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

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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_{50} 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**
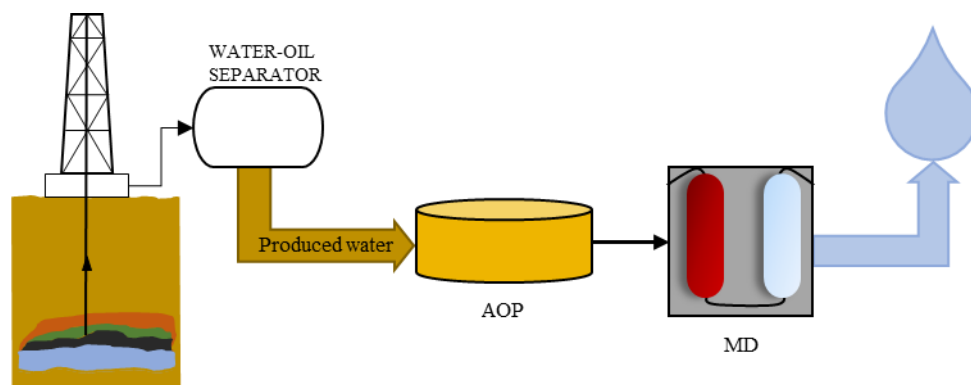
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1. Introduction

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

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

specific application are being developed (Estrada and Bhamidimarri 2016; Mohammad-Pajooh et al. 2018; Liu et al. 2021). These technologies should be versatile to meet the requirements of low cost and compactness, the latter characteristic being especially important in offshore activities (Kabyl et al. 2020; Liu et al. 2021).

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

$$\Delta P \geq LEP \tag{1}$$

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

100

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

101   where γ is the feed water surface tension, θ 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 γ 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; Coha 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:

125 $$Fe(II) + H_2O_2 \rightarrow Fe(III) + {}^{\bullet}OH + OH^- \tag{1}$$

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.

2. Materials and Methods

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 ($FeSO_4$), 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 (Aquastill,

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 $<C_{10}$ 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	
	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	Maximum ~500
TDS	Sodium chloride	100,000		Typically, 35,000 – 240,000
	Calcium chloride	2,500		
	Magnesium chloride	4,000		
	TOT	106,500		Average ~100,000
pH	5.5			

175

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 Fe(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	FeSO$_4$ (mM)	H$_2$O$_2$ (mM)
MQ H$_2$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 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 µS/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 ± 2 and 25 ± 1 °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 °C). The calibration was performed using standards of potassium

214 phthalate, $NaHCO_3/Na_2CO_3$. 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 °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 µm, 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·× 0.25 mm·× 0.25 µm) was used. The

223 injection port temperature was 270 °C, and the oven temperature program was set as follows:

224 35°C for 5 min, followed by an increase to 260 °C at a rate of 15 °C/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 °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 (4×10^{-4} M) and

232   complexing the Fe(II) with o-phenanthroline (4×10^{-3} M) under acidic conditions (buffer pH =

233   3: H_3PO_4 1 mM, NaH_2PO_4 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^{Fe}/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_{50} 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).

3. Results and Discussion

3.1. *Efficacy of thermal Fenton oxidation on organics removal*

Table 3 and **Figure 1a** summarize the results of the Fenton oxidations in terms of TOC removal and surface tension (ST) values, as a function of the relative addition of iron(II) and H_2O_2. The highest TOC removal rates were obtained with Fe/H_2O_2 ratios between 0.02 and 0.2. At low iron dosage (≤ 0.5 mM, Ox1, Ox6), insufficient catalyst was available in solution, while at high reagent concentrations (Ox7), the reaction was possibly self-inhibited. Previous studies highlighted that a Fe/H_2O_2 molar ratio around 0.02 should avoid self-inhibition reactions while providing high efficiency of oxidation (Voelker and Sulzberger 1996; De Laat and Gallard 1999). Oxidation 3 (Ox3) reached the highest percentage of TOC removal, coinciding with the largest dosage of $FeSO_4$ (5 mM) and a Fe/H_2O_2 ratio of 0.2. However, Ox4 also achieved a high percentage of TOC removal, but with a substantially lower amount of iron(II), namely, 1 mM, corresponding to a Fe/H_2O_2 ratio of 0.04. These conditions also allowed reaching the highest value of ST (69 ± 3.1 dyn/cm), close to the ST measured for pure water (72 ± 1.8 dyn/cm) and substantially higher than that of the PW (50.8 ± 2.7 dyn/cm). Ox4 was thus identified as the most promising oxidation and further tests were conducted using the matrix oxidized under this condition.

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

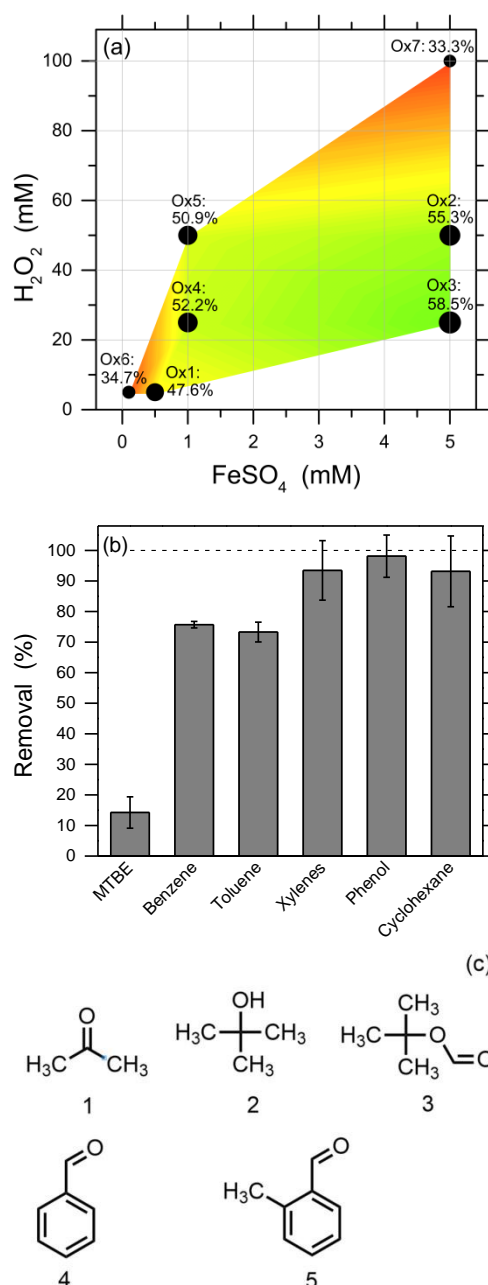| Entry	TOC removal (%)	Surface tension (dyn/cm)
MQ H_2O	-	72 ± 1.8
Produced water	-	50.8 ± 2.7
Ox 1	47.6 ± 0.5	67.8 ± 1.6
Ox 2	55.3 ± 1.3	63.5 ± 1.8
Ox 3	58.5 ± 2.2	60.1 ± 2.3
Ox 4	52.2 ± 2.4	69.5 ± 3.1
Ox 5	50.9 ± 1.7	54.2 ± 2.1
Ox 6	34.7 ± 2.1	68.6 ± 2.0
Ox 7	33.3 ± 2.3	59.3 ± 1.7

14

273

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

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

Organic compounds in the feed matrix may affect the MD step by fouling and by wetting the membrane, hence lowering the desalination efficiency, or by freely passing through the hydrophobic membrane material (PTFE) (Vesterkvist et al. 2012; Pasternak and Kolwzan 2013). Wetting is theoretically described by eq. 1 and experimentally observed with an increase of conductivity in the distillate stream of the MD step (Donaldson et al. 1969; Rezaei et al. 2017). The water flux values presented in **Figure 2a** suggest that the Fenton pre-treatment did not have an effect on the productivity or on the achievable recovery of the MD step under laboratory filtration conditions: the recovery was roughly 75%, upon which the water flux went to zero due to scaling (namely, the deposition of crystals on the membrane or within its pores) and pore blockage. Note that similar productivity was also observed when synthetic PW matrices containing solely salts or solely organics were used as the feed solutions. In the latter case the flux did not go to zero, due to the absence of salt precipitation, but it steadily decreased during the test possibly due to fouling phenomena. Increased conductivity of the distillate solution was measured beginning roughly at 50% recovery for the various feed streams, except that containing only organic compounds; see Figure S4 of the SM. This result suggests that in our study salt passage and possibly wetting were mostly imputable to high salt concentrations, with organics only associated with fouling mechanisms. Salts can crystallize within the pores of the membrane, enlarging them, hence lowering the LEP.
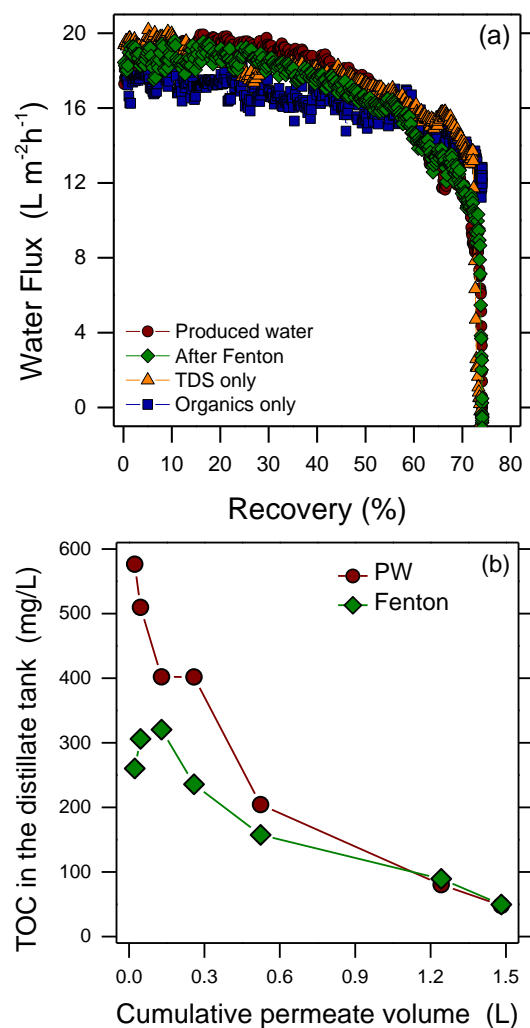
Figure 2 (a) Results of MD filtration tests with different feed solutions: (red circles) synthetic produced water, (blue squares) only the organic content of the synthetic produced water, (orange triangles) only the TDS content of the synthetic produced water, and (green diamonds) the resulting feed after the thermal Fenton oxidation. (b) TOC concentration in the distillate tank (initial volume 1 L) as a function of cumulative permeated volume; the lines connecting the data points are only intended as guides for the eye.

The only organic compounds in the synthetic PW which may induce wetting were humic acids (HA) and the water-miscible compounds (WMC), namely, BTX, MTBE, phenol, and 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 ± 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 fisheri*). 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_{50}

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 ± 0.009 to 0.25 ± 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

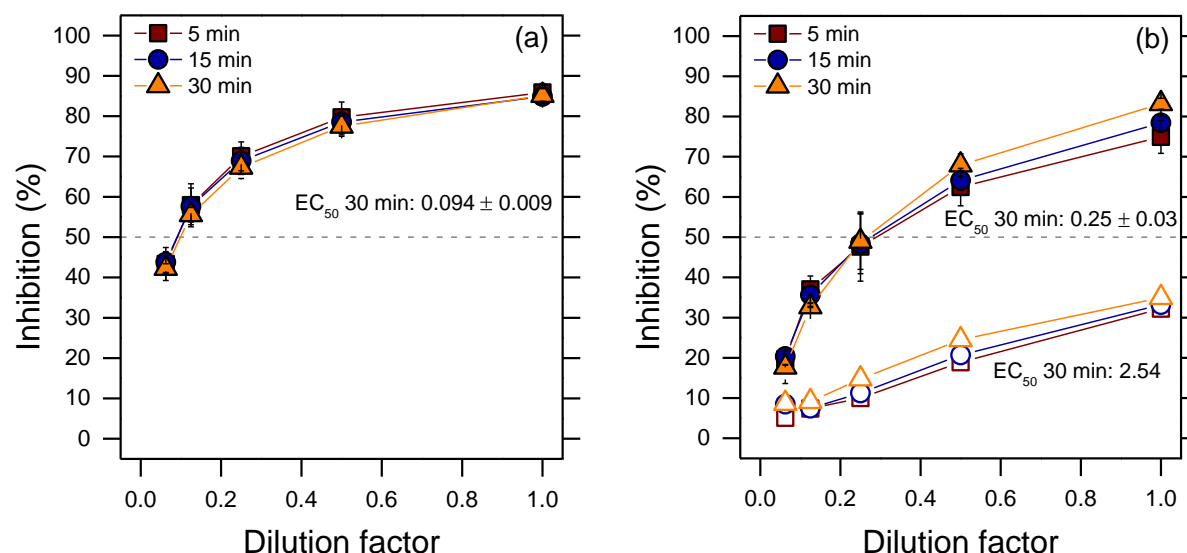384 and over the limit of 80% after 30 min of contact time with the bacteria.

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

21

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_{50} (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_2O_2 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).

425
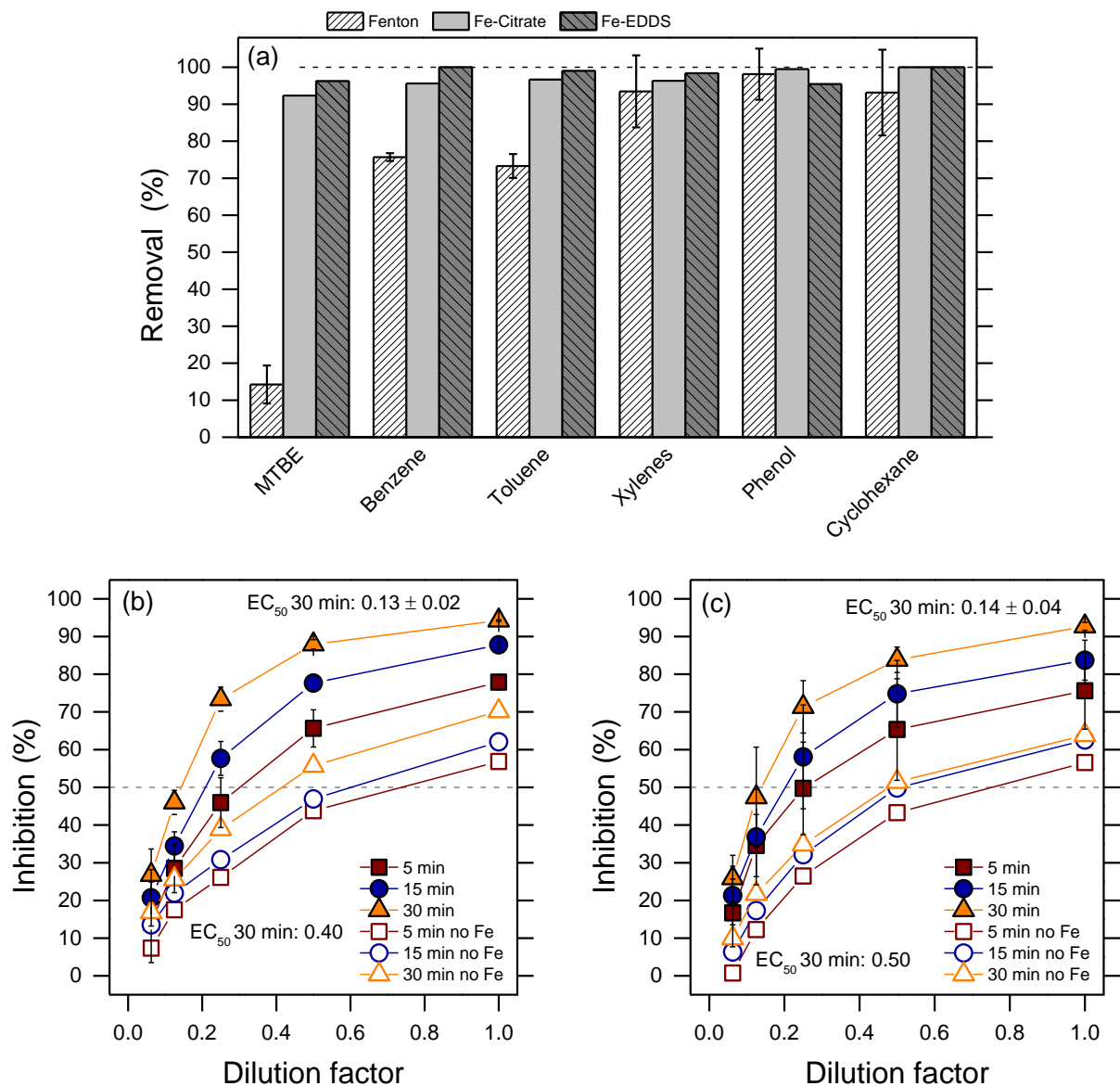
Figure 4 (a) Comparison of the organics removal rate by traditional Fenton and modified

Fenton reactions with citrate and EDDS as iron ligands. Residual toxicity of the final effluent

treated by the coupled system comprising modified-Fenton and MD using (b) Fe-citrate and

(c) Fe-EDDS as catalyst. The open symbols are related to the effluent upon iron sequestration

by EDDS. The toxicity was measured after 5, 15, and 30 minutes of contact with the *Vibrio*

fischeri culture. The dash horizontal line indicates the point where 50% of acute toxicity is

reached; the lines connecting the data points are only intended as guides for the eye.

433

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 ± 0.009 to 0.13 ± 0.02 and to 0.14 ± 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 ± 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

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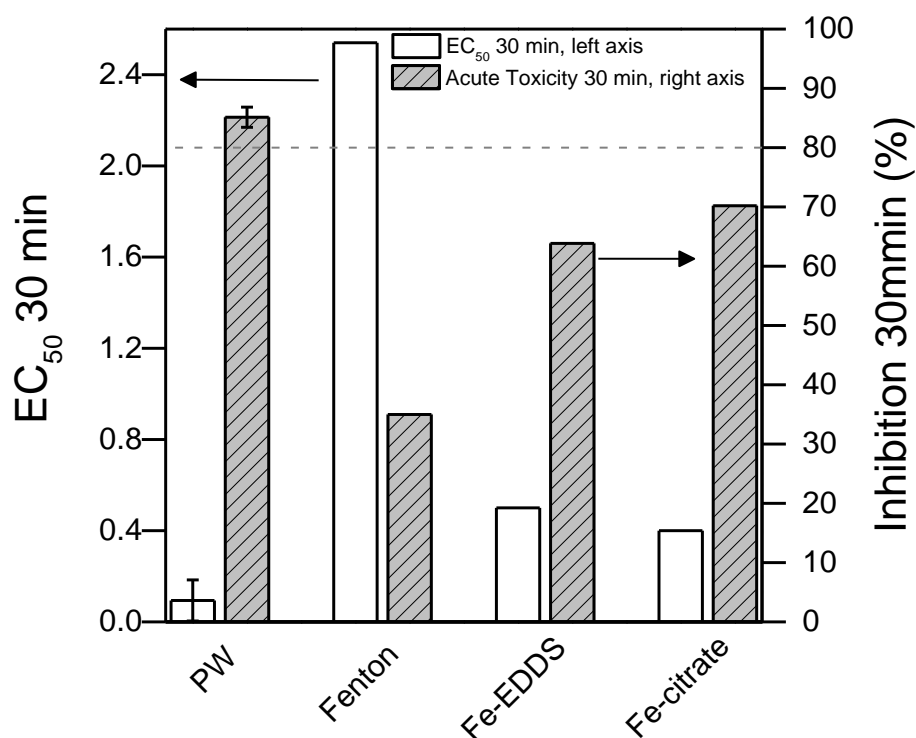easier operational tasks and lower sludge production are important, such as offshore.

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

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

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

Declaration of Competing Interest

507   The authors declare no competing financial interest.

508

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512

Appendix A. Supplementary data.

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

515

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