

1 **Electrochemical degradation of a methyl paraben and propylene**
2 **glycol mixture: interference effect of competitive oxidation and**
3 **pH stability**

4
5 Dawany Dionisio^{a,b}, Manuel A. Rodrigo^b, Artur J. Motheo^{a,*}

6
7
8 ^(a) São Carlos Institute of Chemistry, University of São Paulo, P.O. Box 780, CEP 13560-970,
9 São Carlos, SP, Brazil

10 ^(b) Department of Chemical Engineering, Faculty of Chemical Sciences & Technologies,
11 Universidad de Castilla - La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain

12
13
14
15 *Corresponding author
16 Phone: +55 16 33739932
17 E-mail: artur@iqsc.usp.br

18

19 **Highlights**

20

- 21 • Electrolysis with DSA[®]-Cl₂ anode promotes the oxidation and polymerization of PG.
- 22 • Competitive oxidation is observed for the Mix, decreasing mineralization efficiency.
- 23 • MeP removal might increase in Mix due to its copolymerization with PG oligomers.
- 24 • Buffered acid medium resulted in a higher mineralization of MeP, PG and the Mix.

25

26

27 **Abstract**

28 Endocrine disrupting compounds (EDCs) are one of the many classes of harmful pollutants
29 frequently found in water resources. Even at low concentrations, EDCs might accumulate in
30 the organisms and interfere on numerous processes controlled by hormones. Parabens, for
31 example, are preservatives widely used in pharmaceutical and cosmetic industries, but several
32 studies related them to human breast cancer. It is well-known that electrochemical technologies
33 are an efficient alternative for wastewater treatment, promoting the appropriate destruction of
34 EDCs. However, most studies are applied to single target contaminant solutions, which may
35 neglect the impact from co-existed inorganic/organic pollutants. Based on that, this study aimed
36 to elucidate the interfering effects of two target organic contaminants of very different nature
37 during electrochemical mediated process. For that, methyl paraben (MeP) and propylene glycol
38 (PG) were selected as models of aromatic/phenolic and carboxylate compounds *versus* low-
39 molecular aliphatic alcohols. These two compounds are often together used in preservative
40 blends and cosmetic/pharmaceutical formulations. PG is not a harmful chemical, but it is
41 present in several types of effluents in relatively high concentrations. Thus, it may interfere on
42 the degradation of numerous pollutants of low concentrations. The electrochemical treatment
43 of a mixture containing 100 mg L⁻¹ MeP + 1,000 mg L⁻¹ PG showed that both contaminants
44 suffered interfering effects. The presence of MeP negatively interfered on PG degradation; the
45 carboxylate compound is more easily oxidized even at lower molecular concentration. On the
46 other hand, the presence of PG showed an unexpected positive effect on MeP degradation, that
47 was not reflected on its mineralization. The results indicate that in addition to the expected
48 effect of anodic competition, polymerization and copolymerization reactions also occur in the
49 studied system. The use of an acidic buffer medium increased the removal of both contaminants
50 and favored the oxidation pathway over the polymerization. In this case, the increase in the
51 removal was reflected in the mineralization process, which increased up to 6 times when the
52 mixture was treated in the buffered medium.

53

54 **Keywords**

55 degradation; buffering system; mixed metal oxide anode; polymerization.

56

57 **Introduction**

58 Endocrine disrupting compounds (EDCs) are one of the many classes of harmful pollutants
59 frequently detected in water resources. These chemicals are present in several everyday
60 products and represent a huge threat to the health of animals and humans. Even at low
61 concentrations, EDCs might accumulate in the organisms and interfere on numerous processes
62 controlled by hormones (Bergman et al., 2013; Damstra et al., 2002; Diamanti-Kandarakis et
63 al., 2009). Parabens, for instance, constitute a class of chemical compounds largely used in
64 cosmetic and pharmaceutical industries as antimicrobial preservatives (Bledzka et al., 2014;
65 Haman et al., 2015). In 2004 they were related to human breast cancer, and since then, several
66 studies have reported their adverse effects on the environment and the human and animal health
67 (Dagher et al., 2012; Darbre et al., 2004; Haman et al., 2015; Matwiejczuk et al., 2020; Nowak
68 et al., 2018). However, these substances are still widely used and, consequently, are detected
69 in several environmental sources (Chen et al., 2017; Honda et al., 2018; Li et al., 2015; Marta-
70 Sanchez et al., 2018).

71 It is well-established that conventional methods of wastewater treatment are inefficient for the
72 removal of several classes of chemical pollutants (Rajeshwar and Ibanez, 1997; Sirés et al.,
73 2014). As an alternative, the application of electrochemical methods has proven to be an
74 efficient way to overcome this problem, showing high efficiency for the mineralization of
75 various wastewater types (Brillas, 2021; Deng et al., 2018; Martínez-Huitle et al., 2015;
76 Martínez-Huitle and Panizza, 2018; Paździor et al., 2019).

77 Several studies reported the effectiveness of mixed metal oxides (MMO) anodes for mediated
78 oxidation of organic compounds (Martínez-Huitle and Panizza, 2018; Oliveira et al., 2018;
79 Pointer Malpass and de Jesus Motheo, 2021). Commercial MMO anodes are usually cheap,
80 very robust and stable, and divided into two types: good performance for O₂ or Cl₂ evolution.
81 In the case of matrices containing chloride anions, the latest type of anode is an interesting
82 approach for electrochemical treatment. Active chlorine species (Cl₂, HClO and ClO⁻) are
83 produced in the medium, being capable of oxidizing organic matter and disinfecting solutions
84 contaminated with microorganisms. Besides these species, chemically adsorbed •OH radicals
85 are also produced by MMO electrodes. This is a very powerful oxidant, which due to its non-
86 selective nature presents good efficiency for the mineralization process (Sirés et al., 2014;
87 Trigueiro et al., 2017). Recently, a study using a Ti/Ru_{0.3}Ti_{0.7}O₂ anode showed that the adsorbed

88 •OH radicals played an important role in the oxidation mechanism of methyl paraben, even
89 under the presence of active chlorine species (Dionisio et al., 2020).

90 Besides all studies reported using electrochemical technologies, their real application always
91 faces the challenge of the complexity of the matrix and the effects of the process on it. Many
92 current studies are applied to single target contaminant solutions, which may neglect the impact
93 from co-existing inorganic/organic pollutants. Understanding the effect of the treatment on
94 molecules of different nature, the mechanism of oxidants production and of organics
95 breakdown, the possible parallel reactions and competitions are essential to improve the
96 treatments for specific types of wastewater matrices. Based on that, this study aimed to
97 elucidate the interfering effects of two target organic contaminants of different nature during
98 electrochemical mediated process. For that, methyl paraben (MeP) and propylene glycol (PG)
99 were selected as models of aromatic/phenolic and carboxylate compounds *versus* low-
100 molecular aliphatic compounds.

101 Parabens present structural characteristics that are very common to various water pollutants.
102 Their degradation have been extensively studied by biological methods and several advanced
103 oxidative processes, including electrochemical technologies, as well detailed in recent reviews
104 (Ngigi et al., 2021; Nguyen et al., 2021). Consequently, their main characteristics in several
105 effluents and oxidation mechanisms by several processes are well-known, which is an
106 important feature to consider for a model molecule. On the other hand, PG is a very common
107 cosmetic ingredient, largely used in pharmaceutical and food industries (Martin and Murphy,
108 2000). It is not a harmful chemical, but it is present in several types of wastewater, usually in
109 relatively high concentrations. Thus, it may interfere on the treatments for removing several
110 low concentration pollutants.

111 Parabens and PG are often found together in preservative blends, cosmetic formulations and
112 pharmaceutical manipulations, as so in industrial and domestic wastewaters. The presence of
113 chloride anions in this type of contaminated water is also very common, surpassing the
114 concentrations of other inorganic anions such as sulfate, phosphate and nitrate (Boroski et al.,
115 2009; Carbajo et al., 2015; Friha et al., 2014; Tobajas et al., 2014). Considering this, a
116 commercial MMO anode with high efficiency for Cl₂ evolution was used to study the mediated
117 oxidation of MeP and PG as single targets and as mixture in chloride medium. The results
118 presented contribute to the comprehension of competitive effects of electrochemical treatments
119 in complex matrices.

120

121 **Experimental**

122 *Chemicals.* Methyl paraben and propylene glycol were obtained from Sigma-Aldrich. NaCl
123 (Synth) was used as supporting electrolyte. H₂SO₄, acetonitrile (HPLC grade) and methanol
124 (HPLC grade) were obtained from PanReac. To maintain the solution at pH = 3, a buffer
125 solution of 0.1 M monochloroacetic acid (AnalytiCals) was prepared (named as
126 monochloroacetate buffer, B_{MCAc}). All the solutions were prepared using high-purity water
127 obtained from a Millipore Milli-Q system (resistivity >18M cm at 25 °C) and reactants without
128 any purification.

129 *Working solutions.* Solutions of MeP (100 mg L⁻¹) and PG (1,000 mg L⁻¹) were treated
130 individually and as a mixture (named as Mix) at the proportion 1:10 (w/w). Two different
131 media were used: NaCl 0.15 M and NaCl + B_{MCAc} (0.15 M/0.1 M), both with initial pH = 3
132 (adjusted with HCl and/or NaOH 0.1 M).

133 *Experimental set-up.* Two systems were used in this study. First, to evaluate the degradation
134 of the pollutants and the Mix, a recirculation flow system, described elsewhere (Dionisio et al.,
135 2020), was used to treat 1.7 L of each solution in NaCl medium. The system was constituted
136 of a one-compartment electrochemical cell of 1.2 L capacity, a jacketed reservoir of 1 L
137 capacity and a circulator pump working at 5.0 mL s⁻¹ flow rate. A second set-up was used to
138 evaluate the effect of a buffering system on the electrochemical process. Experiments using
139 NaCl and NaCl + B_{MCAc} media were carried out in a batch system using a jacketed cell with
140 0.6 L of solution. Both systems worked with two electrodes – a commercial DSA[®] of
141 Ti/Ru_{0.3}Ti_{0.7}O₂ (DeNora Brazil) as anode and a Ti plate as cathode – with 54 cm², separated by
142 5 cm. All electrolysis were performed using a Autolab PGSTAT 128N (Metrohm B.V.) and a
143 thermostatic bath (Neslab Instrument RTE-221) to maintain the working solution at 25 °C.

144 *Analytical methods.* The concentration of MeP was determined by liquid chromatography in a
145 HPLC Shimadzu SPD-10A VP, with a Zorbax SB-C18 (25 cm x 4.6 mm) column and UV
146 detector set in 254 nm. The mobile phase was acetonitrile and water (40:60 v/v) at 30 °C and
147 the flow rate was 1 mL min⁻¹. The monochloroacetic acid was monitored in the same
148 chromatographic system, using a Aminex HPX-87H (Bio-Rad) column and H₂SO₄ 0.005 M as
149 mobile phase (1 mL min⁻¹). The temperature of the oven was 25 °C and the detector was set at
150 214 nm. The concentration of PG was monitored by gas chromatography in a GC- 2010 PLUS
151 (Shimadzu) equipped with Carbowax column (30 m x 0.250 mm id x 0.250 mm, Agilent
152 Technologies Inc) and FID detector. The temperature of the injector and the detector were set
153 in 200 °C, and the oven temperature program was: 50 °C for 1 min, then 25 °C min⁻¹ to 200 °C.
154 Nitrogen was the carrier gas, with 1.68 mL min⁻¹ flow rate and 200 kPa. The total organic

155 carbon (TOC) was also determined, using a carbon analyzer Sievers InnovOx, General Electric
156 Company (FAPESP 2014/02739-6).

157

158 **Results and discussion**

159 *Degradation of the single compounds and the Mix*

160 The degradation of methyl paraben as single target contaminant, using DSA-Cl₂ anode and
161 chloride medium, was previously studied and reported elsewhere (Dionisio et al., 2020). Thus,
162 in this study MeP is used as a model molecule to understand the interfering effects of propylene
163 glycol on its degradation. For that, PG was also treated as single target contaminant and then
164 in the Mix with MeP. Both compounds are often used at the proportion 1:10 (w/w, MeP:PG)
165 for preservative blends and cosmetic formulations. To better observe the interfering effects, a
166 solution of 100 mg L⁻¹ MeP + 1,000 mg L⁻¹ PG in chloride medium was studied.

167 **Fig. 1** shows the removal of MeP in chloride medium as a single target component (100 mg L⁻¹)
168 and in the Mix with PG. It is observed that the higher is the applied current density (j_{app}), the
169 faster the complete removal is attained. In this system, the oxidation of organic compounds
170 mainly occurs through active chlorine species generated in the medium, as showed by **Eqs.**
171 **(1)-(3)** (Martinez-Huitle et al., 2015; Sirés et al., 2014 REF). These oxidants are majorly formed
172 at the anodic region and, because of their stability, they are transported to the bulk of the
173 solution. The electroproduction of chlorine gas increases at higher j_{app} values and, therefore,
174 MeP removal is improved.

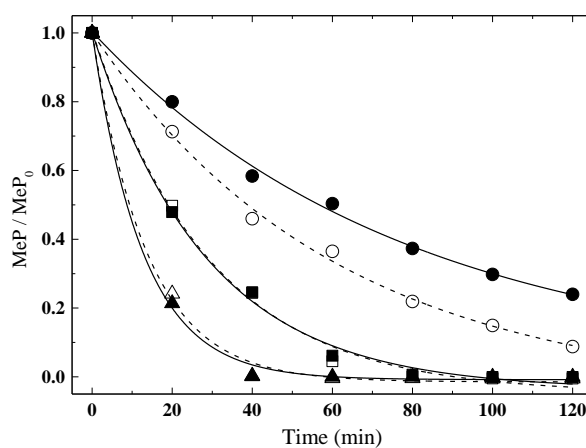


178 It is worth noting that besides the major production of active chlorine species by DSA-Cl₂
179 anodes, chemically adsorbed •OH radicals are also produced in minor scale at the surface of
180 the electrode. In DSA-Cl₂ anodes, •OH radicals are physically adsorbed to the surface due to
181 water electrolysis (**Eq. (4)**). Then, these species can interact with the electrode's surface
182 producing the so-called chemisorbed 'active oxygen' (M=O) (**Eq. (5)**) (Salazar-Banda et al.,
183 2021). In fact, Dionisio *et al.* verified that these hydroxyl radicals play an important role in
184 the early steps of MeP degradation, even in the presence of chlorine species (Dionisio et al.,
185 2020). So, similarly, higher j_{app} improve the production of chemisorbed 'active oxygen',
186 increasing MeP removal.



189 The removal of MeP from the Mix presented similar results to the removal of MeP as single
190 contaminant at higher j_{app} values, achieving complete removal after 80 and 40 min for 5.0 and
191 10 mA cm⁻², respectively. However, at 2.5 mA cm⁻², faster elimination of MeP occurs in the
192 Mix, achieving 91% of removal after 2h, compared to 76% obtained when treated as single
193 target contaminant. The improvement observed in the presence of a second organic compound
194 – propylene glycol in this case – was not expected, but it suggests the occurrence of a parallel
195 reaction that assists removing MeP from the solution.

196



197

198 **Figure 1.** Removal profile of MeP when treated as single target contaminant (full symbols) and as a
199 Mix component (empty symbols) by electrochemical process in NaCl 0.15 M. $j_{app} = (\bullet, \circ)$ 2.5; (\blacksquare, \square)
200 5.0; $(\blacktriangle, \triangle)$ 10 mA cm⁻² at 25 °C.

201

202 In the previous study using MeP as single contaminant (Dionisio et al., 2020), the
203 mineralization process was incomplete, indicating the complexity of the intermediates formed
204 during the degradation. Consequently, the authors reported the formation of an
205 organochlorinated solid product, which could be degraded by the process itself under higher
206 applied current. Similarly, this same solid was produced during the degradation of the Mix in
207 this study, and it was observed its lower accumulation for higher j_{app} .

208 In order to evaluate the interfering effect of PG on MeP degradation, its removal was studied
209 as a single target contaminant (1,000 mg L⁻¹) and in the treatment of the Mix, using the same
210 conditions. Fig. 2 shows that the abatement of PG in the Mix is very low and quite similar in
211 the range of the applied currents, achieving 16-23% of removal (inset). On the other hand,

212 when treated as a single contaminant, it was possible to achieve greater PG removals and the
213 improvement with higher j_{app} values is more significant (30% at 10 mA cm⁻²). These results
214 indicate that PG removal is disfavored in the presence of MeP, which is expected considering
215 a competition between both components.

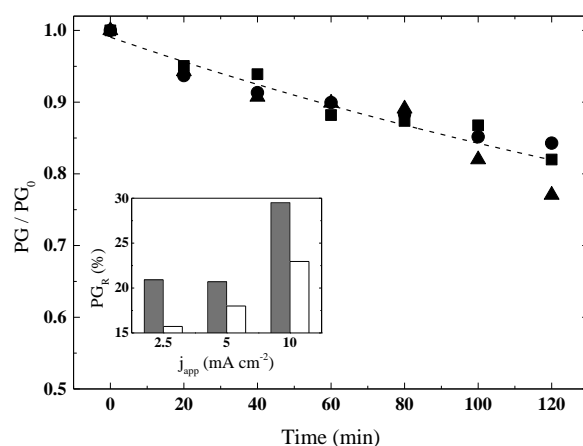
216 So, both contaminants suffered interfering effects when treated as a mixture: while the presence
217 of MeP negatively interfered in PG degradation, the presence of PG showed an unexpected
218 positive effect on MeP degradation (very clear at low applied current, **Fig. 1**). The first effect
219 is relatively common in studies of competitive oxidation. Due to the presence of multiple target
220 contaminants, the oxidant species are not equally distributed to oxidize each organic
221 compound. Usually, it is expected that compounds at higher concentrations are more easily
222 oxidized, mostly because of its better mass transport/distribution in the system. However, at
223 the present case, MeP negatively interfered in PG oxidation due to its structure. Even at a lower
224 molecular concentration (0.66 mM of MeP *versus* 13 mM of PG), the oxidation of an aromatic
225 carboxylate compound, MeP, was preferable over a small aliphatic alcohol, PG, in this system.
226 On the other hand, the positive effect that PG presence caused in MeP degradation is initially
227 not clear and will be considered and discussed in the following sections.

228

229 *Consideration of PG polymerization*

230 As explained before, the main oxidants in the used system are the active chlorine species, which
231 are formed accordingly to the Cl₂ production. If considered the extrapolation that all applied
232 charge is used for the oxidation of Cl⁻ to Cl₂, it is possible to estimate the maximum
233 concentration of chlorine produced (based on Faraday's laws). In this study, chlorine
234 production would be in the range of 3–12 mM (for 2.5–10 mA cm⁻²) after 2h electrolysis, while
235 initial MeP and PG concentrations are maintained at 0.66 and 13 mM, respectively, to all
236 experiments. One should also remember that parallel reactions such as water oxidation and O₂
237 evolution also occur in the system, and that Cl₂ need to be converted into oxidants by **Eqs. (2)-**
238 **(3)**. Therefore, the real concentration of chlorine oxidants might be even lower than this
239 theoretical maximum concentration of Cl₂.

240



241
 242 **Figure 2.** Removal of PG from the Mix at different applied currents (●) 2.5; (■) 5.0; (▲) 10 mA cm⁻²,
 243 in NaCl 0.15 M at 25 °C. **Inset:** Total removal of PG obtained when treated as single target contaminant
 244 (black bars) and as a Mix component (white bars), after 2h electrolysis in NaCl 0.15 M at 25 °C.

245

246 In the case of MeP degradation, its concentration is probably lower than the oxidants
 247 concentration, so a “typical” oxidation process is occurring. However, it is clear that the
 248 chlorine oxidants concentration is lower than PG concentration, which can result in the
 249 occurrence of other parallel reactions. Under this condition, one can also expect that the
 250 chemically adsorbed ‘active oxygen’ (Eq. (5)) plays an even important role in the degradation
 251 process. Due to the high concentration of PG and relatively low concentration of oxidants in
 252 the bulk (stable active chlorine species), it is possible that the main portion of PG is reacting
 253 near to the anodic surface, where greater concentration of oxidant species is found (including
 254 radicals and Cl₂) and also where the direct oxidation process can occur.

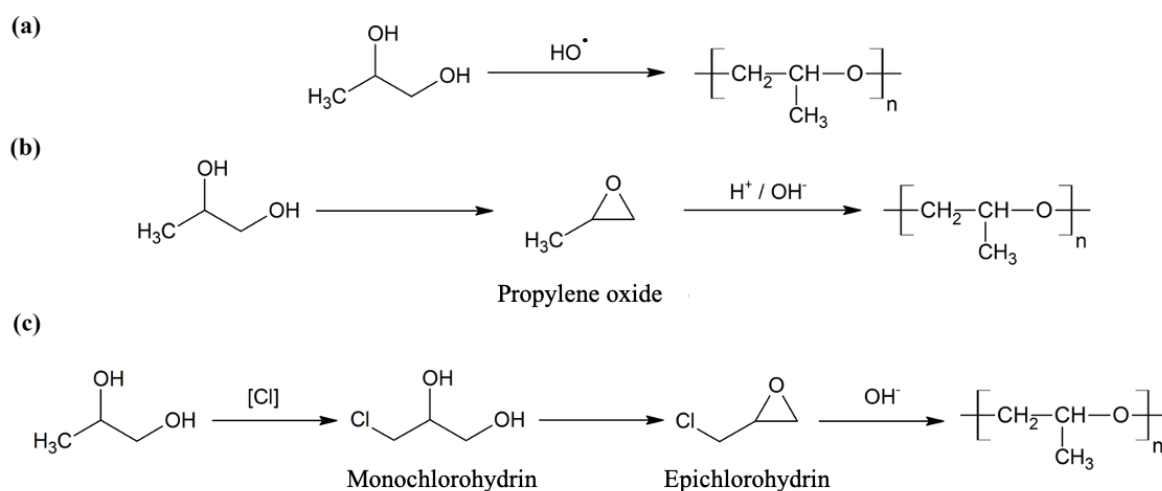
255 Considering the above-described conditions and the results discussed in the previous section,
 256 it is evident the occurrence of some organic parallel reaction(s) that cause the interfering effects
 257 observed. It is well known that PG is an important intermediate on the production of polyether
 258 polyols, which is a polymer class widely used on several industries. Based on that we consider
 259 the possibility that the polymerization of PG is taking place as a parallel reaction in the system
 260 and competing to its oxidation. Below, we propose three polymerization pathways feasible to
 261 occur under the applied conditions in this study:

- 262 i) Free-radical polymerization of PG in the anodic region, where hydroxyl radicals (M(•OH);
 263 M=O) are initiators and PG derived radicals are propagators (Kobayashi and Higashimura,
 264 2003) (Fig. 3a);
- 265 ii) Under the drastic acidic conditions near to electrodes surface, it is possible to occur PG
 266 epoxidation, resulting in propylene oxide. Its polymerization may start via acidic or basic

267 catalysis in aqueous medium, where PG is added to activated oligomers structure (Gagnon,
268 2008; Herzberger et al., 2016; Steiner et al., 1964) (**Fig. 3b**);

269 iii) The presence of activated chlorine species assists the formation of monochlorohydrin,
270 which in a basic medium may produce epichlorohydrin. Under the same conditions,
271 epichlorohydrin is activated by OH^- and added to PG molecules (Bell et al., 2008;
272 Cucciniello et al., 2016; Herzberger et al., 2016; Lu et al., 2015) (**Fig. 3c**).

273



274

275 **Figure 3.** Scheme of three possible polymerization pathways of PG, proposed for the studied
276 electrochemical system: (a) via free-radical, (b) via propylene oxide and (c) via epichlorohydrin.

277

278 This polymerization theory explains the improvement on removal of MeP under the presence
279 of PG (Mix treatment) observed in **Fig. 1** (at 2.5 mA cm^{-2}). Due to its phenolic nature, it is very
280 plausible that MeP and/or its oxidation products are incorporated to the polymer, especially
281 considering the free-radical mechanism proposed (Herzberger et al., 2016; Kobayashi and
282 Higashimura, 2003). It is well-known that oxidative polymerization of phenolic compounds is
283 one of the most common polymerization mechanisms (Kobayashi and Higashimura, 2003). As
284 a result, MeP is consumed from the solution by the copolymerization process with
285 polypropylene, or the consumption of its (phenolic)intermediates shifts the equilibrium to
286 improve MeP oxidation.

287 Considering that is under the lower j_{app} that the greater difference between PG and oxidants
288 concentration is observed (as explained before), 2.5 mA cm^{-2} is probably the main condition
289 that parallel reactions (such as polymerization) can take place. Also, in general, at lower applied
290 currents it is expected lower reactions rate, which in the case of polymerization reactions means

291 the production of longer-chain polymers. This can facilitate the copolymerization process and
 292 might be the reason why synergic removal of MeP from the Mix is only clear at 2.5 mA cm⁻².
 293 Besides longer-chain polymers be favored under lower j_{app} , during PG degradation as single
 294 target contaminant, no solid formation was observed. This indicates that the produced polymer
 295 may presents relatively low molecular weight and some solubility in water (Herzberger et al.,
 296 2016).

297 According to that, the lower removal of PG as a Mix component than as a single contaminant
 298 (Fig. 2) can be attributed to two interfering effects: a decrease in the oxidation and the
 299 polymerization rates. As mentioned, due to its structure MeP molecule is more easily oxidized
 300 than PG, resulting in a competition for oxidant species and a lower oxidation rate of PG. In
 301 addition to that, the copolymerization process might affect the polymerization rate, since the
 302 incorporation of MeP molecules into the PG polymer results in higher removal of MeP from
 303 solution and lower consumption of PG. Ultimately, it is observed that the interference of MeP
 304 on PG degradation is greater than the opposite effect.

305 **Tab. 1** presents the results of TOC removal (%) and energy consumption per unit of TOC mass
 306 (EC) calculated by Eq. (6), where U is the cell voltage (V), I is the applied current (A), t is
 307 time (h), V is volume of working solution (L) and ΔTOC is the experimental TOC decay (in
 308 mg L⁻¹).

$$309 \quad EC (kW h gTOC^{-1}) = \frac{U.I.t}{V.\Delta TOC} \quad (6)$$

310 It is observed a very low removal of organic matter due to the high concentration of PG and
 311 relatively low applied current. Results indicate the formation of a very recalcitrant
 312 intermediate, which is easily explained by the occurrence of polymerization reactions.
 313 However, the removal of TOC also indicates that oxidation takes place in the system, even at
 314 low rates. An increase in j_{app} values did not result in better TOC removals, thus high level of
 315 energy consumption was obtained. This result also evidences the formation of
 316 polymers/copolymers, which inhibits the oxidation process increasing CE.

317 **Table 1.** Total removal of TOC obtained after 2h of electrolysis and the respective energy consumption
 318 when treating PG as a single target contaminant and as a Mix component in NaCl 0.15 M at 25 °C

	j_{app} (mA cm ⁻²)	Removal of TOC (%)	EC (kWh gTOC ⁻¹)
PG	2.5	13	0.008
	5.0	12	0.023
	10	11	0.076

Mix	2.5	2.2	0.054
MeP-PG	5.0	11	0.024
	10	12	0.058

319

320 *Understanding the buffering effect*

321 Measurements of pH after the applied processes showed that the ΔpH values varied depending
 322 on the contaminant (MeP, PG or Mix) and the j_{app} , ranging from 1 to 5 units. Variations on pH
 323 followed the order $\text{PG} > \text{Mix} > \text{MeP}$, which might be related to polymerization process
 324 occurring as main reaction. As a result, chlorine species can accumulate in the medium,
 325 elevating the pH. Similarly, the higher the j_{app} , the higher the ΔpH values observed, because of
 326 the active chlorine species in solution. The speciation of aqueous free chlorine is well-
 327 understood in literature (Deborde and von Gunten, 2008) and a increase in the pH represents
 328 a decrease in the oxidizing power of the solution:

- 329 • $\text{pH} < 1$, there is a mixture of Cl_2 and HClO , where Cl_2 predominates;
- 330 • $1 < \text{pH} < 4$, HClO is predominant over Cl_2 ;
- 331 • $4 < \text{pH} < 7.5$, the mixture is composed of HClO and ClO^- , where HClO predominates;
- 332 • $\text{pH} > 7.5$, the predominant specie is ClO^- , which is the weaker oxidizing agent.

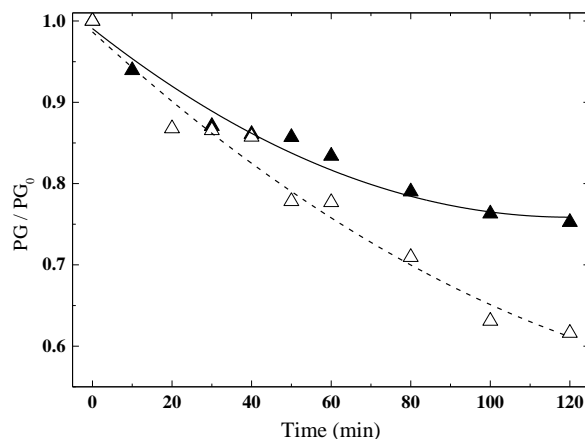
333 According to this, to better understand the process and the occurring interfering effects, the
 334 three solutions (MeP, PG and Mix) were also treated in a buffered medium (0.15 M NaCl +
 335 0.1 M B_{MCAC}) to maintain $\text{pH} = 3$ during all the electrolysis. The following presented results
 336 were performed in a batch system using the same previous electrodes, with 0.6 L of working
 337 solution and only at 2.5 mA cm^{-2} (as described in the Experimental section). The degradation
 338 of MeP as single target contaminant was previously studied in the buffered medium and
 339 showed no differences from the non-buffered solution, achieving complete removal in 80 min
 340 (Dionisio et al., 2020). It is worthy mention that monochloroacetic acid was submitted to
 341 electrochemical treatment under the same applied conditions and no significant degradation
 342 was observed within 2 hours.

343 **Fig. 4** shows that the removal of PG as single contaminant is clearly improved in the presence
 344 of B_{MCAC} , achieving 40% of removal after 2 h of treatment (compared to 25% of removal in the
 345 non-buffered medium). This result can be attributed to the enhancement of both oxidation and
 346 polymerization reactions. As discussed, acidic medium increases the oxidizing power of the
 347 solution, resulting in a better oxidation of PG. Likewise, the formation of Cl^\bullet radicals becomes

348 important when $\text{pH} \leq 3$ (**Eq. (7)**) (Lutze et al., 2015), which favors the polymerization reaction
349 (**Fig. 3c**).



351

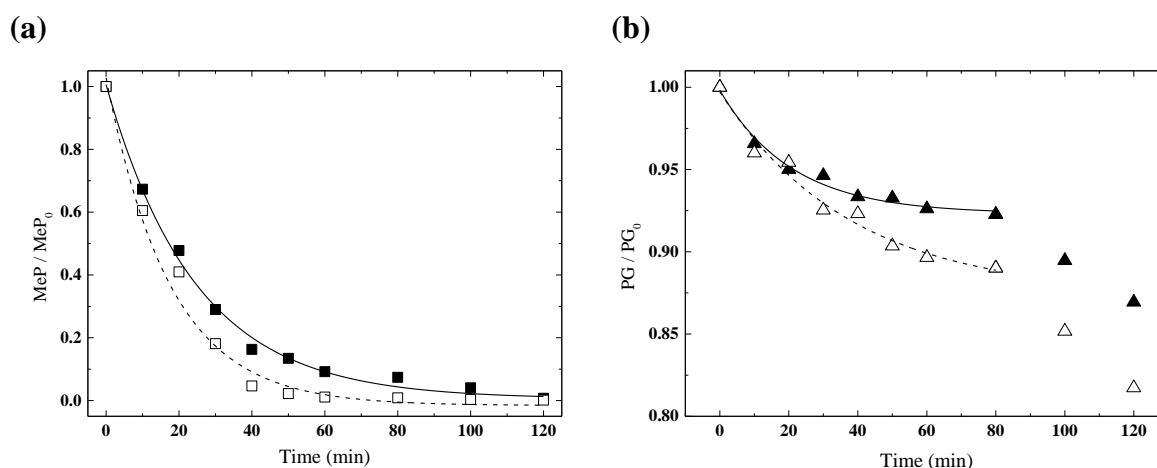


352

353 **Figure 4.** Removal profile of PG when treated as a single target contaminant by electrochemical process
354 in (▲) NaCl 0.15 M and in (△) NaCl + B_{MCAc}. $j_{\text{app}} = 2.5 \text{ mA cm}^{-2}$ at 25 °C.

355

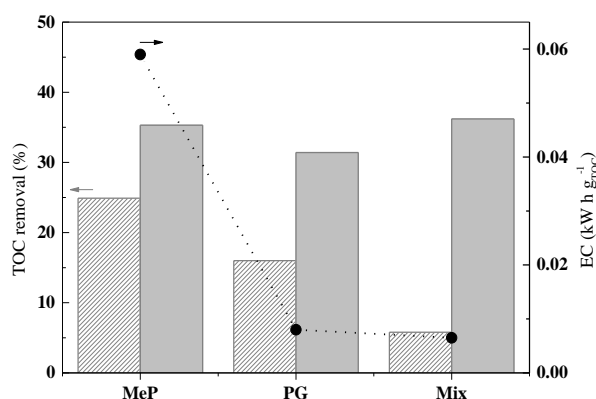
356 The behavior of both contaminants during the treatment of the Mix in the buffered and the non-
357 buffered solutions are presented in **Fig. 5**. As observed for single PG, its removal from the Mix
358 is improved by the constant acidic pH, which results from the enhanced oxidation and/or
359 polymerization reactions (**Fig. 5b**). Nevertheless, the removal percentages are lower than the
360 values obtained for PG degradation as single contaminant, because of the previously discussed
361 interfering effects of MeP. On the other hand, the removal of MeP from the Mix is improved
362 when treated in the buffered medium (**Fig. 5a**), differently from the results reported for single
363 MeP degradation (Dionisio et al., 2020). This effect can be explained by the copolymerization
364 reactions of MeP and/or its degradation products in the presence of PG. Also, since the buffered
365 medium can increase the polymerization rate, the copolymerization effect is also favored. So,
366 the polymerization theory considered before also explain the results obtained in the buffered
367 medium.



368 **Figure 5.** Removal profiles of (a) MeP and (b) PG when treated as Mix components in (■,▲) NaCl
 369 0.15 M and in (□,△) NaCl + B_{MCAc}. $j_{app} = 2.5 \text{ mA cm}^{-2}$ at 25 °C.

370
 371 The TOC removed by the process was also evaluated in this system. The results were obtained
 372 under a considerable low applied current value and with high initial organic carbon content.
 373 Thus, it was not expected to achieve high removal percentages, but actually to observe the
 374 behavior of TOC removal in each of the applied conditions, and its relationship with the
 375 polymerization theory. The removal of TOC represents the extension of the mineralization step,
 376 that is, the oxidation of all organic compounds in the solution. **Fig. 6** shows the TOC removal
 377 of MeP and PG as single target contaminants and as components of the Mix in both buffered
 378 and non-buffered solutions. The acidic medium favored the mineralization process in all
 379 systems, especially in the treatment of the Mix, where almost 40% of TOC removal is achieved
 380 in 2 h.

381 The mechanisms pathway and intermediates formed during the electrochemical oxidation of
 382 MeP and PG are reported in the literature (Dionisio et al., 2020, 2019; Steter et al., 2016, 2014).
 383 In chloride medium, the intermediates formed vary according to the anode composition. Steter
 384 *et al.* used a BDD anode to remove MeP from a sodium-chloride mixture medium. They
 385 detected several organochlorinated compounds of phenolic nature and small polychlorinated
 386 carboxylate compounds, before the mineralization was achieved (Steter et al., 2016). Dionisio
 387 *et al.* used a DSA-Cl₂ anode for MeP degradation and found that OH radicals played an
 388 important role on several steps of the mechanism, as mentioned before. In that study, the main
 389 intermediates were aromatic compounds of phenolic and carboxylate nature, being some of
 390 them chlorinated molecules (Dionisio et al., 2020). In another study *Dionisio et al.* reported
 391 some of the intermediates detected during PG electrooxidation. The main products were small
 392 carboxylic acids such as oxalic, formic, acetic, dichloroacetic acids (Dionisio et al., 2019).



394

395 **Figure 6.** Total removals of TOC achieved after 2h of electrochemical treatment of MeP and PG as
 396 single target contaminants and of the Mix, in NaCl 0.15 M (hatched bars) and in NaCl + B_{MCAc} (solid
 397 bars). $j_{app} = 2.5 \text{ mA cm}^{-2}$ at 25 °C. (●) Energy consumption of the treatment for MeP, PG and Mix in
 398 buffered solution.

399

400 According to those studies, the degradation of both MeP and PG involves the production of
 401 several aromatic and aliphatic carboxylic acids. Therefore, besides the higher oxidizing power
 402 under the acidic medium, it also tends to favor the decarboxylation reactions of intermediates,
 403 which are of great importance on the mineralization pathways. These results indicate that the
 404 interfering effect of polymerization/copolymerization reactions decreases in acidic medium,
 405 prevailing the oxidation of the pollutants. Under this condition, it is possible to oxidize the
 406 mixture with a lower energy consumption than that observed for simple solutions of MeP and
 407 PG.

408 **Tab. 2** compares the results obtained in this study with a few other studies applying
 409 electrochemical advanced oxidation processes to the removal of MeP from aqueous solutions.
 410 All the data showed in the table refer to 120 min of the specific treatment. The applied electrical
 411 charges (Q) were calculated based on the information containing in each paper. Similarly, the
 412 removals of TOC at 120 min were extracted from the figures presented in each study. It is clear
 413 that the total applied current in this work was very low. However, it is interesting to note that
 414 it was possible to achieve similar results of TOC removal. For instance, Fortunato *et al.*
 415 achieved approximately 70% removal of TOC after 2 h of photoelectro-Fenton process (PEF).

416 **Table 2.** Comparison of the TOC removal results obtained for different electrochemical processes
 417 reported in the literature for MeP degradation from aqueous matrices

[Pollutant] (mg L ⁻¹)	Experimental conditions	Process	Q (A h/L)	TOC removal	Ref.
--------------------------------------	-------------------------	---------	--------------	----------------	------

100 MeP	A: DSA-Cl ₂ ; C: Ti; 0.15 M NaCl;	EO	0.453	~ 35%	This study
100 MeP + 1,000 PG	j: 2.5 mA cm ⁻² ; pH: 3; T: 25 °C; V: 0.6 L	EO	0.453	~ 35%	This study
100 MeP	A: Si/BDD; C: Si/BDD; 0.06 M NaCl; j: 30 mA cm ⁻² ; pH: 3;	EO	4.50	~ 30%	(Dionisio et al., 2018)
100 MeP + 1,000 PG	T: 25 °C; V: 1 L	EO	4.50	~ 30%	(Dionisio et al., 2019)
100 MeP	A: Si/BDD; C: Si/BDD; 0.02 M Na ₂ SO ₄ ; j: 30 mA cm ⁻² ; pH: 3;	EO	4.50	< 60%	(Dionisio et al., 2018)
100 MeP + 1,000 PG	T: 25 °C; V: 1 L	EO	4.50	~ 50%	(Dionisio et al., 2019)
76 MeP	A: BDD; C: GDE-modified; 0.05 M Na ₂ SO ₄ ; j: 33.3 mA cm ⁻² ; pH: 2.5; T: 25 °C; V: 0.15 L; [Fe²⁺]: 0.5 mM; UVC 5W	EO	1.33	< 20%	(Fortunato et al., 2020)
		EF	1.33	~ 50%	
		PEF	1.33	~ 70%	
100 MeP	A: Nb/BDD; C: Activated GF (iron supported); 0.01 M Na ₂ SO ₄ ; i: 100 mA; pH: 3; V: 0.15 L.	EF	1.33	96.68%	(Rosales et al., 2018a)
158 MeP	A: BDD; C: GDE; 0.025 M Na ₂ SO ₄ + 0.035 M NaCl; j: 66.7 mA cm ⁻² ; pH: 3; T: 35 °C; V: 0.1 L; [Fe²⁺]: 0.5 mM; UVA 5 W m ⁻²	EO	4.00	< 50%	(Steter et al., 2016)
		EF	4.00	~ 50%	
		PEF	4.00	~ 60%	
158 MeP	A: DSA-Cl ₂ ; C: GDE; 0.025 M Na ₂ SO ₄ + 0.035 M NaCl; j: 66.7 mA cm ⁻² ; pH: 3; T: 35 °C; V: 0.1 L; [Fe²⁺]: 0.5 mM; UVA 5 W m ⁻²	EO	4.00	< 20%	(Steter et al., 2016)
		PEF	4.00	< 50%	

418 **Abbreviations:** A: Anode; C: Cathode; BDD: Boron-doped diamond; DSA-Cl₂: MMO electrode for Cl₂ evolution; GDE:
419 Gas diffusion electrode; EO: Electrochemical oxidation; EF: Electro-Fenton; PEF: Photoelectro-Fenton; GF: Graphite felt.

420

421 However, in that study it was applied almost 3 times the electrical charge used here and a lower
422 initial organic content. In the same study, with single electrochemical oxidation (EO), less than
423 20% of TOC was removed, which is an even lower result than the reported here (Fortunato et
424 al., 2020). Steter *et al.* studied the electrochemical oxidation of MeP and its associations with
425 Fenton and photo-Fenton processes, using several materials as anodes. In the **Tab. 2** it is

426 highlighted the results obtained with BDD and DSA-Cl₂ anodes. The mineralization is more
427 effective using BDD electrode, but when using DSA-Cl₂ the achieved TOC removal by EO is
428 lower than the obtained in this study, even when applying almost 10 times the electrical charge.
429 Another example, that Dionisio *et al.* also studied the removal of the mixture of MeP and PG,
430 using a BDD anode in NaCl and Na₂SO₄ media. The Q value was almost 10 times higher than
431 the applied in this study, and yet similar results of TOC removal were achieved in chloride
432 medium (Steter *et al.*, 2016).

433 There are several other studies using different treatment processes that achieved higher
434 efficiencies of MeP and TOC removals, such as Rosales *et al.* (Rosales *et al.*, 2018b).
435 Independently of the target pollutant or wastewater, it is well-known that the energy
436 consumption is still a major challenge to overcome for the real implementation of
437 electrochemical technologies. In this context, several authors have been studying the use of
438 renewable energies to supply the electrical energy for the water treatments (Ganiyu *et al.*, 2020;
439 Ganiyu and Martínez-Huitle, 2020). This approach is very interesting considering that it could
440 result in more sustainable, eco-friendly and autonomous processes, also reducing the demand
441 of fossil energy. Several studies discuss the application of solar photovoltaic cells, wind and
442 biomass, especially microbial fuel cells, as energy source for different electrochemical
443 technologies. Until now, solar photovoltaic cells have shown more advantages and attracted
444 the attention of most of the studies. Anyhow, these approaches are still under development and
445 are majorly applied to bench-scale systems. Under this perspective, treatment process that
446 apply lower electrical charges, such as this study, gains even more relevance.

447

448 **Conclusions**

449 From the results presented in this study, the following conclusions can be drawn:

- 450 • The electrochemical treatment with the use of DSA[®]-Cl₂ anode was not efficient for the
451 degradation of PG, possibly leading to its polymerization. This process competes with
452 oxidation reactions, inhibiting the removal of organic carbon.
- 453 • The Mix treatment showed that even at a lower molecular concentration the oxidation of
454 an aromatic carboxylate compound was preferable over a small aliphatic alcohol. Also
455 showed the possible effect of MeP incorporation (or its oxidation products) into PG
456 oligomers, resulting in a positive effect on MeP removal from the solution. This may
457 represent a possibility for future studies involving the removal of toxic pollutant from water
458 by their copolymerization with other compounds.

- 459 • The interfering effect of polymerization/copolymerization reactions decreased in acidic
460 medium, prevailing the oxidation and mineralization of the pollutants.
- 461 • Even applying low electrical charges, in the buffered medium, it was possible to achieve
462 100% removal of MeP in 60 min of treatment. Almost 40% of mineralization was attained
463 for the MeP-PG mixture (approximately 6 times better than in the unbuffered solution),
464 which is a result similar to some studies reported in the literature.

465

466 Acknowledgements

467 Authors gratefully acknowledge the financial support from São Paulo Research Foundation
468 (FAPESP), Brazil [2016/04825-2; 2016/19662-1; 2017/10118-0 and 2017/20444-1] and the
469 Spanish Ministry of Economy, Industry and Competitiveness, European Union through project
470 PID2019-107271RB-I00 (AEI/FEDER, UE).

471

472 References

- 473 Bell, B.M., Briggs, J.R., Campbell, R.M., Chambers, S.M., Gaarenstroom, P.D., Hippler, J.G.,
474 Hook, B.D., Kearns, K., Kenney, J.M., Kruper, W.J., James Schreck, D., Theriault, C.N.,
475 Wolfe, C.P., 2008. Glycerin as a renewable feedstock for epichlorohydrin production.
476 The GTE process. *Clean - Soil, Air, Water* 36, 657–661.
477 <https://doi.org/10.1002/clen.200800067>
- 478 Bergman, A., Heindel, J.J., Jobling, S., Kidd, K.A., Zoeller, R.T., 2013. State of the science of
479 endocrine disrupting chemicals - 2012. World Health Organization/ United Nations
480 Environment Programme, Geneva, Switzerland.
- 481 Bledzka, D., Gromadzinska, J., Wasowicz, W., 2014. Parabens. From environmental studies
482 to human health. *Environment International* 67, 27–42.
483 <https://doi.org/10.1016/j.envint.2014.02.007>
- 484 Boroski, M., Rodrigues, A.C., Garcia, J.C., Sampaio, L.C., Nozaki, J., Hioka, N., 2009.
485 Combined electrocoagulation and TiO₂ photoassisted treatment applied to wastewater
486 effluents from pharmaceutical and cosmetic industries. *Journal of Hazardous Materials*
487 162, 448–454. <https://doi.org/10.1016/J.JHAZMAT.2008.05.062>
- 488 Brillas, E., 2021. Recent development of electrochemical advanced oxidation of herbicides. A
489 review on its application to wastewater treatment and soil remediation. *Journal of*
490 *Cleaner Production* 290, 125841. <https://doi.org/10.1016/j.jclepro.2021.125841>
- 491 Carbajo, J.B., Perdigón-Melón, J.A., Petre, A.L., Rosal, R., Letón, P., García-Calvo, E., 2015.
492 Personal care product preservatives: Risk assessment and mixture toxicities with an
493 industrial wastewater. *Water Research* 72, 174–185.
494 <https://doi.org/10.1016/J.WATRES.2014.12.040>
- 495 Chen, J., Pycke, B.F.G., Brownawell, B.J., Kinney, C.A., Furlong, E.T., Kolpin, D.W., Halden,
496 R.U., 2017. Occurrence, temporal variation, and estrogenic burden of five parabens in

497 sewage sludge collected across the United States. *Science of the Total Environment*
498 593, 368–374. <https://doi.org/10.1016/j.scitotenv.2017.03.162>

499 Cucciniello, R., Pironti, C., Capacchione, C., Proto, A., Di Serio, M., 2016. Efficient and
500 selective conversion of glycidol to 1,2-propanediol over Pd/C catalyst. *Catalysis*
501 *Communications* 77, 98–102. <https://doi.org/10.1016/J.CATCOM.2016.01.026>

502 Dagher, Z., Borgie, M., Magdalou, J., Chahine, R., Greige-Gerges, H., 2012. p-
503 Hydroxybenzoate esters metabolism in MCF7 breast cancer cells. *Food and Chemical*
504 *Toxicology* 50, 4109–4114. <https://doi.org/10.1016/j.fct.2012.08.013>

505 Damstra, T., Barlow, S., Bergman, A., Kavlock, R., van der Kraak, G., 2002. Global assessment
506 of the state-of-the-science of endocrine disruptors. World Health Organization,
507 Geneva, Switzerland.

508 Darbre, P.D., Aljarrah, a, Miller, W.R., Coldham, N.G., Sauer, M.J., Pope, G.S., 2004.
509 Concentrations of parabens in human breast tumours. *Journal of Applied Toxicology*
510 24, 5–13. <https://doi.org/10.1002/jat.958>

511 Deborde, M., von Gunten, U., 2008. Reactions of chlorine with inorganic and organic
512 compounds during water treatment-Kinetics and mechanisms: A critical review. *Water*
513 *Research* 42, 13–51. <https://doi.org/10.1016/j.watres.2007.07.025>

514 Deng, Y., Feng, C., Chen, N., Hu, W., Kuang, P., Liu, H., Hu, Z., Li, R., 2018. Research on the
515 treatment of biologically treated landfill leachate by joint electrochemical system.
516 *Waste Management* 82, 177–187. <https://doi.org/10.1016/j.wasman.2018.10.028>

517 Diamanti-Kandarakis, E., Bourguignon, J.-P.P., Giudice, L.C., Hauser, R., Prins, G.S., Soto,
518 A.M., Zoeller, R.T., Gore, A.C., 2009. Endocrine-Disrupting Chemicals: An Endocrine
519 Society Scientific Statement. *Endocrine Reviews* 30, 293–342.
520 <https://doi.org/10.1210/er.2009-0002>

521 Dionisio, D., Motheo, A.J., Sáez, C., Cañizares, P., Rodrigo, M.A., 2019. Competitive Anodic
522 Oxidation of Methyl Paraben and Propylene Glycol: Keys to Understand the Process.
523 *ChemElectroChem* 6, 771–778. <https://doi.org/10.1002/celec.201801332>

524 Dionisio, D., Motheo, A.J., Sáez, C., Rodrigo, M.A., 2018. Effect of the electrolyte on the
525 electrolysis and photoelectrolysis of synthetic methyl paraben polluted wastewater.
526 *Separation and Purification Technology* 208, 201–207.
527 <https://doi.org/10.1016/j.seppur.2018.03.009>

528 Dionisio, D., Santos, L.H.E., Rodrigo, M.A., Motheo, A.J., 2020. Electro-oxidation of methyl
529 paraben on DSA®-Cl2: UV irradiation, mechanistic aspects and energy consumption.
530 *Electrochimica Acta* 338, 135901. <https://doi.org/10.1016/J.ELECTACTA.2020.135901>

531 Fortunato, G. v., Kronka, M.S., dos Santos, A.J., Ledendecker, M., Lanza, M.R.V., 2020. Low
532 Pd loadings onto Printex L6: Synthesis, characterization and performance towards
533 H2O2 generation for electrochemical water treatment technologies. *Chemosphere*
534 259, 127523. <https://doi.org/10.1016/j.chemosphere.2020.127523>

535 Friha, I., Karray, F., Feki, F., Jlaiel, L., Sayadi, S., 2014. Treatment of cosmetic industry
536 wastewater by submerged membrane bioreactor with consideration of microbial
537 community dynamics. *International Biodeterioration & Biodegradation* 88, 125–133.
538 <https://doi.org/10.1016/J.IBIOD.2013.12.015>

539 Gagnon, S.D., 2008. Propylene Oxide and Higher 1,2-Epoxyde Polymers, in: *Encyclopedia of*
540 *Polymer Science and Technology*. John Wiley & Sons, Inc., Hoboken, NJ, USA.
541 <https://doi.org/10.1002/0471440264.pst530>

542 Ganiyu, S.O., Martínez-Huitle, C.A., 2020. The use of renewable energies driving
543 electrochemical technologies for environmental applications. *Current Opinion in*
544 *Electrochemistry* 22. <https://doi.org/10.1016/j.coelec.2020.07.007>

545 Ganiyu, S.O., Martínez-Huitle, C.A., Rodrigo, M.A., 2020. Renewable energies driven
546 electrochemical wastewater/soil decontamination technologies: A critical review of
547 fundamental concepts and applications. *Applied Catalysis B: Environmental* 270.
548 <https://doi.org/10.1016/j.apcatb.2020.118857>

549 Haman, C., Dauchy, X., Rosin, C., Munoz, J.F., 2015. Occurrence, fate and behavior of
550 parabens in aquatic environments: A review. *Water Research* 68, 1–11.
551 <https://doi.org/10.1016/j.watres.2014.09.030>

552 Herzberger, J., Niederer, K., Pohlit, H., Seiwert, J., Worm, M., Wurm, F.R., Frey, H., 2016.
553 Polymerization of Ethylene Oxide, Propylene Oxide, and Other Alkylene Oxides:
554 Synthesis, Novel Polymer Architectures, and Bioconjugation. *Chemical Reviews* 116,
555 2170–2243. <https://doi.org/10.1021/acs.chemrev.5b00441>

556 Honda, M., Robinson, M., Kannan, K., 2018. Parabens in human urine from several Asian
557 countries, Greece, and the United States. *Chemosphere* 201, 13–19.
558 <https://doi.org/https://doi.org/10.1016/j.chemosphere.2018.02.165>

559 Kobayashi, S., Higashimura, H., 2003. Oxidative polymerization of phenols revisited.
560 *Progress in Polymer Science* 28, 1015–1048. [https://doi.org/10.1016/S0079-](https://doi.org/10.1016/S0079-6700(03)00014-5)
561 [6700\(03\)00014-5](https://doi.org/10.1016/S0079-6700(03)00014-5)

562 Li, W.H., Shi, Y.L., Gao, L.H., Liu, J.M., Cai, Y.Q., 2015. Occurrence, fate and risk assessment
563 of parabens and their chlorinated derivatives in an advanced wastewater treatment
564 plant. *Journal of Hazardous Materials* 300, 29–38.
565 <https://doi.org/10.1016/j.jhazmat.2015.06.060>

566 Lu, Y., Wang, R., Zhang, J., Jin, Q., Luo, G., 2015. Evaluation of an improved epichlorohydrin
567 synthesis from dichloropropanol using a microchemical system. *Chinese Journal of*
568 *Chemical Engineering* 23, 1123–1130. <https://doi.org/10.1016/J.CJCHE.2014.10.021>

569 Lutze, H. V, Kerlin, N., Schmidt, T.C., 2015. Sulfate radical-based water treatment in
570 presence of chloride: Formation of chlorate, inter-conversion of sulfate radicals into
571 hydroxyl radicals and influence of bicarbonate. *Water Research* 72, 349–360.
572 <https://doi.org/10.1016/j.watres.2014.10.006>

573 Marta-Sanchez, A.V., Caldas, S.S., Schneider, A., Cardoso, S.M.V.S., Primel, E.G., 2018. Trace
574 analysis of parabens preservatives in drinking water treatment sludge, treated, and
575 mineral water samples. *Environmental Science and Pollution Research*.
576 <https://doi.org/10.1007/s11356-018-1583-4>

577 Martin, A.E., Murphy, F.H., 2000. Glycols, Propylene Glycols, in: *Kirk-Othmer Encyclopedia of*
578 *Chemical Technology*. John Wiley & Sons, Inc., Hoboken, NJ, USA.
579 <https://doi.org/10.1002/0471238961.1618151613011820.a01>

580 Martínez-Huitle, C.A., Panizza, M., 2018. Electrochemical oxidation of organic pollutants for
581 wastewater treatment. *Current Opinion in Electrochemistry* 11, 62–71.
582 <https://doi.org/10.1016/j.coelec.2018.07.010>

583 Martínez-Huitle, C.A., Rodrigo, M.A., Sires, I., Scialdone, O., Martínez-Huitle, C.A., Rodrigo,
584 M.A., Sires, I., Scialdone, O., 2015. Single and Coupled Electrochemical Processes and
585 Reactors for the Abatement of Organic Water Pollutants: A Critical Review. *Chemical*
586 *Reviews* 115, 13362–13407. <https://doi.org/10.1021/acs.chemrev.5b00361>

587 Matwiejczuk, N., Galicka, A., Brzóška, M.M., 2020. Review of the safety of application of
588 cosmetic products containing parabens. *Journal of Applied Toxicology* 40, 176–210.
589 <https://doi.org/10.1002/jat.3917>

590 Ngigi, E.M., Nomngongo, P.N., Ngila, J.C., 2021. Recent methods used in degradation of
591 parabens in aqueous solutions: a review. *International Journal of Environmental*
592 *Science and Technology*. <https://doi.org/10.1007/s13762-021-03228-y>

593 Nguyen, V.-H., Phan Thi, L.-A., Chandana, P.S., Do, H.-T., Pham, T.-H., Lee, T., Nguyen, T.D.,
594 Le Phuoc, C., Huong, P.T., 2021. The degradation of paraben preservatives: Recent
595 progress and sustainable approaches toward photocatalysis. *Chemosphere* 130163.
596 <https://doi.org/10.1016/j.chemosphere.2021.130163>

597 Nowak, K., Ratajczak–Wrona, W., Górška, M., Jabłońska, E., 2018. Parabens and their effects
598 on the endocrine system. *Molecular and Cellular Endocrinology* 474, 238–251.
599 <https://doi.org/10.1016/j.mce.2018.03.014>

600 Oliveira, E.M.S., Silva, F.R., Morais, C.C.O., Oliveira, T.M.B.F., Martínez-Huitle, C.A., Motheo,
601 A.J., Albuquerque, C.C., Castro, S.S.L., 2018. Performance of (in)active anodic materials
602 for the electrooxidation of phenolic wastewaters from cashew-nut processing industry.
603 *Chemosphere* 201, 740–748. <https://doi.org/10.1016/j.chemosphere.2018.02.037>

604 Paździor, K., Bilińska, L., Ledakowicz, S., 2019. A review of the existing and emerging
605 technologies in the combination of AOPs and biological processes in industrial textile
606 wastewater treatment. *Chemical Engineering Journal* 376, 120597.
607 <https://doi.org/10.1016/j.cej.2018.12.057>

608 Pointer Malpass, G.R., de Jesus Motheo, A., 2021. Recent advances on the use of active
609 anodes in environmental electrochemistry. *Current Opinion in Electrochemistry* 27,
610 100689. <https://doi.org/10.1016/j.coelec.2021.100689>

611 Rajeshwar, K., Ibanez, J.G., 1997. *Environmental Electrochemistry: Fundamentals and*
612 *Applications in Pollution Sensors and Abatement*. Elsevier Science.

613 Rosales, E., Buftia, G., Pazos, M., Lazar, G., Sanromán, M.A., 2018a. Highly active based iron-
614 carbonaceous cathodes for heterogeneous electro-Fenton process: Application to
615 degradation of parabens. *Process Safety and Environmental Protection* 117, 363–371.
616 <https://doi.org/10.1016/j.psep.2018.05.014>

617 Rosales, E., Buftia, G., Pazos, M., Lazar, G., Sanromán, M.A., 2018b. Highly active based iron-
618 carbonaceous cathodes for heterogeneous electro-Fenton process: Application to
619 degradation of parabens. *Process Safety and Environmental Protection* 117, 363–371.
620 <https://doi.org/10.1016/j.psep.2018.05.014>

621 Salazar-Banda, G.R., Santos, G. de O.S., Duarte Gonzaga, I.M., Dória, A.R., Barrios Eguiluz,
622 K.I., 2021. Developments in electrode materials for wastewater treatment. *Current*
623 *Opinion in Electrochemistry* 26. <https://doi.org/10.1016/j.coelec.2020.100663>

624 Sirés, I., Brillas, E., Oturan, M.A., Rodrigo, M.A., Panizza, M., 2014. Electrochemical advanced
625 oxidation processes: today and tomorrow. A review. *Environmental Science and*
626 *Pollution Research* 21, 8336–8367. <https://doi.org/10.1007/s11356-014-2783-1>

627 Steiner, E.C., Pelletier, R.R., Trucks, R.O., 1964. A Study of the Polymerization of Propylene
628 Oxide Catalyzed by Anhydrous Potassium Hydroxide. *Journal of the American Chemical*
629 *Society* 86, 4678–4686. <https://doi.org/10.1021/ja01075a031>

630 Steter, J.R., Brillas, E., Sires, I., 2016. On the selection of the anode material for the
631 electrochemical removal of methylparaben from different aqueous media.
632 *Electrochimica Acta* 222, 1464–1474. <https://doi.org/10.1016/j.electacta.2016.11.125>

633 Steter, J.R., Rocha, R.S., Dionísio, D., Lanza, M.R.V. v, Motheo, A.J., 2014. Electrochemical
634 oxidation route of methyl paraben on a boron-doped diamond anode. *Electrochimica*
635 *Acta* 117, 127–133. <https://doi.org/10.1016/j.electacta.2013.11.118>
636 Tobajas, M., Polo, A.M., Monsalvo, V.M., Mohedano, A.F., Rodriguez, J.J., 2014.
637 *Environmental Engineering and Management*.
638 Trigueiro, L.F., Silva, L.M., Itto, L.A.B.D., Oliveira, T.M.B.F., Motheo, A.J., Martínez-Huitle,
639 C.A., Alves, J.J.F., Castro, S.S.L., 2017. Inactivation, lysis and degradation by-products of
640 *Saccharomyces cerevisiae* by electrooxidation using DSA. *Environmental Science and*
641 *Pollution Research* 24, 6096–6105. <https://doi.org/10.1007/s11356-016-7243-7>
642