

1 **Effects of ultrasound irradiation on the electrochemical treatment**
2 **of wastes containing micelles**

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16 **Abstract**

17 This work focuses on the effect of the irradiation of ultrasound during the electrolysis of wastes
18 polluted with micelles. To do this, synthetic wastewater (emulating the ones produced in
19 cosmetic industry) was formulated and it underwent several electrochemical and sono-
20 electrochemical, at low and high frequencies, oxidation assays. Processes were monitored
21 paying attention not only to the changes observed in the organic soluble intermediates and final
22 products, but also to the size of the micelles. Results demonstrate that the presence of surfactant
23 in wastes may interfere on the degradation of pollutants due to the formation of micelles.
24 Nevertheless, 90% of mineralization was achieved by the coupled process of electrolysis and
25 low frequency ultrasound. Furthermore, ultrasound irradiation can contribute to faster turbidity
26 and foam depletion and to retard the formation of perchlorates. Regarding the micelles, it was
27 found that application of ultrasound directly affects the changes on particles size during their
28 destruction which, in turn, influences on the performance of the electrochemical process. A
29 simple phenomenological model is proposed to explain the influence of this irradiation.

30

31 **Keywords**

32 Colloids; diamond anodes; electrolysis; sono-electrolysis

33

34 **Highlights**

- 35 - Electrolysis with diamond anodes can efficiently degrade wastewater polluted with colloids.
- 36 - The presence of surfactants on wastewater interferes on the degradation of pollutants.
- 37 - Cavitation with low frequency US, helps to rearrange micelles into larger particles.
- 38 - Ultrasound may promote important physical effects such as micelles growth and turbidity.

39 **Introduction**

40 Over the last decades, the electrolysis of wastewater has become a really interesting
41 topic of study with hundreds of papers published and many reviews that summarize the state
42 of the art in the technology [1-5]. From those works, it has been concluded that with the use of
43 diamond coatings as anodes it is possible to improve the heterogeneous electrocatalytic process
44 to treat very efficiently most of the pollutants that can be contained in wastewater. Mass
45 transport has become the major handicap in the technology, in which promotion of mediated
46 electrochemical oxidation processes and the improved mechanical design of electrochemical
47 cells are the key paths to face this challenge. In particular, strategies based on the enlarging the
48 electrocatalytic production of oxidants or activating them chemically, photo-chemically or
49 sono-chemically are of interest according to the high number of paper published [6]. Thus,
50 during the electrolytic treatment of wastes, it has been widely studied the electrochemical
51 formation of oxidants such as hydrogen peroxide, ozone, peroxosulfates, peroxocarbonates,
52 peroxophosphates and chlorine. Composition of the waste has a large influence on this
53 production and operation conditions can help to modify it efficiently. Interactions of these
54 oxidants among them in pure electrochemical processes, and also with UV or US in combined
55 treatments, lead to the formation of radicals such as the hydroxyl, sulfate, carbonate and
56 chlorine. This cocktail of oxidants is responsible of the very strong oxidizing conditions
57 produced in the bulk during the electrolysis, being its characterization one of the most
58 interesting contributions to the catalytic understanding of the electrochemical treatments,
59 because sometimes these interactions are synergistic and they contribute to improve the
60 efficiency of the processes, while other they become antagonistic. Explanation is not always
61 related to the nature of the pollutants to be degraded, but also to the composition of the waste
62 and operation conditions applied which are the final responsible of the cocktail of oxidants
63 formed. There are studies about this influence on soluble compounds but to the knowledge of
64 the authors there are no studies focused on the treatment of more complex pollutant such as
65 those present as micelles.

66 On the other hand, and coming back to additional ways of enhancing the performance
67 of electrochemical processes, more recently, the application of concentration processes for
68 pollutants solutions before the degradation is also becoming a very promising alternative [7-
69 10], although this alternative is based on the minimization of the mass transfer problems that
70 typically occurs in the electrochemical cell.

71 Application of ultrasounds in combination with electrolysis has shown contradictory
72 results, suggesting the very complex nature of the processes involved [11-16]. Synergetic
73 effects are not observed in all works, and in some cases the application of US results in an
74 antagonistic effect. At this point, it is important to highlight the difference between the
75 application of low and high frequency ultrasounds [12, 17-21]. Energy of the first type is not
76 enough to promote the formation of oxidants by the rupture of molecules. Nevertheless, it
77 promotes the so-called transient cavitation, in which the violent collapse of bubbles generates
78 extreme conditions of temperature and pressure (hot-spot theory), where radicals such as
79 hydroxyl ($\bullet\text{OH}$), hydrogen ($\bullet\text{H}$) and hydroperoxyl ($\bullet\text{HO}_2$) can be produced. In addition to that,
80 this effect improves the mixing conditions in the cell and, hence, it contributes to minimize the
81 negative effect of mass transport control on the efficiency of the remediation process [12, 21-
82 23]. Opposite, energy of high-frequency ultrasound promotes the stable cavitation effect, in
83 which bubbles collapses are less violent. Under those conditions, bubbles oscillate for longer
84 times, which can improve the formation of radicals but does not improve physical effects [21,
85 22, 24]. However, when the formation of oxidants is huge (and combination of US and
86 electrochemistry favor this formation), interactions between oxidants may contribute to
87 deactivate them, making the process less efficient.

88 A very interesting topic of study in the use of electrolysis is the application of wastes
89 which do not only contain soluble pollutants but also particulate pollutants. Presence of
90 micelles in the waste is a case of very high interest, because several industrial wastewaters
91 contain surfactants on their composition, which can interfere on the efficiency of the treatment.
92 In addition, an important approach on remediation of soils is the soil-washing with surfactants,
93 which simplifies the soil decontamination to a wastewater treatment problem [4]. In this
94 context, the degradation of micelles during the treatment process is not well-studied, in
95 particular paying attention to what happens with the size of the micelles and how this size
96 affects to the efficiency of the treatment. Regarding electrochemical oxidation processes some
97 previous works of our group have tried to shed light on the mechanisms [25-28], but there is a
98 still a long way to have a clear model of the influence of ultrasound on the evolution of these
99 species during the electrochemical degradation of wastes.

100 In order to go further in this topic, this work focuses on the degradation of a synthetic
101 cosmetic waste, which contain not only soluble species but also micelles. In addition to discuss
102 what happened during the electrolysis and sono-electrolysis with soluble organic and inorganic
103 species, the work remarks the importance of the application of ultrasounds in the evolution of

104 micelles and provides a simple mechanistic model to explain the differences between the
105 application of low and high-frequently US. All this is studied in combination with the
106 degradation of methyl-paraben, which is used not only as a model of hazardous pollutant
107 (because of its well-known endocrine disruptor effects) but also as model of soluble aromatic
108 pollutant. The electrolysis of this species in more simple wastes was evaluated in a previous
109 work [29] and here we are going to expand conclusions to systems with a much more complex
110 formulation.

111

112 **Materials and methods**

113 *Chemicals and working solution*

114 Synthetic wastewater (SW) containing high concentrations of organic matter was
115 developed based on real effluents from cosmetic industries [30-33], in which methyl paraben
116 is found. SW was prepared using a commercial micellar water solution (Agua Limpiadora
117 Micelar, Deliplus, Spain), in the concentration of 5 g L⁻¹. To this solution, 100 mg L⁻¹ of methyl
118 paraben and 1 g L⁻¹ of sodium dodecyl sulfate (SDS) were added, both from Sigma-Aldrich.

119 Characterization of the emulsion was based on COD measures (chemical oxygen
120 demand), since the particulate matter would not be accounted for TOC (total organic carbon)
121 analysis (because all samples had to be filtered for carbon analysis). According to that, the
122 micellar water (at the used concentration) represents a COD of 510 mgO₂ L⁻¹, SDS represents
123 about 1350 mgO₂ L⁻¹ and MeP contributes to about 170 mgO₂ L⁻¹. At the end, SW prepared
124 contains COD ~ 2000 mgO₂ L⁻¹ and DOC ~ 400 mgC L⁻¹.

125 Besides the inorganic salts from the micellar water, additional salts were added to the
126 emulsion, guaranteeing the presence of all ions that are common in cosmetic wastewater (**Table**
127 **1**) [30-33]. Na₂SO₄, NaCl and H₂SO₄ were purchased from Panreac, CaCl₂·2H₂O, (NH₄)₂SO₄
128 and Na₃PO₄ from VWR Chemicals and MgSO₄·7H₂O from Sigma-Aldrich. Total
129 concentration of each ion in the final synthetic wastewater is presented in **Table 1** (a portion
130 from the cosmetic micellar water and other added to the emulsion).

131 Chloroform (Sigma-Aldrich), sodium tetraborate decahydrate (VWR Chemicals) and
132 methylene blue (Merck) were used for SDS determination. Acetonitrile, HPLC grade was
133 obtained from VWR Chemicals. All solutions were prepared with high-purity water obtained
134 from a Millipore Milli-Q system (resistivity >18M cm at 25 °C) and all reactants were used as
135 received.

136

137 *Experimental set-up*

138 Experiments were carried out in a bench scale flow system described elsewhere [15].
139 A plate of boron doped diamond (BDD) and a plate of stainless steel were used as anode and
140 cathode, respectively (both with surface area of 75 cm²). A HQ-Power PS3010 power supply
141 (0-30 V, 0-10 A) provided the applied current. A peristaltic pump (PERCOM-I, JP Selecta,
142 Barcelona, Spain) was used to maintain the flow rate at 7 mL s⁻¹ and a thermostatic bath
143 (Digiterm 100, JP Selecta) to maintain 1 L of working solution at 25 °C for 8h of treatment.
144 For the ultrasonic experiments an ultrasound probe was immersed in the glass tank directly
145 acting in the wastewater. Tests were carried out at the acoustic frequencies of 20 kHz (UP200S,
146 Hielscher Ultrasonics GmbH), 1 MHz and 10 MHz (EPOCH 650, Olympus), both equipment
147 with nominal power of 200 W.

148

149 *Analytical techniques*

150 Methyl paraben was monitored by high performance liquid chromatography (Agilent
151 Technologies 1260 chromatographer) with an Eclipse Plus C18 column (3.5µm 4.6 x 100 mm),
152 at 25 °C, and UV detector set in 280 nm. Mobile phase was acetonitrile and water (60:40 v/v)
153 with 1 mL min⁻¹ of flow rate. SDS was quantified according to the method described by Jurado
154 et al. [34] using an Agilent Cary Series UV-Vis spectrophotometer. Dissolved organic carbon
155 (DOC) was determined in a Multi N/C 3100 Analytik Jena analyzer and turbidity was analyzed
156 in a HI93703 microprocessor turbidimeter (HANNA Instruments). Inorganic anions (SO₄⁻²,
157 PO₄⁻³, Cl⁻, ClO₃⁻, ClO₄⁻, Na⁺, NH₄⁺, Ca⁺² and Mg⁺²) were measured by ion chromatography
158 using a 930 Compact IC Flex (Metrohm). The samples for chromatography and carbon analysis
159 (DOC) were previous filtered through a nylon membrane (0.45 µm). Particle size was measured
160 during the electrolysis of SW by laser diffraction analysis in a Mastersizer Hydro 2000SM
161 (Malvern Panalytical).

162

163 *Electric energy per order*

164 Energy consumption of the system was evaluated by electric energy per order according
165 to **Eq. 1** [35], where E_{cell} is the cell potential (V), t is time (h), V is the volume of treated
166 solution (L) and C₀ and C are the initial and final concentration of pollutant.

167

$$168 \quad E_{EO} = \frac{E_{cell.t.1000}}{V.\log(C_0/C)} \quad (1)$$

169

170 **Results and discussion**

171 *Electrochemical treatment*

172 A synthetic wastewater (SW) containing MeP and high concentration of micelles was
173 developed and treated by electrochemical process. In order to observe the behavior of MeP
174 under electrolytic process, the compound was firstly treated individually in sulfate and chloride
175 media, which are the main anions present in the SW. **Fig. 1** shows the removal of MeP in Cl⁻,
176 SO₄²⁻ and SW, during electrolysis.

177 Methyl paraben is completely removed in all systems, however at different times: < 20
178 min, < 1 hour and < 5 hours in Cl⁻, SW and SO₄²⁻, respectively. These great differences are
179 attributed to the main oxidant species generated in each medium. Faster removal in chloride
180 medium is expected due to the chlorination of the organic molecule by active chlorine species,
181 which are electrochemically generated (Cl₂, HClO and ClO[•]) [1, 36]. Hydroxyl radicals are
182 also constantly formed in this medium, however they oxidize organic matter by slower
183 mechanisms (H-abstraction and addition). Conversely, in sulfate medium, besides •OH
184 species, persulfate and sulfate radical anions (SO₄^{•-}) are also produced. These radicals are
185 usually capable to oxidize several pollutants that are refractory towards •OH, because they
186 react predominantly by electron transfer. However, this mechanism is also slower than
187 chlorination and, thus, slower MeP removal is observed [37, 38].

188 Synthetic wastewater contains both Cl⁻ and SO₄²⁻ anions. Thus, all the previously
189 mentioned oxidant species are expected to be formed. In fact, it is observed an intermediate
190 behavior for MeP removal and the result is explained by the greater content of chloride than
191 sulfate. Other authors also observed similar results using BDD anodes. Steter *et al.* [39]
192 compared sulfate and chloride anions as supporting electrolytes, individually and in
193 combination, and found better mineralization results for the combined medium. Frontistis *et*
194 *al.* [40] compared the removal of a pollutant in sulfate and in real wastewater, obtaining faster
195 removal for the more complex matrix. They ascribed those results to the presence of other
196 anions in the wastewater, which contribute to the formation of other oxidant species.
197 Nevertheless, as it was described before, each specie acts through a different mechanism of

198 oxidation, which favors the degradation of compounds of different nature. As a result of that,
199 the oxidation of more organic species may occur, and the efficiency of the process increases.

200 Although the removal of MeP was faster in chloride and SW media, the same is not
201 observed for the total oxidation of organic matter. For the SW, 89% of DOC removal is
202 achieved with 8 hours of treatment, while for MeP in sulfate and chloride solutions 100% of
203 DOC removal is achieved before 5 and 6 hours, respectively. The complexity of the matrix
204 decreases the kinetic of DOC removal and, thus, its mineralization efficiency (**Table 2**). **Fig.**
205 **2a** shows that mineralization, in all media, follows *pseudo*-first order kinetics with two
206 distinctive regions, in which two kinetic constants can be determined: k_1 and k_2 for each regime,
207 respectively (**Table 2**). The kinetic transitions observed are attributed to the nature of oxidants
208 and intermediates generated in the medium, which results in different oxidation mechanisms
209 during the process.

210 Regarding sulfate and chloride media, the difference on the mineralization efficiency
211 is mostly due to the oxidation mechanism. As described before, MeP is rapidly converted to
212 organochlorinated compounds under the presence of HClO/ClO^- . Those intermediates are very
213 stable and more hardly degradable than in the case of sulfate medium, thus lower kinetic rate
214 of mineralization is obtained. Although MeP oxidation in sulfate is slower, the mechanism of
215 degradation consists in the rupture of carbon bonds, which facilitates further mineralization.
216 On the other hand, a more complex kinetic is expected for SW degradation, due to the very
217 high initial DOC and that organic matter is majorly found in the form of micelles. This means
218 that part of the organic content is inside the particles, thus, not accessible to be immediately
219 oxidized. Micelles need to be firstly attacked in order to continuously form smaller particles
220 until their further rupture. At this point, the inner compounds are released to the bulk and can
221 be consumed by the oxidant species.

222 It is important to note that the kinetic change on the SW oxidation curve, is not only
223 explained by the intermediates formation. As the degradation of SDS proceeds, sulfate
224 concentration increases with time, as showed in **Fig. 2b**. Previous works showed that the
225 electrolysis of SDS promotes the releasing of sulfate anions, which can be oxidized to
226 persulfate and improve the removal of organic compounds [41]. In fact, the kinetic transition
227 occurs after 120 min of reaction, in which approximately 50% of SDS was consumed. Hence,
228 the ratio $[\text{SDS}]/[\text{SO}_4^{2-}]$ is significantly changed with regard to the initial ratio, and the oxidation
229 kinetic of DOC is modified.

230

231 *Effect of ultrasound on electrolysis*

232 As an attempt to improve the efficiency of the process, sonochemistry (SCh) and
233 electrochemistry (ECh) technologies were coupled. Previous studies in our laboratory [42]
234 evaluated the effect of ultrasound irradiation (US) to the oxidation of MeP in sulfate medium,
235 showing that the mineralization is favored by the coupled process (SECh process). The kinetic
236 for dissolved organic carbon removal fitted a *pseudo*-first order with two regions, in which k_1
237 and k_2 are presented in **Table 3**. Under the condition L75, it was observed an improvement of
238 35% and 60% for k_1 and k_2 , respectively, and also, the complete mineralization was attained in
239 3 hours compared to 4 hours for electrochemical process. In addition to those results, it can be
240 considered that SW is a much more complex matrix, in which ultrasound could present
241 different effects. For instance, earlier researchers stated that the presence of surfactant can
242 enhance the cavitation phenomenon by reducing the surface tension [17, 22], which may
243 improve the formation of radicals and, thus, the removal of pollutants.

244 According to that, ultrasound frequencies of 20 kHz, 1 MHz and 10 MHz were directly
245 irradiated into the synthetic wastewater during electrolysis with 30 mA cm^{-2} . **Fig. 3a** shows
246 MeP oxidation and the total removal of DOC (inset) after the applied processes. The abatement
247 of MeP is not affected by the presence of ultrasound and complete removal is achieved by the
248 time of 1 hour ($Q = 2.5 \text{ A h L}^{-1}$) under all studied conditions. However, previous studies found
249 that single sonochemical process was capable to remove, approximately, 30% of MeP, when
250 low frequency ultrasound was used [42]. In SW, none of the frequencies applied were efficient
251 to oxidize methyl paraben without the combination to electrolysis (not shown), which is
252 possibly a consequence of the higher complexity of the medium. Inset of **Fig. 3a** shows the
253 elimination of DOC after 8 hour of treatment and the respective kinetic constants are presented
254 on **Fig. 3b**. Similar behavior was observed for the kinetic of DOC abatement in the presence
255 and absence of US, in which k_2 is much higher than k_1 . Low frequency enhanced the removal
256 in the second kinetic region, however, k_1 was smaller than in ECh process and the total removal
257 was not favored. Although the attained DOC removals are very similar and not much should
258 be stated, the observed tendency is consistent with the results obtained in previous work for
259 the degradation of MeP in sulfate medium: L75 > H1 > H10 [42]. This could indicate that
260 ultrasound does may improve electrochemical removal of organic matter. However, the applied
261 conditions might not be ideal.

262 At this point, in order to better understand the effects of ultrasound in this system, it is
263 important to verify the behavior of micelles in the emulsion. For that, particle size was
264 monitored during the electrolysis with and without US irradiation (**Fig. 4a**). It was expected
265 that, as the degradation proceeds, micelles would be attacked, promoting a decrease on their
266 size until the rupture, as it was found by Santos, *et al.* [26]. However, it is observed, for all
267 conditions, an increase on the size of the micelles before their decrease. It was recently reported
268 that micelle size evolution is an interfacial phenomenon strongly dependent on the solution
269 agitation, due to the formation of air/water interfaces [43]. Under the applied conditions,
270 electrolysis generates high concentration of gases (oxygen and chlorine), resulting in a huge
271 amount of bubbles and great stirring of the emulsion. This effect is responsible for the
272 increasing on particle size as proposed on **Fig. 4b**. Surfactant molecules will form micelles,
273 which in the presence of gas bubbles will incorporate these, initiating the growth process;
274 surfactant molecules adsorb to the air/water interfaces may produce bigger micelles by
275 coalescence. Moreover, when current density is doubled (to 60 mA cm^{-2}) for ECh process,
276 particles size increase 2.5 times and the time in which the phenomenon occurs is 3 times
277 shortened, which is explained by the even more intense generation of gases in the medium.

278 A recent study showed that ultrasound can accelerate micelle growth by an order of
279 magnitude with respect to agitation by vortex [44]. Cavitation effect enhance the production of
280 bubbles, which increases the interfaces air/water. In addition, US acts on electrogenerated gas
281 bubbles, promoting their faster rupture, which contributes to micelles evolution (**Fig. 4b**). The
282 growth of cavitation bubbles promotes the fast adsorption of micelles on the interface; the
283 further collapse will lead to a reorganization of the surfactants and the inner content of micelles
284 (hydrophobic compounds), in which higher particles may be formed. In fact, it is possible to
285 see that under the presence of 20 kHz ultrasound (L75), particle size increased more than 7
286 times with relation to E30, and the time of maximum size decreased by half. According to this,
287 it is possible to explain the kinetic of DOC removal observed on **Fig. 3b** for L75. Due to the
288 large micelle size, it is more difficult to break these particles and release organic compounds
289 into the bulk for oxidation, thus, the initial kinetic rate (k_1) is the lowest. However, after 120
290 min of treatment, no more particles are detected, which means that all compounds are dissolved
291 in the solution and can be oxidized. At this point, k_2 increases for all conditions, being the
292 effect more remarkable for L75, that is almost 10 times greater than k_1 and is 30% higher than
293 E30 k_2 .

294 Low frequency ultrasound promotes an effect known as transient cavitation, in which
 295 generated bubbles are unstable and their collapse is very rapid and violent. As a result, great
 296 amount of energy is released, producing extreme conditions in which $\bullet\text{OH}$ radicals and H_2O_2
 297 can be formed by water sonolysis (**Eq. 2-3**). In addition to those, species such as $\text{Cl}\bullet$ and
 298 $\text{SO}_4\bullet$ can also be produced from chlorine and persulfate anions (**Eq. 4-5**), contributing to the
 299 oxidation of organic compounds [22, 45, 46]. At high concentration of micelles, the produced
 300 bubbles are surrounded by particles; at the point of their collapse the energy released
 301 contributes to the reorganization of micelles, inhibiting the sonochemical effect of production
 302 of radicals. After the removal of particles, at 120 min, kinetic constant of DOC removal on L75
 303 increases due to the cavitation contribution to the oxidation.

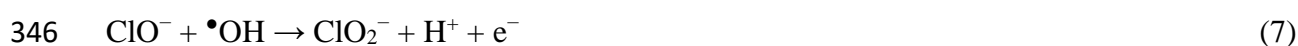


308 On the other hand, inset of **Fig. 4a** shows that the micelles growth happens in a smaller
 309 scale when 1 and 10 MHz are applied. High frequency ultrasound promotes a stable cavitation,
 310 in which bubbles oscillation is slow, resulting in a higher lifetime and a non-violent collapse
 311 [21, 22]. This may be the explanation for the smaller size of micelles observed for H1 and H10
 312 tests. Under those conditions, it seems that US acts on the electrogeneration of gas bubbles,
 313 promoting their oscillation for a longer period and inhibiting the evolution of micelles size
 314 (**Fig. 4b**). This effect is still unclear and more studies should be carried out in order to elucidate
 315 its mechanism. Anyhow, those results are also in agreement with the kinetic constants
 316 presented in **Fig. 3b**, in which the difference between E30 and high frequency experiments (H1
 317 and H10) is not remarkable. Even after the removal of particles, the stable cavitation
 318 phenomenon does not favor the formation of radicals, and no improvement is achieved on
 319 oxidation. Nevertheless, considering that 1 MHz is the boundary between low and high
 320 frequency ultrasound, both cavitation effects will take place at certain levels, hence, a small
 321 increase on particle size is observed at the first 10 min of degradation. This is in agreement
 322 with the previous findings [42], in which the synergistic effect of coupling US and ECh process
 323 followed the order: L75 > H1 > H10.

324 **Fig. 5a** shows the degradation of SDS by ECh and SECh process. As already
 325 mentioned, SDS molecules are majorly found in the form of micelles. The presence of oxidants,

326 will promote the degradation of SDS without breaking the particles, in a first moment. This is
 327 consistent with the first hours of treatment, in which SDS concentration decreases. However,
 328 it is observed a point in which the concentration of SDS slightly increase, approximately about
 329 5 h of treatment. In order to confirm this behavior, an electrochemical test was carried out at
 330 60 mA cm⁻² (inset), where the effect can be clearly seen. These results suggest that SDS
 331 concentration decreases, in a first moment, not only by its degradation, but also by a physical
 332 process. It was possible to observe the formation of foam during the oxidation processes which
 333 means that SDS is being removed from the emulsion. As the degradation proceeds, micelles
 334 are removed and the concentration of SDS decreases in solution; this promotes the dissolution
 335 of foam and the migration of SDS back to solution, rising its concentration. Regarding US
 336 effect, as expected, L75 showed better results on SDS oxidation and removal of foam. In fact,
 337 this was the only condition in which none foam was observed at the end of the treatment, as
 338 will be further discussed.

339 On **Fig. 5b** is presented the production of perchlorate anions in each system. As it is
 340 well known, the formation of ClO₄⁻ is a consequence of the use of diamond anodes in chloride
 341 medium (**Eq. 6-9**). The application of US delayed its formation in more than 1 hour for the
 342 condition L75 and the final concentration is 7 times lower than for electrochemical process.
 343 This is an important result considering that perchlorate is very harmful to human health and
 344 ecosystems [1, 47].



349 For processes with first-order rate constants, it is possible to determine the necessary
 350 energy to degrade the contaminant by one order of magnitude, according to **Eq. 1**. **Table 4**
 351 compares the electric energy per order of organic matter removal for the electrochemical
 352 process individually and coupled to ultrasound. At this point it is clear that, due to the high
 353 content of micelles on the SW emulsion, its treatment consists on several effects, such as
 354 effective stirring, production and dissolution of foam, reorganization of micelles, varying its
 355 size, rupture of micelles, elimination of particles and oxidation of organic compounds.
 356 Considering this, energy consumption is even more interesting, because involves the necessary
 357 energy for both physical and chemical processes. At low frequency (L75), less energy was

358 required to achieve complete mineralization, which means that the oxidation process is more
359 efficient. As discussed before, this is mainly due to the higher generation of oxidants under the
360 presence of transient cavitation.

361 As mentioned at the beginning, the developed SW is a white silky emulsion, allowing
362 the study of micelles behavior under electrochemical treatment and irradiation of ultrasound.
363 Hence, it is also important to consider the physical aspect of the treated wastewater. SDS
364 promotes the aggregation of particles and, as a consequence, the initial turbidity of SW was
365 very high (~ 500 FTU).

366 **Fig. 6** shows the depletion of turbidity during the treatments. It can be seen that
367 irradiation of ultrasound directly affects the physical aspect of the wastewater; the lower the
368 frequency, the faster is the decrease on the turbidity. This results are better seen on the
369 experiments without current application. As discussed before, violent cavitation is resulted
370 from the application of high intensity acoustic field (low frequency), and, under this condition,
371 the bubbles can act as mechanical forces, which can induce the aggregation or disaggregation
372 of particles [48]. This last effect is related to the decrease of turbidity and might facilitate the
373 degradation of organic matter, by increasing the surface area of the particles. As the acoustic
374 intensity decreases, transient cavitation turns to stable cavitation and the collapse of the bubbles
375 is less powerful. As a result, disaggregation of particles is not promoted and turbidity takes
376 more time to be removed.

377 Another physical aspect of the solution that needs to be taken into account is the
378 formation of foam in the glass tank, during the applied treatments for the SW, mentioned
379 before. This was an expected outcome, considering the high concentration of SDS under the
380 circulation of solution and the electro evolution of gases. The dissolution of this foam was
381 observed and after the 8 hours, its remaining quantity in the reservoir was different for each
382 treatment. It was not possible to measure the reminiscent amount of foam, however, some
383 important aspects were noted: in SCh processes, a clear final solution was obtained after using
384 20 kHz, while for the other frequencies the final samples were still white turbid; for ECh and
385 SECh processes, the final solutions were clear, however only with 20 kHz there was no foam
386 at the end of the experiment. These observations reinforce that low frequency ultrasound was
387 the better choice to combine with electrolysis for the studied system. At this point, it is possible
388 to state that although ultrasound did not promote a huge improvement in the chemical oxidation
389 of the wastewater, it does improve the physical aspect of it, which is also important to consider
390 for the disposable of effluents.

391

392 **Conclusions**

393 From this work, the following conclusions can be drawn:

394 - Electrochemical process with diamond electrodes is efficient for the treatment of cosmetic
395 industry wastewater, attaining almost 90% of mineralization in 8h.

396 - The presence of surfactants in the wastewater interferes on the degradation of pollutants.
397 High concentrations of micelles may make more complex the oxidation of hydrophobic
398 organic compounds, since they are only released to the aqueous phase after the micelles
399 rupture.

400 - Ultrasound did not improve electrochemical oxidation. In a complex wastewater, ultrasound
401 energy will firstly promote physical processes, such as particle size growth and depletion of
402 turbidity and foam, before it contributes to chemical effects (activation of oxidants).

403 - Under great content of micelles, high evolution of bubbles may promote the coalescence of
404 micelles. Cavitation of low-frequency ultrasound helps to rearrange micelles into larger
405 particles, which interferes on their stability and may facilitate the degradation.

406 Besides the work showed important results regarding the effect of surfactant in wastewater and
407 the behavior of micelles under electrochemical and sonochemical treatments, there is still room
408 for this topic. Some additional research with hydrophobic pollutants needs to be explored, in
409 order to better understand the possible interfering effects of surfactants and micelles on
410 wastewater.

411

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415 acknowledged.

416 **References**

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563 **Table 1** Amount of ions added to the working solution and initial ionic composition of the synthetic
 564 wastewater

| Ions | Concentration added (mg L⁻¹) | Total concentration in the SW (mg L⁻¹) |
|-------------------------------|--|--|
| Cl ⁻ | 900 | 1000 |
| SO ₄ ⁻² | 160 | 430 |
| PO ₄ ⁻³ | 13 | 40 |
| Na ⁺ | 620 | 920 |
| NH ₄ ⁺ | 26 | 28 |
| Ca ⁺² | 60 | 60 |
| Mg ⁺² | 20 | 40 |

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567 **Table 2** Removal of DOC by electrochemical process and its respective kinetic constants in all studied
 568 media

| | DOC removal (%) | k₁ (10⁻³ min⁻¹) | k₂ (10⁻³ min⁻¹) |
|------------------------------------|------------------------|---|---|
| Cl⁻ | 100 (5 h) | 3.9 | 13 |
| SO₄²⁻ | 100 (4 h) | 7.4 | 15 |
| SW | 89 (8 h) | 2.7 | 5.6 |

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570

571 **Table 3** Kinetic constants of DOC removal of MeP (100 mg dm⁻³) in sulfate medium (3.0 mg dm⁻³) for
 572 electrochemical process with 30 mA cm⁻² (E30) and the coupled processes with ultrasound at 20 kHz
 573 and 75% of power (L75), 1 MHz (H1) and 10 MHz (H10).

| | | E30 | L75 | H1 | H10 |
|------------------------------------|--|------------|------------|-----------|------------|
| SO₄²⁻ | k ₁ (10 ⁻³ min ⁻¹) | 7.4 | 10 | 7.2 | 8.3 |
| | k ₂ (10 ⁻³ min ⁻¹) | 15 | 24 | 16 | 25 |

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578 **Table 4** Energy consumption per order of DOC removal for electrochemical process with 30 mA cm^{-2}
579 (E30) and the coupled processes with ultrasound at 20 kHz (L75), 1 MHz (H1) and 10 MHz (H10)

| Experiment | E_{EO} (kWh/m³/order) |
|-------------------|--|
| E30 | 63 |
| L75 | 51 |
| H1 | 64 |
| H10 | 66 |

580