by the NESMD system, Q<sub>solar</sub> (W/m<sup>2</sup>) is ambient solar radiation, and A<sub>m</sub> 420 (m<sup>2</sup>) is the surface area of the NESMD membrane. Tables 2-3 list the values of the GOR for all 421 422 the experiments. As shown in Tables 3-4, decreasing the feed flow rates from 3.8 L/h (cross-flow velocity of 0.03 m/s) to 1.8 L/h (cross-flow velocity of 0.016 m/s) resulted in increasing the 423 GOR from 0.32 (experiment of 7/9/2020) to 0.54 (7/12/2020) and 0.66 (7/16/2020). The lower 424 feed flow rate to the top channel resulted in higher residence time that led to more sunlight 425 absorption, and consequently higher vapor flux. 426

427

#### 428 Conclusions

A nanophotonics enhanced solar membrane distillation (NESMD) reactor having a total effective 429 membrane surface area of  $0.2 \text{ m}^2$  with an internal heat recovery system has been designed. 430 developed, and tested without an external heater or external condenser. Hence, the solar 431 collection, membrane distillation, heat recovery, and condensation all happened inside the 432 NESMD reactor. A complete design, process flow diagram, electrical diagram, and material 433 selection have been outlined. In this study, natural reverse osmosis brine from the brackish 434 desalination plant at El Paso TX, USA (TDS 17,220 – 18,550 mg/L) has been desalinated by 435 using the NESMD reactor. The current research validates the applicability of NESMD to 436

desalinate natural RO brine and maximize the water recovery from the RO systems using onlysolar energy. The preliminary field data released the following findings:

- The NESMD reactor continuously operated for five to six hours outdoor each of three days with no operational problems. This is a good indication of the durability and mechanical integrity of the NESMD system as well as the photothermal coating stability.
- The NESMD was able to produce clean and pure water (conductivity, lower than 15  $\mu$ S cm-1) from the high concentrate brackish RO discharge brine (conductivity, 18.47-19.53 mS cm<sup>-1</sup>)
- The average feed TDS was approximately 18 g/L with an average TDS removal of
  99.5%, producing product water with an average TDS of70 mg/L, meeting the World
  Health Organization (WHO) drinking water standard.
- Steady-state average membrane flux of 0.46-0.65 kg m<sup>-2</sup> hr<sup>-1</sup> was observed at a solar
   intensity of 585-827 W/m<sup>2</sup> without an external condenser.
- Lowering the feed flow rate to the evaporation channel has a positive effect on increasing
  the GOR;
- The energy balance analysis showed that heat losses compose up to 64% of the overall solar heat amount, and that would be required extensive strategic energy management.
- The technology is still in an early stage and more improvements are required to improve
   productivity. One of the key improvement strategies is to recover the latent heat of the
   vapor using the concept of the multi-effect as well as concentrating the sunlight.
- 457

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- 462 **Conflict of Interest**
- 463 The authors declare no conflict of interest

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