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Evaluation of Fenton and modified Fenton oxidation coupled with membrane distillation for produced water treatment: Benefits, challenges, and effluent toxicity

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(Article begins on next page)

1 **Evaluation of Fenton and modified Fenton oxidation**
2 **coupled with membrane distillation for produced water**
3 **treatment: Benefits, challenges, and effluent toxicity**

4
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18

19 **ABSTRACT**

20 Membrane distillation is a promising technology to desalinate hypersaline produced waters.
21 However, the organic content can foul and wet the membrane, while some fractions may pass
22 into the distillate and impair its quality. In this study, the applicability of the traditional
23 Fenton process was investigated and preliminarily optimized as a pre-treatment of a synthetic
24 hypersaline produced water for the following step of membrane distillation. The Fenton
25 process was also compared to a modified Fenton system, whereby safe iron ligands, i.e.,
26 ethylenediamine-N,N'-disuccinate and citrate, were used to overcome practical limitations of
27 the traditional reaction. The oxidation pre-treatments achieved up to 55% removal of the
28 dissolved organic carbon and almost complete degradation of the low molecular weight toxic
29 organic contaminants. The pre-treatment steps did not improve the productivity of the
30 membrane distillation process, but they allowed for obtaining a final effluent with
31 significantly higher quality in terms of organic content and reduced *Vibrio fischeri* inhibition,
32 with half maximal effective concentration (EC₅₀) values up to 25 times those measured for
33 the raw produced water. The addition of iron ligands during the oxidation step simplified the
34 process, but resulted in an effluent of slightly lower quality in terms of toxicity compared to
35 the use of traditional Fenton.

36

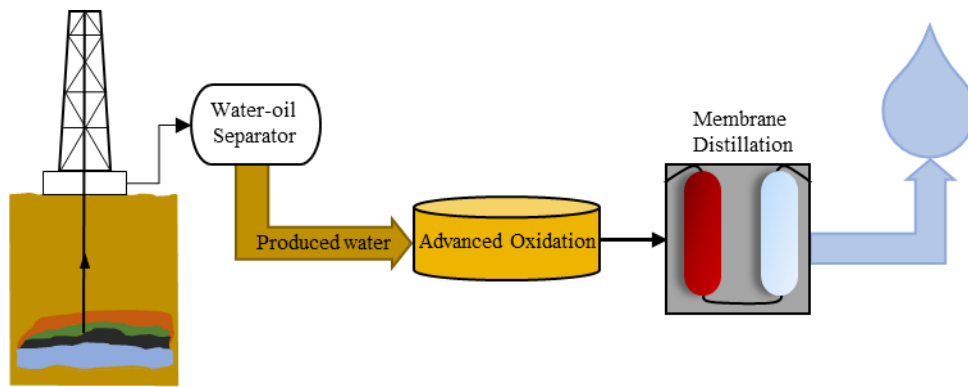
37 **Keywords:** membrane distillation; produced water; advanced oxidation; iron ligands;
38 ecotoxicity

39 **HIGHLIGHTS**

- 40 • Thermal and modified Fenton degraded target contaminants in produced water.
- 41 • The oxidative pre-treatment decreased organics in the membrane distillation effluent.
- 42 • Coupled oxidation and membrane distillation decreased the toxicity of the final effluent.
- 43 • Traditional Fenton pre-treatment provided the best effluent in terms of toxicity.
- 44 • Modified Fenton nearly degraded all target contaminants in hypersaline solutions.

45

46 **GRAPHICAL ABSTRACT**



47

48

49 **1. Introduction**

50 Despite the current transition to more sustainable sources of energy, oil and gas extraction
51 still plays a significant role in the energy sector and wastewater treatment is quickly emerging
52 as one of the most significant challenges of this industry. Indeed, the so-called produced
53 water (PW) is the largest waste stream generated in oil and gas extraction activities
54 (Ahmadun et al., 2009). Considering both onshore and offshore sites, the global PW
55 production has increased from 150 million to around 300 million barrels per day from 1990
56 to 2015 (Ahmadun et al., 2009; Liu et al., 2021). The average water cut, namely, the amount
57 of water volume produced per oil volume, is roughly 3:1 (Ahmadun et al., 2009; Jimenez et
58 al., 2018; Liu et al., 2021; McCormack et al., 2001). As oilfields age during the current
59 energy transition, the water cut will also increase, together with wastewater treatment
60 difficulties (Igunnu and Chen, 2014). PW is a highly complex matrix, rich in organic and
61 inorganic compounds, with widely diverse composition as a function of geological formation,
62 age of the oilfield, and type of hydrocarbon product being extracted (Ahmadun et al., 2009;
63 Estrada and Bhamidimarri, 2016). However, the major compounds are typically dispersed
64 oils, dissolved organics (e.g., phenols, benzene, toluene, xylenes), dissolved minerals (e.g.,
65 sodium chloride, calcium and magnesium salts), and natural organic matter (NOM)
66 (Ahmadun et al., 2009; Al-Ghouti et al., 2019; Coha et al., 2021; Estrada and Bhamidimarri,
67 2016; Jimenez et al., 2018; Kabyl et al., 2020; Liu et al., 2021; Neff et al., 1992).

68 The oil and gas industry faces increasing pressure to limit its environmental footprint
69 (Mohammad-Pajooch et al., 2018). Expensive treatment trains for a multi-contaminated water,
70 as well as water scarcity and increasing international attention to environmental issues, are
71 the drivers pushing this industry to use water more sustainably, bringing along the concepts
72 of water reuse and safe water discharge. As a result, innovative, environmentally focused,
73 and reliable methods of meeting water treatment demands, capable of operating in this

74 specific application are being developed (Estrada and Bhamidimarri, 2016; Liu et al., 2021;
75 Mohammad-Pajooch et al., 2018). These technologies should be versatile to meet the
76 requirements of low cost and compactness, the latter characteristic being especially important
77 in offshore activities (Kabyll et al., 2020; Liu et al., 2021). One of the target parameters that
78 needs abatement to allow for water reuse or safe discharge is salinity, which presents average
79 values of 50-100,000 ppm in PW (Coha et al., 2021; Estrada and Bhamidimarri, 2016). Such
80 salt concentration can plug the reinjection well or may be toxic if PW is discharged in the
81 environment without desalination (Aquilina, 2012; Ariono et al., 2016; Canedo-Arguelles et
82 al., 2019; Chen et al., 2016; Kleinitz et al., 2001; Liu et al., 2021). Membrane distillation
83 (MD) is a promising emerging technology, capable to extract high-quality effluents from
84 hypersaline solutions using low-grade energy and with relatively low capital cost, due to the
85 absence of high pressure and high temperature components (Chen et al., 2017; Han et al.,
86 2017; Howell, 2004; Lin et al., 2014; Shaffer et al., 2013). In recent studies, MD was
87 successfully tested on hypersaline PW (Han et al., 2017; Li et al., 2014; Ricceri et al., 2019).
88 However, since the MD membranes are highly hydrophobic (PTFE and PVDF membranes
89 are generally used), this process may present important practical limitations in the presence of
90 a large and broad content of organic compounds, such as for typical PW (Estrada and
91 Bhamidimarri, 2016; Gonzalez et al., 2017). Organics may either induce wetting phenomena
92 or freely pass through the hydrophobic membrane and end up in the final effluent (Chen et
93 al., 2017; Franken et al., 1987; Kargbo et al., 2010; Wang et al., 2018). Wetting phenomena
94 in MD occur when the transmembrane pressure (ΔP) exceeds the liquid entry pressure (LEP),
95 according to eq. (1), thus allowing the contaminated feed water to pass undisturbed through
96 the porous membrane (Franken et al., 1987; Horseman et al., 2021a; Ricceri et al., 2019).

$$97 \quad \Delta P \geq LEP \quad (1)$$

98 LEP is defined according to eq. (2):

99
$$LEP = -\frac{2B\gamma\cos\theta}{r} \quad (2)$$

100 where γ is the feed water surface tension, θ is the intrinsic contact angle between the feed
101 water and the solid membrane material, r is the equivalent pore radius, and B is a geometric
102 factor accounting for the noncylindrical nature of the membrane pore geometry ($B = 1$ for
103 perfectly cylindrical pores). A low surface tension γ reduces also $\cos\theta$, thus facilitating
104 membrane pore wetting. The degradation of toxic organic compounds in the feed solution
105 both increases its surface tension and thwarts their interaction with the hydrophobic
106 membrane, potentially allowing for a more efficient MD process and a more effective
107 management of the PW.

108 The list of available technologies and processes counts a plethora of options to remove or
109 partially degrade organic compounds (Adewumi et al., 1992; Ahmadun et al., 2009; Chang et
110 al., 2019a; Chang et al., 2019b; Estrada and Bhamidimarri, 2016; Liu et al., 2021; Shang et
111 al., 2019; Tang et al., 2021). Activated carbon adsorption and sand filtration are low-cost
112 treatment processes; however, they produce harmful waste since they do not degrade the
113 toxic organic compounds. Biological treatment is not effective toward biorecalcitrant organic
114 compounds, such as benzene, toluene, xylenes (BTX), and requires large plants with long
115 retention times, hence not available for offshore platforms (Ayed et al., 2017).
116 Electrochemical, photocatalytic, and ozone-based oxidations are growing rapidly, but they
117 are still currently associated with high capital costs and with difficulties in practical
118 implementation (Ahmadun et al., 2009; Bessa et al., 2001; Cocha et al., 2021; Dalmacija et al.,
119 1996; Ma and Wang, 2006; Ricceri et al., 2019; Shokrollahzadeh et al., 2012). Among
120 advanced oxidation processes (AOPs), the Fenton reaction involves the use of iron sulfate
121 and hydrogen peroxide to generate highly reactive hydroxyl radicals able to oxidize almost

122 all the organic compounds (Coha et al., 2021; Haber et al., 1934; Miklos et al., 2018). The
123 main reaction is as follows:



125 The Fenton process is a promising candidate to treat PW both onshore and offshore since it is
126 versatile, characterized by high kinetics also at room temperature, and capable to remove
127 organics from a multi-contaminated matrix (da Silva et al., 2015; Jiménez et al., 2019;
128 Jiménez et al., 2017; Jin and Davarpanah, 2020; Ruiz-Aguirre et al., 2017; Zhai et al., 2018).
129 This method has some limitations, mainly the need for acidic pH to avoid iron hydroxide
130 precipitation, and the production of sludge once neutral pH is restored (Diya'uddeen et al.,
131 2012). A modified Fenton process encompassing the addition of an iron ligand helps
132 overcoming these precise challenges (Chahbane et al., 2007; Farinelli et al., 2020; Farinelli et
133 al., 2019; Messele et al., 2019). However, the literature lacks reports about the application of
134 Fenton processes carried out in presence of iron ligands to treat PW.

135 The first objective of this work is to evaluate a coupled system including Fenton (or
136 modified Fenton) pre-oxidation and MD to desalinate PW and to allow for an easy
137 management of the final effluent. This sequence is applied to treat a synthetic PW that
138 mimics the effluent from primary treatment, which typically includes de-oiling and flotation
139 or sedimentation. A thermal Fenton reaction is first applied as a potential PW oxidation step
140 and as a pre-treatment for MD desalination. The study gives insight into the relationship
141 between the content of organics and the performance of the membrane distillation step by
142 comparing a raw feed stream with the feed subject to Fenton oxidation. Furthermore, the
143 performance of traditional Fenton is compared with that of modified Fenton systems. To this
144 purpose, non-toxic and biodegradable organic ligands, namely, citrate and EDDS, are added
145 in PW at unadjusted pH to assess the ability of iron-ligand complexes to act as effective
146 oxidation catalysts (Chen et al., 2019; Tandy et al., 2006; Van Devivere et al., 2001). The

147 safety of the final desalinated effluent from the coupled system is then fully evaluated
148 through acute toxicity measurements.

149

150

151 **2. Materials and Methods**

152 *2.1. Chemicals, membrane, and produced water preparation*

153 All the organic contaminants, the iron ligands, i.e., sodium citrate and EDDS, ferrous
154 sulfate (FeSO_4), hydrogen peroxide (30% w/w), HCl, and NaOH, were purchased from
155 Sigma-Aldrich (Milan, Italy). Sodium chloride, sodium sulfate, and sodium bicarbonate were
156 acquired from Carlo Erba (Milan, Italy). All the solutions needed for the acute toxicity
157 analysis, namely, the reconstitution, the diluent, and the osmotic solutions were purchased
158 from Modern Water (London, UK). The freeze-dried *Vibrio fischeri* culture was purchased
159 from Ecotox LDS (Cornaredo (MI), Italy). Type I ultrapure water was used for the
160 experiments. A commercially available polytetrafluoroethylene (PTFE) membrane (Aquastill,
161 Sittard, Netherlands) was deployed in MD filtration tests.

162 The composition of the synthetic PW was based on published values of real wastewaters
163 and is listed in **Table 1**, together with the resulting total organic carbon (TOC) and total
164 dissolved solids (TDS) values (Coha et al., 2021; Estrada and Bhamidimarri, 2016; Olsson et
165 al., 2013). Humic acids and a liquid petroleum jelly consisting of paraffins were used as
166 representative compounds for natural dissolved organic matter and oil & grease, respectively
167 (Lester et al., 2015). Xylenes, benzene, toluene, and methyl *tert*-butyl ether (MTBE) were
168 selected as representative volatile organic compounds (VOCs) (Coha et al., 2021).
169 Cyclohexane was added as representative of the $<C_{10}$ hydrocarbon fraction (Estrada and
170 Bhamidimarri, 2016; Lester et al., 2015). Phenol was added as representative substance for

171 the common phenols content in PW. The TDS included sodium, calcium, and magnesium
 172 chlorides. All the components were added into water and the matrix was sonicated at room
 173 temperature for 1 h to enhance solubilization and mixing.

174

175 **Table 1** Composition of the synthetic produced water, compared with the reference real
 176 streams. The matrix includes representative pollutants to mimic typical TOC and TDS values.

Parameter	Component	Synthetic produced water		Real produced water
		Concentration (ppm)	Equivalent TOC (ppm)	Concentration (ppm)
TOC	Paraffins	200.0	Not dissolved	Maximum ~500
	Humic acids	200.0	60.0	
	Cyclohexane	2.0	1.8	
	Phenol	2.5	1.9	
	Xylenes	1.0	1.0	
	Benzene	12.0	11.3	
	Toluene	4.0	3.4	
	MTBE	260.0	178.0	
	TOT	681.5	257.4	
TDS	Sodium chloride	100,000		Typically, 35,000 – 240,000
	Calcium chloride	2,500		
	Magnesium chloride	4,000		
	TOT	106,500		
pH	5.5			Average ~100,000

177

178 2.2. Oxidation conditions

179 All the oxidation reactions were performed at room temperature (25 ± 2 °C) under gentle
 180 stirring for a total duration of 1 h, using different ratios of hydrogen peroxide and catalyst.
 181 The catalyst was iron(II) in the case of the traditional Fenton process, and a complex ligand-
 182 iron(II) in the case of modified Fenton. To promote organics oxidation, three additions of
 183 hydrogen peroxide (0, 20, 40 min) were carried out, each one consisting of a 1/3 aliquot of
 184 the desired total amount. The dosages of iron sulfate and hydrogen peroxide are listed in
 185 **Table 2** for the traditional Fenton system; in these cases, the pH of the synthetic PW was

186 adjusted to ~3 (HCl). At the end of the reaction, the pH was increased to ~10 by addition of
187 NaOH and this step caused the precipitation of Fe(OH)₃. After the sedimentation of the
188 precipitate at 4 °C overnight, the supernatant was collected and used for analysis and as a
189 feed matrix for the following MD filtration tests.

190

191 **Table 2** Traditional Fenton dosages in tests operated at different oxidation conditions.

Entry	FeSO ₄ (mM)	H ₂ O ₂ (mM)
MQ H ₂ O	-	-
Produced water	-	-
Ox 1	0.5	5
Ox 2	5.0	50
Ox 3	5.0	25
Ox 4	1.0	25
Ox 5	1.0	50
Ox 6	0.1	5
Ox 7	5.0	100

192

193 To perform the modified Fenton oxidations, the iron-ligand complexes, namely, Fe-
194 EDDS and Fe-citrate were spiked in the synthetic PW from a stock solution containing 0.1 M
195 of iron(II) and 0.1 M of individual ligand. The pH was not adjusted and was equivalent to ~4
196 upon addition of Fe-EDDS and to ~5 upon addition of Fe-citrate. No precipitate formation
197 was observed in these systems. The resulting samples were used for analysis and as feed for
198 the following MD filtration tests without further processing.

199 *2.3. Membrane distillation tests*

200 The MD tests were performed in direct contact configuration using a lab-scale batch
201 system (Ricceri et al., 2019). The feed and distillate streams were circulated counter-currently
202 on their respective sides of the membrane. A constant crossflow rate of 1.66 L/min (0.278
203 m/s crossflow velocity) was maintained during the tests. The housing cell comprised a 250-
204 mm long, 50-mm wide, and 2-mm deep rectangular channel for a total active membrane area

205 of 125 cm². The flux across the membrane was computed by recording the change in weight
206 of the distillate tank in time through a computer-interfaced balance. Initial volumes of ~1.9 L
207 and 1 L were used for the feed and distillate streams, respectively, unless otherwise stated.
208 Water was used in the distillate side, with specific conductivity always below 20 μS/cm. The
209 specific conductivity in the distillate tank was measured continuously during each test by a
210 conductivity meter (COND 7+, XS Instruments, Italy). The temperature of the feed and
211 distillate tanks were maintained constant throughout the experiments, at respective values of
212 50 ± 2 and 25 ± 1 °C, by means of a thermostatic water bath and a chiller.

213 *2.4. Analytical methods*

214 The TOC of the matrices was measured using a Shimadzu TOC-L analyzer (catalytic
215 oxidation on Pt at 680 °C). The calibration was performed using standards of potassium
216 phthalate and of NaHCO₃/Na₂CO₃. The headspace, solid phase microextraction technique
217 (HS-SPME) was chosen as extraction method before carrying out the GC-MS analysis.
218 Following each reaction experiment, the vials were left in a thermostatic bath at 50 °C for 10
219 min to promote the transfer of all the relevant compounds into the gas-phase headspace.
220 Then, a SPME fiber (df 75 μm, fiber assembly carboxen/polydimethylsiloxane, Supelco) was
221 inserted through the septum of the cap and was left in the headspace for 10 min, before
222 withdrawing it for the subsequent GC-MS analysis. Samples were analyzed on an Agilent
223 6890 GC system coupled with an Agilent 5973 mass selective detector (MSD). For the
224 chromatographic separation, a Zebron-5MS capillary column (30 m × 0.25 mm × 0.25 μm)
225 was used. The injection port temperature was 270 °C, and the oven temperature program was
226 set as follows: 35 °C for 5 min, followed by an increase to 260 °C at a rate of 15 °C/min (total
227 run time 25.33 min). Helium was used as carrier gas at a constant flow of 1 mL/min, and the
228 injector was held in splitless mode. The interface temperature was 270 °C and the ionization

229 energy was 70 eV. The molecular structures of the by-products were identified by means of
230 mass spectrum library.

231 The determination of the residual iron in solution was carried out by a spectrophotometric
232 procedure adapted from previous literature (Goncalves et al., 2020; Harvey et al., 1955). The
233 total iron was determined by reducing the Fe(III) to Fe(II) with ascorbic acid (4×10^{-4} M) and
234 complexing the Fe(II) with o-phenanthroline (4×10^{-3} M) under acidic conditions (buffer pH =
235 3: H₃PO₄ 1 mM, NaH₂PO₄ 3 mM). The Fe(II) was determined without performing the
236 reduction step, and Fe(III) was obtained as the difference between total iron and Fe(II). The
237 calibration was obtained using a commercial standard solution of Fe(III) (1000 mg^{Fe}/L,
238 Sigma-Aldrich). The spectrophotometric analyses were performed using a Varian CARY 100
239 Scan double-beam UV–vis spectrophotometer, using quartz cuvettes with 10 mm path length
240 and working at a wavelength of 510 nm. Surface tension measurements were performed with
241 a digital tensiometer (K10, Krüss): the measurements were repeated three times on each
242 sample.

243 2.5. Toxicity analysis

244 All the toxicity experiments were performed with a Microtox Model 500 analyzer (Milan,
245 Italy). The analysis was performed with the bioluminescence inhibition assay using the
246 marine bacterium *Vibrio fischeri*. Samples were tested in a medium containing 2% sodium
247 chloride, and the luminescence was recorded after 5, 15, and 30 min of incubation at 15 °C.
248 The luminescence inhibition percentage was determined by comparison with a non-toxic
249 control. The toxicity curves and the values of EC₅₀ were obtained from the software
250 (MicrotoxOmni). The pH of all the samples was adjusted in the range 6-8 before the analysis.
251 The method used for the toxicity analysis is the method APAT-IRSA 8030 (APAT, 2003).
252 All the samples obtained at the end of the oxidation experiments were quenched with catalase
253 in order to avoid the detrimental effect of the residual hydrogen peroxide on the toxicity

254 measurements; see Figure S1 of the Supplementary Material (SM). Moreover, the samples
255 after the oxidation experiments were quantified for residual iron content and EDDS was
256 added in EDDS:Fe molar ratio of 1:1, to prevent the toxic effect of the residual iron in
257 solution (see Figure S2 in SM).

258

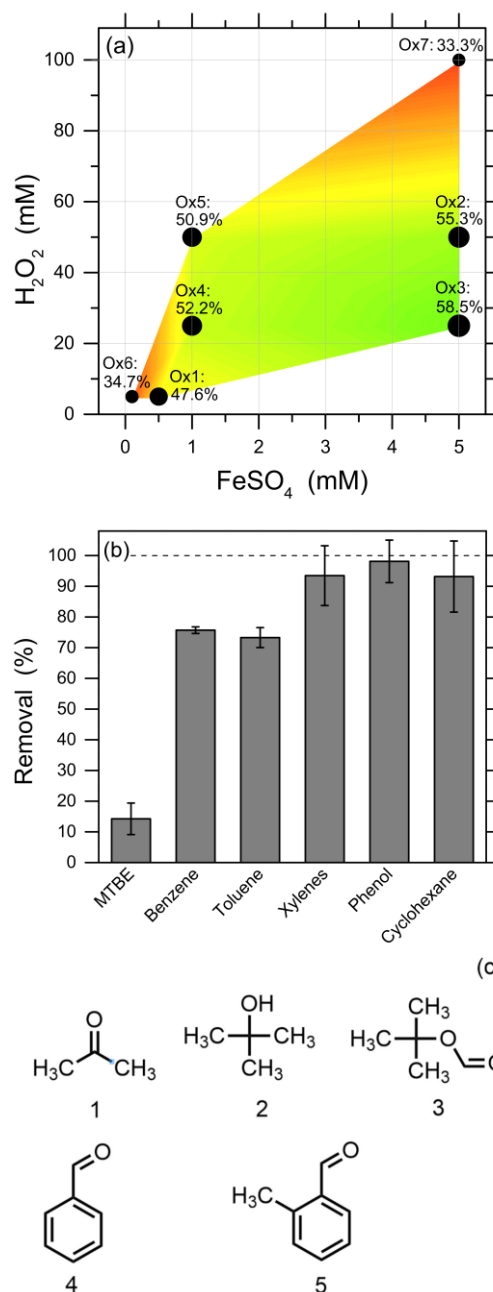
259 3. Results and Discussion

260 3.1. Efficacy of thermal Fenton oxidation on organics removal

261 **Table 3** and **Figure 1a** summarize the results of the Fenton oxidations in terms of TOC
262 removal and surface tension (ST) values, as a function of the relative addition of iron(II) and
263 H₂O₂. The highest TOC removal rates were obtained with Fe/H₂O₂ ratios between 0.02 and
264 0.2. At low iron dosage (≤ 0.5 mM, Ox1, Ox6), insufficient catalyst was available in solution,
265 while at high reagent concentrations (Ox7), the reaction was possibly self-inhibited. Previous
266 studies highlighted that a Fe/H₂O₂ molar ratio around 0.02 should avoid self-inhibition
267 reactions while providing high efficiency of oxidation (De Laat and Gallard, 1999; Voelker
268 and Sulzberger, 1996). Oxidation 3 (Ox3) reached the highest percentage of TOC removal,
269 coinciding with the largest dosage of FeSO₄ (5 mM) and a Fe/H₂O₂ ratio of 0.2. However,
270 Ox4 also achieved a high percentage of TOC removal, but with a substantially lower amount
271 of iron(II), namely, 1 mM, corresponding to a Fe/H₂O₂ ratio of 0.04. These conditions also
272 allowed reaching the highest value of ST (69 ± 3.1 dyn/cm), close to the ST measured for
273 pure water (72 ± 1.8 dyn/cm) and substantially higher than that of the PW (50.8 ± 2.7
274 dyn/cm). Ox4 was thus identified as the most promising oxidation and further tests were
275 conducted using the matrix oxidized under this condition.

276 **Table 3** Resulting TOC removal rates, and surface tension values of the oxidized matrix in
277 tests operated at different oxidation conditions.

Entry	TOC removal (%)	Surface tension (dyn/cm)
Type I H ₂ O	-	72.0 ± 1.8
Produced water	-	50.8 ± 2.7
Ox 1	47.6 ± 0.5	67.8 ± 1.6
Ox 2	55.3 ± 1.3	63.5 ± 1.8
Ox 3	58.5 ± 2.2	60.1 ± 2.3
Ox 4	52.2 ± 2.4	69.5 ± 3.1
Ox 5	50.9 ± 1.7	54.2 ± 2.1
Ox 6	34.7 ± 2.1	68.6 ± 2.0
Ox 7	33.3 ± 2.3	59.3 ± 1.7



278

279 **Figure 1.** (a) Graphical representation of the relationship between TOC removal and reagent
 280 dosage. The green color represents higher values of TOC removal. (b) Percentage of
 281 degradation of the parent organic contaminants in the synthetic produced water after Fenton
 282 reaction (Ox4, 60 min). The percentage of degradation was obtained by computing the target
 283 peaks area detected by GC-MS. (c) Chemical structures of the residual by-products
 284 preconcentrated onto the fiber during the SPME extraction and detected by GC-MS at the end
 285 of the Fenton reaction (Ox4, 60 min).

286 The solution obtained after Fenton oxidation Ox4 was further characterized through GC-
287 MS analysis. Figure S3 in the SM presents the chromatograms and the profile of target
288 substance degradation observed after 20, 40, and 60 min of oxidation. **Figure 1b** summarizes
289 the degradation efficiency after 60 min toward various organic contaminants. A near total
290 degradation of phenol, xylenes, and cyclohexane was observed. The oxidation process
291 degraded benzene and toluene with a yield around 75%. However, only a portion of MTBE
292 was degraded, and this result may also explain the residual TOC after Ox4 (see **Table 3**).
293 Indeed, MTBE contributes to a large part of the total TOC of the synthetic PW (see **Table 1**).
294 The major challenge for the high efficacy of the Fenton reaction in a hypersaline PW is
295 arguably the ability of humic acids and chloride to scavenge the hydroxyl radical (Goldstone
296 et al., 2002; Kiwi et al., 2000), although humic acids may also favor the Fe(III)-Fe(II)
297 recycling (Vione et al., 2004). Nevertheless, the observed TOC removal rates and the yield of
298 degradation of target parent substances suggest the high potential of the Fenton reaction to
299 reach suitable levels of decontamination, also in the presence of a significant amount of
300 scavengers.

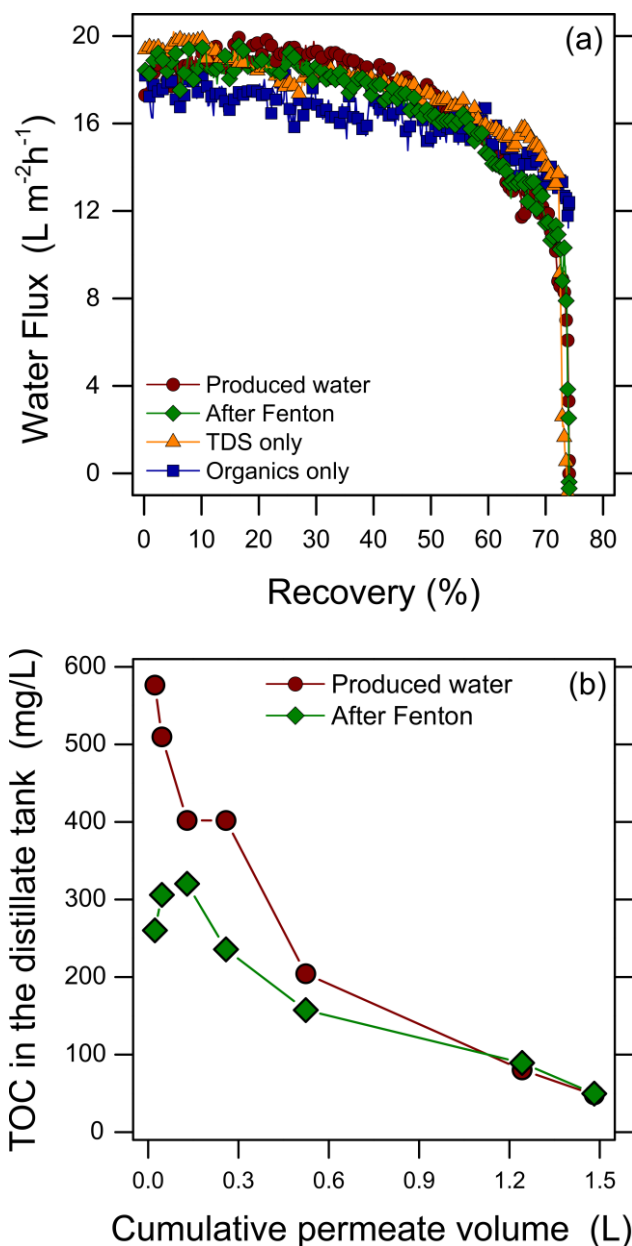
301 The GC-MS also allowed detection of the main volatile by-products of the Fenton process
302 (**Figure 1c**). Based on the molecular structure, the compounds labeled as 1, 2 and 3 in **Figure**
303 **1c** reasonably derived from MTBE, while 4 and 5 likely derived from toluene and o-xylene,
304 respectively. Note that the identified by-products were more hydrophilic than the starting
305 contaminants, thus explaining the observed increase in ST. The relatively high percentage of
306 TOC removal together with the formation of more hydrophilic by-products are promising
307 conditions to obtain an improved feed solution of an MD step.

308

309 *3.2.Evaluation of thermal Fenton oxidation as a pre-treatment for membrane distillation*

310 Organic compounds in the feed matrix may affect the MD step by fouling and by wetting
311 the membrane, hence lowering the desalination efficiency, or by freely passing through the
312 hydrophobic membrane material (PTFE) (Pasternak and Kolwzan, 2013; Vesterkvist et al.,
313 2012). Wetting is theoretically described by eq. 1 and experimentally observed with an
314 increase of conductivity in the distillate stream of the MD step (Donaldson et al., 1969;
315 Rezaei et al., 2017). The water flux values presented in **Figure 2a** suggest that the Fenton
316 pre-treatment did not have an effect on the productivity or on the achievable recovery of the
317 MD step under laboratory filtration conditions: the recovery was roughly 75%, upon which
318 the water flux went to zero due to scaling (namely, the deposition of crystals on the
319 membrane or within its pores) and pore blockage. Note that similar productivity was also
320 observed when synthetic PW matrices containing solely salts or solely organics were used as
321 the feed solutions. In the latter case the flux did not go to zero, due to the absence of salt
322 precipitation, but it steadily decreased during the test possibly due to fouling phenomena. The
323 fouling phenomena in MD are mostly governed by hydrophobic interactions between organic
324 compounds and the MD membrane material (PTFE). These interactions cause the deposition
325 and attachment of macromolecules on the membrane surface, thus impairing the MD process
326 by influencing the behavior of water at the membrane/solution interface and by partly
327 covering the surface pores (Horseman et al., 2021b). Increased conductivity of the distillate
328 solution was measured beginning roughly at 50% recovery for the various feed streams,
329 except that containing only organic compounds; see Figure S4 of the SM. This result suggests
330 that in our study salt passage and possibly wetting were mostly imputable to high salt
331 concentrations, with organics only associated with fouling mechanisms. Salts can crystallize
332 within the pores of the membrane, enlarging them, hence lowering the LEP. Since wetting is
333 observed when the transmembrane pressure overcomes the LEP, the lower is the LEP, the

334 lower is the transmembrane pressure needed to let unpurified liquid water freely pass across
335 the membrane.



336

337 **Figure 2** (a) Results of MD filtration tests with different feed solutions: (red circles) synthetic
338 produced water, (blue squares) only the organic content of the synthetic produced water,
339 (orange triangles) only the TDS content of the synthetic produced water, and (green
340 diamonds) the resulting feed after the thermal Fenton oxidation. (b) TOC concentration in the
341 distillate tank (initial volume 1 L) as a function of cumulative permeated volume; the lines
342 connecting the data points are only intended as guides for the eye.

343 The only organic compounds in the synthetic PW which may induce wetting were humic
344 acids (HA) and the water-miscible compounds (WMC), namely, BTX, MTBE, phenol, and
345 cyclohexane. HA are amphiphilic and may partly act as surfactants, which tend to create
346 liquid water channels through the pores of the membrane (Horseman et al., 2021b); however,
347 they do not present a clear separation between the hydrophobic and hydrophilic portion of the
348 molecule, and can virtually maintain a repulsive behavior for liquid water after the interaction
349 with the hydrophobic membrane. This can result in fouling, but not necessarily in wetting
350 (Horseman et al., 2021a; Klavins and Purmalis, 2010; Wang et al., 2018). This observation
351 has been rationalized with the generally high aromatic fraction of typical HA molecules, with
352 low-density hydrophilic functional groups. On the other hand, WMC may induce wetting by
353 lowering the ST of the solution. A solution containing hydrophobic WMC may be
354 characterized by a lower ST than pure water (see **Table 3**). As LEP is correlated to the ST of
355 the solution (see Eq. 2), it decreases as ST decreases, with higher chances of wetting.
356 However, since no wetting from organic compounds was detected in this study, it is
357 reasonable to assume that the ST threshold needed to observe wetting under the condition of
358 this study was lower than the ST value of the synthetic PW (50.8 ± 2.7 dyn/cm). The fact that
359 organic fouling did not cause wetting may be rationalized with the short duration of the lab
360 experiments, which were run for approximately 8 h before the observed drop in water flux
361 due to scaling. The slow kinetics of fouling phenomena in such a system may require longer
362 filtration times to show wetting effects and should become important at real scale during
363 operation. Note that paraffins form a different phase, hence they cannot lower the ST of the
364 solution or create water bridges within the membrane pores, but only freely pass through the
365 PTFE membrane by virtue of their hydrophobic nature.

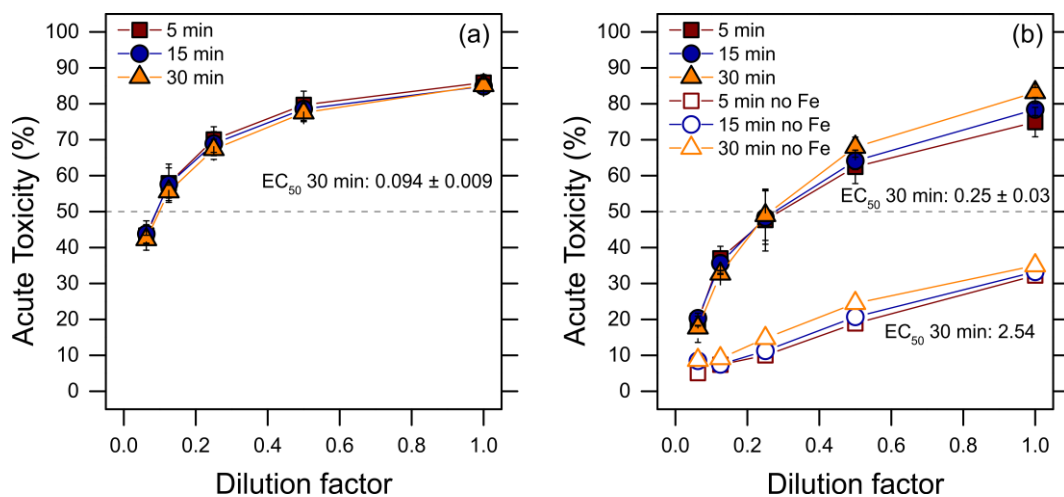
366 While the Fenton pre-treatment did not provide specific advantages in terms of
367 productivity, which was governed by salt concentration and partly affected by fouling, or of

368 prevention of wetting, which was not observed even for the use of untreated PW as feed
369 stream, oxidation had beneficial effect in terms of MD effluent quality and toxicity. The
370 results in **Figure 2b** suggest a clear reduction of the TOC in the distillate when desalinating
371 the feed matrix subject to Fenton reaction; see Figure S5 of the SM for the chromatograms of
372 the final effluent treated only in MD and by the coupled Fenton-MD system. As expected, the
373 MD process did not separate water from volatile WMC or non-aqueous oils. The first data
374 points in **Figure 2b** showed a high TOC passage, justifiable considering an instantaneous
375 passage of a fraction of the organic content, specifically, paraffins and WMC. Subsequently,
376 the TOC in the distillate tank decreased steadily by dilution with the nearly pure water vapor
377 permeating the membrane. The lower amount of TOC measured upon oxidation of the feed
378 stream with Fenton is imputable to both the mineralization of a fraction of toxic compounds
379 (~52% of mineralization, **Table 3**) and the transformation of organic substances to more
380 hydrophilic compounds, which are less prone to pass through the hydrophobic membrane.
381 Fenton oxidation may also provide beneficial effects in terms of MD performance at real
382 scale by thwarting fouling phenomena that would occur at longer time scales, but this effect
383 could not be observed in this study (Abdel-Karim et al., 2021; Siyal et al., 2017).

384 *3.3.Effect of the coupled system on the toxicity of the final effluent*

385 A general index of the safety of an effluent is its toxicity. Toxicity is also a legislated
386 parameter, allowing or denying the discharge of an effluent in the sewage system. According
387 to the Italian regulations (D.Lgs. 152/2006), the acute toxicity limit to discharge an effluent
388 in the sewage system is 80% of the inhibition of the target microorganism (in this case,
389 *Vibrio fischeri*). The synthetic PW of this study presented an acute toxicity around 100%
390 (Figure S6a of the SM), a value also expected for most of the real PW due to the wide variety
391 and large concentrations of contaminants typically present. Both organics and concentrated
392 salts may present large toxic effects, hence they both require a specific treatment. **Figure 3**

393 presents the residual acute toxicity of the effluent treated with only MD and with the coupled
 394 Fenton-MD system, expressed in term of dilution factor of the original samples. The EC_{50}
 395 value was used as a comparative parameter of the quality of different effluents, and it is
 396 defined as the half maximal effective concentration, namely, the concentration required to
 397 obtain 50% of microorganism inhibition. Therefore, the higher the EC_{50} value, the lower the
 398 toxicity. EC_{50} increased significantly (from a dilution factor of 0.094 ± 0.009 to 0.25 ± 0.03)
 399 when the effluent was oxidized and then desalinated, compared to a stream that was not pre-
 400 treated, i.e., the coupled system gave lower toxicity. However, when tested as is, the residual
 401 toxicity of the effluent was still high and over the limit of 80% after 30 min of contact time
 402 with the bacteria.



403
 404 **Figure 3.** Residual toxicity of the effluent expressed in term of dilution factor of the original
 405 sample (a) after MD treatment only, and (b) upon treatment by the coupled Fenton-MD
 406 system (solid data points) with and (empty data points) without Fe sequestration. The toxicity
 407 was measured after 5, 15, and 30 minutes of contact (in red, blue, and orange, respectively)
 408 with the *Vibrio fischeri* culture. The dash line indicates the point where 50% of acute toxicity
 409 is reached.

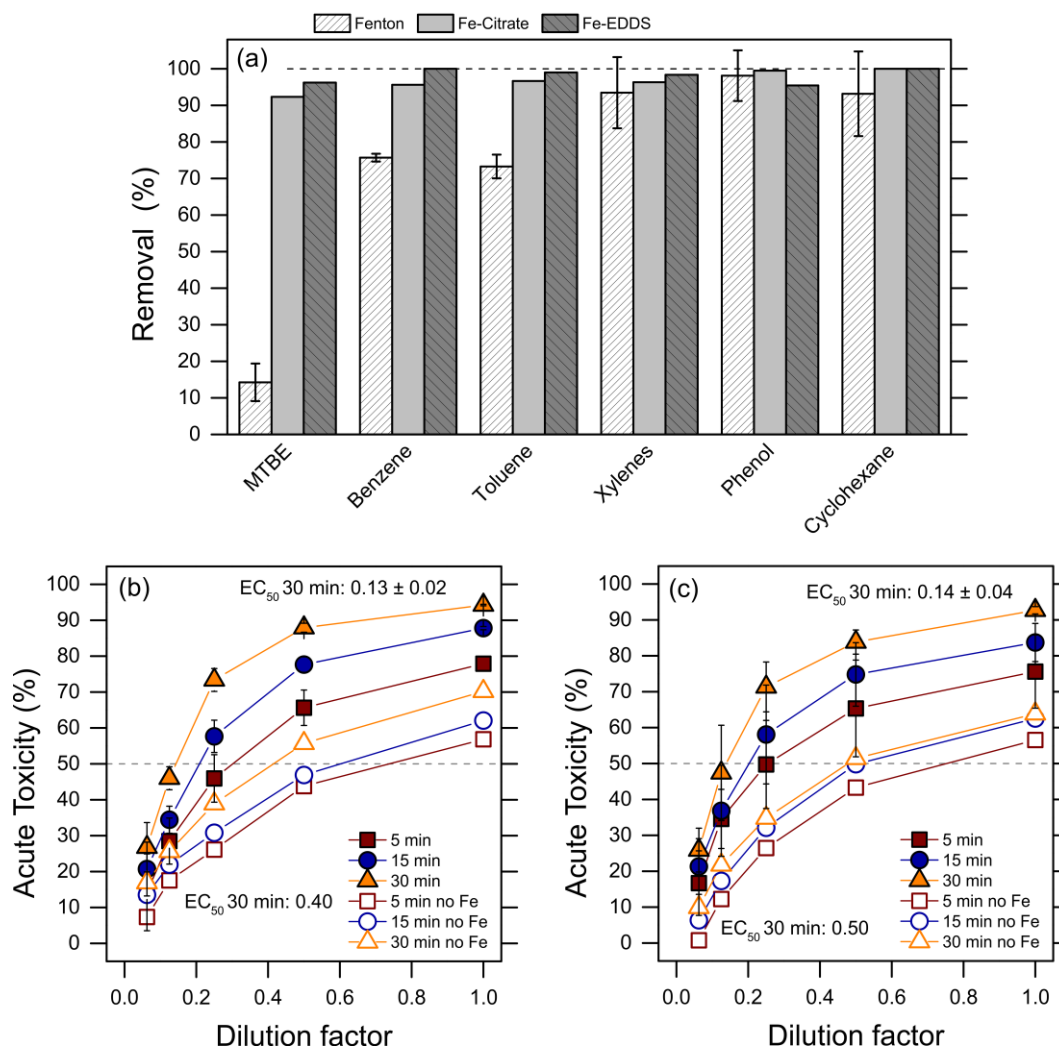
410

411 To understand the relative contribution to toxicity of the different contaminants, toxicity
412 experiments were carried out with individual components (Figures S6 and S7 of the SM).
413 Low toxicity was associated with HA and paraffins, while higher toxic effects were related to
414 parent WMC, which however were degraded effectively by Fenton. CaCl_2 and MgCl_2 also
415 showed negligible toxicity, while NaCl showed some toxicity only at concentrations >50 g/L,
416 that is, far above the concentration measured after MD desalination. On the other hand,
417 $\text{Fe}^{\text{II}}\text{SO}_4$ showed significant toxicity: residual iron may thus be responsible for the toxicity
418 observed for the effluent from Fenton and MD treatments. However, by addition of EDDS in
419 molar ratio 1:1 to residual iron (0.26 mM), the acute toxicity of iron was shut down (see
420 Figure S2 and S7 in SM for the toxicity of Fe-EDDS and iron, respectively) and that of the
421 effluent markedly decreased (from $\sim 80\%$ to $\sim 40\%$), with a substantial increase in EC_{50} (from
422 a dilution factor of 0.25 ± 0.03 to ~ 2.5). Remaining toxicity after this post-treatment step may
423 be reasonably attributed to the residual WMC and to the by-products of Fenton oxidation.
424 Note that in this study EDDS was added to mask the toxic behavior of residual iron, which
425 confirms that residual metal concentration causes toxicity in the effluent. Different strategies
426 to remove residual iron may be implemented in real plants, for example, its precipitation at
427 basic pH. Cleaner and more novel steps may involve enhanced ion exchange resins and the
428 use of adsorbents, such as magnetic nanoparticles (Khatri et al., 2017).

429 *3.4. Comparison between traditional Fenton and Fenton process with iron ligands*

430 Iron ligands keep iron in solution without the need for pH adjustment to 3 and limit the
431 production of sludge, thus potentially allowing for a more streamlined operation compared to
432 the traditional Fenton process. Citrate and EDDS were chosen as non-toxic (Figure S2 of the
433 SM) ligands and the Fe-citrate and Fe-EDDS systems were applied as catalysts (Zhang et al.,
434 2016). The optimized condition in terms of Fe-ligand to H_2O_2 molar ratio corresponded to the
435 dosages relative to Ox7 in **Table 2**; each ligand was dosed equimolarly with iron. The results

436 summarized in **Figure 4a** suggest higher degradation efficiency of the modified Fenton
 437 systems toward WMC with respect to the traditional thermal Fenton.



438
 439 **Figure 4** (a) Comparison of the organics removal rate by traditional Fenton and modified
 440 Fenton reactions with citrate and EDDS as iron ligands. Residual toxicity of the final effluent
 441 treated by the coupled system comprising modified-Fenton and MD using (b) Fe-citrate and
 442 (c) Fe-EDDS as catalyst. The open symbols are related to the effluent upon iron sequestration
 443 by EDDS. The toxicity was measured after 5, 15, and 30 minutes of contact with the *Vibrio*
 444 *fischeri* culture. The dash horizontal line indicates the point where 50% of acute toxicity is
 445 reached; the lines connecting the data points are only intended as guides for the eye.

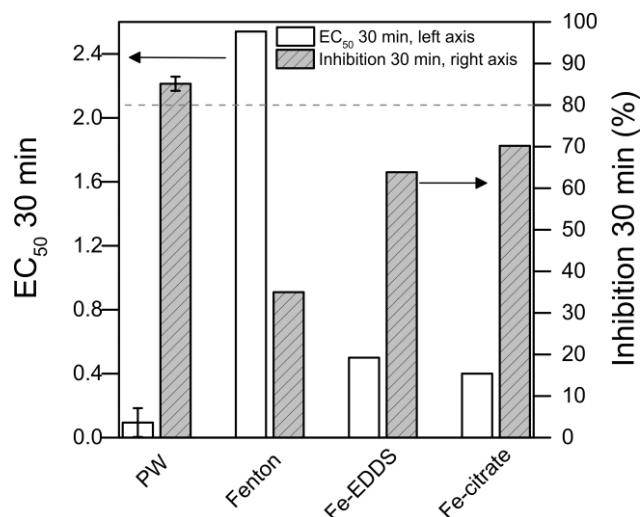
446

447 Specifically, the modified Fenton processes achieved near complete degradation of all
448 WMC, including MTBE that was instead not removed by the classic Fenton reaction; see also
449 the chromatograms and percentage of substrates removal at different oxidation times in
450 Figures S8, S9, and S10 (SM).

451 Despite the higher percentage of degradation of the target contaminants, the modified
452 Fenton reaction did not show further beneficial effect on the MD process in terms of
453 productivity and effluent quality compared to traditional Fenton; see Figure S11 of the SM.
454 With regard to EC_{50} , the quality of the effluent treated with the coupled system including
455 modified Fenton and MD clearly increased compared to the PW treated only with MD,
456 specifically, from a dilution factor of 0.094 ± 0.009 to 0.13 ± 0.02 and to 0.14 ± 0.04 in the
457 case of Fe-citrate and Fe-EDDS, respectively (see **Figure 4b and c**). However, the EC_{50} was
458 lower compared with the residual toxicity observed in the system that included the traditional
459 Fenton oxidation (0.25 ± 0.03), possibly due to the formation of more toxic by-products, e.g.,
460 N-(2-aminoethyl) aspartic acid (Zhang et al., 2016). When the contribution to toxicity of the
461 residual iron (residual iron was 0.27 and 1.30 mM for Fe-citrate and Fe-EDDS, respectively)
462 was prevented by EDDS addition, the acute toxicity of the effluent clearly decreased (from
463 ~90% to ~70% in both cases) and the EC_{50} further increased (to 0.4 and 0.5 for Fe-citrate and
464 Fe-EDDS, respectively). At the end of the process, the effluent treated with the Fe-EDDS-
465 based Fenton system presented a slightly better quality in terms of toxicity than that treated
466 with the Fe-citrate system, consistently with the slightly higher degradation efficiency of the
467 former compared to the latter.

468 **Figure 5** offers a final evaluation of the toxicity parameters from the various treatments.
469 The traditional Fenton coupled with the MD desalination was the best in terms of effluent
470 toxicity. However, the modified Fenton-MD coupled systems were able to overcome some of
471 the practical limitations of the traditional Fenton while still providing an effluent with

472 suitable quality for safe discharge as sewage (toxicity <80%). The modified Fenton oxidation
473 may be more advisable for applications whereby easier operational tasks and lower sludge
474 production are important, such as offshore.



475
476 **Figure 5** Summary of the residual toxicity and EC₅₀ values of the various effluents treated
477 with both MD and oxidation processes after 30 minutes of contact with the *Vibrio fischeri*
478 culture. The dash line is relative to the value of 80% of acute toxicity, namely, the regulated
479 legislative limit for safe discharge into the sewage system in Italy.

480

481 **4. Concluding remarks, challenges, and implications**

482 This work evaluated the impact of traditional and modified Fenton oxidations for the
483 abatement of highly toxic organic contaminants and as pre-treatment options for the
484 subsequent desalination of hypersaline produced waters by membrane distillation. Fe-citrate
485 and Fe-EDDS were used as inexpensive, easy to handle, environmentally friendly and
486 biodegradable systems in the modified Fenton processes. All the oxidative processes
487 provided relatively high degradation efficiency toward target contaminants also in the
488 presence of typical scavengers of the Fenton reaction, namely, chloride and humic acids. The
489 observable beneficial effects of an oxidative pre-treatment were not evident in terms of MD

490 productivity, fouling, or wetting, but directly translated into lower permeation of organics
491 during distillation and in a significantly lower toxicity of the desalinated effluent.
492 Specifically, the EC₅₀ and the acute toxicity (inhibition % of target organisms) were used as
493 indexes for the evaluation of the quality of the final effluent.

494 In conclusion, the coupled oxidation-MD systems to treat PW allow a much less toxic
495 effluent compared to the initial PW toxicity. All the final effluents obtained in this study may
496 be safely discharged in the sewage system and treated within the civil wastewater treatment
497 trains, according to the Italian legislation. The oxidation processes are promising for PW
498 treatments since they are able to degrade the toxic initial target contaminants almost
499 completely. Moreover, the modified Fenton process is able to effectively treat PW while
500 overcoming the practical limitations of traditional Fenton (sludge production and acidic pH).
501 The Fenton processes add iron in the effluent environment, this metal being associated with
502 intrinsic toxicity; thus, the toxicity associated with the residual iron needs to be properly
503 addressed and managed in real plants. A wide range of options are available to remove iron
504 and the best-fitting one should be selected case-by-case. Moreover, the oxidations struggle in
505 achieving complete mineralization of all the organics in PW, thus some potentially toxic by-
506 products may be formed. Therefore, an accurate monitoring of the by-products may be
507 necessary, possibly also enforcing some control on the reaction pathway, to evaluate in each
508 case the possibility to safely discharge the final effluent to a civil wastewater treatment plant
509 and in case to specifically target the most troublesome by-products in a tertiary treatment
510 step.

511

512 **CRedit authorship contribution statement**

513 **Giulio Farinelli:** Conceptualization, Data curation, Formal analysis, Investigation,
514 Methodology, Visualization, Writing - original draft. **Marco Coha:** Data Curation, Formal
515 analysis, Investigation, Methodology, Visualization, Writing - review & editing. **Marco**
516 **Minella:** Data curation, Validation, Methodology, Writing - review & editing. **Debora**
517 **Fabbri:** Resources, Supervision, Writing - review & editing. **Marco Pazzi:** Formal analysis,
518 Methodology. **Davide Vione:** Resources, Supervision, Writing - review & editing. **Alberto**
519 **Tirafferri:** Funding acquisition, Project administration, Resources, Supervision,
520 Visualization, Writing - review & editing.

521

522 **Declaration of Competing Interest**

523 The authors declare no competing financial interest.

524

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528

529 **Appendix A. Supplementary data.**

530 Supplementary material related to this article can be found, in the online version.

531

532

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