Coupling ultrasound to the electro-oxidation of methyl paraben synthetic wastewater: effect of frequency and supporting electrolyte

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Abstract

In this paper, single electrolysis with diamond electrode is studied and compared to its coupling with sonolysis for the degradation of methyl paraben (MeP). Complete mineralization of MeP was achieved for both processes, in chloride and sulfate media. Results showed that, although the oxidation of pollutant is faster in the presence of chloride, sulfate medium favored the mineralization. Ultrasound irradiation enhanced the removal of organic matter due to the activation of oxidant species in both supporting electrolytes. Moreover, the formation of Cl_2 in chloride medium, improves the ultrasound cavitation effect, promoting faster depletion of TOC (total organic carbon) in the first hour of treatment. Regarding the formation of more toxic products, all possible organochlorinated intermediates were removed and chlorates and perchlorates only start to be produced after total removal of TOC. Additionally, the coupling to ultrasound accelerates the destruction of intermediates and delays the formation of ClO_3^- and ClO_4^-. Low and high ultrasound frequencies were evaluated and were found to produce different effects of cavitation, which affect the electrolysis in different ways. The final result will be a balance between those effects and, thus, an optimal frequency may be observed for distinctive systems.

Keywords

Methyl paraben, diamond anodes, electrolysis, sonolysis

Highlights

- Complete mineralization of methyl paraben is achieved in sulfate and chloride media;

- Sulfate medium favored the removal of TOC;

- Enhancement of electrolysis by the coupling to sonolytic process;

- Cavitation effects of low and high intensities are balanced in an optimal frequency;

- Low frequency ultrasound promotes the activation of persulfate.

Introduction

Mehyl paraben (MeP) is one of a series of preservatives, which are esters of *p*-hydroxybenzoic acid and include among others, methyl, ethyl, propyl, butyl and benzyl parabens. This compound is widely used in pharmaceutical drugs, cosmetics and personal care products, singly or in combination to other preservatives, in order to achieve the intended antimicrobial effect [1, 2]. In 2004, parabens were firstly related to human breast cancer by Darbre *et al.* [3], fact that was further confirmed by Dagher *et al.* in 2012 [4]. Since the first publication, numerous studies have been reported about environment outcomes and the effects on human health resulted from the exposure to those substances [1, 5-10]. Those studies described potential estrogenic and carcinogenic activity of parabens, which classifies them as endocrine disrupting chemicals (EDCs).

Although parabens are still used, mainly in cosmetic products, the concern regarding the adverse effects on human health has led to a gradually restriction on their usage. Besides the fact that most countries do not have regulations to parabens usage, several organizations, such as US Food and Drug Administration (FDA), World Health Organization (WHO), European Union (EU) and Scientific Society on Costumer Safety (SCCS), have stablished low concentration limits of those compounds in the case of some types of products. For instance, the content of ethyl and butyl parabens in cosmetics was changed from 0.4% to 0.14% in all EU members in 2014, and these values were also applied in several South America countries [10-12]. In this context, several industries have been replacing parabens to other preservatives with a police of "paraben-free" products. However, parabens are still largely detected in various environmental matrices [12-15], which has led to the contamination of potable water and increased the exposure of humans to those compounds.

In order to remove emerging contaminants, such as parabens, from water and wastewater, the scientific community has invested in the development and enhancement of advanced oxidation processes (AOPs) [16-18]. These processes are based on the generation of hydroxyl radicals ($^{\bullet}$OH), which are highly reactive (E^0 = 2.8 V) and promote the degradation of organic pollutants. Fenton process, photolysis, ozonation and other AOPs are very efficient for the removal of certain pollutants, however not necessarily effect for the complete depletion of organic matter on the treatment of more recalcitrant substances. For that purpose, electrochemical AOPs have shown promising results on the total removal of organic contaminants from water [19-21]. For instance, Wang *et al.* [22], Dantas *et al.* [23], Li *et al.* [24] have studied the degradation of the antibiotic sulfamethoxazole (SMX) by Fenton,

76   ozonation and electrochemical processes, respectively, and found that total SMX can be
77   removed by the applied treatments. However, removal of TOC (total organic carbon) is
78   different for each case: with Fenton reaction 83% of TOC was removed, ozonation promoted
79   only 10% of TOC removal and electrochemical process achieved 91% of mineralization.
80   Additionally, Amorim *et al*. [25] studied electrochemical degradation of SMX in the presence
81   of trimethoprim, being both pollutant completely removed and 90% of TOC reduced.

82   On electrochemical process, organic compounds can be directly oxidized by electron transfer
83   on the surface of the electrode, or indirectly oxidized by $^{\bullet}OH$ or other oxidizing agents. In the
84   second case, oxidants are electrochemically produced on the anode and can react with organic
85   compounds at the mediations of the electrode or extend the oxidation to the bulk of the solution.
86   In most scenarios both oxidation mechanisms simultaneously occur and can be explored
87   according to the objective of the treatment. Most recently, researchers have been exploring the
88   coupling of technologies, in order to improve the efficiency of electrochemical treatments.
89   Electro-Fenton process [21, 26], electrolysis irradiated by UV light [27-29] and
90   electrochemistry combined to sonochemistry [30-32] can be highlighted, where in most cases
91   better results are observed for the coupled processes due to a synergistic effect. As a result of
92   the coupling, more oxidant agents can be produced and, most important, it can be promoted
93   the activation of such species, which means that highly reactive species can be formed from
94   poorly reactive oxidants.

95   Sonochemical processes are based on the irradiation of ultrasound through an aqueous medium.
96   The resultant effect is the so-called cavitation phenomena, which consists on the formation,
97   expansion and implosion of bubbles. The energy released in this cavitation process is the
98   principle of sonochemistry, in which the most accepted theory states that at the point of bubble
99   implosion, conditions of thousands of kelvins and hundreds of atm are produced (hot-spot
100 theory). This conditions are very short-lived but sufficient to promote the generation of
101 radicals, such as hydroxyl ($^{\bullet}OH$), hydrogen ($^{\bullet}H$) and hydroperoxyl ($HO_2^{\bullet}$) [33-35]. Coupling
102 sonochemical to electrochemical technology it is possible to improve the formation of radicals,
103 activate oxidants and also favor the mass-transfer process [30, 36, 37].

104 However, ultrasound irradiation as a wastewater treatment is still considered an emergent
105 technology and more need to be known about frequency and power effects, pH, influence of
106 complex matrices and set-up of the sonolytic system used [38, 39]. According to that, this study
107 aims to enhance electrolysis by the coupling of ultrasound, but more importantly, it focuses on
108 the understanding of cavitation effect on electrogenerated oxidant species. For that, the

109　degradation of methyl paraben, as a model molecule, was carried out under the presence of

110　different supporting electrolytes and different conditions of ultrasound frequency.

111

112　**Materials and methods**

113　*Chemicals*

114　All solutions were prepared using high-purity water obtained from a Millipore Milli-Q system

115　(resistivity >18M cm at 25 ℃). Methyl paraben and the reactants for determination of oxidants

116　(KI, $Na_2S_2O_3$, NaOH, As_2O_3 and starch solution (1%)) were purchased from Sigma-Aldrich.

117　Supporting electrolytes Na_2SO_4 and NaCl were obtained from Panreac, as well as, H_2SO_4 used

118　for pH adjustment. Acetonitrile, from VWR Chemicals, was used as mobile phase for HPLC

119　analysis. All reactants were used as received.

120　*Experimental set-up*

121　Experiments were carried out in a bench scale flow system operating in a discontinuous mode.

122　Electrochemical reactor is coupled to a peristaltic pump (PERCOM-I, JP Selecta, Barcelona,

123　Spain) and to a jacketed glass vessel, used to store 1 L of solution. The cell is equipped with a

124　plate of boron doped diamond (BDD) as anode and a plate of stainless steel as cathode (both

125　with surface area of 75 cm^{-2}) and a HQ-Power PS3010 power supply (0-30 V, 0-10 A) provided

126　the applied current. A thermostatic bath (Digiterm 100, JP Selecta) was used to maintain the

127　solution temperature at 25 ℃. Tests using ultrasound were carried out at three different acoustic

128　frequencies: 20 kHz (UP200S, Hielscher Ultrasonics GmbH), 1 MHz and 10 MHz (EPOCH

129　650, Olympus). The ultrasound probe was immersed in the glass tank directly acting in the

130　working solution.

131　*Analytical techniques*

132　High performance liquid chromatography (Agilent Technologies 1260 chromatographer) was

133　used to monitor the concentration of methyl paraben with an Eclipse Plus C18 column (3.5μm

134　4.6 x 100 mm), at 25 ℃, and UV detector set in 280 nm. Mobile phase was acetonitrile and

135　water (60:40 v/v) with 1 mL min^{-1} of flow rate. Total organic carbon (TOC) was determined

136　in a Multi N/C 3100 Analytik Jena analyzer. Measurements of pH and conductivity were

137　carried out in a GLP22 CRISON and GLP 31 CRISON, respectively. Oxidizing power of the

138　solution was determined by iodometric titration. Inorganic anions (Cl^-, ClO_3^- and ClO_4^-) were

139　measured by ion chromatography using a 930 Compact IC Flex (Metrohm) and hypochlorite

140　was determined by titration, with a solution of As_2O_3 in 2.0 M NaOH.

141 *Synergistic index*

142 Synergistic index (SI), **Eq. 1**, was used to evaluate the effect of coupling ultrasound to

143 electrolysis. Parameters k_{p1-p2}, k_{p1} and k_{p2} are the kinetic constants for the coupled process and

144 the individual processes 1 and 2, respectively.

145 $$SI = \frac{k_{p1-p2}}{k_{p1}+k_{p2}}$$ (1.)

146

147 **Results and discussion**

148 **Fig. 1** shows the removal of MeP obtained in sulfate and chloride medium by the individual

149 and coupled processes. Sonochemical process (SCh) showed a very low efficiency to the

150 oxidation of MeP, achieving 26 and 30% of removal in chloride and sulfate media,

151 respectively. The propagation of ultrasound in a liquid occurs by the vibration of the molecules

152 in the medium, which produces small variations of pressures and cycles of alternate expansions

153 and compressions [40]. In the case of water saturated with air, the acoustic cavitation effect

154 will be produced, creating favored conditions to the formation of radical oxidants [33, 39].
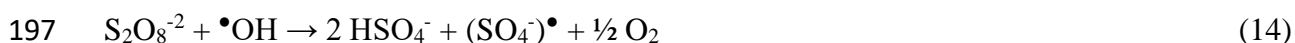
155 Under the studied conditions it is expected the formation of $^{\bullet}OH$, H_2O_2 and O_3 from water

156 sonolysis according to the **Eqs. 2-9** (where the symbol)**))** represents the ultrasound waves).

157 Moreover, in chloride medium, it is also possible the formation of active chlorine species (**Eqs.**

158 **10-12**) [35, 41]. Hence, the faster MeP removal observed in chloride medium, for SCh process,

159 can be explained by the higher concentration of oxidants and the rapid production of

160 organochlorinated compounds (characteristic of oxidation by chlorine species).

161 $H_2O +))) \rightarrow H^{\bullet} + {}^{\bullet}OH$ (2)

162 $O_2 +))) \rightarrow 2\,O^{\bullet}$ (3)

163 $2\,{}^{\bullet}OH \rightarrow H_2O_2$ (4)

164 $H^{\bullet} + O_2 \rightarrow HO_2^{\bullet}$ (5)

165 $HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$ (6)

166 $H^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2$ (7)

167 $O^{\bullet} + O_2 \rightarrow O_3$ (8)

168 $H^{\bullet} + O_2 \rightarrow {}^{\bullet}OH + O^{\bullet}$ (9)

169 $Cl^- +))) \rightarrow Cl_2$ (10)

170 $Cl_2 + 2\ OH^- \rightarrow ClO^- + H_2O + Cl^-$ (11)

171 $ClO^- + H^+ \rightleftharpoons HClO^-$ (12)

172 Electrochemical processes, individually (ECh) and coupled to sonolysis (SECh), completely

173 removed MeP. However, under the applied conditions, it was not possible to observe an

174 improvement on the efficiency for the coupled process. Different characteristics for the MeP

175 degradation in sulfate and chloride media were expected, as observed for diamond electrolysis

176 in a previous work [27]. The main species generated in each system are $SO_4^{-\bullet}$ and ClO^-, which

177 results in different mechanism of oxidation. Sulfate radical has a redox potential comparable

178 to that of $^\bullet OH$ (2.6 and 2.8 V *vs.* normal hydrogen electrode, NHE, respectively) and its main

179 oxidation mechanism is by electron transfer, which promotes the formation of organic radicals

180 and its further rupture of bonds, resulting in high elimination of organic matter [42, 43]. On the

181 other hand, hypochlorite anions will rapidly convert the pollutant into organochlorinated

182 compouds by the addition of Cl atoms to its structure [44].

183 Although no improvement was observed for MeP removal, the SECh process accelerated the

184 oxidation of total organic matter, as it is shown in **Fig. 2** and **Tab. 1**. Two kinetic regions of

185 *pseudo*-first order can be observed in the case of electrolytic processes, with k_1 and k_2 as the

186 kinetic constants for each region. This transition is explained by the nature of the generated

187 intermediates, which seem to be easily oxidized by the present oxidant agents than the initial

188 pollutant [27]. No removal of TOC was achieved with SCh during the 8 hours of treatment (the

189 negative value of kinetic constant is attributed to the dispersion of the points), but complete

190 mineralization was attained for ECh and SECh in less than 5 hours. The coupled process

191 showed an improvement on the oxidation of organic matter due to the sonochemical activation

192 of oxidants. In sulfate medium, $SO_4^{-\bullet}$ is produced by the homogeneous cleavage of the

193 electrogenerated persulfate (**Eq. 13**), which is more efficient than persulfate itself.

194 Additionally, the radicals produced by water sonolysis can also react with persulfate and

195 contribute to radical sulfate yield (**Eqs. 14** and **15**) [45, 46].

196 $S_2O_8^{-2} +))) \rightarrow 2\ (SO_4^-)^\bullet$ (13)

197 $S_2O_8^{-2} + {}^\bullet OH \rightarrow 2\ HSO_4^- + (SO_4^-)^\bullet + \frac{1}{2}\ O_2$ (14)

198 $S_2O_8^{-2} + {}^\bullet H \rightarrow HSO_4^- + (SO_4^-)^\bullet$ (15)

199 On the other hand, an interesting behavior is observed for chloride medium: in a first moment,

200 TOC removal is highly favored. However, after 1 hour of treatment, the removal rate decreases.

201 In order to better understand this result, it is necessary to take into account the nature of
202 oxidants species formed and the possible effect of ultrasound on it. It is well known that in an
203 electrochemical bath, chloride anions are oxidized to chlorine gas. As it was mentioned, the
204 effects of ultrasound are related to the gas dissolved into the water [34, 41, 46]. Higher
205 concentration of gases, may improve the cavitation effect, however after a certain time the
206 solution will be saturated and this improvement will decrease its significance. In addition to
207 this, ultrasound can promote the formation of $Cl^{\bullet}$ and $Cl_2^{-\bullet}$ species (**Eq. 16** and **17**), which are
208 strong oxidants for many organic compounds [47]. The slower rate in the second kinetic region
209 could be attributed to the nature of the intermediates formed, which can be less reactive with
210 relation to the oxidants present in the medium.

211 $$Cl_2 +))) \rightarrow 2\ Cl^{\bullet} \tag{16}$$

212 $$Cl^{\bullet} + Cl^- \rightleftharpoons Cl_2^{-\bullet} \tag{17}$$
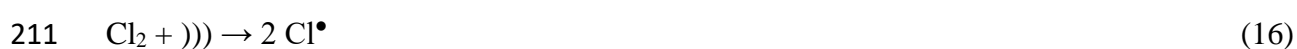
213 Considering that two regions of kinetics can be observed, it is not possible to determine one
214 synergistic index (SI) for all the treatment (**inset of Fig. 2**). In a first moment chloride medium
215 is better, with an SI 4.5 times higher than sulfate. On the other hand, for the second region,
216 sulfate medium presented an SI 5.6 times higher than chloride. These results are important to
217 guess the conditions in which ultrasound may have more influence and this can be an important
218 step for future studies, where an optimization of those conditions could be evaluated.

219 It is well-known and described the formation of chlorate and perchlorate in electrolysis of
220 chlorine using BDD electrodes (**Eqs. 18-21**) [21, 48, 49]. In addition to the fact that those
221 species have a lower oxidant potential, which decrease the process efficiency, they are also
222 related to serious health problems and, thus, are not desired to be produced. **Fig. 3** shows the
223 speciation of the oxochloranions detect in ECh and SECh processes. Although no formation of
224 oxochloranions were verified for sonolysis, it is possible to observe a decrease of the chloride
225 concentration, which is attributed to the formation of Cl_2 and in agreement with the results and
226 discussion of **Fig. 1**. The behavior of production / consumption of chlorine species are similar
227 for ECh and SCEh; however, it is important to note that the coupling of ultrasound delays the
228 formation of perchlorate and that this only starts after all TOC was removed, at 4 hours of
229 treatment (**Fig. 2**). Hence, considering the batch system studied, seems feasible the application
230 of electrochemical process coupled to ultrasound during 4 hours, minimizing the adverse
231 production of chlorate and perchlorate.

232 $$Cl^- + {}^{\bullet}OH \rightarrow ClO^- + H^+ + e^- \tag{18}$$

$$233 \quad ClO^- + {}^\bullet OH \rightarrow ClO_2^- + H^+ + e^- \qquad (19)$$

$$234 \quad ClO_2^- + {}^\bullet OH \rightarrow ClO_3^- + H^+ + e^- \qquad (20)$$

$$235 \quad ClO_3^- + {}^\bullet OH \rightarrow ClO_4^- + H^+ + e^- \qquad (21)$$

236   Considering that the coupling of sonolysis to electrochemical treatment showed faster

237   mineralization of organic matter with a decrease on the formation of chlorate species, it was

238   investigated the effect of ultrasound frequency on the system. The frequency applied has an

239   important role on the critical size of the bubbles and, thus, on the cavitation phenomena. Three

240   acoustic frequencies were studied: 20 kHz (power ultrasound), with 20% and 75% of power

241   (conditions referred as L20 and L75), 1 MHz (high frequency ultrasound) (referred as H1) and

242   10 MHz (diagnostic ultrasound) (referred as H10).

243   **Fig. 4** shows the removal of MeP and TOC obtained for SECh process. Single sonolytic process

244   resulted in low removal of MeP and none removal of TOC. Negative values observed for 10

245   MHz (**Fig. 4a**) are attributed to error of the method, meaning that no removal was achieved

246   under this condition. Lower frequency showed better MeP removals: at 20 kHz approximately

247   30% was attained for both power percentages, while at 1 MHz only 7% was removed. SECh

248   treatment seems to slightly enhance ECh results, however it was not possible to observe great

249   variations of efficiency for different frequencies, as it was expected. Frequency does not seem

250   to affect the MeP removal (**Fig. 4a**), in which total oxidation is achieved with approximately 4

251   hours for all electrochemical processes. However, at the second kinetic region of TOC removal

252   (**Fig. 4b**), it is possible to observe different rates: at L75 and at H1, complete mineralization is

253   attained with 3 hours, while for other conditions 4 hours were necessary. Moreover, the kinetic

254   constant calculated for L75 is 1.5 times higher than for H1 (1.42 compared to 0.93 h^{-1}).

255   As it was already stated, ultrasound will directly influence the gas dissolved in the working

256   solution, because of the cavitation phenomena. Cavitation bubbles have three sites in which

257   chemical reactions can take place: inside the bubble, where temperatures are very high and

258   thermal reactions can occur; the gas-liquid interface, in which hydrophobic compounds are

259   more concentrated; and the bulk of the solution [39, 50, 51]. If volatile intermediates are

260   produced, they can be oxidized inside the bubbles and, thus, the effect of the ultrasound will

261   be more remarkable. As a matter of fact, phenol is a typical product of the degradation of MeP

262   [52] and that is the main reason why the differences between applied frequencies can only be

263   seen in the second region of TOC kinetics.

264 Synergistic index was calculated for each applied frequency in terms of MeP removal and TOC

265 mineralization (**Fig. 5**). First, it is important to highlight that SI does not consider the time

266 needed to remove all MeP or organic matter. This means that although SI is higher for L20 and

267 H10 conditions, at L75 and H1 complete mineralization was achieved 1 hour faster than in the

268 other conditions. Hence the order of efficiency can be summarized as L75 > H1 > L20 > H10.

269 These results indicate that there is an optimal ultrasound frequency in which the degradation is

270 favored, as it was previous observed in the literature [53-55].

271 At lower frequencies, ultrasound promotes the so-called transient cavitation, in which the

272 bubbles are very unstable and the collapses are more violent, leading to sites of high

273 temperature and pressure. At this point, it can be expected high production of radicals by

274 sonolysis and the activation of oxidants. On the other hand, at high frequencies, the cavitation

275 bubbles are stable and its collapse is less violent. Besides the lower cavitation intensity, radicals

276 are still produced inside the bubbles, and its longer stability permits that those radicals escape

277 to the bulk solution and react with organic compounds [34, 35, 53]. It is estimated that under

278 transient cavitation, 10% of the radicals escape to the bulk solution; under stable cavitation this

279 percentage could be improved [34]. Therefore, the optimal frequency will be a balance between

280 the effects of transient and stable cavitation. It is plausible to consider that under the applied

281 conditions, the high frequencies effect compensates the low frequencies one and thus, a very

282 small difference is observed in the final result.

283 As an attempt to clarify the role of ultrasound on the mediated oxidation, sonochemical tests

284 were carried out in the presence of persulfate at the different frequencies. For that, 12.5 g L^{-1}

285 of sodium persulfate were added to the synthetic wastewater studied before (100 mg L^{-1} of

286 MeP + 3.0 g L^{-1} of Na_2SO_4) and ultrasound was applied for 8 hours, point in which the

287 concentration of MeP and TOC were measured. **Tab. 2** shows that persulfate itself is capable

288 to remove approximately 60% of MeP and 35% of organic matter. The irradiation of low

289 frequency ultrasound enhances the oxidation and almost total mineralization is achieved. In the

290 absence of ultrasound, persulfate is the only oxidant in the medium; on the other hand, in the

291 sonolytic process $^{\bullet}OH$ is generated and $SO_4^{-\bullet}$ is produced by the activation of persulfate, as it

292 was already discussed. However, for 1 MHz and 10 MHz, the efficiency of the process

293 significantly decreases compared to persulfate alone. This result suggests that, under these

294 conditions, ultrasound is not only not activating the persulfate, but also inhibiting this oxidant,

295 which could be explained by **Eqs. 22** and **23** [56]. Water sonolysis occurs even at high

296 frequencies, thus, hydrogen peroxide is produced from the recombination of radicals (**Eqs. 4**,

297 **6** and **7**) and will react with persulfate. Additionally, even though the main source of sulfate
298 radical is suppressed (persulfate sonolysis, **Eq. 13**), it may still be produced, at smaller
299 concentrations, by the reaction of persulfate with $^\bullet$OH and $^\bullet$H (**Eqs. 14** and **15**); however, they
300 can also be consumed by H_2O_2.

301 $$S_2O_8^{-2} + \rightarrow 2\ H^+ + 2\ SO_4^{2-} + O_2 \tag{22}$$

302 $$(SO_4^-)^\bullet + H_2O_2 \rightarrow H^+ + SO_4^{2-} + HO_2^\bullet \tag{23}$$

303 In conclusion, low frequency ultrasound (transient cavitation) activates persulfate, producing
304 $SO_4^{-\bullet}$, that in addition to $^\bullet$OH, from water sonolysis, improve organic matter degradation. On
305 the other hand, high frequency ultrasound (stable cavitation) is not able to activate persulfate
306 and also can inhibit its action by the H_2O_2 produced from water sonolysis. These is in
307 agreement with the observations of Ferkous *et al*. [45], which studied the persulfate oxidation
308 of naphthol blue black enhanced by ultrasound and stated that persulfate-enhanced effect was
309 more remarkable at 20 kHz than at 585 kHz. In addition, most studies of ultrasound activation
310 of persulfate only studied low frequency, mainly 20 kHz, obtaining very promising results [57-
311 60].

312 At this point, it is important to remember that electrochemical cell behaves as a cocktail of
313 species and not only persulfate and hydroxyl radicals are acting; all species can suffer the
314 effects of violent and/or stable cavitation in different ways. Irradiation of ultrasound will not
315 only produce more oxidants, but also influences on the kinetics of all reactions, increasing or
316 decreasing their kinetic rates. Furthermore, physical effects can take place other than the
317 chemical ones. For instance, violent cavitation, in transient regime, can also improve the mass-
318 transport of species, which will improve the electrochemical process. These points reinforce
319 the theory that the optimal ultrasound frequency to enhance an electrochemical system will be
320 a balance between the effects of transient and stable cavitation, which represents a combination
321 of all factors involved. Although it was expected higher improvement for the coupled process
322 and greater differences between the applied frequencies, the results presented and discussed
323 give an essential indication of how ultrasound acts in the studied system. It is also important to
324 take into account that the system studied is simple and MeP is a model molecule, with a
325 relatively easy oxidation.

326

327 **Conclusions**

328   The coupling of ultrasound to electrolysis was studied for the degradation of methyl paraben

329   synthetic wastewater, where the influence of supporting electrolyte and acoustic frequencies

330   were evaluated. From that, the following conclusions can be drawn:

331   • The target pollutant was completely mineralized by single electrolysis with diamond anodes

332   and coupled to ultrasound. However, while removal of MeP is faster in the presence of

333   chloride, its mineralization is more efficient in sulfate medium, due to the nature of the

334   oxidant species generated in each condition.

335   • The mineralization of the wastewater by single electrolysis and coupled to ultrasound fits

336   well to *pseudo*-first order kinetics, although two regions can be distinguished. The transition

337   point between regions and the relation between k_1 and k_2 will depend on the reactivity of

338   the intermediates formed and the nature of the main oxidant specie in the medium.

339   • The combination of electrolysis and sonolysis has a synergistic effect on the abatement of

340   organic matter, in both chloride and sulfate media, due to the improvement on mediated

341   oxidation.

342   • Ultrasound promotes different effects of cavitation at low and high frequencies. Hence,

343   there is an optimal frequency for different systems, in which those effects are balanced. It

344   is possible that, under specific conditions, the high frequencies effect compensates the low

345   frequencies one and thus, a very small difference is observed in the final result.

346   • Sonochemical tests showed that low frequency ultrasound can activate persulfate oxidants

347   to form radical species, which highly improves the oxidation. However, it also suggests that

348   high frequencies are not efficient on the activation of persulfate and also inhibit its oxidative

349   action by converting it into sulfate anions.

350

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