Electrolytic and electro-irradiated technologies for the removal of chloramphenicol in synthetic urine with diamond anodes

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Abstract

Hospital effluents are a major source for the occurrence of pharmaceuticals in the environment. In this work, the treatment of synthetic urine polluted with chloramphenicol is studied by using three different conductive-diamond electrochemical oxidation technologies: electrolysis (single electrolysis), photoelectrolysis and high-frequency ultrasound sonoelectrolysis. These technologies were evaluated at 10 and 100 mA cm^{-2}. Results shows that not only chloramphenicol but also other organics contained in urine are completely mineralized by electrolysis. Ammonium is the main inorganic nitrogen species formed and it can react with the electrogenerated hypochlorite, favouring the formation of chloramines. These species prevent the potential formation of perchlorate from chlorides contained in urine at low current densities (10 mA cm^{-2}) and delay its

occurrence at high current densities (100 mA cm^{-2}). On the other hand, irradiation of ultraviolet (UV) light or high-frequency ultrasound (US) produce changes in the performance of the electrolytic treatment, but these changes are not as important as in other cases of study shown in the literature. Nonetheless, the effect of electroirradiated technologies seems to be higher and depends on the type of pollutant when working at low current densities (10 mA cm^{-2}). It is positive in the case of the degradation of the antibiotic and the uric acid and negative in the case of urea where there is a clear antagonistic effect. Production of oxidants increases with the current density although in lower ratio than expected. These results are of great importance because clearly point out that electrolytic technologies can be applied to minimize the diffuse pollution associated to pharmaceuticals before discharge into municipal sewers.

Keywords: chloramphenicol; urine; diamond; electrolysis; sonoelectrolysis; photoelectrolysis

Highlights

- Chloramphenicol can be completely removed from urine using CDEO
- Organic compounds contained in urine can be fully mineralized during CDEO.
- Irradiation of UV light or HF-US does not always improve performance of single CDEO
- Chloramines are formed during the electrolysis of urine
- Production of perchlorates can be avoided operating at low current densities

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1. Introduction

In recent years, many works have confirmed the efficiency and robustness of the application of Conductive-Diamond Electrochemical Oxidation (CDEO) for the mineralization of effluents containing organic pollutants such as alcohols (Cañizares et al. 2005, Panizza and Cerisola 2004), carboxylic acids (Cañizares et al. 2003, Bensalah et al. 2012, Scialdone et al. 2008), dyes (Faouzi et al. 2006, Saez et al. 2007), pharmaceuticals (Domínguez et al. 2012, Salazar et al. 2016, Garcia-Segura et al. 2015, Zhao et al. 2009) or pesticides (Rubí-Juárez et al. 2016a, Brillas et al. 2004, Pereira et al. 2015, Rodrigo et al. 2014, Samet et al. 2010). The high efficiency of CDEO is attained thanks to the great chemical and electrochemical stability of diamond electrodes, the high over-potential for electrolysis of aqueous solutions and the enhanced production of oxidants such as peroxosulfates, peroxophosphates, peroxocarbonates, hypochlorite and hydrogen peroxide (Rodrigo et al. 2014, Cañizares et al. 2009, Sánchez-Carretero et al. 2011a, Cotillas et al. 2011, Sires et al. 2014). In this way, the efficiency of electrolysis (single electrolysis) may be improved by coupling UV or US irradiation technologies with CDEO (dos Santos et al. , Sáez et al. 2014a, Lorimer et al. 2004, Osugi et al. 2005, Cotillas et al. 2016a, Rubí-Juárez et al. 2016b). Thus, photoelectrolysis and high-frequency sonoelectrolysis may lead to the formation of free radicals in the bulk solution from the activation of the electro-generated oxidants, whereas sonoelectrolysis at low frequency contributes to increase the transport of pollutants to the electrode surface, minimizing the effect of diffusion limitations.

The presence of pharmaceuticals in aquatic environment has attracted the attention of the scientific community, and antibiotics are the most commonly pharmaceuticals found in the environment due to their high consumption (Kümmerer 2009a, b, Feng et al. 2013). Here, chloramphenicol is a widely used broad spectrum antibiotic because it has low cost and it presents excellent antibacterial properties to inhibit both Gram-positive and Gram-negative bacteria (Podzelinska et al. 2010, Chen et al. 2015). However, the low biodegradability of this compound in sewage treatment plants may cause serious toxic effects in humans such as severe aplastic anaemia (Kim et al. 2009, Verlicchi et al. 2013, Trovó et al. 2014).

Hospital effluents represent a major source for the entrance of pharmaceuticals into environment, because they may content some pharmaceuticals in concentrations as high as several mg dm^{-3}. In fact, these effluents are known to be at least 5-15 more toxic than urban effluents (Kümmerer 2001, Verlicchi et al. 2015). Nevertheless, except for some particular wastes, discharge of hospital effluents is rarely concerned by legal regulations. Therefore, they are typically discharged into the municipal sewer system and treated together with other domestic and industrial flows in a municipal wastewater treatment facility (WWTF), before being discharged into environment (Verlicchi et al. 2010). In the WWTF, these pollutants undergo physical-chemical and biological treatments, which often are not efficient with these anthropogenic chemicals. For this reason, there is a growing concern about this type of treatment, since it is becoming clearer than the dilution with surface water should not represent the proper action to mitigate potential adverse of pharmaceutical residues in the environment (Verlicchi et al. 2015). Furthermore, only a fraction of the administered pharmaceuticals may be metabolized by the human body and the remaining pharmaceutical quantity enters into the water cycle as the parent compound and/or its metabolites via excretion, mainly in urine (55-80%) and to a lesser extent the

faeces (4-30%) (Al Aukidy et al. 2014, Jjemba 2006). Consequently, dedicated treatments for hospital effluents are starting to become recommended by many authors worldwide.

With this background, this paper focuses on the evaluation of the removal of chloramphenicol (chosen as antibiotic model) in synthetic urine media by CDEO based EAOP (Electrochemical Advanced Oxidation Process), in order to simulate the treatment of pharmaceuticals originating from hospital effluents. According to literature, the degradation of chloramphenicol has been previously evaluated in aqueous solutions by different EAOP technologies. Thus, very high removal ratios are reported, such as the 83.3% of chloramphenicol degradation from aqueous media by enhanced the efficiency of Fenton's reaction (Wu et al. 2016), the 87.30% of chloramphenicol degradation from 0.2 M Na_2SO_4 media by electrolysis treatment with Al-doped PbO_2 electrode (Chen et al. 2015), the 96.1% of chloramphenicol degradation from the effluent of a beef cattle operation by persulfate activated by zero valent iron (Nie et al. 2015) or the total degradation of chloramphenicol from 0.05 M Na_2SO_4 media by solar photoelectro-Fenton with BDD anode (Garcia-Segura et al. 2014). Nevertheless, to the best knowledge of the authors, chloramphenicol degradation from human urine media has not been studied yet. Likewise, irradiated assisted CDEO has never been applied before for the treatment of this antibiotic. Hence, in this work, our efforts are focused on the clarification of the influence of the current density (10 - 100 mA cm^{-2}) on the mineralization process by three highly efficient electrochemical advanced oxidation processes, based on CDEO: single electrolysis, photoelectrolysis and high-frequency sonoelectrolysis. This two current densities were proposed as boundary cases of study, according to previous works of our group (Canizares et al. 2007) which confirmed a totally different behaviour of electrochemical processes at these two different current density values. Thus, in the

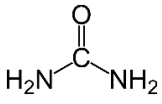
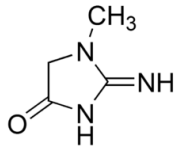
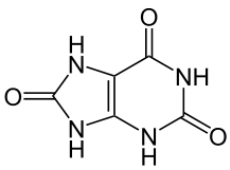
electrolyses at 10 mA cm^{-2} the mediated effects of hydroxyl radicals on performance are not expected to be as important as in the case of 100 mA cm^{-2}.

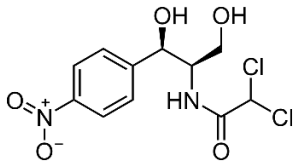
2. Material and methods

2.1. Chemicals

Chloramphenicol, urea, creatinine and uric acid were of analytical grade (> 98% purity) from Sigma-Aldrich. Other chemicals employed were analytical grade and purchased from Sigma-Aldrich. Table 1 shows details of synthetic urine media based on the composition given by Dbira et al. (Dbira et al. 2015). Sulfuric acid utilized to adjust the initial pH from 8.0 to 5.6 was analytical grade purchased from Merck. All solutions were prepared with double deionized water obtained from a Millipore Milli-Q system, with resistivity 18.2 MΩ cm at 25°C.

Table 1. Composition of the synthetic matrix used in this study.

Name	**Molecular formula**	**Molecular structure**	**Concentration (mg dm^{-3})**	
Urea	CH_4N_2O		3333.34	Synthetic urine (Dbira et al. 2016)
Creatinine	$C_4H_7N_3O$		166.67	
Uric acid	$C_5H_4N_4O_3$		50.00	
Potassium chloride	KCl		1000.00	

Magnesium sulfate	$MgSO_4$		170.00	
Calcium Phosphate	$(Ca)_3(PO_4)_2$		28.34	
Sodium carbonate	Na_2CO_3		166.67	
Diammonium hydrogen phosphate	$(NH_4)_2HPO_4$		83.34	
Chloramphenicol	$C_{11}H_{12}Cl_2N_2O_5$		100.00	Antibiotic

129

130 **2.2. Experimental procedures**

131 Electrolysis experiments were carried out in a single compartment electrochemical cell
132 working under batch-operation mode (Cañizares et al. 2002). Circular boron doped
133 diamond (BDD) plates (purchased from WaterDiam in France, formerly Adamant
134 Technologies) with a geometric area of 78 cm^2 were used as electrodes, and the inter-
135 electrode gap between both electrodes was 9 mm. Photoelectrolysis experiments were
136 carried out by immersing an UVG ERG-11 lamp (Baquias Cabre i Berga, S.L) in the bulk
137 solution. Sonoelectrolysis experiments were carried out by immersing an Epoch 650
138 ultrasound horn (Olympus), emitting 10 MHz and maximum ultrasonic power of 200 W.
139 A Delta Electronika ES030-10 power supply (0-30V, 0-10A) provided the electric
140 current.

141 Synthetic wastewater was prepared with 100 mg dm^{-3} of antibiotic and synthetic urine as
142 supporting electrolyte. All experiments were carried out under galvanostatic conditions

and the current densities applied were 10 and 100 mA cm^{-2}. The synthetic wastewater was stored in a glass tank (1 dm^{-3}).

2.3 Analytical techniques.

High performance liquid chromatography was used to determine the concentration of different organics using an Agilent 1200 series coupled a DAD detector. A ZORBAX Eclipse Plus C18 analytical column was used and its temperature was maintained at 25ºC. The mobile phase consisted of 2 % acetonitrile / 98 % aqueous solution with 0.1 % of formic acid, applying a flow rate of 1.0 cm^3 min^{-1}, an injection volume of 10 μL and a DAD detection wavelength of 235 nm to determine creatinine and uric acid. Furthermore, the mobile phase consisted of 50 % methanol / 50 % water, applying a flow rate of 0.6 cm^3 min^{-1}, an injection volume of 20 μL and a DAD detection wavelength of 270 nm to determine chloramphenicol.

The urea concentration was determined by a spectrophotometric method using the Cary Series UV-Vis Spectrophotometer (Agilent Technologies). This method is based on the yellow-green color produced when p-dimethylaminobenzaldehyde is added to urea in dilute hydrochloric acid solution (Watt and Chrisp 1954).

Ions concentrations were measured by ion chromatography using a Metrohm 930 Compact IC Flex coupled to a conductivity detector. A Metrosep A Supp 7 column was used to determine anions, using a mobile phase consisting of 85:15 v/v 3.6 mM Na_2CO_3/acetone with a flow rate of 0.8 cm^3 min^{-1}. In addition, a Metrosep A Supp 4 column was used to analyze cations, using a mobile phase consisting of 1.7 mM HNO_3 and 1.7 mM 2,6-pyridinedicarboxylic acid with a flow rate of 0.9 cm^3 min^{-1}. The

166 temperature of the oven was 45 and 30ºC for the determination of anions and cations,
167 respectively. The volume injection was 20 µL.

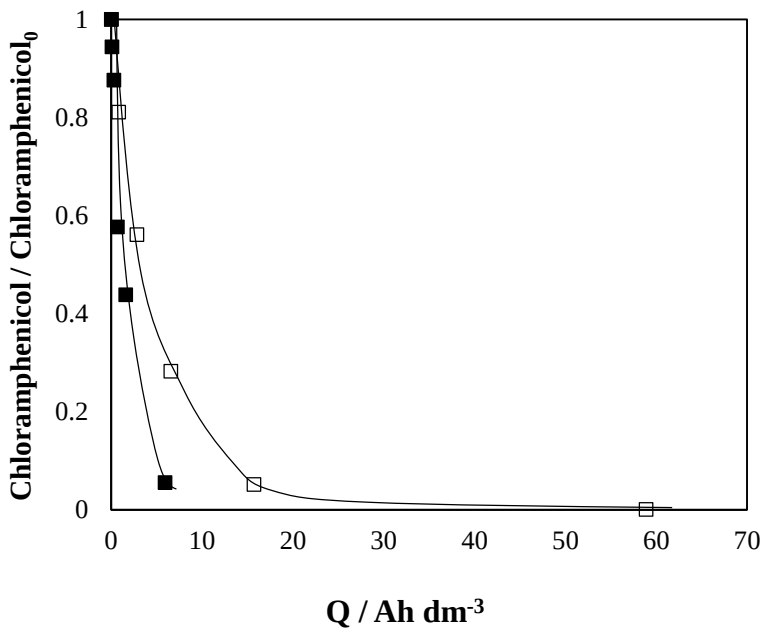
168 TOC concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer.
169 Hypochlorite was analyzed by titration with 0.001 M As_2O_3 in 2 M NaOH (Wilpert 1957,
170 Freytag 1959). Oxidants (hypochlorite, persulfate, percarbonate, peroxodiphosphate,
171 ozone, hydrogen peroxide…) were determined iodometrically according to Kolthoff &
172 Carr (Kolthoff and Carr 1953). The pH and conductivity were measured using a CRISON
173 pH25+ and CRISON CM35+, respectively.

174 The intermediates generated from the organic products were extracted with ethyl acetate
175 within a ratio pollutant/solvent of 0.6 w/w. Then, both phases were stirred using a vortex
176 mixer during 5 minutes and after that, samples were centrifuged during 15 minutes at
177 4,000 rpm. The organic phase was analyzed by GC-MS using a Thermo Scientific DSQ
178 II Series Single Quadrupole GC-MS with a NIST05-MS library. The column was a polar
179 TR-WAXMS (30 m x 0.25 mm x 0.25 µm). The temperature ramp was 70ºC for 1 min,
180 30ºC min^{-1} up to 300 ºC and hold time 5 minutes. The inlet, source and transfer line
181 temperatures were 250, 200 and 300ºC, respectively.

182

183 **3. Results and discussion**

184 Figure 1 shows the variation of chloramphenicol concentration during the single
185 galvanostatic electrolysis of synthetic urine containing 100 mg dm^{-3} of this antibiotic at
186 10 and 100 mA cm^{-2}.



187

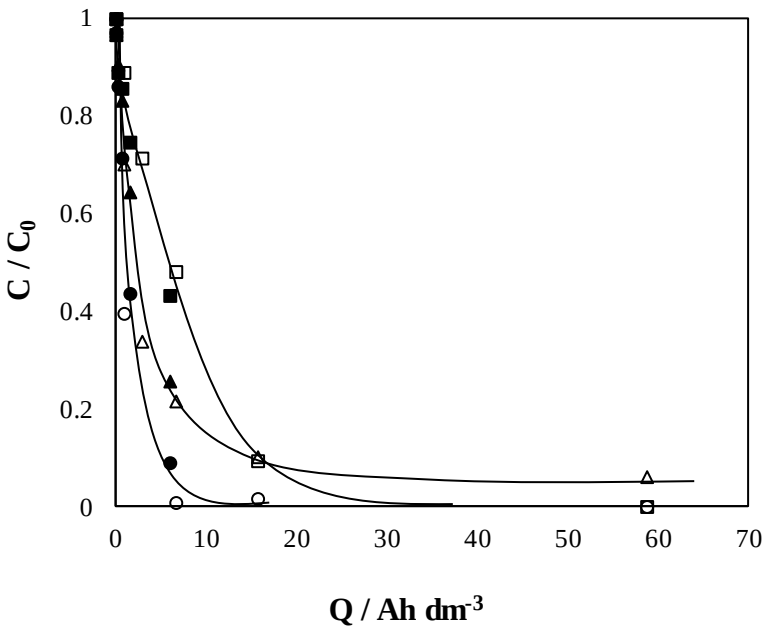
188 **Figure 1.** Influence of the current density on the chloramphenicol degradation as function
189 of the applied electric charge during electrolysis process in synthetic urine. (■) 10 mA
190 cm^{-2}; (□) 100 mA cm^{-2}.

191

192 Results show that chloramphenicol may be completely degraded by electrolysis at both
193 current densities applied. However, the process efficiency is quite different and it depends
194 on the current density applied. Here, the 95% removal of chloramphenicol was achieved
195 with an applied electric charge of 5.0 Ah dm^{-3} at a current density of 10 mA cm^{-2} whereas
196 the same removal percentage was reached at approx. 15 Ah dm^{-3} when operating at 100
197 mA cm^{-2}. Then, the degradation of chloramphenicol in synthetic urine during the
198 electrolysis at the lowest current density is 3 times more efficient than the electrolysis
199 carried out with the highest current density. This is in agreement with other results shown
200 in literature for the degradation of other antibiotics such as sulfamethoxazole (Martín de
201 Vidales et al. 2012), amoxicillin (Panizza et al. 2014, Sopaj et al. 2015) or tetracycline
202 (Wu et al. 2012) and even with other very different organic species (Sires et al. 2014). It
203 clearly indicates that electrolysis is diffusion-controlled and hence that processes

204 occurring in the nearness of the electrode surface are quite important. This lose in
205 efficiency is related to the increase in the rate of side reactions such as water oxidation
206 and/or inorganic oxidants production, which despite of having indirect influence on the
207 degradation of the organic, produces a fall in the efficiency of the overall process.

208 At this point, it is important to take in mind that not only the antibiotic is degraded during
209 the electrolysis but also the other organic components of urine may undergo degradation
210 during the electrolysis process. Then, Figure 2 shows the evolution in the concentration
211 of the organics contained in the synthetic urine, during the electrolysis process at both 10
212 and 100 mA cm^{-2}. These organic compounds are presented in the synthetic urine in very
213 different ranges of concentrations (3333.34 mg dm^{-3} of urea, 166.67 mg dm^{-3} of creatinine
214 and 50.00 mg dm^{-3} of uric acid) and the graph shows the changes observed in the
215 normalized concentrations.



216

217 **Figure 2.** Influence of the current density on degradation of the organic compounds
218 presented in synthetic urine as function of the applied electric charge during electrolysis

process. (■) urea; (▲) creatinine; (●) uric acid. Filled symbols: 10 mA cm^{-2}; empty symbols: 100 mA cm^{-2}.

The first important observation is that urea, creatinine and uric acid are totally depleted during the two electrolyses. Furthermore, and opposite to what it was observed with the antibiotic, no significant influence of the current density is observed on the degradation of urea and creatinine, because the data obtained at 10 and 100 mA cm^{-2} are almost overlapped, meaning that the same charge is required to remove a similar percentage of these organics. On the other hand, in the case of uric acid, the oxidation seems to be more efficient at the highest current density. Hence, current density affects in a different way to the four organic molecules contained in the urine and the only way to explain these differences is by considering the effect of the different oxidants produced on the electrochemical cell on the chemical reactivity of the four organics, which, in fact, it is a competitive oxidation. Specifically, hypochlorite (Eqs. (1)-(3)), peroxosulfate (Eq. (4)), peroxodiphosphate (Eq. (5)) or percarbonate (Eq. (6)) can be generated from the ions present in the effluent. These species attack each organic compound with different efficiency depending on its chemical structure (Cotillas et al. 2018). In this context, aromatic and cyclic molecules which present more functional groups are more easily degraded by oxidants. Therefore, the concentration of these species plays a key role on the removal of all organics present in the effluent.

$$2\ Cl^- \rightarrow Cl_2 + 2\ e^- \quad (1)$$

$$Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+ \quad (2)$$

$$HClO \leftrightarrows H^+ + ClO^- \quad (3)$$

$$2\ SO_4^{2-} \rightarrow S_2O_8^{2-} + 2\ e^- \quad (4)$$

$$2\ PO_4^{3-} \rightarrow P_2O_8^{2-} + 4\ e^- \quad (5)$$

$$2\ CO_3^{2-} \rightarrow C_2O_6^{2-} + 2\ e^- \quad (6)$$

Concentration of different oxidizing species is shown in Figure 3, where it can be seen that the higher the current density, the higher is the oxidants concentration produced ("cocktail" of hypochlorite, peroxosulfate, hydrogen peroxide…). However, it is important to take in mind that the measured oxidants are those which have not reacted and, hence, it is assumed that many other species could be involved in the oxidation of the organics contained in the urine.

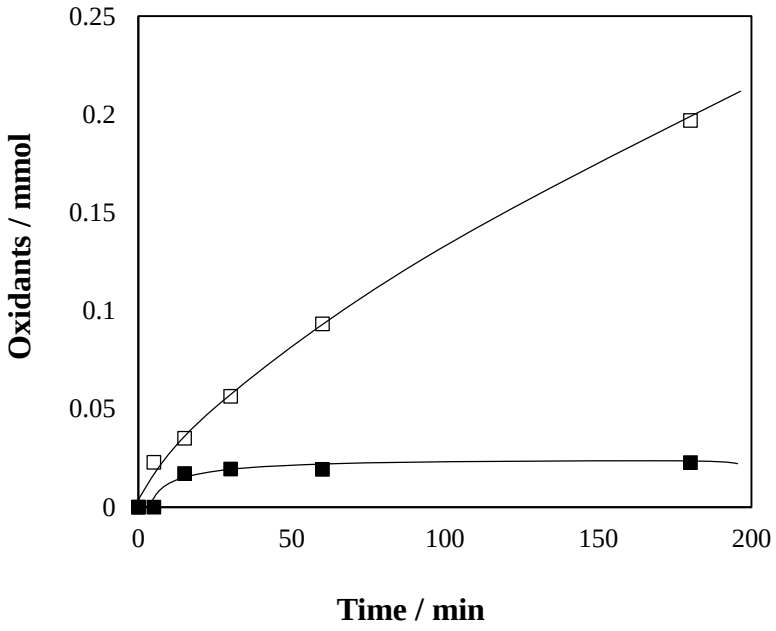


Figure 3. Oxidants electrogenerated as function of the operation time during the electrochemical treatment of chloramphenicol in synthetic urine. Filled points: 10 mA cm^{-2}; empty points: 100 mA cm^{-2}.

In recent works, it has been demonstrated that irradiation of wastes during the electrolysis influences on the results of the treatment, because of the activation of the oxidants

produced on the electrode surface during the treatment. Thus, as an example, the efficiency of the oxidation of sulfate radicals obtained by photolysis of peroxosulfate is known to be several log-units above the efficiency of the raw peroxosulfate. However, irradiation of UV or high-frequency US does not always show a positive synergistic effect and sometimes antagonistic effects are clearly observed (Cotillas et al. 2016b). For this reason, and in order to clarify this effect on the treatment of urine polluted with antibiotic, the treatment of chloramphenicol in synthetic urine has been also studied during the photoelectrolysis with ultraviolet light (254nm/11W) and the sonoelectrolysis with continuous emission of ultrasounds (10MHz/200W). In order to compare the degradation rate of organic compounds for the different electrochemical processes, the experimental data were fitted to a first order kinetic (Eq. (7)).

$$Ln\frac{[A]}{[A]_0} = -k \cdot t \qquad (7)$$

Figure 4 shows the kinetic constants calculated for the degradation of chloramphenicol, urea, creatinine and uric acid during different electrochemical processes at current densities of 10 and 100 mA cm^{-2}.

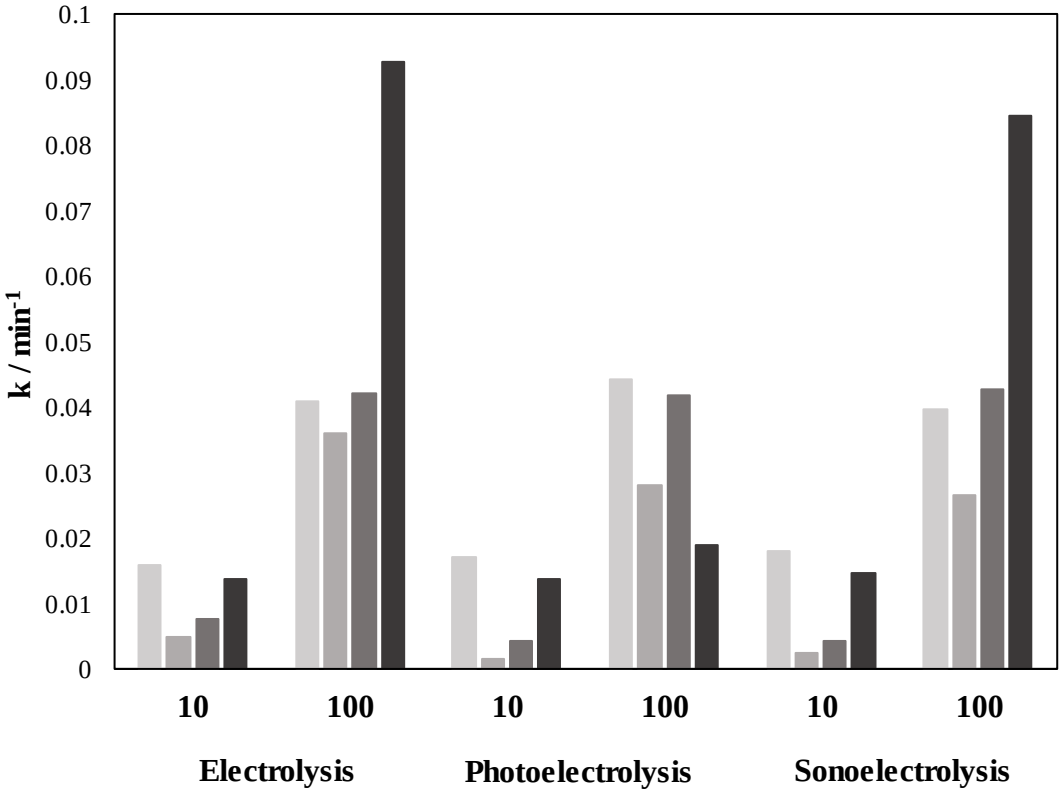


Figure 4. Kinetic constants calculated for the organic compounds presented in aqueous solution as function of the electrochemical processes studied at different current densities (mA cm^{-2}). (▫) chloramphenicol, (▪) urea, (▪) creatinine, (■) uric acid.

Kinetic constants significantly depend on the current density and on the particular pollutant studied. In comparing the effect of the current density, it can be observed that changing by one log-unit the current density only produces an increase in the oxidation ratio by a factor of 2-3, clearly indicating that processes are less efficient at highest current densities. In comparing the oxidation of pollutants, it is important to point out that the antibiotic and the uric acid are more easily oxidized than urea and creatinine, and that this later compound (creatinine) becomes more easily oxidized (in comparison with the other three) at the highest current density. Activation of oxidants by irradiation does not always

show a positive effect. In fact, irradiation has a clear negative effect on the degradation of urea at both current densities and on the degradation of creatinine at the lowest current density. Conversely, it has a positive effect on the degradation of the antibiotic and the uric acid at low current density, although this positive effect is not observed at 100 mA cm^{-2}. Results are in agreement with previous works and indicate that it is very important to make experimental work in order to evaluate if the application of UV light or US is positive for the treatment of a given waste (Sáez et al. 2014b, dos Santos et al. 2016, Martínez-Huitle et al. 2015).

Once clarified the effect of irradiation on the raw organics contained in the initial urine, it is important to focus the attention on other organic species, that is, the intermediates produced during the treatment. In a first approach, TOC can give valuable information about them. Thus, Figure 5 depicts the evolution of TOC concentration during the tests.

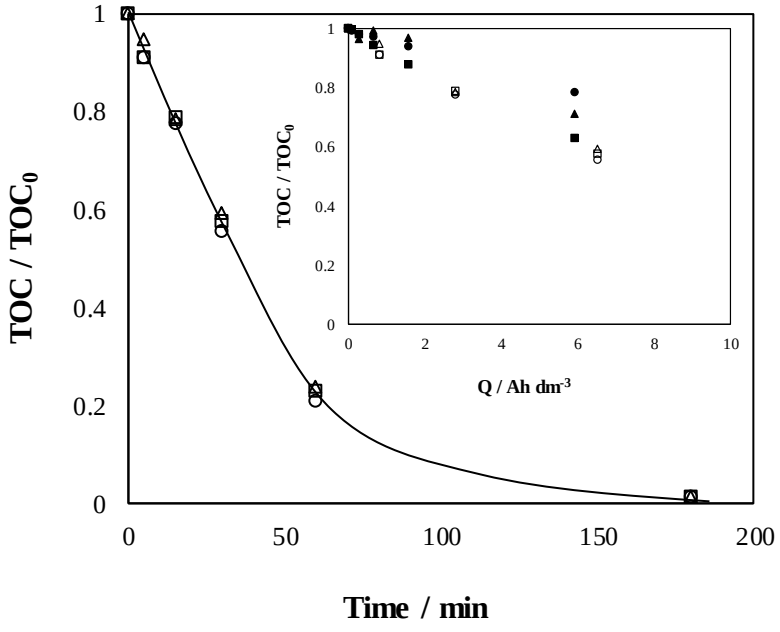
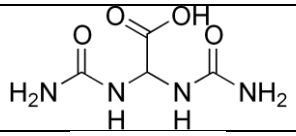
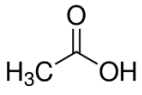
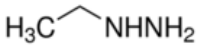
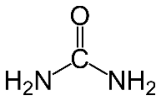


Figure 5. TOC decay as function of the operation time during the electrochemical treatment at 100 mA cm^{-2} of chloramphenicol in synthetic urine. Onset: Influence of the current density on the TOC decay as unction of the applied electric charge during the electrochemical treatment at 10 mA cm^{-2} (Full points) and 100 mA cm^{-2} (empty points). Electrochemical processes: (■,□) Electrolysis; (●,○) Photoelectrolysis; (▲,△) Sonoelectrolysis.

The total mineralization of the TOC contained in the urine can be attained after 180 minutes of electrolysis (by applying electric charges of nearly 60 Ah dm^{-3}). In addition, TOC depletion shows the same efficiency for the three electrochemical technologies studied at 100 mA cm^{-2} as the experimental data lay over the same line. Onset of the Figure compares the efficiency of the different treatments at the two current densities and points out that differences in the mineralization are more important at 10 mA cm^{-2}, where the irradiation of US, and especially of UV, lead to a lower mineralization efficiency. Thus, the TOC removal after passing an electric charge of 6.0 Ah dm^{-3} was 38.08 %, 28.47 % and 21.85 % for electrolysis, sonoelectrolysis and photoelectrolysis, respectively.

The slight differences observed in the removal of the organic compounds studied and TOC have to be explained by the formation of reaction intermediates during the electrochemical processes, which entail a slower removal of TOC than each initial organic compound. In this context, Table 2 summarizes the main intermediates formed during the three electrolytic technologies used for the oxidation of chloramphenicol in synthetic urine and detected by GC-MS.

Table 2. Main intermediates formed during the single electrolysis treatment of chloramphenicol in synthetic urine.

Compound	Molecular structure	M_w (g mol^{-1})	Retention time (min)	Main fragmentation ions (m/z)
Allantoic acid		176	32.36	44, 60
Acetic acid		60	12.85	43, 45, 60
Ethyl-Hydrazine		60	12.83	43, 45, 60
Urea		60	4.45	17, 61

The number of intermediates found in this work is much lower than that reported in other works focused on the mineralization of chloramphenicol in aqueous media by different EAOPs. Thus, during the electrochemical oxidation with a Al doped PbO_2 electrode, the most important intermediates identified were 4-(2-Amino-1,3-dihydroxy-propanyl)-nitrobenzene, 2,2-Dichloro-N-[1,3-dihydroxy-1-(4-hydroxyphenyl)-propan-2-yl] acetamide, 4-(2-Amino-1,3-dihydroxy-propanyl)-phenol, 4-(2-Nitro-1,3-dihydroxy-propanyl)-nitrobenzene, 4-Nitro-(2R)-hydroxy(phenyl) ethanoic acid, 4-(2-Nitro-1,3-dihydroxy-propanyl)-phenol, 4-Nitrobenzoic acid, 4-Hydroxy-(2R)-hydroxy(phenyl) ethanoic acid, 4-Hydroxybenzoic acid, hydroquinone, 1,4-Benzoquinone, dichloroacetic acid, maleic acid, fumaric acid, succinic acid, acetic acid, oxalic acid and formic acid (Chen et al. 2015). On the other hand, the by-products obtained from the electrochemical oxidation of urea in aqueous solution with BDD anode were reported to be NO_3^-, NH_4^+ and volatile N-compounds (Cataldo Hernández et al. 2014). Likewise, the degradation of uric acid in aqueous solution by conductive-diamond electrochemical oxidation was

reported to generate oxalic acid and urea as intermediates (Dbira et al. 2016). Furthermore, the degradation of creatinine in aqueous solution with immobilized titanium dioxide photo-catalysts was reported to identify as primary intermediates compounds such as dimethyl creatinine, creatol, methyl guanidine, guanidine and urea (Antoniou et al. 2009).

Opposite to other EAOPs, CDEO based technologies are known for the formation of very small quantities of intermediates because of the very harsh oxidation conditions produced that made the raw pollutants contained in a waste undergo a very rapid oxidation (Rodrigo et al. 2010).

Figure 6 shows the evolution of chlorine species at the two current densities evaluated. It is worth to remark that chlorine is known to exhibit a high reactivity during electrolysis (Lacasa et al. 2012a, Sánchez-Carretero et al. 2011b, Brito et al. 2016). Thus, the electrochemical oxidation of chloride generates hypochlorite (Eqs. (1)-(3)) and, in using diamond electrodes, the formation of hydroxyl radicals from water oxidation (Eq. (8)) promotes the formation of chlorate and perchlorate (Eqs. (9)-(11)), as well. Furthermore, the electrogenerated hypochlorite may chemically reacts with ammonium ion presents in solution, favouring the production of chloramines, nitrogen trichloride (Eqs. (12)-(14) and dinitrogen.

$$H_2O \rightarrow \cdot OH + H^+ + e^- \quad (8)$$

$$ClO^- + \cdot OH \rightarrow ClO_2^- + H^+ + e^- \quad (9)$$

$$ClO_2^- + \cdot OH \rightarrow ClO_3^- + H^+ + e^- \quad (10)$$

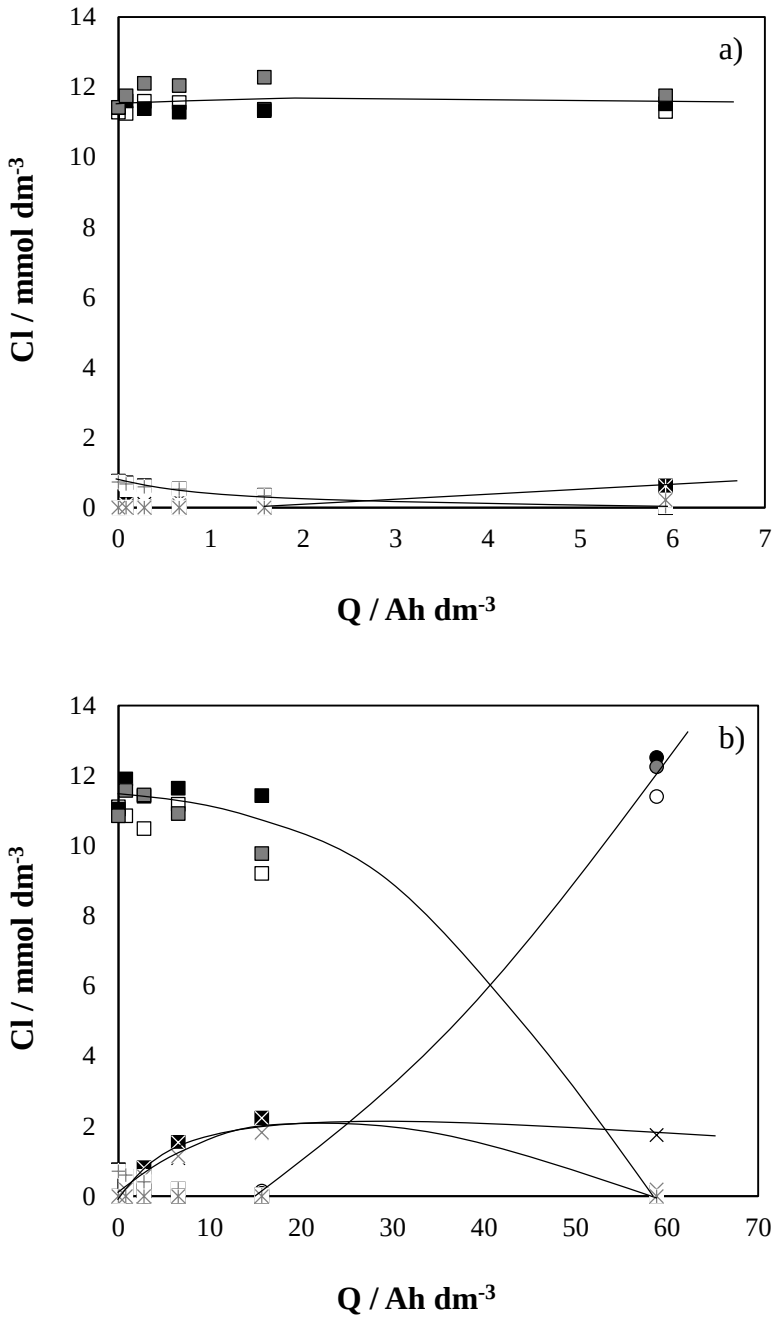
$$ClO_3^- + \cdot OH \rightarrow ClO_4^- + H^+ + e^- \quad (11)$$

$$NH_4^+ + ClO^- \rightarrow NH_2Cl + H_2O \quad (12)$$

$$NH_2Cl + ClO^- \rightarrow NHCl_2 + H_2O \quad (13)$$

364 $NHCl_2 + ClO^- \rightarrow NCl_3 + OH^-$ (14)

365



366

367 **Figure 6.** Influence of the current density on the evolution of chlorine species as function
368 of the applied electric charge during the electrolysis process of chloramphenicol in
369 synthetic urine at (a) 10 mA cm^{-2} and (b) 100 mA cm^{-2}. (■) chloride, (▲) hypochlorite,
370 (♦) chlorate, (●) perchlorate, (×) chloramines, (+) organic chloride, (*) chlorine gas.

Black symbols: electrolysis, white symbols: photoelectrolysis; grey symbols: sonoelectrolysis.

Results obtained in this work indicate that there are no significant differences among the evolution of chlorine speciation during the three CDEO based electrolysis. This means that irradiation of UV or US does not result in significant changes in the concentration of species, despite it is known that both technologies promote the formation of chlorine radicals. Opposite, current density seems to behave as a very important parameter and results obtained at 10 and 100 mA cm^{-2} are completely different. Anyhow, it is worth taking in mind that the progress of reaction is completely different, because the electric charge applied is ten times higher at 100 mA cm^{-2} (all tests were carried out for 3 hours of electrolysis). At the lowest current density, concentration of chloride remains almost constant over the complete tests and only chloramines are formed. As it is known, sequential formation of mono, dichloramine and nitrogen trichloride ends with the regeneration of chloride ions and the formation of gaseous nitrogen. No chlorates or perchlorates are generated, which becomes a major advantage taking into account the hazardousness of both species (Bergmann et al. 2009, Bergmann et al. 2015) and indicates that a high content of ammonium in solution and low current densities can be a way to prevent, or at least minimize, the appearing of these two species. Results obtained working at 100 mA cm^{-2} are completely different. Production of chloramines and nitrogen trichloride is also observed, resulting in this case in higher concentration in the bulk. Likewise, within a long period of the tests, formation of chlorates and perchlorates is prevented, although, eventually the concentration of perchlorate increases suddenly and total conversion of chloride into perchlorate is attained. Initially, this was the expected outcome of the electrolysis with diamond. However, the prevention in their formation at low current density and the delay at high current densities clearly indicate that presence

of species capable of reacting with hypochlorite (like the nitrogen species contained in urine in very high concentrations) is a very interesting mechanism to avoid the formation of chlorates and perchlorates. As it is well-known, formation of these hazardous species is becoming nowadays one of the most important weaknesses of CDEO-based technologies.

Figure 7 focuses on the changes in the concentration of nitrogen species during the electrolysis at 10 mA cm^{-2} and 100 mA cm^{-2}. The total initial nitrogen was 1660.52 mg dm^{-3}, which corresponds to 1.06 % of N-NH_4^+, 93.68 % of N-CH_4N_2O, 3.73 % of N-$C_4H_7N_3O$, 1.00 % of N-$C_5H_4N_4O_3$ and 0.52 % of N-$C_{11}H_{12}Cl_2N_2O_5$. Here, the organic nitrogen has been considered as the total sum of nitrogen contained in the urea, creatinine, uric acid and chloramphenicol. Regarding the reactivity of the inorganic nitrogen species, in previous works (Lacasa et al. 2012a, Lacasa et al. 2012b, 2011), it was reported that nitrites play a key role in the nitrogen speciation during electrolysis processes because they can be reduced and/or oxidized towards the formation of gaseous nitrogen (Eqs. (15)-(19)) and/or nitrates (Eqs. (15) and (20)) depending on values of applied electric charge, pH and electrode materials. Likewise, it is reported that nitrates can be easily reduced electrochemically to ammonium ions, while ammonium ions are almost electrochemically inactive (Amstutz et al. 2012, Kim et al. 2005, Kapałka et al. 2011), and they can only be oxidized chemically by active free chlorine (Eqs. (12)-(14)). In this context, organic nitrogen release mainly evolved into nitrites at low values of applied electric charge whereas nitrates and ammonium ions are generated from organic nitrogen release at high values of applied electric charge.

$$3\ NO_2^- + 2\ H^+ \leftrightarrow 2\ NO + NO_3^- + H_2O \quad (15)$$

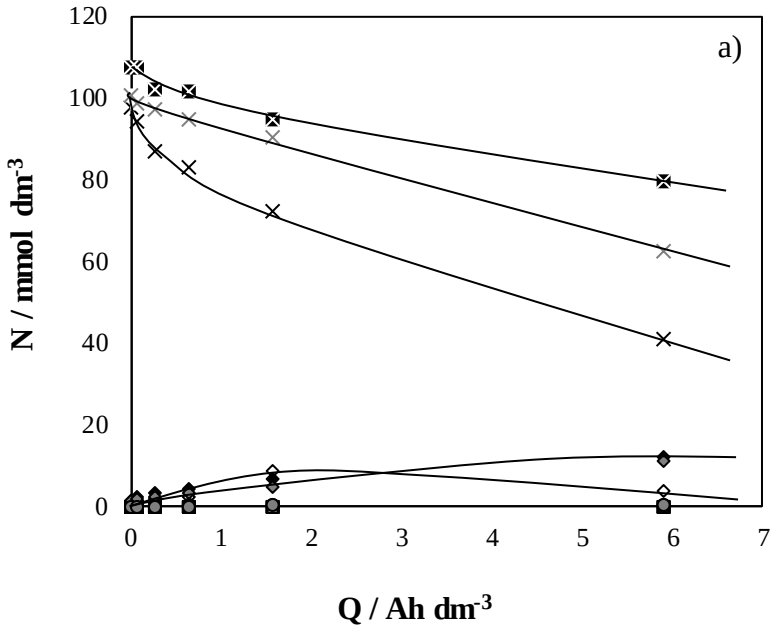
$$2\ NO + O_2 \rightarrow 2\ NO_2 \leftrightarrow N_2O_4 \quad (16)$$

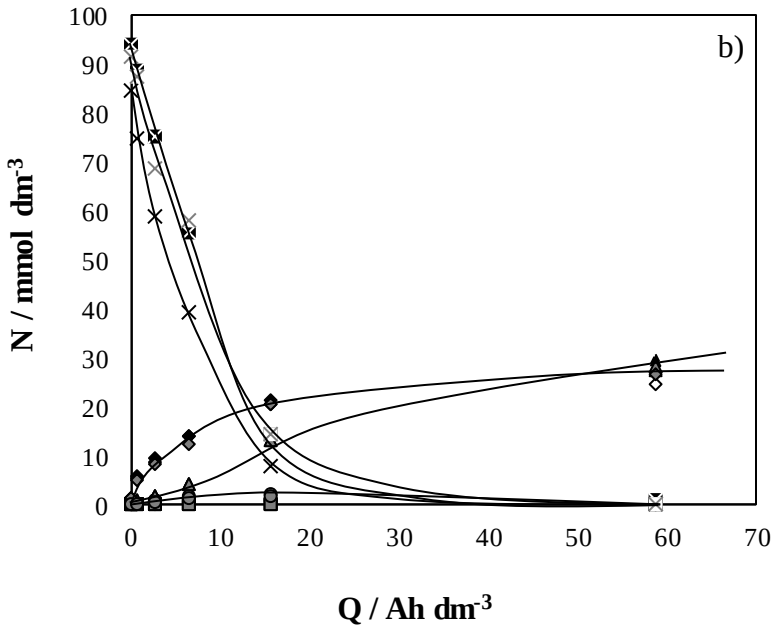
$$3\ NO \rightarrow N_2O + NO_2 \quad (17)$$

421 $NO + NO_2 \leftrightarrow N_2O_3$ (18)

422 $NO_2 + O_2 + NO \leftrightarrow N_2O_5$ (19)

423 $NO_2^- + \frac{1}{2} O_2 \rightarrow NO_3^-$ (20)





424

425 **Figure 7.** Influence of the current density on the evolution of nitrogen species as function
426 of the applied electric charge during the electrolysis process of chloramphenicol in
427 synthetic urine at (a) 10 mA cm^{-2} and (b) 100 mA cm^{-2}. (■) nitrite, (▲) nitrate, (♦)

amonium, (●) chloramines, (×) organic nitrogen. Black symbols: electrolysis, white symbols: photoelectrolysis; grey symbols: sonoelectrolysis.

Experimental results show how organic nitrogen is totally transformed into inorganic species over the tests, being slightly more efficient the conversion of organic nitrogen in the non-irradiated technology, both at high and low current densities. Ammonium is the primary species measured in the bulk and low concentration of nitrates and nitrites are also formed. Likewise, as pointed out before, ammonium is transformed into chloramines and nitrogen trichloride during the test, explaining the decrease in the total amount of nitrogen because of the formation of dinitrogen.

Finally, Table 3 depicts the electrochemical production of oxidant species during the six electrolysis tests.

Table 3. Maximum concentration of oxidants (mmol) produced after three hours of electrolysis.

j (mA cm^{-2})	**Electrolysis (mmol)**	**Photoelectrolysis (mmol)**	**Sonoelectrolysis (mmol)**
10	0.023	0.022	0.015
100	0.197	0.145	0.147

As it was explained in Figure 3, oxidant concentration increases over the electrolysis up to a plateau, which indicates that the rates between oxidant production and consumption in oxidation reactions is balanced. As observed, this maximum concentration depends on the current density, although the ratio obtained between oxidants at the two values tested

446 is lower than the ratio of current densities, suggesting that oxidants are more active at the
447 highest current densities because its concentration is higher. Likewise, the irradiation of
448 high-frequency US or UV light leads to lower steady-state concentrations of oxidants,
449 pointing out the effect of the activation by formation of radicals. At this point, it is
450 important to take in mind that the presence of oxidants is not a direct indicative of their
451 action but just the opposite. Thus, only are measured the oxidants that have not reacted
452 under given experimental conditions.

453

454 **4. Conclusions**

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

456 - CDEO can attain the total mineralization of chloramphenicol in urine. It also
457 attains the mineralization of the other three organic species contained in the urine
458 (uric acid, urea and creatinine). It means that this technology may be promising
459 for the treatment of hospital effluents, helping to avoid the diffusion of
460 pharmaceutical products in the environment if used before discharge to municipal
461 sewers.
462 - Irradiation of UV light or high-frequency US produce changes in the performance
463 of the electrolytic treatment but these changes are not as important as in other
464 cases of study shown in the literature. At low current densities, the effect seems
465 to be higher and depends on the type of pollutant. It is positive in the case of the
466 degradation of the antibiotic and the uric acid and negative in the case of urea.
467 - Current density has a significant influence on the performance of the CDEO based
468 technologies. Removal rate increases with current density although in lower ratio
469 than expected (lose of efficiency). At low current densities, the formation of

chlorates and perchlorates is prevented. Ammonium is the main nitrogen species formed during the electrolysis and the formation of chloramines by combination of hypochlorite and ammonium is a key reaction in the system. Production of oxidants increases with current density.

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