



23 since it acts as a competitor for active chlorine species and so reducing the  
24 mineralization rate.

25 **Keywords:** Actual wastewater, advanced oxidation processes, Electro-oxidation,  
26 Fenton-like processes, Hydroxyl radicals.

## 27 **1. Introduction**

28 Nowadays society's lifestyle encourages a high rate of consumption of natural water  
29 resources, meaning that an inadequate management will lead to a certain degree of  
30 scarcity in the long term. Specifically, chemical industry undergone a strong  
31 development owed to a growing demand for new products to satisfy the needs of the  
32 consumers. The manufacture of drugs, personal care products or pesticides and  
33 fertilizers to improve agricultural production, jointly with other organic substances  
34 widely used in modern life, has led to the appearance of new water contaminants, either  
35 at high concentrations ( $\text{mg L}^{-1}$ ) in industrial wastewaters or at much lower  
36 concentrations ( $\text{ng-}\mu\text{g L}^{-1}$ ) in urban wastewaters (known as micro-contaminants, MCs).  
37 MCs effect on the environment is under study, but their toxicity and high persistence  
38 have been widely demonstrated. They are difficult to assimilate for microorganisms  
39 thus being accumulated and active in the environment for long periods of time and with  
40 still unknown effects on the discharge ecosystems (Patel et al., 2019). That situation  
41 motivates arisen, development and application of new highly oxidizing technologies  
42 (Kanakaraju et al., 2018), aiming the degradation of these compounds of emerging  
43 concern and even, depending to their organic load and complexity of the wastewater,  
44 enhancing the biodegradability of the whole effluent.

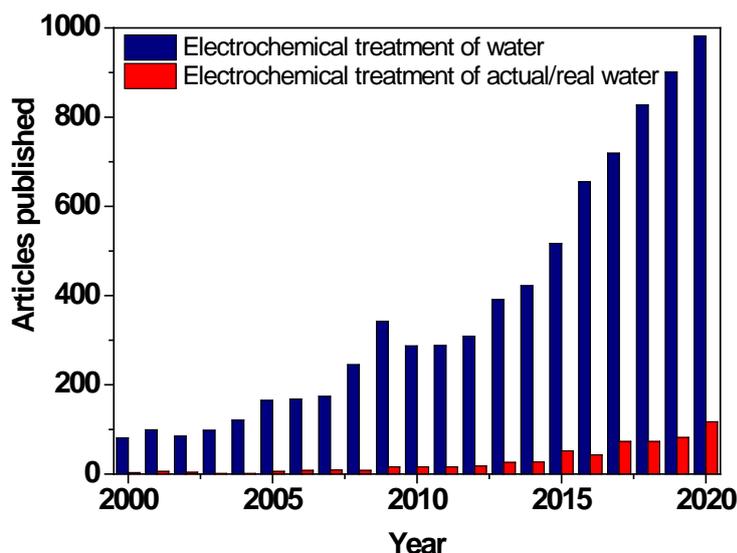
45 In this context, electrochemical processes pose a versatile, useful and powerful tool for  
46 the depuration of a wide variety of wastewaters, since only by applying an electric

47 current or electrode potential a broad spectrum of organics can be eliminated. They can  
48 be applied as a tertiary treatment for the degradation of MCs as well as for the suitable  
49 depuration of very complex industrial wastewaters with high toxic organic load and/or  
50 low biodegradability, being applied as a pre-treatment until making the effluent enough  
51 biocompatible (Urriaga et al., 2018; Mousset et al., 2020). In fact, electrochemical  
52 processes pose an appropriate complement to other technologies such as membrane  
53 systems, since the high ionic content of membrane rejections facilitates the flow of  
54 electrons obtaining lower energy consumptions compared with other less saline  
55 effluents (Pan et al., 2019; Soriano et al., 2020).

56 Some electrochemical processes have been widely used at industrial scale. For instance,  
57 electrocoagulation implies an advantage over the conventional coagulation-flocculation  
58 physicochemical process, since avoids the addition of chemical reagents by the use of  
59 sacrificial electrodes, generating a lower amount of sludge, and presenting higher  
60 efficiency in colloids removal (Barrera-Díaz et al., 2014) and even in pharmaceuticals  
61 removal (Zaied et al., 2020). Despite involving great advantages such as an easy control  
62 of the process and therefore easy automatization as well as the absence of external  
63 reagents, other processes such as electrochemical oxidation, photoelectro-Fenton (PEF)  
64 or photoelectrocatalysis have not been evaluated further than at laboratory scale and  
65 very often by using model wastewaters.

66 Making an overview of the current literature (from year 2000 to nowadays), more than  
67 7500 articles have been published on the use of electrochemical treatments for water  
68 purification with a significant increase since 2012 (Fig.1). Most of these works are  
69 mainly focused on the development of new materials for the manufacture of electrodes  
70 and the effectiveness achieved in the degradation of a reference contaminant in a simple  
71 water matrix. However, works addressing the application of these electrochemical

72 processes in actual water matrices are a few hundreds (Moreira et al., 2017). Therefore,  
73 it is evident the scarcity of studies facing these technologies under a realistic approach  
74 and for the purification of complex water matrices, which has limited the possibilities of  
75 electro-oxidative systems from a commercial standpoint.



76

77 **Fig. 1.** Publications from Scopus DataBase focused on the study of electrochemical  
78 processes since 2000 (revised on November 2020).

79 It is important to note that, from the inorganic ions naturally contained in waters, a large  
80 amount and variety of oxidizing species can be generated, which entails an intrinsic  
81 improvement over the basic studies in model waters using a supporting electrolyte  
82 whose only function is to allow the transition of electrons. This was evidenced in  
83 Garcia-Segura et al. (2018) where the efficiency of the electro-oxidative process as a  
84 treatment for actual effluents from different sources was reported, revealing the  
85 fundamental role of active chlorine species (ACS) for the degradation of organic matter.

86 Furthermore, some electrogenerated species are photoactive, which means that just by  
87 irradiating the solution (usually with short wavelength light) the generation of different

88 oxidizing species could be promoted, which would result in an increase of the  
89 contaminant degradation rate. This means that it is necessary to carry out an evaluation  
90 of these electrochemical systems under actual conditions with real effluents as obtained  
91 results may significantly diverge from those performed under model/simulated  
92 conditions.

93 Few works are focused on covering the gap between small and large scale systems such  
94 as the one published by Garcia-Rodriguez et al. (2020), which shows the possible  
95 strategies to be followed depending on the type of water to be treated, emphasizing the  
96 importance of process optimization and cost-efficiency. Furthermore, regarding photo-  
97 electro-chemical processes, the study of Mousset and Dionysiou (2020) reviews the  
98 possible configurations of electrochemical photo-reactors and the work of Brillas et al.  
99 (2021) focuses on a more efficient use of light in this type of electro-chemical systems.

100 The present study deals with the application of solar-assisted electrochemical processes  
101 on actual industrial and municipal wastewaters, discussing their performance as well as  
102 their main mechanisms, especially focusing on persistent contaminants and MCs.

## 103 **2. Electro-oxidation processes**

104 Electro-oxidation can be addressed directly or indirectly. During direct electro-  
105 oxidation, target contaminants are adsorbed on the anode surface where they are directly  
106 oxidized by the transfer of electrons from the molecule to the anode avoiding the  
107 intervention of any mediator. This treatment is possible as long as the applied potential  
108 is low and keeps below the potential of oxygen evolution reaction, characteristic of the  
109 specific material that conform the anode. Very often the process is governed by  
110 adsorption so, as a consequence, degradation kinetics are low and strongly depend on  
111 the anode electrocatalytic activity (Panizza, 2010). Moreover, another drawback of the

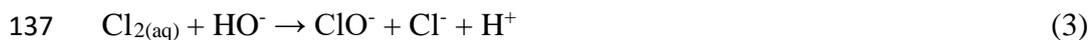
112 application of low potentials is evidenced by a decrease on the anode activity when time  
113 of operation is increasing due to the formation of a layer of polymers from contaminants  
114 or degradation by-products on the surface. This phenomenon is known as poisoning or  
115 deactivation (Panizza, 2010). Likewise, polymers can be eliminated by the application  
116 of a highly oxidative potential, thus regenerating the anode surface (Comninellis, 1994;  
117 Panizza, 2010).

118 In indirect electro-oxidation, the oxidizing species are electrogenerated on the anode but  
119 react in the bulk solution to oxidize organic compounds, so they can be considered as  
120 the intermediaries transferring electrons between the anode and the organic  
121 contaminants allowing the degradation of organics in the bulk solution, even far of the  
122 anode surface. These oxidizing species can be generated from two sources, from the  
123 intermediates generated as result of the oxygen evolution reactions (hydroxyl radicals,  
124 •OH) or from the inorganic ionic species dissolved in water (chloride could produce  
125 chlorine). The type and concentration of oxidant produced depends on the wastewater  
126 composition but also on the width of the potential window of the electrode material. For  
127 this reason non-active anodes, and specifically boron-doped diamond (BDD) anodes,  
128 are able to generate different oxidants (Rychen et al., 2010), though in active anodes the  
129 main oxidant generated is chlorine (Sáez et al., 2018).

## 130 2.1 Electrochlorination

131 One of the main inorganic ions that can be naturally found in waters is chloride. When a  
132 contaminated water containing this ion undergoes an electrochemical depuration  
133 process it follows two pathways: on the electrode surface via adsorbed chloro radicals  
134 (reaction (1)) and by ACS (reactions (2 - 4)) (Panizza and Cerisola, 2009).





139 The solution pH determines the species of active chlorine that will be present in  
140 wastewater. At pH below 7.55 (pKa), the main specie is HClO ( $E^0 = 1.49$  V) and at  
141 higher pH values,  $\text{ClO}^-$  ( $E^0 = 0.86$  V) is predominant (reaction (4)). Despite the wide  
142 use of these ACS for the degradation of organics, electrochemical and chemical  
143 reactions occurring during the electro-oxidative process are partially unknown (Panizza  
144 and Cerisola, 2009).

145 This electrochemically-assisted chlorine treatment, commonly known as  
146 electrochlorination, presents several advantages regarding conventional chlorination  
147 where ACS are added as a reagent (Martinez-Huitle and Brillas, 2009): (i) Transport  
148 and storage of chlorine are not necessary, thus avoiding the risk associated; (ii) Organics  
149 removal is faster than in chemical oxidation; (iii) Overall operation costs are lower.

150 As the treatment starts, ACS react with organic matter as soon as they are  
151 electrogenerated so free available chlorine (FAC) concentration remains low, however  
152 when the organic matter is completely eliminated, FAC begins to accumulate and so  
153 oxidation process ends. When a BDD anode is used for the removal of organics in a  
154 wastewater with high content on chloride, its high over-potential for oxygen evolution  
155 leads in the generation of a huge amount of  $\bullet\text{OH}$ , thus promoting the oxidation of FAC  
156 to undesired chlorine by-products (reactions (5 - 7)) (Bergmann, 2010; Groenen  
157 Serrano, 2018). In such a case, the oxidative power of the process is reduced and water  
158 toxicity increases entailing a serious risk for the ecosystems and human beings. To  
159 avoid this effect, it is recommended to work at low potentials with BDD anodes so

160 diminishing the generation of ACS and  $\bullet\text{OH}$  reducing the possible reaction between  
161 both.



## 165 2.2. Electro-oxidation by other inorganic anions

166 When water purification is carried out by electro-cells with high oxygen evolution over-  
167 potential anodes, organic contaminants are removed mainly by the oxidizing action of  
168 electrogenerated  $\bullet\text{OH}$ . However, if the effluent to be treated is an actual wastewater  
169 with sulphate, carbonate and phosphate ions, they can be oxidized on the anode surface  
170 as described by reactions (8 - 10) (Cuerda-Correa et al., 2020):



174 The main advantage of these electrogenerated oxidants is that they are dissolved in the  
175 aqueous solution, so that oxidative process extends beyond the areas adjacent to the  
176 anode, thus avoiding the limitation of mass transfer on anode surface and increasing the  
177 efficiency of the process (Panizza and Cerisola, 2009). In fact, at the beginning of the  
178 treatment in which the concentration of organic pollutants is high, no significant  
179 differences are found regarding the presence or absence of sulphate, carbonate and  
180 phosphate ions. Nevertheless, when the concentration of organics is low and so the

181 system is limited in the adjacent area to the anode, the degradation process will be faster  
 182 in wastewater with higher content of sulphate, carbonate or phosphate ions.

183 Farhat et al. (2017) evaluated the effect of this ionic species on the degradation process  
 184 of 100 mg L<sup>-1</sup> of resorcinol by using different salt solutions whose main components  
 185 were chloride, sulphate and nitrate. Different contaminant degradation rates were  
 186 observed with only a single anion compared to a combination of them. Moreover,  
 187 Ganiyu and Gamal El-Din (2020) studied the treatment of oil sand wastewater through  
 188 electro-oxidation with BDD anodes, detecting the formation of radical and non-radical  
 189 oxidant species, namely BDD(<sup>•</sup>OH), SO<sub>4</sub><sup>•-</sup>, CO<sub>3</sub><sup>•-</sup>, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, C<sub>2</sub>O<sub>6</sub><sup>2-</sup> and active chlorine.  
 190 They confirmed their generation and their contribution in the overall organics  
 191 degradation.

192 Considering the strong effect that these dissolved ionic species can have on a  
 193 wastewater depuration by electro-oxidation, it is necessary to deepen on the application  
 194 of electrochemical treatments to actual waters, whose natural compositions are highly  
 195 variable. A summary of the main and most recent studies in which electro-oxidation has  
 196 been applied for the depuration of actual industrial wastewaters is shown in Table 1.

197 **Table 1.** Main studies addressing application of electro-oxidation for the depuration of  
 198 industrial wastewater effluents. COD: chemical oxygen demand.

Wastewater	Electrodes	Operating Conditions	Removal %	Reference
Herbicide wastewater	PbO <sub>2</sub> anode - Ti cathode gap: 1 cm	<i>j</i> : 4 A dm <sup>-2</sup> pH: 4 V: 1 L	87% of COD	(Zhang et al., 2020)
Sugar beet wastewater	BDD anode/Stainless steel cathode A= 109 cm <sup>2</sup> gap: 1 cm	<i>j</i> : 49.1 mA cm <sup>-2</sup> pH: 5 t: 294 min V: 1 L Adding NaCl	75% of COD	(Sharma and Simsek, 2020)

RO concentrate of petrochemical industry	Nb-BDD anode / stainless steel AISI 304L cathode A: 0.01 m <sup>2</sup>	j: 20 mA cm <sup>-2</sup> pH: 8 t: 5 h V: 1.5 L	71% of COD	(Wohlmut h da Silva et al., 2019)
RO concentrate of print and dyeing wastewater	PbO <sub>2</sub> -Ti anode / Ti mesh-plate cathode. A: 300 cm <sup>2</sup> gap: 1 cm	j: 10 mA cm <sup>-2</sup> pH: 8.3 t: 40 min V: 1 L Q <sub>sp</sub> : 2.45 Ah L <sup>-1</sup>	72% of COD	(Wang et al., 2018)
Washing machine effluent	Nb-BDD anode/Ti cathode A: 63.5 cm <sup>2</sup>	j: 16.6 mA cm <sup>-2</sup> t: 360 min V: 1 L	71% of COD	(Durán et al., 2018)
	Nb-BDD anode/Ti cathode A: 63.5 cm <sup>-2</sup>	j: 66.6 mA cm <sup>-2</sup> t: 180 min Adding 7 g L <sup>-1</sup> of Na <sub>2</sub> SO <sub>4</sub>	88.5% of COD	
Oxyfluorfen solution, raw (234 mg L <sup>-1</sup> ) and ultrafiltration retentate	BDD anode / Stainless Steel AISI 304 cathode A: 78 cm <sup>2</sup> gap: 9 mm	j: 500 mA cm <sup>-2</sup> V: 0.6 L 590 kWh kg <sup>-1</sup> Adding 1 g L <sup>-1</sup> of Na <sub>2</sub> SO <sub>4</sub>	50% of Oxyfluorfen raw solution	(Acosta-Santoyo et al., 2020)
Winery wastewater	BDD anode / Stainless Steel cathode A: 5 cm <sup>2</sup>	j: 60 mA cm <sup>-2</sup> t: 420 min V: 0.1 L	64% of COD	(Candia-Onfray et al., 2018)
Petroleum wastewater (Phenol)	28 Graphite anodes / 21 Stainless Steel cathodes A: 126 cm <sup>2</sup> gap: 2 cm	j: 3.5 mA cm <sup>-2</sup> pH: 7.5 - 9 t: 15 min V: 19.2 L E: 0.79 kWh m <sup>-3</sup>	49-60 % of COD 100% Phenol	(Abou-Taleb et al., 2020)
Textile wastewater	2 Ti-RuO <sub>2</sub> anodes / 2 Al cathodes A: 85 cm <sup>2</sup> each gap: 1 cm	j: 1.66 A pH: 5.49 t: 80 min V: 1.5 L E: 0.68 Wh	80% of COD 97% color	(Kaur et al., 2017)
Methiocarb and Bisphenol A in sanitary landfill leachate	Si-BDD anode / Stainless Steel cathode A: 10 cm <sup>2</sup> gap: 0.3 cm	j: 300 A m <sup>-2</sup> pH: 8.5 t: 2 h V: 200 mL	>99% of Methiocarb and Bisphenol A	(Fernandes et al., 2020)

199

200 According to these studies, electro-oxidation is quite effective for the elimination of

201 organic compounds in complex waters, which would facilitate their subsequent

202 biological treatment or even safe disposal to the Environment. However, as both  $\bullet\text{OH}$   
203 and FAC would be present, the formation of chlorates and perchlorates in effluent  
204 toxicity is an additional major challenge that must be tackled. This means that, at the  
205 end of the treatment, it is necessary to evaluate the potential risks caused by these  
206 chlorinated substances, in view of the potential end-use of the treated effluent.

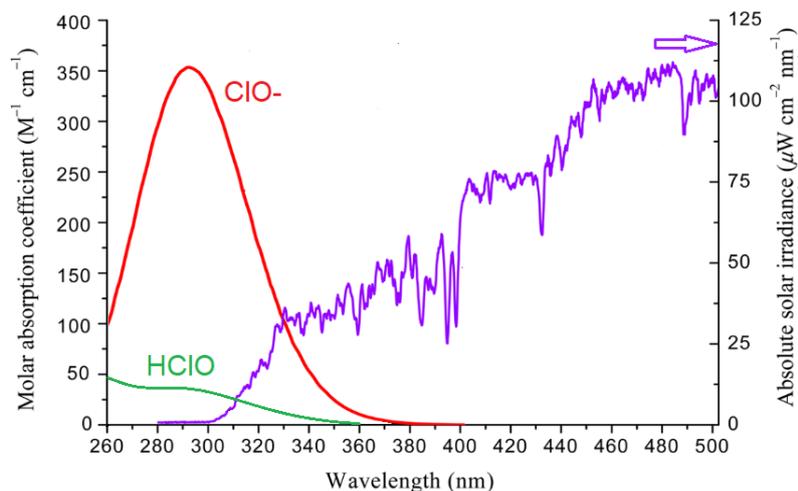
### 207 2.3. Electro-oxidation combined with light irradiation

208 Many of electrogenerated species on the anode surface can be activated by different  
209 methods, being the irradiation with light the most widely applied. New species with a  
210 high oxidizing power could be generated, leading to an increase in the treatment  
211 efficiency. This is the case of ACS which undergo photolysis when radiation is applied  
212 generating active radicals as  $\text{Cl}\bullet$  ( $E^0 = 2.4 \text{ V}$ ) and  $\bullet\text{OH}$  following reaction (11) in the  
213 case of  $\text{HClO}$  and reactions (12) and (13) for  $\text{ClO}^-$ .



217 These reactions have been studied in detail mainly in the UV-C range at 254 nm of  
218 wavelength (Feng et al., 2007). However, ACS photolysis could occur at other longer  
219 wavelengths depending on the molar absorption, probably with lower quantum  
220 efficiency (Fig. 2). In fact,  $\text{ClO}^-$  photolysis could take place even under solar radiation  
221 since the molar absorption of  $\text{ClO}^-$  overlaps with UV-B and UV-A region of the solar  
222 spectrum (from 280 to 400 nm) (Shu et al., 2014). This suggests that sunlight can be  
223 applied in solutions containing ACS at pH higher than 7.5 aiming an enhancement in

224 the treatment oxidative capacity, which is known as solar-assisted anodic oxidation  
225 (solar-assisted AO).



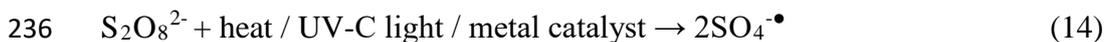
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227 **Fig. 2.** Molar absorption of HClO and ClO<sup>-</sup> vs solar irradiance spectrum at noon.

228

Modified from Shu et al 2014 (Shu et al., 2014).

229 On the other hand, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, an alternative oxidant to H<sub>2</sub>O<sub>2</sub> also widely studied, that can  
230 be activated either by increasing temperature, by adding a transition metal catalyst or by  
231 irradiating with light at 254 nm (reaction (14)), produces SO<sub>4</sub><sup>•-</sup> (with a very high redox  
232 potential E<sup>0</sup> = 2.5 – 3.1 V, in the same range as •OH). For this reason, sulphate-based  
233 treatments has been described in depth in literature for the removal of MCs and for  
234 bacteria inactivation (Sánchez-Montes et al., 2020). However, mechanism involving  
235 SO<sub>4</sub><sup>•-</sup> generation and its role during electro-oxidative treatment is still under study.



237 Combination of an electrochemical treatment with a light source, whether artificial as a  
238 lamp or natural as sunlight, leads to the promotion of electrogenerated oxidative species  
239 to still more oxidizing ones. Therefore, efficiency of electrochemical processes could be

240 enhanced jointly with a reduction on the energy costs, which is one of the major  
241 drawbacks of electro-oxidative treatments (Matzek and Carter, 2016; Dewil et al., 2017)

242 Despite the potential of these treatments, they have not yet been studied in depth with  
243 actual wastewaters, with only a few studies in literature addressing the combination of  
244 electro-oxidation with a light source. Sierra-Sanchez et al. (2020) studied a comparison  
245 between the degradation of acetaminophen in a NaCl solution ( $2.5 \text{ g L}^{-1}$ ) by electro-  
246 oxidation in the dark or illuminated with a UV-C lamp, obtaining higher degradation  
247 rates under illumination. In Sanchez-Montes et al. (2020) it was also studied the  
248 degradation of a model contaminant (glyphosate) in NaCl ( $2 \text{ g L}^{-1}$ ) by an electrochemical  
249 cell illuminated with a UV-C lamp. However, that work addressed the behavior of the  
250 system when using dimensionally stable anodes (DSA) or BDD, reporting a total  
251 mineralization of glyphosate with DSA/UV-C but releasing chlorates. Luo et al. (2020)  
252 studied the removal of four different bisphenol analogues but in this case,  $\text{Na}_2\text{SO}_4$  was  
253 used as supporting electrolyte, thus the formation of chlorate and perchlorates was  
254 avoided. The results reported synergistic effects when combining UV-C and BDD,  
255 increasing the degradation rate regarding UV-C and BDD stand-alone process and even  
256 a toxicity reduction. One of the studies nearest to actual operating conditions was  
257 published by Aravind et al. (2018), addressing the depuration of textile effluents. This  
258 work confirmed the generation of oxyl radicals by electron paramagnetic  
259 analysis and evidenced the improvement entailed in the elimination of COD. In  
260 addition, the light-assisted treatment resulted in lower amounts of chlorinated organic  
261 compounds and in the absence of toxicity at the end of the treatment.

262

263

### 264 **3. Electro-Fenton and photo electro-Fenton processes.**

265 Electrochemistry is presented as a versatile tool for Fenton's reaction (reaction (15))  
266 control. The combination of both is known as electro-Fenton (EF) process. In this  
267 treatment, the anode generates oxidant species on its surface and simultaneously,  
268 electrogeneration of H<sub>2</sub>O<sub>2</sub> occurs by two-electron reduction of O<sub>2</sub> on the cathode  
269 surface (reaction (16)), thus only with the addition of an iron salt, Fenton reaction is  
270 promoted. Furthermore, Fe<sup>3+</sup> obtained after Fenton reaction can be also reduced to Fe<sup>2+</sup>  
271 on the cathode, regenerating the catalyst (reaction (17)) (Brillas et al., 2009; Sirés et al.,  
272 2014) which is able to react again with electrogenerated H<sub>2</sub>O<sub>2</sub>, closing the cycle of the  
273 catalytic process (Brillas, 2020). By means of the applied energy to the electrochemical  
274 cell, the generation of oxidant species as well as Fenton reagents can be controlled,  
275 allowing adapting the treatment according to the target wastewater characteristics.



279 The selection of the cathode material is of outmost relevance for H<sub>2</sub>O<sub>2</sub>  
280 electrogeneration since it requires the use of specific and selective materials with a high  
281 over-potential for H<sub>2</sub> evolution. Specifically, the most used materials are the carbon-  
282 based, such as carbon-polytetrafluoroethylene (carbon-PTFE), carbon felt, reticulated  
283 vitreous carbon or graphene, which are good electrical conductors, non-toxic, stable,  
284 moderate cost and show a high over-potential for H<sub>2</sub> evolution with a low catalytic  
285 activity for H<sub>2</sub>O<sub>2</sub> reduction (Oturán and Oturán, 2018). To facilitate the cathodic  
286 production of H<sub>2</sub>O<sub>2</sub> it is convenient to have as much oxygen in solution as possible

287 thus, in filter-press cells, it is common to install an air chamber in the back side of the  
288 cathode, working in a slightly higher pressure than water flow forcing the diffusion of  
289 oxygen to the aqueous solution. These kinds of electrodes are known as Gas Diffusion  
290 Electrodes (GDE).

291 EF process was the first technology considered as an electrochemical advanced  
292 oxidation process (EAOP), presenting several advantages (Plakas and Karabelas, 2017):  
293 (i) The in situ generation of reagent entails cost saving as well as avoid risks associated  
294 to their transport and storage; (ii) The oxidation of contaminants can be easily  
295 controlled by means of varying the current or potential applied; (iii) Easy automation  
296 and monitoring of operating parameters.

297 EF can also be enhanced by the application of a light source, not only due to the  
298 activation of electrogenerated species, but due to the regeneration of Fe<sup>2+</sup> from Fe<sup>3+</sup>  
299 generated during Fenton reaction (reaction (18)) ensuring the feasibility of the reaction.  
300 This process is known as PEF when the irradiation source is a lamp and solar photo  
301 electro-Fenton (SPEF) when it is developed under sunlight (Roccamante et al., 2019).



303 Nonetheless, most of the published studies address EF, PEF and SPEF process at  
304 laboratory scale, with small systems treating low volumes of simulated wastewater,  
305 focusing mainly on the development of new electrode materials. This evidences the lack  
306 of studies carried out at larger scale and with complex water matrices, which would  
307 serve as a preliminary step to the scale-up and future penetration of these systems into  
308 the market. Among the most recent works treating actual wastewater with EF and SPEF  
309 is the one developed by Mousset et al. (2018) in which 0.4 L of an electronic industry  
310 effluent was treated by EF at pH 3, but adding 50 mM of K<sub>2</sub>SO<sub>4</sub> in order to facilitate

311 the electrochemical process as well as reducing electrical energy consumption. In that  
312 work, the removal of total organic carbon (TOC) achieved 94%. Salazar et al. (2019),  
313 addressed the removal of Acid Blue 29 from an industrial textile wastewater by SPEF at  
314 a pre-pilot scale and acidic pH by adding Na<sub>2</sub>SO<sub>4</sub>. After 6 h applying a current density  
315 of 25 mA cm<sup>-2</sup> and a UV energy of 30 W m<sup>-2</sup>, 93% of TOC was eliminated. Guelfi et al.  
316 (2019) obtained similar results, removing 0.208 mM of bentazon spiked in an urban  
317 wastewater effluent fortified with Na<sub>2</sub>SO<sub>4</sub> with SPEF at pH 3.

318 Regarding the application of EF and SPEF in actual wastewaters at circumneutral pH, it  
319 must be highlighted the new trend on studying the use of iron complexing agents to  
320 maintain iron in solution as a new challenge for this technology. Only a few works have  
321 already addressed this new approach (Ye et al., 2020; Salmerón et al., 2021).

#### 322 **4. Addressing the challenge of solar electrochemical treatments applied** 323 **under actual operating conditions**

324 As mentioned in the previous sections, solar electrochemical studies conducted with  
325 actual wastewaters are scarce, and if considering its combination with a light source, the  
326 number of works published is even lower. This fact has hampered the development of  
327 light-assisted electrochemical systems at pre-industrial level. Moreover, it would be  
328 highly recommended to use, whenever possible, a renewable resource such as solar  
329 energy as light source instead of artificial lamps.

330 In this context, Plataforma Solar de Almería (PSA) has recently addressed the  
331 application of electrochemical processes for the treatment of actual wastewaters,  
332 assessing the possible improvements achieved by the combination of solar  
333 photoreactors with an electrochemical pilot plant (Salmerón et al., 2019). The efficiency  
334 of a SPEF pilot plant in the degradation of a mixture of two MCs, pentachlorophenol

335 (PCP) and terbutryn (TBT), contained in several aqueous matrices has been studied.  
336 The first approach was the simplest one, 50 mM of Na<sub>2</sub>SO<sub>4</sub> dissolved in distilled water,  
337 then a highly saline simulated effluent and finally an actual highly saline wastewater.  
338 The main objective was to verify the improvement in the performance of solar-assisted  
339 electrochemical processes by treating actual wastewaters, with a great variety of ions  
340 able to generate different radicals, when applying also a natural solar light source.

341 Complementarily, the treatment of two industrial effluents by means of a commercial  
342 electrical cell assisted by solar energy was also studied in order to demonstrate that a  
343 higher concentration of photo-active ions implies a higher performance of the system  
344 and the requirement of lower electrical energy to achieve target treatment goals.

#### 345 4.1 Materials and Analyses

346 PCP and TBT were selected as model compounds considering the list of priority MCs  
347 reported in Directive 39/2013. Water matrices were spiked with a mixture stock solution  
348 of PCP and TBT (from Sigma-Aldrich) at initial concentrations between 100 – 200 µg  
349 L<sup>-1</sup>. Fe<sup>3+</sup>:EDDS complex, (EDDS: Ethylenediamine-N,N'-disuccinic acid) in a  
350 concentration rate of 0.1:0.2 mM, was prepared by adding Iron (III) sulfate x-hydrate  
351 (~75% pure) from Panreac to acidified water (pH 2.8) and maintaining stirring and  
352 darkness. After, the desired amount of EDDS (from Sigma-Aldrich) was added stirring  
353 vigorously until the solution took a very intense yellow colour indicating the proper  
354 formation of the complex.

355 Wastewaters treated in this work addressed from a saline solution to a highly actual  
356 saline wastewater (Table 2), increasing gradually the water complexity to evaluate the  
357 influence of the ionic content in the behavior of the oxidation system.

358

359 **Table 2.** Main characteristics of the wastewaters treated by electrochemical processes  
 360 assisted by solar energy.

	50mM Na <sub>2</sub> SO <sub>4</sub>	High salinity simulated effluent, HSSE	High salinity actual effluent, HSAE	Low salinity industrial wastewater, LSIW	High salinity industrial wastewater, HSIW
Conductivity (mS cm <sup>-1</sup> )	8.2	5.5 - 6	6.1 - 6.8	28	71
Turbidity (NTU)	-	-	9 - 45	308	N.A.
pH	6.2	8.7	8 - 8.6	7.4	7.2
DOC (mg L <sup>-1</sup> )	48	48	43 - 78	2040	2300
<i>Main ionic species</i>					
SO <sub>4</sub> <sup>-</sup> (mg L <sup>-1</sup> )	4800	1465	390 - 660	8245	29150
Cl <sup>-</sup> (mg L <sup>-1</sup> )	-	555	1180 - 1960	4470	7930
NH <sub>4</sub> <sup>+</sup> (mg L <sup>-1</sup> )	-	18	46 - 76	2670	9940

N.A. Non available; DOC Dissolved organic carbon.

361

362 MCs concentration was monitored by an UPLC/UV Agilent Series 1200 equipped with  
 363 a ZORBAX Eclipse XDB-C18 analytical column. Analytical method consist on formic  
 364 acid 25 mM in ultrapure water as eluent A and acetonitrile as eluent B. The gradient  
 365 starting with 10% of eluent B, reaching 100% of B in 14 min at a flow rate of 1 mL min<sup>-1</sup>  
 366 <sup>1</sup>. Re-equilibration time was 3 min. Column temperature was 30° C and sample injection  
 367 volume was 100 µL.

368 In the case of industrial wastewater, the efficiency of the treatment was assessed in  
 369 terms of DOC elimination. This parameter was measured in a Total Organic Carbon  
 370 Analyser TOC-V CSN from Shimadzu equipped with an ASI-V sampler after filtration  
 371 through 0.45 µm nylon filter.

## 372 4.2 Experimental Setup

373 Ultraviolet radiation (UV) was measured with a CUV 5 UV radiometer from KIPP &  
 374 ZONEN, located at PSA (Spain) and tilted 37° (the same as the CPC solar photo-

375 reactor), according to the latitude. Equation (19) provides the accumulative solar UV  
376 energy applied in the treatment. This parameter allows comparison between different  
377 solar processes (Malato et al., 2003).

$$378 \quad Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \cdot \overline{UV}_{G,n} \cdot A_i / V_t; \quad \Delta t_n = t_n - t_{n-1} \quad (19)$$

379  $Q_{UV,n}$  (kJ L<sup>-1</sup>) is the accumulated UV energy per unit of volume,  $\overline{UV}_{G,n}$  (W m<sup>-2</sup>) is the  
380 average solar ultraviolet radiation ( $\lambda < 400$  nm) measured between  $t_n$  and  $t_{n-1}$  being  $n$  the  
381 number of sample,  $A_i$  is the irradiated surface and  $V_t$  is the total volume.

382 The SPEF pilot plant installed at PSAis conformed by an electrochemical cell from  
383 Electro-MP cells with a BDD anode on a niobium substrate and a carbon-PTFE GDE  
384 cathode, both with an active area of 0.010 m<sup>2</sup>. The cell is connected to a compound  
385 parabolic collector (CPC) solar photo-reactor with 10 borosilicate glass tubes (4.5 cm  
386 inner diameter) corresponding to 23 L of illuminated volume and 2 m<sup>2</sup> of irradiated  
387 surface. Working conditions were established according to Salmerón et al. (2019) and  
388 75 L of effluent was treated in each experiment.

389 Commercial DSA pilot plant comprised an electrochemical cell with five DSA anodes,  
390 with a total active surface of 0.324 m<sup>2</sup>, connected to a CPC solar photo-reactor with 24  
391 borosilicate glass tubes (3.2 cm inner diameter) achieving an illuminated volume of 22  
392 L and an illuminated area of 3.08 m<sup>2</sup>. Operating conditions were established following  
393 the manufacturer's recommendations and so applying a current density of 25 mA cm<sup>2</sup>.  
394 The maximum treatment capacity of the system per batch is 38 L.

395

396

397

## 398 4.2 Results and discussion

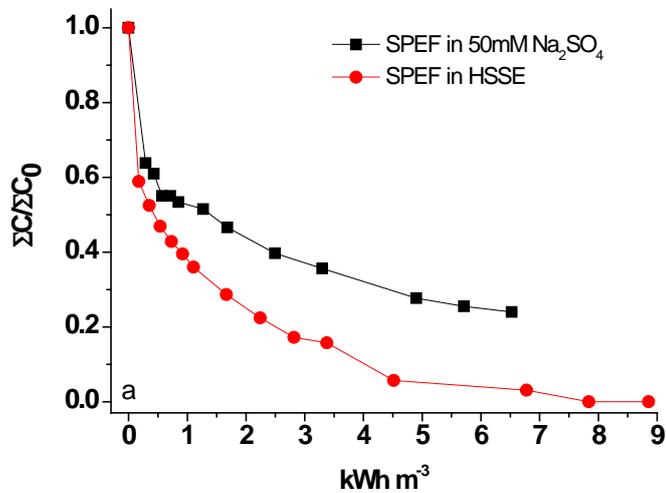
### 399 4.2.1 Solar photoelectron-Fenton pilot system

400 Experiments performed by adding 50 mM of Na<sub>2</sub>SO<sub>4</sub> as supporting electrolyte, as well  
401 as those with HSSE, were spiked with 200 µg L<sup>-1</sup> of PCP and TBT, respectively, while  
402 HSAE were spiked with 100 µg L<sup>-1</sup> of each MCs, closer to actual wastewater  
403 conditions. All SPEF tests were performed at natural pH, thus iron was maintained in  
404 solution by using EDDS as complexing agent and so entailing an increase in DOC of 24  
405 mg L<sup>-1</sup>.

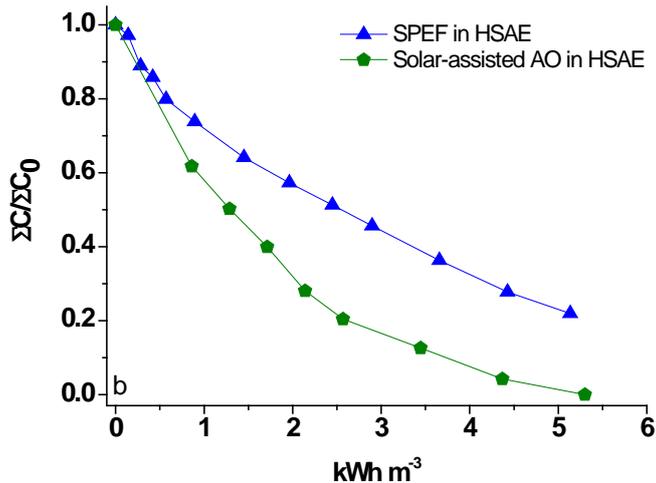
406 At the end of the treatment with 50 mM of Na<sub>2</sub>SO<sub>4</sub>, 80% MCs degradation was not  
407 attained (Fig. 3a), after applying 6.5 kWh m<sup>-3</sup> and a Q<sub>UV</sub> of 10 kJ L<sup>-1</sup>. In HSSE,  
408 degradation was faster, requiring only 2.8 kWh m<sup>-3</sup> and a Q<sub>UV</sub> of 5.3 kJ L<sup>-1</sup> to achieve  
409 80% of degradation of the sum of the MCs (PCP and TBT), even when the water had  
410 lower conductivity (Table 2), the electric consumption was also lower. The main  
411 difference was that HSSE contained more than 500 mg L<sup>-1</sup> chloride, thus not only •OH,  
412 were generated at the anode but also the presence of ACS (reactions (1 - 4)), which, in  
413 turn, could be activated by sunlight, increased significantly the oxidizing capacity of the  
414 system. In fact, in Sanchez-Montes et al. (2020) it was reported the conversion of 76%  
415 of HClO into radicals (reaction (11)) after 1 hour of treatment when irradiated with a 9  
416 W UV-C lamp. In the case of sunlight, the irradiation available to interact with the ACS  
417 is in the UV-A and UV-B range as shown in Fig. 2. Therefore, it is possible that the  
418 conversion efficiency into radicals would be lower than with UV-C lamps, but with the  
419 advantage of using a green and renewable energy source.

420 Regarding HSAE, the concentration of chlorides was higher than in HSSE, however it  
421 contained higher organic matter background (43 – 78 mg L<sup>-1</sup> of DOC) which competed

422 with MCs for radicals and other oxidative species, slowing down the degradation  
 423 process (Ferreira et al., 2020). As it is shown in Fig. 3b, at the end of the SPEF  
 424 treatment of HSAE, 80% removal of the sum of MCs was not reached. Aiming to  
 425 reduce the organics dissolved in the effluent, the treatment in HSAE was addressed by  
 426 solar-assisted AO and thus the use of EDDS was avoided. Then, 80% of removal of  
 427 MCs was attained after applying 2.6 kWh m<sup>-3</sup> and 6.6 kJ L<sup>-1</sup> of accumulated UV energy.



428 (a)



429 (b)

430 **Fig. 3.** Degradation profile of the sum of both MCs (PCP and TBT) a) at 200 µg L<sup>-1</sup>  
 431 each dissolved in 50 mM of Na<sub>2</sub>SO<sub>4</sub> and in HSAE treated by SPEF at pilot plant scale,

432 b) at  $100 \mu\text{g L}^{-1}$  each in HSAE treated by SPEF and solar-assisted AO at pilot plant  
433 scale.

#### 434 *4.2.2 Dimensionally Stable Anodes pilot system*

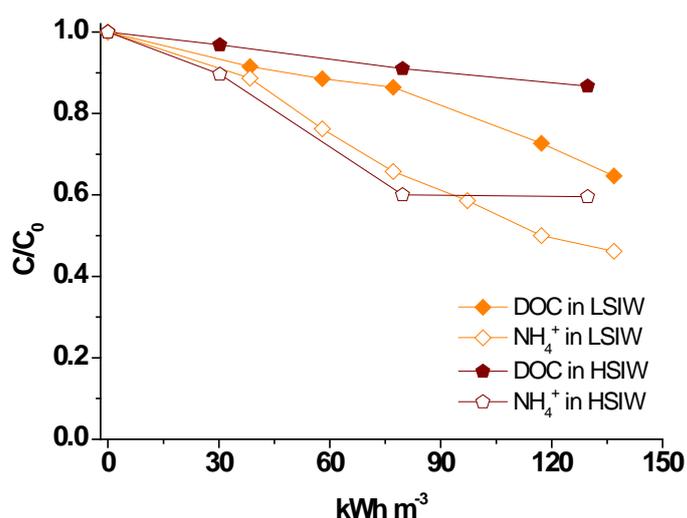
435 On the other hand, non-biodegradable industrial effluents is one of the main depuration  
436 challenges that must be faced by advanced technologies, not because the vast volume  
437 produced but due to the high concentration of organic matter content (in the range of g  
438  $\text{L}^{-1}$  of DOC) which includes a huge amount of unknown hazardous and persistent  
439 compounds. Electro-oxidation efficiency for mineralization of this highly complex  
440 actual effluents is very low, however it can be improved when applying a light source,  
441 as it was reported by (Alfonso-Muniozguren et al., 2020) for slaughterhouse  
442 wastewater.

443 In the present study, the efficiency of DSA-based system assisted by solar energy was  
444 evaluated for the treatment of a complex wastewater, showing the results in terms of  
445 DOC and  $\text{NH}_4^+$  removal. As shown in Fig. 4, the effectiveness of electrochemical  
446 processes (solar-assisted AO) on mineralization is very low, being necessary a huge  
447 amount of energy ( $> 100 \text{ kWh m}^{-3}$  of electrical energy and  $>100 \text{ kJ L}^{-1}$  of  $Q_{\text{UV}}$ ) to  
448 remove less than 50% of DOC. For this reason, instead of considering solar-assisted AO  
449 as the unique treatment option, it could be applied as a pretreatment to improve  
450 biodegradability enough in order to subsequently combine with a lower costly  
451 biological treatment as it has been demonstrated in recent published studies (Ferreira et  
452 al., 2020; Salmerón et al., 2020).

453 Furthermore, and contrary to what it could be expected, higher DOC degradation rate  
454 was obtained in LSIW than in HSIW despite having a greater conductivity and a higher  
455 chloride concentration. This can be explained by the very high concentration of  $\text{NH}_4^+$  in

456 HSIW (9940 mg L<sup>-1</sup>), which reacts rapidly with ACS thus reducing their availability to  
457 oxidize organic matter (Wahman, 2018) or to generate radicals.

458 Therefore, application of electrooxidation processes should take into account the specific  
459 characterization of target wastewater. As in DSA electrodes the main electrogenerated  
460 oxidizing species are ACS, the effect of NH<sub>4</sub><sup>+</sup> is even more detrimental in these systems  
461 than in those with electrodes with a higher oxygen evolution over-potential and so able  
462 to generate •OH, as BDD electrodes. This effect was also reported previously in Tirado  
463 et al. (2018), where 95.2% of total nitrogen was abated with an RuO<sub>2</sub>-based active  
464 anode while 41.5% with BDD.



465

466 **Fig. 4.** DOC and NH<sub>4</sub><sup>+</sup> removal in LSIW and HSIW (Table 2) by solar-assisted AO  
467 with a DSA system.

## 468 5. Conclusions

469 The application of electrochemical treatments to actual wastewaters depuration poses an  
470 enhancement on the oxidative power of the system, since available dissolved inorganic  
471 ions could be precursors of different oxidative species. Research on electrochemical  
472 processes must be upgraded to the treatment of actual wastewaters as

473 artificial/simulated saline solutions are far away of possible realistic industrial  
474 applications. Furthermore, ammonium content in wastewaters is an essential parameter  
475 to determine the efficiency of generated ACS by electrochemical processes.

476 Combination of an electrochemical system with a light source entails an enhancement  
477 on degradation rates due to the generation of new oxidizing species, not only in classical  
478 electrooxidation processes but also in electrochemical treatments based in Fenton,  
479 Fenton-like and photo-Fenton where regeneration of  $\text{Fe}^{2+}$  is an important issue.

480 Considering the high electrical energy consumption (and related costs) that could imply  
481 the application of electrochemical systems, a further challenge to be faced in the near  
482 future is their combination with other technologies, either to supply the cells with a  
483 renewable electrical energy source or to combine directly with solar irradiation.

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