

1 **Membrane Desalination and Water Re-use for Agriculture: State of the Art and Future Outlook**

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9 **Abstract**

10 Membrane-based desalination technologies for agricultural applications are widely applied in
11 many countries around the world. Sustainable and cost-effective desalination technologies, such
12 as reverse osmosis (RO), membrane distillation, forward osmosis, membrane bioreactor, and
13 electrodialysis, are available to provide treated water, but the pure water product does not
14 contain the required level of nutrients to supply agricultural fields. This can be overcome by the
15 use of blended water to meet the required quality of irrigation water for crop production, which
16 is expensive in areas lacking in freshwater resources. The adoption of a hybrid system offers many
17 advantages, such as generating drinking water and water enriched with nutrient at low cost and
18 energy consumption if natural power is used. This review focusses on summarizing the current
19 and recent trends in membrane desalination processes used for agricultural purposes. The
20 challenges being faced with desalinating seawater/brackish water and wastewater are discussed.
21 A specific focus was placed on the viability of hybrid desalination processes and other advanced
22 recovery systems to obtain valuable irrigation water. A comparison between various membrane
23 desalination technologies in terms of treatment efficiency and resource recovery potential is

24 discussed. Lastly, concluding remarks and research opportunities of membrane technologies are
25 analyzed. We concluded that the ED process can be utilized to minimize the energy requirements
26 of other membrane technologies. The MD coupled with ED system can also be utilized to generate
27 high quality irrigation water at low energy requirement. The FO-ED hybrid system exhibited
28 excellent performance and very low energy consumption as compared to other hybrid systems.

29

30 **Key words:** Water desalination, membrane technology, hybrid system, agriculture, crop
31 production

32

33 **Highlights**

34 1-Membrane desalination technologies play a major role in satisfying increasing demand on
35 irrigation water for fertigation.

36 2- Seawater and wastewater are the most common inlet source for treatment processes to
37 provide valuable nutrient water.

38 3- Desalinated water integrated desalination processes can become a continuous water source
39 for crop growth.

40 4- Low energy desalination process for fertigation by electro dialysis combined with forward
41 osmosis hybrid process.

42 5- Efforts should be increased to decrease cost and energy consumption by using renewable
43 power resources.

44

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52 1. Introduction	

53 The global demand for drinking water, food security concerns, and climate change effects on
54 farming have motivated scientific communities to search for alternative resource management
55 strategies [1, 2]. Since petroleum resources are being reduced, most countries have looked for
56 agriculturally produced materials to be used for manufacturing and trade, which imposes further
57 demand on crops [3]. The consumption of plant waste is a promising resource for energy
58 extraction and conversion to electricity [3]. The existing demands on these agricultural products
59 are expected to increase in the future, imposing challenges to developing nations. It has become
60 necessary to explore additional water resources to increase agricultural materials production and
61 support ever-growing requirements [4, 5]. There is an intensive use for irrigated water estimated
62 at 70% of total usage, followed by industrial utilization, around 21%, and domestic use around 9%
63 [1].

64 There has been a renewed interest in the treatment of wastewater to irrigate crops in
65 greenhouses. Membrane based desalination processes used to treat wastewater are reverse
66 osmosis (RO) [6, 7], nanofiltration (NF) [8], membrane bioreactor [9, 10], membrane distillation
67 (MD) [11], and electrodialysis [12]. For example, to remove nitrogen from wastewater, high
68 energy input is required around 45 MJ per kg nitrogen to extract nitrogen gas [11]. NF membranes
69 can be used to separate various nutrients such as ammonium, phosphate, and potassium from
70 sewage sludge [8], achieving a high rejection rate of these nutrients at low hydraulic pressure.
71 However, the wastewater feed solution is composed of various chemical species which may result
72 in fouling and membrane deterioration. Fouling is created due to the adherence of solutes and
73 particulates on the membrane surface leading to cake layer formation and pore clogging [13, 14].
74 Another study reported that there were limited wastewater resources and that its price is high in
75 many developing countries. Thus, researchers shifted to desalinate natural groundwater or
76 brackish water for crop growth due to availability and low salinity ($5 \leq S \leq 5 \text{ g/kg}$) [15].

77 To maximize the agricultural output and minimize impacts on natural water resources, many
78 countries are beginning to utilize irrigated water produced from different saline water sources to
79 cope with high food production demands [16]. Some potential solutions are to develop low cost
80 and climate-independent water resources for fertigation, which are related to desalination
81 technologies. Efficient desalination technologies for irrigated agriculture depends on water
82 desalination and wastewater reclamation [17]. Many countries have started using desalinated
83 water for agricultural purposes to meet their water needs. For instance, Spain consumed 22%
84 used of desalinated water for fertigation from a total desalination capacity of 1.4 million m³/day
85 [16], whilst Kuwait has a desalination capacity higher than 1 million m³/day and 13% for
86 fertigation. Still, only 0.5% of desalinated water overall is currently being used for fertigation. Italy
87 and Bahrain implemented a desalination capacity of 64,700 m³/day and 620,000 m³/day while
88 they used only a small proportion of desalinated water of 1.5% and 0.4% for agriculture. The USA
89 and Qatar used only 1.3% and 0.1% of desalinated water for agricultural purposes.

90 Brackish water desalinated via RO is the most common practice due to high purity product water
91 [18, 19]. Additionally, brackish water can be desalinated by other membrane-based desalination
92 processes such as NF [20, 21], ion exchange resins [20], forward osmosis system (FO) [22], closed-
93 circuit reverse osmosis (CCRO) [23], and electrodialysis reversal (EDR) system [24]. Monovalent-
94 selective electrodialysis reversal (MS-EDR) has been employed to concentrate sodium chloride
95 from seawater [15]. Among these desalination technologies, RO is the leading system for
96 seawater desalination due to minimum energy expenditure relative to other desalination
97 processes [25, 26]. When the seawater was replaced by brackish water in a BWRO plant at Almeria
98 Cuevas de Almanzora, the product water was used for fertigation [18]. The most important
99 advantage of this process was the generation of a variety of water qualities, which could be used
100 as irrigation water and for golf land irrigation. The potable water can also be obtained by mixing

101 the permeate stream with raw water. Spain and Australia depend on SWRO desalination
102 technology for seawater desalination to produce irrigation water for agricultural uses. Australia
103 pioneered the use of reverse osmosis capable sub-surface drip irrigation (ROSDI) for fertigation
104 [17]. This process does not require high hydraulic pressure because it operates based on tension
105 on the soil side to draw water into the system. An acceptable amount of water-rich nutrients of
106 around 0.25 and 1.5 L/h.m² and salt rejection of around 50% were achievable. Some hurdles
107 associated with the RO process hampered its utilization for agricultural aspects. For instance, the
108 desalinated water does not contain an acceptable amount of nutrients or boron or chloride for
109 irrigation water, a high quantity of brine is discharged to the sea, harmful gases may be released
110 into the air, the excess sodium affected the soil and productivity and energy consumption and
111 cost are high [18]. Moreover, recovery strategies have been suggested to concentrate nutrients
112 and ensure suitable quality of irrigation water. Some of these methods are adsorbents such as
113 carbon-based adsorbents [27] and sepiolite [28] along with membrane technologies such as FO
114 [29] and RO processes [30].

115 This paper is a timely critical review of recent advances in membrane-based desalination
116 technologies for producing agricultural irrigation from saline water and wastewater. It addresses
117 the main limitations associated with membrane-based treatment processes development. It
118 discusses the performance of advanced membrane technologies during seawater/brackish water
119 desalination and wastewater reclamation in terms of treatment efficiency and resource recovery
120 potential. It also highlights the potentiality of the hybrid desalination process and other
121 complementary processes for recovering nutrients. Finally, conclusions and remaining drawbacks
122 that need to be further investigated are summarized.

123

124 **2. Applicability of membrane desalination technologies for fertigation**

125 Membrane technology is the leading process for treating seawater and wastewater, providing
126 sustainable development and targeted process efficiency [17]. Many countries over the world
127 have begun to use membrane technology to produce water-rich nutrients for agriculture. Nutrient
128 concentrations by membrane technology is a powerful treatment option for combined production
129 of crops and potable water [20]. One of the advantages of membrane desalination in agriculture
130 is the generation of additional water resources, known as irrigation water. During the late 1950s
131 to the 1980s, asymmetric cellulose acetate membrane was the first membrane used for the RO
132 process [31]. After that, the development of RO membranes continued to enhance the
133 performance of membrane desalination processes. Although the high cost of the RO process
134 remains the major hurdle to the application of RO to seawater desalination and reuse, RO
135 membranes are the most technically viable membranes for producing irrigation water [32]. For
136 agricultural fields, RO membranes or membranes in the hybrid system can generate a high
137 quantity of drinking water and water suitable for irrigated agriculture at relatively low cost and
138 environmental effects [17]. RO membrane can also be used to desalinate brackish water, with the
139 cost estimated to be a third that of seawater desalination [20]. Several industrial seawater and
140 brackish water plants were developed by TEDAGUA to supply irrigation water for agriculture [33].
141 In 1987, RO was operated in the seawater desalination plant located in Gran Canaria [33]. The
142 salinity of the seawater feed was about 34,000 mg/L. The production capacity of irrigation water
143 was 6,900 m³ /d, and a further increase in the capacity by 500 m³ /d was expected in the future.
144 The water permeate had an acceptable level of salinity of about 200 mg/L.

145 Electro-dialysis reversal (EDR) technology was installed in Gran Canaria to produce pure water for
146 agricultural fields [33]. This process is able to desalinate brackish water with a low concentration

147 of around 3,000 mg/L. The predicted energy consumption to treat this brackish water was around
148 1–2 kWh/m³ [33].

149 Membrane distillation is currently being researched to generate irrigation water from seawater.
150 It has been found that the desalinated water recovery was high, resulting in a decrease in the
151 discharge cost per unit of water distillate [20].

152 The membrane bioreactor (MBR) is a widespread technology used to treat municipal wastewater
153 for agricultural purposes [10]. MBR consists of biological processes coupled with membrane
154 filtration to remove organic and inorganic pollutants and microorganisms from wastewater [9,
155 34]. This system can be used in countries that rely on agriculture to grow their economy and can
156 be implemented in rural areas or modern cities. There are many industrial plants around the world
157 able to reclaim wastewater for agricultural fields. An example is an MBR employed to purify
158 wastewater for irrigating vegetables in Chania on the island of Crete [10]. The cost of the MBR
159 system was estimated to be a few cents/m³ to 1 or 2 USD /m³ when treating wastewater to
160 produce irrigation water for food production. This value is assumed to increase based on the
161 water-scarcity factors. The low price of purified water relative to the traditional freshwater would
162 encourage farmers on the island to utilize the purified water and improve water resource
163 management. Mixing MBR and RO effluents could achieve the required quality of irrigation water
164 including acceptable amount of salts [35]. In this way, the reclaimed wastewater has negligible
165 impact on the soil, and there is no need to dispose of the reclaimed wastewater. To that end,
166 membrane technologies are regarded as key elements of providing the feasibility of extracting
167 irrigation water with appropriate salinity for food productivity by either using desalinated water
168 or reclaimed wastewater.

169

170 **3. Water quality required for agricultural irrigation**

171 Water quality plays an important role in determining the suitability of a water supply to be used
172 for agricultural applications. Nowadays, new resources with lower quality are being used for
173 irrigation projects because many good quality water supplies have been intensively used [36].
174 There are some restrictions for using wastewater effluent directly for vegetation, such as negative
175 impacts on the physio-chemical properties of the soil, increasing microbial activity in the soil,
176 aggravation of crop production and yield, and contaminating groundwater with undesired
177 elements [37]. The most significant characteristics in the treated water used as irrigation water
178 are salinity, sodium content, trace elements, excess chloride, and nutrients [38]. High salinity in
179 the irrigation water influence plant health and productivity along with deterioration of the soil
180 structure and properties [38].

181 The product water from the desalination process includes total dissolved solids (TDS) with very
182 low concentrations of less than 20 mg/L, which can be used as drinking water [16]. If the
183 concentration of the inlet fed to the desalination unit is low, the final volume of the permeate
184 could be maximized by blending the permeate with the inlet water, thereby decreasing the unit
185 cost of irrigation water [16].

186 In general, the permeate water has a minimum quantity of calcium and magnesium and is slightly
187 acidic [16]. Therefore, it should be re-mineralized and balanced to reach the required quality for
188 irrigation water. The needed mineral content for agricultural applications is estimated at 0.75 g/L.

189 The essential nutrients for plant growth are N, P, K, Ca, and S [39]. Amongst these elements,
190 Nitrogen (N)/ Phosphorus (P)/ Potassium (K) are the most significant nutrients for mineral or
191 artificial fertilizer. Therefore, the water-soluble fertilizer to be added should contain a suitable
192 quantity of N/P/K nutrients. The concentration of these nutrients in the fertilizer solution depends

193 on the type of crops, cropping seasons, and soil nutrient amounts [40]. The suggested
194 concentration for N / K/ P in the irrigation water is ranged from 50 to 200 mg/L, 15 and 250 mg/L,
195 and up to 1mg/L [37, 41]. According to the United Nations Food and Agricultural Organization
196 (FAO), the recommended concentration of calcium and magnesium in irrigation water is around
197 400 mg/L and 61 mg/L, respectively [42]. Besides, the acceptable phosphorus concentration in
198 the product water from a wastewater plant should be as low as 1.0 mg/L in most countries in
199 which polyphosphates and organic phosphate species derived from orthophosphate compounds
200 are the wastewater [41]. The acceptable level of Mg^{+2} is from 48 to 65 mg/L, while it is around
201 321 mg/L for SO^{-2}_4 constituents [37].

202 The main physicochemical factors for assessing the quality of effluent wastewater are chemical
203 oxygen demand (COD), biochemical oxygen demand (BOD), ammonia-nitrogen, total organic
204 carbon (TOC), and total suspended solids (TSS) [43]. It is, however, impossible to use these
205 physicochemical factors in determining the acute toxicity and genotoxic hazards to aquatic
206 organisms present in the effluent. Aquatic organisms are an effective way to assess the toxic
207 impact of the treated water and evaluate the detoxification efficiencies of many systems [44].
208 Other parameters, such as boron concentration or Sodium Adsorption Ratio (SAR), should be
209 taken into account. The concentration of boron in seawater has been recorded between 4.5 and
210 6.0 mg/L, whilst according to the World Health Organization, the acceptable level of boron in
211 irrigation water is below 0.50 mg/L [32]. The potassium adsorption ratio (PAR) is also used
212 determine water quality. It demonstrates the adverse impact of potassium on soil permeability
213 properties[42]. The water infiltration issue is known as relative to SAR (Sodium Adsorption Ratio)
214 with reference to electrical conductivity. Sodium toxicity can be measured based on RSC (residual
215 sodium carbonate), SSP (soluble sodium percentage), and ESP (exchangeable sodium percentage)
216 [38].

217 Blending of the treated water with freshwater can minimize the concentration of toxic
218 compounds and make it reusable for fertigation. This method is successful in reducing the sodium
219 toxicity because its adsorption in the soil depends on the proportion of monovalent (Na^+) and
220 divalent (Ca^{+2}) cations [38]. When diluting the treated water, the soil would prefer to adsorb the
221 divalent salts like calcium and magnesium ions more than the monovalent sodium.

222

223 **4. Challenges in membrane technology development**

224 The most important challenges in the membrane desalination and wastewater treatment
225 industries involve the characteristics of the feed solution, the standard quality of the treated
226 water, materials development, process advancement, brine discharge, energy consumption,
227 operational and capital costs of facilities and instruments [11, 45].

228 The desalinated water should possess low salinity, meeting the quality standard, and the required
229 nutrient levels for irrigation water. This is because the desalinated water or treated wastewater
230 containing a high concentration of total dissolved solids (TDS) like Sodium (Na^+) and Chlorine (Cl^-)
231 can deteriorate soil properties, inhibit crop productivity and affect negatively the environment
232 [45, 46]. On the other hand, the desalinated water may miss some important mineral nutrients
233 for plant growth, and hence adding complementary minerals to the desalinated water is essential
234 [26]. Other very important problems are the product water quality accuracy, the difference in
235 nutrient requirements for targeted crops, and demand. In light of this, recovery methods for
236 concentrating nutrients should be utilized to ensure a product of acceptable quality for
237 agricultural fields. Another drawback is the emission of CO_2 into the atmosphere, which estimated
238 to be 0.9 kg CO_2 per cubic liter of purified wastewater [11].

239 Membrane technology based on electricity and thermal energy, such as
240 electrodialysis/electrodialysis reversal, reverse osmosis, and membrane distillation, are energy-
241 intensive processes and very expensive [46-48]. The thermal desalination process is not cost-
242 effective, and hence it is rarely used for brackish water desalination. The cost of ion exchange
243 membranes in the voltage-driven membrane process is higher than for RO [49]. In parallel, the
244 salt separation efficiency is low when using seawater as the feed solution compared to the RO
245 process. Therefore, some developing countries cannot afford these desalination technologies for
246 irrigated agriculture. Additional issues are the high electrical resistance of the membrane causes
247 a reduction in the non-Ohmic voltage [49]. This occurs when voltages move across the membrane,
248 thereby influencing the energy expenditure of the system. This electrical resistance is strongly
249 correlated with the solution concentration. The membrane perm-selectivity can be reduced due
250 to severe concentration polarization phenomena arising from the solute leakage. Since this
251 process is operated using two electrodes, a large size and quantity of the electrodes are required
252 for industrial plants [50]. This increases the operating and investment costs, and therefore, it is
253 difficult to be commercially acceptable for water desalination.

254 The MD process is not practical for brackish water due to high energy consumption [20]. However,
255 it might be effective for desalinating high salinity brackish water (up to 15,000 mg/L) or seawater.
256 In comparison, anaerobic membrane bioreactors (An-MBRs) combined with low-pressure
257 microfiltration (MF) or ultrafiltration (UF) has shown low rejection towards dissolved organic
258 carbon [51]. The treated water has quality like that for effluent generated through aerobic
259 treatment [52]. However, membrane fouling causes high energy demands and therefore this
260 technology is not suitable for energy recovery.

261 Pressure driven membrane processes, especially RO, suffer from fouling due to complex feed
262 streams (such as municipal wastewater) impacting the long-term performance of the membrane

263 and the management of brine discharge [48, 53]. This can cause the accumulation of various
264 constituents on the membrane surface. This leads to low water permeation and poor water
265 quality, thereby increasing energy input. However, if the feed pressure is raised to ensure
266 consistency of the water flux, this imposes an additional energy requirement [38, 53]. It has been
267 suggested that the energy expenditure and overall cost could be reduced if the membrane pore
268 size is increased. Therefore, when operating a brackish water feed with a salinity of 15,000 mg/L,
269 the estimated total cost to generate irrigation water approached 0.13 \$/m³ along with an
270 investment cost of \$17.54 million.

271 On the other hand, the salt rejection was decreased from 97% to 88% resulting in irrigation water
272 of unacceptable quality. Even though the RO membrane achieves good quality desalination water
273 when utilizing seawater/brackish water membranes, some of the removed mineral nutrients
274 (calcium, magnesium and sulfate) are necessary for plant growth [17]. As boron, which can retard
275 plant growth, can transmit easily through the RO membrane, a second RO cycle in many industrial
276 plants is needed. It has been highlighted that boron concentration can be further reduced from
277 1.5 to 0.5 mg/L in the nutrient water through multistage RO, electrodialysis and adsorption-
278 membrane filtration hybrid systems [54]. The Ashkelon and Palmahim seawater desalination
279 plants in Israel produced high quality desalinated water with boron concentration lower than 0.4
280 mg/L [55]. Municipal wastewater includes a high quantity of colloidal particles, suspended solids
281 and dissolved organics, which induces membrane fouling [38]. In this respect, a pre-treatment
282 process is needed to decrease the concentration of these species. Another significant concern is
283 brine disposal which contains high concentration of different salt species. This causes adverse
284 impacts on the aquatic ecosystem.

285 Osmotic gradient processes, such as FO, have potential for agricultural irrigation. Although the
286 individual FO process requires lower energy input and less influenced by fouling, it has some

287 disadvantages, like the separation of the draw solution and loss of nutrients [56, 57]. To separate
288 the draw solution effectively, a post-treatment strategy is required, which increases energy
289 consumption. The solute leakage allows accumulation of solute in the feed solution leading to
290 reduced effective osmotic pressure gradient and fouling/scaling on the membrane surface, which
291 reduces the productivity and lifetime of the membrane [58-60]. When the draw solution is being
292 diluted through the support layer as a result of the convective flow of water across the selective
293 layer, a severe dilutive internal concentration polarization occurs [61, 62]. Thus, there is a drop in
294 the osmotic pressure gradient leading to low water permeation. If using fertilizer as draw solute,
295 the draw solution will require further dilution to meet the quality standard of irrigation water [29,
296 56, 63].

297

298 **5. Water nutrient production from seawater/brackish water**

299 ***5.1 Pressure-driven membrane process***

300 **5.1.1 RO process**

301 Over the years, pressure-driven membranes, such as RO and NF membranes, have been used for
302 desalinating saline water for agricultural purposes and drinking water consumption [19]. The
303 common characteristics of pressure driven membrane applications is outlined in Table.1.

304 RO has the greatest total capacity worldwide relative to other membrane technologies. RO
305 membranes have a high rejection rate towards salt, high water permeation, and good tolerance
306 at very high hydraulic pressure. Improvement in membrane materials and fabrication of
307 membrane modules with a large surface area per unit volume has led to a reduced price of
308 membrane and water production cost [64]. In parallel, the recovery ratio was improved from 35%
309 in the 1990s to around 45% now, and it can be further increased to 60% when using the second

310 pass RO process. RO membrane can be utilized to desalinate seawater with salinity in the range
311 of 2.5 to 35 g/L for agricultural irrigation and drinking water extraction at a cost of US\$0.50/m³ to
312 US\$1.00/m³ [65]. Seawater desalination plants in Israel, such as Sorek, Hadera, and Ashkelon,
313 were the top seawater desalination globally due to high water capacity of around 540,000,
314 456,000, and 392,000 m³/day respectively [17]. Another plant located in Australia, operated
315 through a two-pass reverse osmosis membrane system, provided 17% of potable water to 1.6
316 million users in Perth [20, 66]. The seawater plant required energy input between 4 and 12
317 kWh/m³. All these factors contribute to high operating costs as the energy is responsible for 30–
318 50% of the operation cost. The Australian RO plant produced a high amount of concentrated
319 brine, as much as 55–60% of the total feed stream [20].

320 Owing to the above restrictions, brackish water with lower salinity has replaced seawater to
321 obtain irrigation water. The first commercialized brackish water desalination plant was first
322 operated in 1979 [65]. The total water capacity was about 20–21 m³/h when using water with
323 salinity in the range of 4–15 g/L. Earlier, PA TFC RO membranes were used in six brackish water
324 desalination plants, and the performance of this membrane was investigated in terms of
325 permeate water quality [67]. All plants achieved similar productivity with little variation in the
326 water capacity and cost per cubic meter of treated water. The water recovery was adjusted at
327 83% for plant-D and at 70% for plant B. Excellent performance of the RO membrane was observed,
328 providing water permeate at the required standard for irrigation water. The results revealed that
329 the membrane was effective in removing nitrate reaching 50 mg/l in the purified water, and the
330 fluoride concentration was at an acceptable level according to WHO and PS standards. The
331 chloride, sulfate, sodium, magnesium and potassium concentrations in the purified water of all
332 plants met the quality standard for potable water. Production capacity approached 640 m³/day
333 upon raising the flow rate to 80 m³/h.

334 Garcia et al. [68] used Polyamide Thin-Film Composite (PA TFC) (BW30-400 Filmtec™) membrane
335 to treat groundwater well brackish water with a salinity of about 3.1 and 7.8 g/L to generate
336 irrigation water. The design of the RO system is provided in Fig.1. The membrane generated
337 product water with acceptable salinity for fertigation. It was found that membrane scaling and
338 frequent chemical cleaning affected the water recovery and energy consumption. The fractional
339 water recovery decreased to 0.6 due to scaling. Another problem was an increase in the feed
340 pressure by 980.67 kPa after 40,000 h running time. The specific energy consumption was
341 relatively high at around 1.4 and 1.7 kWh/m³ after 5 years, along with the specific cost of water.
342 Ismail et al.[69] investigate RO to desalinate brackish water (groundwater) with various salinities
343 (1,000-3,000 mg/L). Desalinated water from feed with a salinity of 500 mg/L contained a sufficient
344 concentration of nutrients for crop production. Therefore, the RO permeate caused an increase
345 of 56% and 73% in crop yield. The yield and profit of crops were maximum when using the treated
346 water with this feed.

347

348 **5.1.2 NF process**

349 In comparison with RO membranes, the NF membrane can be operated under lower hydraulic
350 pressure leading to lower energy consumption and cost [70]. Birnhack et al. [71] utilized TFC NF
351 membranes in a pilot-scale seawater desalination unit to concentrate Mg⁺² ions while reducing
352 the addition of unnecessary seawater ions such as Cl⁻, Na⁺, B, Br⁻ in the treated water for crop
353 production. The principle of this NF desalination process involved circulating seawater across the
354 NF membrane, while Mg⁺²-rich brine was added into the treated water. It was observed that the
355 highest salt rejection rate approached 97% when raising the hydraulic pressure to 28 bar at a
356 recovery ratio of 40%. However, the rejection rate declined to 90%, 94%, 95% when increasing

357 the recovery ratio at varying hydraulic pressure of 10, 18, 28 bar respectively. The concentration
358 ratio between Mg^{+2} : Na^{+1} was decreased upon increasing the recovery ratio, but there was a
359 negligible change at high hydraulic pressure.

360 Ghermandi et al. [70] investigated the viability of the NF membrane in purifying brackish
361 groundwater with salinity of 1,577 mg/L for agricultural farms. A comparison between NF and RO
362 membranes was also carried out. According to simulation data, the NF permeate had higher
363 concentrations of the required nutrients such as calcium (14.1 mg/L), magnesium (7.9 mg/L), and
364 sulfate (33.5) than RO permeate, which were within the quality standard for irrigation water. It
365 was suggested that when using the NF membrane, lower brackish water volume by 34% was
366 needed compared to the RO membrane. However, using NF permeate was assumed to increase
367 the biomass activity by 18% while the RO permeate had an insignificant impact.

368 Lew et al. [72] examined the performance of various membranes, such as NF with 86% rejection
369 and high flux, NF membrane with 91% rejection and medium flux, RO membrane with 99.7%
370 rejection and high flux, RO membrane with 99.2 % rejection and very high flux. An analytic
371 hierarchy process (AHP) model and the multi-dimension scaling (MDS) models were used to find
372 out the optimal design of the membrane process for brackish water desalination. The theoretical
373 outcomes indicated that the NF membrane with low rejection and high flux was likely to have the
374 best performance and produce irrigation water with sufficient nutrients concentration. This water
375 product showed a low sodium absorption ratio (SAR). Both the NF membranes consumed low
376 energy of 0.26 and 0.20 kWh/m³, respectively, and hence low investment cost.

377 NF membranes were also used in a desalination plant in Saudi Arabia because they are less prone
378 to fouling relative to PA TFC RO membranes [65, 73]. It was reported that the salinity of the
379 desalinated water decreased from 45,460 to 28,260 mg/L, and the chloride concentration was

380 lowered from 21,587 to 16,438 mg/L. The NF membrane achieved maximum rejection rate of
381 sulfate (SO_4^{2-}) of up to 99% while it was lowered to 98%, 92%, and 44% for magnesium (Mg^{+2}),
382 calcium (Ca^{+2}), and bicarbonate (HCO_3^-), respectively. The hardness of the desalinated water was
383 lowered from 7,500 to 220 mg/L. The desalinated water contained less than 2 mg/L of SO_4^{2-} , 29
384 mg/L of Mg^{+2} , 40 mg/L of Ca^{+2} , and 17 mg/L of HCO_3^- , which is lower than the recommended
385 concentration level for drinking water.

386 Although the NF membrane generates high water permeation under low hydraulic pressure, the
387 membrane can separate divalent ions only, while allowing the permeation of monovalent ions.
388 Thus, the irrigation water ends up with a low concentration of required nutrients such as SO_4^{2-}
389 and Mg^{+2} and a high concentration of unwanted monovalent ions such as Na^+ and Cl^- .

390

391 **5.1.3 FO process**

392 Fertilizer drawn FO processes for fertigation has been given much attention. A diverse range of
393 commercial fertilizers can be utilized as a draw solution, which when diluted can be used in
394 irrigation water [74]. Because the high amount of nutrients in the diluted draw exceeds the quality
395 standard of irrigation water it requires further dilution. This FDFO process needs a perfect
396 membrane to separate different types of nutrients effectively. However, most of the developed
397 membranes are not yet commercialized [22, 59]. For example, Lotfi et al. [75] used a TFC hollow
398 fiber membrane and brackish water feed to generate irrigation water as demonstrated in Fig.(2).
399 The draw solutions were inorganic fertilizers including ammonium sulfate (SOA) $(\text{NH}_4)_2\text{SO}_4$,
400 calcium nitrate (CAN) $\text{Ca}(\text{NO}_3)_2$, mono-ammonium phosphate (MAP) $\text{NH}_4\text{H}_2\text{PO}_4$, diammonium
401 hydrogen phosphate (DAP) $(\text{NH}_4)_2\text{HPO}_4$. Since the polyamide selective layer is negatively charged,
402 the divalent salts like Ca^{+2} and Mg^{+2} were efficiently separated and accumulated on the membrane

403 surface, causing scaling. Also, Ca^{+2} could be transferred to the feed solution due to the reverse
404 solute flux and interaction with nutrients such as SO_4^{+2} , creating gypsum scaling (CaSO_4) on the
405 membrane surface. Other nutrients with small hydrated ionic radii, like NO_3^- and NH_4^+ , were
406 poorly rejected and permeated rapidly through the membrane to the feed solution. The forward
407 diffusion of nutrients such as Ca^{+2} or Mg^{+2} to the draw solution which interacted with phosphate
408 resulted in calcium phosphate scaling. This adversely affected the membrane performance and
409 the quality of the water permeate. The SOA fertilizer draw solution achieved the highest water
410 flux around 11.2 LMH While CAN and DAP solutions had the lowest water flux of 10.4 and 8.7
411 LMH.

412 Phuntsho et al. [63] used a cellulose triacetate (CTA) FO membrane and eleven commercial
413 fertilizer draw solutions such as urea, ammonium nitrate (NH_4NO_3), $(\text{NH}_4)_2\text{SO}_4$, Monoammonium
414 phosphate (MAP), potassium chloride (KCl), potassium nitrate (KNO_3), Monopotassium phosphate
415 (KH_2PO_4), calcium nitrate $\text{Ca}(\text{NO}_3)_2$, sodium nitrate (NaNO_3), Diammonium phosphate
416 $(\text{NH}_4)_2\text{HPO}_4$, ammonium nitrate (NH_4Cl) for brackish water desalination including blended
417 solutions. It was highlighted that when blending two or three fertilizers in the draw solution, the
418 product water contained a lower concentration of nitrogen, phosphorus, potassium (NPK)
419 nutrients relative to the individual fertilizer draw solution. KCl and $\text{NH}_4\text{H}_2\text{PO}_4$ draw solution
420 included only a small quantity of N nutrient (0.61 g/L), P nutrient (1.35 g/L), and K nutrient (1.70
421 g/L) as compared to which individual fertilizer draw solution having a high concentration of the
422 single nutrient. However, it was observed that there was a significant nutrient loss due to reverse
423 solute flux. For example, the urea draw solution experienced a high drop by 65% in the amount
424 of N nutrient relative to other draw solutions. The membrane performance was also influenced
425 by mixing two fertilizer draw solutions as the osmotic pressure, and water permeation was
426 decreased compared to that of individual draw solutions.

427 Kim et al. [76] evaluated the performance of PA (TFC) FO membrane in an FDFO system using RO
428 brine as a feed solution and ammonium sulfate (SOA), calcium nitrate (CAN), di-ammonium
429 phosphate (DAP), potassium nitrate (KNO_3) as draw solutions. The membrane separation
430 performance was affected by scaling and reverse solute flux at a varying rate. For example, the
431 lowest water flux, along with reverse solute flux, was assigned to the KNO_3 draw solution. The fast
432 transfer of calcium ions and accumulation in the feed solution lead to the most significant
433 membrane scaling (calcium nitrate). The solute leakage of nutrients ordered from the lowest to
434 highest as follows, SOA (2%), DAP (5%), CAN (4%), and KNO_3 (21%). Interestingly, KNO_3 showed
435 the highest nutrient loss due to its high extraction capacity, which accelerated the reverse solute
436 flux. In terms of water recovery rate, a maximum recovery rate was observed for the DAP draw
437 solution (95%), followed by SOA (80%), KNO_3 (79%), and CAN (70%). The draw solution with low
438 concentration and high osmotic pressure had the highest extraction capacity according to the
439 osmotic equilibrium. As a result, the total recovery rate grew significantly. In term of N/P/K
440 nutrients, the final product water contained higher concentrations of N (268.40 mg/L) from CAN,
441 N (201.19 mg/L) and P (222.45 mg/L) from DAP, N (230.63 mg/L) from SOA, N (114.76 mg/L) and
442 K (320.33 mg/L) from KNO_3 . This indicated that the nutrient solution needs further dilution by
443 potable water to lower the concentration of phosphorous and potassium nutrients while the
444 nitrogen nutrient concentration meets the recommended standard for irrigation water. The FO
445 membrane was effectively cleaned using 5% citric acid yielding a complete recovery of the initial
446 water flux.

447 Sahebi et al. [77] evaluated the performance of pressure-assisted FDFO using a flat sheet cellulose
448 triacetate (CTA) FO membrane, brackish water feed (10,000 mg/L) and four fertilizer draw
449 solutions ($(\text{NH}_4)_2\text{SO}_4$, $\text{NH}_4\text{H}_2\text{PO}_4$ and KCl) for fertigation. It was revealed that the membrane
450 achieved higher water permeation corresponding 7.38, 8.62, and 9.42 LMH for 0.1 mol/L

451 $\text{NH}_4\text{H}_2\text{PO}_4$, KCl, and $\text{NH}_4\text{H}_2\text{PO}_4$, respectively at a hydraulic feed pressure of 10 bar. This was related
452 to to 1928%, 345%, and 237% growth in the water permeation upon using 0.1 mol/L draw
453 solutions as compared to 38%, 29%, and 69% at a draw solution concentration of 3 mol/L. This
454 additional water flux produced when using a low concentration of the draw solution at high
455 hydraulic pressure, improved the draw solution dilution beyond the osmotic equilibrium point. A
456 small reduction in the specific reverse solute flux was noticeable when increasing the hydraulic
457 pressure to 10 bar. For instance, the specific reverse solute flux was reduced from 0.77 g/L and
458 0.60 g/L for NaCl and KCl, respectively, at 0 bar to 0.49 g/L and 0.45 g/L at 10 bar. Therefore, the
459 final water product contained acceptable nutrient concentrations for direct irrigation without the
460 need for a post-treatment stage to lower the fertilizer concentrations.

461 Recently, Lima et al. [78] proposed a new principle of FO desalination that depends on a
462 subsurface irrigation procedure for fertigation. It involves using irrigation pipes made of the BW30
463 RO membrane and FO 8040 FO membrane. The brackish water feed rich-nutrients passed through
464 the pipes to the soil and crops, which decreases soil deterioration and yield. It was found that the
465 FO membrane supplied the soil with a higher amount of water permeate than that for the RO
466 membrane after six days. For instance, the FO membrane produced 11 times higher water balance
467 leading to efficient soil hydration as compared to that for the RO membrane. The soil treated
468 with RO permeate was dried after the third day and remained dry throughout the experiment. To
469 that end, the FO membrane performed better, and its productivity is complying with the control
470 membrane for the duration of the experiment.

471

472 **5.2 Chemical-driven membrane processes**

473 **5.2.1 Electrodialysis (ED)**

474 A new membrane-based technology rarely used for seawater/brackish water desalination is
475 electro-dialysis. There are two types of electro-membrane processes, reverse electro-dialysis (EDR)
476 and electro-deionization (EDI) for desalinating low salinity streams.

477 The ED system is operated based on converting the salinity gradient between the concentrated
478 solution (i.e., seawater) and diluted solution (i.e., river water) into voltages using ion-exchange
479 membranes [49, 79]. In this system, cation and anion exchange membranes are arranged
480 alternately and isolated from each other by spacers to make channels. Fig. (3) shows the normal
481 EDR stack model where the ion flux transports from the concentrated stream to the diluted
482 stream, the selective membrane allows the penetration of cations across a cation exchange
483 membrane (CEMs) and the anions across an ion-selective anion membrane (AEMs). This leads to
484 the generation of an ionic current through the multi-membranes in which can be converted into
485 voltage due to reactions occurring on the electrode [79]. The electricity can be collected using an
486 electrical conversion device. In 2015–2016, the first ED/EDR and EDI electro-membrane process
487 plants were operated using saline water as a feed solution. An EDR plant implemented in South
488 Africa produced water capacity in the range of few tens of m³/day up to 10,000 m³/day from the
489 brackish water inlet.

490 Eberhard et al. explored the feasibility of the electro-dialysis process for separating micronutrients
491 such as copper chloride and copper sulfate from brackish water and coal seam gas water [80]. The
492 electro-membrane had an active area of 207 cm², and 20 cell pairs, including the cation/anion
493 membranes in alternated series, were employed. One of the important findings is that the
494 rejection rate of the copper and the sulfate reached 98 % and 100%, respectively, after three
495 hours of operation time at 23 °C. In comparison, the removal efficiency of both the copper and
496 sulfate was faster than that for NaCl with a rejection rate of around 72%. The water content in
497 the diluted solution was reduced by only 10%, which minimized brine disposal. The theoretical

498 work suggested that the mass /charge ratio of Sulphur ion with large ionic radii could reveal the
499 separation efficiency. For instance, the ions with small ionic radii can be removed rapidly as
500 compared to that with larger ionic radii. The diluted solution contained 3.0 mg/L of copper
501 nutrients and 2.7 g TDS/L, which can be used directly for fertigation.

502 Zhang et al. [81] studied the possibility of using a novel selector-dialysis membrane to separate
503 ions having the same charge signs. He attempted to separate divalent ions such as SO_4^{2-} from
504 monovalent, such as Cl^- , via the same membrane. The feed was composed of a mixture saline
505 solution ($\text{NaCl}/\text{Na}_2\text{SO}_4$) with initial concentrations of 7.61, 0.32, 4.48, and 0.43 mmol L⁻¹ for all
506 ions, respectively. The membrane achieved excellent selectivity at the highest pH. When
507 increasing the pH value, the current efficiency of the selector-dialysis system was also increased.
508 There was a strong correlation between sulfate concentration and pH value. The membrane was
509 capable of concentrating sulfate to 4 and 3.5 mmol L⁻¹ at the optimal conditions of current
510 densities (31.2 and 46.8 A m⁻²) and a pH of 10. The purity of sulfate in the product water was
511 higher than 85% at a current efficiency of greater than 50%. This indicated that the selector-
512 dialysis system was viable for separating monovalent ions (Cl^-) from multivalent ions (SO_4^{2-}), and
513 therefore, the final product water can be used for agricultural irrigation.

514 A new approach for brackish water desalination is using monovalent selective cation exchange
515 membranes in the ED process. This special membrane can be fabricated by adding a poly-cation
516 layer on the membrane surface to reject monovalent salts such as Na and Cl while retaining
517 divalent salts such as Ca, Mg, and SO_4 ions. A recent work described the use of this membrane for
518 desalinating brackish water to obtain irrigation water containing the required amount of mineral
519 nutrients [82]. To select the best performing commercial monovalent selective ion exchange
520 membranes (MIEM) in removing the monovalent ions, the process conditions were optimized,
521 and the effect of membrane selectivity was investigated. All MIEM membranes exhibited superior

522 selectivity for sulfate than chloride. The performance of these membranes was more efficient
523 than monovalent selective cation exchange membranes when using brackish water with low
524 conductivity. It was noticed that the anionic membranes purchased from MVK and CMS exhibited
525 the good perm-selectivity for Ca^{+2} and Mg^{+2} . The removal ratio of these cations was about 80%
526 and 70%, respectively, while it was only 37- 48% for Na ions. An anionic membrane manufactured
527 by CSO produced superior monovalent perm-selectivity of less than 1 upon using brackish water
528 with conductivities of less than 4.5 dS/m. The removal ratio of Na^{+1} , Ca^{+2} and Mg^{+2} amounted to
529 52%, 44%, and 24%, respectively. To achieve the best selectivity of monovalent ions, the current
530 densities should be maintained lower than the limiting current corresponding to sodium
531 concentration. When the total salinity of the product water decreased by 50%, the removal
532 efficiency of Cl and SO_4^{-2} was as high as around 90% and 12% for CSO membranes-modified with
533 polyethyleneimine. Lastly, the SAR in the final product water was 2.3 making it suitable as
534 irrigation water for crop production. It was concluded that this novel procedure facilitated the
535 generation of irrigation water, which provides another water resource for fertigation and
536 eliminates negative effects on the environment.

537

538 ***5.2.2 Capacitive Deionization (CDI) process***

539 Capacitive Deionization is a desalination technology that depends on an electrical capacitance to
540 separate or release charged ions from/into solutions [47, 83]. Both CDI and ED had a similar
541 operating principle, especially the ions, transfer through the solution and across the membrane.
542 However, CDI does not need a membrane and is considered a low-pressure process. This means
543 that the CDI process is competing with the pressure-driven processes (RO) and temperature-
544 driven processes (MD), which is capable of producing pure water at a lower operating cost [50].

545 The principle of the CDI can be explained as follows [49, 84]. We can see in Fig. (4) that a saline
546 solution passes into a channel between capacitive electrodes that are separated by an ion-
547 selective layer. This selective layer is used to increase the voltage efficiency and improve the
548 performance of the system. The transfer of ions towards the capacitive electrodes is induced by
549 applying an electrical potential difference between the electrodes. Thereafter, the ions are
550 adsorbed on this electrode, and hence the ions from the feed solution are removed. As a result,
551 the feed solution becomes almost free of salt ions providing pure water. It should be mentioned
552 that, at the saturation point of the electrode, the salt ions are released from the electrode and
553 transported through a purge stream to the channel. This causes the accumulation of ions in the
554 solution generating a concentrated brine. The most widely used applications are seawater
555 desalination, brackish water desalination, wastewater reclamation, and water softening [47, 83].
556 Industrial plants for numerous applications are operated in the Netherlands and China, achieving
557 water capacity around up to 2000 m³/h [85].

558 The CDI process for brackish water desalination has been evaluated in two stages [86]. In the first
559 stage, the electro-sorption capacity of the lab-scale CDI rig was assessed. In the second stage, the
560 salinity removal efficiency and energy consumption were investigated for the prototype CDI
561 system in the Wilora area, Australia. The possibility of implementing this system in this field with
562 a temperature of 45 °C and humidity of 80% was explored along with, the separation efficiency of
563 the system. The theoretical data indicated that there was an increase in the electro-sorption
564 capacity and adsorption rate constant upon increasing the feed concentration. The electro-
565 sorption rate was 48.29% for a salt solution having a concentration of 1500 mg/L. The selectivity
566 of the system was excellent, and the highest salinity removal was achieved at the lowest flow rate
567 (1.0 L/min). The removal efficiency of metal ions and non-metal ions was roughly 89%, 85%, 73%,
568 84%, 74%, and 80% for Ca⁺², Mg⁺², Na⁺, Nitrate, and Arsenic, respectively. Raising the flow rate to

569 7.0 L/min yielded a minimum energy expenditure of about 1.89 kWh/m³ for the desalinated
570 water. A total water recovery around 75 to 80% was achievable. These findings make the CDI
571 system a potential alternative for desalinating brackish water.

572 To further improve the removal efficiency, Liu et al. [87] developed membrane capacitive
573 deionization (m-MCDI). Here, the electrodes were manufactured from carbon nanotubes
574 incorporating a cation exchange polymer (Polyethyleneimine (PEI)) and an anion exchange
575 polymer (dimethyl diallyl ammonium chloride (DMDAAC)). It was found that the new electrodes
576 achieved high removal efficiency for NaCl of 93%, greater than that for other CDI systems. A CDI
577 unit using carbon nanotube electrodes and MCDI unit with commercial anion and cation exchange
578 membranes had a lower removal efficiency of 25% and 74% under the same electrical current of
579 1.2 V and solution conductivity of 50 μ S/cm. The modified MCDI also achieved superior electro-
580 sorption of 0.159 mmol/g and charge efficiency of 0.70 at less than 2.0 V. At the same time, the
581 commercial MCDI cell demonstrated an electro-sorption behavior around 0.114 mmol/g and 0.53.
582 This enhancement can be attributed to incorporation ion-exchange polymers, which adhered
583 strongly to the electrodes leading to lower co-ion expulsion impact compared to the commercial
584 MCDI system.

585 More recently, Bales et al. [85] developed a simulation model to predict the performance of the
586 MCDI process and combined it into an agricultural economics model. In this model, the
587 environmental conditions in Australia and a crop-water-salinity function were used to estimate
588 crop yield and profits. The MCDI consisted of an ion exchange membrane attached to each carbon
589 electrode to eliminate the passage of ions during the recharge cycle. The current adsorption
590 remained constant at zero-volt desorption leading to reduced energy consumption relative to
591 commercial CDI. According to the theoretical information, this system can be utilized to irrigate
592 many valuable crops, and it can be optimized based on the environmental conditions of any

593 agricultural area. Different salinity limits were used according to thresholds for different crops of
594 4.2 dS/m, 5.5 dS/m, 4.4 dS/m, 14 dS/m, and 8.5 dS/m for grapes, oranges, almonds, apples, and
595 tomatoes for a 60 ha crop and investment period of 10 years. The cost of the treated water was
596 varied in each scenario, and it was estimated to be less than AUD\$ 1/kL. Therefore, this cost-
597 effective MCDI system is feasible to desalinate brackish water providing irrigation water after
598 further dilution by freshwater.

599

600 **6. Water nutrient production from industrial wastewater**

601 ***6.1 Pressure-driven membrane process***

602 An alternative source of water for many agricultural applications is treating different types of
603 wastewater. Pressure driven membrane processes are effective methods for wastewater
604 treatment due to high productivity and selectivity towards organic and inorganic contaminants
605 [88]. Bunani et al. [38] used brackish water reverse osmosis (AK-BWRO) and seawater reverse
606 osmosis (AD-SWRO) membranes in an RO system to generate irrigation water from mixed
607 secondary treated urban effluent. The performance of this membrane was tested under a
608 hydraulic pressure of 10 bar. It was observed that both the membranes exhibited good rejection,
609 and adjusting the pressure showed an insignificant impact on the rejection efficiency. At 10 bar,
610 the BWRO membrane achieved rejection of 94.6%, 95.2%, 85.8%, 76.4%, and 91.3%, respectively
611 against conductivity, salinity, chemical oxygen demand (COD), total organic carbon (TOC) and
612 color whereas these values were 98.3%, 98.3%, 84.6%, 69.7%, and 86.6%, for the BWRO
613 membrane. The water permeation was varied for both the membranes as the AK-BWRO
614 membrane permeate approached 38.0 LMH. The AD-SWRO membrane permeate was as low as
615 3.81 LMH, and it was maximized to 14.8 LMH at 20 bar. The AK-BWRO membrane showed the

616 best water quality with higher water recovery. When adding 20-30% of secondary treated urban
617 effluent to 70–80% of the final product water, acceptable SAR values of around 6.41–7.67 and
618 7.36–8.31 with EC_w values of 1.62–2.25 dS/m and 1.52 to 2.10 dS/m for AD-SWRO and AKBWRO
619 membranes were achieved. Therefore, this mixture solution was suitable for fertigation meeting
620 the standard of irrigation water.

621 Ranganathan et al. [89] assessed the behavior of RO for purifying tannery wastewater and stated
622 the cost analysis of this process. It was confirmed that the RO membrane was efficient in
623 separating organic components and the total dissolved salts in the desalinated water. The
624 membrane demonstrated a rejection rate of 93-98%, 92-99%, and 91-96% for TDS, sodium, and
625 chloride, respectively. It was suggested that the wastewater was recovered by 70-85%, and the
626 TDS in the desalinated water approached 118-438 mg/L, meeting the quality standard of potable
627 water. The overall operating and maintenance costs of the RO unit were low.

628 UF membrane was also examined for treating wastewater under two different experimental
629 conditions of “stressed operating conditions” against “conventional operating conditions” [43].
630 The stressed operating conditions phase consisted of three typical process cycles while the
631 conventional operating conditions consisted of one typical process cycle. Experimental results
632 showed that the desalinated water from both the conditions contained a minimum amount of
633 Total Suspended Solids (TSS) < 10 mg/L; Chemical Oxygen Demand (COD) < 100 mg/L and
634 *Escherichia coli* < 10 CFU/100 mL. The quality of this desalinated water satisfied the Italian
635 guidelines for irrigation water produced from wastewater. However, the desalinated water
636 obtained using the conventional operating condition satisfied the quality standard of irrigation
637 water issued by the State of California. This desalinated water was free of TSS and turbidity while
638 the total coliforms were less than 2.2 CFU/100 mL. This can be ascribed to a localized membrane
639 pore micro-enlargement mechanism that controlled the permeability and transmembrane

640 pressure during the experiment. Consequently, a thin cake layer created on the membrane
641 surface contributed insignificantly to the fouling and pore blocking. The treated water from both
642 the conditions did not include any *E. coli* microorganisms. It was suggested that the conventional
643 operating condition is the best option for operating the UF membrane in the process of achieving
644 a good quality of irrigation water.

645 Balcioglu et al. [90] made a study of using different membranes (FM UP020, FM UP005, NF 270,
646 NF 90, and Desal 5DL) to treat baker's yeast wastewater for agricultural irrigation. The effect of
647 the operating conditions on fouling, water permeation reduction, and quality of the permeate
648 was explored. Membrane separation performance and fouling analysis suggested that the Desal
649 5DL and NF 270 membranes were feasible for treating baker's yeast wastewater due to excellent
650 rejection rate, reduced flux declines, and low water contact angles. This is because the Desal 5DL
651 membrane achieved a removal efficiency of 90%, 87%, higher than 88% for the COD, chloride,
652 total dissolved solids, respectively. NF 90 membrane demonstrated rejection efficiency against
653 total dissolved solids around 88%. The NF membranes showed total hardness and sulfate removal
654 efficiency in the range of 70–98% and 97–99%. The removal efficiency of chloride corresponded
655 to 13%, 25%, and 87% chloride removal for NF 270, Desal 5DL, and NF 90 membranes,
656 respectively. However, the chloride was not rejected by the FM UP020 membrane. The NF
657 membrane rejected the suspended solids completely, while the UF membrane showed rejection
658 of only 75–81%. The FM UP020 membrane exhibited poor color rejection, which was above the
659 discharge limit values while the NF membrane rejected the color completely. In terms of fouling
660 impacts, the water flux reduction was dropped by 68% for the FM UP005 membrane, while NF
661 270 and Desal 5DL membrane achieved the lowest water flux reduction around 5% only. Similarly,
662 the Desal 5DL membrane had better antifouling property at operating parameters of pH 7, 12 bar,

663 and 25 °C as compared to other membranes. The product water purified by two NF 90 passes met
664 the standard regulations for irrigation water.

665

666 **6.2 FO process**

667 In the FO process, the feed water will be converted to nutrient water for agricultural purposes
668 when using a fertilizer draw solution and, therefore, there is no need for a recovery system to
669 separate the draw solution [91]. Research was conducted using three commercial all-purpose
670 solid fertilizers with concentrations ranged from 1.0-3.0 mol/L to draw pure water from
671 wastewater [92]. The performance of a commercial cellulose triacetate membrane with an active
672 area of 0.0025 m² was evaluated in terms of water permeation and water recovery. The nutrient
673 concentrations in both the draw and feed solutions and nutrient loss were analyzed and the
674 energy required to operate the FDFO system was optimized. The results revealed that the fertilizer
675 DS-F1 (N=24/P=8/K=16) was the best performing draw solution when using wastewater as the
676 feed solution due to the low concentration of urea. Also, water extracted was around 324 mL,
677 which amounted to 41% of the total water required to dilute irrigation water within 72 hours of
678 running time. Likewise, the highest water permeation approached 4.2 LMH while the reverse
679 solute flux was estimated at 92%, 98%, 75%, and 81% for NH₄-N, TN, K, and P nutrients. The final
680 diluted draw solution (F-1) included N from NH₄ at 12.0 mmol, N from urea of around 30.6 mmol,
681 P nutrient around 5.9 mmol, K nutrient around 16.5 mmol. Phosphorus was rejected by the FO
682 membrane leading to a high amount in the feed solution, but the amount of total nitrogen and
683 potassium increased in the FS due to reverse solute flux. Finally, reducing the flow rate from 100
684 to 10 mL min⁻¹ resulted in energy consumption reduction from 1.86 to 0.02 kWh m⁻³. Although

685 the reverse solute flux was challenging, the commercial solid fertilizers as a draw solution showed
686 potential for obtaining irrigation water from wastewater.

687 Li et al. [44] used the PA TFC FO membrane to treat landfill leachate containing a high amount of
688 undesired species such as dissolved organic matter, inorganic components, heavy metals, and
689 other compounds. Different concentrations of the NH_4HCO_3 draw solution and the flow rate were
690 investigated. The water recovery rate corresponded to 91.6% within 72 hours, which is higher
691 than that for the Changsheng Bridge Landfill plant located in Nanan District, Chongqing, China.
692 The water permeation increased to 6.7 LMH when increasing the DS concentration to 3.0 mol/L.
693 However, it declined after 5 hours. When the flow rate was raised to 8.4 cm/s, the water
694 permeation was increased to 7.5 LMH due to improved fluid shear stress at the membrane leading
695 to a thin boundary layer. As a result, the accumulation of solute and concentration polarization
696 was mitigated across the membrane. After 48 running hours, the product water was free of the
697 metals Hg, As, Cr, Cd, Pb, had no odor and negligible precipitates, pH within the recommended
698 value, minimum TOC (42.2 mg L^{-1}) and chloride (38.5 mg L^{-1}). The product water met the standard
699 regulation of commercial liquid fertilizer, and therefore it can be reused for fertigation.

700 Iskander et al. [93] estimated the energy consumption of the FO system for purifying landfill
701 leachate. Several operating parameters, such as the draw solution concentration and flow rate,
702 were optimized. The treatment performance and energy consumption were compared when
703 varying the landfill leachate properties. Cellulose triacetate commercial membrane was tested in
704 the FO process, and the effect of membrane fouling on energy expenditure was also explored.
705 Experimental data showed that the water recovery rate increased from $63.8 \pm 7.7 \text{ mL}$ to $277.3 \pm$
706 3.8 mL when using concentrated draw solution (3.0 mol/L). The reverse solute flux was slightly
707 increased from 4.60 ± 0.59 to $5.37 \pm 1.15 \text{ gMH}$. It was observed that raising the flow rate to 110
708 mL/min at a draw solution concentration of 1.0 mol/L resulted in higher energy requirements

709 estimated at $0.276 \pm 0.033 \text{ kW h m}^{-3}$. This energy expenditure was minimized to $0.005 \pm 0.000 \text{ kW}$
710 h m^{-3} upon decreasing the flow rate to 30 mL/min, increasing the water recovery rate, and higher
711 draw solution concentration of 3.0 mol/L. The fouling was easily removed from the membrane
712 through osmotic backwashing. Simultaneously, the leachate with a low amount of pollutants
713 required low energy consumption due to high water recovery. The FO process can be used to
714 lower the volume of leachate whilst extracting highly pure water for direct reuse.

715 Very recently, Volpin et al. [94] proposed a new concept of the FO process as MgSO_4 and $\text{Mg}(\text{NO}_3)_2$
716 fertilizer draw solution was employed to dewater synthetic human urine. The diagram of the
717 fertilizer driven FO process is shown in Fig. (5). It was assumed that the reverse solute flux of Mg^{+2}
718 would trigger P-recovery through struvite precipitation. Next, the leakage and precipitation of
719 urea in the Mg-fertilizer draw solution will increase the amount of N nutrients. Also, a lower
720 volume of urine at the end of the experiment leading to enhanced productivity in downstream
721 processes for N-recovery. The $\text{Mg}(\text{NO}_3)_2$ draw solution produced higher water flux by 3-fold (31
722 LMH) as compared to that for the MgSO_4 draw solution at a concentration of 1.0 mol/L because
723 of high mass transfer through the FO membrane. Similarly, the reverse solute flux was higher at
724 0.89 g/L for $\text{Mg}(\text{NO}_3)_2$ draw solution and 0.1 g/L for MgSO_4 draw solution. It was reported that the
725 urea was not rejected completely by the PA TFC FO membrane, but it was recovered in the Mg-
726 based draw solution. The volume of urine was decreased to 60%, which can promote efficiency in
727 downstream processes. Accordingly, a high amount of nutrients amounted to 40% of the P as
728 struvite fertilizer, and 50% of the N in the urine were recovered when urine was concentrated by
729 60%. The agricultural companies can be supplied with solid struvite as the diluted fertilizer can be
730 utilized as irrigation water for green walls, parks, and farms. The new development of the FO
731 process opened an opportunity to effectively extract nutrients from human urine and reused for
732 sustainable agriculture.

733 **6.3 Temperature-driven membrane system**

734 The basic concept of MD lies in the thermally driven transference process across a hydrophobic
735 membrane [56]. A wide range of commercial membranes was used as the MD membrane such as
736 polypropylene (PP), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), and
737 polyethylene (PE) [95]. The selection of membrane configuration (flat sheet or capillary) and type
738 depends on the MD application, if highly pure water or concentration of the ionic solution is
739 required. The most important characteristics of MD membranes are high hydrophobicity, high
740 porosity; pore size ranged from several nanometers to few micrometers, small pore size
741 distribution, high liquid entry pressure, thick single-layer to produce low thermal conductivity,
742 antifouling material and excellent chemical and thermal stabilities [96, 97]. In comparison with
743 pressure-driven membranes, the MD process needs low hydraulic pressure, produces a high
744 water recovery rate, integrates with natural energy to generate heat, thereby reducing energy
745 consumption [95]. The MD process is effective in extracting nutrients from wastewater effluent.
746 For example, Zarebska et al. [98] made a study on the removal of ammonia from swine manure
747 and examined the membrane anti-fouling resistance. In this study, tubular polypropylene
748 membrane and a liquid fraction of undigested manure as feed solution were used in the FO
749 system. The feed solution contains valuable nutrients such as potassium, ammoniacal nitrogen,
750 sodium, phosphorus, sulphur, calcium, magnesium and iron for plant growth. During the test,
751 there was a fast drop in the ammonia flux from $42 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ to $3 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. This is because of
752 reduction in the ammonia partial pressure after 25 hours of operation time. It was found that the
753 membrane was affected by accumulation of proteins, some inorganic components such as O, S,
754 Fe, Na, Mg, K and microorganisms leading to serious fouling. This resulted in altering the surface
755 characteristics and the membrane surface was converted from hydrophobic to hydrophilic in

756 nature, thereby hampering the separation of ammonia. The fouling layer was thick (10-15 mm)
757 after a week of running the experiment.

758 To improve the membrane performance for rejecting ammonia, research was carried with a
759 modified direct contact membrane distillation (MDCMD) process to remove ammonia from
760 municipal wastewater [99, 100]. The PVDF membrane was operated in the system, and its
761 characteristics were 80% porosity, mean pore size of 0.22 μm , liquid entry pressure of 250 kPa,
762 and water contact angle of 87°. This membrane was tested in three different process modes: a
763 conventional direct contact MD, a hollow fiber membrane contactor, and a modified DCMD
764 apparatus. The influence of operating conditions such as feed pH, temperature, flow rate, and
765 concentration on the ammonia stripping was explored. It was observed that the removal
766 efficiency of ammonia for direct contact membrane distillation (DCMD), hollow fiber membrane
767 contactors (HFMCs), and MDCMD modes amounted to 52%, 88%, and 99.5% after 105 minutes of
768 running time, respectively. This meant that MDCMD was the best process for removing ammonia
769 from water/wastewater. A negligible effect on the removal efficiency of ammonia and the
770 distillate flux was noticed at an optimal feed pH value of 12.2. However, adjusting the cross-flow
771 velocity from 0.15 to 0.5 m/s caused an increase in the water flux from 5.75 to 11.75 LMH and
772 high diffusion of ammonia through the membrane leading to improved vapor mass transfer.
773 When raising the feed temperature and feed flow rate, separation efficiency towards ammonia
774 and the water permeation were enhanced. However, the separation efficiency was independent
775 of the initial feed ammonia concentration in the MDCMD process.

776 Macedonio et al. developed a PVDF MD membrane and compared its performance with two
777 polypropylene MD commercial membranes for treating saline oily wastewater [101]. The impact
778 of feed temperature and hydrodynamic conditions on the rejection efficiency was studied.
779 Furthermore, an economic analysis was performed to determine the viability of the direct contact

780 MD process for saline oily wastewater treatment. The experimental results demonstrated that
781 the new PVDF2 membrane had the highest water flux of 6.0 LMH and rejection rate of TDS and
782 total carbon of 99.8% and 90.6%, respectively. Overall, the rejection rate was greater than 99.0%
783 and 90.0% against TDS and TC for all the fabricated membrane modules. The distillate included
784 TDS, Total carbon (TC), total inorganic carbon (TIC), total organic carbon, and conductivity of
785 about 415 mg/L, 91.36 mg/L, 48.46 mg/L, TOC= 42.9 mg/L, and 614 $\mu\text{s}/\text{cm}$ respectively. The cost
786 analysis showed that the water production cost of the PVDF-2 membrane reached 0.72 $\$/\text{m}^3$ at a
787 recovery rate of 70%, the temperature of the produced water passed to the unit was 50°C, and
788 the lifespan was 10 years. The cost was higher of about 1.28 $\$/\text{m}^3$ when the temperature of the
789 produced water passed to the plant reached 20 °C and lifespan of 5 years. Thus, these findings
790 proved that the developed membrane is a cost-effective alternative method for industrial
791 wastewater treatment.

792

793 ***6.4 Membrane bioreactor (MBRs) process***

794 Membrane bioreactor (MBR) has been commonly used for wastewater treatment as an
795 alternative process to traditional treatment systems due to a simple design and high-quality
796 product effluent [102]. It consists of a classical biological sludge process coupled with a micro- or
797 ultrafiltration membrane module. The biological process is used to decompose the waste species
798 or microorganisms while the membrane separates the water from the mixed liquor [103, 104].
799 The membrane has pore diameter ranged from 0.01 to 0.1 μm to reject contaminants and
800 bacteria, so it was an alternative method to gravity sedimentation system in the biological sludge
801 process. The practicality of the MBR process has been shown through lab and pilot plants for
802 wastewater applications.

803 Matosic et al. [105] studied the performance of a pilot MBR plant with a hollow fiber membrane
804 for treating wastewater from a soft drinks production facility compared with the performance of
805 a traditional treatment process (biological activated sludge system). The biological activated
806 sludge process failed to completely remove COD, leading to a high concentration in the effluent.
807 The MBR performed better in rejecting organic contents, and the amount of COD and TOC was
808 decreased by 94% in the effluent. This can be attributed to the higher concentration of activated
809 sludge biomass in the bioreactor governed by the rejection of these species by the hollow fiber
810 membrane. The membrane was effective in removing total suspended solids and other
811 contaminants, which improved the quality of the effluent. The initial water permeation was 5.43
812 LMH but declined due to fouling. The fouling was caused by a high amount of total hardness and
813 high pH value in the influent, leading to precipitation of scale precursors. The most severe fouling
814 was after the first 10 days of the operating period, and then it decreased slowly. The initial water
815 permeates value was restored after chemical cleaning via hypochlorite, acid, and alkaline
816 solutions. For instance, the water recovery rate reached 72% when immersing the membrane in
817 a hypochlorite solution. The superiority of the MBR treatment proved its feasibility in treating
818 wastewater rather over the traditional treatment process.

819 Prieto et al. [106] invented a gas-lift anaerobic membrane bioreactor (GI-AnMBR) for household
820 wastewater treatment. The performance of the GI-AnMBR was evaluated, and a comparison
821 between membrane fouling mitigation strategies was addressed. PVDF UF membrane combined
822 suspended-growth bioreactor and synthetic household wastewater was used for the treatment
823 operation over 100 days. It was found that the highest water flux corresponded to 18 LMH at a
824 constant cross-flow velocity of 0.3 m/s and constant transmembrane pressure, and the water flux
825 was independent of the higher cross-flow velocity. This means that the membrane permeate was
826 controlled by mass transfer resistance across the membrane during the process. After 100 days

827 of the operation period, the water permeation declined to 10-15 LMH. Fouling was alleviated by
828 backwash cleaning every week. A further improvement in the water flux was achieved by to
829 backwash cleaning every 4 hours. There was an excellent removal efficiency against sewage
830 organic matter as the removal efficiency of COD and organic carbon removal approached up to
831 98% and 95%. Methane as biogas was released around 4.5 L/d, which is beneficial for energy
832 recovery and membrane cleaning. The product water contained 95.5% of the cumulative recovery
833 for nitrogen and 93.4% of the cumulative recovery for phosphorous after 100 d of running time.
834 Therefore, the product water included an acceptable amount of nutrients from sewage organic
835 matter, and it can be used for fertigation depending on the specific nutritional requirements of
836 the crop.

837 Bolzonella et al. [107] highlighted the results of 10 years of investigations on the performance and
838 feasibility of the MBR process for removing various contaminants from industrial wastewater. The
839 MBR system was effective in rejecting solids, nutrients, and micropollutants as the removal
840 efficiency of nitrogen, phosphorus, and heavy metals was 80%, >60%, and 10-15%, respectively,
841 whilst COD was reduced from 100 mg/L to < 40 mg/L. The removal efficiency of the toxic
842 compound ,2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), was superior as the concentration
843 decreased to <0.5 pg/L in 60% of the samples while the concentration of other dioxins was less
844 than 10 pg/L. The removal efficiency of organic pollutants was enhanced when using a high
845 concentration in the influent while there were no *E. coli* bacteria in the effluent. The total
846 coliforms in the effluent ranged from 0 to 240 MPN/100 mL in the MBR-1 and higher around 13
847 and 460 MPN/100 mL in the MBR-2. Therefore, the treated water had high quality, and was
848 appropriate to be reused directly or after treatment with another method. The operating and
849 maintenance costs were reduced significantly to between 0.11 and 0.15 USD/m³, which indicated

850 the workability of the system in treating wastewater and reuse of the treated water in the
851 Mediterranean Region.

852

853 **7 Application of hybrid systems for agriculture**

854 The development and performance of existing integrated systems in different agricultural
855 applications are discussed.

856 ***7.1 Seawater/brackish water desalination***

857 ***7.1.1 RO integrated system***

858 To reach the required quality of irrigation water, some membrane processes need an additional
859 pass to recover nutrients. For instance, seawater desalination plants use several passes to polish
860 the desalinated water and remove boron and chloride [32]. When using low hydraulic pressure
861 and neutral pH, the removal efficiency of boron was 83%. The removal efficiency of boron can be
862 maximized to 99% when using high hydraulic pressure and pH 10.5 [108]. Generally, the second
863 RO pass requires high energy consumption of about 0.5 kWh/m³ [32]. A SWRO industrial plant
864 used multiple RO passes to effectively reject boron and chloride from the treated water [32].
865 However, energy consumption is a crucial hurdle for the SWRO facility for generating irrigation
866 water. The pre-treatment or post-treatment stage of the RO membrane can consume energy of
867 0.7-0.9 kWh/m³. This accelerated the total energy consumption for the facility reaching 3–7
868 kWh/m³ of produced water.

869 Altaee et al. [109] explored the efficiency of RO membranes as a post-treatment stage coupled to
870 a NF system to recover nutrients from seawater with a salinity of 35,000 mg/L to improve the
871 quality of irrigation water. The NF/RO process did not efficiently separate the NO⁻³ nutrient, and
872 hence it was mixed with KNO₃ to increase the rejection. The solution contained KNO₃ as the main

873 component, and a high rejection by the RO membrane was noticeable. When two BWRO
874 membrane passes were used to recover nutrients from the $\text{Ca}(\text{NO}_3)_2$ draw solution, the
875 membrane achieved high rejection, and another RO cycle was also applied to provide an
876 acceptable level of NO_3^- and K^+ nutrients in the product water. It was important to use two RO
877 stages for recovering the nutrients, and the permeate was further recovered to obtain the
878 required concentration of NO_3^- and K^+ nutrients in the final product water. In the first RO pass, a
879 high rejection rate of around 99.5% was achieved for monovalent ions while it was decreased to
880 90% for MgCl_2 and KNO_3 . However, the BW30-440i RO membrane exhibited the greatest rejection
881 rate of about 99% against monovalent ions, but the power expenditure was relatively high. The
882 final product water contained the recommended level of nutrients for agricultural irrigation when
883 two RO stages were used as the recovery processes. It was reported that when increasing the
884 recovery rate, the energy expenditure was minimized. The specific energy consumption for the
885 RO recovery stage was 3.0 kWh/m^3 , which was lower than for a conventional RO desalination
886 plant.

887 To recover nutrients in the desalinated water with minimum energy, Atab et al. [110] applied an
888 adsorption cycle (AD) after the RO membrane process. The layout of this hybrid system is
889 presented in Fig. (6). Although the temperature influenced the performance of the RO membrane,
890 increasing the temperature to 85°C led to the high water capacity of the AD cycle of about 6.3
891 m^3/day . The salinity can affect membrane performance, but there was a negligible impact on the
892 AD cycle. It was found that this desalination plant generated $24,000 \text{ m}^3/\text{day}$ of irrigation water
893 with salinity less than 1600 mg/L . The total water recovery achieved was around 65% for the
894 hybrid system. The estimated energy consumption of the hybrid system at a water recovery of
895 45% was about 0.8 kWh/m^3 . This resulted in a reduced cost of around $0.54 \text{ \$/m}^3$ as compared to
896 the stand-alone RO system. The significance of desalination by combining RO and a post-

897 treatment method is not only to minimize the energy expenditure but also to enhance the quality
898 of irrigation water.

899

900 **7.1.2 FO integrated system**

901 FO coupled with another membrane-based process could be beneficial and comparable to the RO
902 process in terms of operating cost and energy saving. The FO integrated process has potential in
903 treating complex impaired water sources from the oil and gas industry, brine desalination, and
904 drilling flow back water [111]. Many earlier patents reported the use of the FO combined heating
905 process to extract a volatile fertilizer solution from the product water [48]. In this respect, a dual-
906 stage of the FO/heating process was used for seawater/brackish water desalination. The heating
907 system was employed to recover a volatile fertilizer draw solution, including ammonia and carbon
908 dioxide. The theoretical results indicated that the hybrid system consumed power of 0.25 kWh/m³
909 at a water recovery rate of 64%. Also, the energy consumption was very high for the heating
910 recovery system approaching 75 kWh/m³, which hindered the feasibility of this recovery strategy.
911 Other drawbacks are the high reverse solute flux and the accumulation of ammonia in the product
912 water.

913 A closed-loop FO-NF hybrid system could be an effective process for seawater desalination, with
914 the NF stage used to recover the nutrients from a fertilizer draw solution [112]. Experimental
915 results showed that the water permeation of the hybridized FO-NF process reached 10 LMH, while
916 the solute rejection by the FO membrane was as high as 99.4% for all the tested draw solutions.
917 The solute rejection by the NF membrane was lower, around 97.9%.

918 Furthermore, dual NF passes were applied to purify the diluted draw solution obtaining high-
919 quality potable water. According to Chekli et al. [48], the second stage is necessary to remove Na⁺

920 and Ca^{2+} from the diluted draw solution completely. Another negative impact is that the passage
921 of salt solution through the membrane may deteriorate the lifespan of the membrane. After that,
922 the final product water contained a minimum amount of TDS of about 113.6 mg/L, which is lower
923 than the recommended level for drinking water (500 mg/L).

924 Phuntsho et al. [111] reported the effect of operating conditions on each other in a closed-circle
925 large-scale FDFO-NF hybrid process according to the mass balance of the flow rates, the draw and
926 the feed solutions. The theoretical information suggested that when the capacity and feed
927 concentration in the FO/NF hybrid system are constant, the initial flow rate of the draw solution
928 was inversely proportional to the initial concentration of the draw solution or other way around.
929 The mass flow rate of the draw solution is correlated to the concentration of the feed solution
930 and the constant capacity of the closed-cycle FO/NF plant. The data shows that when one of the
931 conditions or both got higher, the mass flow rate can be grown, causing an increase in the
932 concentration of the diluted draw solution and the energy requirements of the NF recovery
933 system. Besides, the initial concentration and the flow rate of the draw solution were crucial
934 conditions. They can influence the water recovery rate of the NF system, thereby imposing a
935 higher energy input. One of the practical hurdles is the nutrients loss and accumulation in the
936 concentrated feed solution resulting in highly concentrated brine exceeding the standard limit for
937 brine disposal. This issue can occur when running the FDFO system at a high recovery rate, and
938 therefore a highly selective membrane is needed to minimize the reverse solute flux. Since the
939 electricity requirement and operating cost are not validated for the closed-loop hybrid system, a
940 quantitative economic analysis and energy consumption estimation are essential for the large-
941 scale plant.

942 **7.1.3 MD integrated system**

943 Widespread studies on MD hybrid processes in various applications have been reported for its
944 high contribution to treat complex impaired water, high rejection towards different organic and
945 inorganic components, improve water recovery, recover valuable nutrients, alleviate
946 fouling/scaling, reduce brine disposal, low energy if natural power source used, and cost-effective
947 [113]. It has been utilized in many fields such as seawater desalination, wastewater treatment,
948 agriculture, oily wastewater, landfill leachate, and pharmaceutical industry [113, 114]. Because
949 the commercial membrane provided high quality and stable permeate, thereby improving the
950 efficiency of the processes and preventing the drawbacks that hampered its realization in large-
951 scale operations [114]. An example is the hybrid MD- crystallizer, which is capable of recovering
952 various mineral nutrients from seawater and wastewater and can improve the production of
953 drinking water by up to 95% [113]. The function of a crystallizer is to reach the supersaturation
954 level of the saline solution to capture solid salts in a tank through water recovery. The most
955 common salt nutrients extracted from seawater and wastewater brine are sodium (NaCl, Na₂SO₄,
956 and Na₂CO₃), calcium (CaCO₃, CaSO₄), and magnesium (MgSO₄, MgOH). Ji et al. utilized the hybrid
957 MD- crystallizer to obtain NaCl from RO brines. The performance of the hybrid system was
958 investigated in terms of crystallization kinetics, productivity, controlled size and shape distribution
959 of the solid nutrient salts. A comparison between actual and synthetic RO brine was carried out
960 to understand the impact of organic matter dissolved in raw seawater on the water permeate,
961 suspension density, and nucleation and growth rates of NaCl. The results revealed that when using
962 synthetic RO brine, the system captured 21 kg/m³ of NaCl crystals having common cubic shape
963 with size ranged from 20 to 200 μm. The system achieved much higher water recovery factor of
964 90%. However, when using actual brine, the growth rate of NaCl crystals was reduced by 15–23%
965 as compared to that for the synthetic brine. The dissolved organic matter in the real brine
966 influenced the water flux and the quantity of salt crystals and the reduction was estimated at 20%

967 and 8.0 %, respectively. Consequently, a pre-treatment step before the RO is necessary to remove
968 dissolved organic matter and avoiding their effects on the MD membrane. Since the
969 supersaturation of the solution was effectively controlled along with the polarization issue,
970 nucleation process and hydrodynamics, the distillate permeate during 100 hours in the MD
971 process was stable.

972 Recovering nutrients can also be done by MD. The hybrid MD process can continuously re-
973 concentrate the diluted solution and, at the same time generating drinking water in the outlet
974 side. Suwaileh et al. [56] explored the efficiency of using the FO-MD hybrid process to treat
975 brackish water and recover nutrients from fertilizer draw solution. It was assumed that the
976 thermal heating for operating the MD system could be supplied from a renewable power source,
977 such as solar heating, to reduce the overall energy requirement. The salinity of the feed solution
978 and concentration polarization had no effect on the removal efficiency of the MD membrane. It
979 was observed that when using a low salinity feed solution of 0.5 mol/L of KCl fertilizer draw
980 solution, the water permeation reached 7.7 LMH. This flux value dropped to 4.9 LMH when using
981 a high concentration feed solution of 1.4 mol/L. the average salt rejection was as high as >99.4%
982 when using feed concentrations ranging from 0.1 to 0.8 mol/L. The water permeate had a
983 conductivity value of less than 500 $\mu\text{S}/\text{cm}$, which satisfied the recommended standard of the
984 drinking water. At an optimum temperature of 60 °C, the MD membrane produced distillate
985 permeate around 5.7 LMH and excellent salt rejection around 99.55%. This can be attributed to
986 low membrane fouling as the FO removed most of the salts from the feed solution before fed the
987 MD process. Furthermore, the energy consumption was minimized significantly from 7.06
988 KWh/m^3 to 1.1 KWh/m^3 which confirmed the potentiality of the hybrid system in the separation
989 of salts and recovering the fertilizer draw solution. The final product water can be directly used
990 for fertigation.

991 The MD integrated PRO process is beneficial to recover the draw solution with low energy
992 expenditure. Through using the osmotic power gradient process (PRO), the energy consumption
993 can be reduced, and the concentration of the draw solution can be maximized to enhance power
994 exploitation [115]. Lin et al. investigated the performance of an advanced closed-loop system
995 involving PRO coupled MD to regenerate the low and highly concentrated feed solutions and
996 produce drinking water. The PRO was used to extract useful power via a hydro-turbine. It was
997 found that the energy efficiency of the system approached 9.8%, equivalent to 81.6% of the
998 Carnot efficiency when using 60 °C for the hot stream, 20 °C for the cold stream, and 1.0 mol/L
999 NaCl feed solution. However, increasing the concentration of the feed solution led to greater
1000 theoretical energy efficiency. It should be said that the experimental energy could be lower than
1001 the theoretical energy efficiency due to the impact of various operating conditions. Besides,
1002 operating different concentrations of feed solutions in the range of 1.0, 2.0, and 4.0 mol/kg NaCl
1003 needed very high hydrostatic applied pressure around 46, 100, and 220 bar in the PRO system. As
1004 a result, the PRO membrane can be deformed at high hydraulic pressure yielding lower water flux,
1005 poor salt rejection, low energy generation, and high membrane replacement cost. Thus, the
1006 development of membrane with high mechanical strength is essential to take advantage of the
1007 great power output at high feed solution concentration.

1008

1009 **7.1.4 ED integrated system**

1010 RED is a voltage-driven process that produces electricity from a salinity gradient, and it can be
1011 combined with the NF or MD membrane process [113]. The ED process has been found to be a
1012 potential process for obtaining concentrated brine, although the monovalent ion-selective
1013 membrane is expensive. Liu et al. [116] employed a novel NF-ED hybrid system in which the NF

1014 membrane was to separate divalent ions like SO^{2-}_4 while the ED was to re-concentrate the water
1015 permeates from the NF. The applied pressure and feed stream concentration caused a reduction
1016 in the water flux and salt rejection. A slow increase in the water flux at higher applied pressure
1017 was noticeable due to membrane compaction. When using artificial seawater with a salinity of
1018 88,000 mg/L at a hydraulic pressure of 32 bar, water permeation of 57.5 LMH was achieved. It
1019 was indicated that the NF membrane almost completely rejected SO^{2-}_4 from the brine solution.
1020 However, the rejection rate was lower of about 40% and 87% for Ca^{+2} and Mg^{+2} salt nutrients. The
1021 NF membrane showed poor rejection of less than 5% against monovalent ions such as Cl^- , K^+ and
1022 Na^+ . High concentration of Ca^{+2} were detected in the NF water permeate of 392 mg/L, which
1023 minimized ED membrane fouling when used as a feed solution in the ED process. When the NaCl
1024 was concentrated to 160 g/L at 15 V for over 5 hours in the ED system, the greatest water recovery
1025 was around 70%. This brine solution contained a total amount of mineral nutrients (K^+ , Ca^{+2} , and
1026 Mg^{+2}) around 5 g/L of the total TDS. The energy consumption was approximately 0.6 kW h/m³ for
1027 the NF system, and it was higher, around 1.4 kW h/kg NaCl for the ED process. To that end, the
1028 hybrid NF-ED system could be a prospective strategy to re-concentrate high salinity NaCl from
1029 seawater desalination brine.

1030 The MD coupled RED can generate concentrated brine in the outlet, freshwater product, and
1031 power output. Long et al. [117] studied the performance of innovated MD-RED hybrid system
1032 using low-grade heat sources varying from 40 °C to 80 °C and the NaCl feed solution with different
1033 salinities of 1.0, 2.0, 3.0, 4.0, and 5.0 mol/kg. The concentrated brine from the MD fed to the ED
1034 to convert the mixing energy to electricity, thereby minimizing the energy consumption of the
1035 hybrid system. The operating conditions influencing the performance of the process were
1036 optimized. The energy efficiency of this hybrid system was also determined to evaluate its viability
1037 for the large-scale plant. In the analysis, the distribution of the mass flow rate and heat through

1038 the MD membrane was determined using the mass and heat transfer models. The energy
1039 efficiency of the MD system depends on the operating temperature and concentration of the feed
1040 solution. It was observed that the energy efficiency approached 1.15% at a temperature of 20 °C
1041 and 60 °C for the cold and the hot compartments, respectively, and feed NaCl concentration of 5
1042 mol/kg. In the RED system, the efficiency of currents to extract low-grade heat was around 1.2%,
1043 with the regenerative efficiency being 50%. This calculated energy efficiency confirmed the
1044 feasibility of the system to generate low-grade heat that can be converted to electricity. However,
1045 to further maximize the extractable power, the electrode material should be improved. Since the
1046 properties of both the MD and RED membranes play an important role in determining the total
1047 energy efficiency of the process, advanced conductive materials for the membranes can be used.
1048 This hybrid technology has potential for harvesting natural power to heat water, which can be
1049 utilized for industrial and agricultural applications.

1050 Recently, the hybrid MD-RED system was examined by Tufa et al. [118] for seawater desalination
1051 to generate freshwater production and power output. In this study, high energy efficiency was
1052 generated of 49% when operating the MD system with the temperature of the hot stream around
1053 60 °C and synthetic seawater feed concentration around 0.5 mol/L NaCl, whilst the specific energy
1054 consumption was slightly reduced at 8%. The resultant brine from the MD with a salinity of about
1055 5.0 mol/L NaCl was transferred to the RED system to boost the extractable power. It was reported
1056 that the power density approached 2.2 W/m² membrane pairs. This indicated that increasing the
1057 MD brine concentration to 5.0 mol/L caused an increase in the attainable energy from the RED
1058 system compared to RO brine (1.0 mol/L NaCl) in combination with seawater (0.5 mol/L NaCl).
1059 Overall, this reliable and cost-effective hybrid system offers several advantages, such as low brine
1060 discharge, harvesting low-grade heat to produce electricity, and is useable in various desalination
1061 processes where high-power input is needed.

1062

1063 **7.2 Wastewater treatment**

1064 **7.2.1 RO integrated system**

1065 Another water resource is secondary effluent wastewater, and treatment is required to remove
1066 pathogens, dissolved solids, and other pollutants to allow the water to be reused in sustainable
1067 agriculture. RO membrane-based process is frequently utilized for wastewater treatment globally,
1068 due to process enhancements, small footprint, uncomplicated maintenance, high water capacity,
1069 and workable process [6]. Among pressure-driven processes, UF coupled with RO is proven to be
1070 an effective hybrid system for wastewater reclamation. In line with this, Oron et al. [119] used a
1071 pilot plant composed of the UF membrane to separate suspended matter, organic matter, and
1072 microorganisms while the complementary RO membrane was used to reject total dissolved solids
1073 (TDS). After 681 hours of operation, the UF permeate showed very low turbidity of less than 1.0,
1074 low organic matter (BOD = 6.6 mgO₂/l, and COD =64 mgO₂/l), and was free of fecal coliforms.
1075 Next, the UF permeate entered the RO system for further purification resulting in water permeate
1076 with low organic matter (BOD = 4.8 mgO₂/l and COD = 16 mgO₂/l), lowered salts (TDS=69.8 mg/L,
1077 Cl⁻ = 65.6 mg/L, Na⁺ = 42 mg/L, K⁺ = 10.4 mg/L, Ca⁺² = 6.6, Mg⁺² = 4.4, N-NH⁺=10.8 mg/L, and PO₄ =
1078 1.8 mg/L). Treatment by RO membrane produced water permeate that is suitable for agricultural
1079 applications meeting the quality guidelines for irrigation water. The RO permeate with minimum
1080 dissolved solids, and the lowest SAR value was applied directly to a crop field. This type of treated
1081 effluent had a negligible effect on the groundwater salinization and enrichment with undesired
1082 nitrates. Despite that, the permeate from stabilization ponds, including high contents of organic
1083 matter and a medium level of salinity, led to a higher crop yield.

1084 Shanmuganathan et al. [120] integrated the NF process with the RO process to treat biologically
1085 treated sewage effluent aiming at producing irrigation water. The results indicated that the NTR
1086 729HF membrane achieved the greatest rejection rate towards bivalent ions around 99% for SO_4^{2-} ,
1087 62% for Ca^{+2} , and Mg^{+2} . However, a very low rejection was observed for monovalent ions like
1088 Na^+ , Cl^- and NO_3^- of about 19%, 11%, and 5%, respectively. The NF membrane separated most of
1089 the organic matter with a rejection rate around 76–95%, and the permeate contained only 0-0.8
1090 mg/L of DOC. However, the concentration of pharmaceuticals and personal care products, Na^+
1091 (202 mg/L), Cl^- (110 mg/L), and SAR level, were still higher than the allowable level for irrigation
1092 water. Therefore, further treatment using the RO membrane was conducted, yielding maximum
1093 rejection rate reaching > 99%, 99%, 98%, and 88% for Na^+ , Cl^- , SO_4^{2-} , Ca^{+2} , Mg^{+2} , and NO_3^- ,
1094 respectively. The RO membrane rejected valuable nutrients required for crops, and hence 10% of
1095 feed water was blended with 90% of RO permeate. The final irrigation water included an
1096 acceptable SAR value of 6 and concentrations of Na^+ (40 mg/L) and Cl^- (15.5 mg/L). The hybrid
1097 system has potential for the removal of pharmaceutical and personal care products from effluent
1098 wastewater to produce high-quality irrigation water and which will not contaminate soil and
1099 groundwater.

1100 Later, NF and RO hybrid system was investigated to purify MBR treated wastewater to reuse for
1101 agricultural applications [35]. The analysis of the water permeates from the NF and RO processes
1102 was performed based on different international standards. It was found that the water permeate
1103 from NF is not suitable for irrigation water because the SAR level is 25.7, which may hinder the
1104 crop growth and affect the soil permeability. It is most likely that poor rejection of Na^+ and Cl^- and
1105 high rejection of Ca^{+2} and Mg^{+2} by the NF membrane caused great SAR value. A second pass with
1106 RO was utilized to reduce the SAR value and create irrigation suitable water. The RO permeate
1107 showed the lowest concentrations of mineral nutrients, such as Na^+ (7.83 mg/L) Cl^- (4.96 mg/L),

1108 PO_4 (<0.05 mg/L), Ca^{+2} (1.56 mg/L), Mg^{+2} (0.06 mg/L), K^+ (0.93 mg/L), salinity of 0.37g/L, and low
1109 SAR value of 12.5. The turbidity of the permeate was reduced from 0.81 to 0.23, satisfying the
1110 acceptable level for irrigation water. As the sodium concentration was higher than calcium and
1111 magnesium, the water infiltration problem was low. The RO blended MBR with a ratio of 2:1
1112 achieved the best SAR value of (5.30) and low salinity (0.57 g/L). By using this optimum ratio 2:1
1113 of the product water, it can be reused directly for fertigation, improved waste management, and
1114 is cost-effective.

1115

1116 **7.2.2 FO integrated system**

1117 FO treatment process using fertilizer draw solution is attractive because the fertilizer draw
1118 solution can be used directly or blended with potable water to irrigate crops. Several studies have
1119 been carried out utilizing the FDFO integrated process to treat wastewater due to excess of
1120 valuable nutrients for plant growth [48]. However, the diluted draw solution should be mixed with
1121 potable water [121]. This is challenging because in many parts of the world freshwater resources
1122 are limited. Therefore, the FDFO process, combined with another treatment process, can
1123 minimize nutrient concentrations in the diluted draw solution reaching the quality of irrigation
1124 water. MBR has been used commonly for wastewater reclamation giving clean water having
1125 adequate nutrients concentration for fertigation [17]. For example, the combination of FDFO and
1126 an anaerobic membrane bioreactor (AnMBR) was employed to treat wastewater and generate
1127 irrigation water for hydroponics [121]. Firstly, the optimum water recovery rate was determined
1128 by using Bio-methane potential (BMP) measurements. The performance of a wide range of
1129 fertilizer draw solutions in terms of water flux, water recovery, reverse salt flux, and final nutrient
1130 concentrations were evaluated in the FDFO when using synthetic municipal wastewater as the

1131 feed solution. Biogas generation was increased when increasing the water recovery, and the
1132 recovery rate of 95% demonstrated the greatest cumulative biogas production. It was reported
1133 that the water flux was strongly correlated to the water recovery, and therefore the performance
1134 of both KCl and NH₄Cl draw solutions was similar. Among the tested fertilizer draw solutions, the
1135 KCl and NH₄Cl fertilizer draw solutions generated the highest water permeation of 21.1 LMH
1136 followed by KNO₃ with 13.2 LMH. The KH₂PO₄ and ammonium phosphate dibasic (DAP) exhibited
1137 lowest water flux of about 13.3 LMH. Similarly, the highest water recovery achieved for NH₄Cl and
1138 KCl reaching 42.2% and 38.6%. The ammonium sulphate showed the highest water recovery rate
1139 around 76% followed by KH₂PO₄ with water recovery around 75% after hydraulic cleaning. The
1140 MAP and SOA fertilizer draw solutions exhibited the lowest reverse solute flux around 1.0 and 1.7
1141 gMH, respectively. Although the MAP fertilizer liquid included minimum final nutrient
1142 concentration (N=54.1 mg/L/P= 10.8 mg/L / K=0 mg/L), it still needs further dilution by fresh water
1143 to reach irrigation water quality.

1144 Another proposed desalination technology for leachate treatment is the combined chemical
1145 precipitation method and the FO process. Wu et al. [122] proposed using a pre-treatment strategy
1146 involving the addition of carbonate to improve the struvite precipitation and purity, followed by
1147 the FO desalination process as presented in Fig. (7). The researchers investigated three aspects to
1148 evaluate the performance of the new hybrid system. Firstly, the struvite recovery from landfill
1149 leachate, and the influence of the pretreatment method on recovery rate was sought. It was
1150 essential to understand how the pre-treatment stage impacted water recovery behavior in the FO
1151 system. Lastly, the optimal arrangement of chemical pretreatment, struvite precipitation, and FO
1152 water recovery was also assessed. When adding the calcium into the landfill leachate, the
1153 magnesium was precipitated as pure struvite. Then, the FO process was used to minimize the
1154 volume of wastewater, which eliminated the use of another post-treatment stage and reduced

1155 the investment cost. After applying the pre-treatment step with a molar ratio of 1:1.4 for Ca^{+2} :
1156 CO_3^{-2} , the Mg^{+2} leakage was decreased by $24.1 \pm 2.0\%$ while the rejection efficiency of Ca^{+2}
1157 amounted as $89.5 \pm 1.7\%$. The high amount of Mg^{+2} can be recovered of about $98.6 \pm 0.1\%$, and
1158 traces of $\text{PO}_4^{-3}\text{-P}$ detected in the solution of less than 25 mg/L under the condition of (Mg + Ca
1159 residual): P molar ratio of 1:1.5 and pH 9.5. The struvite product created from the process showed
1160 crystal structure and composition mimicking the commercial struvite (19.3% Mg and 29.8% P).
1161 When using 4.0 mol/L NaCl draw solution in the FO system, the water extracted was around 621.5
1162 mL over 95 hours of operational time, meaning 36.6% of recovery efficiency. The FO was capable
1163 of lowering the volume of wastewater by 37%. The optimal system configuration was chemical
1164 pre-treatment-FO- struvite recovery for the best FO performance.

1165 The FO process can also be integrated with the bioelectrical process to control brine production
1166 and extract more pure water from wastewater. During the FO operation, the wastewater feed
1167 gets concentrated, and the brine caused more mass transfer resistance for the pure water, which
1168 is controlled by the osmotic difference through the FO membrane [123]. A microbial desalination
1169 cell (MDC) can be coupled with the FO system to further desalinate the diluted draw solution from
1170 the FO system and generate irrigation water. For example, Yuan et al. [124] used the MDC-FO
1171 hybrid system to improve the efficiency of the FO to treat wastewater over 16 hours, as illustrated
1172 in Fig. (8). The working principle depends on the blending the anode effluents together and using
1173 them as the feed solution for the FO process. Two different solutions were produced from the FO
1174 process. The concentrated feed solution is fed to the cathode of the MDC to remove the COD
1175 whilst the diluted draw solution was purified in the desalination cell of the MDC. The influence of
1176 initial COD, salt concentration, and hydraulic retention time were investigated to study the
1177 practicality of the hybrid system. In the hybrid system, a synthetic anode solution involving 750
1178 mg/L COD, 35 g/L NaCl solution at the MDC anode, and HRT of 12 h was utilized. It was reported

1179 that the hybrid system produced a lower wastewater volume estimated by 64% due to water
1180 permeation in the FO and evaporation on the cathode as compared to the stand-alone MDC
1181 system (14%). The conductivity reduction in saline water (HRT) was improved by 2-fold as
1182 compared to individual MDC systems. The removal efficiency towards COD approached 93%, and
1183 the conductivity reduction improved to 99.4% when using a low concentration of NaCl. The
1184 efficiency of the hybrid system was promising, which makes it an appropriate desalination process
1185 for brackish water or as a pre-treatment method for hypersaline solution and wastewater.

1186

1187 **7.2.3 MD integrated system**

1188 Wastewater treatment by a MD membrane is an excellent opportunity to eliminate the technical
1189 barriers of the RO process. It can be coupled with another membrane process providing fresh
1190 water for industrial uses, for fertigation, and for domestic uses. Several studies highlighted that
1191 purified municipal wastewater could be reused for irrigation because it contains high quantities
1192 of nutrients for crop growth [17]. A group of researchers assessed the performance of a bench-
1193 scale FO–MD system to treat for direct sewer mining [125] as shown in Fig. (9). They studied the
1194 efficiency of the process based on water permeation and the rejection rate of trace organic
1195 contaminants (TrOC). Experimental data showed that the water flux was stable upon using natural
1196 sewage as the feed solution in the hybrid process at water recovery up to 80%. The removal rate
1197 of trace organic contaminants was high in the range of 91 to 98%. The high rejection of TrOC can
1198 be ascribed to the solute–membrane interaction of the FO membrane and, in the case of the MD
1199 membrane, was due to the volatility of these species. When the water recovery was increased,
1200 there was an increase in the TrOCs concentration in the draw solution. The TrOCs accumulation
1201 in the draw solution was probably due to the variation in the removal efficiency between the FO

1202 and MD membranes. To avoid this issue, activated carbon adsorption or ultraviolet oxidation can
1203 be used to separate these contaminants completely, achieving rejection of more than 99.5%. It
1204 was noted that the energy expenditure was high due to operating the MD at a temperature
1205 between 20 °C and 40 °C. In this respect, it can be a promising process for agricultural purposes in
1206 arid areas where renewable power is available.

1207 Xie et al. [126] employed a similar approach to separate phosphorus nutrient and freshwater from
1208 digested sludge centrate using a 1.5 mol/L MgCl₂ as draw solution. The bidirectional flux of
1209 magnesium and protons induces struvite precipitation. The role of FO was to concentrate
1210 orthophosphate and ammonium for phosphorus recovery when creating struvite
1211 (MgNH₄PO₄·6H₂O). MD was utilized to regenerate the draw solution and obtain fresh water from
1212 the digested sludge centrate. A reduction in the water permeation obtained from the FO
1213 membrane due to fouling was observed; however, after the first and second cleaning stages, the
1214 water recovery was 82% and 68%, respectively. As a result, a high amount of water permeate was
1215 fed to the MD, which exhibited stable water permeation. The hybrid system achieved an excellent
1216 rejection of inorganic salts (ammonium and orthophosphate), organic matter (TOC and total
1217 nitrogen, TN). Because the magnesium transferred from the draw solution to the concentrated
1218 digested sludge and protons diffused in the forward direction, the struvite crystals were created.
1219 A decrease in the pH of the feed solution and the accumulation of magnesium facilitated the
1220 formation of struvite crystals. Thus, the hybrid system was effective in extracting phosphorus
1221 nutrients in the form of struvite precipitate.

1222 A recent study was reported by Volpin et al. [114] using an FO-MD hybrid system to recover
1223 nutrients like nitrogen, phosphorous, and potassium from human urine. The optimization and
1224 performance of the hybrid system were explored. A novel protocol was developed to minimize
1225 the nitrogen transfer to the MD outlet, thereby obtaining water products for direct irrigation. The

1226 operating conditions in the FO, like urine pH and draw solution concentration, were optimized.
1227 The feed temperature, nitrogen concentration, and membrane properties were optimized for the
1228 MD process. It was noted that the FO water permeates ranged from 31.5 to 28.7 LMH upon
1229 utilizing 2.5 mol/L NaCl as a draw solution while the nitrogen flux was very low at 1.4 g/L. The
1230 nitrogen flux as $\text{NH}_3/\text{NH}_4^+$ /Urea dropped significantly by 33% when decreasing the hydraulic
1231 pressure at the draw solution side to 2.0 bar, but a decline in the water flux by 42% was noticeable.
1232 When the feed solution became acidic (pH =6-7), the nitrogen rejection by both the FO and MD
1233 membranes was improved. The importance of acidification was to maintain a high rejection of
1234 nitrogen and to prevent the hydrolysis of urine. The MD membrane achieved maximum distillate
1235 permeate of 16 LMH due to high porosity and hydrophobicity. The ammonia vapor pressure was
1236 raised due to the high concentration of ammonia and inlet temperature of 60 °C. The membrane
1237 pore size and thickness controlled the transport of ammonia through the membrane. It was
1238 concluded that this dual separation process was reliable for wastewater treatment in space
1239 application and nutrient regeneration for urban applications.

1240

1241 **7.2.4 ED integrated system**

1242 The membrane desalination technology operated based on thermodynamic reaction is an
1243 attractive method for converting extractable power to electricity that created with water recovery
1244 [127]. It is recognized that the accumulation of various nutrients on the feed stream due to
1245 reverse solute flux and salinity build-up from the membrane rejection is one of the key challenges
1246 in the FO process. To avoid this technical hurdle, the ED system was coupled to an FO system for
1247 further treatment of the concentrated feed solution and therefore controlling the salinity build-
1248 up on the feed stream [128]. The combination of FO and ED processes delivered a remarkable

1249 advantage for wastewater treatment. Zou et al. [129] followed this strategy to desalinate
1250 wastewater using $(\text{NH}_4)_2\text{HPO}_4$, fertilizer draw solution. A schematic of the hybrid system is
1251 demonstrated in Fig. (10). In the FO system, the influence of draw solution concentration on the
1252 water recovery and reverse solute flux was investigated. In the ED system, the removal efficiency,
1253 regeneration of the fertilizer draw solution, and energy consumption using different applied
1254 voltages was also studied. Experimental findings demonstrated that the FO process generated a
1255 stable water recovery volume around 375.5 mL when utilizing concentrated fertilizer draw
1256 solution (2.0 mol/L). A minimum specific reverse solute diffusion of 0.063 g/L and 0.083 g/L for
1257 $\text{NH}_4\text{-}^+\text{N}$ and $\text{PO}_4\text{-}^3\text{-P}$ nutrients, respectively, was observed upon using 1.0 mol/L draw solution. The
1258 negligible concentration of Na^+ , Cl^- , and organic constituents was detected in the diluted draw
1259 solution, and therefore the diluted draw solution is reusable for fertigation. At the optimum
1260 applied current of 3.0 V, the ED showed excellent water recovery of $96.6 \pm 3.0\%$ reverse-fluxed
1261 draw solution. The specific energy consumption of the hybrid system was very low of about 0.72
1262 kWh m^{-3} and 0.35 kWh m^{-3} (55.7% reduction) when applying 2.5 V and 3.0 V, respectively. The
1263 synergistic cooperation of both processes achieved excellent water recovery and consistent
1264 performance.

1265 Ippersiel et al. [130] integrated an ED system with an air stripping method to concentrate
1266 ammonia nutrients followed by direct aeration or vacuum to separate the volatile ammonia from
1267 the concentrate solution by an acidic trap. The aim was to extract concentrated nitrogen fertilizer
1268 from liquid swine manure through the addition of acids to eliminate scaling stripping towers. In
1269 the ED process, the optimum applied voltage was 17.5 V resulting in efficient energy expenditure.
1270 The best pH values of the feed solution were ranged from 8.5 to 8.2, facilitating electromigration
1271 of NH_4 . It was noted that the maximum achievable ammonia nitrogen recovered was 21 352 mg/L
1272 in the concentrate solution corresponding 7-folds the concentration in the swine manure. This

1273 value was greater by 33% than that extracted from the open-to-the-atmosphere system. In this
1274 work, 95% of the TAN was recovered from the swine manure utilizing a closed-to-the-atmosphere
1275 system. The increase in concentration of the solution was hindered during the process due to the
1276 transport of the pure water from the diluted stream governed by electroosmosis and osmosis.
1277 When the concentrate reservoir was exposed to vacuum, the ammonia recuperated was around
1278 14.5% of the theoretical value of the NH_3 in the concentrate solution relative to 6.2% only when
1279 applying aeration. However, effective energy usage caused a lower concentration gradient
1280 between the concentrate and the diluted solutions by a factor of 10. This caused the presence of
1281 swine manure TAN traces in the diluted solution after shutting down the process. The pH of the
1282 concentrate solution should be increased to more than 8.6 further to improve the volatilization
1283 of NH_3 toward the acid trap.

1284 Vecino et al. [131] proposed using liquid-liquid membrane contactors (LLMCs) to re-concentrate
1285 ammonia from wastewater as ammonium salts (NH_4NO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$). Two different
1286 concentrations of ammonia fertilizer as feed solutions (1.7 g/L, N= 0.33% (w/w)-4.0 g/L, N= 0.14%
1287 (w/w)) were used to create ammonium salts by an acid stripping solution (nitric and phosphoric
1288 acid). After that, the ED system was connected to the LLMCs for further desalination of the LLMCs
1289 permeate and obtaining product water depicting the quality of irrigation water. In this work, over
1290 29.0 hours of LLMCs experiment, the ammonia concentration declined to 0.03% (w/w) of nitrogen
1291 at 360 mg NH_3 /L when utilizing high initial concentration of fertilizer feed solution. However, the
1292 ammonia concentration was further reduced to 0.02% (w/w) of nitrogen around 240 mg NH_3 /L
1293 over 12.5 hours when using a low initial concentration of fertilizer feed solution. After that, the
1294 ED was capable of concentrating these ammonium salts by a factor of 1.6 ± 0.3 , which created a
1295 liquid fertilizer contained 15.6% (w/w) and $16.2 \pm 1.2\%$ nitrogen as NH_4NO_3 by Fujifilm membranes
1296 and a PCell, respectively. Under constant applied current of 7 V., The estimated energy

1297 consumption was as low as 0.21 ± 0.08 kWh/kg ammonium salt and $93.1 \pm 4.2\%$ of faradaic yield.
1298 This indicated that this novel hybrid system is a promising technology for the valorization and
1299 recovery of ammonia nutrients from wastewater solutions.

1300

1301 **8 Conclusions**

1302 Water desalination and wastewater treatment could have useful impacts on fertigation and
1303 environment providing additional water resources and regenerating poor-quality water.
1304 Membrane technologies can supply water for agriculture and increasing food production. The
1305 stand-alone or hybrid RO and FO membrane-based processes are proven to be the most effective
1306 desalination technologies used in many countries around the world. Due to the efficient
1307 separation performance, low fouling tendency, reduced energy expenditure, widespread for
1308 saline water desalination and wastewater treatment, they can provide fertilizer solution and
1309 irrigation water with an acceptable level of nutrients for fertigation. The stand-alone RO and
1310 electrodialysis are available, have effective performance, and can provide high quality nutrient
1311 water, but the water production cost is still higher than that for common technologies used for
1312 agriculture. A potential approach to desalinate hypersaline feed solution is the MD system. It can
1313 produce high quality water, but it should be blended with liquid nutrients to reach the acceptable
1314 standard of irrigation water. Also, the MD system requires high thermal energy which increases
1315 the energy consumption and the operating cost. The MBR process generates water enriched
1316 nutrients from wastewater effluent and can be reused immediately for fertigation. On the other
1317 hand, membrane fouling is a serious problem due to high concentration of complex wastewater
1318 and the energy consumption of the system is considered high. Thus, the operating and
1319 maintenance costs are high due to frequent replacement of the membrane and high energy
1320 demand. Furthermore, hybrid FO process can achieve efficient nutrient recovery and low energy
1321 consumption only if natural energy is available for recycling of the draw solution. Integrating MD
1322 with another membrane desalination technology is promising for nutrient recovery when RO
1323 brine is used as the feed solution. This is because the concentrated brine is valuable source of
1324 mineral nutrients and therefore no need to discharge high volume of brine to the sea. Other
1325 technologies such as MD and ED processes will be applied for agricultural purposes where natural

1326 energy is abundant and can be utilized to reduce the energy requirements and overall cost.
1327 Among stand-alone and hybrid desalination technologies evaluated in this review, FO coupled ED
1328 processes showed superior performance efficiency and minimum energy expenditure around
1329 0.35 kWh m⁻³. Although these membrane technologies for treating saline water or wastewater
1330 are expensive, they could be cost-effective when producing nutrient water for fertigation,
1331 increasing crop production, and enhancing the quality of crop yield. To that end, all these
1332 membrane-based desalination technologies require advances in irrigation water practices,
1333 reducing the need for freshwater supply resources, and maximizing water reusability efficiency.
1334

1335

1336 9 Future prospects

1337 The membrane in an individual treatment process has often failed in providing the required
1338 quality for irrigation water for diverse types of feed salinities. The additional purification of the
1339 diluted draw solution to reach the quality water nutrient can be achieved using another
1340 desalination technology process. The recovery system should possess minimum energy
1341 expenditure and efficient output. The recovery process combined with the desalination process
1342 is necessary in some cases to re-concentrate the draw solution, extract valuable nutrients, and
1343 produce drinking water. Other merits are accelerating the water production, decreasing the
1344 energy requirement, recover nutrients from hypersaline solution and wastewater, and lowering
1345 the volume of brine and wastewater for discharge. The hybrid desalination systems in this review
1346 generated product water with varying qualities depending on the availability of freshwater
1347 resources, the type of crops, and soil. However, if a perfect draw solution in the FO system
1348 provided water nutrients suitable for direct irrigation, the recovery method can be ignored, and
1349 minimal power is needed. For instance, the FO integrated MD system can potentially generate
1350 irrigation water and drinking water when using a complex wastewater stream or brine containing

1351 nutrients and a thermolytic fertilizer draw solution. The implementation of the FO-MD process in
1352 the industry needs special consideration related to promoting system design and heat recovery.
1353 The use of a heat exchanger can improve the energy efficiency of the system [132]. Besides, this
1354 system can be considered energy-wise, cost-effective, and low environmental impacts, especially
1355 if low-grade heat source or natural power such as effective solar absorber, waste heat,
1356 geothermal heating, is supplied to the recovery system. The production of vapor by solar energy
1357 can be increased through efficient solar absorptive materials like carbon nanomaterials,
1358 plasmonic materials, metal oxide nanomaterials, and non-thermal-conductive material such as
1359 wood and foams. Currently, research is directed to maximize energy efficiency by determining
1360 latent heat recovery [132]. The improvement of latent heat recovery depends on optimizing the
1361 system design.

1362 Another promising technology is the MD coupled ED system to recover nutrients and convert the
1363 thermal potential of MD brine and energy of mixing to electricity. To fulfill commercial potential
1364 for the MD-ED hybrid process, on-site optimization of membrane-based processes through the
1365 mobile pilot plant can be an effective suggestion for evaluating the operating parameters. Many
1366 works devoted to developing novel electrode materials like pseudocapacitive and carbon
1367 materials with superior electrical conductivity, fast rapid adsorption, and desorption of salts, and
1368 high salt adsorption capacity to promote the system efficiency [49, 132, 133]. Increasing the
1369 electrode capacitance is important because a lower amount of applied voltage would be required,
1370 and a certain amount of charges would be stored [132].

1371 Another important aspect is developing revolutionary anti-fouling TFC membranes by
1372 impregnation of antibacterial nanomaterials like graphene oxide, carbon nanotubes, catalytic
1373 nanoparticles such as titania (TiO₂), silver or copper nanoparticles [134]. The long-term
1374 performance of the membranes can be further increased by removing foulants and their

1375 precursors through transparent exopolymer particles (TEP), and novel modification strategies
1376 such as layer-by-layer assembly, polymer grafting, zwitterionic coating with easy to scale up
1377 procedure and multifunctionality [135]. An alternative method to alleviate fouling is using a pre-
1378 treatment stage such as UF or MF membrane, but this practice can impose an additional energy
1379 cost. Therefore, employing real-time monitoring is a promising option to monitor fouling in early-
1380 stage, and its effectiveness needs to be tested during large-scale operations on-site [135].

1381 As most of the alteration strategies consider improving the surface properties, other membranes
1382 (i.e., FO and RO) suffer internal fouling. To reduce internal fouling effects, designing and tailoring
1383 the porous support layer is essential [61]. A balanced permeability–selectivity tradeoff can be
1384 achieved when incorporating one-dimensional (1-D) nanotubes, two-dimensional (2-D)
1385 nanosheets, and biomimetic channels into membranes [132]. The water flow through the
1386 additional channels in the membrane governed by the improved diffusion under slip flow
1387 conditions. This slip flow conditions created when the water molecules interacted with the
1388 channel surface yielding a nonzero velocity and failure of no-slip boundary condition.

1389 For MD membranes, the selection of membrane materials and characteristics is important to
1390 mitigate chemical deterioration and improving thermal conductivity. An advanced glass
1391 membrane showed excellent thermal and chemical efficiencies as compared to polymeric
1392 membranes [136]. The thermal efficiency can also be enhanced by incorporating self-healing
1393 metal nanoparticles or carbon-based sunlight absorbers into the MD membrane [118],
1394 photothermal surface coatings like plasmonic nanoparticles [132]. Furthermore, membranes with
1395 high hydrophobicity are required to reduce wetting, fouling, scaling, and purer condensate. Prior
1396 research suggested that scaling can be minimized when exposing the membrane to
1397 superhydrophobic fluorosilicone coatings [136], but the stability and separation performance in
1398 long-term experiments necessitate further investigations.

1399 For the ion exchange membrane, high water–solute selectivity of higher than 95% and a low
1400 resistance material with a price less than 4 €/m² are the main elements to promote the membrane
1401 separation performance [137]. The performance of membranes incorporating polyolefin,
1402 polyaryletherketones, halogenated polyethers, polyethylene, and poly(arylene ether sulfone)
1403 opened room for further explorations. Moreover, researches should be dedicated to optimizing
1404 the stack design involving spacers and electrodes. The design and evaluation of new geometries
1405 and shapes of spacers to decrease pressure loss and polarization phenomena are necessary [49].
1406 In parallel, a novel stack design involving manifolds layout can ameliorate the solution flow
1407 distribution in the feed channels and should be tested in a real application. It is possible to
1408 enhance the fluid dynamics, mixing behavior of the feed stream, lower resistance, and pressure
1409 drop employing by using an ion-exchange membrane with optimum geometry leading to
1410 extraordinary power output [137]. To exploit a large amount of natural power from the low-grade
1411 heat source, a closed-loop RED system is workable, especially when it is integrated with another
1412 desalination technology achieving low overall energy consumption [137]. To achieve
1413 commercialization of the hybrid system, accurate thermo-economic analysis, and cost assessment
1414 for a pilot plant in the field are needed [138]. Also, establishing thermodynamic models to
1415 evaluate the performance of the membrane and overall process is needed for scaling up the
1416 process and realization in the agricultural industry.

1417 Although these membrane-based techniques present several challenges, they could be a viable
1418 option to produce irrigation water for agricultural applications. The prospect of implementing
1419 industrial plants with optimal operating conditions and system design does not depend only on
1420 the important requirements for each desalination process but also makes the membrane the most
1421 significant factor for water generation in the agriculture industry.

1422

1423

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1425

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1429

1430 **Figure Captions**

1431 Figure.1: A diagram of the BWRO desalination plant located in the island of Gran Canaria [68].

1432

1433 Figure.2: A schematic diagram of the semi-pilot scale fertilizer drawn FO system (FDFO) utilizing
1434 hollow fiber membrane module. The lumen side of the hollow fiber membrane made of PA TFC
1435 active layer on top of the polyethersulfone (PES) support layer on the outer shell of the fiber.
1436 Adapted with permission from Lotfi et al.[75].

1437 Figure.3: The common stack unit consisted of cation exchange membranes (CEMs) and anion
1438 exchange membranes (AEMs) arranged in alternating sequences. The electrochemical potential
1439 is produced when passing each high concentration compartment (HCC) and low concentration
1440 compartment (LCC) generated by aligning alternatively both membranes. The salinity difference
1441 between both solutions allowed the transfer of ions from the membrane to electrodes. This
1442 resulted in a redox reaction to extract electricity. Adapted with permission from Tufa et al. [137].

1443 Figure.4: The design of the capacitive de-ionisation system. A circulation pump is used to drive
1444 the solution to the cell and the effluent return to the inlet tank with a volume of 25 liter. The cell
1445 is supplied with the required voltage via a power supply. The temperature of the solution was
1446 kept constant at 25 °C and the flow rate was fixed at 0.5 L/min. Reproduced with permission from
1447 Mossad et al. [86].

1448 Figure.5: A schematic diagram of the fertilizer driven FO unit (FDFO). It consists of a membrane
1449 cell with dimensions of 2.6 cm width x 7.7 cm length x 0.3 cm depth. The membrane active area
1450 is of about 20.02 cm². The draw solution container is placed on a digital scale to calculate the
1451 permeate volume. Both conductivity and pH meters were connected to the feed container to
1452 measure the pH and conductivity of the feed solution. Reproduced with permission from Volpin
1453 et al. [139].

1454 Figure.6: A schematic diagram of the RO combined adsorption system. The RO rig involves of
1455 several vessels containing membrane modules, pressure exchanger that generate energy from
1456 rejected solution to circulation pump. The adsorbent was made of Silica gel type-RD. Adapted
1457 with permission from Atab et al. [110].

1458 Figure.7: The lab-scale unit of chemical precipitation pre-treatment procedure integrated the FO
1459 process. The FO process was arranged in three different modes: 1- FO – calcium pretreatment -
1460 struvite precipitation (C1), 2- calcium pretreatment - FO - struvite precipitation (C2) and 3- calcium
1461 pretreatment - struvite precipitation - FO (C3). Adapted with permission from Wu et al. [122].

1462 Figure.8: A diagram showing the microbial desalination cells (MDCs) and forwards osmosis (FO)
1463 hybrid system. CEM is the cation exchange membrane while AEM is the anion exchange
1464 membrane. Adapted with permission from Yuan et al. [124].

1465 Figure.9: The design of the FO–membrane distillation (MD) process composed of FO membrane
1466 channel, a direct contact MD membrane compartment, pumps, temperature monitoring sensors.
1467 Adapted with permission from Xie et al. [140].

1468 Figure.10: A schematic diagram of the FO–Electrodialysis (ED) hybrid process with a semi-
1469 continuous configuration. Adapted with permission from Zou et al. [129].

1470

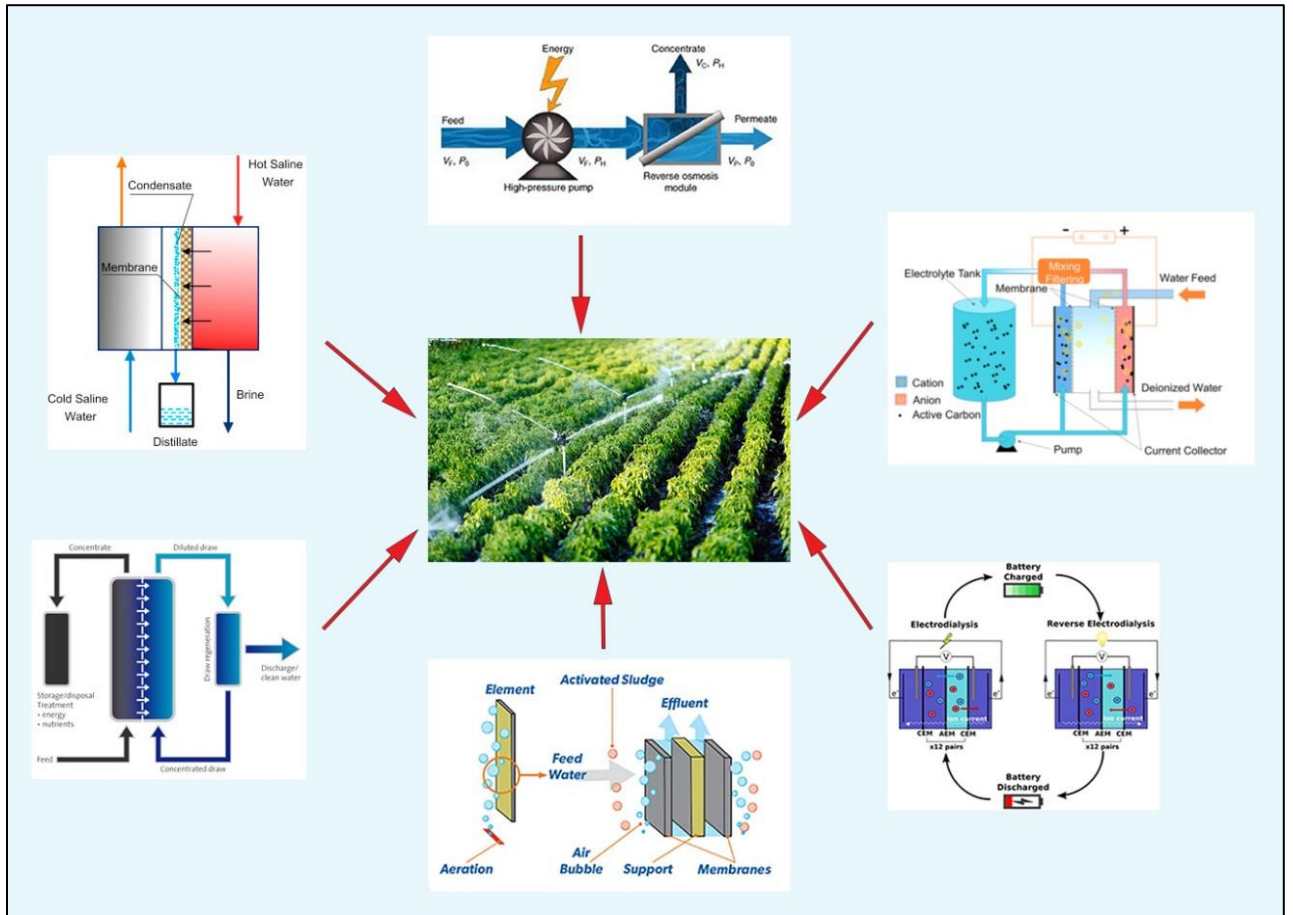
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1474 Figures

1475 Graphical abstract



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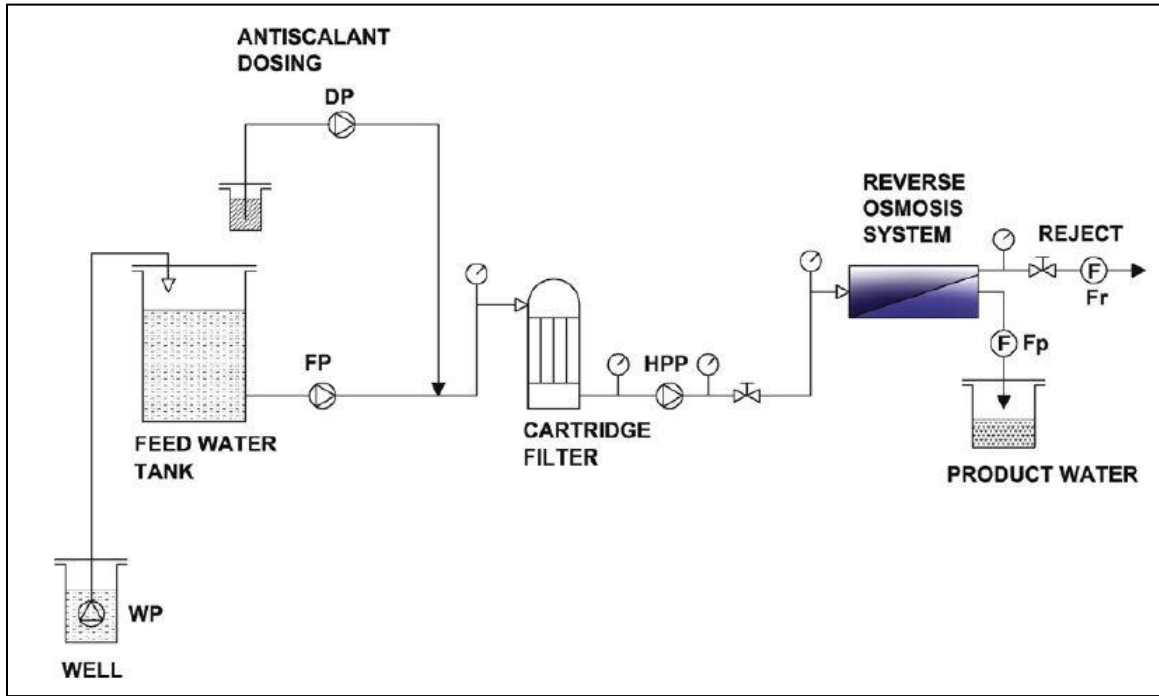
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1484 **Figure.1**



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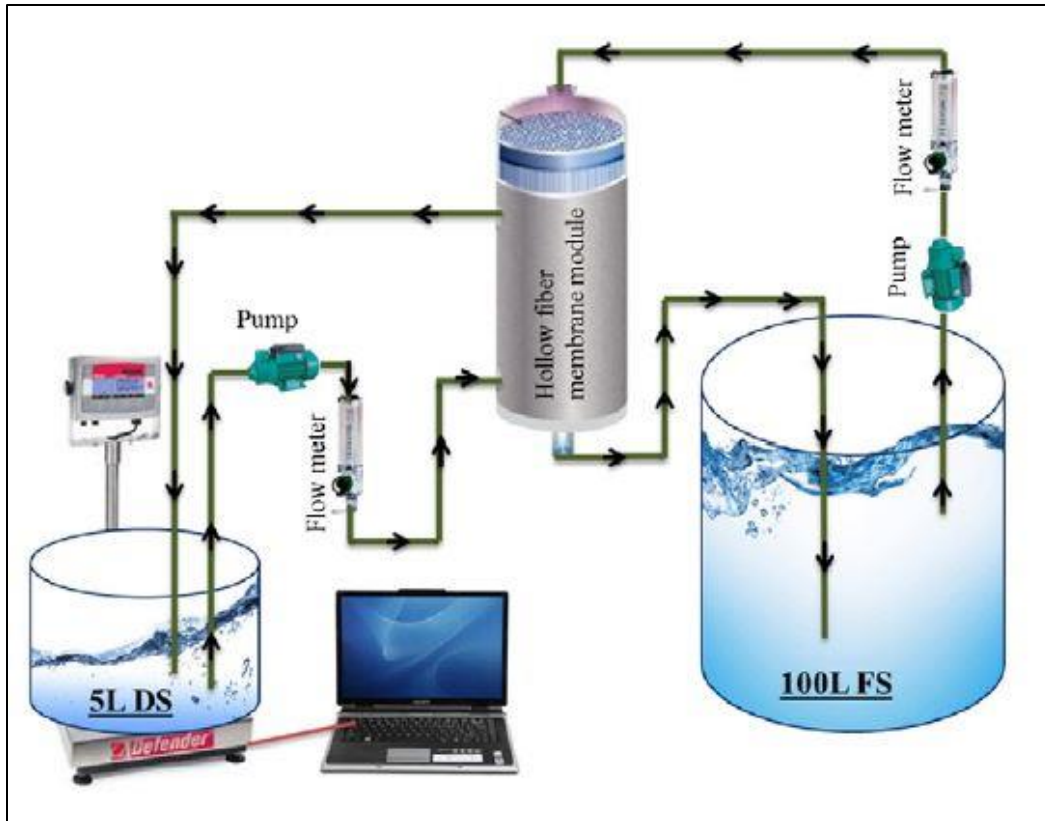
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1493 **Figure.2**

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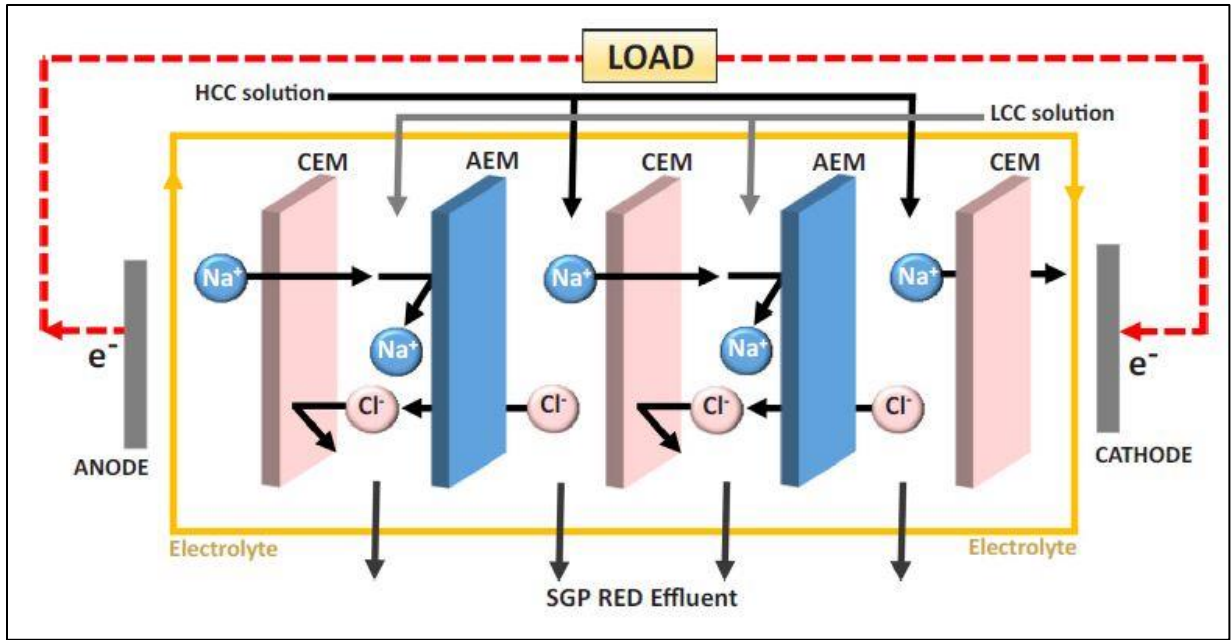
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1503 **Figure.3**

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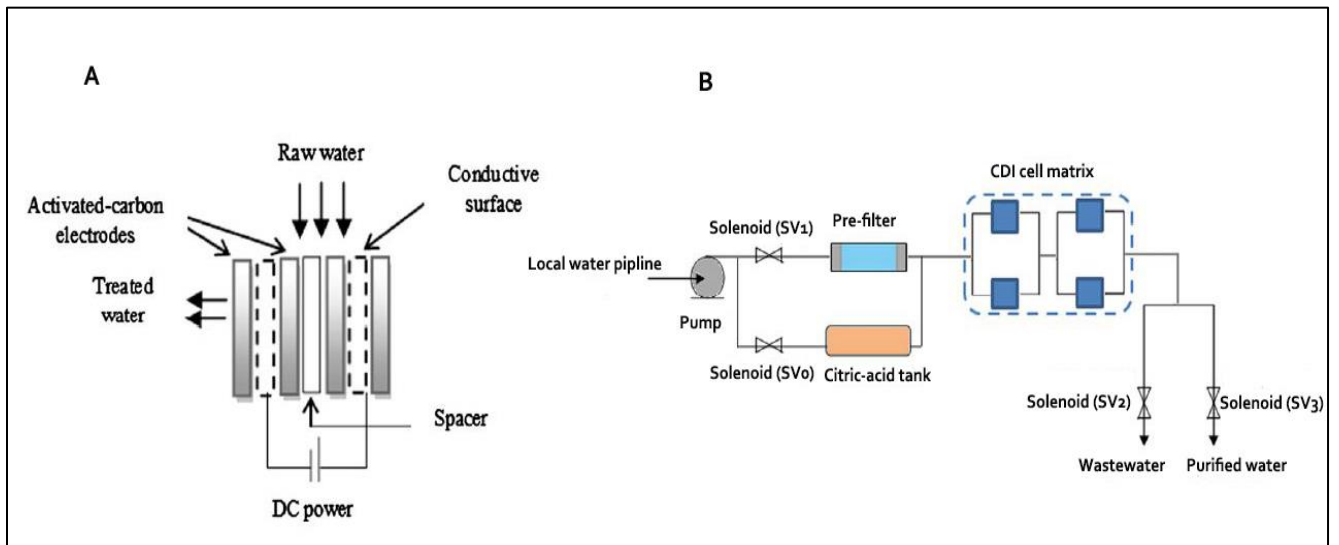


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1507 **Figure.4**

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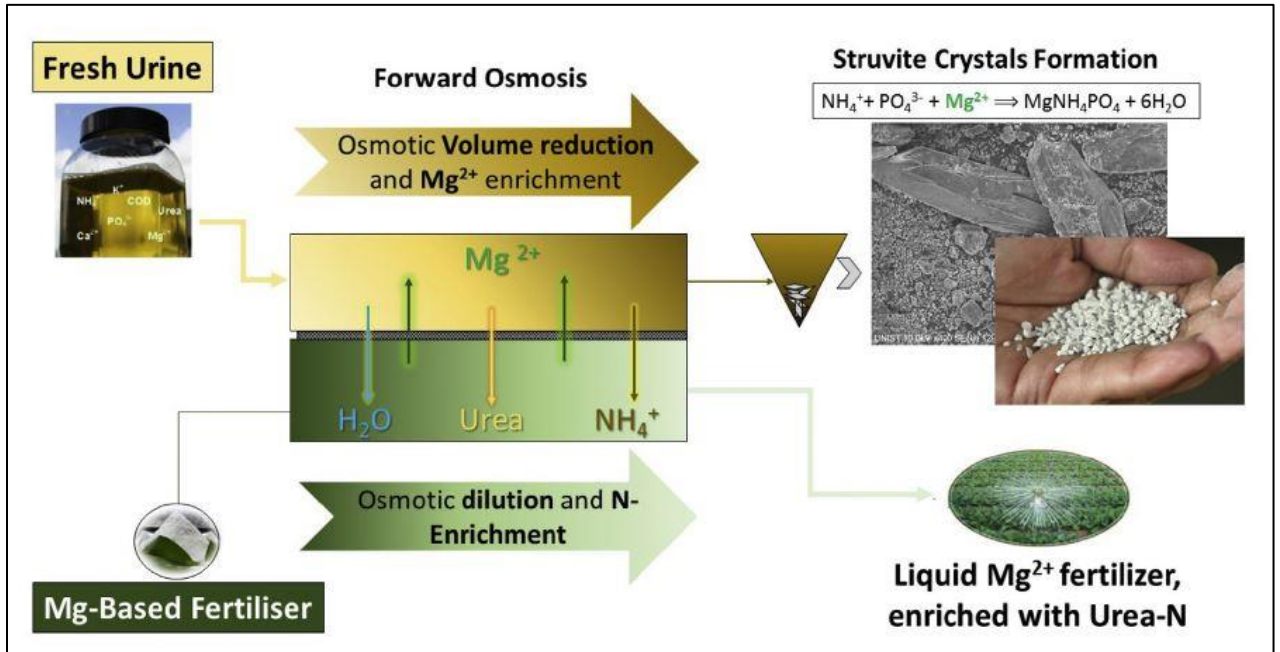
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1512 Figure.5

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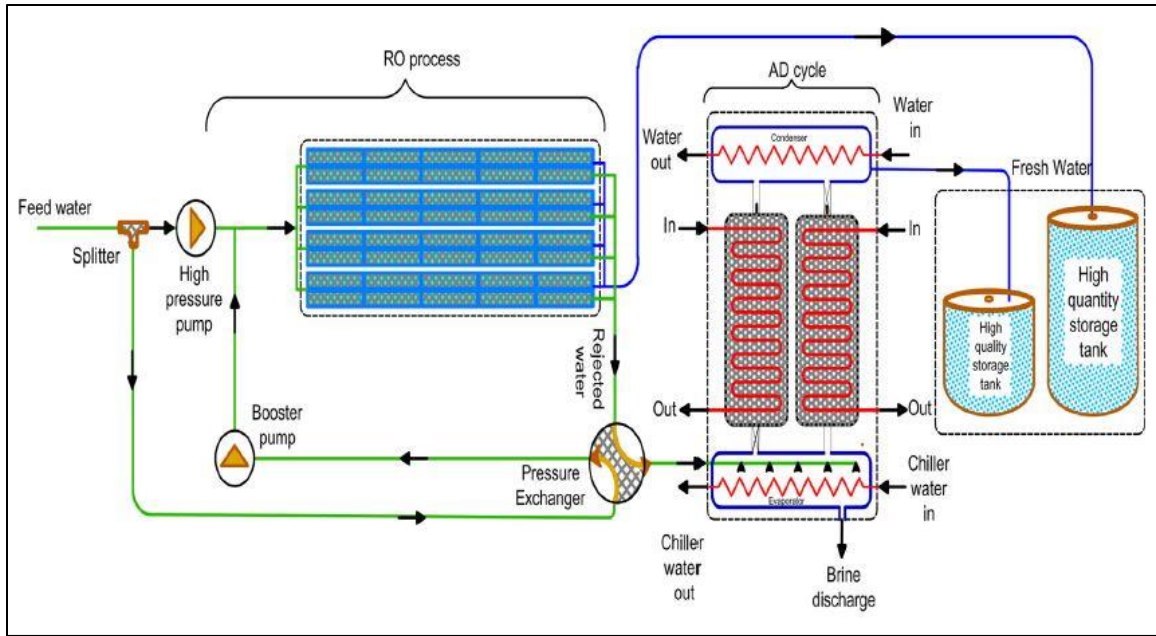
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1523 Figure.6

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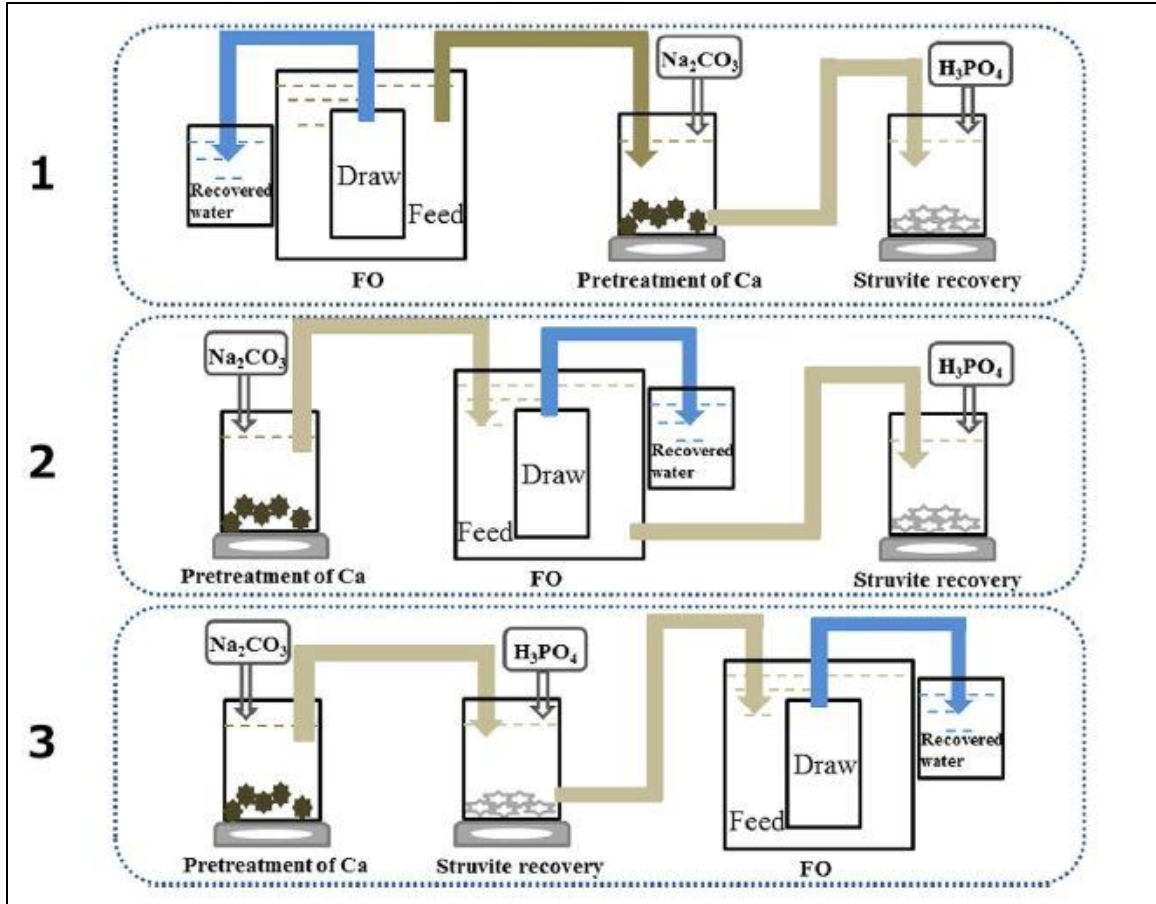
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1536 **Figure.7**

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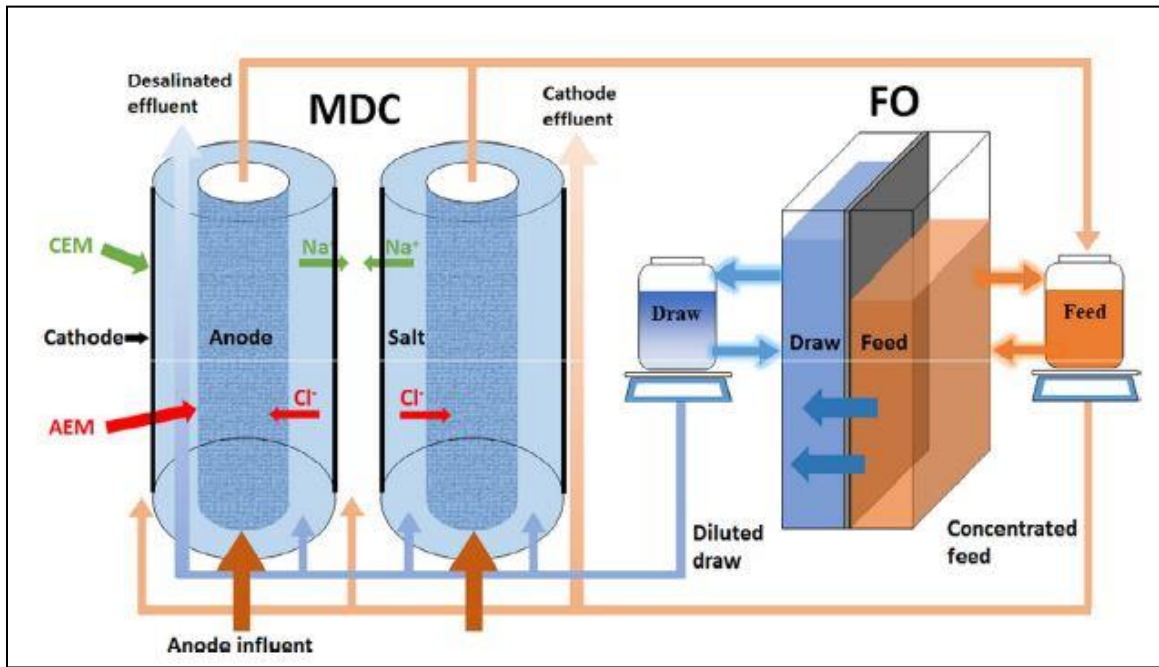
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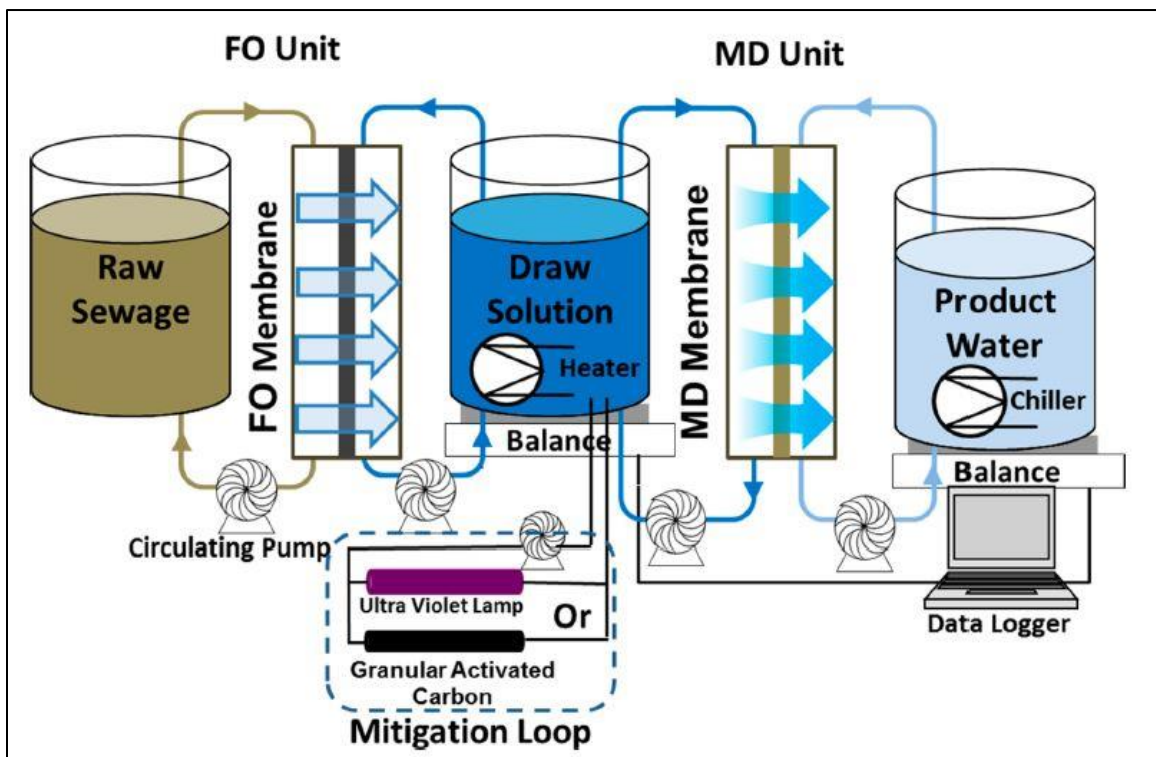
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1545 Figure.8



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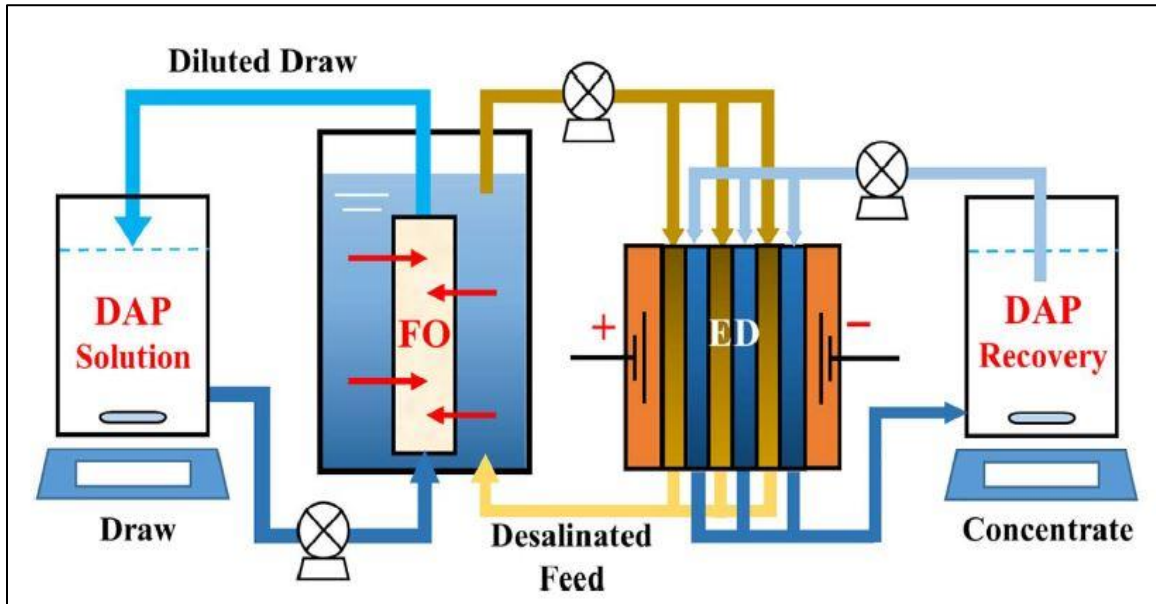
1547 Figure.9



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1550 **Figure.10**



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1555 **List of tables**

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1557 Table.1: The important properties of pressure driven membrane processes which is classified into
1558 reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF).

1559 Reproduced with permission from Pangarkar et al. [95].

1560

Membrane technology	Applied pressure (kPa)	Minimum particle size removed	Pollutant removal (type, average removal efficiency%)
Microfiltration	30–500	0.1–3 μm	Turbidity (>99%); bacteria (>99.99%)
Ultrafiltration	30–500	0.01–0.1 μm	Turbidity (>99%); bacteria (>99.99%); TOC (20%)
Nanofiltration	500–1000	200–400 daltons	Turbidity (>99%); color (.98%); TOC (>95%); hardness (>90%); sulfate (>97%); virus (>95%)
Reverse osmosis	1000–5000	50–200 daltons	Salinity (>99%); color and DOC (>97%); nitrate (85–95%); pesticide (0–100%); As, Cd, Cr, Pb, F removal (40–98%)

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