

25 (11.12 A m⁻²) than that required with BDD anodes. Finally, the influence of cell flow path
26 and flow rate have been studied. Results show that the performance of the process
27 strongly depends on the characteristics of the initial effluent (E. Coli concentration and
28 Cl⁻/NH₄⁺ initial ratio) and that a cell configuration cathode (inlet)-anode (outlet) and a
29 higher flow rate enhance the removal of the turbidity from the treated effluent.

30

31

32 **Keywords:** BDD, DSA, aluminium bipolar electrode, electrodisinfection,
33 electrocoagulation, integrated process.

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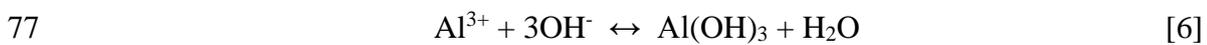
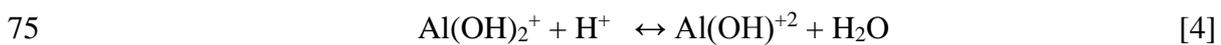
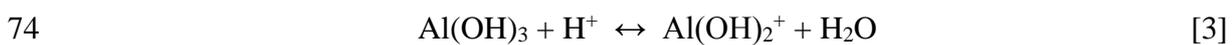
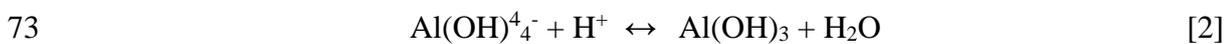
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54 **1. Introduction.**

55 Municipal wastewater treatment facilities usually make it possible to reduce the organic
 56 matter, nitrogen and phosphorous content of municipal wastewaters. Nevertheless, the
 57 water demand is increasing and the availability of high-quality water is being lowered
 58 due to the intensive use of water resources. For this reason, the regeneration and reuse of
 59 treated wastewaters is becoming a research topic of the major interest for addressing water
 60 shortage (Zhang and Farahbakhsh, 2007; Joss et al., 2011; Pisarenko et al., 2012;
 61 Molinos-Senante et al., 2011).

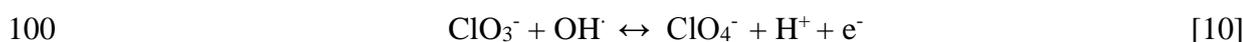
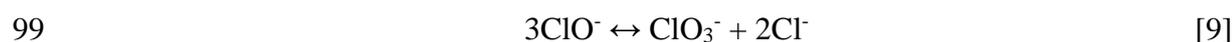
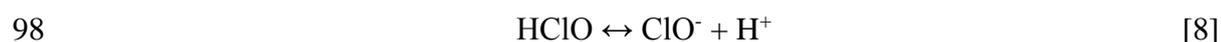
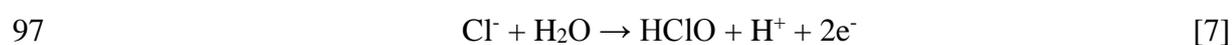
62 For the case of municipal wastewaters, the reclamation of a previously treated water
 63 effluent may imply the reduction of the microbiological concentration, turbidity,
 64 conductivity and/or suspended solids, depending on the characteristics of the raw effluent.
 65 Among the different technologies available to face these challenges, electrochemical
 66 techniques have attracted high interest due to the great results obtained in synthetic
 67 wastewater treatment (Rodrigo et al., 2010; Yavuz et al., 2010; Pikaar et al., 2011a,b;
 68 Lacasa et al., 2011a; Martín de Vidales et al., 2012).

69 One of the electrochemical technologies most studied in wastewater treatment is
 70 electrocoagulation. This technique consists of the addition of coagulant species by means
 71 of the electrodisolution of a sacrificial electrode usually [Eqs. 1-6].



78 The species formed during the process can be different depending on the pH and the metal
79 concentration (Gregory et al., 2001; Duan et al., 2003; Cañizares et al., 2006). The
80 electrocoagulation is a process currently used in the elimination of contaminants in waters
81 and wastewaters, e.g. colloids (Larue et al., 2003; Trompette et al., 2008), emulsions
82 (Cañizares et al., 2008) or anions (Lacasa et al., 2011b, c; Muruganathan et al., 2004).
83 Moreover, electrodisinfection has been proven efficient in the removal of microorganism
84 (Martínez-Huitile et al., 2008). During the process, oxidizing species are formed by the
85 electrooxidation of the ions contained naturally in the wastewater (Cañizares et al., 2009a;
86 Bergmann, 2010; Cotillas et al., 2011; Ghernaout et al., 2011). The main oxidant
87 generated during the electrodisinfection process of a wastewater containing chlorides is
88 hypochlorite [Eq. 7-8]. This oxidant allows to carry out the most popular method of
89 electrodisinfection, called electrochlorination. Also, hypochlorite can suffer a
90 disproportion to chlorate [Eq. 9] during the electrochemical process, and this chlorate can
91 be oxidized to perchlorate easily [Eq. 10] because the chlorate disproportion to
92 perchlorate is a slow reaction that implies high temperatures. On the other hand, the
93 hypochlorite formed can react with other species present in wastewater such as
94 ammonium. The products of this reaction are combined chlorine species called
95 chloramines [Eqs. 11-13].

96



103 $\text{NHCl}_2 + \text{HClO} \leftrightarrow \text{NCl}_3 + \text{H}_2\text{O}$ [13]

104

105 These species (free and combined chlorine species) oxidize the microorganisms in a
106 process that usually begins with the lysis of the cell membrane (Jeong et al., 2006). The
107 generation of oxidizing species may take place in the electrode surface (direct synthesis)
108 or in the wastewater bulk by the production of hydroxyl radicals (indirect synthesis).

109 However, one of the drawbacks of the electrochemical technology is still the high cost of
110 operation of some of them and the high investment cost, which is strongly dependant on
111 the cost of the electrode materials. For this reason, different alternatives should be
112 explored to diminish these costs and make electrochemical processes more cost-effective
113 and energy efficient.

114 In this context, process integration emerges as a good alternative to minimize the costs
115 related to energy consumption as well as the investment in electrochemical process. This
116 process integration represents the union, in one single stage, of basic operations that are
117 traditionally carried out separately. This process integration allows working towards the
118 intensification of water treatment processes. Thus, many authors have studied the
119 performance of different combined processes and they have improved them in order to
120 minimize the operation costs. An interesting approach was carried out by Linares-
121 Hernández et al. (2010), who described a combined electrocoagulation-electrooxidation
122 treatment for industrial wastewater and by Durante et al. (2011) that proposed a
123 combination of electrocoagulation and advanced oxidation process for removal of Cr-
124 EDTA from wastewaters. However, these works presented processes that combine
125 different techniques in successive steps but not in the same experimental set-up.

126 More recently, Mahvi et al. (2011) proposed an electrocoagulation/electrooxidation-
127 electroflotation reactor for the simultaneous removal of ammonia and phosphate from

128 synthetic wastewater. In this work, the experimental set-up comprises one reactor with
129 two different units: one electrochemical and one more for separation using aluminium,
130 stainless steel and RuO₂/Ti as electrodes. With this system, it is possible to remove
131 efficiently both phosphate and ammonia at pH values close to neutrality.

132 The aim of this work is to study the performance of an electrodisinfection/
133 electrocoagulation integrated cell for the treatment of actual treated wastewaters from the
134 WWTF of Ciudad Real (Spain). In addition, it is aimed to quantify the effect of several
135 parameters, such as the current density and the electrode material in order to determine
136 the optimum operation conditions to perform the regeneration of treated effluents.

137

138 **2. Material and methods.**

139 In this section, the analytical techniques, the experimental setup and the experimental
140 procedure in the electrodisinfection/electrocoagulation process are described.

141 **2.1 Analytical techniques.**

142 Nitrogen and chloride inorganic anions (NO₃⁻, NO₂⁻, Cl⁻, ClO⁻, ClO₂⁻, ClO₃⁻, ClO₄⁻)
143 were measured by ion chromatography using Shimadzu LC-20A equipment column,
144 Shodex IC I-524A; mobile phase, 2.5 mM phthalic acid at pH 4.0; flow rate, 1.0 ml
145 min⁻¹). In the case of hypochlorite, its peak interferes with the chloride one; therefore, the
146 determination was carried out by titration with As₂O₃ in NaOH 2 M. The same ion
147 chromatography equipment (column, Shodex IC YK-421; mobile phase, 5.0 mM tartaric,
148 1.0 mM dipicolinic acid and 24.3 mM boric acid; flow rate, 1.0 ml min⁻¹) was used to
149 measure the nitrogen inorganic cation (NH₄⁺). Inorganic chloramines have been measured
150 following the DPD standard method described in literature (APHA-AWWA-WPCF,
151 1998).

152 The faecal coliforms of the wastewaters were estimated using the most probable number
153 (MPN) technique (APHA-AWWA-WPCF, 1998). The microorganism counts were
154 carried out by the multiple-tube-fermentation technique (24 h of incubation at 44 °C)
155 using five tubes in each dilution (1:10, 1:100, and 1:1000).

156 Total aluminium concentration was measured off-line using an inductively coupled
157 plasma spectrometer (Liberty Sequential, Varian) according to a standard method
158 (APHA-AWWA-WPCF, 1998) (plasma emission spectroscopy). In order to evaluate the
159 total metal concentration, samples were diluted to 50:50, v/v using 4 N HNO₃ so as to
160 ensure the total solubility of the metal.

161 Turbidity was measured using a 115 Velp Scientifica turbidimeter according to a standard
162 method described in literature (APHA-AWWA-WPCF, 1998).

163

164 **2.2 Experimental setup.**

165 The electrodisinfection/electrocoagulation process was carried out in a single-
166 compartment electrochemical cell (Figure 1). This cell is a filter-press type, where a
167 perforated aluminium plate is placed between anode and cathode. This Al foil acts as a
168 bipolar electrode, in which the face that confronts the anode works as cathode and vice
169 versa. Thus, the side of the Al foil which confronts the cathode is dissolved, allowing the
170 generation of Al species for the electrocoagulation process. Boron Doped Diamond
171 (BDD) (Adamant Technologies, Switzerland) and Dimensional Stable Anodes (DSA)
172 (DSA-O₂, DeNora, Italy) were used as anodes and stainless steel (SS) (AISI 304)
173 (Mervilab, Spain) as cathode. BDD was circular with a geometric area of 78.5 cm² and
174 DSA was rectangular with a geometric area of 100 cm². The wastewater was stored in a
175 glass tank and the amount of water treated was 4000 ml.

176 With this configuration, it is possible to carry out, simultaneously, the disinfection of the
177 effluent (due to the oxidants produced on the anode) and the electrocoagulation of the
178 target waste water (due to the dissolution of the Al bipolar electrode).

179 The system works in total recirculation mode, with a peristaltic pump (JP Selecta Percom
180 N-M328) continuously recycling the target waste water. An agitation system assures the
181 homogeneity of the system. The power supply is a Delta electronika ES030-10. The
182 temperature of the system is kept constant by means of a thermostated bath and a heat
183 exchanger (a detailed plot of the experimental set-up is included as supplementary
184 material, Fig. SM-1).

185

186 **2.3. Target effluents.**

187 The WWTP treat the wastewater of an average-sized town (75000 p.e.) located in the
188 center of Spain. The influent is a domestic wastewater without a significant industrial
189 contribution. The main characteristics of the samples used in this work are shown in
190 supplementary material (Tables SM-1 and SM-2).

191

192 **3. Results and discussion.**

193 Within the present work, the influence of the current density, the anode material and the
194 cell configuration on the process performance was evaluated.

195

196 **3.1. Electrodisinfection-electrocoagulation of synthetic wastewater polluted with** 197 **kaolinite.**

198 Fig. 2 shows the evolution of the turbidity during the ED-EC process of wastewaters
199 containing kaolinite with BDD and DSA anodes. Kaolinite has been selected as pollutant
200 because it is a colloid type which is presented in domestic and industrial wastewaters
201 (Cañizares et al., 2007). The concentration of kaolinite chosen simulates the average
202 turbidity of urban wastewaters and the Z potential value of kaolinite solutions is similar
203 than that measured in these wastewaters. As it can be observed, the turbidity decreases
204 with the applied electric charge and can be completely removed for applied electric
205 charges of 0.014 Ah dm^{-3} for BDD anodes and 0.018 Ah dm^{-3} when using DSA as anode
206 material. This behavior can be explained by the generation of aluminium species due to
207 the electrodisolution of the bipolar electrode [Eq. 1] and the subsequent formation of
208 soluble and insoluble species of this metal [Eqs. 2-6]. The pH during the process was
209 maintained around 7.3, being at these conditions aluminium hydroxide precipitates the
210 dominant species (Cañizares et al., 2009b). With this distribution of aluminium species,
211 the particles are retained in suspension and the main mechanism of coagulation is sweep
212 flocculation.

213 Moreover, a different performance of the process was observed depending on the anode
214 material. The applied electric charge necessary to completely remove the turbidity with
215 BDD anodes is lower than the charge required with DSA (Fig. 2). This behavior can be
216 explained due to the special characteristics of BDD anodes that require higher electric
217 potential than DSA anodes to obtain the same value of the current density (Quiroz Alfaro
218 et al., 2006). This higher electric potential required during the ED-EC process with BDD
219 anodes is the responsible for the more efficient electrodisolution of the bipolar electrode
220 for this anode material and thus, for the better behavior in terms of the removal of
221 turbidity.

222

223 **3.2. Electrodisinfection-electrocoagulation of urban wastewaters.**

224 Once the performance of the electrocoagulation process has been evaluated for the
225 treatment of synthetic wastewaters, the next step consisted in the treatment of actual
226 wastewaters by the integrated electrodisinfection-electrocoagulation that is presented in
227 this work.

228 Fig. 3 shows the evolution of the concentration of E. Coli during the ED-EC process of
229 an actual effluent of a WWTF (Ciudad Real, Spain) using BDD or DSA anodes. The
230 current density applied was 6.65 A m^{-2} for BDD anode and 5.61 A m^{-2} when using DSA
231 as anode material. These values of current density have been selected because they are
232 typical standard values in wastewater treatment (Cano et al., 2011). As it can be observed,
233 the E. Coli concentration decreases with the applied electric charge following a
234 exponential trend characteristic of the electrochemical processes that follow a first-order
235 kinetics. However, the use of BDD anodes allows the complete elimination of the
236 microorganisms, while with DSA anodes it is not possible to remove completely the E.
237 Coli at similar current densities.

238 Chloride and sulphate are the most important anions that are present in the target
239 wastewaters. Sulphate concentration was observed to be constant throughout the tests,
240 meanwhile the concentration of chloride was observed to decrease. This decrease in the
241 concentration of chloride is due to its oxidation to produce species in higher oxidation
242 state (hypochlorite, chlorate) [Eqs. 7-9]. At this point, it is noteworthy the key effect of
243 the pH due to its role in the speciation of chlorine (Sánchez-Carretero et al., 2011). The
244 pH during the process was maintained constant around 8 (see Fig. SM-2 in the
245 supplementary material) because of the buffering behavior of the designed non-divided
246 cell. For this reason, the pH changes, due to the production of H^+ ions (water oxidation)
247 are somehow offset by the production of OH^- (water reduction). These pH values shift

248 the equilibrium of HClO dissociation [Eq. 8] to the production of ClO⁻. Moreover, the
249 complex matrix of the actual effluents selected also exhibit a buffering behavior which
250 help to maintain the pH around these values. Under these conditions, the formed
251 hypochlorite can react with ammonium to form chloramines [Eqs. 11-13]. Although, the
252 electrodisinfection process can take place on the electrode surface due to the
253 electroadsorption of E. Coli on the anode (direct electrodisinfection) (Golub et al., 1987),
254 these free and combined chlorine species seem to play a key role in the disinfection
255 process which is carried out in the electrochemical cell (indirect electrodisinfection).
256 Thus, Fig. 4 shows the speciation of chlorine during the electrodisinfection process with
257 BDD and DSA anodes.

258 The first oxidant produced in the electrochemical cell is hypochlorite [Eq. 7-8], a
259 compound commonly used in wastewater treatment to prevent algae formation and
260 specially, as disinfectant. As it can be observed, there is an increase in the concentration
261 of hypochlorite until a maximum value from which this concentration decreases. The
262 increase within the first stage of the process corresponds to the previously mentioned
263 electrooxidation of chlorides [Eq. 7]. On the other hand, the decrease observed with the
264 applied electric charge can be explained because of several overlapped effects: the lysis
265 of the cellular membrane of E. Coli, causing its death; the reduction of the hypochlorite
266 on the cathode of the cell (non divided reactor), the oxidation of hypochlorite to chlorates
267 or the reaction of hypochlorite with other ions present in wastewater such as ammonium
268 [Eqs. 10-12]. As it has been commented, the result of this last reaction is combined
269 chlorine species (chloramines).

270 Chloramines present also disinfection capacity but avoid the potential formation of
271 trihalomethanes (one of the disadvantages of hypochlorite) due to their lower reactivity
272 (Lyon et al., 2012). The formation of chloramines and the reaction rate depend on the

273 $\text{ClO}^-/\text{NH}_4^+$ ratio and the pH (White, 1992; Mackay et al., 1999). Hypochlorite-ammonium
274 molar ratios from 1.5:1 to 2:1 and pHs around 8 favor the formation of chloramines.

275 At this point, it is important to highlight that the use of BDD anodes (Fig. 4.a) leads to
276 the generation of chlorate [Eq. 9] while DSA anodes (Fig. 4.b) only make it possible to
277 generate hypochlorite [Eq. 7], being this compound less aggressive to human health than
278 chlorates. The production of chlorate can be explained due to the role of hydroxyl radicals
279 during the electrooxidation of chloride solutions with BDD anodes (Sánchez-Carretero et
280 al., 2011). On the contrary, DSA behaves as an active electrode, on which surface the
281 hydroxyl radicals generated during the water oxidation process are adsorbed (Quiroz
282 Alfaro et al., 2006). Thus, the use of DSA is advantageous in respect of BDD for the
283 regeneration of treated wastewater effluents, due to the potential toxicity of chlorate.
284 Regarding the production of perchlorate, the low current densities used with both
285 electrodes and the low conversions achieved to chlorates, do not allow the generation of
286 perchlorate by the electrooxidation of chlorates (Sánchez-Carretero et al., 2011). Due to
287 the production of low amounts of chlorate, the applied electric charge should be limited
288 to prevent the formation of high concentrations of chlorates (maximum Q of 0.051 Ah
289 dm^{-3} for a current density of 6.65 A m^{-2}). Moreover, it is noteworthy that the formation
290 of trihalomethanes during the electrodisinfection process was discarded by gas
291 chromatography, which can be explained in terms of the low concentration of oxidized
292 chlorine species due to the low value of the current densities selected.

293 Fig. 5 shows the evolution of the turbidity in urban wastewaters with the applied electric
294 charge using BDD and DSA anodes in the same experimental test. As it can be observed,
295 there is a slight decrease in the turbidity with the applied electric charge using BDD
296 anodes. This behavior, as previously explained in the process with synthetic wastewaters,
297 is directly related to the aluminium which is dissolved from the bipolar Al electrode. The

298 total aluminium concentration follows a linear trend with the applied electric charge
299 reaching a final value of 5.69 mg l⁻¹ and the pH during the process was maintained in 8.5.
300 This value indicates that the main species of aluminium are insoluble hydroxides. In
301 addition, this pH value is within the range established by the regulation for wastewater
302 reclamation so it is not necessary a subsequent neutralization process.

303 On the other hand, the turbidity remains practically constant during the process with DSA
304 anodes. This is due to the fact that the applied electric potential is too low to permit the
305 generation of sufficient concentration of coagulant species (maximum concentration of
306 1.84 mg l⁻¹), which confirms the behavior observed in the treatment of synthetic effluents.
307 Thus, for DSA electrodes, it is necessary to work at higher values of current density to
308 carry out the simultaneous removal of turbidity and E. Coli. In the case of pH, this value
309 was maintained in 8.02, once again within the range established by the RD 1620/2007,
310 the regulation for reclamation of wastewaters in Spain.

311

312

313

314 **3.2.1. Influence of the current density.**

315 In order to optimize the operating conditions for the ED-EC cell, the process was carried
316 out at increasing current densities. Thus, Fig. 6 shows the evolution of the concentration
317 of E. Coli with the applied electric charge during the ED-EC process of an actual effluent
318 with BDD (Fig. 6.a) and DSA (Fig. 6.b) anodes at different current densities.

319 As it can be observed, it is not possible to remove the E. Coli when working at current
320 densities lower than 6.65 Am^{-2} with BDD anodes (Fig. 6.a). However, at a current density
321 equal to 6.65 Am^{-2} , the electrodisinfection with BDD anodes makes it possible to
322 completely remove the E. Coli at an applied electric charge of 5.5 mAh dm^{-3} . This fact,
323 as it has been previously mentioned, is due to the generation of disinfectant species during
324 the electrodisinfection process. This result indicates that it is not necessary a high energy
325 consumption to remove the faecal coliforms present in the urban wastewater. Specifically,
326 the required energy consumption for the complete removal of E. Coli for this specific
327 effluent is only 36.7 W m^{-3} of treated effluent, considering an average voltage of 6.3 V
328 throughout the test. Finally, it can be seen that the efficiency of E. Coli removal does not
329 clearly depend on the value of the working current density. Nevertheless, it is worth
330 mentioning that the tests were carried out with actual effluents with different initial E.
331 Coli concentrations (detailed in Figure captions) and the required electric charge to
332 remove it completely is higher for higher initial concentrations.

333 However, the concentration of oxoanions in high oxidation state increases with the
334 current density due to the generation of hydroxyl radicals, which react with the
335 hypochlorite to form chlorates [Eq. 9] (see Supplementary material, Fig. SM-3). On the
336 other hand, the current densities used in all the experiments do not allow the formation of
337 perchlorates regardless of the current density applied as it is necessary higher current
338 densities and higher values of electric charges to achieve the electrooxidation of chlorate
339 to perchlorate (Sánchez-Carretero, 2011). As it has been previously commented, the use
340 of BDD anodes in the ED-EC process is restricted by the generation of chlorates during
341 the disinfection. The presence of chlorates is not limited in the Spanish legislation to
342 wastewater reuse. However, there exists a Ministerial Order (SAS/1915/2009) that limits
343 the presence of chlorate in $700 \text{ } \mu\text{g dm}^{-3}$ to human water consumption. According to this

344 strict limit, the presence of chlorates in the reclaimed wastewater during the ED-EC
345 process allows the use of BDD anodes at maximum current density of 6.65 A m^{-2} and at
346 applied electric charge of 0.015 Ah dm^{-3} . Regarding the formation of combined chlorine
347 species, the concentration of chloramines increases with the current density due to the
348 fact that the hypochlorite concentration generated in wastewater is higher and favors the
349 reaction with ammonium.

350 In the case of the electrodisinfection with DSA anodes (Fig. 6.b), it can be observed that
351 it is not possible to remove the E. Coli when working at similar current densities as for
352 BDD anodes. Nevertheless, the E. Coli is completely removed when working at a current
353 density of 11.12 Am^{-2} with DSA anodes, following a first order kinetics. In this case, the
354 main oxidant formed with DSA anodes is hypochlorite, which does not develop to other
355 chlorine oxoanions at higher oxidation state (chlorates or perchlorates).

356 The value of the current density required for the complete removal of microorganisms
357 with DSA is greater than that obtained with BDD anodes. This behavior, as discussed
358 earlier, is due to the different characteristics of DSA and BDD anodes. At this point, it is
359 worth mentioning that the formation of trihalomethanes has been discarded regardless of
360 the current density and the anode material used.

361 The selected wastewaters were taken at the outlet of the secondary clarifier of a WWTF,
362 being their content in organic matter low. The total organic carbon (TOC), measured in
363 all samples, was very low and did not significantly decrease with the applied electric
364 charge (Anode: BDD; j : 6.65 A m^{-2} ; TOC_0 : 9.19 mg dm^{-3} . Anode: DSA; j : 11.12 A m^{-2} ;
365 TOC_0 : 17.22 mg dm^{-3}). This behavior can be explained in terms of the low current
366 densities applied, which are not sufficient to remove efficiently the organics by their
367 oxidation on BDD or DSA anodes (Rodrigo et al., 2010). Furthermore, the

368 electrocoagulation process also requires higher current densities than that used in the ED-
369 EC process to generate high concentrations of coagulant species and thus conduct an
370 efficient removal of the dissolved organic matter (Cañizares et al., 2008). At this point, it
371 is worth mentioning that the main aim of this study is the assessment of the
372 electrodisinfection/electrocoagulation process of an effluent from a municipal WWTF in
373 terms of E. Coli and turbidity removal, being the process of TOC removal mainly
374 confronted in the secondary biological treatment of this WWTF.

375 Fig. 7 shows the evolution of the turbidity with the applied electric charge during the ED-
376 EC process at different current densities using BDD and DSA anodes. As it can be
377 observed, the turbidity remains constant at low current densities with BDD and DSA
378 anodes, and does not decrease regardless of the applied electric charge. This behavior can
379 be explained because it is necessary a minimum concentration of aluminium species to
380 decrease the turbidity of wastewater by the electrocoagulation process. In the case of
381 BDD anodes (Fig. 7.a), at current densities from 6.65 Am^{-2} there is a decrease in the
382 turbidity with the applied electric charge but in no case it is completely removed. As
383 discussed earlier, this decrease observed is due to the generation of aluminium species by
384 the electrodisinfection of the bipolar electrode [Eqs. 1-6].

385 On the other hand, during the ED-EC process with DSA anodes (Fig. 7.b) there is a
386 decrease in the turbidity with the applied electric charge from current densities of 11.12
387 Am^{-2} due to a higher metal concentration in wastewater (see Fig. SM-2 in the
388 supplementary material). This value of current density is higher than the value obtained
389 with BDD anodes to decrease the turbidity and the reason for this, as commented earlier,
390 is the different electric potential generated with DSA and BDD anodes. This result implies
391 that the use of BDD anodes, at the same current density than with DSA, facilitates the

392 generation of the coagulant species in high concentration by the rapid electrodisolution
393 of the bipolar electrode and, consequently, the elimination rate of the turbidity is higher.

394 At this point, it is noteworthy that the value of the pH during the ED-EC process with
395 both BDD and DSA anodes at different current densities was maintained constant at a
396 value around 8 due to the buffering effect typical of electrocoagulation processes
397 (Cañizares et al., 2009b).

398 Finally, according to the data obtained during the ED-EC process at different current
399 densities, the removal of E. Coli in wastewaters seem to be directly related with the
400 generation of oxidant species in wastewater. Thus, at very low current densities (2.16 A
401 m^{-2} for BDD anodes and 5.61 A m^{-2} for DSA anodes), the percentage of elimination of E.
402 Coli is null and under these operating conditions, it has not been observed the generation
403 of hypochlorite or others oxidizing species. On the opposite, when working at higher
404 current densities (6.65 A m^{-2} for BDD anodes and 11.12 A m^{-2} for DSA anodes), the E.
405 Coli is completely removal and it has been observed the occurrence of chlorine oxidizing
406 species.

407

408 **3.2.2. Influence of the flow path.**

409 The experiments thus far have been carried out with a cell configuration cathode (inlet)-
410 anode (outlet) (C-A). Next, the cell configuration was changed (from anode to cathode,
411 A-C) in order to evaluate the influence of the flow path on the process performance.

412 Thus, Fig. 8 shows the evolution of the concentration of E. Coli and turbidity with the
413 applied electric charge during the ED-EC process with a cell configuration A-C. As it can
414 be observed, the E. Coli is completely removed at an applied electric charge of 45 mAh

415 dm^{-3} for BDD anode and 10 mAh dm^{-3} when using DSA as anode. Although this value of
416 the applied electric charge is lower than that required with the configuration C-A for BDD
417 anodes, it may occur due to the lower initial concentration of E. Coli (5400 vs. 200000
418 CFU/100 ml) and not to a better performance of the disinfection process.

419 Regarding chlorine speciation, the concentration of chloramines (3 ppm vs. 1.7 ppm) is
420 higher for the configuration A-C, meanwhile the concentration of chlorate was found to
421 be higher for the path flow C-A (10 ppm vs. 6 ppm). On the one hand, this result should
422 be related to the initial ratio $\text{Cl}^-/\text{NH}_4^+$, which was equal to 4.6 for C-A and to 3.5 for A-
423 C. This lower chloride to ammonium ratio promotes the formation of chloramines for the
424 test carried out with the A-C flow path. Moreover, at the cell configuration C-A, the
425 newly-formed oxidants leave the cell and they are more difficultly reduced in the
426 electrochemical cell, which could explain the higher chlorate concentration found for this
427 flow path.

428 Regarding the turbidity, this parameter remains constant with the applied electric charge
429 when working with a cell configuration A-C and BDD anodes. Moreover, it was found
430 an initial increase in the turbidity due to the lower aluminum concentration that was
431 generated in this test. This behavior can be explained in terms of a better mass transfer
432 from the Al foil when the flow path is C-A. With this configuration, the side of the bipolar
433 electrode that faces the inlet of the reactor behaves as anode. As this side (facing the inlet)
434 does present a higher turbulence than the one which face the outlet of the electrochemical
435 cell, the better performance of the C-A configuration is somehow expected.

436 In respect of the ED-EC process with DSA anodes and a configuration cell A-C, not
437 significant differences were observed with the experiment carried out with a
438 configuration C-A.

439

440 **3.2.3 Influence of the flow rate.**

441 Fig. 9 shows the evolution of the concentration of E. Coli and the turbidity with the
442 applied electric charge during the ED-EC process with BDD and DSA anodes using a
443 feed flow rate of $30 \text{ dm}^3 \text{ h}^{-1}$ (vs. $50 \text{ dm}^3 \text{ h}^{-1}$ of the previous tests). As it can be observed,
444 for a flow rate of $30 \text{ dm}^3 \text{ h}^{-1}$ the applied electric charge necessary to completely remove
445 the E. Coli from the target effluent is lower than that required with a flow rate of 50 dm^3
446 h^{-1} for BDD anodes (23 mAh dm^{-3} vs. 72 mAh dm^{-3}). This behavior can be explained, as
447 previously commented for the influence of the cell configuration, due to that the initial
448 concentration of E. Coli in wastewater is higher for a flow rate of $50 \text{ dm}^3 \text{ h}^{-1}$ (200000 vs.
449 3500 CFU/100 ml). Furthermore, the selection of a lower flow rate leads to the generation
450 of higher chloramines concentration than that obtained with a feed flow rate of $50 \text{ dm}^3 \text{ h}^{-1}$
451 ¹. This fact is due to a higher residence time in the reactor of the hypochlorite and
452 ammonium ions. For the same reason, the concentration of chlorine species in high
453 oxidation state is lower than that obtained at feed flow rate of $50 \text{ dm}^3 \text{ h}^{-1}$.

454 Regarding to the electric charge required to completely remove the E. Coli at $30 \text{ dm}^3 \text{ h}^{-1}$
455 with DSA anodes, this value is higher than that obtained at $50 \text{ dm}^3 \text{ h}^{-1}$. This behavior can
456 be explained on the basis of a lower concentration of disinfectants species formed during
457 the process due to the appearance of mass transfer limitations related to the lower value
458 of the working flow rate.

459 Regarding the turbidity, this parameter decreases with the applied electric charge during
460 the experiments with BDD and DSA anodes. However, the final value of turbidity
461 achieved in both cases (BDD and DSA) is higher than that obtained with a flow rate of
462 $50 \text{ dm}^3 \text{ h}^{-1}$. Moreover, there is an initial increase in the turbidity due to the lower

463 aluminum concentration that was generated in the test with DSA anodes. This behavior
464 and the lower decrease in the turbidity can be explained due to the lower mass transfer
465 coefficient related to the flow rate of $30 \text{ dm}^3 \text{ h}^{-1}$.

466

467 **4. Conclusions.**

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

- 469 - The electrodisinfection/electrocoagulation process, with BDD or DSA anodes and
470 perforated aluminium bipolar electrodes, allows removing simultaneously the E.
471 Coli and the turbidity present in urban wastewater at low current densities.
472 However, the applied electric charge necessary to remove the turbidity is higher
473 than the required to eliminate the E. Coli.
- 474 - Chlorine species in high oxidation state are formed due to the oxidation of the raw
475 chlorides of the target wastewaters. Also, the presence of ammonium in urban
476 wastewater favors the generation of combined chlorine species which present
477 disinfectant capacity. Both hypochlorite and chloramines are found to be the main
478 responsible of the oxidation process. Moreover, it has been discarded the
479 formation of trihalomethanes in wastewater.
- 480 - The use of BDD anodes leads to the generation of chlorine species at high
481 oxidation state (chlorates) when working above a current density and a value of
482 the applied electric charge (j : 6.65 A m^{-2} ; Q : $0.016 \text{ A h dm}^{-3}$). Thus, the use of
483 BDD anodes is limited to work under these thresholds of current density and
484 applied charge in order to prevent the formation of high concentrations of chlorate.
- 485 - The pH of the wastewater is maintained constant (around 8) during the ED-EC
486 process, due to the buffering effect of the ED-EC process.

487 - A flow path C-A and a higher flow rate enhances the mass transfer of the system,
488 allowing to reach a more efficient removal of the turbidity of the treated effluent.

489

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619

620 **List of Figures**

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625 **Figure 3.** Evolution of the E. Coli with the applied electric charge during the ED-EC
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644 **Figure 7.** Variation of the turbidity with the applied electric charge at different current
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649 pH: 8.02; ● 11.12 A m⁻²; Turbidity₀: 14 NTU; pH: 8.04; □ 25.49 A m⁻²; Turbidity₀: 17
650 NTU; pH:7.83). (T: 25°C; 50 l h⁻¹).

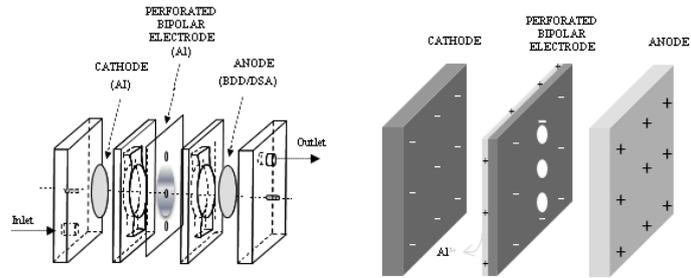
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658 Coli₀: 2100 CFU/100 ml; Turbidity₀: 7 NTU; j: 10.62 A m^{-2} ; pH: 7.77).

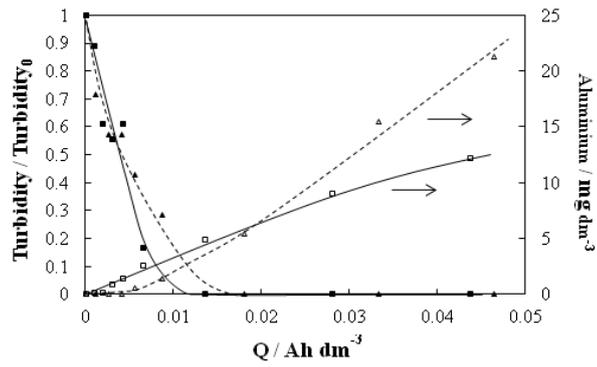
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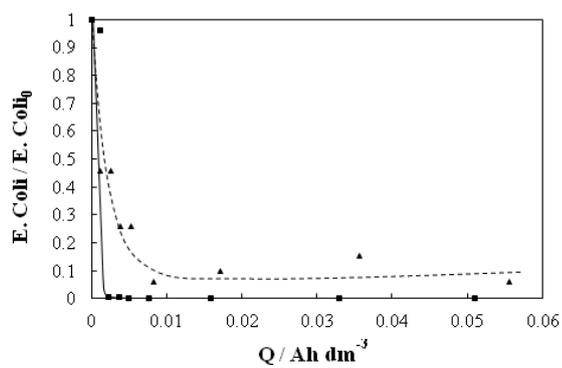
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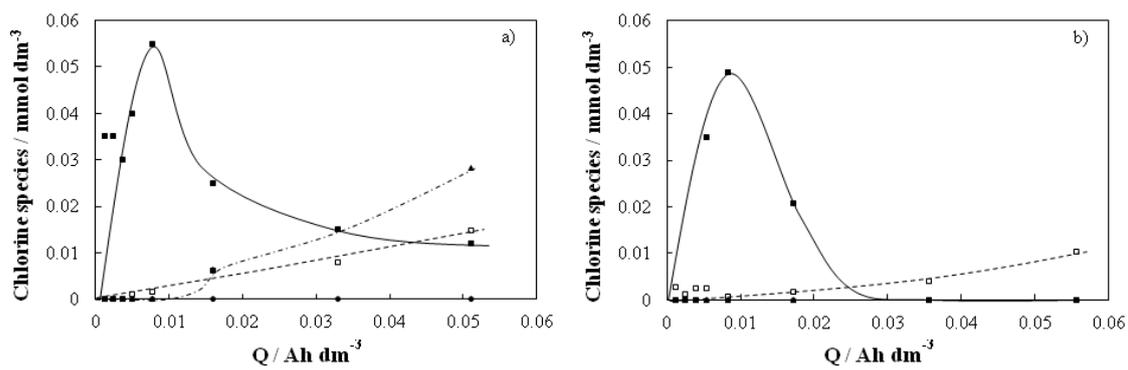
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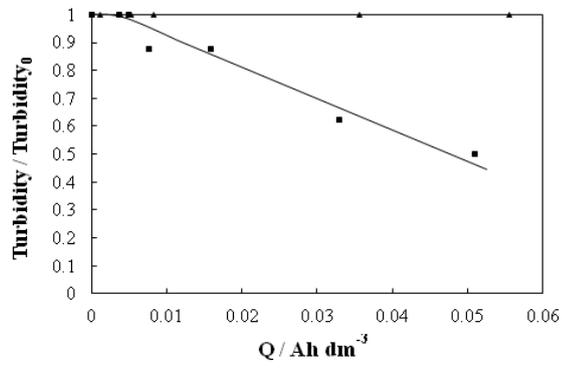
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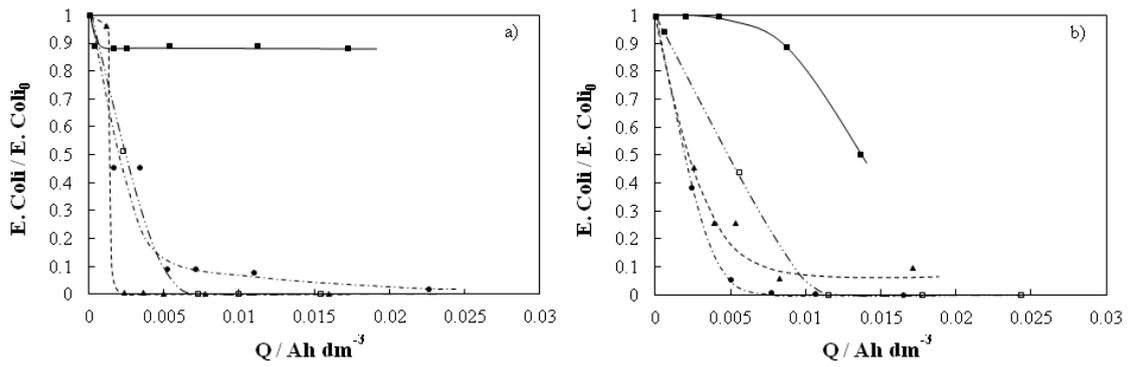
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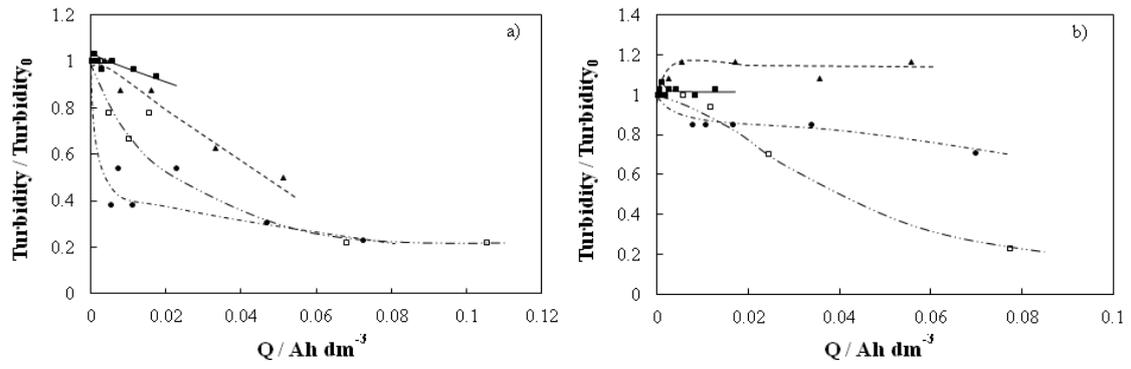
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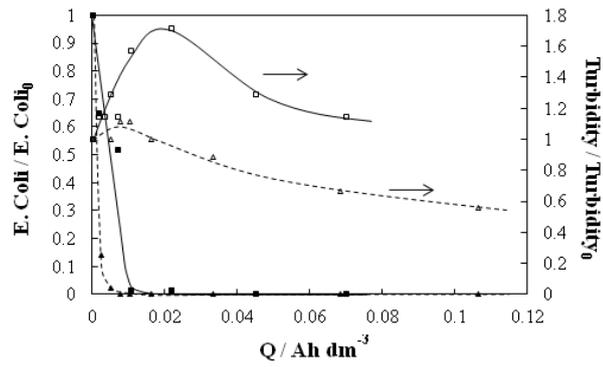
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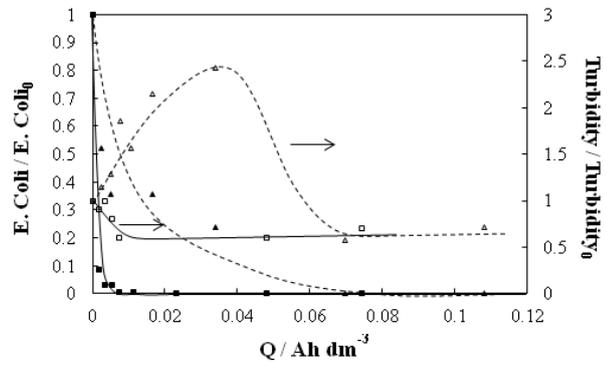
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