Effect of bipolar electrode material on the reclamation of urban wastewater by an integrated electrodisinfection/electrocoagulation process

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Abstract.

This work presents an integrated electrodisinfection/electrocoagulation (ED-EC) process for urban wastewater reuse that employs iron bipolar electrodes. Boron doped diamond (BDD) was used as the anode and stainless steel (SS) as the cathode. A perforated iron plate was introduced between the anode and cathode to function as a bipolar electrode. This ED-EC combined cell makes it possible to conduct the simultaneous removal of microbiological content and elimination of turbidity from urban wastewater. The results show that current densities greater than or equal to 6.70 Am^{-2} enable complete disinfection of the effluent and the removal of more than 90% of its initial turbidity. Hypochlorite and chloramines formed during the ED-EC process were found to be the main compounds responsible for the disinfection process. Furthermore, a cell configuration of cathode (inlet)-anode (outlet) improves the process performance by enhancing turbidity removal. Finally, the influence of the bipolar electrode material (iron or aluminium) was assessed. The results indicate that the efficiency of the electrodisinfection process depends mainly on the anodic material and is not influenced by the material of the bipolar electrode. In contrast, the removal of turbidity is more efficient when using iron as a bipolar electrode, especially at low current densities, due

to the formation of a passive layer on the aluminium that hinders the dissolution of the bipolar electrode.

Keywords: BDD, iron bipolar electrode, electrodisinfection, electrocoagulation, integrated process.

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1. Introduction.

In recent years, electrochemical engineering has experienced great advances due to the development of new electrode materials. For this reason, electrochemical technologies have been widely used in wastewater treatment processes such as the removal of nutrients (Bektas et al., 2004; Lacasa et al., 2011; Tran et al., 2011; Zaleschi et al., 2013), disinfection of wastewater effluents (Cano et al., 2011; Ghernaout et al., 2011; Cui et al., 2013) and degradation of organic compounds (Martínez-Huitle and Brillas, 2009; Alves et al., 2013).

The choice of an appropriate electrode material is a matter of major importance to ensure the success of an electrochemical process. In the case of coagulation, a technology applied in urban wastewater treatment and reclamation (Pouet and Grasmick, 1995; Rodrigo et al., 2010), aluminium and iron are the most commonly used electrode materials (Farhadi et al., 2012; Mohora et al., 2012; Dubrawski et al, 2013). For the treatment of various target effluent types, the different behaviours of iron and aluminium electrodes have been assessed in the electrocoagulation of textile waste (Kobya et al., 2003; Zongo et al., 2009), baker's yeast wastewaters (Kobya et al, 2008) and leachate (Ilhan et al, 2008), among others. The results obtained have proven that the efficiency of the electrode material is directly dependent on the nature of the wastewater being treated. Specifically, iron electrodes have proved more efficient for Chemical Oxygen Demand (COD) removal during the treatment of textile wastewaters, whereas the use of aluminium electrodes had led to higher elimination percentages in the treatment of leachate and baker´s yeast wastewaters.

Electrochemical disinfection has become a good alternative for the removal of microbiological content in wastewater (Martínez-Huitle and Brillas, 2008; Ghernaout and Ghernaout, 2010; Pérez et al, 2010). This process consists mainly of the elimination of

faecal coliforms present in water through two potential mechanisms: the electroadsorption of *Escherichia coli* (*E. coli*) on the electrode surface (direct disinfection) (Golub et al, 1987; Ninomiya et al, 2013) and the formation of disinfectant species that attack and eliminate *E. coli* (indirect disinfection) (Schmalz et al, 2009; Bergmann, 2010). Again, the selection of the appropriate anode material for the electrodisinfection process can affect the nature of the oxidising species formed; the most common anode materials are boron doped diamond (BDD) and dimensionally stable anodes (DSA) (Jeong et al, 2009; Gusmao et al, 2010; Haaken et al, 2012).

In the context of wastewater regeneration by electrochemical processes, our research group recently demonstrated the technical viability of a combined reactor for the simultaneous disinfection and removal of turbidity in actual effluents from municipal wastewater treatment facilities, WWTF (Cotillas et al, 2013). In that work, the combined electrodisinfection/electrocoagulation cell proposed was equipped with aluminium bipolar electrodes. This cell was able to completely remove the microbiological content in urban wastewaters at low applied electric charges (0.008 Ah dm^{-3}) and low current densities (6.65 A m^{-2}). In addition, this cell facilitated a decrease in the turbidity of wastewater by the electrodissolution of the aluminium bipolar electrode and the subsequent formation of coagulant species. However, the applied electric charge required to reduce the turbidity was found to be higher than that necessary to disinfect the urban wastewaters.

One of the key elements of the cell, which strongly affects the removal of turbidity, is the material of the bipolar electrode. For this reason, and with the aim of optimizing the efficiency of the proposed cell, it is necessary to confront a detailed study of the influence of the bipolar electrode material on the process performance. Likewise, the comparison

of the behaviour of both materials can provide valuable information for the treatment of actual wastewater by combined electrochemical processes involving electrocoagulation.

Based on these results, the main aim of the present work was to study the influence of the bipolar electrode material (iron or aluminium) on the performance of an integrated electrodisinfection/electrocoagulation process for the regeneration of urban wastewater from the WWTF of Ciudad Real (Spain). The effects of the current density and cell flow path on the process performance were also studied using iron as a bipolar electrode material.

2. Material and methods.

This section describes the analytical techniques, experimental setup and experimental procedure for the electrodisinfection/electrocoagulation process.

2.1 Analytical techniques.

The total iron and aluminium concentration was measured off-line using an inductively coupled plasma spectrometer (Liberty Sequential, Varian) (detention limit <1.5 ppb) according to a previously published standard method (APHA-AWWA-WPCF, 1998) (plasma emission spectroscopy). To evaluate the total metal concentration, samples were diluted to 50:50 (v/v) using 4 N HNO_3 to ensure total solubility of the metal.

Turbidity was measured using a 115 Velp Scientifica turbidimeter (measuring accuracy: ±2%) according to a standard method described in the literature (APHA-AWWA-WPCF, 1998). This measurement was carried out after sedimentation (30 min without agitation,

typical settle time in reclamation of wastewaters) and filtration (0.45 μm filter) of the samples.

Nitrogen and chloride inorganic anions (NO_3^-, NO_2^-, Cl^-, ClO^-, ClO_2^-, ClO_3^-, ClO_4^-) were measured by ion chromatography using a Shimadzu LC-20A equipped with a Shodex IC I-524A column; mobile phase, 2.5 mM phthalic acid at pH 4.0; flow rate, 1.0 ml min^{-1} (concentration accuracy: ±0.5%). The peak corresponding to hypochlorite interferes with that of chloride; therefore, the determination of hypochlorite was carried out by titration with 0.001 M As_2O_3 in 2.0 M NaOH (Wilpert, 1957; Freytag, 1959). This method consists of a redox determination to selectively quantify the hypochlorite concentration, specifically, it is based on the redox reaction between the hypochlorite and arsenite. Hypochlorite is reduced to chloride by the continuous addition of arsenite whereas this last one is oxidized to arsenate. The pretreatment of the samples consists of the addition of 2 ml of 2.0 M NaOH in order to increase the pH.

The same ion chromatography equipment (Shodex IC YK-421 column; mobile phase, 5.0 mM tartaric, 1.0 mM dipicolinic acid and 24.3 mM boric acid; flow rate, 1.0 ml min^{-1}) was used to measure the nitrogen inorganic cation (NH_4^+). Inorganic chloramines were measured following the DPD standard method described in the literature (APHA-AWWA-WPCF, 1998).

The faecal coliforms from wastewaters were estimated using the most probable number (MPN) technique (APHA-AWWA-WPCF, 1998) (confidence level: 95%). Microorganism counts were carried out by the multiple-tube-fermentation technique (24 h of incubation at 44 °C) using 5 tubes at each dilution (1:10, 1:100, and 1:1000).

The presence of trihalomethanes (THMs) was evaluated by gas chromatography (detention limit <0.2 ppb) using a SPB 10 column (30 m x 0.25 mm; macroporous

150 particles with 0.25 μm diameter). Injection volume was set to 1 μL. Chloroform was the
151 only trihalomethane that could be generated because chloride is the only halogen that was
152 detected in the target wastewater. The presence of adsorbable organically bound halogens
153 using BDD anodes has been quantified in literature when working at current densities
154 higher than 25 A m^{-2} (Schmalz et al., 2009; Haaken et al., 2012). Nevertheless, these
155 halogenated organic derivates were not measured in the present work due to the low initial
156 average organic matter in the target effluents (TOC_0: 25 mg dm^{-3}; COD_0: 30 mg dm^{-3})
157 and also to the low values of the current densities selected (1.90-9.38 A m^{-2}), which
158 according to previous works prevent the formation of organochlorinated species (Cano et
159 al., 2011; Cano et al., 2012).

160

161 **2.2 Experimental setup.**

162 The electrodisinfection/electrocoagulation process was carried out in a single-
163 compartment electrochemical cell. In brief, this cell was a filter-press type in which a
164 perforated iron plate (2 mm thickness) was placed between the anode and cathode. The
165 electrode gap between anode and cathode was 27 mm and between anode or cathode and
166 the perforated bipolar electrode was 12.5 mm. The internal volume of the electrolysis cell
167 was 150 mL. The Fe foil acted as a bipolar electrode; the face exposed to the anode
168 worked as a cathode, and vice versa. Thus, the side of the Fe foil that faced the cathode
169 dissolved, allowing the generation of Fe species for the electrocoagulation process. BDD
170 (Adamant Technologies, Switzerland) was used as the anode material, and stainless steel
171 (SS) (AISI 304) (Mervilab, Spain) was used for the cathode. Both electrodes (BDD and
172 SS) were circular, with a geometric area of 78.5 cm^2. The wastewater was stored in a
173 glass tank, stirred by an overhead stainless steel perforated flat plate stirrer (squared, 49

174 cm^2 of area). The stirrer speed was low (100 rpm) in order to prevent floc breakage. The
175 amount of water treated was 4000 ml.

176 The system worked in total recirculation mode, with a peristaltic pump (JP Selecta
177 Percom N-M328) continuously recycling the target wastewater. The volumetric
178 recirculation flow was 50 dm^3 h^{-1} during the experiments. All tests were carried out in
179 discontinuous mode. At this mode of operation, the production of oxidant and disinfectant
180 species is cumulative and it is related to the total Q (A h dm^{-3}) applied at a given moment.

181 Agitation ensured the homogeneity of the system. The power supply was a Delta
182 Elektronika ES030-10. The temperature of the system was kept constant (25ºC) by a
183 thermostatised bath and a heat exchanger. The samples were collected in the glass tank
184 and the sample volume was 100 ml. The *E. coli* and chlorine compounds (free and
185 combined) were measured immediately. In this way, it is not necessary the addition of
186 reagents (e.g. $Na_2S_2O_3$) to stop the reaction between microorganisms and disinfectant
187 species and therefore, the experimental error of the measure is minimized.

188

189 **2.3. Target effluents.**

190 The WWTF treats the wastewater of an average-sized town (Ciudad Real, 75000 p.e.)
191 located in the centre of Spain. The influent is domestic wastewater without a significant
192 industrial contribution. In order to minimize the influence of the characteristics of the
193 target effluent, several tests were carried out with the same sample and the samples were
194 taken in several consecutive days with similar weather conditions.

195 The average chemical and biological composition characteristics of the samples used in
196 this work is shown in Table 1.

197 **3. Results and discussion.**

198 Within the present work, the influences of the current density, cell configuration and
199 bipolar electrode material on the process performance were evaluated.

200

201 **3.1. General behaviour of the ED-EC cell with Fe bipolar electrodes.**

202 Fig. 1.a shows the change in concentration of *E. coli* in an actual urban effluent during
203 the ED-EC process at an applied current density of 6.70 A m^{-2}. As can be observed, the
204 concentration of *E. coli* decreases with the applied electric charge following first-order
205 kinetics (k = 0.3625 min^{-1}). This result can be related to several processes that occur
206 simultaneously in the electrochemical cell. As discussed in the introduction, the removal
207 of *E. coli* can take place on the anode surface by electroadsorption of microorganisms
208 (direct disinfection). However, the more advantageous electrode materials for this process
209 are fibrous carbon and graphite materials in the form of felt or cloth (Golub et al, 1987).
210 Microorganisms can also be removed by the generation of disinfectant species due to the
211 electrooxidation of ions naturally present in wastewater (indirect disinfection) (Schmalz
212 et al, 2009; Bergmann, 2010). One of the most common inorganic ions in municipal
213 treated wastewaters is chloride, which can be oxidised to hypochlorite, chlorate and
214 perchlorate according to Eqs. 1 to 4. The concentrations of these species (and
215 chloramines) are presented in Fig. 1.b.

216 $$Cl^- + H_2O \rightarrow HClO + H^+ + 2e^- \quad [1]$$

217 $$HClO \leftrightarrow ClO^- + H^+ \quad [2]$$

218 $$2HClO + ClO^- \rightarrow ClO_3^- + 2H^+ + 2Cl^- \quad [3]$$

219 $$ClO_3^- + OH^\cdot \rightarrow ClO_4^- + H^+ + e^- \quad [4]$$

220 Hypochlorite is the first chlorine compound formed by the electrooxidation of chloride
221 [Eq. 1-2]; it has been widely used in drinking water disinfection processes (Bergmann et

al, 2008). There is an initial increase in the hypochlorite concentration with the application of the electric charge, followed by a decrease. The first trend observed is due to the electrooxidation of chlorides present in wastewater, as mentioned previously. The subsequent decline may be due to the elimination of *E. coli*, the oxidation of hypochlorite to chlorates [Eq. 3] or the reaction of the electrogenerated hypochlorite with other compounds such as ammonium to form chloramines [Eqs. 5-7].

$$NH_3 + HClO \leftrightarrow NH_2Cl + H_2O \quad [5]$$

$$NH_2Cl + HClO \leftrightarrow NHCl_2 + H_2O \quad [6]$$

$$NHCl_2 + HClO \leftrightarrow NCl_3 + H_2O \quad [7]$$

As can be observed, the concentration of combined chlorine species increases with the applied electric charge (Fig. 1.b), becoming the main disinfectant product at an applied electric charge of 0.050 Ah dm^{-3}. The presence of ammonium in the target effluent and the consequent formation of chloramines is positive preferable due to the less reactive and less aggressive nature of these compounds compared to hypochlorite. These properties make the formation of organochlorinated species, which are harmful to human health, less favourable (Lyon et al, 2012; Farré et al, 2013; Wang et al, 2013).

The pH did not vary appreciably during the test (average pH of 8.0) due to the undivided nature of the proposed reactor and its resulting buffering behaviour. At this pH, the free chlorine present in wastewater takes the form of hypochlorite ions, and the formation of combined chlorine compounds is favoured (White, 1992; Mackay et al, 1999). Moreover, because the pH is not altered, a subsequent neutralisation process (a step commonly required in conventional coagulation processes) is not necessary.

The presence of chlorine compounds in high oxidation states has been detected, specifically the formation of chlorates at high applied electric charges. Chlorates are

formed by the electrooxidation of hypochlorite, and their presence should be avoided in wastewater because they are detrimental to human health. Regarding this point, it must be highlighted that the evolution of chlorides to chloramines or chlorates and perchlorates could be influenced by the initial composition of the target wastewater. In this context, Pérez et al. (2012) reported the behaviour of chloride during the electrocatalytic treatment of ammonium from synthetic solutions and landfill leachates using BDD anodes. They concluded that a high initial chloride concentration (from 5,000 to 20,000 mg/L) favours the production of free chlorine and the subsequent generation of inorganic chloramines avoiding the formation of perchlorates, while a low initial concentration of chlorides (lower than 2,000 mg/L) promotes the evolution of chlorides to chlorates and perchlorates. Taking into account the low concentration of chloride of the target effluents selected in the present work (around 200 mg/L), the presence of chlorate at certain current densities is in accordance with the results previously presented in literature.

For this reason, the maximum applied electric charge allowed during the ED-EC process is 0.020 Ah dm^{-3}. At this applied electric charge, disinfection is guaranteed, but the production of chlorates is avoided.

Moreover, it is important to note that trihalomethanes, which could be formed due to the reaction of hypochlorite with the soluble organic matter of the target wastewater (TOC_0: 24 mg dm^{-3}; COD_0: 28 mg dm^{-3}), were not detected over the entire range of applied electric charges in the test.

The second key parameter monitored throughout the test is turbidity. Fig. 2 shows the evolution of this variable with the applied electric charge. The initial turbidity value is 14 NTU, and this parameter decreases with the applied electric charge, reaching a final value of 1 NTU (93% turbidity removal). The observed behaviour is due to the generation of

soluble and insoluble coagulant species by the electrodissolution of the anodic side of the bipolar iron electrode [Eqs. 8-16].

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad [8]$$

$$2Fe^{2+} + \tfrac{1}{2} O_2 + H_2O_2 \rightarrow Fe^{3+} + 2OH^{-} \quad [9]$$

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2 \quad [10]$$

$$2Fe(OH)_2 + \tfrac{1}{2} O_2 + H_2O \rightarrow 2Fe(OH)_3 \quad [11]$$

$$Fe(OH)_4^{-} + H^{+} \leftrightarrow Fe(OH)_3 + H_2O \quad [12]$$

$$Fe(OH)_3 + H^{+} \leftrightarrow Fe(OH)_2^{+} + H_2O \quad [13]$$

$$Fe(OH)_2^{+} + H^{+} \leftrightarrow Fe(OH)^{+2} + H_2O \quad [14]$$

$$Fe(OH)^{+2} + H^{+} \leftrightarrow Fe^{+3} + H_2O \quad [15]$$

$$Fe^{3+} + 3OH^{-} \leftrightarrow Fe(OH)_3 + H_2O \quad [16]$$

The total electrodissolved iron increases during the experiment, reaching a final value of 76.1 mg dm^{-3}. The nature of the iron species formed depends mainly on the pH and metal concentration of the wastewater (Gregory and Duan, 2001; Duan and Gregory, 2003; Cañizares et al, 2006; Cañizares et al, 2009). As discussed earlier in this manuscript, the pH was naturally maintained at approximately 8 during the experiment. Thus, under these operating conditions and according to the literature cited above, the dominant coagulant species are insoluble hydroxide precipitates, and the mechanism of coagulation is sweep flocculation.

3.2. Influence of the key working variables on process performance.

In this section, the influence of current density and flow path on the performance of the cell was evaluated.

294

295 *3.2.1. Current density*

296 One of the most studied parameters in electrochemical processes is the current density
297 because this parameter can be directly related to the efficiency of reactions that occur on
298 the anode surface (Lacasa et al, 2012). Fig. 3 shows the changes in the *E. coli*
299 concentration during the ED-EC of urban wastewaters at different current densities.

300 As can be observed, the concentration of faecal coliforms decreases with the applied
301 electric charge, following first-order kinetics independent of the current density applied.
302 However, current densities equal to or greater than 6.70 Am^{-2} are required to achieve the
303 complete removal of *E. coli*. As previously demonstrated, the main compounds
304 responsible for the disinfection process are the disinfectant species electrogenerated
305 throughout the test. To shed light on the importance of the generation of these
306 electrogenerated species and the role that current density plays in their synthesis, Fig. 4
307 presents the concentration of free (Fig. 4.a) and combined (Fig. 4.b) chlorine species as a
308 function of the applied electric charge.

309 As can be observed, during the experiments conducted at 1.90 and 4.13 Am^{-2}, the
310 maximum concentrations of free and combined chlorine species were 0.005, 0.010 mmol
311 Cl dm^{-3} (free) and 0.003, 0.010 mmol Cl dm^{-3} (combined), respectively. For a current
312 density of 6.70 Am^{-2}, the concentrations of both free and combined chlorine increased
313 dramatically, explaining the higher efficiency of the disinfection process at this current
314 density. In contrast, the maximum concentration of chlorine species detected at 9.38 Am^{-2}
315 is lower than that observed at 6.70 Am^{-2}. This result can be explained in terms of the
316 higher initial concentration of *E. coli* (31,000 vs. 22,000 CFU 100 ml^{-1}) in the test carried
317 out at 9.38 Am^{-2}, which may result in a higher consumption of disinfectant and, thus, a
318 lower detected concentration.

With regard to the formation of chlorates and perchlorates, it was observed that the former is detected when working at current densities from 6.70 Am^{-2} and charges higher than 0.020 Ah dm^{-3}. Perchlorate is not synthesised and the presence of trihalomethanes was not detected at any of the current densities studied.

Fig. 5 shows the evolution of turbidity with the charge applied at increasing current densities. As can be observed, the turbidity removal efficiency increases markedly with current density until the applied current density reaches 6.70 Am^{-2}. This enhanced performance is related to the higher efficiency of electrodissolution of the iron bipolar electrode. Thus, the final total iron concentration that was electrodissolved increased from 4.96 to 76.1 mg dm^{-3} when the current density increased from 1.90 to 6.70 Am^{-2}. In contrast, the trends observed during the experiments carried out at 6.70 and 9.38 Am^{-2} are very similar, although it is possible to completely remove the turbidity of the target effluent at the highest current density using an applied electric charge of 0.046 Ah dm^{-3}.

Finally, with respect to the change in pH, the behaviour observed for all current densities studied is similar to that described in section 3.1; pH is naturally maintained at approximately 8 due to the buffering effect of the undivided reactor.

In light of these results, it can be stated that the optimal current density for the proposed EC-ED process with iron bipolar electrodes is 6.70 Am^{-2}. At this current density, it is possible to conduct an efficient disinfection process together with significant removal of turbidity. However, with the initial parameters of the treated effluent (*E. coli*$_0$: 22000 CFU $100ml^{-1}$; *turbidity*$_0$: 14 NTU), the process is limited to a maximum applied electric charge of 0.020 Ah dm^{-3} to avoid the generation of chlorates. At this value of electric charge, the maximum removal of turbidity (close to 90%) is already reached, so this restriction on the maximum allowable electric charge is not a constraint on the removal

of initial turbidity of the target effluent. This optimal current density could undergo modifications if the initial composition of the target wastewater is drastically changed.

Finally, it is important to note that some authors (Yan et al., 1993; Kraft at al., 1999) have reported the formation of calcareous deposits on the cathode surface during the treatment of wastewaters containing Ca^{2+} and Mg^{2+}, due to the local increase in the pH that takes place on the cathode (water reduction). However, this deposition of calcareous deposits on the cathode surface was not observed in the present work. Moreover, the cell voltage did not increase during the treatment, indicating that the properties of the cathode surface were not modified. To explain this result, it is important to highlight that the calcium concentration is lower than that reported by other researchers (Kraft et al., 1999). Likewise, the low current densities used in the present work (maximum current density of 9.38 A m^{-2} vs. 100 A m^{-2} of Kraft et al., 1999) reduce the formation of OH^- on the cathode surface, preventing the formation of calcareous deposits.

3.2.2. Influence of the flow path.

In the first approach to the design of the combined EC-ED reactor using aluminium bipolar electrodes (Cotillas et al, 2013), it was observed that the flow path played an important role in the performance of the process. In the present work, the experiments presented thus far were conducted with a cathode-anode (C-A) cell configuration: the target wastewater enters the electrochemical reactor near the cathode and exits near the anode (see Fig. SM-1 in the supplementary material). Fig. 6 shows the change in *E. coli* concentration (Fig. 6.a) and turbidity (Fig. 6.b) with respect to the applied electric charge at different cell configurations.

As can be observed, there were no significant differences in the disinfection efficiency of the combined reactor when the flow path was changed. Thus, the microbiological content decreased during the ED-EC process, achieving total removal of faecal coliforms at low applied electric charges for both cell configurations.

Turbidity decreased with the applied electric charge, reaching a final value lower than 3 NTU in both cases (C-A: Final turbidity = 1 NTU; A-C: Final turbidity = 2 NTU). However, the process was more efficient with a C-A cell configuration because of the higher concentration of iron species formed (C-A: 76.1 mg Fe dm^{-3}; A-C: 55.5 mg Fe dm^{-3}). This behaviour was previously described when using Al bipolar electrodes and can be attributed to the improvement in mass transfer in the electrochemical cell when the wastewater enters through the cathode side of the reactor and directly hits the anodic side of the bipolar electrode. This event increases the turbulence inside the reactor (on the anodic face) and favours the electrodissolution process.

3.3. Influence of the bipolar electrode material on the ED-EC process.

As previously mentioned, the main aim of the present work is to evaluate the effect of the bipolar electrode material on the performance of the combined ED-EC cell. This comparison between the results obtained with Al and Fe electrodes could be useful for further optimisation of the combined process. Fig. 7 shows the percentage removal of *E. coli* (Fig. 7.a) and turbidity (Fig. 7.b) using aluminium and iron bipolar electrodes at three different applied electric charges and similar current densities.

As shown in Fig. 7.a, the *E. coli* are completely removed at low applied electric charges, regardless of the material used for the bipolar electrode, with the differences in elimination rate between the Al and Fe electrodes being negligible (iron: k = 0.3625 min^{-}

390 [1]; aluminium: k = 0.3516 min^{-1}). The initially higher removal of *E. coli* by the iron
391 electrodes at a very low applied electric charge (0.001 Ah dm^{-3}) can be related to a slight
392 difference in the initial microbiological concentration of the effluent (iron: 22000 CFU
393 100 ml^{-1}; aluminium: 24000 CFU 100 ml^{-1}). During the experiment with aluminium
394 bipolar electrodes, the maximum concentrations of free and combined chlorine species
395 were 0.055 and 0.015 mmol Cl dm^{-3}, respectively, while concentrations of 0.069 (free)
396 and 0.046 mmol Cl dm^{-3} (combined) were achieved with iron bipolar electrodes. The
397 differences observed in chlorine speciation, specifically in combined chlorine species, are
398 related to the initial concentration of ammonium in wastewater (aluminium: 23.095 mg
399 NH_4^+ dm^{-3}; iron: 43.434 mg NH_4^+ dm^{-3}). The higher initial ammonium concentration
400 enhances its reaction with the electrogenerated hypochlorite, resulting in a higher
401 concentration of chloramines in wastewaters when working with iron bipolar electrodes.
402 These results indicate that the disinfection process is mainly influenced by the anode
403 material of the electrochemical cell (BDD in both cases) rather than the material of the
404 bipolar electrode.

405 In contrast, the percentage of turbidity removal (Fig. 7.b) was strongly influenced by the
406 material of the bipolar electrode. The initial turbidity in wastewater was 8 NTU during
407 the process conducted with aluminium bipolar electrodes and 14 NTU when working with
408 iron electrodes. The elimination of turbidity during the experiment performed with iron
409 bipolar electrodes was higher when compared to aluminium electrodes. For example, at
410 the highest applied electric charge evaluated (0.050 Ah dm^{-3}), the use of iron electrodes
411 achieved an elimination of 92.86%, while aluminium electrodes removed 50%.

412 The superior turbidity removal with the use of iron electrodes can be explained by the
413 higher concentration of dissolved iron in comparison to aluminium, presented in Fig. 8.a.
414 Specifically, the total iron concentration achieved was 1.362 mmol Fe dm^{-3} whereas 0.210

mmol Al dm^{-3} was obtained when working with aluminium electrodes at the same applied electric charge (0.050 Ah dm^{-3}).

The different efficiencies of Al and Fe dissolution in the ED-EC reactors can be explained by passivation of the aluminium bipolar electrode under the conditions studied. It has been well reported in the literature that aluminium can suffer from passivation due to the formation of an $Al_2O_3/Al(OH)_3$ layer on the anode surface (Mechelhoff et al, 2013). This passivation resulted in lower Al dissolution rates from the bipolar electrodes and subsequently less efficient performance of the reactor in turbidity removal.

Theoretically, the presence of chloride, a well-known pitting promoter, should increase the dissolution rate of the Al electrodes (Szklarska-Smialowska, 1986). Nevertheless, to promote the dissolution of the passive layer by the pitting effect of chlorides, it is necessary to apply a potential greater than the so called pitting potential (Lee and Pyun, 2000). Thus, when working at low current densities (as in Fig. 7), the passivation of the Al electrode dominated over the pitting effect of the chloride present in the target wastewater. When a comparison of process performance was carried out at a higher current density (and consequently at a higher applied potential), the efficiency of the dissolution of the bipolar electrodes became similar (data presented in Fig. 8.b) due to the breakage of the passive layer of the Al electrode.

Taking into account that disinfection can be efficiently conducted at low current densities and low applied electric charges, the performance of the combined ED-EC process is optimised when working with Fe bipolar electrodes, which avoid the formation of a passive layer that would hinder the efficiency of the turbidity removal process.

Finally, the energy consumption per unit volume was calculated by means of the specific electrical charge passed (Q, kAh m^{-3}) and the average potential difference between anode (BDD) and cathode (SS) [Eq. 17].

$$W\ (kWh\ m^{-3}) = Q \cdot V \quad [17]$$

The energy consumption has been only calculated for the current densities in which the *E. coli* has been completely removed (6.70 A m^{-2} and 9.38 A m^{-2}). The results show that it is necessary 0.030 and 0.080 kWh m^{-3} to achieve the total disinfection of the effluent for current densities of 6.70 A m^{-2} and 9.38 A m^{-2}, respectively. The differences observed in the required energy consumption can be related to the differences between the initial concentrations of microorganisms in wastewater (j: 6.70 A m^{-2}, *E. coli*$_0$: 22000 CFU $100ml^{-1}$; j: 9.38 A m^{-2}, *E. coli*$_0$: 31000 CFU $100ml^{-1}$). However, the energy consumption necessary to obtain a reclaimed water is lower than 0.1 kWh m^{-3} regardless the current density applied and the initial characteristics of the wastewater.

4. Conclusions.

From this work, the following conclusions can be drawn:

- The integrated electrodisinfection/electrocoagulation process with BDD anodes and perforated iron bipolar electrodes allows complete disinfection of the effluent with simultaneously high percentages of turbidity removal.
- Hypochlorite and chloramines have been identified as the main compounds responsible for the disinfection process. In addition, the presence of chlorates has

been detected for current densities greater than 6.70 Am^{-2} and applied electric charges greater than 0.020 Ah dm^{-3}.

- A change in the flow path of the cell does not affect the efficiency of the electrodisinfection process. Instead, a flow path from C-A enhances the electrodissolution of the Fe foil and increases the rate of turbidity removal by electrocoagulation.
- The bipolar electrode material does not significantly affect the efficiency of the disinfection process. In contrast, Fe bipolar electrodes exhibit better performance in the removal of turbidity at the low current density required to disinfect the target effluent, which is due to the formation of a passive layer when Al is selected as the bipolar electrode material.

Acknowledgements

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List of Figures

Figure 1. Variation of the *E. coli* concentration (1.a) and chlorine species (1.b) with the applied electric charge during the ED-EC process. ■ Cl-ClO^-; ▲ Cl-ClO_3^-; ● Cl-ClO_4^-; □ Cl-Chloramines. (Anode: BDD; Cathode: SS; Bipolar electrode: Iron; j: 6.70 A m^{-2}; *E. coli*$_0$: 22,000 CFU $100ml^{-1}$; T: 25ºC; pH: 8.05).

Figure 2. Variation of the turbidity and the iron concentration with the applied electric charge during the ED-EC process. (Anode: BDD; Cathode: SS; Bipolar electrode: Iron; j: 6.70 A m^{-2}; *E. coli*$_0$: 22,000 CFU $100ml^{-1}$; T: 25ºC; pH: 8.05).

Figure 3. Variation of the *E. coli* with the applied electric charge at different current densities during the ED-EC process of urban wastewater. ■ 1.90 A m^{-2}; *E. coli*$_0$: 90,000

CFU 100 ml^{-1}; pH: 7.98; ▲ 4.13 A m^{-2}; *E. coli*$_0$: 35,000 CFU 100 ml^{-1}; pH: 8.06; ● 6.70 A m^{-2}; *E. coli*$_0$: 22,000 CFU 100 ml^{-1}; pH: 8.05; □ 9.38 A m^{-2}; *E. coli*$_0$: 31,000 CFU 100 ml^{-1}; pH: 8.35. (Anode: BDD; Cathode: SS; Bipolar electrode: Iron; T: 25ºC).

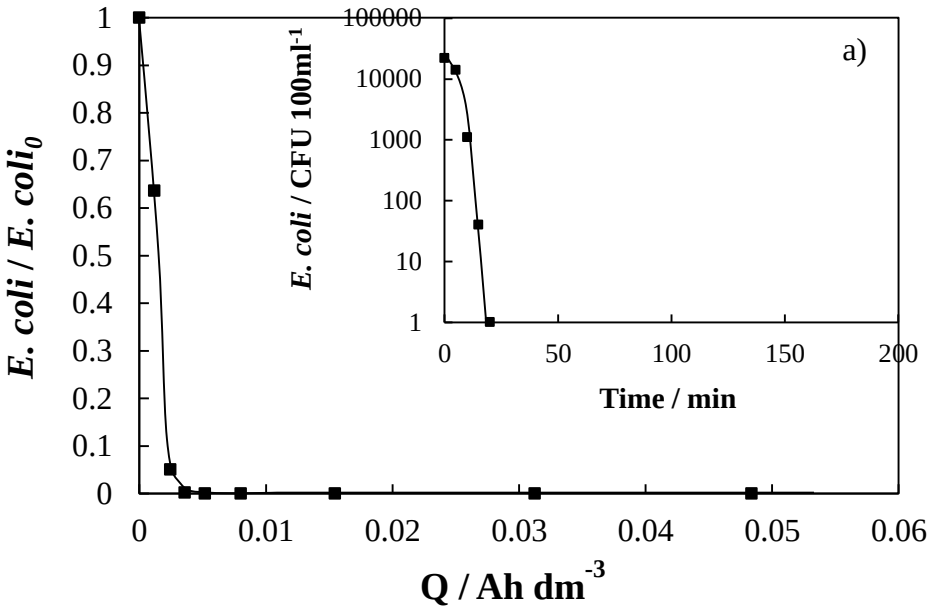
Figure 4. Evolution of chlorine species with the applied electric charge at different current densities during the ED-EC process of urban wastewater. (a) Free chlorine. Black points: Cl-ClO^-; Grey points: Cl-ClO_3^-; White points: Cl-ClO_4^-. (b) Combined chlorine. ■ 1.90 A m^{-2}; ▲ 4.13 A m^{-2}; ● 6.70 A m^{-2}; ♦ 9.38 A m^{-2}. (Anode: BDD; Cathode: SS; Bipolar electrode: Iron; T: 25ºC).

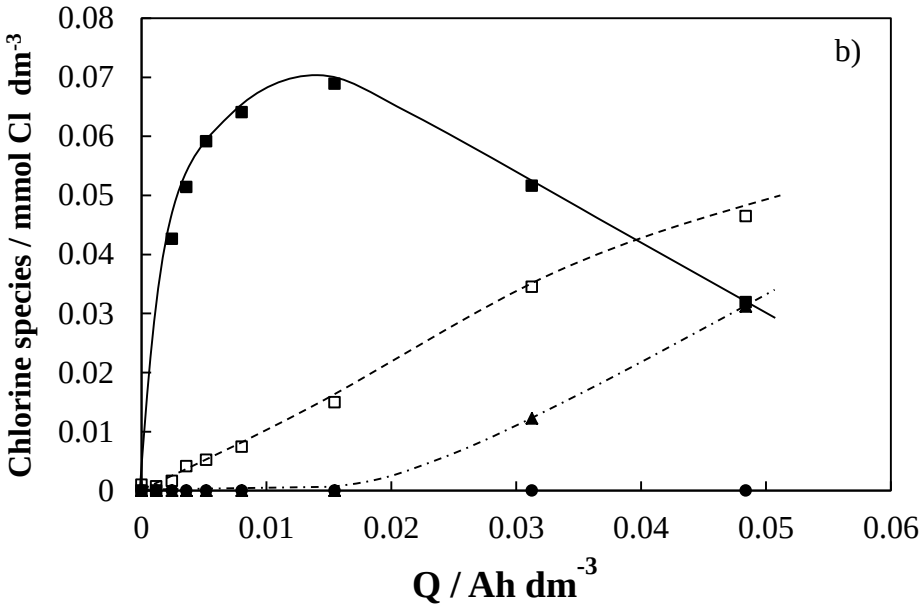
Figure 5. Variation of the turbidity with the applied electric charge at different current densities during the ED-EC process. ■ 1.90 A m^{-2}; Turbidity$_0$: 13 NTU; pH: 7.98; ▲ 4.13 A m^{-2}; Turbidity$_0$: 15 NTU; pH: 8.06; ● 6.70 A m^{-2}; Turbidity$_0$: 14 NTU; pH: 8.05; □ 9.38 A m^{-2}; Turbidity$_0$: 13 NTU; pH: 8.35. (Anode: BDD; Cathode: SS; Bipolar electrode: Iron; T: 25ºC).

Figure 6. Variation of the *E. coli* (black points) and the turbidity (white points) with the applied electric charge during the ED-EC process of urban wastewater with different cell configurations. ■□ C-A (j: 6.70 A m^{-2}; *E. coli*$_0$: 22,000 CFU 100ml^{-1}; Turbidity$_0$: 14 NTU; T: 25ºC; pH: 8.05). ▲Δ A-C (j: 6.76 A m^{-2}; *E. coli*$_0$: 35,000 CFU 100ml^{-1}; Turbidity$_0$: 16 NTU; T: 25ºC; pH: 8.35). (Anode: BDD; Cathode: SS; Bipolar electrode: Iron; T: 25ºC).

Figure 7. Removal of *E. coli* concentration (a) and the turbidity (b) at three different applied electric charges and with different bipolar electrode materials. Black bars: iron bipolar electrode (j: 6.70 A m^{-2}; *E. coli*$_0$: 22,000 CFU 100ml^{-1}; Turbidity$_0$: 14 NTU; T: 25ºC; pH: 8.05), hatched bars: aluminium bipolar electrode (j: 6.62 A m^{-2}; *E. coli*$_0$: 25,000 CFU 100ml^{-1}; Turbidity$_0$: 8 NTU; T: 25ºC; pH: 8.50). (Anode: BDD; Cathode: SS; T: 25ºC).

Figure 8. Evolution of the metal concentration electrodissolved with the applied electric charge during the ED-EC process. (a) ■ Aluminium; j: 6.62 Am^{-2} □ Iron; j: 6.70 Am^{-2}. (b) ■ Aluminium; j: 127.32 Am^{-2} □ Iron; j: 116.59 Am^{-2}. (Anode: BDD; Cathode: SS; T: 25ºC).





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691 **Figure 1**
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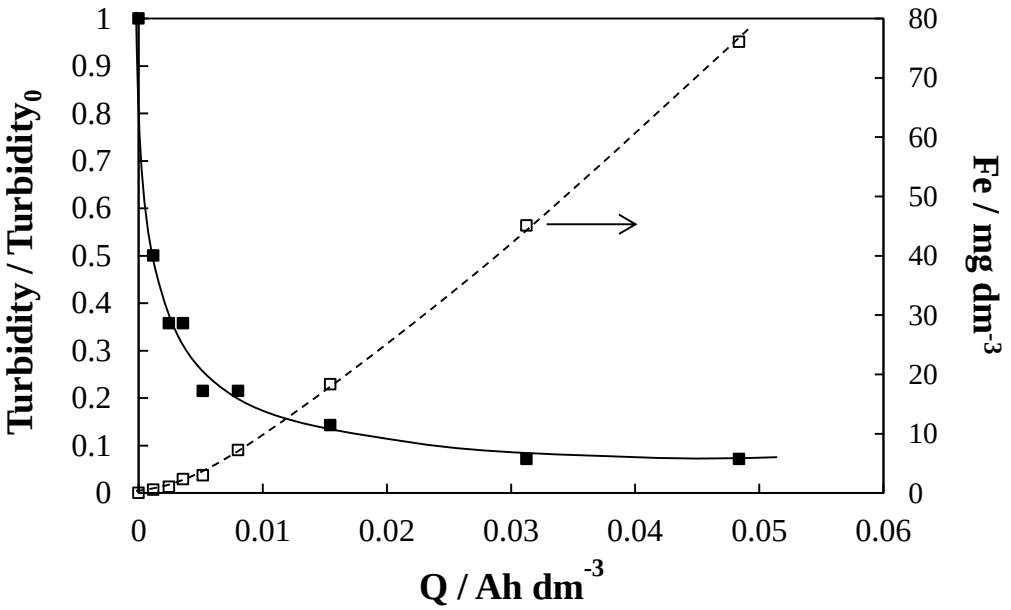

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703 **Figure 2**
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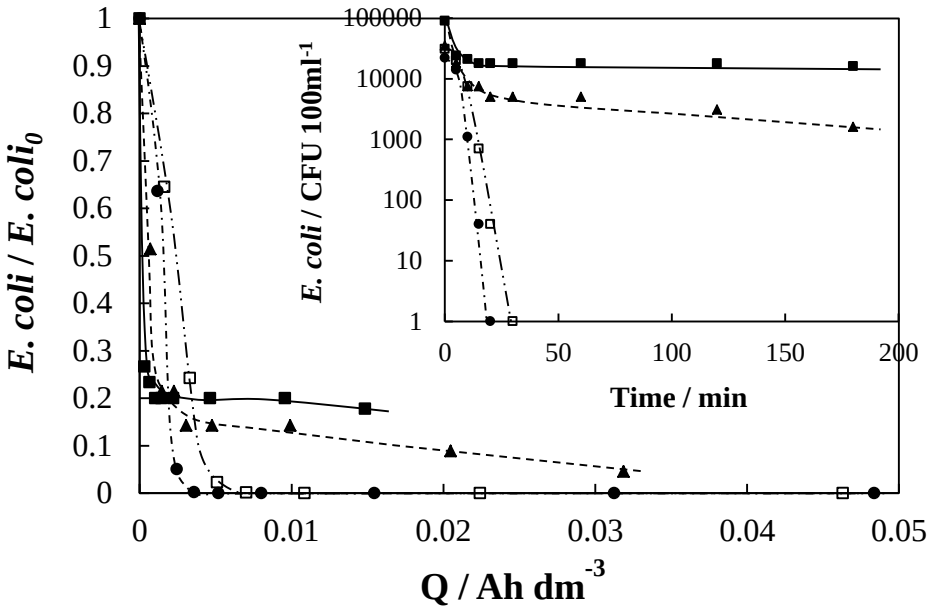
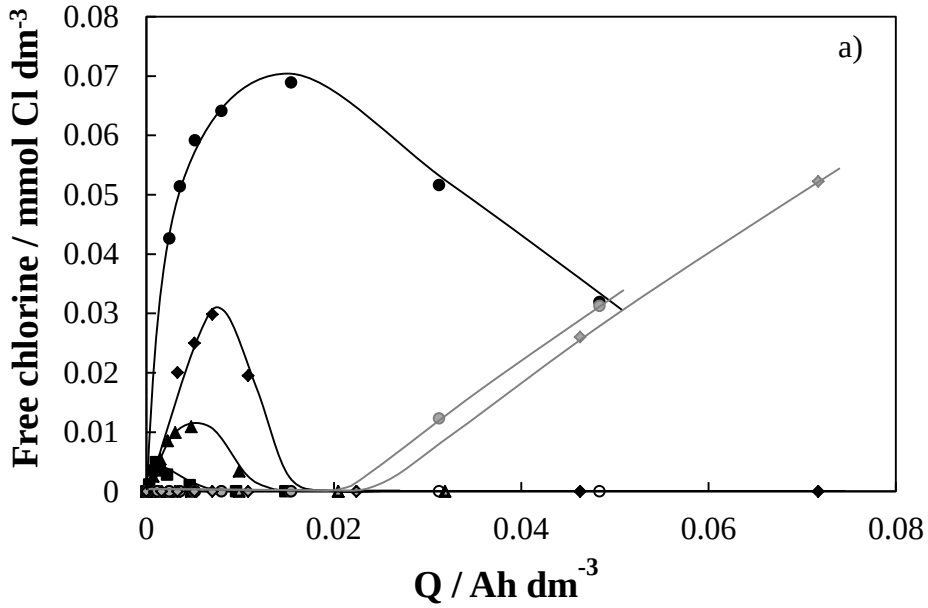

E. coli / E. coli0
Q / Ah dm-3
E. coli / CFU 100ml-1
Time / min
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0.01
0.02
0.03
0.04
0.05
100000
10000
1000
100
10
50
100
150
200

Figure 3


a)
Free chlorine / mmol Cl dm-3
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
0.02
0.04
0.06
0.08
Q / Ah dm-3

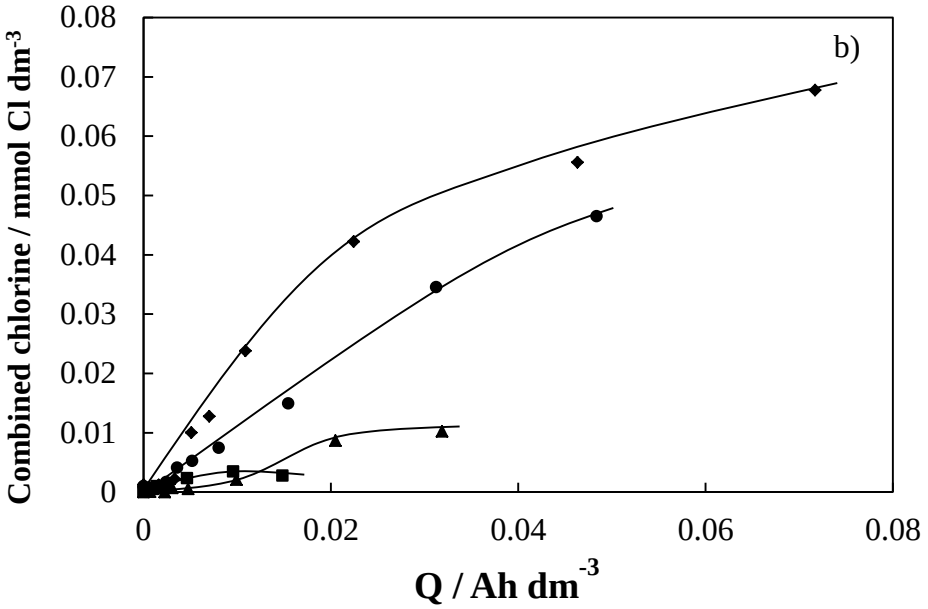
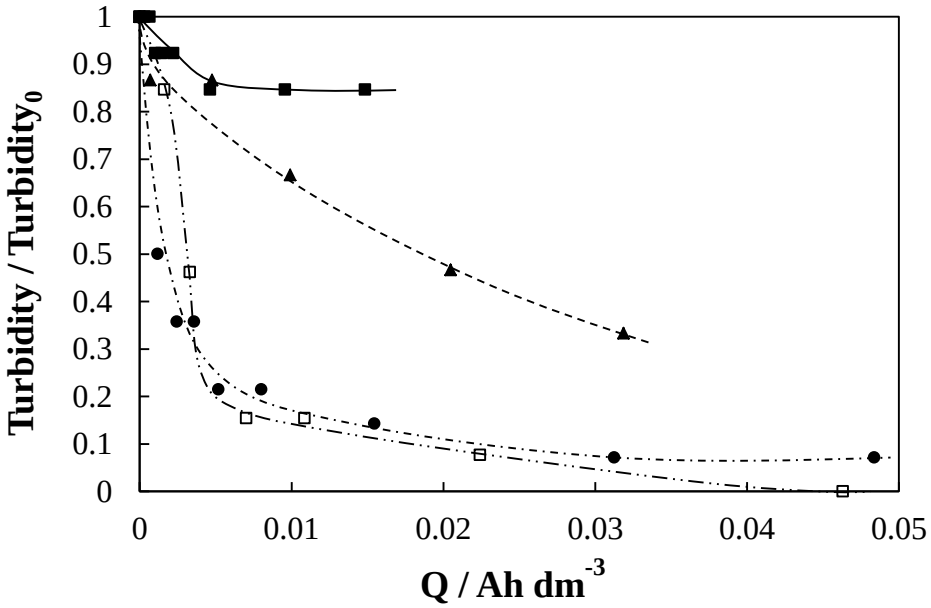

b)
Combined chlorine / mmol Cl dm-3
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
0.02
0.04
0.06
0.08
Q / Ah dm-3

Figure 4


Turbidity / Turbidity0
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0.8
0.7
0.6
0.5
0.4
0.3
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0
0
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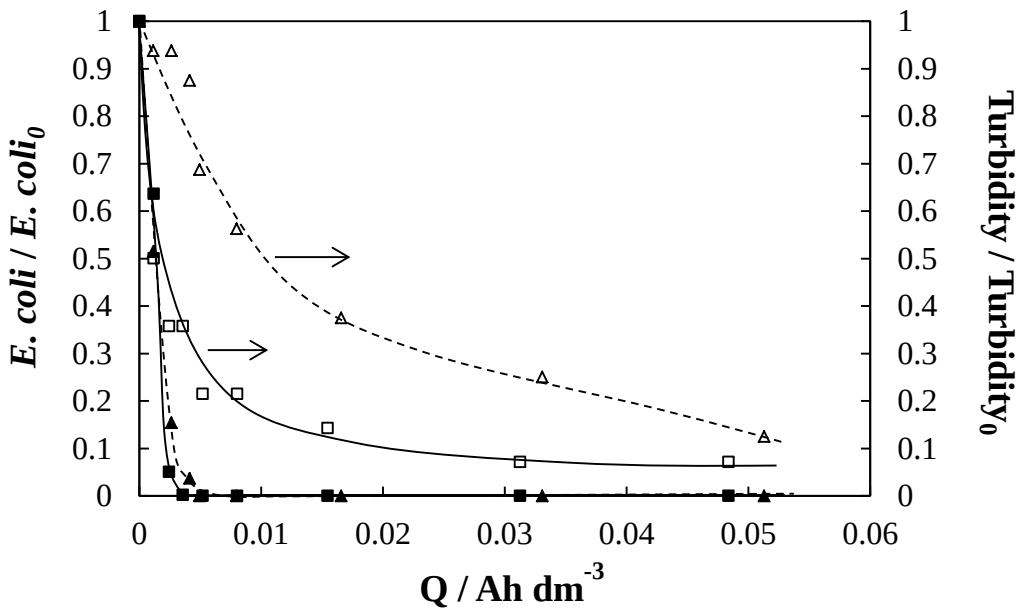
0.02
0.03
0.04
0.05
Q / Ah dm-3

Figure 5


E. coli / E. coli0
Turbidity / Turbidity0
Q / Ah dm-3
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0.1
0.2
0.3
0.4
0.5
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0.9
1
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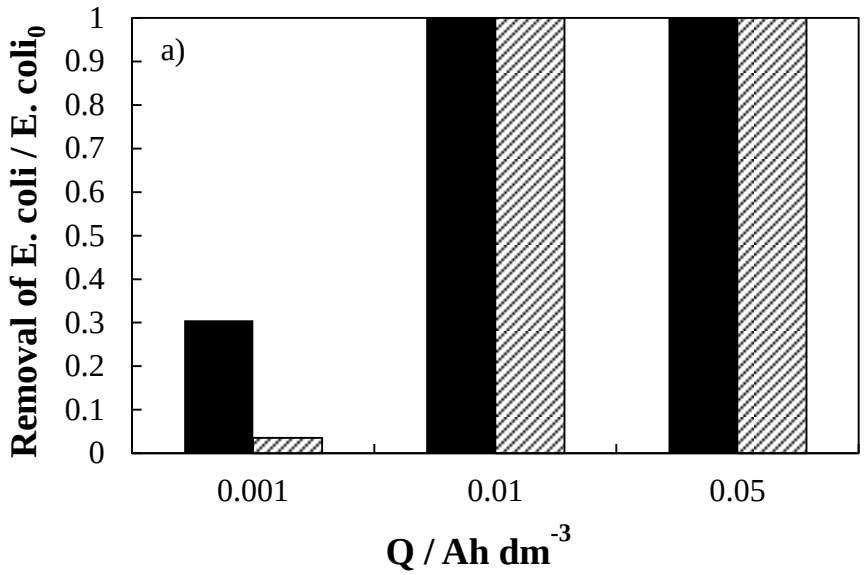
0.03
0.04
0.05
0.06

Figure 6



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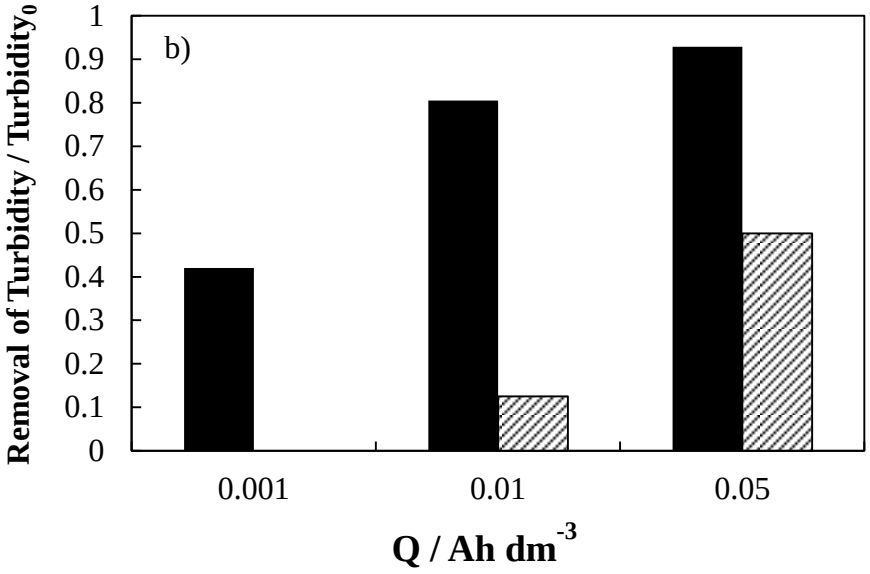

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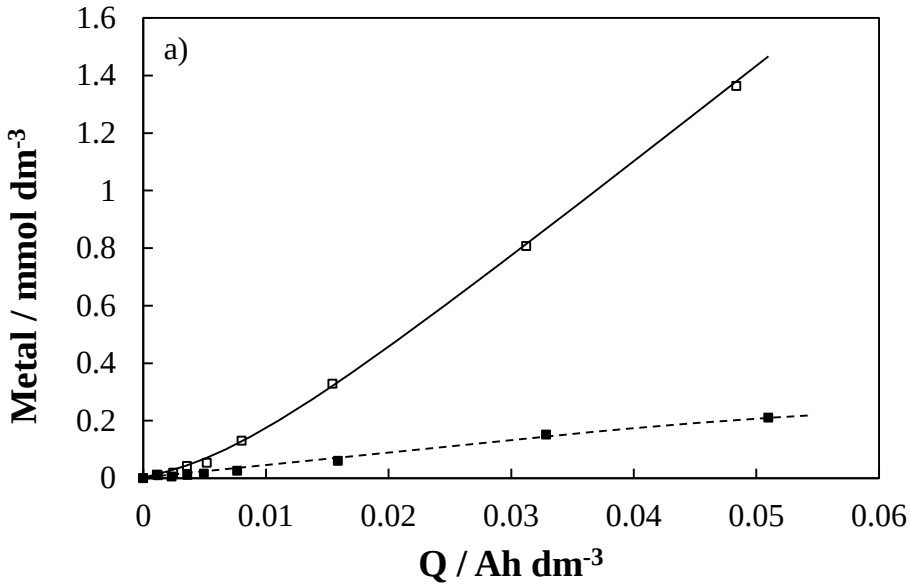
a)
Metal / mmol dm-3
Q / Ah dm-3
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
0.01
0.02
0.03
0.04
0.05
0.06

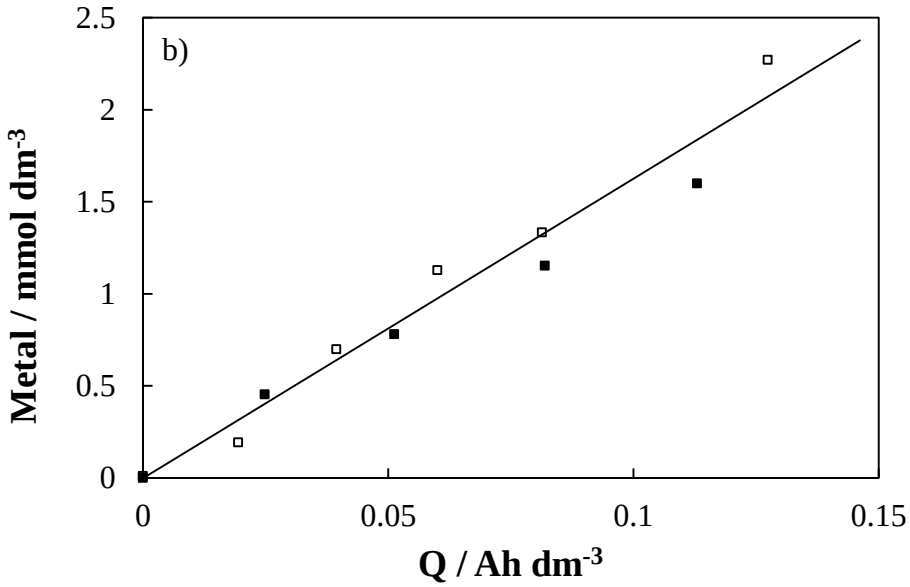
b)
Metal / mmol dm-3
Q / Ah dm-3
0
0.5
1
1.5
2
2.5
0.05
0.1
0.15

Figure 8

List of Tables

Table 1. Average composition of target wastewater.

Parameter	Value
Chloride (mg dm^{-3})	204.850
Nitrate (mg dm^{-3})	23.740
Sulphate (mg dm^{-3})	334.595
Ammonium (mg dm^{-3})	43.434
Iron (mg dm^{-3})	n. d.
Aluminium (mg dm^{-3})	n. d.
Turbidity (NTU)	13-15
TSS (mg dm^{-3})	7-10
TOC (mg dm^{-3})	25
E. coli (CFU $100ml^{-1}$)	22000-90000

n. d. – non detectable
TSS – Total suspended solids
TOC – Total organic carbon