

1 **A novel application of membrane distillation to facilitate nickel recovery from**
2 **electroplating wastewater**

3 Submitted to

4 **Environmental Science and Pollution Research**

5 Hung C. Duong^{a,b,*}, Thao M. Pham^b, Son T. Luong^b, Ky V. Nguyen^b, Diu T. Nguyen^b, Ashley J.
6 Ansari^c, and Long D. Nghiem^a

7 ^a Centre for Technology in Water and Wastewater, University of Technology Sydney, Ultimo,
8 NSW 2007, Australia

9 ^b Le Quy Don Technical University, Hanoi, Vietnam

10 ^c Strategic Water Infrastructure Laboratory, School of Civil, Mining and Environmental
11 Engineering, University of Wollongong, Wollongong, NSW 2522, Australia

12
13
14
15
16
17
18 _____
19 * Corresponding authors:

20 Hung Cong Duong, email hungcongduong@hotmail.com; Tel: +84 357 593243

22 **Abstract:** In many years, the nickel electroplating technique has been applied to coat nickel on
23 other materials for their increased properties. Nickel electroplating has played a vital role in our
24 modern society, but also caused considerable environmental concerns due to the mass discharge of
25 its wastewater (i.e. containing nickel and other heavy metals) to the environment. Thus, there is a
26 strong need for treating nickel electroplating wastewater to protect the environment and in tandem
27 recover nickel for beneficial use. This study explores a novel application of membrane distillation
28 (MD) for the treatment of nickel electroplating wastewater for a dual purpose: facilitating the nickel
29 recovery and obtaining fresh water. The experimental results demonstrate the technical capability
30 of MD to pre-concentrate nickel in the wastewater (i.e. hence facilitate the subsequent nickel
31 recovery via chemical precipitation or electrodeposition) and extract fresh water. At a low
32 operating feed temperature of 60 °C, the MD process increased the nickel content in the wastewater
33 by more than 100-folds from 0.31 to 33 g/L with only a 20% reduction in the process water flux
34 and obtained pure fresh water. At such high concentration factors, the membrane surface was
35 slightly fouled by inorganic precipitates; however, membrane pore wetting was not evident,
36 confirmed by the purity of the obtained fresh water. The fouled membrane was effectively cleaned
37 using a 3% HCl solution to restore its surface morphology. Finally, the thermal energy analysis of
38 the combined MD–chemical precipitation/electrodeposition process revealed a considerable
39 reduction in energy consumption of the nickel recovery process.

40 **Keywords:** membrane distillation (MD); nickel recovery; nickel electroplating wastewater
41 treatment; membrane wetting.

42 1. Introduction

43 Nickel electroplating plays an important role in our modern society. Given its excellent
44 chemical and physical properties, in many applications, nickel is coated on the surface of other
45 metallic and non-metallic materials by electroplating to increase their strength and resistance to
46 corrosion or degradation, and to provide decorative appearance. However, the growth of nickel
47 electroplating industries has also resulted in considerable environmental and health concerns
48 (Coman V., Robotin B. and Ilea P. 2013, Almazán-Ruiz F.J., Caballero F., Cruz-Díaz M.R., Rivero
49 E.P., Vazquez-Arenas J. and González I. 2015). A typical nickel electroplating process involves
50 three main steps including surface pre-treatment, electrodeposition, and product post-treatment.
51 Amongst these steps, post-treatment (i.e. product rinsing) entails the discharge of large volumes of
52 rinse water (i.e. electroplating wastewater) containing nickel and other heavy metals at various
53 concentrations to the environment. Long-term exposure to nickel polluted environments resulting
54 from nickel electroplating wastewater discharge can lead to numerous health problems such as
55 contact dermatitis, lung fibrosis, heart attack, kidney diseases, and even cancer (Denkhaus E. and
56 Salnikow K. 2002, Kasprzak K.S., Sunderman F.W. and Salnikow K. 2003). In this context, there
57 has been mounting interest in the treatment of nickel electroplating wastewater for simultaneous
58 environmental pollution prevention and beneficial recovery of nickel.

59 Several methods, most notably including chemical precipitation and electrodeposition, have
60 been explored to treat nickel electroplating wastewater (Njau K.N., Woude M.v., Visser G.J. and
61 Janssen L.J.J. 2000, Giannopoulou I. and Panias D. 2007, Blais J.-F., Djedidi Z., Cheikh R., D.
62 Tyagi R. and Mercier G. 2008, Giannopoulou I. and Panias D. 2008, Barakat M.A. 2011, Coman
63 V., Robotin B. and Ilea P. 2013) (Table 1). In chemical precipitation treatment of nickel
64 electroplating wastewater, nickel is converted to insoluble nickel hydroxide by elevating pH to
65 9–10, and the precipitated nickel hydroxide is subsequently removed from the wastewater. The
66 chemical precipitation treatment of the electroplating wastewater can achieve a nickel removal rate
67 as high as 99.76% (Giannopoulou I. and Panias D. 2007, 2008). It is noteworthy that the chemical
68 precipitation method requires pre-concentrating and heating the nickel electroplating wastewater
69 (i.e. 65–95 °C) to achieve a maximum nickel removal rate (Giannopoulou I. and Panias D. 2007,
70 2008). In the electrodeposition treatment, nickel from the electroplating wastewater is deposited
71 onto cathodes in an electrolyser. Nickel can be recovered from the wastewater in the form of
72 metallic nickel, nickel oxide, or nickel hydroxide depending on the wastewater composition and
73 the electrolysis conditions (Njau K.N., Woude M.v., Visser G.J. and Janssen L.J.J. 2000, Orhan

74 G., Arslan C., Bombach H. and Stelter M. 2002, Coman V., Robotin B. and Ilea P. 2013). Similar
 75 to chemical precipitation, the efficiency of the electrodeposition treatment of nickel electroplating
 76 wastewater is strongly affected by the temperature and the initial nickel concentration of the
 77 wastewater. A more concentrated nickel electroplating wastewater at an elevated temperature leads
 78 to increased nickel recovery rate and enhanced current efficiency (Orhan G., Arslan C., Bombach
 79 H. and Stelter M. 2002, Coman V., Robotin B. and Ilea P. 2013).

80 **Table 1.** Treatment of nickel electroplating wastewater for removal and recovery of nickel.

Method	Operating conditions	Removal efficiency (%)	Ref.
Chemical precipitation			
		–	
Chemical precipitation	- Initial Ni concentration: 0.6 g/L - pH: 9.8 - Temperature:	99.74	Giannopoulou & Panias 2007
Electrodeposition	- Initial Ni concentration: 0.3–2.4 g/L - Current density: 8–500 A/m ² - pH: 6.32 - Temperature: 20 °C	–	Njau et al. 2000

81 Membrane distillation (MD) has recently emerged as a feasible process for treatment and
 82 concentration of challenging waters (Abdelkader S., Gross F., Winter D., Went J., Koschikowski
 83 J., Geissen S.U. and Bousselmi L. 2018, Nguyen N.C., Chen S.-S., Jain S., Nguyen H.T., Ray S.S.,
 84 Ngo H.H., Guo W., Lam N.T. and Duong H.C. 2018, Plattner J., Kazner C., Naidu G., Wintgens
 85 T. and Vigneswaran S. 2018). MD is a hybrid process that combines thermal distillation and
 86 membrane separation (Drioli E., Ali A. and Macedonio F. 2015, González D., Amigo J. and Suárez
 87 F. 2017). The MD process uses a hydrophobic and microporous membrane to separate a feed water
 88 and a fresh distillate stream. Due to its hydrophobic nature, the MD membrane prevents the
 89 permeation of liquid water (i.e. hence dissolved salts and non-volatile compounds) while allowing
 90 for the transport of water vapor through membrane pores. The driving force for the water vapor
 91 transport across the membrane pores is a water vapor pressure gradient induced by a temperature
 92 difference between two sides of the membrane. Unlike other pressure-driven membrane separation
 93 processes, MD is negligibly affected by the osmotic pressure and the salinity of the feed water.
 94 Thus, the MD process can concentrate saline waters up to their salt saturation limits. Moreover,

95 because the MD process mainly relies on thermal energy and can be efficiently operated at mild
96 temperatures (i.e. with feed water temperature ranging from 40 to 80 °C), waste heat and solar
97 thermal energy available on site can be sourced to power the MD process and thus reduce water
98 treatment costs. Given these notable attributes, the MD process has been successfully demonstrated
99 for the [treatment and concentration of various challenging wastewaters](#) including [wastewaters from](#)
100 [textile, dyeing, and dairy industries](#), brines following the reverse osmosis (RO) treatment of
101 seawater and oil/gas produced water (Duong H.C., Chivas A.R., Nelemans B., Duke M., Gray S.,
102 Cath T.Y. and Nghiem L.D. 2015, Duong H.C., Duke M., Gray S., Nelemans B. and Nghiem L.D.
103 2016), draw solutions of forward osmosis (FO) (Nguyen N.C., Chen S.-S., Jain S., Nguyen H.T.,
104 Ray S.S., Ngo H.H., Guo W., Lam N.T. and Duong H.C. 2018), and liquid desiccant solutions used
105 in air-conditioning systems (Duong H.C., Hai F.I., Al-Jubainawi A., Ma Z., He T. and Nghiem
106 L.D. 2017, Duong H.C., Álvarez I.R.C., Nguyen T.V. and Nghiem L.D. 2018).

107 A critical condition for the MD process to maintain its separation efficiency is the absence of
108 liquid water in the membrane pores (Han L., Tan Y.Z., Netke T., Fane A.G. and Chew J.W. 2017,
109 Rezaei M., Warsinger D.M., Lienhard V J.H. and Samhaber W.M. 2017, Wang Z. and Lin S. 2017,
110 Velioglu S., Han L. and Chew J.W. 2018, Wang Z., Chen Y., Sun X., Duddu R. and Lin S. 2018).
111 This condition is underpinned by the hydrophobicity of the membrane surface and the surface
112 tension of the feed water. During the MD process of challenging waters, contaminants (i.e.
113 surfactants and organic additives) and precipitated salts in the feed water might interact with the
114 membrane surface and alter its hydrophobicity and reduce the water surface tension at the
115 membrane pore entrance, resulting in the intrusion of liquid water into the membrane pores (Han
116 L., Tan Y.Z., Netke T., Fane A.G. and Chew J.W. 2017, Wang Z. and Lin S. 2017, Wang Z., Chen
117 Y., Sun X., Duddu R. and Lin S. 2018). The intrusion of liquid water into membrane pores is
118 termed as membrane wetting in the MD process. Membrane wetting reduces the active membrane
119 surface area for water evaporation and leads to the salt leakage through the membrane, thus
120 deteriorating the separation efficiency of the MD process (Duong H.C., Duke M., Gray S., Cath
121 T.Y. and Nghiem L.D. 2015, Duong H.C., Duke M., Gray S., Cooper P. and Nghiem L.D. 2016,
122 Sanmartino J.A., Khayet M., García-Payo M.C., El-Bakouri H. and Riaza A. 2017).

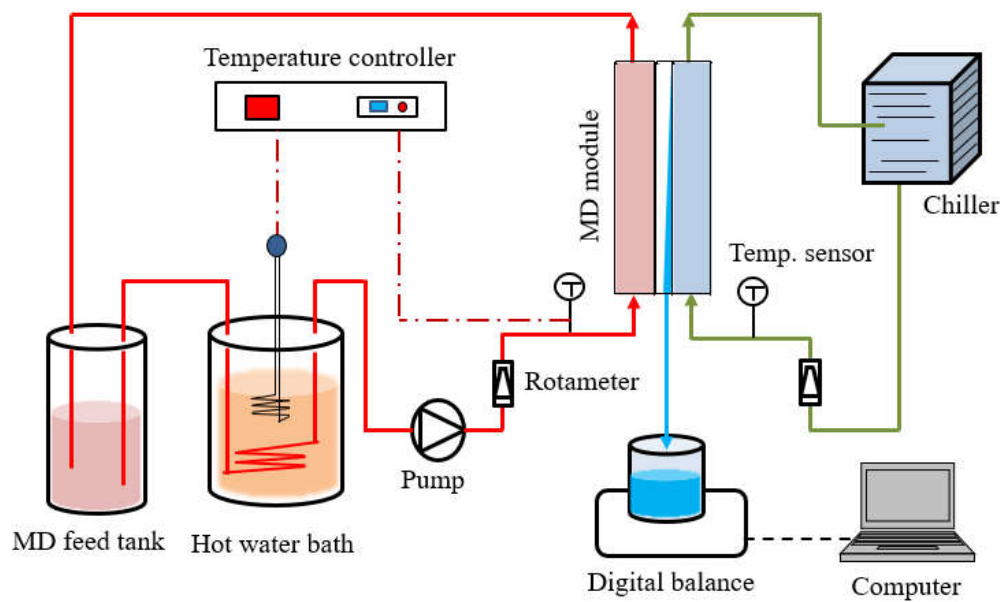
123 This study aims to evaluate the feasibility of the MD process for concentrating nickel
124 electroplating wastewater for subsequent nickel recovery via chemical precipitation or
125 electrodeposition. Real nickel electroplating wastewater was first characterised and long-term MD
126 experiments of the electroplating wastewater were conducted to assess the performance of the MD
127 process during the concentration of the wastewater. The obtained MD distillate and the

128 concentrated wastewater were subsequently examined to determine their suitability for beneficial
129 reuse. Finally, potential for reduction in the thermal energy consumption of combined
130 MD–chemical precipitation/electrodeposition was analysed to highlight the benefits of the MD
131 process for the treatment of nickel electroplating wastewater.

132 **2. Materials and methods**

133 **2.1. Membrane distillation system**

134 A lab-scale MD system was used in this study (Fig. 1). The system consisted of an air gap MD
135 membrane module with a flat-sheet [polytetrafluoroethylene \(PTFE\)](#) membrane purchased from
136 Porous Membrane Technology (Ningbo, China). The specifications of the PTFE membrane and air
137 gap MD membrane module are shown in Table 1. The nickel electroplating wastewater solution
138 was heated using a hot water bath before entering the feed channel of the membrane module. As
139 the wastewater solution travelled along the feed channel, water evaporated at the membrane surface
140 and hence the wastewater solution was concentrated. The concentrated wastewater was then
141 returned to the feed tank. Water vapour generated at the feed membrane surface permeated through
142 membrane pores to the distillate channel due to the vapour pressure gradient caused by the
143 temperature difference between the feed and the distillate channels. When water vapour reached
144 the coolant plate, it condensed into distillate and bled out of the membrane module by gravity into
145 a distillate tank placed on a digital balance connected with a computer. Chilled water was circulated
146 along the coolant channel to maintain the temperature of the coolant plate. Temperature sensors
147 and rotameters were placed before the inlets of the feed and coolant channels to measure
148 temperature and circulation rates, respectively. A heating element connected to a temperature
149 control unit and a chiller were employed to regulate the feed and coolant temperatures.



150
151 **Fig. 1.** Schematic diagram of the air gap MD system.

152 The nickel electroplating wastewater was collected from a nickel electrodeposition (i.e. using
153 the Watts nickel electroplating solution) factory in Hanoi, Vietnam. The wastewater (25 L) was
154 filtered using 0.45 μm filter papers prior to its treatment using the MD process.

155 **Table 2.** Specifications of the PTFE membrane and the air gap membrane module.

<i>The flat-sheet PTFE membrane:</i>	
Membrane thickness (μm)	60
Membrane pore size (μm)	0.2
Membrane porosity (%)	90
<i>The air gap membrane module:</i>	
Length of the channels (cm)	14.5
Width of the channels (cm)	9.5
Active membrane surface area (cm^2)	137.8
Thickness of the feed channel (mm)	3.0
Thickness of the coolant channel (mm)	3.0
Thickness of the distillate channels (mm)	1.0
Condenser material	Aluminium
Spacer material	Polypropylene
Gasket material	Silicone rubber
Module cell material	Acrylic

156 2.2. Analytical methods

157 Cation concentrations of the nickel electroplating wastewater and the distillate extracted from
158 the MD process were analysed using an ICP-MS system (Agilent 7500CS, USA). The plating
159 wastewater anion contents (e.g. sulphate and chloride) were determined using conventional

160 analytical methods. Briefly, sulphate in the wastewater was precipitated by adding excessive
161 barium nitrate at 70 °C. The precipitate was then filtered and dried in an oven at 800 °C for one
162 hour. The weight of the dried barium sulphate precipitate was measured to calculate the sulphate
163 content of the plating wastewater. The wastewater chloride content was then determined based on
164 the cations and sulphate contents given the electroneutrality condition of the wastewater solution.
165 The electrical conductivity and pH of the nickel electroplating wastewater and the distillate
166 obtained from the MD process were measured using a conductivity-pH meter (Hatch, USA).

167 Surface characteristics of membranes were analysed using a Scanning Electron Microscope
168 (Hitachi SEM-4800, Japan) and a Contact Angle Measure (CAM 200, Finland). Prior to the SEM
169 analysis, the membranes were coated with a thin layer of gold. For the contact angle measurement,
170 deionised (DI) water was used as the reference liquid.

171 **2.3. Experimental protocols**

172 MD treatment of the electroplating wastewater solution was conducted at inlet feed and coolant
173 temperature of 60 and 25 °C, respectively, with feed and coolant circulation rates of 0.3 L/min (i.e.
174 equivalent to a cross-flow velocities of 0.045 m/s). The MD experiment of the electroplating
175 wastewater feed was conducted at daytime only and the MD system was switched off at night
176 without rinsing the system with fresh water. The process water flux and distillate electrical
177 conductivity were regularly measured throughout the experiment. The MD process was finally
178 terminated after the wastewater had been concentrated by 100-folds (as the minimum feed water
179 volume to run the process was 200 ml) or until water flux reduced to zero. Then, the membrane
180 was disassembled from the module and kept for subsequent membrane surface analysis and
181 membrane cleaning effectiveness evaluation. An additional MD experiment using a DI water feed
182 solution was conducted under the same operating conditions to determine the process baseline
183 water flux.

184 A fouled membrane coupon (i.e. 2 × 5 cm) was used to evaluate the effectiveness of membrane
185 cleaning using a 3% HCl solution. The membrane coupon was submerged in the cleaning solution
186 at 25 °C for 5 minutes under mild agitation. After cleaning, the membrane was rinsed with DI water
187 and air-dried prior to the SEM and contact angle analysis.

188 3. Results and discussions

189 3.1. Characterisation of nickel electroplating wastewater

190 The characterisation results of the nickel electroplating wastewater (Table 2) confirmed that the
191 Watts plating solution had been used in the electrodeposition process. The wastewater had pH,
192 electrical conductivity, and total dissolved solids of 6.8, 1,006 $\mu\text{S}/\text{cm}$, and 1,100 mg/L,
193 respectively. The total suspended solids content of the wastewater was 4.0 mg/L, and the
194 wastewater was mainly composed of nickel (310.58 mg/L), sulphate (418.0 mg/L), and chloride
195 (341.3 mg/L). These characterisation results indicated that the electroplating wastewater was
196 neither dilute enough for environmentally safe direct discharge nor concentrated enough for
197 efficient nickel recovery (Njau K.N., Woude M.v., Visser G.J. and Janssen L.J.J. 2000, Orhan G.,
198 Arslan C., Bombach H. and Stelter M. 2002, Peng C., Jin R., Li G., Li F. and Gu Q. 2014, Almazán-
199 Ruiz F.J., Caballero F., Cruz-Díaz M.R., Rivero E.P., Vazquez-Arenas J. and González I. 2015).
200 Thus, the wastewater needed to be pre-concentrated to facilitate nickel recovery in the subsequent
201 chemical precipitation or electrodeposition process. [Alternatively, the electroplating wastewater](#)
202 [can be diluted using fresh water for safe discharge to the environment. Nevertheless, this alternate](#)
203 [method is not encouraged given the more stringent water pollution laws and regulations and](#)
204 [increased nickel cost.](#)

205 **Table 3.** Characteristics of the nickel electroplating wastewater.

<i>General characteristics</i>	
Conductivity ($\mu\text{S}/\text{cm}$)	1,006
pH	6.8
Total dissolved solids (mg/L)	1,100.0
Total suspended solids (mg/L)	4.0
<i>Ion concentrations (mg/L)</i>	
Nickel	310.58
Manganese	6.41
Calcium	3.48
Zinc	1.70
Magnesium	1.19
Sulphate	418.0
Chloride	341.3

206 3.2. MD treatment of the nickel electroplating wastewater

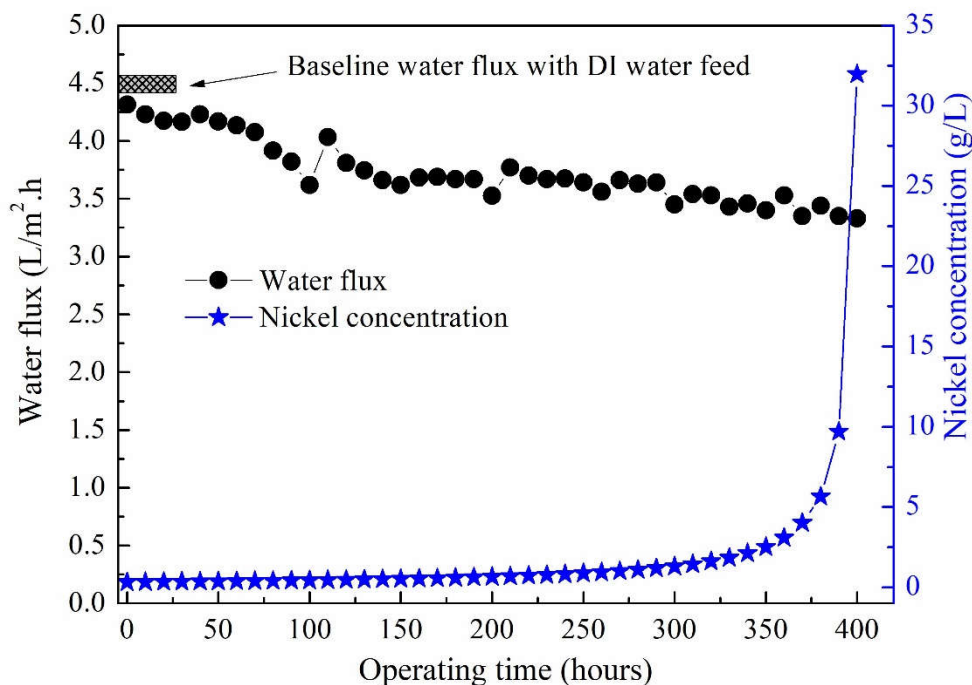
207 The viability of MD for the treatment of nickel electroplating wastewater was assessed based
208 on the process water flux, risk of membrane fouling and wetting, nickel concentration efficiency

209 and the obtained distillate quality. The experimental results demonstrated that the MD process was
210 capable of pre-concentrating the electroplating wastewater to facilitate the subsequent nickel
211 recovery and to produce quality distillate in tandem.

212 3.2.1. *Water flux during the MD treatment of nickel electroplating wastewater*

213 Water flux of the MD process was slightly affected by nickel salts in the electroplating
214 wastewater (Fig. 2). Initially, the MD process with the wastewater feed (i.e. with a low nickel
215 concentration of 0.31 g/L) achieved a water flux similar to that obtained during the baseline
216 experiment using DI water as the feed. During the concentration process, as the distillate was
217 extracted from the wastewater feed, the nickel concentration of the wastewater feed increased. For
218 the first 350 hours, the nickel concentration increased at small rates given the large volume of the
219 wastewater feed compared to the distillation rate. The last 50 hours of the operation witnessed an
220 exponential increase in the nickel concentration after the wastewater feed volume had been
221 significantly reduced. On the other hand, the water flux gradually decreased throughout the MD
222 concentration of the wastewater feed. At the completion of the process, although the nickel
223 concentration had been increased by more than 100-folds, the process water flux only reduced
224 approximately by 20% compared to the initial value (i.e. from 4.3 to 3.3 L/m²·h).

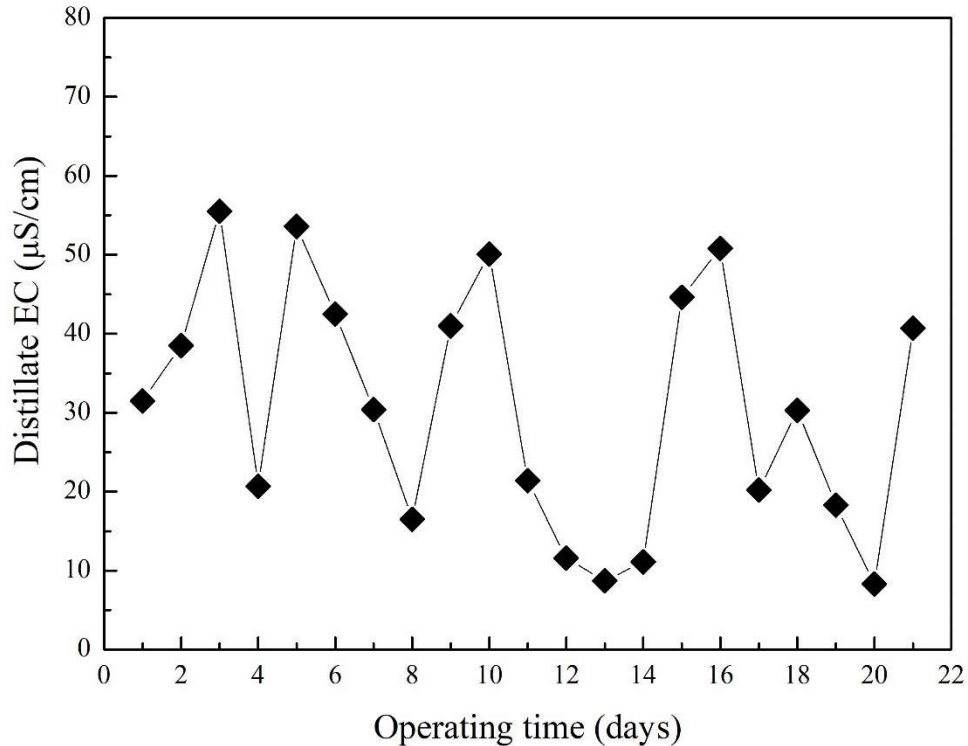
225 The marginal impact of salt concentrations on the MD process water flux demonstrates the
226 superiority of MD over pressure-driven membrane processes (i.e. RO) for concentrating the plating
227 wastewater. During MD, salts in the feed water only affect the process water flux by reducing water
228 vapour pressure and increasing viscosity of the feed water. Hence, the influence of reduced water
229 vapour pressure and increased viscosity on MD water flux is negligible compared to the impact of
230 increased osmotic pressure on RO water flux. Indeed, successful applications of MD for the
231 concentration of hyper saline water feeds, including RO brines from seawater and oil/gas produced
232 water desalination (Duong H.C., Chivas A.R., Nelemans B., Duke M., Gray S., Cath T.Y. and
233 Nghiem L.D. 2015, Peng Y., Ge J., Li Z. and Wang S. 2015, Zhang P., Knötig P., Gray S. and
234 Duke M. 2015, Duong H.C., Duke M., Gray S., Nelemans B. and Nghiem L.D. 2016), draw
235 solutions for the forward osmosis (FO) process (Xie M., Nghiem L.D., Price W.E. and Elimelech
236 M. 2013, Li X.M., Zhao B., Wang Z., Xie M., Song J., Nghiem L.D., He T., Yang C., Li C. and
237 Chen G. 2014), and liquid desiccant solutions for air conditioning systems (Duong H.C., Hai F.I.,
238 Al-Jubainawi A., Ma Z., He T. and Nghiem L.D. 2017, Chen Q., Kum Ja M., Li Y. and Chua K.J.
239 2018, Duong H.C., Álvarez I.R.C., Nguyen T.V. and Nghiem L.D. 2018), have been demonstrated.



240
 241 **Fig. 2.** Water flux and nickel concentration during the MD process of the electroplating wastewater.
 242 Operating conditions: feed temperature (T_{feed}) = 60 °C, coolant temperature ($T_{coolant}$) = 25 °C, feed
 243 and coolant circulation rates = 0.3 L/min.

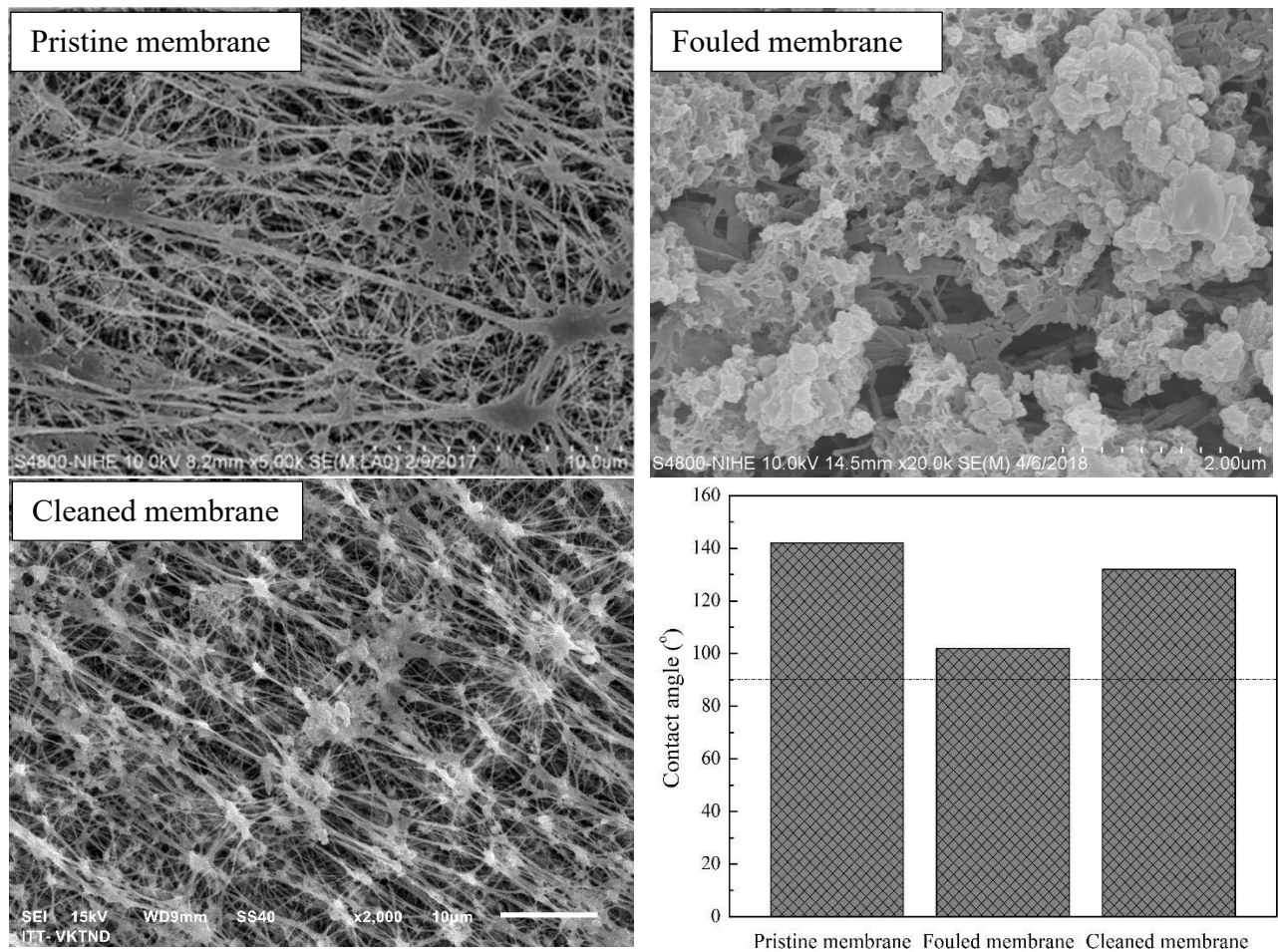
244 *3.2.2. Membrane fouling and wetting during MD treatment of nickel electroplating wastewater*

245 The MD process demonstrated a strong resistance to membrane wetting during the treatment of
 246 the nickel electroplating wastewater. Throughout the MD concentration process of the plating
 247 wastewater, the electrical conductivity of the obtained distillate was always below 60 $\mu\text{S}/\text{cm}$ (Fig.
 248 3), confirming that membrane pore wetting did not occur. The non-wetting condition of the
 249 membrane pores during the MD process of the plating wastewater was also verified by the gradual
 250 decline in water flux (Fig. 2). It is noteworthy that when the membrane pores are wetted, salts from
 251 the electroplating wastewater feed will penetrate through the membrane pores to contaminate the
 252 distillate, inevitably increasing the distillate electrical conductivity. Wetting of the membrane pores
 253 also reduces the active membrane surface for water evaporation, thus leading to a noticeable
 254 decline in the process water flux. The variation in the daily measured distillate electrical
 255 conductivity might be attributed to the corrosion of the aluminium condenser plate and the
 256 measurement errors.



257
 258 **Fig. 3.** Variation in the distillate electrical conductivity (EC) during the MD process of the nickel
 259 electroplating wastewater. Operating conditions: feed temperature (T_{feed}) = 60 °C, coolant
 260 temperature (T_{cool}) = 25 °C, feed and coolant circulation rates = 0.3 L/min.

261 SEM analysis of the membrane surface revealed that inorganic salts had precipitated on the
 262 membrane surface (Fig. 4). **These precipitated inorganic salts might be mainly composed of nickel**
 263 **and sulphate given their dominant concentrations in the electroplating wastewater feed (Table 3).**
 264 However, the impact of the precipitate layers on the process water flux and distillate electrical
 265 conductivity was negligible (Figs. 2&3). This can be attributed to the fact that the MD process was
 266 operated at a low hydrostatic pressure; thus, the precipitate layers formed on the membrane surface
 267 were porous and loose. These porous and loose **inorganic** precipitate layers could be effectively
 268 removed by cleaning the fouled membrane with the 3% HCl solution. Indeed, the SEM image of
 269 the fouled membrane surface after membrane cleaning was similar to that of a pristine membrane
 270 (Fig. 4). **The effectiveness of membrane cleaning using acidic cleaning agents for inorganic**
 271 **precipitates in the MD process has been previously reported .**



272 **Fig. 4.** SEM images and contact angles of a pristine membrane, the fouled membrane, and the
 273 fouled membrane after cleaning with 3% HCl solution.

274 Contact angle measurement results also demonstrated strong resistance to membrane fouling
 275 and wetting of the MD process for nickel electroplating wastewater (Fig. 4). Compared to the
 276 pristine membrane, the fouled membrane exhibited a lower water contact angle (i.e. 102° compared
 277 to 142°); however, this value was still far above the hydrophobicity threshold (i.e. 90°) for MD
 278 membranes, preventing the membrane pores from being wetted. Moreover, given the ease of
 279 membrane cleaning with the HCl solution, the fouled membrane surface after cleaning could
 280 mostly restore its original hydrophobicity (i.e. with a contact angle of 132°). The marginal
 281 reduction in contact angle of the cleaned membrane compared to that of the pristine membrane was
 282 because of changes in membrane pore structures under the influence of temperature during the MD
 283 process. Slight decline in membrane hydrophobicity has been observed during the MD process
 284 even with fresh water feed (Ge J., Peng Y., Li Z., Chen P. and Wang S. 2014). It is noteworthy the
 285 raw nickel electroplating wastewater contained organic additives. These organic additives might

286 have posed some challenges to the MD process as they could attach to the membrane surface and
 287 alter the membrane hydrophobicity. However, pre-filtering the nickel electroplating wastewater
 288 with 0.45 μm filter papers effectively reduced its organic content, thus preventing the MD process
 289 from membrane wetting. This is consistent with results reported in previous studies on the MD
 290 treatment of seawater whereby organic matters in seawater were effectively removed by filter
 291 papers (Duong H.C., Cooper P., Nelemans B. and Nghiem L.D. 2015, Duong H.C., Cooper P.,
 292 Nelemans B., Cath T.Y. and Nghiem L.D. 2016).

293 3.2.3. Characteristics of the MD distillate and concentrated nickel electroplating solution

294 Results in this study prove the capability of MD for producing high-quality distillate from the
 295 nickel electroplating wastewater. The ICP-MS analysis results demonstrated that the MD distillate
 296 contained very low concentrations of metals with a total concentration of around 2.0 mg/L (Table
 297 4). The distillate can be reused as rinsing water to reduce the water footprint of the electroplating
 298 process or safely discharged to the environment (Almazán-Ruiz F.J., Caballero F., Cruz-Díaz M.R.,
 299 Rivero E.P., Vazquez-Arenas J. and González I. 2015).

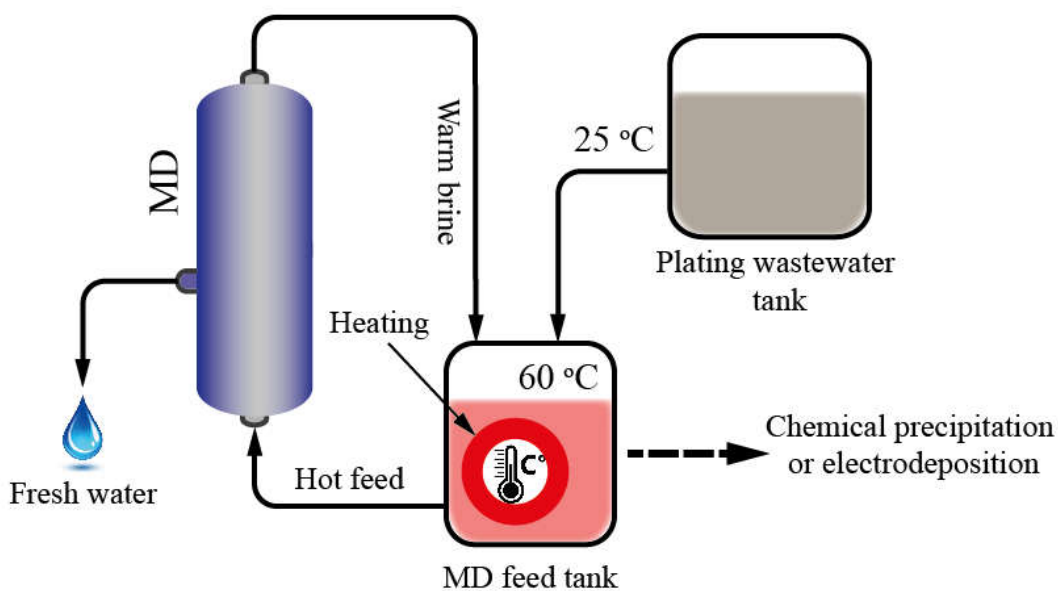
300 **Table 4.** Cation concentrations of the MD distillate.

<i>Cations</i>	<i>Concentration (mg/L)</i>
Nickel	1.141
Wolfram	0.799
Calcium	0.386
Magnesium	0.076
Zinc	0.002
Strontium	0.001

301 In addition to producing the high-quality distillate, the MD process could elevate the nickel
 302 concentration in the wastewater to facilitate the subsequent recovery of nickel via chemical
 303 precipitation or electrodeposition. The concentrated wastewater had nickel concentration of 33 g/L,
 304 which was in the optimal range of nickel concentration required for efficient chemical precipitation
 305 or electrodeposition (Coman V., Robotin B. and Ilea P. 2013). Moreover, the sensible heat
 306 remained in the hot concentrated electroplating wastewater can be utilized to reduce the thermal
 307 energy demand of the chemical precipitation/electrodeposition process.

308 **3.3. Thermal energy consumption analysis of the combined MD–chemical**
309 **precipitation/electrodeposition of nickel electroplating wastewater**

310 The combined MD–chemical precipitation/electrodeposition process for treatment of nickel
311 electroplating wastewater can offer considerable benefits with respects to thermal energy
312 consumption reduction. MD concentration of the nickel electroplating wastewater can be operated
313 in brine recycling mode (i.e. batch mode): the warm brine leaving the MD module is returned to
314 the MD feed tank to continuously increase the nickel concentration in the feed tank (Fig. 5). As the
315 warm brine is returned to the feed tank, its sensible heat can be recovered to reduce the thermal
316 energy demand of the MD process (Duong H.C., Cooper P., Nelemans B. and Nghiem L.D. 2015,
317 Swaminathan J. and Lienhard J.H. 2018). When the nickel concentration in the feed tank reaches
318 33 g/L, the MD process is terminated, and the chemical precipitation/electrodeposition process can
319 be initiated. The residual heat contained in the MD concentrated wastewater (i.e. at 60 °C) can be
320 utilised to facilitate the optimal nickel removal/recovery in the chemical
321 precipitation/electrodeposition process, thus obviating the need for heating the concentrated
322 wastewater. Our calculation reveals that the thermal energy saving from heating the concentrated
323 MD brine (from 25 °C to 60 °C) to recover 1 kg of nickel from the brine (i.e. given the nickel
324 concentration of 33 g/L and the recovery ratio of 90%) during the chemical
325 precipitation/electrodeposition process can be as high as 1,370 kWh.



326
327 **Fig. 5.** Schematic diagram of a combined MD–chemical precipitation/electrodeposition process
328 for nickel recovery.

329 4. Conclusions

330 This study explored a novel MD application for the treatment and concentration of nickel
331 electroplating wastewater to facilitate beneficial reuses. The experimental results demonstrated the
332 technical viability of MD for treatment of the nickel electroplating wastewater prior to nickel
333 recovery via chemical precipitation or electrodeposition. At a feed and coolant temperature of 60
334 and 25 °C, respectively, the MD process could increase the nickel concentration of the
335 electroplating wastewater from 0.31 to 33 g/L. At high concentration factors (i.e. 100 folds), the
336 process water flux experienced a slight reduction (i.e. by 20%), and the membrane surface was
337 slightly fouled by inorganic precipitates. However, no evidence of membrane pore wetting during
338 the MD concentration of the electroplating wastewater was observed, as demonstrated by the purity
339 of the obtained distillate. The surface morphology of the fouled membrane was effectively restored
340 by rinsing the fouled membrane with the 3% HCl solution. The combined MD–chemical
341 precipitation/electrodeposition process for the treatment of the nickel electroplating wastewater can
342 offer considerable benefits with respects to thermal energy consumption reduction because the
343 sensible heat of the warm MD concentrated wastewater can be utilised in chemical
344 precipitation/electrodeposition.

345 References

- 346 Abdelkader S., Gross F., Winter D., Went J., Koschikowski J., Geissen S.U. and Bousselmi L.
347 (2018), Application of direct contact membrane distillation for saline dairy effluent treatment:
348 performance and fouling analysis, *Environmental Science and Pollution Research*.
- 349 Almazán-Ruiz F.J., Caballero F., Cruz-Díaz M.R., Rivero E.P., Vazquez-Arenas J. and González
350 I. (2015), Nickel recovery from an electroplating rinsing effluent using RCE bench scale and RCE
351 pilot plant reactors: The influence of pH control, *Chemical Engineering Research and Design* 97:
352 18-27.
- 353 Barakat M.A. (2011), New trends in removing heavy metals from industrial wastewater, *Arabian*
354 *Journal of Chemistry* 4: 361-377.
- 355 Blais J.-F., Djedidi Z., Cheikh R., D. Tyagi R. and Mercier G. (2008). Metals Precipitation from
356 Effluents: Review.
- 357 Chen Q., Kum Ja M., Li Y. and Chua K.J. (2018), Thermodynamic optimization of a vacuum multi-
358 effect membrane distillation system for liquid desiccant regeneration, *Applied Energy* 230: 960-
359 973.

- 360 Coman V., Robotin B. and Ilea P. (2013), Nickel recovery/removal from industrial wastes: A
361 review, *Resources, Conservation and Recycling* 73: 229-238.
- 362 Denkhaus E. and Salnikow K. (2002), Nickel essentiality, toxicity, and carcinogenicity, *Critical*
363 *Reviews in Oncology / Hematology* 42: 35-56.
- 364 Drioli E., Ali A. and Macedonio F. (2015), Membrane distillation: Recent developments and
365 perspectives, *Desalination* 356: 56-84.
- 366 Duong H.C., Álvarez I.R.C., Nguyen T.V. and Nghiem L.D. (2018), Membrane distillation to
367 regenerate different liquid desiccant solutions for air conditioning, *Desalination* 443: 137-142.
- 368 Duong H.C., Chivas A.R., Nelemans B., Duke M., Gray S., Cath T.Y. and Nghiem L.D. (2015),
369 Treatment of RO brine from CSG produced water by spiral-wound air gap membrane distillation -
370 A pilot study, *Desalination* 366: 121-129.
- 371 Duong H.C., Cooper P., Nelemans B., Cath T.Y. and Nghiem L.D. (2016), Evaluating energy
372 consumption of membrane distillation for seawater desalination using a pilot air gap system,
373 *Separation and Purification Technology* 166: 55-62.
- 374 Duong H.C., Cooper P., Nelemans B. and Nghiem L.D. (2015), Optimising thermal efficiency of
375 direct contact membrane distillation via brine recycling for small-scale seawater desalination,
376 *Desalination* 374: 1-9.
- 377 Duong H.C., Duke M., Gray S., Cath T.Y. and Nghiem L.D. (2015), Scaling control during
378 membrane distillation of coal seam gas reverse osmosis brine, *Journal of Membrane Science* 493:
379 673-682.
- 380 Duong H.C., Duke M., Gray S., Cooper P. and Nghiem L.D. (2016), Membrane scaling and
381 prevention techniques during seawater desalination by air gap membrane distillation, *Desalination*
382 397: 92-100.
- 383 Duong H.C., Duke M., Gray S., Nelemans B. and Nghiem L.D. (2016), Membrane distillation and
384 membrane electrolysis of coal seam gas reverse osmosis brine for clean water extraction and NaOH
385 production, *Desalination* 397: 108-115.
- 386 Duong H.C., Hai F.I., Al-Jubainawi A., Ma Z., He T. and Nghiem L.D. (2017), Liquid desiccant
387 lithium chloride regeneration by membrane distillation for air conditioning, *Separation and*
388 *Purification Technology* 177: 121-128.
- 389 Ge J., Peng Y., Li Z., Chen P. and Wang S. (2014), Membrane fouling and wetting in a DCMD
390 process for RO brine concentration, *Desalination* 344: 97-107.
- 391 Giannopoulou I. and Panias D. (2007), Copper and nickel recovery from acidic polymetallic
392 aqueous solutions, *Minerals Engineering* 20: 753-760.
- 393 Giannopoulou I. and Panias D. (2008), Differential precipitation of copper and nickel from acidic
394 polymetallic aqueous solutions, *Hydrometallurgy* 90: 137-146.

- 395 González D., Amigo J. and Suárez F. (2017), Membrane distillation: Perspectives for sustainable
396 and improved desalination, *Renewable and Sustainable Energy Reviews* 80: 238-259.
- 397 Han L., Tan Y.Z., Netke T., Fane A.G. and Chew J.W. (2017), Understanding oily wastewater
398 treatment via membrane distillation, *Journal of Membrane Science* 539: 284-294.
- 399 Kasprzak K.S., Sunderman F.W. and Salnikow K. (2003), Nickel carcinogenesis, *Mutation
400 Research/Fundamental and Molecular Mechanisms of Mutagenesis* 533: 67-97.
- 401 Li X.M., Zhao B., Wang Z., Xie M., Song J., Nghiem L.D., He T., Yang C., Li C. and Chen G.
402 (2014), Water reclamation from shale gas drilling flow-back fluid using a novel forward osmosis-
403 vacuum membrane distillation hybrid system, *Water Science and Technology* 69: 1036-1044.
- 404 Nguyen N.C., Chen S.-S., Jain S., Nguyen H.T., Ray S.S., Ngo H.H., Guo W., Lam N.T. and Duong
405 H.C. (2018), Exploration of an innovative draw solution for a forward osmosis-membrane
406 distillation desalination process, *Environmental Science and Pollution Research* 25: 5203-5211.
- 407 Njau K.N., Woude M.v., Visser G.J. and Janssen L.J.J. (2000), Electrochemical removal of nickel
408 ions from industrial wastewater, *Chemical Engineering Journal* 79: 187-195.
- 409 Orhan G., Arslan C., Bombach H. and Stelter M. (2002), Nickel recovery from the rinse waters of
410 plating baths, *Hydrometallurgy* 65: 1-8.
- 411 Peng C., Jin R., Li G., Li F. and Gu Q. (2014), Recovery of nickel and water from wastewater with
412 electrochemical combination process, *Separation and Purification Technology* 136: 42-49.
- 413 Peng Y., Ge J., Li Z. and Wang S. (2015), Effects of anti-scaling and cleaning chemicals on
414 membrane scale in direct contact membrane distillation process for RO brine concentrate,
415 *Separation and Purification Technology* 154: 22-26.
- 416 Plattner J., Kazner C., Naidu G., Wintgens T. and Vigneswaran S. (2018), Removal of selected
417 pesticides from groundwater by membrane distillation, *Environmental Science and Pollution
418 Research* 25: 20336-20347.
- 419 Rezaei M., Warsinger D.M., Lienhard V J.H. and Samhaber W.M. (2017), Wetting prevention in
420 membrane distillation through superhydrophobicity and recharging an air layer on the membrane
421 surface, *Journal of Membrane Science* 530: 42-52.
- 422 Sanmartino J.A., Khayet M., García-Payo M.C., El-Bakouri H. and Riaza A. (2017), Treatment of
423 reverse osmosis brine by direct contact membrane distillation: Chemical pretreatment approach,
424 *Desalination* 420: 79-90.
- 425 Swaminathan J. and Lienhard J.H. (2018), Design and operation of membrane distillation with feed
426 recirculation for high recovery brine concentration, *Desalination* 445: 51-62.
- 427 Velioğlu S., Han L. and Chew J.W. (2018), Understanding membrane pore-wetting in the
428 membrane distillation of oil emulsions via molecular dynamics simulations, *Journal of Membrane
429 Science* 551: 76-84.

- 430 Wang Z., Chen Y., Sun X., Duddu R. and Lin S. (2018), Mechanism of pore wetting in membrane
431 distillation with alcohol vs. surfactant, *Journal of Membrane Science* 559: 183-195.
- 432 Wang Z. and Lin S. (2017), Membrane fouling and wetting in membrane distillation and their
433 mitigation by novel membranes with special wettability, *Water Research* 112: 38-47.
- 434 Xie M., Nghiem L.D., Price W.E. and Elimelech M. (2013), A Forward Osmosis–Membrane
435 Distillation Hybrid Process for Direct Sewer Mining: System Performance and Limitations,
436 *Environmental Science & Technology* 47: 13486-13493.
- 437 Zhang P., Knötig P., Gray S. and Duke M. (2015), Scale reduction and cleaning techniques during
438 direct contact membrane distillation of seawater reverse osmosis brine, *Desalination* 374: 20-30.
- 439 Abdelkader S, Gross F, Winter D, Went J, Koschikowski J, Geissen SU, Bousselmi L (2018)
440 Application of direct contact membrane distillation for saline dairy effluent treatment: performance
441 and fouling analysis. *Environ. Sci. Pollut. Res.* <https://doi.org/10.1007/s11356-018-2475-3>.
- 442 Almazán-Ruiz FJ, Caballero F, Cruz-Díaz MR, Rivero EP, Vazquez-Arenas J, González I (2015)
443 Nickel recovery from an electroplating rinsing effluent using RCE bench scale and RCE pilot plant
444 reactors: The influence of pH control. *Chem. Eng. Res. Des.* 97: 18-27.
- 445 Barakat MA (2011) New trends in removing heavy metals from industrial wastewater. *Arab. J.*
446 *Chem.* 4: 361-377.
- 447 Blais JF, Djedidi Z, Cheikh R, D. Tyagi R, Mercier G (2008) Metals Precipitation from Effluents:
448 Review. *Pract. Period. Hazard. Toxic Radio. Waste Manag.* 12: 135-149.
- 449 Chen Q, Kum Ja M, Li Y, Chua KJ (2018) Thermodynamic optimization of a vacuum multi-effect
450 membrane distillation system for liquid desiccant regeneration. *Appl. Energ.* 230: 960-973.
- 451 Coman V, Robotin B, Ilea P (2013) Nickel recovery/removal from industrial wastes: A review.
452 *Resour. Conserv. Recyc.* 73: 229-238.
- 453 Denkhaus E, Salnikow K (2002) Nickel essentiality, toxicity, and carcinogenicity. *Crit. Rev.*
454 *Oncol. Hematol.* 42: 35-56.
- 455 Drioli E, Ali A, Macedonio F (2015) Membrane distillation: Recent developments and
456 perspectives. *Desalination* 356: 56-84.
- 457 Duong HC, Álvarez IRC, Nguyen TV, Nghiem LD (2018) Membrane distillation to regenerate
458 different liquid desiccant solutions for air conditioning. *Desalination* 443: 137-142.
- 459 Duong HC, Chivas AR, Nelemans B, Duke M, Gray S, Cath TY, Nghiem LD (2015) Treatment of
460 RO brine from CSG produced water by spiral-wound air gap membrane distillation - A pilot study.
461 *Desalination* 366: 121-129.
- 462 Duong HC, Cooper P, Nelemans B, Cath TY, Nghiem LD (2016) Evaluating energy consumption
463 of membrane distillation for seawater desalination using a pilot air gap system. *Sep. Purif. Technol.*
464 166: 55-62.

- 465 Duong HC, Cooper P, Nelemans B, Nghiem LD (2015) Optimising thermal efficiency of direct
466 contact membrane distillation via brine recycling for small-scale seawater desalination.
467 Desalination 374: 1-9.
- 468 Duong HC, Duke M, Gray S, Cath TY, Nghiem LD (2015) Scaling control during membrane
469 distillation of coal seam gas reverse osmosis brine. J. Membr. Sci. 493: 673-682.
- 470 Duong HC, Duke M, Gray S, Cooper P, Nghiem LD (2016) Membrane scaling and prevention
471 techniques during seawater desalination by air gap membrane distillation. Desalination 397: 92-
472 100.
- 473 Duong HC, Duke M, Gray S, Nelemans B, Nghiem LD (2016) Membrane distillation and
474 membrane electrolysis of coal seam gas reverse osmosis brine for clean water extraction and NaOH
475 production. Desalination 397: 108-115.
- 476 Duong HC, Hai FI, Al-Jubainawi A, Ma Z, He T, Nghiem LD (2017) Liquid desiccant lithium
477 chloride regeneration by membrane distillation for air conditioning. Sep. Purif. Technol. 177: 121-
478 128.
- 479 Ge J, Peng Y, Li Z, Chen P, Wang S (2014) Membrane fouling and wetting in a DCMD process
480 for RO brine concentration. Desalination 344: 97-107.
- 481 Giannopoulou I, Panias D (2007) Copper and nickel recovery from acidic polymetallic aqueous
482 solutions. Miner. Eng. 20: 753-760.
- 483 Giannopoulou I, Panias D (2008) Differential precipitation of copper and nickel from acidic
484 polymetallic aqueous solutions. Hydrometallurgy 90: 137-146.
- 485 González D, Amigo J, Suárez F (2017) Membrane distillation: Perspectives for sustainable and
486 improved desalination. Renew. Sust. Energ. Rev. 80: 238-259.
- 487 Han L, Tan YZ, Netke T, Fane AG, Chew JW (2017) Understanding oily wastewater treatment via
488 membrane distillation. J. Membr. Sci. 539: 284-294.
- 489 Kasprzak KS, Sunderman FW, Salnikow K (2003) Nickel carcinogenesis.
490 Mutat. Res. Fund. Mol. Mech. Mut. 533: 67-97.
- 491 Li XM, Zhao B, Wang Z, Xie M, Song J, Nghiem LD, He T, Yang C, Li C, Chen G (2014) Water
492 reclamation from shale gas drilling flow-back fluid using a novel forward osmosis-vacuum
493 membrane distillation hybrid system. Wat. Sci. Tech. 69: 1036-1044.
- 494 Nguyen NC, Chen S-S, Jain S, Nguyen HT, Ray SS, Ngo HH, Guo W, Lam NT, Duong HC (2018)
495 Exploration of an innovative draw solution for a forward osmosis-membrane distillation
496 desalination process. Environ. Sci. Pollut. Res. 25: 5203-5211.
- 497 Njau KN, Woude Mv, Visser GJ, Janssen LJJ (2000) Electrochemical removal of nickel ions from
498 industrial wastewater. Chem. Eng. J. 79: 187-195.

- 499 Orhan G, Arslan C, Bombach H, Stelter M (2002) Nickel recovery from the rinse waters of plating
500 baths. *Hydrometallurgy* 65: 1-8.
- 501 Peng C, Jin R, Li G, Li F, Gu Q (2014) Recovery of nickel and water from wastewater with
502 electrochemical combination process. *Sep. Purif. Technol.* 136: 42-49.
- 503 Peng Y, Ge J, Li Z, Wang S (2015) Effects of anti-scaling and cleaning chemicals on membrane
504 scale in direct contact membrane distillation process for RO brine concentrate. *Sep. Purif. Technol.*
505 154: 22-26.
- 506 Plattner J, Kazner C, Naidu G, Wintgens T, Vigneswaran S (2018) Removal of selected pesticides
507 from groundwater by membrane distillation. *Environ. Sci. Pollut. Res.* 25: 20336-20347.
- 508 Rezaei M, Warsinger DM, Lienhard V JH, Samhaber WM (2017) Wetting prevention in membrane
509 distillation through superhydrophobicity and recharging an air layer on the membrane surface. *J.*
510 *Membr. Sci.* 530: 42-52.
- 511 Sanmartino JA, Khayet M, García-Payo MC, El-Bakouri H, Riaza A (2017) Treatment of reverse
512 osmosis brine by direct contact membrane distillation: Chemical pretreatment approach.
513 *Desalination* 420: 79-90.
- 514 Swaminathan J, Lienhard JH (2018) Design and operation of membrane distillation with feed
515 recirculation for high recovery brine concentration. *Desalination* 445: 51-62.
- 516 Velioglu S, Han L, Chew JW (2018) Understanding membrane pore-wetting in the membrane
517 distillation of oil emulsions via molecular dynamics simulations. *J. Membr. Sci.* 551: 76-84.
- 518 Wang Z, Chen Y, Sun X, Duddu R, Lin S (2018) Mechanism of pore wetting in membrane
519 distillation with alcohol vs. surfactant. *J. Membr. Sci.* 559: 183-195.
- 520 Wang Z, Lin S (2017) Membrane fouling and wetting in membrane distillation and their mitigation
521 by novel membranes with special wettability. *Water Res.* 112: 38-47.
- 522 Xie M, Nghiem LD, Price WE, Elimelech M (2013) A Forward Osmosis–Membrane Distillation
523 Hybrid Process for Direct Sewer Mining: System Performance and Limitations. *Environ. Sci.*
524 *Technol.* 47: 13486-13493.
- 525 Zhang P, Knötig P, Gray S, Duke M (2015) Scale reduction and cleaning techniques during direct
526 contact membrane distillation of seawater reverse osmosis brine. *Desalination* 374: 20-30.