

1 **Conductive diamond sono-electrochemical disinfection** 2 **(CDSED) for municipal wastewater reclamation**

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6 **Abstract**

7 In the present work, the disinfection of actual effluents from a municipal wastewater
8 treatment plant (WWTP) by a conductive diamond sono-electrochemical process was
9 assessed. First, efficiency of single electrodisinfection process with diamond anodes
10 (without the contribution of ultrasounds) was studied, finding that the total disinfection
11 can be attained at current charges applied below 0.02 kA h m^{-3} . It was also found that the
12 main disinfection mechanism is the attack of *E. coli* by the disinfectants produced in the
13 electrochemical cell and that the production of chlorates is avoided when working at
14 current densities not higher than 1.27 A m^{-2} . Next, a marked synergistic effect was found
15 when coupling ultrasound (US) irradiation to the electrochemical system (sono-
16 electrochemical disinfection). This increase in the disinfection rate was found to be
17 related to the suppression of the agglomeration of *E. coli* cells and the enhancement in
18 the production of disinfectant species.

19
20 **Keywords:** Conductive diamond, ultrasound, electrodisinfection, wastewater
21 reclamation, integrated process.

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24 **1. Introduction.**

25

26 Over the last decades, electrochemical processes have been extensively studied for the
27 remediation of wastewaters [1, 2]. They exhibit high pollutant degradation rates, small
28 dependence on added chemicals and sufficient robustness to be applied in many different
29 environments [3].

30 Nowadays, reclaiming of urban wastewaters is one of the most promising alternative
31 sources to provide water for many different uses such as irrigation, repletion of aquifers
32 or industrial activities, and many researchers are doing a great effort for the development
33 of new technological approaches. Disinfection is the key process for this technology and
34 nowadays it has become a hot research topic because of its significant challenges: it is
35 necessary not only to develop processes that kill microorganisms contained in wastewater
36 in an economical, persistent and efficient way but also to avoid the formation of hazardous
37 disinfection by-products [4].

38 Within the broad spectrum of disinfection technologies, electrolysis has emerged as a
39 very interesting alternative, in particular when boron doped diamond electrodes (BDD)
40 are applied. This technology (CDEO, conductive-diamond electrochemical oxidation)
41 was proved to be efficient in wastewater treatment processes for the oxidation of many
42 different pollutants, including refractory organics [5-7] and also in disinfection processes
43 [8-10]. However, those studies focused on the treatment of synthetic wastewaters,
44 avoiding different problems that may occur during the treatment of actual effluents. In
45 addition, electrochemical processes using BDD electrodes have exhibited a marked
46 integration capability with other treatment technologies as it is the case of electro-Fenton
47 [11, 12], photoelectro-Fenton [13] and photo-electrolytic processes [14].

48 Another technique that has been used in disinfection processes is the irradiation with
49 ultrasounds (US), a process that is usually called sonochemical disinfection [15, 16].

50 Sonochemical disinfection (SCD) is based on the production of hot spots with highly
51 reactive free radicals and in the capacity to break agglomerates of microorganisms [17].
52 In addition, the performance of sonochemical processes can be easily enhanced by
53 coupling ultrasounds with other oxidation and disinfection techniques such as
54 electrochemical oxidation with BDD [18] and platinum anodes [19], TiO₂ particles [20,
55 21] or photo-oxidation processes [22].

56 Thus, the combination of sonochemical techniques and CDEO in conductive-diamond
57 sono-electrochemical disinfection (CDESD) processes is a specially promising research
58 topic in the field of water disinfection. Synergistic effects of the integration of both
59 techniques should be expected due to the capacity of CDEO to generate active oxidant
60 species (potential disinfectants) and that of sonochemical processes to enhance this
61 production and also to destroy microorganisms clusters (which can then be more exposed
62 to the disinfectants generated). To the best of the authors' knowledge, no previous
63 attempts of coupling both technologies in a disinfection process of actual effluents have
64 been carried out.

65 Thus, the aim of the present work is to study the potential synergistic effect of coupling
66 ultrasound irradiation with conductive-diamond electrochemical oxidation on the
67 disinfection of actual effluents from municipal WWTP. In a first approach, the
68 electrochemical disinfection of actual effluents by conductive diamond anodes was
69 confronted. Next, US irradiation was coupled with the electrochemical disinfection
70 system in order to evaluate the potential synergies of both techniques. The effect of the
71 most important parameters (current density for CDEO and power irradiated and cycle
72 duration for US irradiation) in the performance of the CDESD process was also evaluated.

73

74 **2. Material and methods.**

75 **2.1 Analytical techniques.**

76 Faecal coliforms were estimated using the most probable number (MPN) technique [23].

77 Microorganism counts were carried out by the multiple-tube-fermentation technique (24
78 h of incubation at 44 °C) using 5 tubes at each dilution (1:10, 1:100, and 1:1000).

79 Nitrogen and chloride inorganic anions (NO_3^- , NO_2^- , Cl^- , ClO^- , ClO_2^- , ClO_3^- , ClO_4^-)
80 were measured by ion chromatography using a Shimadzu LC-20A equipped with Shodex
81 IC I-524A column; mobile phase, 2.5 mM phthalic acid at pH 4.0; flow rate, 1.0 ml
82 min^{-1}). The peak of hypochlorite interferes with that of chloride; therefore, the
83 determination of hypochlorite was carried out by titration with As_2O_3 in 2 M NaOH. The
84 same ion chromatography equipment (Shodex IC YK-421 column; mobile phase, 5.0 mM
85 tartaric, 1.0 mM dipicolinic acid and 24.3 mM boric acid; flow rate, 1.0 ml min^{-1}) was
86 used to measure the nitrogen inorganic cation (NH_4^+).

87 Inorganic chloramines were measured following the DPD standard method described in
88 the literature [23].

89 Occurrence of trihalomethanes (CHCl_3 , CHBrCl_2 , CHBr_2Cl , CHBr_3) was followed using
90 a SPB 10 column (30 m x 0.25 mm; macroporous particles with 0.25 μm diameter).

91 Injection volume was set to 1 μL .

92 **2.2 Experimental setup.**

93 The electrodisinfection and sono-electrodisinfection processes were carried out in a
94 single-compartment electrochemical cell. Boron doped diamond (BDD) (Adamant
95 Technologies, Switzerland) was used as anode and stainless steel (SS) (AISI 304)
96 (Mervilab, Spain) as cathode. Both electrodes (anode and cathode) were circular with a
97 geometric area of 78.5 cm^2 and the electrode gap was 3 mm.

98 Wastewater was stored in a glass tank (2.5 dm³). The ultrasound generator (UP200S,
99 Hielscher Ultrasonics GmbH, Germany) is equipped with a horn (40 mm diameter, 100
100 mm length, 12 Wcm⁻², 24 kHz) that is located inside the glass tank. The maximum power
101 of ultrasound is 200 W and the output can be continuous or pulsed with duty cycle ranging
102 from 10 to 100%.

103 The system works in total recirculation mode, with a peristaltic pump (JP Selecta Percom
104 N-M328) continuously recycling the target wastewater. The power supply is a Delta
105 Electronika ES030-10. Temperature of the system is kept constant by means of a
106 thermostatised bath (JP Selecta, Digiterm 100) and a heat exchanger (Fig. 1).

107

108 **2.3. Experimental procedure.**

109 Bench-scale electrolyses of 2000 cm³ of wastewater were carried out under galvanostatic
110 conditions. The current density applied ranged from 1.27–6.37 A m⁻². The cell voltage
111 did not vary during electrolysis, indicating that conductive-diamond layers did not
112 undergo appreciable deterioration or passivation phenomena. Prior to use in galvanostatic
113 electrolysis assays, the electrode was polarized for 10 min in a 5,000 mg dm⁻³ Na₂SO₄
114 solution at 150 A m⁻² to remove any kind of impurity from its surface.

115

116 **2.4. Target effluents.**

117 The WWTP treat the wastewater of an average-sized town (75,000 p.e.) located in the
118 centre of Spain. The influent is domestic wastewater without a significant industrial
119 contribution. The average chemical characteristics of the samples used in this work are
120 shown in Table 1.

121

122 **3. Results and discussion.**

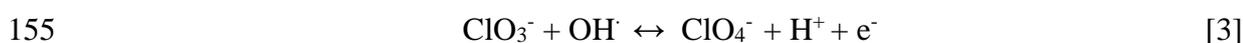
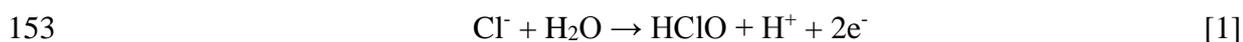
123 **3.1. Electrodisinfection of actual effluents from WWTP.**

124 Fig. 2.a shows the changes in concentration of *E. coli* with the operation time and applied
125 electric charge during galvanostatic electrolyses at three values of current density. As it
126 can be observed, in all cases it is possible to completely disinfect the effluents for values
127 of current charge applied below 0.02 Ah dm^{-3} . The disinfection process follows a first
128 order kinetics (respect to the concentration of *E. coli*), characteristic of disinfection by
129 chemicals. Although CDEO processes are typically mass transfer controlled [24], the key
130 process to explain the disinfection in electrochemical systems is the production of
131 disinfectant and not the transport of microorganism to the nearness of the anode surface.
132 At this point, and as expected because of the higher production of oxidants, *E. coli* is
133 more efficiently removed when working at current densities higher than 1.27 A m^{-2} .

134 In order to quantify the effect of the current density on the rate of the process, these data
135 have been fitted to a first order kinetic model, being the results shown in Fig. 2.b. As it
136 can be observed, kinetic rate constant follows an almost linear trend with the applied
137 current density. This result implies that the system is not working under mass transfer
138 limitations and confirms that the disinfection is basically a mediated process. In order to
139 shed light on the production of these oxidants species, changes in the concentration of
140 chlorine oxoanions in the bulk are shown in Fig. 3.

141 As it can be observed, hypochlorite is the primary species produced. This time-course of
142 hypochlorite has been described in literature [25]: it behaves as a clear reaction
143 intermediate with an initial increase and a subsequent decrease in the concentration. The
144 initial increase in its concentration can be explained by the oxidation of chloride ions on
145 the anode surface (Eq. 1). The subsequent decrease in the concentration of hypochlorite
146 can be described in terms of several simultaneous processes: 1) the oxidation of

147 hypochlorite to oxoanions in higher oxidation state (chlorate and perchlorate), as
148 described by Eqs. 2 and 3; 2) the reaction of hypochlorite with ammonium ions to form
149 chloramines (Eqs. 4 to 6); 3) the oxidation of E. coli cellular membrane leading to the
150 disinfection of the effluent; 4) the reduction of hypochlorite in the cathode of the cell
151 (non-divided equipment); 5) the reaction of hypochlorite with dissolved organic matter to
152 form organochlorated compounds (mainly trihalomethanes).

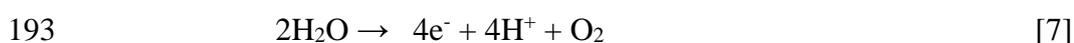


159 These five possible processes compete in the bulk during electrolysis and they exhibit
160 different behavior regarding disinfection, being positive the formation of hypochlorite
161 and chloramines, and negative the production of chlorates and perchlorates. As it can be
162 observed in Figure 3, perchlorate is not produced within the entire range of conditions
163 tested in the present work. Unfortunately, the formation of chlorate is promoted at the two
164 highest current densities (3.82 A m⁻² and 6.37 A m⁻²) and this fact may be explained in
165 terms of the role of hydroxyl radicals produced on BDD during the electrooxidation of
166 chloride solutions [26]. On the contrary, when working at the lowest current density (1.27
167 A m⁻²), neither chlorate nor perchlorate are produced in the cell.

168 Regarding combined chlorine species, the production of chloramines is a desired process
169 because these products act as disinfectant and simultaneously prevent the formation of
170 trihalomethanes, due to its lower reactivity when compared to hypochlorite [27]. Fig. 4

171 shows the changes in the concentration of chloramines (mono-, di- and trichloroamine)
172 in the bulk with respect to the applied electric charge for the three current densities
173 studied. As it can be observed, chloramines are produced at the whole range of current
174 densities used in this work and the rate of production does not seem to depend importantly
175 on the applied current density. Moreover, it was observed that both monochloramine and
176 dichloramine are the main combined chlorine species that are produced in the
177 electrochemical cell.

178 At this point, it is important to note that, according to the literature [28], when the weight
179 of chlorine to ammonia nitrogen is lower to 5:1, and at pH 7 to 8, free chlorine is converted
180 almost completely to monochloramine. Rate of dichloramine formation increases for
181 lower values of pH and at higher ratios of chlorine to ammonia nitrogen (10:1) and the
182 formation of trichloramine (nitrogen trichloride) is favored at strongly acidic pH values
183 and at chlorine to nitrogen ratios equal or higher than 15:1. From the viewpoint of
184 disinfection, monochloramine is the most active and so the most desired species, and
185 nitrogen trichloride is non active and so its production should be prevented. In the
186 electrolyses studied, pH (data not shown) was maintained between 7.4 and 7.7 throughout
187 the tests and the weight ratio of chlorine to ammonia was far below 5:1 (initial ammonium
188 concentration around 30 mg dm⁻³). At these conditions, and according to the information
189 previously mentioned, the formation of di- and trichloramine in the bulk solution should
190 be negligible, so their production should be taking place in the vicinity of the anode
191 surface, where the pH is locally more acid, because of the well known oxygen evolution
192 reaction (Eq. 7).



194 Regarding the unwanted production of organohalogenated derivatives, samples were
195 measured by gas chromatography, but no species were found (detection limit <0.2 ppb)
196 in any of the tests performed in the present work.

197

198 **3.2. Sono-electrochemical disinfection of actual effluents.**

199 Once the performance of the electrodisinfection process was studied, the next step of this
200 research consisted of coupling an ultrasound transducer to the system, looking for an
201 increase in the rate of the disinfection process irradiating US and even for synergy
202 between both processes. These tests were done working at the lowest current density
203 tested in the first part of the work (1.27 A m^{-2}) because at these conditions, it was checked
204 that it was possible to completely disinfect the effluent avoiding the unwanted occurrence
205 of hazardous chlorate and perchlorate.

206 Fig. 5.a shows the changes in the normalized concentration of *E. coli* vs. time for different
207 doses of US irradiated in this CDSED and it also shows results obtained for a single SCD
208 test, carried out with the purpose of comparison. As it can be observed, single SCD
209 decreases the initial concentration of *E. coli* but conditions produced in the bulk are not
210 hard enough to completely disinfect the effluent. According to the literature [29, 30], US
211 irradiation is able to inactivate bacteria and destroy agglomerates of bacterial flocs by
212 several physical, mechanical and chemical mechanisms related to acoustic cavitation. The
213 most significant are: 1) pressure gradients induced by cavitation close to the bacterial cell
214 wall; 2) shear forces; 3) chemical oxidation by radicals; 4) production of H_2O_2 due to
215 sonochemical degradation of water. Furthermore, it has been reported [31] that low
216 frequency ultrasounds (from 20 to 38 kHz), as it is the case of the present work, result in
217 higher disinfection rates than high frequency ultrasounds.

218 On the contrary, Fig. 5.a shows that it is possible to completely disinfect the effluent when
219 single SCD and CDEO electrodisinfection processes are coupled in CDSED processes.
220 In addition, it can be observed that the disinfection rate increases when increasing US
221 applied power (Fig. 5.b). As it can be observed, if the decrease in the *E. coli* concentration
222 is fitted to a first order model, the disinfection rate constant continuously increased from
223 a value of 0.0242 min^{-1} for the electrochemical process to 0.1428 min^{-1} for an US applied
224 power of 200 W.

225 Apart from the applied power, another important parameter is the US emission cycle,
226 defined as the fraction of time in which the US transducer is irradiating US. To carry out
227 this study, US powers of 50 W and 200 W and cycles of 0.5 and 1 were selected. Fig. 6
228 shows the changes in the disinfection rate constant (data fitted to a first order kinetics) for
229 different combinations of power irradiated and cycle of emission.

230 As it can be observed, the higher the power applied to the solution and the longer the
231 cycle of US emission, the higher the rate of the disinfection process. In addition, it can be
232 observed that the rate constant obtained when coupling US and the electrochemical
233 process is clearly much higher than the sum of the rates of the individual processes. This
234 implies that the integrated CDSED process exhibits a marked synergistic effect with
235 respect to the application of the two single technologies. Besides, the disinfection rate
236 constant calculated for an applied power of 200 W and a cycle of 0.5 is similar to that
237 obtained for a power applied of 50 W and a cycle of 1. This result means that the
238 performance of the process does not only depend on the accumulated US power but also
239 on the cycle duration (in fact on the pause of the US emission). This might be explained
240 in terms of a negative effect of the interruption in the emission of US irradiation in the
241 promotion of turbulence and in the formation of radicals.

242 The synergistic effect observed can be explained in terms of the effect of US irradiation
243 in the agglomeration of *E. coli* cells. As it has been described in literature, US can
244 suppress the agglomeration of microorganisms and then increase the exposure of *E. coli*
245 to the main disinfection process. Specifically, a synergistic effect has been described
246 when coupling ultrasounds to UV irradiation [32] and to chemical dosing of low
247 concentrations of chlorine [33]. Thus, at the light of these previous results shown in the
248 literature, results obtained in the present work can be explained in terms of a prevention
249 of the agglomeration of *E. coli* with the use of US, making them more accessible to the
250 disinfectants produced electrochemically (hypochlorite and chloramines).

251 Furthermore, it has been described [34] that the use of US can also enhance the production
252 of oxidants in CDEO processes. To check this enhancement, the concentration of oxidants
253 synthesized in the electrochemical cell was also measured with and without irradiation of
254 US. No oxidants were synthesised throughout the single SCD process. Regarding the
255 CDESED, Fig. 7 compares the concentration of oxidants formed (free and combined
256 chloride) during the single CDEO and the CDESED irradiated with the highest US power
257 (200 W and cycle of 1).

258 Although the initial rate of both free and combined chlorine does not depend on the use
259 of US, it can be clearly observed that the maximum concentration of these disinfectant
260 species increases when coupling US to the CDEO process. The synergistic effect in the
261 production of oxidants can be described in terms of the huge concentration of energy that
262 is produced when US irradiation is applied to an aqueous solution, producing high local
263 temperatures that can result in higher concentrations of hydroxyl radicals in the bulk
264 solution [34, 35]. These hydroxyl radicals can oxidize chloride ions to produce
265 hypochlorite (Eq. 8). A very interesting observation is that US radiation does not promote

266 the formation of chlorates and perchlorates, probably due to the low working current
267 density of the present work.



269 Thus, the suppression of the agglomeration of *E. coli* together to the improvement in the
270 maximum concentration of hypochlorite and chloramines explained the synergistic effect
271 observed when coupling US radiation to an electrochemical disinfection process. These
272 findings are in accordance with the main disinfection mechanism previously proposed in
273 section 3.1 for the single CDEO disinfection, that is, a disinfection process mediated by
274 the chlorine disinfectant species synthesised in the electrochemical cell.

275 **4. Conclusions**

276 The main conclusions to be drawn from the present manuscript are:

277 - Single CDEO can attain the complete removal of *E. coli* from the effluents of municipal
278 WWTP with applied electric charges below 0.02 Ah dm⁻³. The main disinfection
279 mechanism is the attack of electrogenerated chlorine disinfection products (mainly
280 hypochlorite and chloramines) to the *E. coli*. In order to avoid the formation of chlorates,
281 it is necessary to work at current densities not greater than 1.27 A m⁻².

282 - A marked synergistic effect in the disinfection rate was found when coupling an US
283 irradiation with CDEO in combined CDSSED processes. This increase in the disinfection
284 rate is related to the suppression of the agglomeration of *E. coli* cells and the enhancement
285 in the production of chlorine disinfectant products. The improvement in the disinfection
286 rate obtained in the combined process is directly related to the ultrasound irradiation
287 power transmitted to the bulk solution.

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294

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411 **List of Tables**

412 **Table 1.** Composition of target wastewater.

Ion	Concentration (mg dm⁻³)
Chloride (Cl ⁻)	144.413
Sulphate (SO ₄ ²⁻)	231.984
Ammonium (NH ₄ ⁺)	35.046

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431 **List of Figures**

432 **Fig. 1.** Experimental set-up.

433

434 **Fig. 2.** Influence of current density on the electrodisinfection of urban wastewaters. **(a)**
435 Evolution of *E. coli* with the operation time and applied electric charge. **(b)** Variation of
436 kinetic constant with the applied current density. (Black points: 1.27 A m^{-2} ; grey points:
437 3.82 A m^{-2} ; white points: 6.37 A m^{-2} ; *E. coli*: $16000 \text{ CFU } 100\text{ml}^{-1}$; Anode: BDD;
438 Cathode: SS; T: $25 \text{ }^\circ\text{C}$).

439

440 **Fig. 3.** Evolution of free chlorine species with the applied electric charge during the
441 electrodisinfection of urban wastewaters. (●) ClO^- ; (■) ClO_3^- ; (▲) ClO_4^- . (Black points:
442 1.27 A m^{-2} ; grey points: 3.82 A m^{-2} ; white points: 6.37 A m^{-2} ; *E. coli*: $16000 \text{ CFU } 100\text{ml}^{-1}$;
443 Anode: BDD; Cathode: SS; T: $25 \text{ }^\circ\text{C}$).

444

445 **Fig. 4.** Evolution of combined chlorine species with the applied electric charge during the
446 electrodisinfection of urban wastewaters. (■) NH_2Cl ; (▲) NHCl_2 ; (●) NCl_3 . (Black
447 points: 1.27 A m^{-2} ; grey points: 3.82 A m^{-2} ; white points: 6.37 A m^{-2} ; *E. coli*: $16000 \text{ CFU } 100\text{ml}^{-1}$;
448 Anode: BDD; Cathode: SS; T: $25 \text{ }^\circ\text{C}$).

449

450 **Fig. 5. (a)** Variation of *E. coli* in urban wastewaters with the operation time. (▲)
451 Sonodisinfection (200 W ; *E. coli*: $2400 \text{ CFU } 100\text{ml}^{-1}$); (■) electrodisinfection (0 W ; *E.*
452 *coli*: $16000 \text{ CFU } 100\text{ml}^{-1}$); (●) sonoelectrodisinfection. (Black points: 32 W US ; *E. coli*:
453 $16000 \text{ CFU } 100\text{ml}^{-1}$; grey points: 128 W US ; *E. coli*: $24000 \text{ CFU } 100\text{ml}^{-1}$; white points:
454 200 W US ; *E. coli*: $16000 \text{ CFU } 100\text{ml}^{-1}$) **(b)** Variation of kinetic constant with the power
455 of ultrasound (j: 1.27 A m^{-2} ; Anode: BDD; Cathode: SS; T: $25 \text{ }^\circ\text{C}$).

456

457 **Fig. 6.** Variation of the disinfection rate constant with the power of US irradiated. Striped
458 bars: electrodisinfection without ultrasound; grey bars: sono-disinfection with cycle 1;
459 white bars: sono-electrodisinfection with cycle 0.5; black bars: sono-electrodisinfection
460 with cycle 1; j: 1.27 A m^{-2} ; Anode: BDD; Cathode: SS; T: $25 \text{ }^\circ\text{C}$).

461

462 **Fig. 7.** Production of chlorine oxoanions as a function of the charge applied per unit
463 volume of electrolyzed solution (Q_{ap}) with conductive- diamond anodes (■) ClO^- (●)
464 chloramines. Empty symbols: electrodisinfection; filled symbols: sono-
465 electrodisinfection; j: 1.27 A m^{-2} ; power US: 200 W ; Anode: BDD; Cathode: SS; T: 25
466 $^\circ\text{C}$.

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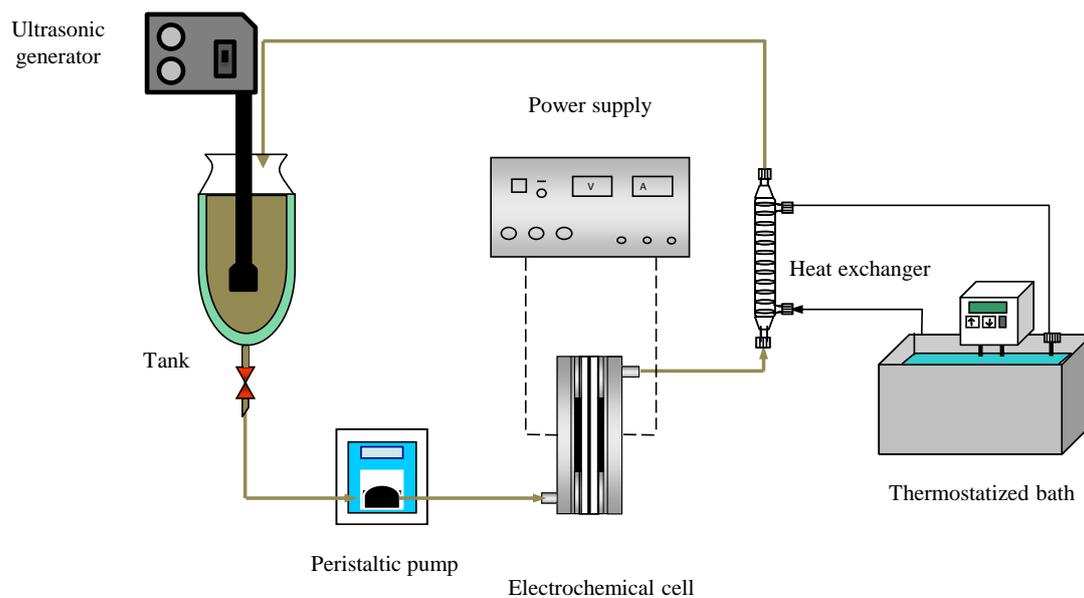
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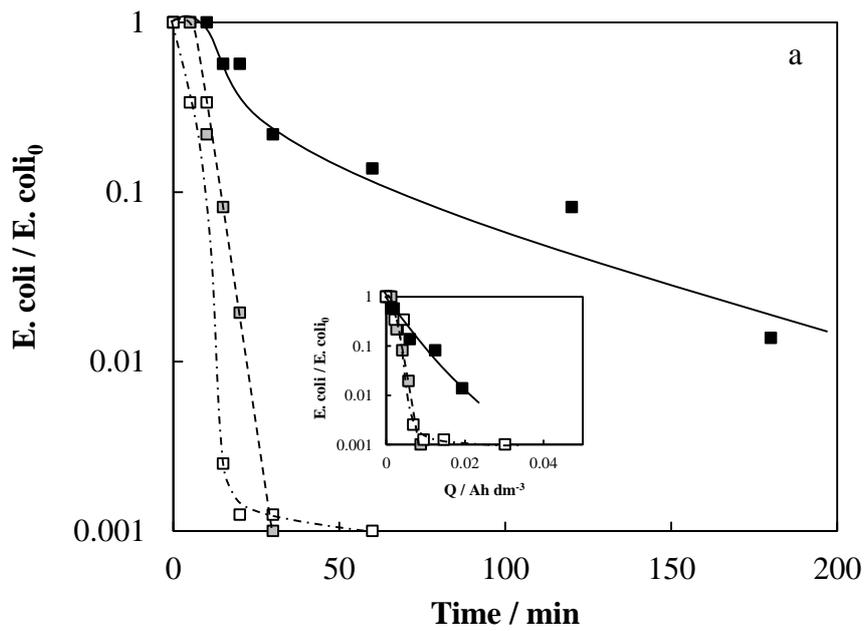
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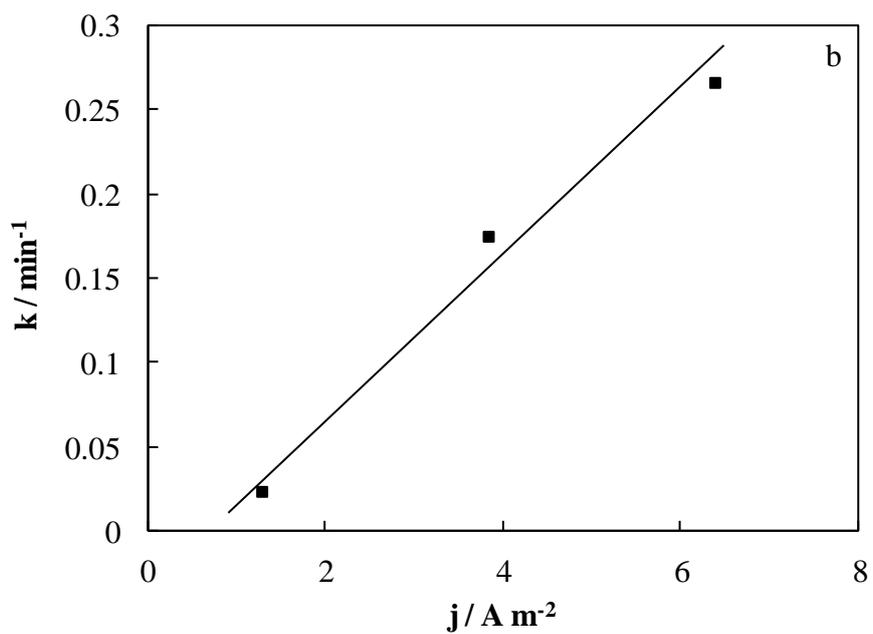


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Figure 1



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Figure 2

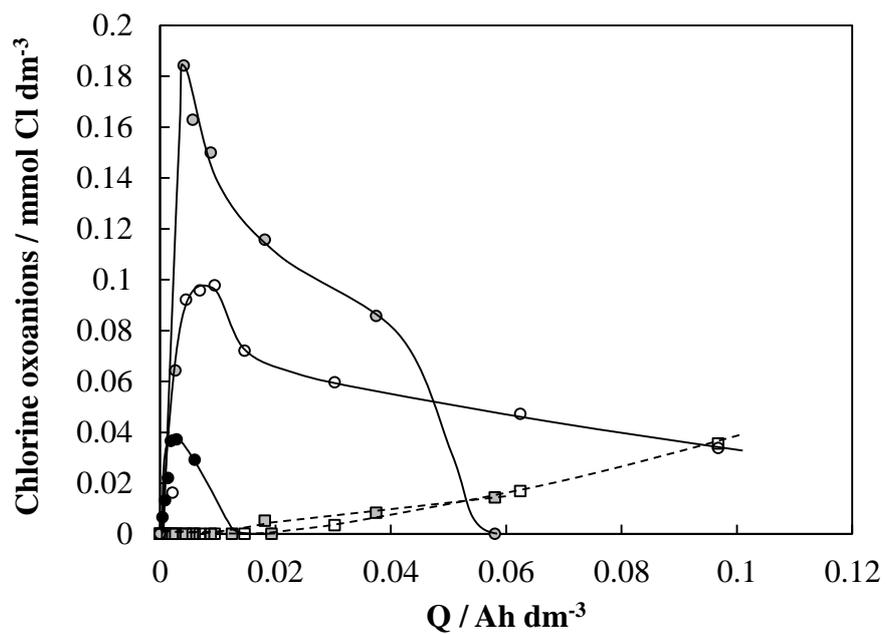


Figure 3

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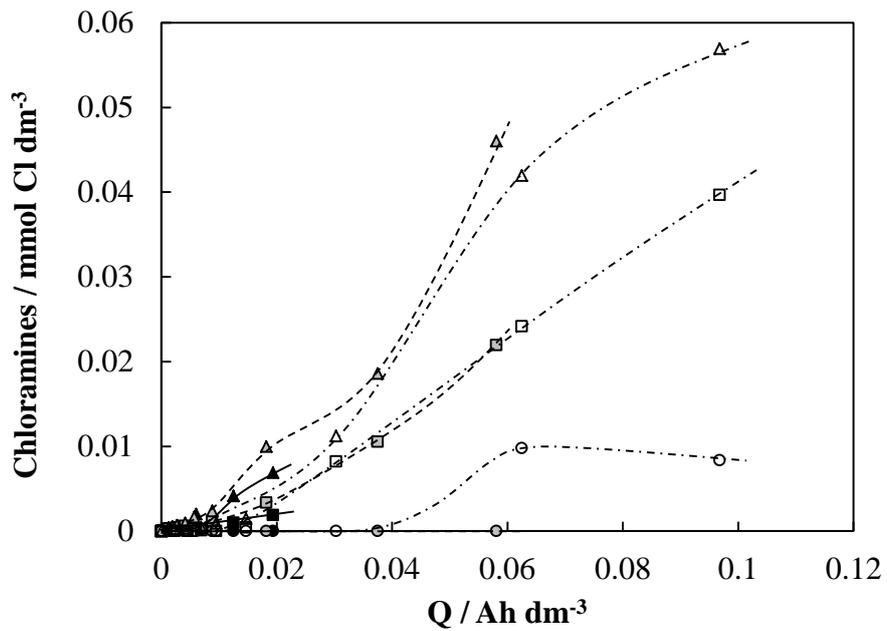
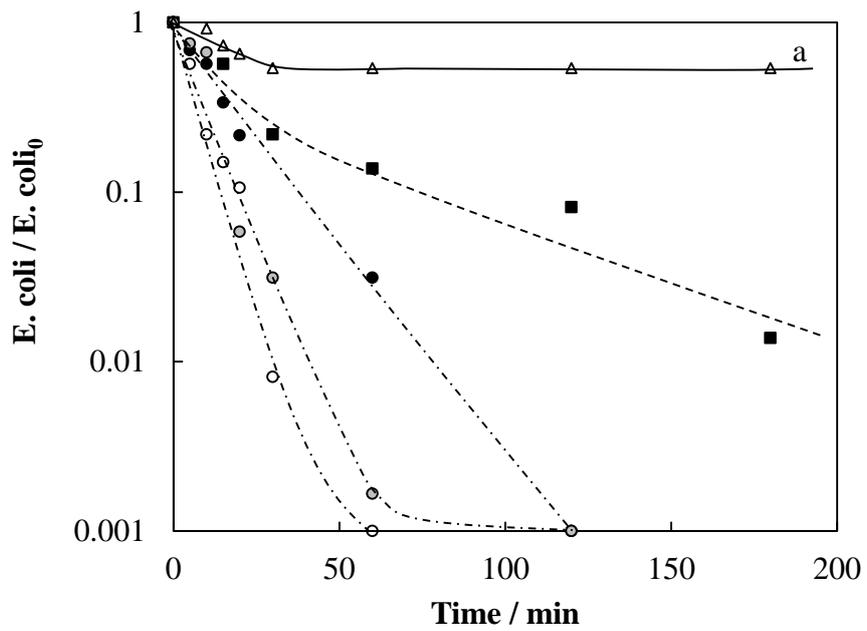
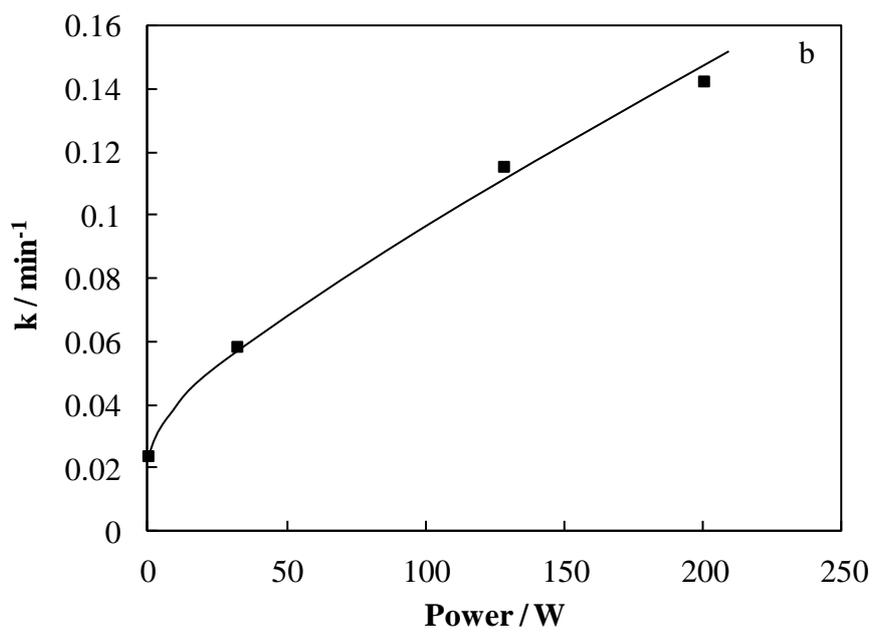


Figure 4

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Figure 5

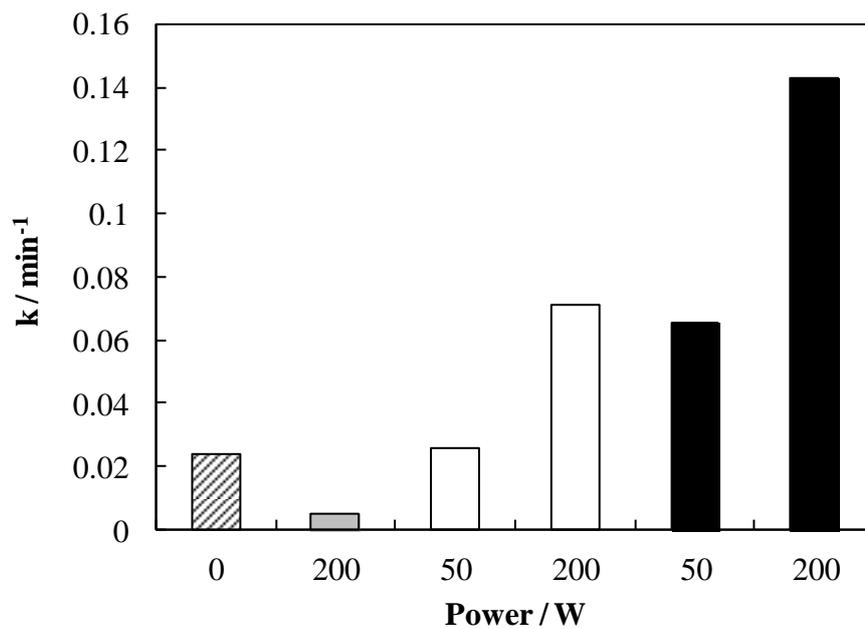
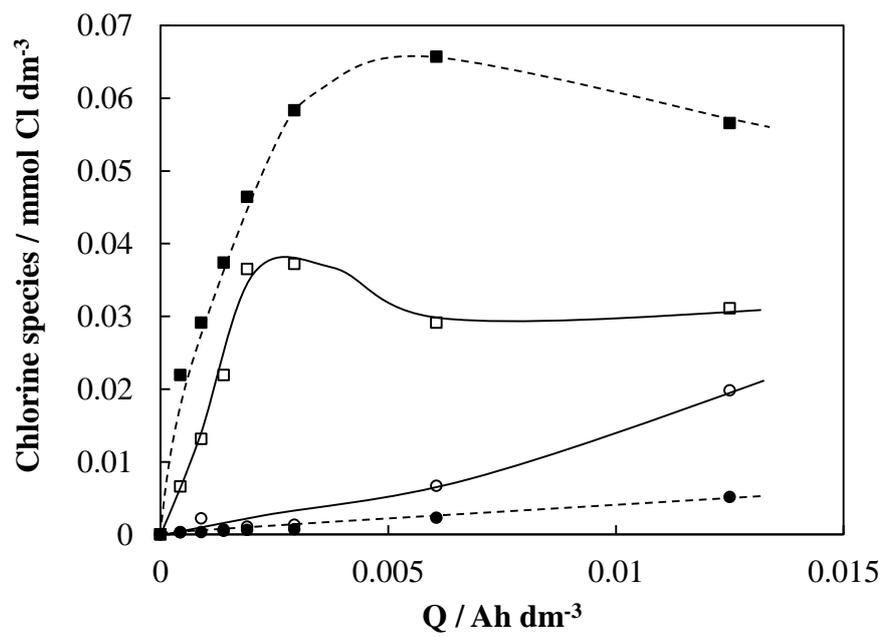


Figure 6

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Figure 7