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# Enhanced solar evaporation using a photo-thermal umbrella for wastewater management

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# Abstract

Zero-Liquid Discharge (ZLD) is an emerging wastewater management strategy that maximizes water recovery for reuse and produces a solid waste, thereby lowering the environmental impact of wastewater disposal. Evaporation ponds harvest solar energy as heat for ZLD, but require large land areas due to low evaporation rates. Here, we demonstrate a passive and non-contact approach to enhance evaporation by more than 100% using a photo-thermal device that converts sunlight into mid-infrared radiation where water is strongly absorbing. As a result, heat is localized at the water's surface through radiative coupling, resulting in a better utilization of solar energy with a conversion efficiency of 43%. The non-contact nature of the device makes it uniquely suited to treat a wide range of wastewater without contamination, and the use of commercial materials enables a potentially low cost and highly scalable technology for sustainable wastewater management, with the added benefit of salt recovery.

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1 The World Economic Forum recognizes water crises as a major global risk that has arisen from the depletion of natural freshwater resources due to agricultural, industrial and municipal use, while 2 generating vast amounts of wastewater.<sup>1</sup> This poses a sustainability challenge that currently threatens 3 4 four billion people worldwide and is expected to become more severe with population growth and economic development.<sup>2,3</sup> Desalination of seawater and inland brackish water has emerged as a solution 5 6 to meet this increasing water demand. However, desalination plants produce concentrated brine as a 7 byproduct, disposal of which is detrimental to land vegetation and the aquatic ecosystem, thereby having a significant environmental impact.<sup>4,5</sup> Thus, there has been a push towards maximizing water recovery 8 9 for reuse from industrial wastewater and desalination brine to achieve Zero Liquid Discharge (ZLD) 10 such that the final waste is a solid. At present, ZLD involves a series of treatment processes that (i) reduce the volume of wastewater using membrane-based systems or thermal brine concentrators, and (ii) 11 12 reduce concentrated brine to a solid waste using a crystallizer or an evaporation pond<sup>6</sup> (Supplementary 13 Fig. 1).

14 The choice for this final step of ZLD depends upon various factors including concentrated brine volume and composition, energy requirement, local climate and land costs.<sup>7,8</sup> A crystallizer is a complex 15 mechanical system that requires high-grade heat and electricity resulting in a large energy consumption 16 17 and capital cost. Although crystallizers have a small site footprint, their operating costs depend heavily 18 on the composition of wastewater, which can be exorbitant for highly scaling water (e.g. wastewater containing large amounts of silica).<sup>9</sup> In contrast, evaporation ponds are artificial brine disposal ponds 19 20 with very large surface area (>1000 m<sup>2</sup>) that harness solar energy to passively evaporate water from any 21 waste stream, resulting in low energy and operating costs. Currently, evaporation ponds are implemented 22 in China, Australia, Europe (Mediterranean), the Middle East and some areas of the U.S. where they are 23 economically viable owing to inexpensive land and a suitable climate (arid or semi-arid, high solar flux).<sup>6,9,10</sup> Although they offer a tremendous advantage of being suitable for different wastewater 24 25 streams, capital costs are high due to the large land footprint required for natural evaporation. This footprint is inversely proportional to the evaporation rate, which is inherently low due to the passive nature and inefficient use of solar energy in these ponds. To reduce environmental impact (*i.e.*, smaller areal footprint) and capital costs, evaporation enhancement in brine disposal ponds is essential, and different approaches have been implemented in this regard.<sup>11,12</sup>

30 Active methods of enhancement include Wind-Aided Intensified Evaporation (WAIV) and droplet spraying, while passive techniques include the use of solar radiation absorbing organic dyes, wetted 31 floating fins and salt tolerant plants.<sup>7,8,12</sup> These methods have been shown to enhance evaporation rates 32 33 by up to 35%, while WAIV has shown a 50% enhancement at high salinities but requires continuous 34 electric pumping making it an active system. Recently, a new passive approach for solar evaporation 35 enhancement has emerged where the emphasis is to avoid wastefully heating a large volume of water and instead perform surface heating by localizing solar heat at the water-air interface.<sup>13,14</sup> Various prototypes 36 using nanomaterial-based absorbers and bio-inspired structures exploiting surface heating have since 37 been reported, with solar-vapor conversion efficiencies of over 90% for these floating structures.<sup>15-20</sup> 38 39 While these devices are suitable for solar stills and steam generation applications, their continuous 40 operation in high salinity wastewater (such as evaporation ponds) causes salt precipitation at the surface in contact with water, resulting in deterioration of the optical and wicking properties over time.<sup>16</sup> Thus, 41 42 there is a need to develop *non-contact* and *passive* technologies for enhanced solar evaporation that can 43 reduce the footprint of evaporation ponds and eliminate contamination from fouling and scaling. Recently, Cooper et al. proposed a non-contact device for solar steam generation,<sup>21</sup> however their design 44 45 was focused on generating superheated steam, rather than increasing evaporation rates which is critical 46 to achieve a low cost ZLD technology. Furthermore, given the large areas of evaporation ponds, design 47 simplicity and scalability are key considerations.

Here, we demonstrate a novel and scalable surface heating approach that enhances evaporation by over a 100% under one sun (1000 W  $m^{-2}$ ), with the potential to increase evaporation by 160% compared to traditional evaporation ponds through optimized thermal design. The system relies solely on radiative

51 coupling using a photo-thermal conversion device that comprises a selective solar absorber and a 52 blackbody emitter. Since this photo-thermal device shields the water in an evaporation pond from direct sunlight, we refer to it as a "solar umbrella." We design a lab-scale prototype to experimentally 53 54 demonstrate the potential of the solar umbrella to enhance evaporation from concentrated brines. Using 55 thermal models validated by these lab-scale experiments as well as outdoor testing under natural 56 sunlight, we predict the performance of a large-scale evaporation pond for sustainable wastewater disposal. By enhancing the evaporation two-fold,<sup>22</sup> the land required for disposing the same volume of 57 58 wastewater is halved, which has a significant environmental impact.

# 59 Radiative heat localization

60 Efficient utilization of solar energy for evaporation is limited by the transparency of water at visible and near-IR wavelengths owing to its low absorption coefficient of 0.01 m<sup>-1</sup> (Supplementary Note 1). In other 61 words, a depth of 100 m is required for complete absorption of solar radiation by water,<sup>23</sup> while 62 traditional evaporation ponds have typical depths ranging from 0.5 - 2 m.<sup>24</sup> In this case, a large fraction 63 (~60%) of incident solar flux is used in the volumetric or sensible heating of bulk water as shown in 64 Figure 1a. Although the temperature of water increases as sunlight is absorbed, that increase is 65 66 distributed in the whole volume of liquid (large thermal mass) resulting in a lower temperature at the 67 water surface, as compared to the case where all the radiation is absorbed at the surface. As a result, the 68 transient thermal response of traditional evaporation ponds is slow, which when coupled with the diurnal 69 variation of solar radiation, results in low evaporation rates. At mid-IR and larger wavelengths however, the absorption coefficient of water increases by several orders of magnitude to 10<sup>4</sup> m<sup>-1</sup>, and 70 71 consequently, radiation is absorbed within a 100 µm layer, *i.e.*, heat is localized at the surface. Given 72 that evaporation is a surface phenomenon, by shifting solar radiation to mid-IR and larger wavelengths, 73 higher surface temperatures can be achieved, which in turn enhances the evaporation rate. This mid-IR radiation can be obtained from a heated blackbody - as an example, a blackbody with a temperature 74 75 <150 °C emits ~99.9% of radiation at wavelengths above 2 µm that is absorbed in a thin layer of water

 $\sim 100 \ \mu m$  (Supplementary Fig. 2). We achieve the shifting of solar radiation to mid-IR wavelengths by utilizing a photo-thermal converter comprising a selective solar absorber and a blackbody emitter shown in Figure 1b. When used as a solar umbrella over a water surface such as an evaporation pond, the overall system efficiency ( $\eta$ ) is:

80 
$$\eta = \left(\frac{\dot{m}h_{fg}}{q_{solar}}\right) = \eta_1 \times \eta_2 \times \eta_3 = \left(\frac{\alpha_s q_{solar} - \varepsilon_s \sigma T_{abs}^4}{q_{solar}}\right) \left(\frac{F\varepsilon_b \sigma T_{abs}^4}{\alpha_s q_{solar} - \varepsilon_s \sigma T_{abs}^4}\right) \left(\frac{\dot{m}h_{fg}}{F\varepsilon_b \sigma T_{abs}^4}\right)$$
(1)

81 where  $\dot{m}$  is the water evaporation rate,  $h_{fg}$  is the latent heat of vaporization and  $q_{solar}$  is the incident solar 82 flux. There are three parts to this efficiency:  $\eta_1$  represents the absorber optical efficiency,  $\eta_2$  incorporates 83 the emitter efficiency as well as the radiative coupling between the solar umbrella and water surface, and 84  $\eta_3$  represents the fraction of incident radiation on the water surface that is used in evaporation.



**Fig 1: Surface heating using a photo-thermal (solar) umbrella. a** Schematic of a conventional evaporation pond where incoming sunlight is volumetrically absorbed, causing a bulk water temperature increase that leads to evaporation. **b** Rendering of the proposed solar umbrella (spectrally selective absorber and blackbody emitter) that converts incoming sunlight into mid-IR radiation where water is strongly absorbing, thereby increasing surface temperature and evaporation rate while the bulk remains at a lower temperature. **c** Schematic of the lab-scale prototype of an evaporation pond comprising water in an acrylic tank separated from the solar umbrella by an air gap and tested under a solar simulator. **d** Energy balance and modes of heat transfer for the umbrella and water, where the red region represents non-contact heat localization at the surface.

85 Equation (1) can be used to guide the material selection and design of the solar umbrella. To obtain a 86 high  $\eta_1$  (*i.e.*, to minimize optical losses), the top surface of the umbrella is coated with a spectrally 87 selective solar absorber characterized by a high solar absorbtance,  $\alpha_s$ , from 0.2 – 2.5 µm and a near-zero thermal emittance,  $\varepsilon_s$ , at wavelengths larger than 2.5  $\mu m^{25}$  (Supplementary Note 2 and Supplementary 88 Fig. 3). This reduces radiation losses to the ambient and achieves efficient conversion of sunlight into 89 heat at an equilibrium temperature of  $T_{abs}$ . To obtain a high  $\eta_2$  (*i.e.*, low thermal losses from the photo-90 91 thermal converter), the bottom surface of the umbrella is coated with a black emitter characterized by a 92 high IR emittance,  $\varepsilon_b$ , which is placed above the water surface with a large radiation view factor, F;  $\sigma$  is the Stefan-Boltzmann constant. Furthermore, a convective cover can be used to reduce losses from the 93 surface of the umbrella as it heats up. Finally, to obtain a high  $\eta_3$ , thermal losses from water via 94 95 conduction, convection and radiation must be minimized such that a majority of the energy is used for 96 evaporation. To test the effectiveness of the non-contact surface heating approach, we designed a lab-97 scale prototype shown in Figure 1c that consists of two sub-systems, namely the solar umbrella and a 98 water tank that represents an evaporation pond. Figure 1d shows the energy balance for the overall 99 system in a real application.

# 100 Lab-scale demonstration

In the lab-scale prototype shown in Figure 1c, the solar umbrella is positioned above the water surface to obtain a view factor larger than 0.8 (Supplementary Note 3 and Supplementary Fig. 4). Under one-sun illumination from a solar simulator (1000 W m<sup>-2</sup>), the temperature of the solar umbrella increases rapidly and reaches a steady-state value of  $T_{abs} = 70$  °C in less three minutes (Supplementary Fig. 5). The 105 corresponding increase in the temperature of pure water due to radiative heating from the hot emitter is shown in Figure 2a. The water surface temperature rises steadily from 22.5 °C to 40 °C in one hour, 106 while the bulk water temperature increases only by 2.5 °C in that period. To mimic concentrated 107 108 wastewater in evaporation ponds, the experiment was repeated with a saturated salt solution (25 wt. % 109 NaCl), which has over 7x the concentration of seawater. Similar trends were observed for the brine, with a 20 °C temperature rise at its surface in one hour, thereby demonstrating radiative heat localization 110 111 using the solar umbrella. The presence of salts such as NaCl that absorb near-IR radiation increases the brine temperature  $\sim 2$  °C higher than pure water. To facilitate a comparison with traditional evaporation 112 113 ponds where water is illuminated directly by sunlight, the same setup was used without the solar 114 umbrella, and corresponding temperatures are shown in Figure 2b. In this case, due to the small 115 absorption coefficient of water at solar wavelengths, the solar flux is volumetrically absorbed resulting in 116 only a 5 °C temperature rise throughout the water in one hour.

117 Given that evaporation varies with surface temperature, the mass change due to evaporation was measured for each case at an ambient temperature,  $T_{\infty} = 25$  °C and a relative humidity of 50%. Figure 2c 118 119 shows the evaporation rates under one sun after subtracting the evaporation in an otherwise identical but dark environment (0.07 kg m<sup>-2</sup> h<sup>-1</sup>). Without the solar umbrella, pure water absorbs sunlight 120 volumetrically that increases evaporation to 0.3 kg m<sup>-2</sup> h<sup>-1</sup> compared to the dark case (Supplementary 121 Fig. 5). With the solar umbrella however, the evaporation increases to 0.62 kg m<sup>-2</sup> h<sup>-1</sup> as a higher surface 122 temperature is achieved; this represents over a two-fold enhancement under the same input solar flux in 123 this passive system. The evaporation rate and surface temperature achieved here are comparable to other 124 125 surface heating approaches in literature that use self-supporting floating structures (single layer absorbing devices without an insulating foam).<sup>26-28</sup> The saturated NaCl brine showed an evaporation rate 126 of 0.49 kg m<sup>-2</sup> h<sup>-1</sup> with surface heating compared to 0.22 kg m<sup>-2</sup> h<sup>-1</sup> with bulk heating, both of which 127 represent a ~21% reduction compared to pure water. This is expected as vapor pressure decreases with 128 129 salinity but is partially compensated by the higher temperature of brine compared to pure water; we note

that this reduction is for an extreme case as the salt concentration is at its saturation limit. To demonstrate continuous operation, brine evaporation experiments were performed for a 3-hour period under a constant solar flux of 1000 W m<sup>-2</sup> resulting in precipitation and recovery of salts, as shown in Figure 2d. The effect of the photo-thermal umbrella on water evaporation was also investigated under low optical concentrations of 2, 3 and 5 suns. As expected, higher evaporation rates up to 1.6 kg m<sup>-2</sup> h<sup>-1</sup> were measured at higher input fluxes (Supplementary Fig. 6). These low optical concentrations can be achieved with passive non-tracking concentrators.<sup>29</sup>



**Fig. 2: Lab-scale experimental results. a** Surface and bulk temperature of pure water (solid line) and 25 wt. % NaCl brine (dashed line) over one hour with the solar umbrella showing localized heating at the surface. **b** Surface and bulk temperatures of pure water without the solar umbrella showing volumetric heating. Inset images are captured using an IR camera after 10 minutes of illumination for visualization of surface vs. volumetric heating with and without the solar umbrella, respectively (IR images are for qualitative observation only; temperature measurements were made with thermocouples as shown in Fig. 1c). **c** Mass change due to evaporation for pure water under direct illumination (volumetric heating)

compared to evaporation of pure water and NaCl brine with the solar umbrella (surface heating). **d** Evaporation rate over a three-hour period with the solar umbrella for pure water (solid line) and 25 wt. % brine (dashed line) showing a 21% reduction due to salinity. The inset shows precipitated salt crystals from the walls of the water tank owing to evaporation of water from brine to achieve ZLD. All experiments are conducted under one sun (1000 W m<sup>-2</sup>) at an ambient temperature of 25 °C and relative humidity of 50%.

137 For the case of pure water, the experimentally measured values are used to calculate sub-system efficiencies from Equation (1):  $\eta_1 = 91\% \eta_2 = 74\%$  and  $\eta_3 = 63\%$ , resulting in an overall solar-thermal 138 evaporation efficiency of 43% under one sun. This compares favorably with single-layer floating 139 evaporation structures<sup>20,30</sup> and has the added benefit of being non-contact thus eliminating contamination 140 141 from the wastewater. The absorber efficiency of 91% can be explained by accounting for optical losses 142 due to reflection (5%) and thermal radiation (4%) from the selective absorber surface. The emitter efficiency of 74% is due to an emittance view factor less than unity ( $\varepsilon_b = 0.94$  and F ~0.85) in the lab-143 144 scale prototype, as well as convection losses from the umbrella. The latter can be minimized with a 145 sophisticated convective cover design or with an evacuated absorber that is commonly used in domestic 146 solar hot water heaters. Finally, an evaporation efficiency of 63% indicates that thermal losses via 147 conduction, convection and radiation from the water compete with and reduce the energy available for evaporation (Supplementary Fig. 8). Furthermore, mass transport is hindered by the closeness of the 148 149 umbrella to the water surface resulting in a diffusion-limited prototype, as discussed in the modeling 150 section (Supplementary Note 4). This yields an overall solar-thermal evaporation efficiency of 43%which is higher than the 24.6% efficiency of the contactless solar evaporation structure,<sup>21</sup> owing to 151 152 higher evaporation rates achieved with the solar umbrella (Supplementary Note 7 and Supplementary 153 Table 1). Furthermore, the solar-thermal efficiency of volumetrically heated water, *i.e.*, without the umbrella, under the same solar flux is  $\sim 20\%$  based on the experimentally measured evaporation rate 154 (Figure 2c), which is consistent with literature.<sup>18</sup> This confirms the superior performance of surface-155 156 based heating for solar evaporation.

#### 157 Brine evaporation under natural sunlight

158 To demonstrate continuous or long-term operation with high salinity wastewater (25 wt. % NaCl 159 solution) and to validate the performance of the solar umbrella in real conditions (varying solar flux and wind), brine evaporation experiments were performed for five days under natural sunlight in Berkeley, 160 161 California as shown in Figure 3a. The solar flux was recorded over an 8-hour period and averaged over 162 all five days as shown in Figure 3b, the corresponding temperature of the umbrella and water surface are displayed in Figure 3c. Under a peak solar flux of 750 W m<sup>-2</sup>, the solar umbrella temperature rises to 75 163 164 °C, which in turn results in a water surface temperature of over 45 °C. Evaporation occurs at the water surface and the generated vapor diffuses into the air gap and through the holes in the umbrella, leaving 165 behind salt deposits along the walls of the acrylic tank. There is no visible contamination or salt 166 deposition on the emitter surface even after several days (Supplementary Fig. 7). This confirms that the 167 solar umbrella can be used as a fouling-resistant device for brine concentration towards zero-liquid 168 169 discharge.



**Fig. 3: Outdoor testing of solar umbrella. a** Photo of the experimental setup for water evaporation from a saturated salt solution (25 wt% NaCl) over five days. **b** Solar flux measured over an 8-hour window in Berkeley, CA. **c** Temperature of the solar umbrella (emitter) and brine surface corresponding to the solar flux. All experiments are conducted under natural sunlight in Berkeley, CA at an ambient temperature of 20-24 °C and relative humidity of 40-50%.

#### 170 Thermal model validation

- 171 To estimate heat losses in the lab-scale prototype and to make predictions for optimized device design, a
- thermal model was developed using COMSOL Multiphysics (Supplementary Note 5). The evaporation
- 173 was modeled as a boundary heat flux:

# $q_{evap} = h_{evap}(T_s - T_{\infty}) = \dot{m}h_{fg}$

174 where  $q_{evap}$  is the heat loss due to evaporation characterized by an effective heat transfer coefficient,  $h_{evap}$ 175 (which is a function of temperature). Using the experimentally measured  $\dot{m}$  and  $T_s$  values obtained at 176 different optical concentrations (Supplementary Fig. 6), an average value of  $h_{evap} = 28$  W m<sup>-2</sup> K<sup>-1</sup> is 177 extracted, which is within the range of reported values for floating structure prototypes.<sup>13</sup> The low value 178 corresponds to a diffusion-limited evaporation process,<sup>19,31</sup> which is attributed to the large mass transport 179 resistance owing to the geometry of the lab-scale prototype (Supplementary Fig. 9 and 10).

180 The simulated cross-sectional temperature profile of water in the acrylic tank receiving infrared radiation 181 from the hot emitter at steady-state is shown in Figure 4a. Heat localization results in a higher temperature of 42 °C at the surface, while the bulk temperature remains close to ambient at 25 °C. Figure 182 183 4b shows the transient temperature over an hour, which matches the experimentally measured values, 184 thereby confirming the validity of the thermal model. From this analysis, conduction from the water surface into underlying bulk water was calculated to be 21%, convection from the walls of the acrylic 185 186 tank was 6%, and radiation from the walls was 11%. This leaves 62% of the energy incident on the water surface for evaporation, which is in good agreement with  $\eta_3$  obtained from the experimentally measured 187 188 evaporation rate. We note here that due to the small size of the lab-scale prototype, side walls of the 189 acrylic tank contribute to a 17% parasitic loss (convection and radiation) implying that higher 190 evaporation efficiencies are achievable in a larger system.

191 Next, the validated thermal model is used to make performance predictions under different conditions. 192 For instance, on cloudy or winter days, when the solar flux can be as low as 300 W m<sup>-2</sup>, the umbrella can 193 still reach 45 °C and heats the water surface to enhance evaporation. Furthermore, by eliminating 194 convective losses from the umbrella surfaces (*e.g.* evacuated absorber), the steady-state temperature of 195 the solar umbrella can exceed 100 °C under one sun as shown in Figure 4c. This in turn increases 196 blackbody emission to the water surface, resulting in a temperature rise of over 50 °C at its surface as shown in Figure 4d. Given that the vapor pressure of water increases by 70% from 40 to 50 °C, higher
efficiencies and evaporation rates can be obtained using an evacuated umbrella.



**Fig. 4: Thermal model validation and performance prediction for Solar Umbrella. a** Cross-sectional temperature profile of water in an acrylic tank with solar umbrella modeled using COMSOL that shows localized heating to a steady state surface temperature of 42 °C due to a large absorption coefficient  $(10^4 \text{ m}^{-1})$  at mid-IR wavelengths. **b** Water surface and bulk temperatures simulated over one hour (solid lines) and overlaid with experimentally measured temperatures (open symbols) that confirms the validity of the thermal model. **c** Simulated temperature of the solar umbrella at various solar fluxes indicate that convection losses limit the performance, and **d** the corresponding simulated water surface temperature predictions show that even at low solar fluxes, the water surface temperature increases and can reach 55 °C if an evacuated system is used.

#### **199 Performance prediction for evaporation ponds**

- 200 The validated thermal model can also be applied to predict the performance of the solar umbrella on
- 201 large-area evaporation ponds. In existing ponds, the diurnal variation of solar radiation causes a time
- delay of a few hours between the highest solar intensity and maximum brine temperature as sunlight is

203 volumetrically absorbed and used for the sensible heating of water. As a result, the transient response is 204 slow and the evaporation rate is small, thereby requiring large land areas to dispose wastewater. In 205 evaporation ponds having a white salt precipitate layer at the bottom, this is exacerbated due to further losses by reflection and conduction to the ground,<sup>32</sup> resulting in even lower solar-thermal evaporation 206 207 efficiencies. A common approach to address this is the addition of colored organic dyes (e.g., naphthol 208 green and methylene blue) that increase the solar absorption of water during the day. This method has 209 been shown to create a  $\sim 3$  °C increase in brine surface temperature which enhances the evaporation by up to 35%, but at night these dyes lead to lower surface temperatures.<sup>32,33</sup> The solar umbrella can serve as 210 211 an alternative to these colored dyes and minimize the time lag caused by volumetric heating through 212 localizing heat in a small thermal mass at the evaporation surface (Supplementary Fig. 12). In other 213 words, the rapid thermal response of the umbrella under sunlight can increase water surface temperature, 214 thereby increasing evaporation. To investigate the effectiveness of this approach for a real pond, the aforementioned validated COMSOL model was modified to mimic a typical evaporation pond depth of 215 0.5 m,<sup>7,32</sup> exposed to an ambient of 22 °C and 50% relative humidity. Under one sun, the solar umbrella 216 reaches a steady-state temperature of 70 °C, resulting in a thermal emission of ~750 W m<sup>-2</sup> to the surface 217 218 of the pond. The resulting water surface temperature (Supplementary Fig. 11) accounting for (3) 219 losses due to natural convection, evaporation and radiation is shown in Figure 5a. From these 220 temperatures, time dependent evaporation is predicted using:

$$\dot{m} = h_m(\rho_s - \rho_\infty)$$

where  $h_m$  is the mass transfer coefficient for evaporation,  $\rho_s$  is the combined vapor-air density at the water surface and  $\rho_{\infty}$  is the corresponding ambient density. For fixed ambient conditions),  $\rho_{\infty}$  is known,  $h_m$  is extracted from lab-scale experiments as an average value of 0.0042 m s<sup>-1</sup> (comparable with data on evaporation from a stagnant water surface<sup>34</sup>), and an increase in the surface temperature from 20 to 40 °C results in a three-fold increase in  $\rho_s$ . This in turn results in a higher evaporation rate as shown in Figure 5a for pure water, where the daily evaporation rate is obtained by integrating the time and temperature-

dependent mass flux yielding ~9.8 kg m<sup>-2</sup> day<sup>-1</sup>. To account for the salinity of brines, the evaporation is 227 reduced by 21% to 7.8 kg m<sup>-2</sup> day<sup>-1</sup> based on experimentally observed evaporation rates for pure water 228 and saturated NaCl in the lab-scale prototype. However, it has been reported that for a salinity of 25 wt. 229 230 % and at similar ambient conditions to the one modeled here, evaporation is reduced between 18 – 22%;<sup>35</sup> thus a fixed reduction of 21% is valid for this analysis. We also note that in real ponds  $h_m$  can be 231 232 higher as limitations of the lab-scale prototype are surpassed due to advective mass transport 233 (Supplementary Fig. 10) and due to the presence of wind, as well as other factors such as low humidity in arid regions that increase evaporation. The main advantage of the solar umbrella is its fast response 234 that allows for efficient evaporation during the 8-hour illumination window, with over a 100% 235 236 enhancement compared to volumetrically heated brines under similar ambient conditions over a diurnal cycle.<sup>35-38</sup> An evacuated umbrella may be used for further performance enhancement as discussed in 237 Figure 4c and 4d, and in this case, a daily evaporation of 14.3 kg  $m^{-2}$  day<sup>-1</sup> can be obtained (or 11.3 kg  $m^{-2}$ 238  $^{2}$  dav<sup>-1</sup> accounting for brine salinity). This leads to a ~160% enhancement in evaporation compared to 239 240 traditional ponds, thus surpassing the performance of organic dyes and WAIV, as shown in Figure 5b.



**Fig. 5: Simulated performance of evaporation ponds for ZLD. a** Simulation of water surface temperature and evaporation rate over a diurnal cycle; the shaded region represents sunlight incident on the solar umbrella, resulting in heat localization at the water surface and a corresponding rise in temperature. The evaporation rate is calculated at each temperature, and the brine evaporation rate under these conditions is obtained as a 21% reduction from pure water evaporation. **b** Daily evaporation enhancement (relative to a traditional volumetrically heated pond under 1 sun) by passive methods

including radiation absorbing dyes, solar umbrella and an evacuated solar umbrella at a relative humidity of 50% and ambient temperature of 20 °C.

Finally, we vary the pond depth to evaluate conditions under which bulk heating can attain temperatures similar to surface heating with the solar umbrella (Supplementary Note 6). The model indicates that a pond depth of ~0.1 cm would be required to compete with surface heating, which is unrealistically small for a ZLD evaporation pond (Supplementary Fig. 12).

245 In summary, we report a new photo-thermal approach to improve the efficiency of solar evaporation by leveraging the inherently strong infrared absorption of water that causes heat localization in a thin layer 246 247  $(<100 \mu m)$  at the surface. The system is passive and non-contact, and comprises a commercially 248 available selective solar absorber and a spray-on black paint emitter. Surface heating results in over a 249 100% enhancement in evaporation compared to volumetric heating which translates into a lower land 250 requirement, and a 43% solar-thermal efficiency is achieved under one sun. The non-contact radiative 251 coupling eliminates risk of fouling and contamination from wastewater streams, making this system 252 uniquely suited for long-term implementation in brine disposal ponds for achieving zero-liquid 253 discharge, as demonstrated with a saturated salt solution. Furthermore, by reducing thermal losses (primarily convection from the absorber surface), the umbrella temperature can be increased 254 significantly, thereby enabling high temperature vapor or steam generation under one sun. Other 255 256 potential applications of the photo-thermal umbrella is in solar stills where vapor generated can be 257 condensed to produce drinking water for off-grid communities. The design simplicity lends itself to a 258 scalable solution for the sustainable management and disposal of wastewater.

#### Methods

*Materials and characterization*: The selective solar absorber was obtained from Almeco (TiNOX<sub>energy</sub> on aluminum), which has a solar absorptance of 0.95 and thermal emittance of 0.04 at thermal wavelengths that suppresses radiation losses. The black paint was a high emissivity paint (Zynolyte Hi-Temp Paint, Aervoe) that was sprayed in even three layers on the aluminum substrate and cured at 300 °C in a furnace for two hours to achieve an emittance of 0.94 at infrared wavelengths. The optical properties of the spectrally selective absorber and black paint emitter were measured using an FTIR (Thermo Electron Nicolet 5700), coupled with an integrating sphere accessory (Pike Technologies Mid-IR IntegratIR). As the samples were non-transmitting, the absorptance was calculated as unity minus reflectance.

*Experimental setup*: For lab-scale prototype testing, a solar simulator (Newport, 94081A) with an optical filter for AM 1.5G spectrum is used as the solar input. A power meter and thermopile detector (Newport, 919P-030-18) were used to measure the incoming solar flux at the same location as the water tank. The tank is made out of acrylic and comprises an inner pocket (square cross-section with a side length of 35 mm and a 50 mm depth) that is coated in a reflective foil and filled with water. The inner pocket is surrounded by a 20 mm thick acrylic wall on all sides that minimizes thermal losses from the sides of the tank. Two K-type thermocouples were placed in the tank: one  $\sim 2$  mm below the water surface to record the surface temperature,  $T_s$ , and one 40 mm below the surface to record the bulk water temperature,  $T_b$ . The selective absorber-black emitter was mounted on Teflon spacers and placed ~4 mm above the water surface. Another K-type thermocouple was attached to the surface of the emitter to measure its temperature,  $T_{abs}$ , and estimate the blackbody emissive power. Since the substrate is thin ~0.5 mm and metallic, temperatures of the absorber and emitter are equal and remain isothermal over the course of the measurements. A convective shield (bubble wrap) was placed on top of the absorber to reduce convection losses from the hot surface. Holes were drilled in the absorber (covering less than 1% of its area) to allow vapor diffusion into the ambient air. The tank was placed on a balance (A&D, GF-4000) that records the mass loss due to evaporation over time. A hygrometer (Onset, HOBO UX100) was kept next to the balance to measure ambient conditions (temperature,  $T_{\infty}$  and relative humidity). The K-type thermocouples were connected to a data logger (Pico Technologies, USB TC-08) that records temperature as a function of time. A copper aperture was placed above the absorber to limit extraneous light from the solar simulator during experimental testing. As a first step, evaporation under dark conditions was measured for 30 minutes with the simulator shutter closed. Next, the shutter was opened with the incident flux set to 1000 W m<sup>-2</sup>, unless specified otherwise. Mass loss and temperature measurements were made for at least two hours, and values reported in the manuscript are averaged over four runs with the dark evaporation subtracted. Laboratory and outdoor experiments were performed at ambient temperatures between 20-24 °C and a relative humidity of 40-50%.

*Modeling:* A 3D model was developed on COMSOL Multiphysics software to simulate steady-state and transient operating conditions. Both the lab-scale prototype and real evaporation pond simulations were performed using radiation in participating media, and spectral properties of the photo-thermal umbrella were used as inputs along with relevant boundary conditions (Supplementary Note 5).

#### **Data Availability**

The data that support the findings of this study are available in the Supplementary Information, and additional data is available from the corresponding author (<u>rsprasher@lbl.gov</u>) upon request.

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# **Author Contributions**

A.K.M. and I.H. contributed equally to this work. The idea of non-contact radiative heating was conceptualized by R.P. and developed by S.L., S.K. and I.H. A.K.M. and I.H. conducted experiments, developed models and analyzed results. A.K.M., I.H., S.K., and R.P. wrote the paper. R.P supervised the

research.

# **Ethics Declaration**

The authors declare no competing interests.

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