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Classical and recent developments of membrane processes for desalination and natural water treatment

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25 **Abstract:**

26

27 Water supply and water treatment are of major concern all around the world. In this respect,
28 membrane processes are increasingly used and reported for a large range of applications. Desalination
29 by membrane processes are well-established technologies with many desalination plants implemented
30 in coastal areas. Natural water treatment is also well implemented to provide purified water for
31 growing population. This review covers various aspects of desalination: membranes and modules,
32 plants, fouling (scaling, biofouling, algal blooms), cleaning, pre-treatment (conventional and
33 membrane treatments), energy and environmental issues, renewable energies, boron removal and
34 brine disposal. Treatment of natural water focuses on removal of natural organic matter, arsenic, iron,
35 nitrate, fluoride, pesticides and herbicides, pharmaceutical and personal care products. This review
36 underlines that desalination and natural water treatment require identical knowledge: membrane
37 fouling, construction of large plants, cleaning procedures, energy and environmental issues, and that
38 these two different fields can learn from each other.

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41 **Keywords:** water, membrane, membrane process, treatment, desalination, contaminants

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46 1. Introduction

47
48 Due to the increasing need of fresh water both for human consumption and plant irrigation,
49 desalination and treatment of natural water are increasingly developed. For seawater and brackish
50 water desalination, reverse osmosis (RO) has become a major process. Other membrane techniques
51 used for desalination include forward osmosis (FO), membrane distillation (MD) and electrodialysis
52 (ED). Treatment of natural waters (ground and surface waters) is also a major activity in several places
53 in the world. As natural water may contain several contaminants (natural organic matter (NOM), iron,
54 fluoride, etc), their removal is highly needed.

55 This review covers various aspects of desalination, including membranes and modules, typical plants,
56 fouling (scaling, biofouling, algal blooms), cleaning, pre-treatment before RO (conventional and
57 membrane treatments), energy and environmental issues, renewable energies for desalination, boron
58 removal and brine disposal. Treatment of natural water is presented including removal of NOM,
59 arsenic, iron, nitrate, fluoride, pesticides and herbicides, pharmaceutical and personal care products.

60 2. Previous reviews

61
62
63 Due to the huge development of desalination over the past 40 years, several reviews have been
64 proposed. Some of these reviews concern the main aspects of desalination. For example, [Fritzmann et al. \(2007\)](#)
65 [provided a very complete review, including implementation \(membranes, modules, membrane cleaning, energy recovery systems\), raw water characterization \(chemical foulants, particulate fouling, biofouling, organic foulants\), pre-treatment \(chemical, conventional, membrane\), post-treatment \(recarbonation and remineralisation, disinfection, boron removal\), waste management and environmental impact, energy requirement and cost.](#) [Greenlee et al. \(2009\)](#) summarized the history of desalination, composition of feed waters (sea water and brackish water), membrane fouling, membrane cleaning, RO system design, pre-treatment and post-treatment, RO concentrate disposal, alternative energy sources, and costs.

73
74 RO membrane materials for desalination have been the subject of specific review papers ([Lee et al. 2011](#), [Patel et al. 2020](#)). [Lee et al. \(2011\)](#) focused on RO membrane materials for desalination, their development and future potential. Conventional desalination RO membranes include thin film composite membrane, membrane post-synthesis modifications and control of interfacial polycondensation reactions. Among novel desalination RO membranes are polymeric membrane by rigid star amphiphiles, ceramic/inorganic membranes and mixed matrix membranes (nanoparticle/polymeric membranes, carbon nano-tube/polymeric membranes). [Shenvi et al. \(2015\)](#) focused their review on RO membrane materials and modules, and problems associated to RO modules such as scaling, boron removal and brine disposal. [Qasim et al. \(2019\)](#) discussed theories and models related to concentration polarization and membrane transport, membrane modules, membrane cleaning and different pre-treatment technologies, membrane fouling, process design, economic and energy considerations as well as current challenges faced by RO desalination processes.

86
87 Some reviews are devoted to specific aspects of seawater RO desalination. For example, [Miller et al. \(2015\)](#) focuses on environmental issues associated to desalination and solutions proposed and [Ogunbiyi et al. \(2021\)](#) reviewed brine management for water, energy and mineral recovery. Energy required for desalination is one of the most important environmental problem. [Elimelech and Phillip \(2011\)](#), [Kim et al. \(2019\)](#), [Park et al. \(2020\)](#), [Nassrullaha et al. 2022](#) reviewed the possible reductions in energy demand, focusing on advances in materials, and innovative technologies in improving RO performance. [Matin et al. \(2011\)](#) and [\(2019\)](#) focused on biofouling and scaling in RO membranes during seawater desalination. [Villacorte et al. \(2015\)](#) on seawater desalination and harmful algal blooms. [Ghaffour et al. \(2015\)](#), [Kalogirou et al. \(2005\)](#), [Charcosset \(2009\)](#), [Bundschuh et al. \(2021\)](#) reviewed renewable energies for desalination. Other reviews focus on alternative techniques to RO,

97 like FO, MD and ED (Wu et al. 2020, Lee et al. 2020, Awad et al. 2019 Skuse et al. 2021, Ahmed et al.
98 2021).
99

100 Several reviews are also available on the treatment of natural waters, for the removal of specific
101 pollutants, including boron (Hilal et al. 2011), iron (Chaturvedi and Dave 2012), nitrate (Shrimali and
102 Singh 2001), fluoride (Mohapatra et al. 2009, Damtie et al. 2019), pesticides (Plakas and Karabelas
103 2012), and pharmaceutical and personal care products (Yang et al. 2017, Khanzada et al. 2020).

104 The aim of the present article is the provide a state-of-the-art of water treatment by membrane
105 processes by focusing both on seawater (desalination) and natural waters treatment. Both seawater
106 and natural waters contain low amounts of toxic compounds (much less that wastewaters). They are
107 treated by similar processes (RO, NF, UF, MF, etc), raise similar questions (productivity and cost,
108 environmental issues, membrane fouling) and need both the development of similar techniques and
109 new understanding of related phenomena. The review has two main sections. Section 2 is related to
110 desalination and presents membranes and modules used in RO, operation of typical RO desalination
111 plants, pre-treatment prior to RO, other membrane processes for desalination, topics related to energy,
112 environmental issues, boron removal and renewable energies for desalination. The treatment of
113 natural waters is presented in section 4, by focusing on the removal of natural organic matter, arsenic,
114 iron, nitrate, fluor, pesticides and herbicides and finally pharmaceuticals and personal care products.
115 The present review is based on previous reviews and new articles to give a general background in the
116 field of seawater and natural water treatments as well a description of some new findings in this area.
117
118
119

120 3.RO Desalination

121 122 3.1 Introduction

123 Nowadays, water scarcity is one of the most serious global challenges [Elimelech and Phillip 2011].
124 The need for fresh water is a critical problem, as climate change. According to the World Health
125 Organization (WHO), there are more than 2.5 billion people (about 40% of the world's population)
126 that do not have access to drinking water. As a consequence of the growing scarcity of fresh water, the
127 implementation of large desalination plants has been increasing these last years. Generally,
128 desalination processes are categorized into two major types: (1) phase-change/ thermal and (2)
129 membrane processes. Some of the phase-change processes include compression, freezing,
130 humidification/dehumidification and solar stills. Membrane based processes include RO, MD and ED.
131 RO technology has improved considerably in the past two decades, and current desalination plants
132 can desalinate seawater with much less energy than thermal desalination. Currently the largest
133 seawater RO plant in the world is in Ashkelon (Israel), with a production rate of about 110 million m³ /
134 year [Elimelech and Phillip 2011]. RO is driven by the transmembrane pressure like ultrafiltration (UF)
135 and microfiltration (MF), however, in RO the water flux through the membrane is proportional to the
136 applied pressure minus the osmotic pressure of the solution on the membrane side opposite to the
137 feed solution. Desalination is a major application of RO.
138

139 3.2. Membranes and modules [Lee et al. 2011, Fritzmann et al. 2007, Qasim et al. 2019]

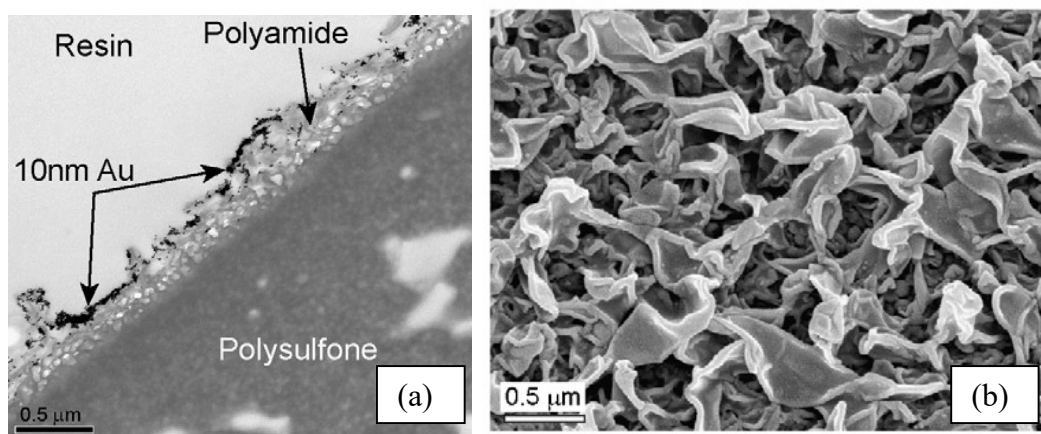
140 RO membranes are usually asymmetric. The support layer protects the membrane from breaking,
141 while the active layer gives the selectivity of the membrane. In the early 1960s, the first asymmetric
142 RO membranes were prepared by Loeb and Sourirajan [1964]. Later, in the early 1970s, the first
143 commercially available RO membranes made of cellulose acetate were introduced into the market.
144 One of the major drawbacks of cellulose acetate membranes is the possibility of membrane
145 deterioration by hydrolysis. In addition, cellulose acetate membranes tend to strongly compact under
146 high pressure and flux as well as overall performance decreases. Although cellulose acetate
147 membranes are still commercially available, thin-film composite membranes are mostly used.

148 In a thin-film composite membrane, the supporting layer is usually an UF or MF membrane made of
149 polysulphone and the active layer from polyamide (Figure 1). These membranes have several
150 advantages like chemical and mechanical stability, resistance to bacteria degradation, and are less
151 influenced by membrane compaction. However, composite membranes are less hydrophilic and
152 therefore have a stronger tendency for fouling than cellulose acetate membranes. During these last 20
153 years, membrane performance has significantly increased with respect to both permeability and salt
154 rejection. The rejection of typical seawater membranes is 99.8%, while flux is around 69 L/(m² day bar).
155 RO polyamide membranes can be produced using monomeric aromatic amines and aromatic acyl
156 halides containing at least three carbonyl halide groups, such as trimesoyl chloride. The four major
157 membrane module suppliers (DOW, Toray, Hydranautics and Toyobo) provide such RO membranes
158 for large scale desalination plants. The FT-30 membrane (DOW FILMTEC™) is produced by reaction
159 of 1,3-benzenediamine and trimesoyl chloride. Its morphology is unique as its pores have the shape of
160 “ridge and valley”. A number of similar membranes are available, e.g. the CPA2 membrane produced
161 by Hydranautics and the UTC-70 by Toray Industries.

162
163 Despite the great improvements in thin-film composite membranes, they still suffer from several
164 limitations [Elimelech and Philip 2011]. Hollow fiber configurations that offer higher packing densities
165 have not been successfully produced. In addition, the surface properties of thin-film composite
166 membranes make them sensible to fouling, which diminishes process performance.

167
168 The spiral wound membrane devices are the most used for RO desalination. They have the following
169 advantages: a high specific membrane surface area, easy scaling up, rather easy changeability, and
170 low replacement costs. In addition, the spiral wound module is the least expensive to produce from
171 flat sheet composite membrane. The current industrial standard element measures 8-in. in diameter.
172 Inside one pressure vessel, 4 to 8 elements are placed in series with a connected permeate collector
173 tube, to minimise piping and reduce the number of pipe connections. Larger modular elements are
174 available for increased desalination capacity. Koch Membrane Systems introduced the large diameter
175 (MegaMagnum™) element with a nominal diameter of 18-in. and 16-in. modules are commercialized
176 by Hydranautics and DOW (FILMTEC™).

177
178



179
180 Figure 1: TEM cross-section of a typical RO membrane (ESPA3, Hydranautics) previously used in a
181 filtration experiment with 10nm gold nanoparticles [Pacheco et al. 2010]. (a) TEM of the membrane
182 cross-section. Gold nanoparticles are used to obtain sufficient contrast for imaging. (b) SEM of the
183 polyamide top surface showing the typical rough ridge and valley structure. (from Pacheco et al. 2010)

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New membranes for RO can be obtained by modifying the membrane surface properties. For many years, various chemical and physical techniques have been developed such as coating the membrane

188 surface with more hydrophilic compounds and chemical treatment. Other surface modification
189 techniques include the use of free radical-, photochemical-, radiation-, redox- and plasma-induced
190 reaction. A key point on membrane science for desalination is to develop antifouling RO membranes.
191 [Zhao et al. \(2020\)](#) summarized the three main strategies to obtain fouling resistant thin-film composite
192 RO membranes: substrate modification before interfacial polymerization, incorporating
193 (hydrophilic/biocidal/antifouling) molecules into the thin layer during interfacial polymerization, and
194 lastly post (surface) modification after interfacial polymerization. Many researches in this field are still
195 going on with promising results in terms of membranes with anti-scaling and anti-fouling properties,
196 although availability, large scale use and long term stability in RO plants need to be confirmed [[Hao et al. 2021](#), [Tian et al. 2021](#)]. Another direction in membrane development for RO is the development of
197 chlorine resistant RO membranes, to eliminate the need of neutralization and improve the resistance
198 to biofouling [[Yao and Zhang 2021](#)].
199

200
201 New materials for RO have also emerged as the consequence of nano-technology science
202 development. These novel membranes include zeolite membranes, thin film nano-composite
203 membranes, carbon nano-tube membranes, and aquaporin-based membranes. These supports present
204 advantages compared to traditional RO composite membranes such as better selectivity, but their
205 availability and application at large scale remain challenging ([Lee et al. 2011](#), [Elimelech and Philip 2011](#), [Al-Najar et al. 2020](#)). In addition, these materials have relatively low impact on increasing energy
206 efficiency ([Patel et al. 2020](#)). Research efforts are still needed to optimize water-salt selectivity rather
207 than membrane permeability to enhance desalination process efficiency.
208
209

210 3.3. Operation

211 A typical RO desalination plant includes RO modules with energy recovery system and open seawater
212 intake. The process includes the following stages (Figure 2):

213 - The abstraction of feed water can be realised either through coast and beach wells or through open
214 seawater intake systems [[Fritzmann et al. 2007](#)]. Abstraction through wells have several advantages:
215 the water quality is better, with less turbidity, and less algae and total dissolved solids. However,
216 wells require more space. In brackish water desalination, the abstraction of feed water is realized
217 through wells.

218 - In the pre-treatment stage, colloids are removed from the feed water and chemicals are added to
219 prevent scaling and fouling. The composition and pH of the intake water are adjusted. Pre-treatment
220 has a major influence on the RO performance by lowering the fouling propensity of the RO
221 membranes. A specific section will be dedicated to pre-treatment.

222 - The pump is used to create the required transmembrane pressure and also to overcome the height
223 differences within pipes in the RO plant. High transmembrane pressures have to be used (up to 7000
224 kPa) due to the high salt concentrations of seawaters. The power required to pump the feed water is
225 directly related to the feed pressure and flow rate [[Greenlee et al. 2009](#)].

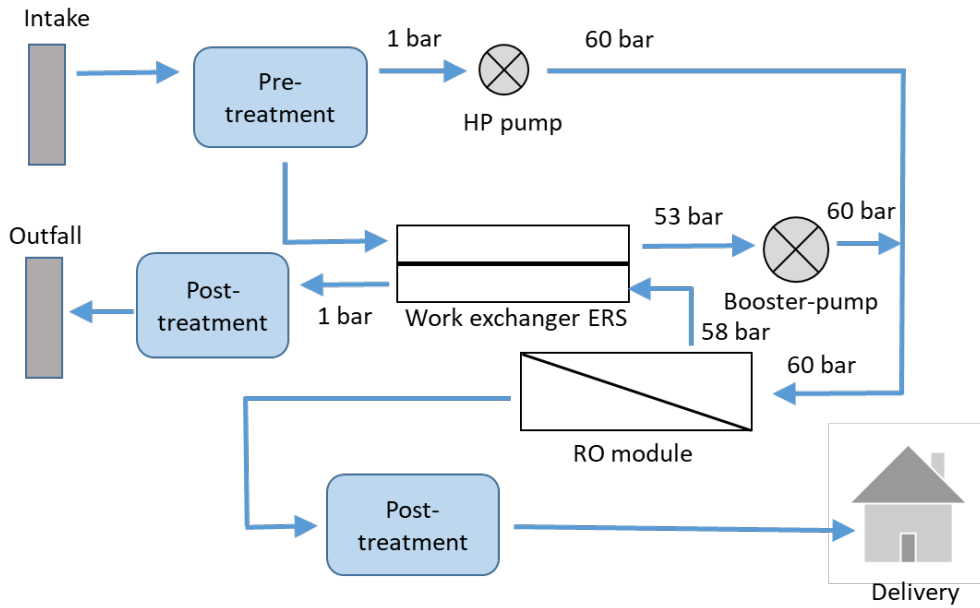
226 - The RO membranes separate salt from water with a rejection of 98–99.5%, depending on the
227 membranes used. Several RO plants operate with either one or two, or four RO passes [[Greenlee et al. 2009](#)]. The choice between one or more RO passes depends on several factors including energy cost,
228 feed water, desired recovery, and product water standards.
229

230 - The energy recovery system is aimed at transferring the potential energy from the concentrate to the
231 feed. Current energy recovery systems operate with efficiencies greater than 95%. Several energy
232 recovery devices are available. The most common use hydraulic power to cause a positive
233 displacement within the recovery device [[Greenlee et al. 2009](#)]. Several RO plants use these devices,
234 like the DWEER (DWEER Technology, Ltd.), PX Exchanger (ERI), or PES (Siemag's Pressure
235 Exchanger System) [[Greenlee et al. 2009](#)].

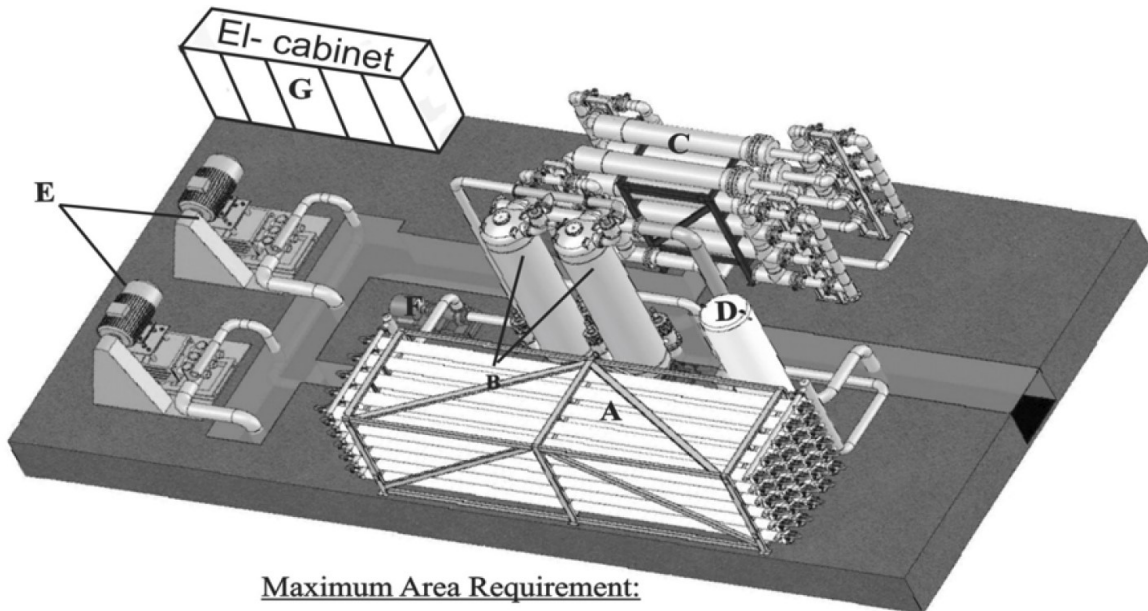
236 In the post-treatment step, permeate is re-mineralised, re-hardened, disinfected by chlorination and
237 adjusted to drinking water standards [[Fritzmann et al. 2007](#)]. Alkalinity is added to water to make it
238 non-aggressive and noncorrosive; it is realized by the dissolution of lime or limestone by carbon

239 dioxide or the addition of a calcium chloride or bicarbonate solution. Disinfection of produced RO
 240 waters is realized by adding chlorine, hypochlorite or sodium hypochlorite. In addition, post-
 241 treatment methods have to be applied for boron removal, to avoid toxic effects of boron on humans
 242 and agriculture. Under standard test conditions, seawater RO high rejection membranes display a
 243 boron rejection between 88 and 91%, BWRO membranes reject between 30% and 80% of the
 244 uncharged boron compound. In general, ion exchange resins are used to remove boron from produced
 245 RO waters. Typically, boron removal using ion exchange resins is performed in one step, with
 246 removal higher than 99 - 99.99 %.

247 In addition, a control system is necessary to maintain a continuous and reliable production.
 248 A typical RO stage installation is shown in Figure 3.



249
 250 Figure 2: Simplified reverse osmosis scheme with energy recovery system. (adapted from Fritzmann et
 251 al. 2007).



Maximum Area Requirement:

Area: 128 m²

Height: 6 m

252

253 Figure 3: Typical RO stage installation. A, pressure vessel, membranes and manifolds; B, pressure
254 recuperator towers; C, bag filters; D, seawater feeding tank; E, high pressure pumps; F, booster pump;
255 G, electro-cabinet. (from Fritzmann et al. 2007.)
256

257

258 3.4 Boron removal

259 Boron is known to be toxic for both humans and plants, even at low concentrations. Although the
260 WHO has increased the recommended maximum concentration (from 0.3, to 0.5 and 2.4 mg/L in 2011),
261 boron removal by RO remains a difficult task as boron is present in seawater in its uncharged boric
262 acid form which can pass through the RO membrane. The increase in pH above the boric acid pKa (9.2
263 at 25 °C) converts boric acid into negatively charged borate anions, enhancing boron rejection by RO
264 membranes [Farhat et al. 2013]. Therefore, RO desalination plants can be implemented in a double-
265 pass configuration, where the pH of the RO permeate obtained from the first pass is chemically
266 increased above the pKa of $B(OH)_3$, and is treated again using RO as a second pass. High boron
267 removal efficiency is then obtained, however, the technique implies higher operating and capital costs
268 [Jung et al. 2020].

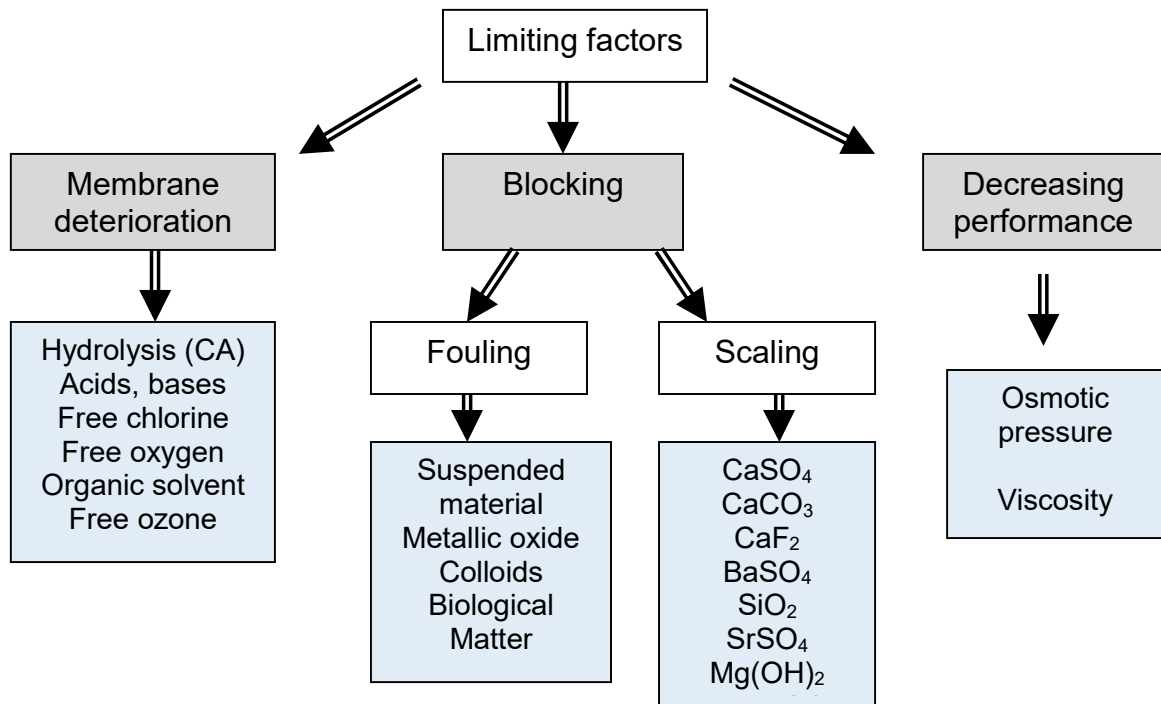
269 Several other techniques are available for boron removal such as ion exchange, chemical precipitation,
270 adsorption, and electrocoagulation [Hilal and Kim 2011]. In RO desalination plants, the most popular
271 technique uses ion exchange resins specifically designed for boron removal. These commercial resins
272 (e.g. Amberlite IRA743, Purolite S108, Diaion CR05) have a macroporous polystyrene matrix on which
273 N-methyl-D-glucamine functional groups are attached. The ion exchange technique is highly efficient
274 for boron removal, but its disadvantages include the use of costly chemicals for regeneration and their
275 disposal [Shenvi et al. 2015].

276 Ion exchange resins can also be used in a hybrid process in which a reactor is associated to a UF or MF
277 membrane (submerged or not) [Kabay et al. 2013]. In most configurations, boron solution and fresh
278 resin are continuously added to the reactor, while saturated resins are removed at the same flowrate
279 by MF [Kabay et al. 2013]. The technique can also be performed without continuous addition of resin
280 [Alharati et al. 2017]. Ion exchange resin with small size are used to increase the kinetics of sorption,
281 consequently boron is retained before passing in the permeate. The major advantages of the technique
282 are that the kinetics and process efficiency are increased.
283

284

285 3.5 Fouling

286 In RO membranes, fouling types are classified as: inorganic salt precipitation (scaling), organic,
287 colloidal, and microbiological (usually bacterial biofilm formation) [Herzberg and Elimelech, 2007]
288 (Figure 4). Fouling is a major phenomenon in RO desalination that results in a significant increase in
289 both operation and maintenance. Fouling include scaling by salts, biofouling by microorganisms and
290 nutrients, and algal blooms.



291
292 Figure 4: Limiting factors to membrane desalination by reverse osmosis. (adapted from Fritzmann et
293 al. 2007)

294
295 *Scaling*

296 During RO, the concentration of different soluble salts increases in the RO feed channel. When the
297 solubility limit of these salts reaches supersaturation, they precipitate and build a thin layer (scale) on
298 the membrane surface which affects the performance of the RO process, decreasing permeate flux and
299 membrane longevity, leading to higher operating costs [Shenvi et al. 2015]. These salts include silica,
300 iron, barium sulfate, calcium carbonate, gypsum. They are present at different concentrations
301 depending on the source of the feed water. For some compounds, scaling can be removed by flushing
302 the membrane with acid, however, it is often not possible to transport the crystalline mud out of the
303 modules, especially in spiral wound modules.

304 Therefore, several pre-treatments have been proposed to prevent scaling. Anti-scaling agents are
305 widely used as they increase the threshold for the onset of scale formation on the membrane surface.
306 They affect the kinetics of mechanisms involve in crystallization : nucleation and growth. Commonly
307 used anti-scalants are organic polymers, surface active reagents, organic phosphonates and
308 phosphates. Commercial anti-scalants are for example Permatreat 510 (blend of polymers and
309 phosphonates), Hypersperse SI 300 UL (multi-polymer), Acumer 5000 (multi-polymer) and Aquafeed
310 EX-105 (an anionic polyelectrolyte) [Semiat et al. 2003]. The inhibition limits are at SiO₂ concentrations
311 in the range of 240 to 300 mg/L. Dosages recommended by the commercial literature range from 3 to
312 15 ppm.

313 Silica scaling is difficult and costly to remove, in particular removal of silica by use of anti-scalants is
314 difficult due to the varying parameters influencing silica precipitation [Shenvi et al. 2015, Thompson
315 et al. 2017]. Carbonate scaling can be avoided as the pH of the feed water is set between 4 and 6.
316 Gypsum scaling can be reduced in inland brackish water feed by increasing levels of bicarbonate.
317 Gypsum scaling can be reduced by adding bicarbonate. Also, mineral scaling can be limited by pre-
318 treatment of the feed by pH adjustment, ion exchange, or nanofiltration (NF)/UF or by a flow reversal
319 mechanism [Pomerantz et al. 2006]. In order to limit mineral scaling in RO, it has to be detected as
320 early as possible. Several methods were developed to monitor flux decline (at constant
321 transmembrane pressure) or transmembrane pressure (at constant water flux) in order to determine

322 the early start of mineral scaling [Thompson et al. 2017]. Such approaches include ultrasonic time-
323 domain reflectometry and electrical impedance spectroscopy. Moreover, direct visual membrane
324 surface monitoring and real-time image analysis can provide detection of onset of mineral scaling, as
325 well as scaling kinetics and scale morphology.

326

327 *Biofouling*

328 Biofilm growth on the RO membrane surface is due the presence of microorganisms and nutrients in
329 water, and the convective permeate flow through the membrane [Herzberg and Elimelech, 2007, Goh
330 et al. 2019]. Biofilm development is a complex event which is influenced by a number of factors
331 including bacteria and membrane properties and operational parameters. The first step in biofilm
332 formation is the transport and attachment of suspended bacterial cells to the solid-liquid interface.
333 Several factors govern the interactions between bacteria and surfaces. Some are linked to the bacteria
334 characteristics such as their hydrophobicity, their fimbriae appendages, their flagellar motility, and
335 lipopolysaccharides and extracellular polymeric materials present at their surface. Other factors
336 concern the surface properties (hydrophobicity, rugosity, etc), the hydrodynamics at the membrane
337 surface and the RO device, and the water properties (pH, presence of multivalent cations and
338 nutrients, and ionic strength).

339

340 Biofouling of RO membranes is always followed by a decrease in permeate water flux, and a decrease
341 in salt rejection may also be observed. Many seawater desalination facilities have been affected by
342 membrane biofouling, such as large desalination plants in Bahrain and US Virgin Islands [Matin et al.
343 2011]. Different strategies may be employed to minimize the effect of biofouling such as feed pre-
344 treatment, membrane treatment and membrane modification. Feed pre-treatment, like UF or MF, and
345 biocide application are aimed at eliminating or minimizing the microbial concentration in the feed
346 stream. Membrane surface modification is aimed at preventing the adhesion of bacteria or/and
347 inactivates them if adsorbed. For example, silver and titania nanoparticles can be added to the
348 membranes to limit biofouling as they have an antibacterial activity.

349

350 *Algal blooms [Villacorte et al. 2015]*

351 Algal blooms are defined by a rapid increase in the population of algae in water. They are frequently
352 referred to as “red tides” due to their vibrant color. Algal blooms are mainly due to natural
353 phenomena, but also to human activities which may increase their frequency and importance. Every
354 coastal countries can be affected. Several algal species may be involved, with different cell size, cell
355 density and effects. Some algal blooms may be harmful as they may produce neurotoxins that are
356 toxic substances for human and animals. They can lead to fish die-offs, cities cutting off water to
357 residents, or states having to close fisheries. Moreover, they can proliferate in very dense
358 concentrations. Algal blooms produce algal organic matter of different types and concentrations
359 which may be exuded by living algal cells and/or released through lyses of dead cells. Transparent
360 exopolymeric particle is a major component of algal organic matter which is highly sticky and a major
361 initiator and/or promoter of biofilm in marine aquatic environments.

362 The adverse effects in seawater RO plants due to algal blooms are particles / organic fouling of pre-
363 treatment systems and biological fouling of RO membranes, mainly due to accumulation of algal
364 organic matter. Toxins which may be produced by algal cells is also a potential issue but only at very
365 low concentrations. The main issues of algal blooms on seawater RO was highlighted in 2008–2009 in
366 the Arabian Gulf region during a catastrophic algal blooms [Richlen et al. 2010]. Several seawater RO
367 plants had to reduce or stop due to fouling of pre-treatment systems and/or due to unacceptable feed
368 water quality.

369 Several pre-treatments are possible but the best solution is to early detect the algal bloom. Thus, the
370 systematic measurement of indicators (e.g. algae and transparent exopolymeric particles) is highly
371 recommended. When possible, subsurface intake is a robust pre-treatment to protect seawater RO
372 plants from the impact of algal blooms. They include wells (vertical, angle, and radial type) and

373 galleries. Subsurface intakes provide pretreatment (filtration on granular media) of the inlet seawater.
374 UF membrane with in-line coagulation is also a very efficient treatment capable of maintaining stable
375 operation and feed water quality even during severe algal blooms.

376
377 Fouling of RO membranes during desalination has been intensively investigated. Future directions
378 include the need for fouling measurement under realistic conditions, studying the interactions
379 between membrane, spacer surface and foulants, and the development of environmentally benign
380 antiscalants [Matin et al. 2019].

381 382 *Cleaning*

383 In RO desalination, membrane fouling occurs due to mineral scaling, colloidal particles or biofoulants
384 [Fritzmann et al. 2007]. Fouling is associated to increased feed channel pressure drop, decreased
385 permeate flux and reduced salt rejection. To restore membrane performance and to avoid membrane
386 damage, membrane cleaning is necessary. In RO desalination, the main cleaning methods are basically
387 the same as in other membrane processes. They include physical and chemical methods [Jiang et al.
388 2017]. The cleaning efficiency can be evaluated by flux recovery resistance and salt removal.

389 For chemical cleaning, a variety of chemical agents are commonly used to clean RO membranes. The
390 selection of the cleaning chemical agents depends on the foulants components, their chemical
391 properties and economic factors. Chemical agents can react with the foulants to reduce the cohesion
392 forces between foulants and adhesion of foulants to membrane surface, making them easy to be
393 removed. The chemical agents commonly used include acids, bases, surfactants and chelating agents.
394 Acids, such as hydrochloric acid, nitric acid and sulfuric acid can remove membrane scaling. Basic
395 solutions can remove an organic fouling layer by hydrolysis and solubilization [Herzberg and
396 Elimelech 2007]. Sequential cleaning protocols with different chemicals can be used to recover
397 membrane performance [Lee et al. 2021].

398 Ethylene diamine tetra acetic acid (EDTA) is a commonly used chelating agent, which is very sensitive
399 to solution pH. Surfactants solubilize macromolecules by forming micelles around them, to facilitate
400 the removal of the foulants from the membrane surface. Sodium dodecyl sulfate (SDS) is a common
401 surfactant used in membrane cleaning. SDS can adhere to organic matter thanks to its hydrophobic
402 part while the hydrophilic head tends to move towards water. SDS can also remove colloidal fouling
403 under proper cleaning conditions. Cleaning efficiency also depends on operational conditions such as
404 cleaning time, crossflow velocity, cleaning solution temperature, and permeation rate.

405 Physical cleaning is mainly performed by rinsing the RO device with water at high shear. Chemical
406 and physical cleaning can be performed at the same time; chemical cleaning solubilizes the foulant
407 layer while physical cleaning flows the foulants away from the membrane surface. Other physical
408 cleanings have been proposed without stopping the RO plant like a backwash cleaning technique,
409 which consist of the intermittent injection of a high salinity solution through the membrane [Qin et al.
410 2010].

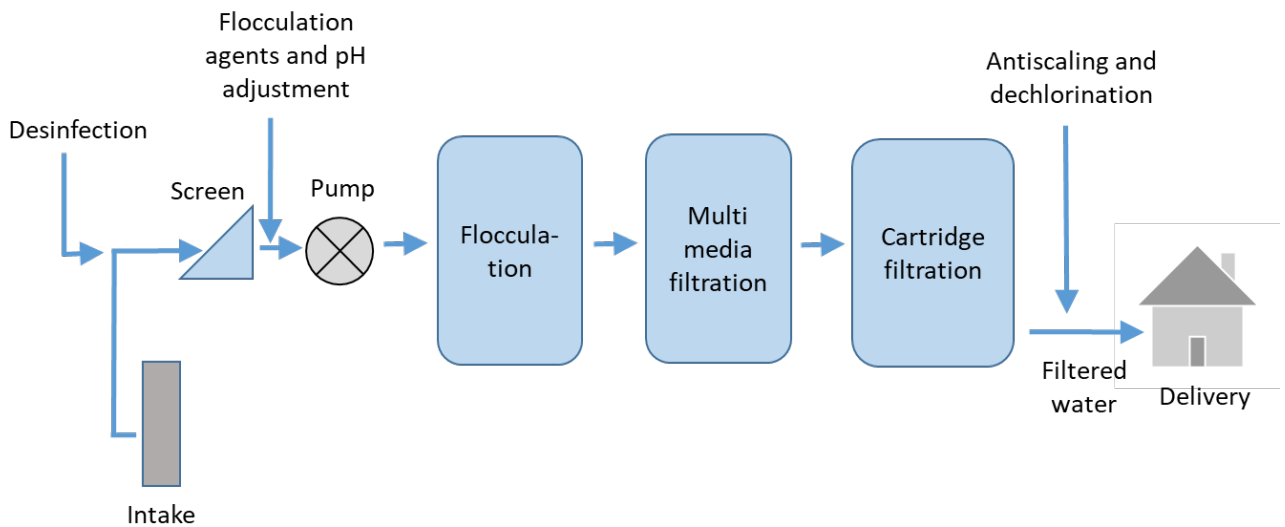
411 412 413 *3.6 Pre-treatment prior to RO*

414 *Conventional treatments*

415 Pre-treatment of the feed water is aimed at reducing fouling potential, increasing RO membrane life,
416 maintaining performance level and minimizing scaling on the membrane surface [Fritzmann et al.
417 2007]. To characterize the fouling potential of the RO feed water, the Silt Density Index (SDI)
418 parameter is generally used. SDI₁₅ values are recommended to be below 3 to minimize fouling.

419 Conventional pre-treatments are chemical and physical techniques without the use of membrane
420 processes. A simplified pre-treatment process scheme is shown in Figure 5. The chemical pre-
421 treatment usually includes: coarse pre-filtration on screens, chlorination, acid addition, coagulation,
422 flocculants, sand filtration, addition of antiscalants and sodium bisulphite (to remove residual

423 chlorine) and cartridge filtration (5–10 μm). The physical pre-treatment usually consists of flocculation
 424 and multimedia filtration followed by cartridge filtration.
 425 Chlorination is aimed at disinfecting the water and preventing biological growth which causes
 426 biofouling of filters and RO membranes. For that purpose, chlorine (sodium hypochlorite or chlorine
 427 gas), is added to the seawater, where chlorine is hydrolysed to hypochlorous acid.
 428 Addition of acid, such as sulphuric acid, is aimed at achieving lower pH values where RO membranes
 429 show better performance. To limit CaCO₃ scaling, the pH is adjusted.
 430 In a conventional pre-treatment, coagulation and flocculation agents are often added to cause
 431 dissolved matter to adsorb on hydroxides. Sedimentation and sand filtration are then used to remove
 432 these agglomerates. To increase the agglomerate size, addition of chemicals is necessary. Coagulants
 433 used are ferric chloride FeCl₃, ferric salts Fe₂(SO₄)₃ or aluminum sulphate Al₂(SO₄)₃, sometimes in
 434 combination with polymers.
 435 Antiscalant agents reduce scaling, that is the precipitation of salts (sulphates, carbonates, calcium
 436 fluoride, etc) on the membrane surface. Depending upon the salt, different scale inhibitors are used.
 437 Sulphuric acid is added to avoid calcium carbonate scaling. Polymeric compounds are commonly
 438 used as antiscalants.
 439 Dechlorination of feed water is realized before RO operation because chlorine residual may damage
 440 the RO membrane by oxidation. Sodium metabisulphite is commonly used for dechlorination.
 441 Activated carbon is also very effective to reduce residual free chlorine.



442
 443 Figure 5: Simplified process scheme of a conventional pre-treatment of feed water process before RO
 444 desalination. (adapted from Fritzmann et al. 2007)
 445

446 *Membrane processes*

447 Pre-treatments of seawater by UF or MF have been proposed since almost 30 years as interesting
 448 alternatives to chemical pre-treatment [Fritzmann et al. 2007]. Suspended particles, colloidal materials,
 449 microalgae, bacteria, viruses and pathogens micro-organisms are removed from seawater, limiting RO
 450 membranes fouling. In addition, UF or MF pre-treatments requires less chemical addition and space in
 451 the RO plant than conventional pre-treatments. They are less sensitive to fluctuations of feed water
 452 quality and supply the RO stage with superior water quality for long-term operation. They are able to
 453 increase the life of RO membrane and can thus lead to overall cost reductions. The efficacy of MF pre-
 454 treatment was for example confirmed in a pilot study conducted at Jeddah Port on the Red Sea (Saudi
 455 Arabia). Pearce et al. [2004] operated UF pre-treatment to RO desalination during a 6-month period of
 456 algal bloom and storms. The water quality obtained was much better than the one observed with the
 457 conventional pre-treatment.

458 The use of NF as pre-treatment before RO can reduce water hardness [Al-Amoudi and Farooque,
 459 2005]. Indeed, NF membranes are negatively charged and rejects divalent ions which can induce

460 scaling [Song et al. 2013]. In addition, NF can also reduce total dissolved salts (TDS) and remove
461 microorganisms, turbidity and organic matter. The first industrial plant using NF as pre-treatment
462 before RO was constructed in Saudi Arabia at the beginning of the 2000's by the Saline Water
463 Conversion Corporation. ()
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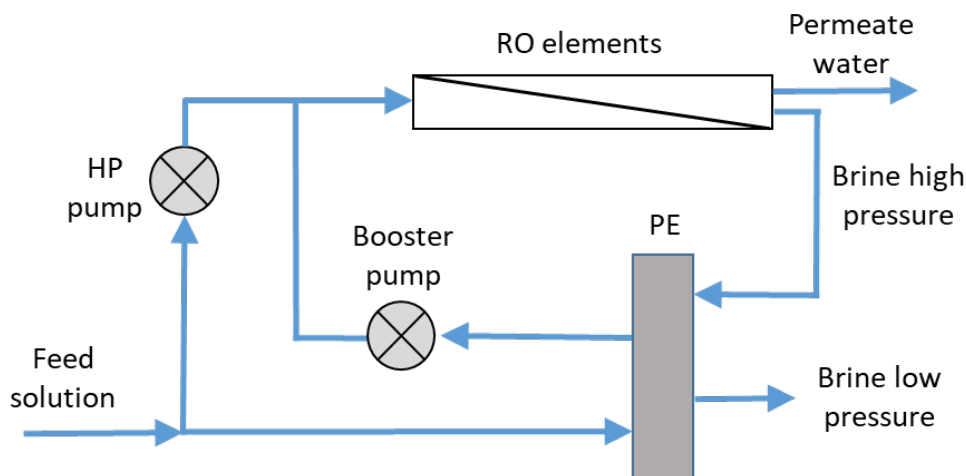
3.7. Energy

467 The energy consumption, in kWh/m³ of product water, is a major parameter characterizing the
468 performance of RO desalination plants [Karabelas et al. 2018, Kim et al. 2019, Park et al. 2020].
469 Depending on seawater salinity the energy consumption of a modern seawater RO system is 3.5-6
470 kWh/m³. The more water is recovered per unit of seawater the more energy is needed, but it can be
471 theoretically reduced below 0.7 kWh/m³. Energy consumption comes from the various parts of the RO
472 desalination plant: feed-water intake, pre-treatment, RO (high-pressure pumps and energy recovery
473 devices), post-treatment and brine treatment/disposal. The largest energy consumption (usually
474 between 60%-80%), depending on feed water, local conditions, technology employed, comes from the
475 main section where RO takes place. Indeed, seawater RO desalination energy consumption is very
476 high because of the low recovery ratio (25-40 %) and the high operating pressure (60-70 bars).
477 Therefore, maximum recovery of energy from the disposed brine is highly needed.

478 Different energy recovery systems are commercially available and have been implemented in several
479 RO plants. For example, Avlonitis et al. [2003] have tested four different energy recovery systems
480 (classical Pelton wheel, turbocharger, pressure exchanger and Pelton wheel commercialized by
481 Grundfos company). These energy recovery systems have been applied in small and medium size RO
482 plants. The most efficient recovery system was found to be the pressure exchanger, by considering the
483 recovery ratio and the specific energy divided by the recovery ratio (Figure 6). Numerous researches
484 are still going to develop new energy recovery systems. For example, Song et al. [2021] introduced a
485 new piston type integrated high pressure pump-energy recovery device, that synchronously
486 pressurizes the feed seawater and recovers the hydraulic energy from the concentrated brine. The
487 utilization of this new device instead of a single high pressure pump is shown to decrease both the
488 payback period and the desalinated water cost.
489

490

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492

493

Figure 6: Pressure exchanger energy recovery system. (adapted from Avlonitis et al. 2003).

494

495

496 The high energy required to run desalination plants remains a major drawback. Therefore, the idea of
497 using renewable energies such as solar, wind, wave, geothermal and hydrostatic pressure, is
498 fundamentally attractive [Kalogirou 2005, Charcosset 2009, Ghaffour et al. 2015, Li et al. 2019,

499 [Bundschuh et al. 2021](#)]. Their applicability strongly depends on the availability of renewable energy
500 resources.
501 Solar energy has been extensively investigated as a potential source of energy for water desalination
502 [[Delgado-Torres and García-Rodríguez 2007](#)]. Solar energy may be used directly in solar stills or may
503 be converted to electricity and then used in either thermal or membrane processes for desalination.
504 Photovoltaic (PV) powered RO systems have been implemented in several places around the world, in
505 countries like Egypt, Jordan, and Australia.
506 Wind is also an interesting source of energy as it is often available in coastal areas. Wind-powered RO
507 plants have been implemented in several countries like Croatia, Norway, and Australia. For example,
508 a wind powered desalination plant was installed on the island of Gran Canaria [[Carta et al. 2003](#)]. The
509 plant includes two wind turbines and a flywheel, which supply the energy to a complete desalination
510 plant (eight RO modules, pre-treatment and post-treatment facilities and control system). A similar
511 plant has been run for more than 15 years by Solaires Canarias S.L. [[Rosales-Asensio et al. 2019](#)]. The
512 cost of the plant was evaluated by assuming the combined use of RO and wind energy, a membrane
513 life time of 10 years, a total capital investment cost of 196 000 euros, and a profitability index of 1.3794.
514 The internal rate of return was found to be as high as 225 %, confirming the interest of such plants.
515 In addition, desalination plants can be supplemented by both wind and solar energies. These plants
516 can be found in several countries like the Sultanate of Oman, Israel, Mexico, and Germany. For
517 example, the DESIRES® (DESalting Island on Renewable multi-Energy Supply) project proposed a
518 floating island with a combination of several renewable energies like wind, solar, and wave
519 [[Stuyfzand and Kappelhof 2005](#)].
520 Wave energy is also a possible energy source, especially in coastal regions and island nations.
521 However, large investment costs render current wave-powered desalination technologies
522 economically unrealistic. Recent researches focus on developing feasible wave-powered RO
523 desalination techniques. For example, [Brodersen et al. \[2022\]](#) studied the feasibility of direct-drive
524 ocean wave-powered batch RO using a modelling approach. Seawater is used as the working fluid in
525 a hydro-mechanical coupling and replaces the RO high-pressure pump with a hydraulic converter for
526 direct-drive. System modelling shows that energy consumption and cost of water are competitive.
527 It is usually recognized that the optimization of energy requirement relies on conventional energy
528 reduction possibilities such as energy recovery systems but also on several aspects including the
529 development of ultra-high permeability membranes and fouling resistant membranes, hybrid systems
530 and renewable-energy driven desalination [[Nassrullah et al. 2020](#)]. Regulations to develop less
531 energy-intensive desalination technologies should also be much helpful to help the implementation of
532 these techniques [[Bundschuh et al. 2021](#)].

533

534

535 3.8. *Environmental issues*

536 The environmental impact of RO desalination is of major concern because of its extensive
537 development these recent years. Several environmental issues are reported mainly attributed to the
538 discharge of a brine of high salinity and high chemical concentration, but also to the influence of the
539 intake on the marine environment, and to emission of air pollutants and greenhouse gases [[Miller et
540 al. 2015](#)]. Several solutions are available to reduce environment issues. For example, the use of
541 subsurface intakes for seawater RO desalination plants limit the use of chemicals in the pre-treatment
542 step and thus environmental issues [[Missimer et al. 2013](#)]. Seawater is then filtered by natural
543 sediments and rocks. The intake may be realized through wells of different geometries like vertical,
544 angle, and radial type or galleries. These structures can be built on the beach or in the seabed.
545 The reject water from the RO desalination plant has a salinity much higher than the seawater, it is
546 called brine or brine-blowdown. The characteristics of the brine are related to the quality of the feed
547 water, the desalination technology, the percent recovery, and the chemical additives used [[Ahmed et
548 al. 2003](#)]. The brine may contain high levels of TDS, organic compounds and chemicals like anti-
549 scalants, antifoulants, acid, etc.

550 The brine is rejected directly into the sea, in evaporation ponds or injected into wells. Direct rejection
551 into the sea influences microalgal, plant and animal life, and may also results in the formation of
552 sludge. The degree of degradation depends on the total volume of the brine being released, its
553 characteristics, the dilution rate prior to discharge, and the characteristics of the receiving water
554 [Alameddine and El-Fadel 2007]. The effect of the brine on the environment also depends on the
555 geometric installation of the discharge outfall. In open and well-mixed water, adverse impacts are
556 noticed mostly within 300 m from the discharge point. The effect is more pronounced in waters that
557 are located in shallow and/or semi-closed bays. Rejection in evaporation ponds is generally realized in
558 inland RO desalination plants (in arid and semi-arid areas) where direct rejection into the sea is not
559 possible and solar energy is abundant. Their drawbacks are the space and surface needed which affect
560 the availability of soils. Dilution of the brine with seawater or water used can reduce the
561 environmental impact.

562 Another option to reduce the environmental impacts associated to the brine, is the extraction of
563 valuable compounds. Recovery of minerals from brines can be realized by precipitation,
564 crystallization, adsorption, membrane distillation, or evaporation [Ogunbiyi et al. 2021]. Hybrid
565 techniques can also be implemented. For example, Ahmed et al. [2003] described the extraction of
566 dissolved minerals from brine by multiple evaporation and cooling. The compounds recovered
567 include gypsum, sodium chloride, calcium carbonate, magnesium hydroxide, calcium chloride, and
568 sodium sulphate which can be used by various industries. Nevertheless, these processes are limited by
569 several disadvantages like high energy consumption, requirement of large amounts of chemicals, and
570 have limited applications at industrial scale level [Ogunbiyi et al. 2021]. Improvements are needed to
571 improve the separation of single elements from the others and to lower the overall cost of the
572 processes to become more attractive.

573
574

575 *3.9 Other membrane processes for desalination*

576 Forward osmosis (FO) and MD are the more advanced alternatives membrane techniques to RO for
577 desalination [Skuse et al. 2021, Ahmed et al. 2021]. They offer several advantages over RO, such as
578 high salt rejection (MD), higher recovery of water (MD), and fewer pre-treatment stages (MD, FO).
579 They are intensively investigated to help their implementation at large scale and improve their
580 feasibility in terms of productivity, cost, lower energy consumption to become competitive with RO.

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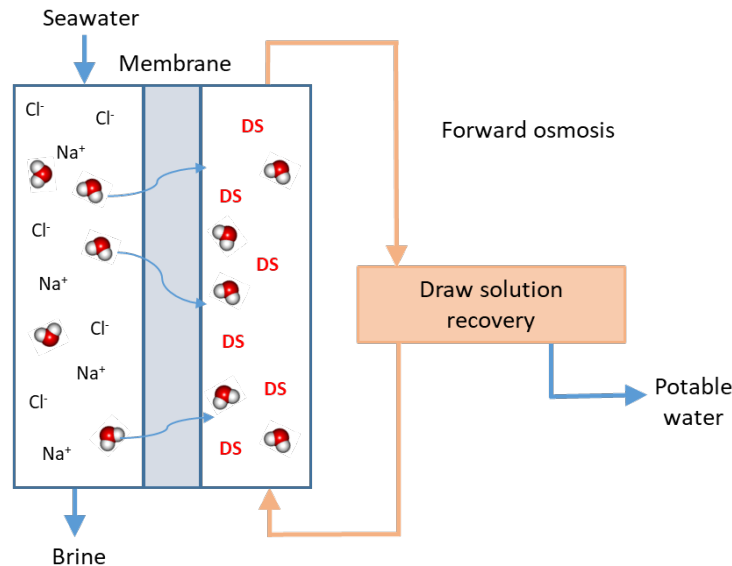
582 *Forward osmosis*

583 FO uses the osmotic pressure difference between seawater and a highly concentrated draw solution
584 (DS) [Awad et al. 2019, Skuse et al. 2021, Ahmed et al. 2021]. The mass transfer is driven by the
585 osmotic pressure gradient through a semi-permeable membrane. Water moves from the seawater
586 across the membrane into the DS, while the salts and other dissolved solids are retained on their
587 respective sides. Once the DS is diluted with fresh water, it is sent to the recovery process to be
588 concentrated. The recovered water is then collected for distribution, while the regenerated DS is sent
589 back to the FO plant (Figure 7). Appropriate selection of DS and its low cost recovery is important for
590 a feasible implementation. Ammonia-based solutions are usually used as the DS and can be recovered
591 by moderate heating (60°C). FO membranes are asymmetric with a thin « active » layer and a support
592 layer. Like in RO, concentration polarisation and fouling happen in FO. Two mechanisms are
593 generally described: internal concentration polarisation inside the membrane pores and external
594 concentration polarisation that happens on both membrane surfaces.

595
596

596 Membranes used in FO are most of the time the asymmetric thin-film composite RO membranes.
597 However, the permeate water flux of these membranes is generally low due to internal concentration
598 polarisation, especially in the dense thin layer. Several materials have been proposed to improve the
599 performances of thin-film composite RO membranes, with the inclusion of nanomaterials such as
600 zeolite, SiO₂ and graphene oxide nanosheets. Nanoparticles can be incorporated into the support

601 (mixed matrix membrane) or in the selective thin layer (thin-film nanocomposite) [Wu et al. 2020].
 602 Like new developments in RO membranes, new membranes for FO are mostly developed at small
 603 scale and for short usage time.
 604
 605



606
 607
 608 Figure 7 : Schematic representation of a Forward Osmosis system
 609

610 Several developments are similar between FO and RO in seawater desalination. UF can be used as an
 611 effective pre-treatment before FO, with addition of ferric chloride coagulation to improve filtration
 612 performance [Brover et al. 2022]. Also, similar strategies are employed to reduce membrane fouling
 613 such as pretreatment, membrane surface modification and choice of appropriate operating conditions
 614 [Lee et al. 2020].
 615

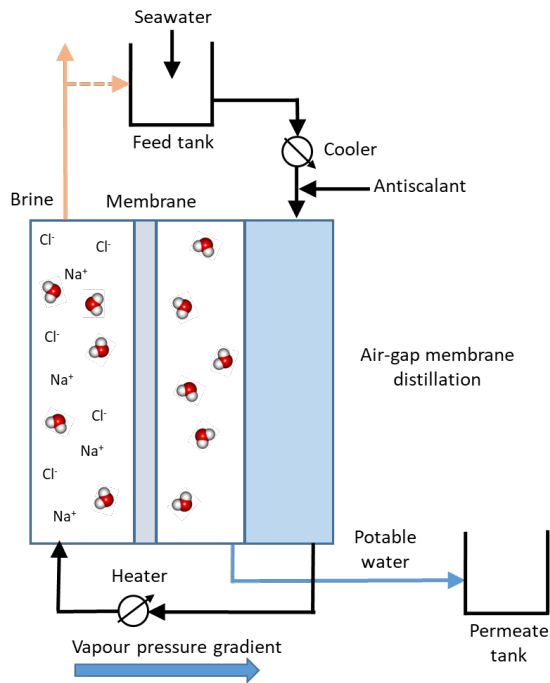
616 Membrane distillation

617 MD is a membrane process which uses hydrophobic microporous membranes. The membrane
 618 separates a hot and cold stream of water, preventing flow of liquid water through the membrane and
 619 allowing flow of water vapour (Figure 8). The temperature difference produces a vapour pressure
 620 gradient which causes water vapour to pass through the membrane and condense on the colder
 621 surface. The water obtained has a very high purity. MD can be conducted in different configurations
 622 that differ by the way the permeate is collected, the mass transfer mechanism through the membrane,
 623 and the driving force [Gryta 2005]. Various configurations of MD are possible like direct contact, air
 624 gap, sweeping gas and vacuum.

625 For desalination, the seawater for example obtained by cooling the condenser foil to 75°C, creates a
 626 water vapour partial pressure difference between the two sides of the membrane and allows the
 627 evaporation through the membrane. The water vapour condenses on the low-temperature side and
 628 distillate is formed. MD can be used as a substitute for desalination processes such as RO [Al-
 629 Obaidani et al. 2008]. The advantages of MD are lower operating pressure and performance not
 630 limited by high osmotic pressure or concentration polarization.

631 The interest of using MD for desalination has been increasing worldwide, especially when coupled
 632 with solar energy. Several MD configurations have been tested and plants have been implemented. In
 633 the first example, two solar thermal MD units were developed and installed in Jordan [Banat et al.
 634 2007]. Each unit consists of flat plate collectors, PV panels, spiral air gap MD module(s), and a data
 635 acquisition system. In the second example, the Memstill® process was developed by TNO
 636 (Netherlands) for desalination of seawater by air gap MD carried out in a counter current flow

637 configuration [Hanemaaijer et al. 2006]. Also, MD can be associated to reverse ED for the valorization
 638 of hypersaline waste brine to implement Zero Liquid Discharge and low-energy desalination (MD)
 639 [Tufa et al. 2019].
 640



641
 642
 643 Figure 8 : Schematic representation of an air-gap Membrane Distillation system
 644
 645

646 *Electrodialysis*

647 ED is an electric field driven membrane process. In an ED module, cation exchange and anion
 648 exchange membranes are alternatively stacked together, separated by flow spacers. ED is
 649 implemented for seawater and brackish water desalination in several plants, in particular small and
 650 medium plants [AlMadani 2003, Al-Amshawee et al. 2020]. The cations migrate from the brackish
 651 water towards the negative electrode through the cation-exchange membranes which allow only
 652 cations to pass. On the other hand, the anions migrate towards the anode through the anion exchange
 653 membranes. Inverters are used to reverse the polarity of the electric field about every 20 min, to limit
 654 scaling. This process is called electro dialysis reversal (EDR). Solar and wind energy can supply ED in
 655 areas where sun and/or wind are highly available. For example, Veza et al. [2004] built an ED/wind
 656 energy plant in Canaria Islands (Spain) for brackish water desalination.

657 In reverse electro dialysis (RED), a similar configuration as in ED allows to generate electrical power
 658 from two salinity gradients [Logan and Elimelech 2012]. The ion-exchange membranes are used for
 659 ion transport with the concentration difference as driving force. ED and REV can be associated for
 660 desalination, as a potential fresh water supply on small islands [Chen et al. 2015].

661 Despite these performances, seawater desalination by ED is generally considered to require a too high
 662 amount of energy to be competitive with RO. New ED configurations were thus proposed like
 663 electrically segmented ED configuration and hydraulically staged (i.e. multistage) ED configuration
 664 [Doornbusch et al. 2021]. The multistage configuration gave an average energy consumption of 3
 665 kWh/m³ over a 18 days period, demonstrating the potential of multistage ED seawater desalination
 666 over RO.

667
 668
 669 4. Removal of specific compounds in natural water

670 4.1 Introduction

671 Seawater is a major source of drinking water. In several countries, another important source of
672 drinking water is groundwater. Due to rocks dissolution and /or industrial pollution, groundwater
673 sources may contain several toxic molecules and particles like synthetic organic chemicals such as
674 pesticides, herbicides, industrial solvents and chemicals, inorganic pollutants such as arsenic, nitrate,
675 and metals, NOM and microorganisms such as protozoa, bacteria and viruses. These contaminants are
676 traditionally removed by technologies like adsorption, coagulation, flotation, ozonation, ion exchange,
677 and pressure driven membrane processes such as MF, UF, NF, RO, and membrane hybrid techniques.
678 These techniques are often similar to those employed for seawater desalination and their advantages
679 and limits are the same, like ease to implement large plants, however associated to fouling problems.

680

681 4.2 Natural organic matter

682 Natural waters contain colloids and NOM, i.e. molecules derived from the degradation of plants and
683 microorganisms. NOM can be divided into dissolved organic matter (DOM) and particulate organic
684 matter (POM). Humic substance is the major fraction of NOM and is generally divided into three
685 species: humic acid, fulvic acids and humin. NOM is a cause of colour in natural water sources, and is
686 not considered to be harmful to humans. However, NOM can generate disinfection by-products
687 (DBPs) during chlorination of the RO system. DBPs are very toxic as they can generate cancers, so they
688 have to be significantly removed before chlorination [Matilainen et al. 2010].

689 NOM removal is realized by coagulation and flocculation followed by sand filtration or direct
690 filtration [Matilainen et al. 2010]. Given more stringent water quality regulations, pressure driven
691 membrane processes such as NF and RO are increasingly used; however, membrane fouling by NOM
692 is a major limitation [Seidel and Elimelech 2002, Cornelissen et al. 2021]. Multivalent cations, such as
693 calcium and magnesium, react with NOM to form complexes, which results in a highly compacted
694 fouling layer associated to rapid flux decline [Seidel and Elimelech 2002]. The rate of deposition onto
695 the NF or RO membrane surface and thus fouling are also controlled by the coupling between the
696 opposite forces of electrostatic repulsion and hydrodynamic force [Seidel and Elimelech 2002].

697 Like in seawater desalination, pre-treatment of fresh water sources can reduce membrane fouling and
698 thus improve the process efficiency [Cornelissen et al. 2021]. For NOM removal, MF or UF can be
699 associated to other processes, such as adsorption on activated carbon, oxidation by iron oxide
700 particles, photocatalysis, ozonation and electrocoagulation [Pontié and Charcosset 2016]. For example,
701 pre-treatment by coagulation immediately before the UF or MF membrane is effective to prevent
702 membrane fouling, and reducing the coagulant dose and the duration of water treatment compared to
703 coagulation alone. However, the removal of NOM can be significantly affected by the type of
704 coagulant, coagulation conditions, type of membrane, filtration conditions, and characteristics of the
705 water to be treated [Matilainen et al. 2010]. Ozonation can also be used in combination with UF or MF
706 to reduce membrane fouling by NOM. Also, catalysts, such as metal oxides, can be used
707 simultaneously. For example, Park et al. [2012] reported NOM removal using a hybrid process that
708 combined ozonation with iron oxide nanoparticles loaded membranes. Their results indicated that the
709 reactive membrane-ozonation process enhanced NOM removal and reduced membrane fouling by
710 generating hydroxyl radicals from the catalytic ozonation.

711 Renewable energies are also interesting alternatives to reduce cost associated to energy consumption
712 in drinking water production systems. Systems based on UF driven by gravity are developed and
713 used at small-scale, especially for decentralized production of drinking water in developing countries
714 [Derlon et al. 2022]. However, these systems are limited by low values of permeate flux (typically
715 lower than 20 L m⁻² h⁻¹) and developments are needed to increase the permeate flux, while
716 maintaining a minimal need of maintenance.

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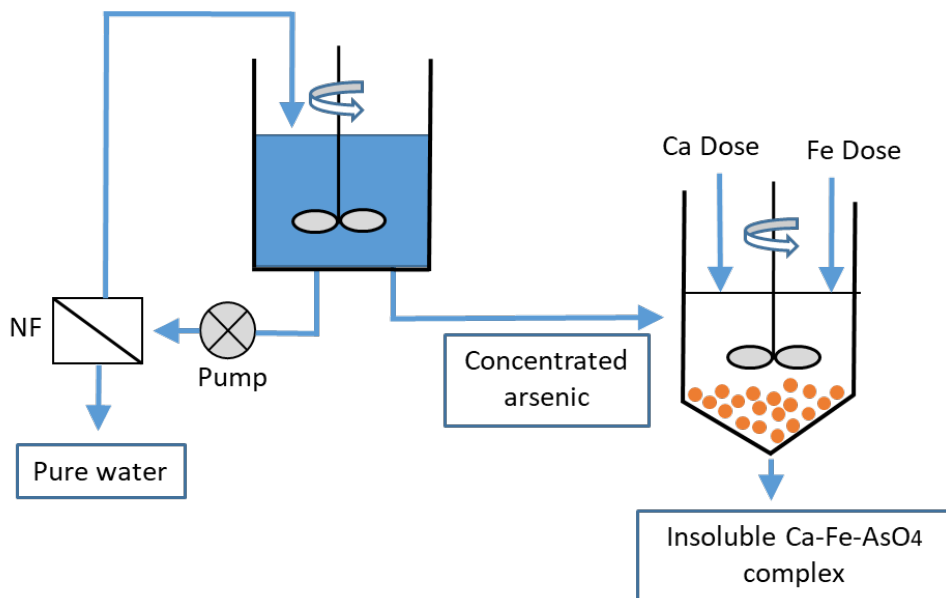
719 4.3 Arsenic

720 In many places around the world, arsenic is present in drinking water due to natural geochemical
721 phenomena or industrial pollution. Intensive consumption of arsenic contaminated water is the cause
722 of various types of human diseases, including respiratory diseases, gastro-intestinal, liver and
723 cardiovascular problems, and increasing risk of cancer. High arsenic concentrations are found in
724 groundwaters at concentrations above the maximum contaminant concentration in countries like
725 China, Bangladesh and India. The maximum arsenic concentration stated by the WHO, US and
726 European Union is 10 mg/L, in other countries like India and China, this concentration may be higher
727 (50 mg/L) [Pal et al. 2014, Park and Choi 2011].

728 Arsenic exists in groundwater in two predominant species: trivalent arsenite As(III) (H_3AsO_3) and
729 pentavalent arsenate As(V) (H_3AsO_4) [Pal et al. 2014]. Both As(III) and As(V) are found in
730 groundwaters. Several processes can be used for arsenic removal, including oxidation, coagulation–
731 precipitation, adsorption, ion exchange, and membrane separation [Park and Choi 2011]. Coagulation
732 and adsorption provide good arsenic removal efficiency.

733 Membrane processes such as NF and RO have been largely used for arsenic removal. The highest
734 removal is obtained by RO, however, RO has a high cost (plants and energy required). NF can remove
735 arsenic under its As(III) form by steric effects as it is uncharged, and As(V) by Donnan and steric
736 effects as it is negatively charged [Pal et al. 2014, Boussouga et al. 2021]. So, waters with high As(III)
737 concentration require a pre-oxidation step realized by chemical oxidation ($KMnO_4$, H_2O_2 , OCl^- and
738 $S_2O_2^{8-}$), Fenton [$Fe(II)/H_2O_2$] or ozone (O_3). Small particles (0.1–1 μm) are then obtained which are
739 removed in a settling basin. For example, Pal et al. [2014] removed trivalent and pentavalent arsenic
740 by cross flow NF following a chemical pre-oxidation step for conversion of trivalent arsenic into
741 pentavalent form, with simultaneous stabilization of arsenic rejects for safe disposal (Figure 9). Ion
742 exchange is also a possible technique, its drawbacks are associated to resin regeneration and costs
743 (resins and plant).

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748 Figure 9: A nanofiltration–coagulation integrated system for separation and stabilization of arsenic
749 from groundwater. (adapted from Pal et al. 2014)

750

751 Hybrid membrane processes are often chosen to improve the process efficiency (arsenic removal, less
752 chemicals, and lower cost). For example, MF is an alternative to coagulation-flocculation-settling,
753 where particles can be removed using a low pressure pump without chemicals and need for large
754 space. The technique was successfully applied to the treatment of groundwater from a city in southern
755 Colorado in the United States and from Sonargan in Bangladesh [Wickramasinghe et al. 2004].

756 Ozonation can also be used as a pre-treatment. For example, [Park and Choi \[2011\]](#) removed As(III)
757 using iron oxide nanoparticles (to promote ozonation) loaded membranes. [Santoro et al. \[2021\]](#)
758 implemented MD, photocatalysis and polyelectrolyte-enhanced UF for the treatment of arsenic
759 contaminated water in the area of Sila Massif (Italy), ensuring a complete removal of arsenic and a
760 rational management of residual contaminants.

761 In several volcanically active regions, like southern Peru, the presence of Arsenic is associated to high
762 boron concentrations [[Regis et al. 2022](#)]. Higher arsenic and boron removal are obtained by an
763 increase in pH. Increasing the pH to 9.5 implies an additional cost that was evaluated to 0.03–0.08
764 \$/m³.

765

766

767 4.4 Iron

768 Iron is often found at high concentrations in ground waters, from 0.5 to 50 mg/L [[Chaturvedi and Dave](#)
769 [2012](#)]. This is mainly due to the dissolution of rocks and minerals. Iron is not toxic for humans,
770 however it has several negative effects for drinking waters, such as unpleasant taste and color; it can
771 also induce the growth of ferro-bacteria. According to the European regulation, the maximal total iron
772 concentration in drinking water is 0.3 mg/L. Iron is mainly found in two states: Fe²⁺ and Fe³⁺.

773

774 Iron can be removed from ground water by several techniques like oxidation/precipitation/filtration,
775 ion exchange, lime softening and membrane processes [[Chaturvedi and Dave 2012](#)].

776 The oxidation/precipitation of soluble Fe²⁺ into insoluble iron hydroxides, especially ferric hydroxide
777 Fe(OH)₃, is realized by adding chemicals (hypochlorite, permanganate) or dissolved gases (oxygen,
778 chlorine, ozone) [[El Azher et al. 2008](#)]. For waters with high iron concentration (> 5 mg/L), aeration is
779 the best way to oxidize the ferrous iron and avoid the use of chemicals. At lower iron concentration,
780 ozonation or chlorination are usually chosen for oxidation. Iron hydroxides particles are then removed
781 by sand filtration to obtain an iron concentration lower than 7 mg/L and then by decantation.

782 Ferric and ferrous ions are not easily retained by NF, UF or MF, so, iron based particles need to be
783 formed before being filtrated. Iron based complexes are obtained using chelating agents [[Chaturvedi](#)
784 [and Dave 2012](#), [Fakhfekh et al. 2017](#)] or oxidation (by biological treatment, sodium hypochlorite addi-
785 tion (prechlorination), potassium permanganate addition or air bubbling, etc) to form ferric hydroxide
786 particles. For example, iron and manganese were removed from groundwater by aeration, chlorine
787 oxidation and MF at a water treatment plant in Taiwan [Chen et al. \[2011\]](#).

788 Different process configurations are possible: (1) the oxidation takes place in a reactor, and the ferric
789 hydroxide suspension is then filtered by UF or MF, (2) the treatment is continuous, the water is added
790 continuously to an aerated reactor and then the ferric hydroxide particles are eliminated by UF or MF
791 [[Fakhfekh et al. 2017](#)], (3) the reactor is coupled to UF or MF, the permeate and retentate being
792 recycled in the reactor without continuous water addition. The second configurations is particularly
793 attractive for groundwater treatment plants.

794

795 4.5 Nitrate

796 Nitrate is found at moderate concentrations in most groundwaters, however, high concentrations are
797 increasing observed around the world, mainly resulting from intensive use of fertilizers. Nitrate is
798 known to be harmful especially to infants and pregnant women [[Shrimali and Singh 2001](#)]. This is due
799 to the potential reduction of nitrate to nitrite ion which can bind with hemoglobin, thus diminishing
800 the transfer of oxygen to the cells resulting in a bluish skin color often called “the blue baby
801 syndrome”. This is a reason why the limit concentration in drinking water has been fixed by the WHO
802 at 50 mg/L.

803 High nitrate concentrations limit the direct use of groundwaters for human consumption in several
804 parts of the world including Saudi Arabia, India and China [[Shrimali and Singh 2001](#)]. For example, in
805 the Nagpur district of Maharashtra in India, about 91% of the villages recorded use groundwater with
806 nitrate concentration between 20 and 100 mg/L and about 7% with concentrations higher than 100

807 mg/L. In Israel, nitrate concentrations higher than 70 mg/L lead to the closure of wells in the coastal
808 aquifers, with an annual water loss of around 24 million m³ [Epsztein et al. 2015].
809 The techniques use for nitrate removal are ion exchange, ED and RO. Removal of nitrate by NF
810 membranes is expected to be low due to the monovalency of nitrate. For example, Van der Bruggen et
811 al. (2001) found nitrate removal around 76% with a NF70 membrane (Dow/Filmtec). This
812 concentration was said to be sufficient to be a first step with ED or RO for complete removal. On the
813 other hand, RO is very efficient for nitrate removal. RO has been implemented successfully in a rural
814 area in South Africa [Schoeman and Steyn 2003]. Indeed, RO was found to remove 98% nitrate-
815 nitrogen, from 42 mg/L to less than 1 mg/L. The RO brine was said to be suitable for stock watering if
816 water recovery was kept low (approximately 50%) and if conditions for stock watering were met in
817 terms of nitrate/nitrogen concentration, TDS and other constituent concentrations. Brine disposal for
818 stock watering is said to be a very convenient and cost effective way of brine disposal in a rural area.
819 However, the drawbacks of RO may be associated to its price and production of concentrated waste
820 brines and their disposal issues [Epsztein et al. 2015].
821 Combination of NF and RO is also a possible alternative. For example, Epsztein et al. [2015] proposed
822 a hybrid NF/RO process for nitrate removal thanks to the ability of NF to remove more chloride and
823 sodium ions than nitrate ions. In a second stage, RO was applied to remove nitrate and the RO
824 permeate was mixed with the side stream of the NF stage to give water with low nitrate concentration,
825 yet with a suitable composition with all required species and minerals. The hybrid process consisting
826 of a single and double NF stages followed by RO was able to reach water recoveries of 91.6% and
827 94.3%, respectively, based on Israeli regulations for drinking water and composition of brines
828 discharged to the sewage.

829 830 4.6 Fluor

831 High fluoride concentrations are mainly found in water sources of countries in North and East Africa,
832 and in India and China [Mohapatra et al. 2009, Dantie et al. 2019]. These high concentrations are due
833 to natural dissolution of rocks and soils and/or mining industries. At high concentrations, fluoride
834 ions may be toxic for human, with more or less negative effects on teeth, bones or brain. Thus, the
835 maximum concentration in drinking water recommended by the WHO is 1.5 mg/L.

836 Water defluoridation techniques include ion exchange, membrane processes, electrocoagulation,
837 coagulation-precipitation and adsorption [Mohapatra et al. 2009, Dantie et al. 2019]. Ion exchange and
838 membrane processes can decrease fluoride concentrations below recommended concentrations. Their
839 drawbacks are their cost and the need to regenerate resins or membranes. Electrocoagulation is a very
840 effective technique for fluoride removal, but it requires much energy, and the dissolution of the anode
841 increases the aluminium concentration in water, which leads to a secondary pollution. The Nalgonda
842 technique is a coagulation-precipitation technique with lime and aluminium as chemicals. This
843 technique is largely implemented in India as it is very effective for fluoride removal. Drawbacks
844 associated to this method include the formation of toxic soluble aluminium complexes, the increase of
845 pH and total dissolved solids, so an additional process is needed to eliminate chemicals. Adsorption is
846 an another technique, which has the advantages of being less expensive and simple to operate, but has
847 the disadvantage to be less effective.

848 NF is the best membrane process to remove fluoride from waters as it very selective [Mohapatra et al.
849 2009]. Indeed, the high hydration of fluoride ions helps that their exclusion by organic NF membranes.
850 For example, with the NF90 membrane, the fluoride concentration in the permeate increased with
851 increasing fluoride concentration in the feed water, but fluoride was reduced to a satisfactory value
852 for all concentrations (up to 1.5 mg/L) [Pontié et al. 2008].

853 Following this theoretical study, Pontié et al. (2013) proposed to first NF plant for defluoridation
854 which was built in Thiadiaye (Senegal) [Pontié et al. 2013]. The skid mounted system was a typical 2
855 stages design plant typical for brackish water treatment, with a water tank of 1 m³ and a membrane
856 area of 1338 m² (36 spiral wound modules of the NF90-400 membrane). Cartridge filters (10 µm) were
857 located upstream of the NF unit in order to limit particulates fouling. The F⁻ concentration in the feed

858 water was 4.7 mg/L. With the NF90 membrane, the fluoride concentration decreased to a value of 0.6
859 mg/L.

860
861

862 *4.7 Removal of pesticides and herbicides*

863 Herbicides and insecticides are intensively used to control weeds (herbicides), insects (insecticides)
864 and plant diseases with may affect the growth, harvest, and marketability of crops [Plakas and
865 Karabelas 2012]. This results in their presence at very small concentrations (pg/L to ng/L) in surface
866 and eventually in groundwaters. The potentially adverse health effects of herbicides and insecticides
867 include increasing risk of cancer, genetic malformations, neuro-developmental disorders and damage
868 of the immune system. Conventional methods such as particle coagulation–flocculation,
869 sedimentation and dual media filtration, are ineffective for removing pesticide residues from water
870 sources. Advanced treatments (like oxidation by H₂O₂ or O₃, and granular activated carbon /filtration)
871 are effective, although their limits are related to saturation of activated carbon, and toxic chemical by-
872 products, which may develop in the GAC filters under some conditions.

873 In these last 20 years, NF and RO membranes were shown to remove of a large number of herbicides,
874 insecticides and fungicides from various waters. Plakas and Karabelas [2012] reviewed the NF and RO
875 membranes employed together with the reported pesticide rejection performance for 49 active
876 substances. Factors affecting the removal of pesticides by NF and RO membranes include membrane
877 characteristics (molecular weight cut-off, membrane material and charge), pesticides properties
878 (molecular weight and size, hydrophobicity/hydrophilicity, polarity), and feed water composition
879 (pH, solute concentration, ionic environment).

880 For example, Zhang et al. [2004] investigated the removal of two pesticides (atrazine and simazine)
881 from different waters (distilled, tap and river water) using four types of NF membranes (DESAL 51
882 HL, DESAL 5 DL, UTC-20, UTC-60). The rejection of atrazine was found higher than the rejection of
883 simazine; and the highest rejections were obtained with the UTC-20 membrane. The rejection of
884 pesticides was higher in river and tap waters than in distilled water, but the water flux was lower.
885 This was explained by ion adsorption inside the NF membrane pores which modifies the rejection
886 rates and water fluxes. In addition, the presence of NOM enhances the adsorption of pesticides onto
887 the membranes surface and increases the size exclusion and electrostatic repulsion. In addition, these
888 authors show that pesticides were completely removed from water while only a small fraction of salts
889 using loose NF membranes (DESAL 51HL, N30F and NF270) in cascades. Rejection of pesticides
890 (aldrin, atrazine, bentazone, dieldrin, and propazine) depended on specific properties of the solutes
891 like molecular size and chemical structure (e.g. hydrophobicity).

892
893

894 *4.8 Pharmaceuticals and personal care products*

895 Pharmaceuticals and personal care products (PPCPs) are well recognized trace contaminants of
896 sewage, rivers, lakes, and groundwater [Yang et al. 2017, Khanzada et al. 2020]. PPCPs can have
897 negative effects for humans and animals mainly because their residues enter and accumulate in food
898 through contamination of water used in culture irrigation. Among pharmaceuticals, we find
899 antibiotics, hormones, analgesics, anti-inflammatory drugs, blood lipid regulators, β - blockers, and
900 cytostatic drugs and as personal care products, preservatives, bactericides/disinfectants, insect
901 repellents, fragrances, and sunscreen ultraviolet (UV) filters. In addition to PPCs, endocrine
902 disrupting chemicals (EDCs) are less specific and interfere with the functioning of natural hormones
903 in animals like fishes [Snyder et al. 2007]. Some natural or synthetic compounds are considered to be
904 EDCs, including pharmaceuticals, pesticides, industrial chemicals, phytoestrogens, and hormones
905 excreted by animals and humans. PPCPs and EDCs are found in natural waters at concentration
906 below 1 μ g/L.

907 Many processes have been proposed for reducing the concentration of PPCPs and EDCs in natural
908 water [Yang et al. 2017, Taheran et al. 2016]. Coagulation, flocculation, and precipitation processes are

909 often ineffective for removing PPCPs and EDCs. Oxidative processes such as chlorination and
910 ozonation can reduce the concentrations of several classes of contaminants; however, their efficacy
911 depends on the contaminant structure and oxidant dose. Biological processes, such as activated
912 sludge, biofiltration, and soil aquifer treatment, can reduce the concentration of PPCPs and EDCs
913 which are biodegradable and/or readily bind to particles. Activated carbon can remove nearly all
914 PPCPs and EDCs; however, their removal capacity is limited by contact time, competition with NOM
915 and contaminant solubility.

916 Many studies have reported the treatment of natural or synthetic waters containing PPCPs and EDCs
917 using RO and NF [Taheran et al. 2016, Snyder et al. 2007]. RO can efficiently remove almost all PPCPs,
918 however its operational cost is relatively high since RO is operated under high pressure. NF
919 membranes have shown high rejection for a wide range of PPCPs, but their performance is influenced
920 by size exclusion, electrostatic and hydrophobic interaction especially in the case of NF membranes
921 with large pore size. Generally, larger molecules with negative charge and higher hydrophilicity are
922 more efficiently rejected. To improve the removal obtained by UF or MF, these membrane processes
923 can be associated with other techniques, such as activated carbon sorption and enzymatic
924 degradation. For example, Snyder et al. [2007] used granular activated carbon (GAC) and powdered
925 activated carbon (PAC) as a pretreatment to membrane separation systems. Both GAC and PAC were
926 effective for removal of PPCPs from water (more than 90% removal). However, the efficacy of GAC
927 was influenced by NOM which competes for binding sites. The authors also underline that the
928 pressures required for RO and NF as well as the thermal regeneration of GAC require significant
929 amounts of energy, which may lead indirectly to greater environmental impacts than the presence of
930 trace contaminants.

931 932 **5. Conclusion**

933 This review presents classical and recent applications of membrane processes in the field of
934 desalination and water treatment. Desalination is a classical and well established technology with
935 many plants built all around the world. Natural water treatment is also largely implemented in areas
936 using natural water as water source. This review presents the main characteristics of these processes
937 by focusing on membranes and devices, plants, membrane fouling, energy consumption, and
938 environmental issues, etc. In that sense, advances in desalination technologies could bring new
939 solutions to natural water treatment. Like in desalination plants, renewable energy could be
940 implemented to decrease energy consumption and environmental issues. Like in desalination,
941 environmental impact assessment could be further evaluated. Comprehension of membrane fouling in
942 desalination could also give valuable data for comprehension and limitation of fouling in natural
943 water treatment. Desalination and natural water treatment are thus closely linked and this can offer
944 new solutions.

945 946 947 **Bibliography**

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