

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

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Evaluation of Fenton and modified Fenton oxidation coupled with membrane distillation for produced water treatment: Benefits, challenges, and effluent toxicity / Farinelli, G.; Cocha, M.; Minella, M.; Fabbri, D.; Pazzi, M.; Vione, D.; Tiraferri, A.. - In: SCIENCE OF THE TOTAL ENVIRONMENT. - ISSN 0048-9697. - 796:(2021), p. 148953.  
[10.1016/j.scitotenv.2021.148953]

*Availability:*

This version is available at: 11583/2915972 since: 2021-07-30T11:04:17Z

*Publisher:*

Elsevier B.V.

*Published*

DOI:10.1016/j.scitotenv.2021.148953

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

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19

20 **ABSTRACT**

21 Membrane distillation is a promising technology to desalinate hypersaline produced waters.  
22 However, the organic content can foul and wet the membrane, while some fractions may pass  
23 into the distillate and impair its quality. In this study, the applicability of the traditional  
24 Fenton process was investigated and preliminarily optimized as a pre-treatment of a synthetic  
25 hypersaline produced water for the following step of membrane distillation. The Fenton  
26 process was also compared to a modified Fenton system, whereby safe iron ligands, i.e.,  
27 ethylenediamine-N,N'-disuccinate and citrate, were used to overcome practical limitations of  
28 the traditional reaction. The oxidation pre-treatments achieved up to 55% removal of the  
29 dissolved organic carbon and almost complete degradation of the low molecular weight toxic  
30 organic contaminants. The pre-treatment steps did not improve the productivity of the  
31 membrane distillation process, but they allowed for obtaining a final effluent with  
32 significantly higher quality in terms of organic content and reduced *Vibrio fischeri* inhibition,  
33 with EC<sub>50</sub> values up to 25 times those measured for the raw produced water. The addition of  
34 iron ligands during the oxidation step simplified the process, but resulted in an effluent of  
35 slightly lower quality in terms of toxicity compared to the use of traditional Fenton.

36

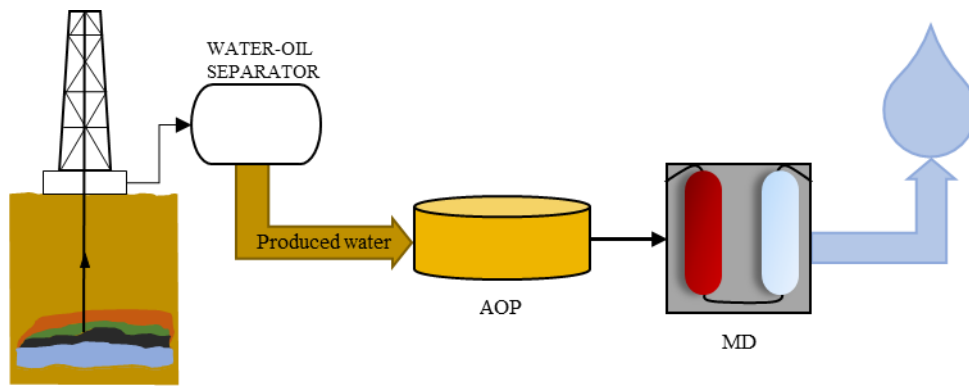
37 **Keywords:** membrane distillation; produced water; advanced oxidation; iron ligands;  
38 ecotoxicity

39 **HIGHLIGHTS**

- 40 • Thermal and modified Fenton degraded target contaminants in produced water.
- 41 • The oxidative pre-treatment reduced organics in the membrane distillation effluent.
- 42 • Coupled oxidation and membrane distillation reduced 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 around 150 million to around 300 million barrels per day from  
56 1990 to 2015 (Ahmadun et al. 2009; Liu et al. 2021). The average water cut, namely, the  
57 amount of water volume produced per oil volume, is roughly 3:1 (McCormack et al. 2001;  
58 Ahmadun et al. 2009; Jimenez et al. 2018; Liu et al. 2021). 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 produced (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) (Neff et  
66 al. 1992; Ahmadun et al. 2009; Estrada and Bhamidimarri 2016; Jimenez et al. 2018; Al-  
67 Ghouti et al. 2019; Kabyl et al. 2020; Cocha et al. 2021; Liu et al. 2021).

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; Mohammad-  
75 Pajoo et al. 2018; Liu et al. 2021). 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 (Kabyl et al. 2020; Liu et al. 2021).

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

$$98 \quad \Delta P \geq LEP \quad (1)$$

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

$$100 \quad LEP = -\frac{2B\gamma\cos\theta}{r} \quad (2)$$

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

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



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



126 The Fenton process is a promising candidate to treat PW both onshore and offshore since it is  
127 versatile, characterized by high kinetics also at room temperature and capable to remove  
128 organics from a multi-contaminated matrix. This method has some limitations, mainly the  
129 need for acidic pH to avoid iron hydroxide precipitation, and the production of sludge once  
130 neutral pH is restored (Diya'uddeen et al. 2012). A modified Fenton process encompassing  
131 the addition of an iron ligand helps overcoming these precise challenges (Chahbane et al.  
132 2007; Farinelli et al. 2019; Messele et al. 2019; Farinelli et al. 2020). However, the literature  
133 lacks reports about the application of Fenton processes carried out in presence of iron ligands  
134 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 (Van Devivere et al. 2001; Tandy et al. 2006; Chen et al. 2019). The

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

## 149 **2. Materials and Methods**

### 150 *2.1. Chemicals, membrane, and produced water preparation*

151 All the organic contaminants, the iron ligands, i.e., sodium citrate and EDDS, ferrous  
152 sulfate (FeSO<sub>4</sub>), hydrogen peroxide (30% w/w), HCl, and NaOH, were purchased from  
153 Sigma-Aldrich (Milan, Italy). Sodium chloride, sodium sulfate, and sodium bicarbonate were  
154 acquired from Carlo Erba (Milan, Italy). All the solutions needed for the acute toxicity  
155 analysis, namely, the reconstitution, the diluent, and the osmotic solutions were purchased  
156 from Modern Water (London, UK). The freeze-dried *Vibrio fischeri* culture was purchased  
157 from Ecotox LDS (Cornaredo (MI), Italy). Type I ultrapure water was used for the  
158 experiments. A commercially available polytetrafluoroethylene (PTFE) membrane (Aquistill,  
159 Sittard, Netherlands) was deployed in MD filtration tests.

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

170 chlorides. All the components were added into water and the matrix was sonicated at room  
 171 temperature for 1 h to enhance solubilization and mixing.

172

173 **Table 1** Composition of the synthetic produced water, compared with the reference real  
 174 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	Not dissolved	Maximum ~500
	Humic acids	200	60	
	Cyclohexane	2	1.8	
	Phenol	2.5	1.9	
	Xylenes	1	1	
	Benzene	12	11.3	
	Toluene	4	3.4	
	MTBE	260	178	
	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

175

## 176 2.2. Oxidation conditions

177 All the oxidation reactions were performed at room temperature under gentle stirring for a  
 178 total duration of 1 h, using different ratios of hydrogen peroxide and catalyst, intended as  
 179 iron(II) in the case of the traditional Fenton process and as the complex ligand-iron(II) in the  
 180 case of modified Fenton. To promote organics oxidation, three additions of hydrogen  
 181 peroxide (0, 20, 40 min) were carried out, each one of a 1/3 aliquot of the desired total  
 182 amount. The dosages of iron sulfate and hydrogen peroxide are listed in **Table 2** for the  
 183 traditional Fenton system; in these cases, the pH of the synthetic PW was adjusted to ~3  
 184 (HCl). At the end of the reaction, the pH was increased to ~10 by addition of NaOH and this

185 step caused the precipitation of  $\text{Fe}(\text{OH})_3$ . After the sedimentation of the precipitate at 4 °C  
186 overnight, the supernatant was collected and used for analysis and as a feed matrix for the  
187 following MD filtration tests.

188

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

Entry	$\text{FeSO}_4$ (mM)	$\text{H}_2\text{O}_2$ (mM)
MQ $\text{H}_2\text{O}$	-	-
Produced water	-	-
Ox 1	0.5	5
Ox 2	5	50
Ox 3	5	25
Ox 4	1	25
Ox 5	1	50
Ox 6	0.1	5
Ox 7	5	100

190

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

### 197 2.3. Membrane distillation tests

198 The MD tests were performed in direct contact configuration using a lab-scale batch  
199 system (Ricceri et al. 2019). The feed and distillate streams were circulated counter-currently  
200 on their respective sides of the membrane. A constant crossflow rate of 1.66 L/min (0.278  
201 m/s crossflow velocity) was maintained during the tests. The housing cell comprised a 250-  
202 mm long, 50-mm wide, and 2-mm deep rectangular channel for a total active membrane area  
203 of 125  $\text{cm}^2$ . The flux across the membrane was computed by recording the change in weight

204 of the distillate tank in time through a computer-interfaced balance. Initial volumes of ~1.9 L  
205 and 1 L were used for the feed and distillate streams, respectively, unless otherwise stated.  
206 Water was used in the distillate side, with specific conductivity always below 20  $\mu\text{S}/\text{cm}$ . The  
207 specific conductivity in the distillate tank was measured continuously during each test by a  
208 conductivity meter (COND 7+, XS Instruments, Italy). The temperature of the feed and  
209 distillate tanks were maintained constant throughout the experiments, at respective values of  
210  $50 \pm 2$  and  $25 \pm 1$   $^{\circ}\text{C}$ , by means of a thermostatic water bath and a chiller.

#### 211 2.4. Analytical methods

212 The TOC of the matrices was measured using a Shimadzu TOC-L analyzer (catalytic  
213 oxidation on Pt at 680  $^{\circ}\text{C}$ ). The calibration was performed using standards of potassium  
214 phthalate,  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ . The headspace, solid phase microextraction technique (HS-  
215 SPME) was chosen as extraction method before carrying out the GC-MS analysis. Following  
216 each reaction experiment, the vials were left in a thermostatic bath at 50  $^{\circ}\text{C}$  for 10 min to  
217 promote the transfer of all the relevant compounds into the gas-phase headspace. Then, a  
218 SPME fiber (df 75  $\mu\text{m}$ , fiber assembly carboxen/polydimethylsiloxane, Supelco) was inserted  
219 through the septum of the cap and was left in the headspace for 10 min, before withdrawing it  
220 for the subsequent GC-MS analysis. Samples were analyzed on an Agilent 6890 GC system  
221 coupled with an Agilent 5973 mass selective detector (MSD). For the chromatographic  
222 separation, a Zebron-5MS capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ) was used. The  
223 injection port temperature was 270  $^{\circ}\text{C}$ , and the oven temperature program was set as follows:  
224 35 $^{\circ}\text{C}$  for 5 min, followed by an increase to 260  $^{\circ}\text{C}$  at a rate of 15  $^{\circ}\text{C}/\text{min}$  (total run time 25.33  
225 min). Helium was used as carrier gas at a constant flow of 1 mL/min, and the injector was  
226 held in splitless mode. The interface temperature was 270  $^{\circ}\text{C}$  and the ionization energy was  
227 70 eV. The molecular structures of the by-products were identified by means of mass  
228 spectrum library.

229 The determination of the residual iron in solution was evaluated by a spectrophotometric  
230 procedure adapted from previous literature (Harvey et al. 1955; Goncalves et al. 2020). The  
231 total iron was determined by reducing the Fe(III) to Fe(II) with ascorbic acid ( $4 \times 10^{-4}$  M) and  
232 complexing the Fe(II) with o-phenanthroline ( $4 \times 10^{-3}$  M) under acidic conditions (buffer pH =  
233 3: H<sub>3</sub>PO<sub>4</sub> 1 mM, NaH<sub>2</sub>PO<sub>4</sub> 3 mM). The Fe(II) was determined without performing the  
234 reduction step, and Fe(III) was obtained as the difference between total iron and Fe(II). The  
235 calibration was obtained using a commercial standard solution of Fe(III) (1000 mg<sup>Fe</sup>/L,  
236 Sigma-Aldrich). The spectrophotometric analyses were performed using a Varian CARY 100  
237 Scan double-beam UV–vis spectrophotometer, using quartz cuvettes with 10 mm path length  
238 and working at a wavelength of 510 nm.

### 239 2.5. Toxicity analysis

240 All the toxicity experiments were performed with a Microtox Model 500 analyzer (Milan,  
241 Italy). The analysis was performed by evaluating the bioluminescence inhibition assay using  
242 the marine bacterium *Vibrio fischeri*. Samples were tested in a medium containing 2%  
243 sodium chloride, and the luminescence was recorded after 5, 15, and 30 min of incubation at  
244 15 °C. The luminescence inhibition percentage was determined by comparison with a non-  
245 toxic control. The toxicity curves and the values of EC<sub>50</sub> were obtained from the software  
246 (MicrotoxOmni). The pH of all the samples was adjusted in the range 6-8 before the analysis.  
247 The method used for the toxicity analysis is the method APAT-IRSA 8030 (APAT 2003). All  
248 the samples obtained at the end of the oxidation experiments were quenched with catalase in  
249 order to avoid the detrimental effect of the residual hydrogen peroxide on the toxicity  
250 measurements; see Figure S1 of the Supplementary Material (SM). Moreover, the samples  
251 after the oxidation experiments were quantified for residual iron content and EDDS was  
252 added in EDDS:Fe molar ratio of 1:1, to prevent the toxic effect of the residual iron in  
253 solution (see Figure S2 in SM).

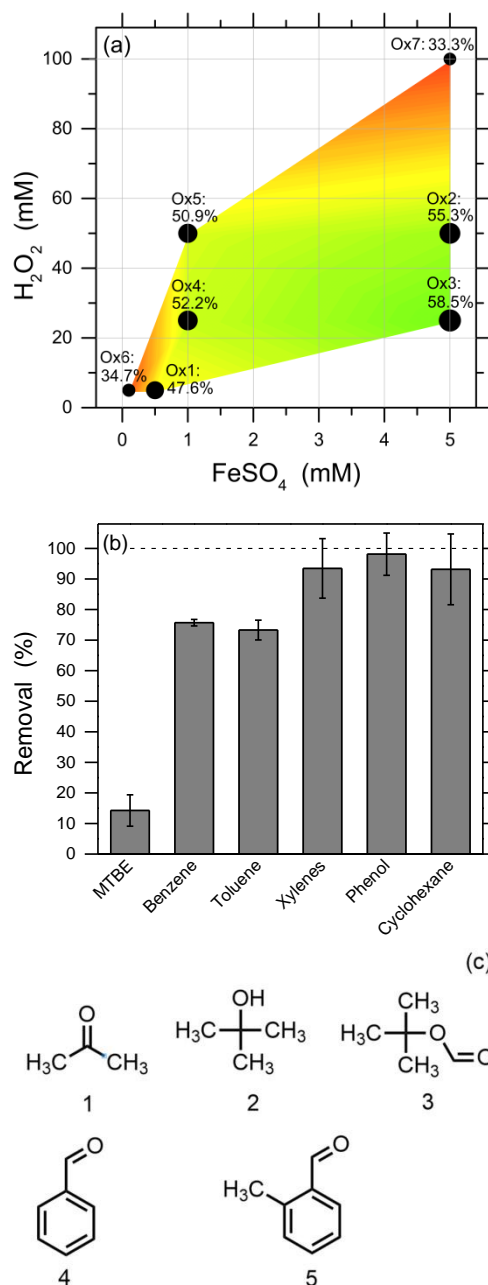
### 254 3. Results and Discussion

#### 255 3.1. Efficacy of thermal Fenton oxidation on organics removal

256 **Table 3** and **Figure 1a** summarize the results of the Fenton oxidations in terms of TOC  
257 removal and surface tension (ST) values, as a function of the relative addition of iron(II) and  
258 H<sub>2</sub>O<sub>2</sub>. The highest TOC removal rates were obtained with Fe/H<sub>2</sub>O<sub>2</sub> ratios between 0.02 and  
259 0.2. At low iron dosage ( $\leq 0.5$  mM, Ox1, Ox6), insufficient catalyst was available in solution,  
260 while at high reagent concentrations (Ox7), the reaction was possibly self-inhibited. Previous  
261 studies highlighted that a Fe/H<sub>2</sub>O<sub>2</sub> molar ratio around 0.02 should avoid self-inhibition  
262 reactions while providing high efficiency of oxidation (Voelker and Sulzberger 1996; De  
263 Laat and Gallard 1999). Oxidation 3 (Ox3) reached the highest percentage of TOC removal,  
264 coinciding with the largest dosage of FeSO<sub>4</sub> (5 mM) and a Fe/H<sub>2</sub>O<sub>2</sub> ratio of 0.2. However,  
265 Ox4 also achieved a high percentage of TOC removal, but with a substantially lower amount  
266 of iron(II), namely, 1 mM, corresponding to a Fe/H<sub>2</sub>O<sub>2</sub> ratio of 0.04. These conditions also  
267 allowed reaching the highest value of ST ( $69 \pm 3.1$  dyn/cm), close to the ST measured for  
268 pure water ( $72 \pm 1.8$  dyn/cm) and substantially higher than that of the PW ( $50.8 \pm 2.7$   
269 dyn/cm). Ox4 was thus identified as the most promising oxidation and further tests were  
270 conducted using the matrix oxidized under this condition.

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

Entry	TOC removal (%)	Surface tension (dyn/cm)
MQ H <sub>2</sub> O	-	$72 \pm 1.8$
Produced water	-	$50.8 \pm 2.7$
Ox 1	$47.6 \pm 0.5$	$67.8 \pm 1.6$
Ox 2	$55.3 \pm 1.3$	$63.5 \pm 1.8$
Ox 3	$58.5 \pm 2.2$	$60.1 \pm 2.3$
Ox 4	$52.2 \pm 2.4$	$69.5 \pm 3.1$
Ox 5	$50.9 \pm 1.7$	$54.2 \pm 2.1$
Ox 6	$34.7 \pm 2.1$	$68.6 \pm 2.0$
Ox 7	$33.3 \pm 2.3$	$59.3 \pm 1.7$



273

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



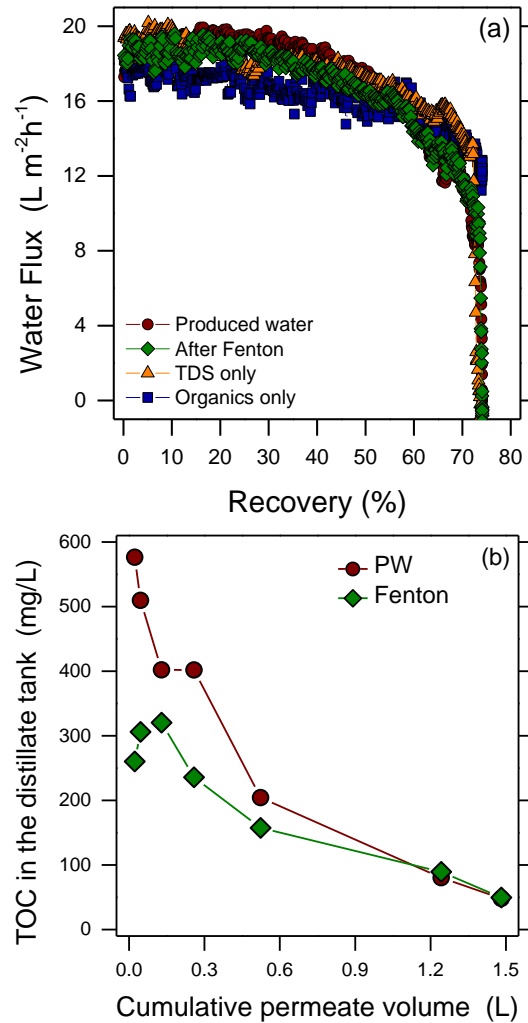
281 The solution obtained after Fenton oxidation Ox4 was further characterized through GC-  
282 MS analysis. Figure S3 in the SM presents the chromatograms and the profile of target  
283 substance degradation observed after 20, 40, and 60 min of oxidation. **Figure 1b** summarizes  
284 the degradation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

296 The GC-MS also allowed detection of the main volatile by-products of the Fenton process  
297 (**Figure 1c**). Based on the molecular structure, the compounds labeled as 1, 2 and 3 in Figure  
298 S3 reasonably derived from MTBE, while 4 and 5 likely derived from toluene and o-xylene,  
299 respectively. Note that the identified by-products were more hydrophilic than the starting  
300 contaminants, thus explaining the observed increase in ST. The relatively high percentage of  
301 TOC removal together with the formation of more hydrophilic by-products are promising  
302 conditions to obtain an improved feed solution of an MD step.

303

304 3.2. *Evaluation of thermal Fenton oxidation as a pre-treatment for membrane distillation*

305 Organic compounds in the feed matrix may affect the MD step by fouling and by wetting  
306 the membrane, hence lowering the desalination efficiency, or by freely passing through the  
307 hydrophobic membrane material (PTFE) (Vestervik et al. 2012; Pasternak and Kolwzan  
308 2013). Wetting is theoretically described by eq. 1 and experimentally observed with an  
309 increase of conductivity in the distillate stream of the MD step (Donaldson et al. 1969; Rezaei  
310 et al. 2017). The water flux values presented in **Figure 2a** suggest that the Fenton pre-  
311 treatment did not have an effect on the productivity or on the achievable recovery of the MD  
312 step under laboratory filtration conditions: the recovery was roughly 75%, upon which the  
313 water flux went to zero due to scaling (namely, the deposition of crystals on the membrane or  
314 within its pores) and pore blockage. Note that similar productivity was also observed when  
315 synthetic PW matrices containing solely salts or solely organics were used as the feed  
316 solutions. In the latter case the flux did not go to zero, due to the absence of salt precipitation,  
317 but it steadily decreased during the test possibly due to fouling phenomena. Increased  
318 conductivity of the distillate solution was measured beginning roughly at 50% recovery for  
319 the various feed streams, except that containing only organic compounds; see Figure S4 of  
320 the SM. This result suggests that in our study salt passage and possibly wetting were mostly  
321 imputable to high salt concentrations, with organics only associated with fouling  
322 mechanisms. Salts can crystallize within the pores of the membrane, enlarging them, hence  
323 lowering the LEP.



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

330

331 The only organic compounds in the synthetic PW which may induce wetting were humic  
 332 acids (HA) and the water-miscible compounds (WMC), namely, BTX, MTBE, phenol, and  
 333 cyclohexane. HA are amphiphilic and may partly act as surfactants; however, not presenting

334 a clear separation between the hydrophobic and hydrophilic portion of the molecule, they can  
335 virtually maintain a repulsive behavior for liquid water after the interaction with the  
336 hydrophobic membrane, thus resulting in fouling, but not necessarily in wetting (Klavins and  
337 Purmalis 2010; Wang et al. 2018; Horseman et al. 2021). On the other hand, WMC may  
338 induce wetting by lowering the ST of the solution. However, since no wetting from organic  
339 compounds was detected in this study, it is reasonable to assume that the ST threshold needed  
340 to observe wetting under the condition of this study was lower than the ST value of the  
341 synthetic PW ( $50.8 \pm 2.7$  dyn/cm). The fact that organic fouling did not cause wetting may be  
342 rationalized with the short duration of the lab experiments, which were run for approximately  
343 8 h before the observed drop in water flux due to scaling. The slow kinetics of fouling  
344 phenomena in such a system may require longer filtration times to show wetting effects and  
345 should become important at real scale during operation. Note that paraffins form a different  
346 phase, hence they cannot lower the ST of the solution or create water bridges within the  
347 membrane pores, but only freely pass through the PTFE membrane by virtue of their  
348 hydrophobic nature.

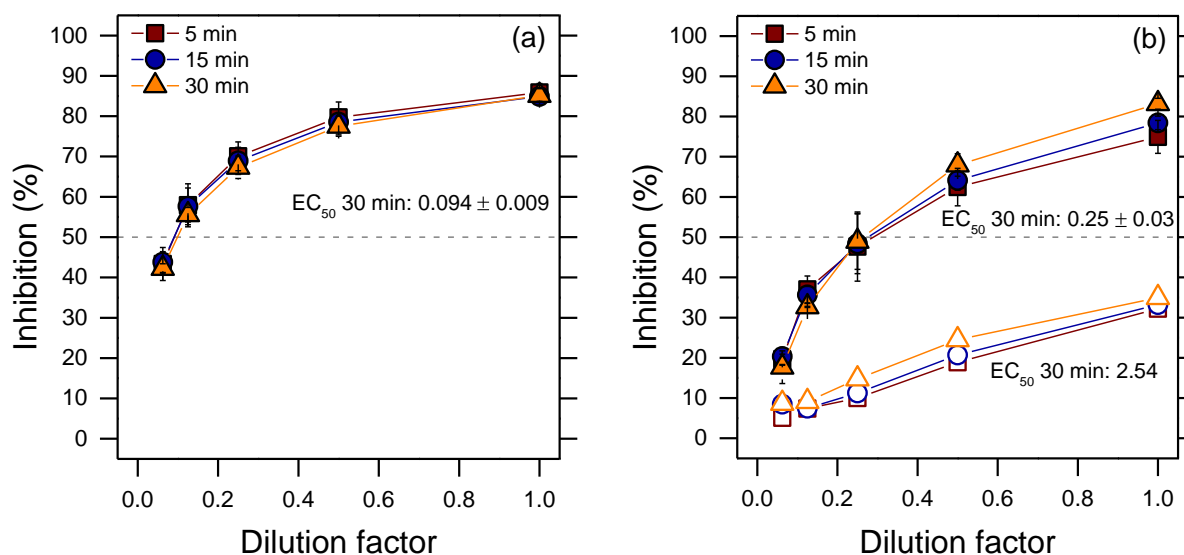
349 While the Fenton pre-treatment did not provide specific advantages in terms of  
350 productivity, which was governed by salt concentration and partly affected by fouling, or of  
351 prevention of wetting, which was not observed even for the use of untreated PW as feed  
352 stream, oxidation had beneficial effect in terms of MD effluent quality and toxicity. The  
353 results in **Figure 2b** suggest a clear reduction of the TOC in the distillate when desalinating  
354 the feed matrix subject to Fenton reaction; see Figure S5 of the SM for the chromatograms of  
355 the final effluent treated only in MD and by the coupled Fenton-MD system. As expected, the  
356 MD process did not separate water from volatile WMC or non-aqueous oils. The first data  
357 points in **Figure 2b** showed a high TOC passage, justifiable considering an instantaneous  
358 passage of a fraction of the organic content, specifically, paraffins and WMC. Subsequently,

359 the TOC in the distillate tank decreased steadily by dilution with the nearly pure water vapor  
360 permeating the membrane. The lower amount of TOC measured upon oxidation of the feed  
361 stream with Fenton is imputable to both the mineralization of a fraction of toxic compounds  
362 (~52% of mineralization, **Table 3**) and the transformation of organic substances to more  
363 hydrophilic compounds, which are less prone to pass through the hydrophobic membrane.  
364 Fenton oxidation may also provide beneficial effects in terms of MD performance at real  
365 scale by thwarting fouling phenomena that would occur at longer time scales, but this effect  
366 could not be observed in this study.

### 367 3.3. *Effect of the coupled system on the toxicity of the final effluent*

368 A general index of the safety of an effluent is its toxicity. Toxicity is also a legislated  
369 parameter, allowing or denying the discharge of an effluent in the sewage system. According  
370 to the Italian regulations (D.Lgs. 152/2006), the acute toxicity limit to discharge an effluent  
371 in the sewage system is 80% of the inhibition of the target microorganism (in this case,  
372 *Vibrio fischeri*). The synthetic PW of this study presented an acute toxicity around 100%  
373 (Figure S6a of the SM), a value also expected for most of the real PW due to the wide variety  
374 and large concentrations of contaminants typically present. Both organics and concentrated  
375 salts may present large toxic effects, hence they both require a specific treatment. **Figure 3**  
376 presents the residual acute toxicity of the effluent treated with only MD and with the coupled  
377 Fenton-MD system expressed in term of dilution factor of the original samples. The EC<sub>50</sub>  
378 value was used as a comparative parameter of the quality of different effluents, and it is  
379 defined as the half maximal effective concentration, namely, the concentration required to  
380 obtain 50% of microorganism inhibition. This parameter increased significantly (from a  
381 dilution factor of  $0.094 \pm 0.009$  to  $0.25 \pm 0.03$ ) when the effluent was oxidized and then  
382 desalinated, compared to a stream that was not pre-treated, i.e., the coupled system gave

383 lower toxicity. However, when tested as is, the residual toxicity of the effluent was still high  
384 and over the limit of 80% after 30 min of contact time with the bacteria.



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

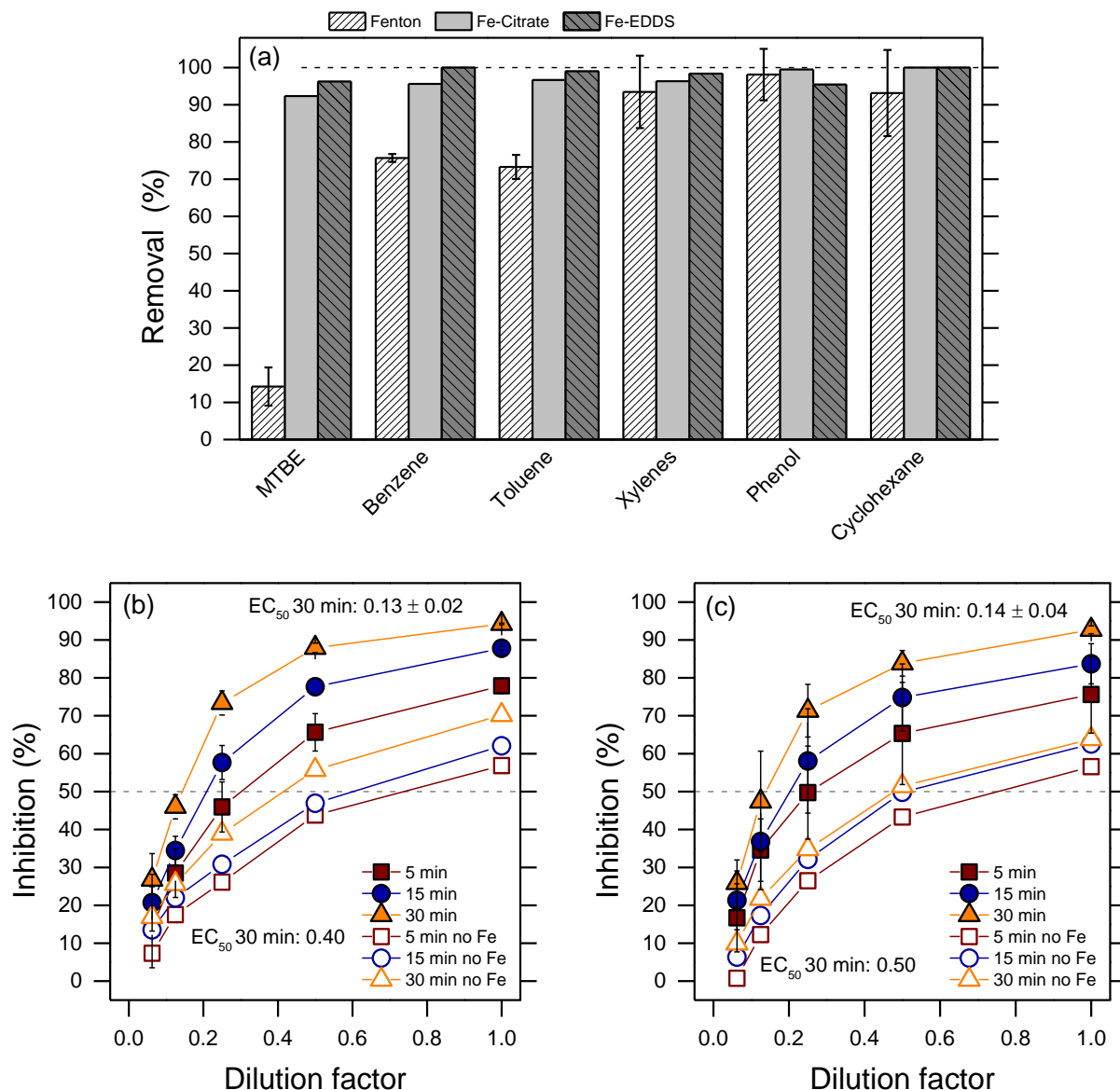
391

392 To understand the relative contribution to toxicity of the different contaminants, toxicity  
393 experiments were carried out with individual components (Figures S6 and S7 of the SM).  
394 Low toxicity was associated with HA and paraffins, while higher toxic effects were related to  
395 parent WMC, which however were degraded effectively by the Fenton oxidation. Calcium  
396 and magnesium chloride also showed negligible toxicity, while sodium chloride showed  
397 some toxicity only at concentrations  $>50$  g/L, that is, far above the concentration measured  
398 after the MD desalination. On the other hand, iron (II) sulfate showed a significant toxicity:  
399 residual iron may thus be responsible for the toxicity observed for the effluent from Fenton

400 and MD treatments. Indeed, by addition of EDDS in molar ratio 1:1 to the residual iron (0.26  
401 mM), the acute toxicity of iron was shut down (see Figure S2 and S7 in SM for the toxicity of  
402 Fe-EDDS and iron, respectively) and that of the effluent markedly decreased (from ~80% to  
403 ~40%), accompanied with a substantial increase in EC<sub>50</sub> (from a dilution factor of 0.25 ± 0.03  
404 to ~2.5). The remaining toxicity after this post-treatment step may be reasonably attributed to  
405 the residual WMC and to the by-products of Fenton oxidation. Note that in this study EDDS  
406 was added to mask the toxic behavior of the residual iron, which confirms the fact that  
407 residual metal concentration causes toxicity in the effluent. However, different strategies to  
408 remove the residual iron may be implemented in real plants, for example, its precipitation  
409 under basic pH. Cleaner and more novel steps may involve enhanced ion exchange resins and  
410 the use of adsorbents, such as magnetic nanoparticles (Khatri et al. 2017).

#### 411 3.4. *Comparison between traditional Fenton and Fenton process in the presence of iron* 412 *ligands*

413 Iron ligands keep iron in solution without the need for the pH adjustment to 3 and limit  
414 the production of sludge, thus potentially allowing for a more streamlined operation  
415 compared to the traditional Fenton process. Citrate and EDDS were chosen as non-toxic  
416 (Figure S2 of the SM) ligands and the Fe-citrate and Fe-EDDS systems were applied as  
417 catalysts (Zhang et al. 2016). The optimized condition in terms of Fe-ligand to H<sub>2</sub>O<sub>2</sub> molar  
418 ratio corresponded to the dosages relative to Ox7 in **Table 2**; each ligand was dosed  
419 equimolarly with iron. The results summarized in **Figure 4a** suggest higher degradation  
420 efficiency of the modified Fenton systems toward WMC with respect to the traditional  
421 thermal Fenton. Specifically, the modified Fenton processes achieved near complete  
422 degradation of all WMC, including MTBE that was instead not removed by the classic  
423 Fenton reaction; see also the chromatograms and percentage of substrates removal at different  
424 oxidation times in Figures S8, S9, and S10 (SM).



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



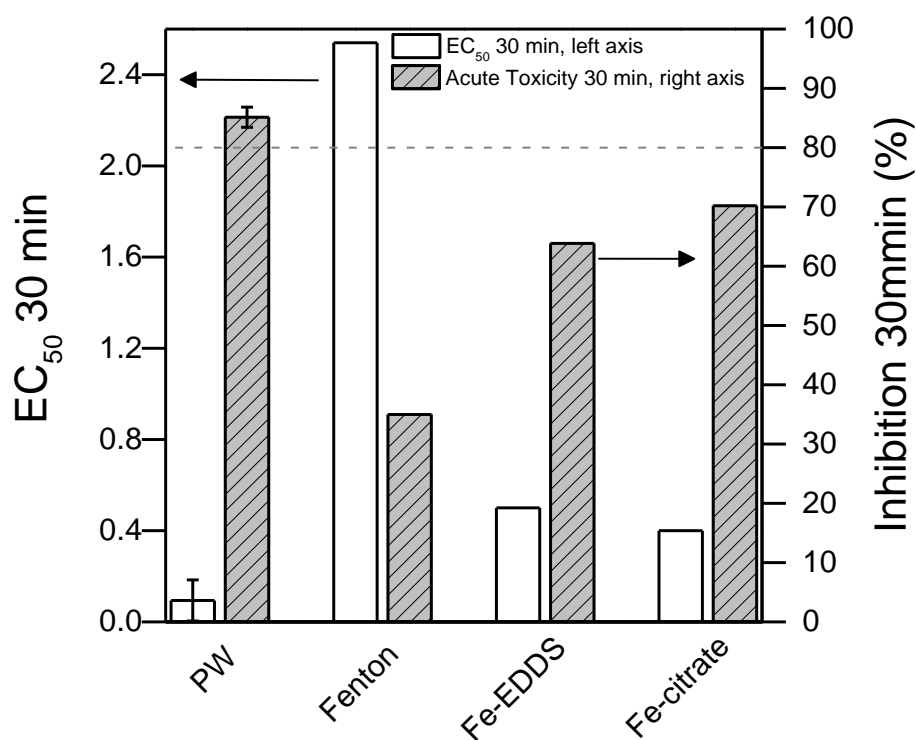
434 Despite the higher percentage of degradation of the target contaminants, the modified  
435 Fenton process did not show further beneficial effect on the MD process in terms of  
436 productivity and effluent quality compared to traditional Fenton; see Figure S11 of the SM.  
437 With regard to  $EC_{50}$ , the quality of the effluent treated with the coupled system including  
438 modified Fenton and MD clearly increased compared to the PW treated only with MD,  
439 specifically, from a dilution factor of  $0.094 \pm 0.009$  to  $0.13 \pm 0.02$  and to  $0.14 \pm 0.04$  in the  
440 case of Fe-citrate and Fe-EDDS, respectively (see **Figure 4b and c**). However, the  $EC_{50}$  was  
441 lower compared with the residual toxicity observed in the system that included the traditional  
442 Fenton oxidation ( $0.25 \pm 0.03$ ), possibly due to the formation of more toxic by-products  
443 (Zhang et al. 2016). When the contribution to toxicity of the residual iron (residual iron was  
444 0.27 and 1.30 mM for Fe-citrate and Fe-EDDS, respectively) was prevented by EDDS  
445 addition, the acute toxicity of the effluent clearly decreased (from ~90% to ~70% in both  
446 cases) and the  $EC_{50}$  further increased (to 0.4 and 0.5 for Fe-citrate and Fe-EDDS,  
447 respectively). At the end of the process, the effluent treated with the Fe-EDDS-based Fenton  
448 system presented a slightly better quality in terms of toxicity than that treated with the Fe-  
449 citrate system, consistently with the slightly higher degradation efficiency of the former  
450 compared to the latter.

451

#### 452 **4. Concluding remarks, challenges, and implications**

453 This work evaluated the impact of traditional and modified Fenton oxidations for the  
454 abatement of highly toxic organic contaminants and as pre-treatment options for the  
455 subsequent desalination of hypersaline produced waters by membrane distillation. Fe-citrate  
456 and Fe-EDDS were used as inexpensive, easy to handle, environmentally friendly and  
457 biodegradable systems in the modified Fenton processes. All the oxidative processes

458 provided relatively high degradation efficiency toward target contaminants also in presence  
 459 of typical scavengers of the Fenton reaction, namely, chloride and humic acids. The  
 460 observable beneficial effects of an oxidative pre-treatment were not evident in terms of MD  
 461 productivity, fouling, or wetting, but directly translated into lower permeation of organics  
 462 during distillation and in a significantly lower toxicity of the desalinated effluent.  
 463 Specifically, the EC<sub>50</sub> and the acute toxicity (inhibition % of target organisms) were used as  
 464 indexes for the evaluation of the quality of the final effluent. The target values of acute  
 465 toxicity should be below the regulated limit of 80%. **Figure 5** offers a final evaluation of the  
 466 toxicity parameters from the various treatments. The traditional Fenton coupled with the MD  
 467 desalination was the best in terms of toxicity. However, the modified Fenton-MD coupled  
 468 systems were able to overcome some of the practical limitations of the traditional Fenton  
 469 while still providing an effluent with suitable quality for safe discharge as sewage (toxicity  
 470 <80%). The modified Fenton oxidation may be more advisable for applications whereby  
 471 easier operational tasks and lower sludge production are important, such as offshore.



472

473 **Figure 5** Summary of the residual toxicity and EC<sub>50</sub> values of the various effluents treated  
474 with both MD and oxidation processes after 30 minutes of contact with the *Vibrio fischeri*  
475 culture. The dash line is relative to the value of 80% of acute toxicity, namely, the regulated  
476 legislative limit for a safe discharge in the sewage system in Italy.

477

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

495

496 **CRedit authorship contribution statement**

497 **Giulio Farinelli:** Conceptualization, Data curation, Formal analysis, Investigation,  
498 Methodology, Visualization, Writing - original draft. **Marco Coha:** Data Curation, Formal  
499 analysis, Investigation, Methodology, Visualization, Writing - review & editing. **Marco**  
500 **Minella:** Data curation, Validation, Methodology, Writing - review & editing. **Debora**  
501 **Fabbri:** Resources, Supervision, Writing - review & editing. **Marco Pazzi:** Formal analysis,  
502 Methodology. **Davide Vione:** Resources, Supervision, Writing - review & editing. **Alberto**  
503 **Tiraferri:** Funding acquisition, Project administration, Resources, Supervision,  
504 Visualization, Writing - review & editing.

505

## 506 **Declaration of Competing Interest**

507 The authors declare no competing financial interest.

508

## 509 **Acknowledgments**

510 This work was performed with the support of Politecnico di Torino  
511 (58\_RBA17TIRALB).

512

## 513 **Appendix A. Supplementary data.**

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

515

516

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