Conductive Diamond electrochemical oxidation of caffeine-intensified biologically treated urban wastewater

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Abstract

In this work, the usefulness of Conductive Diamond Electrochemical Oxidation (CDEO) to degrade caffeine in real urban wastewater matrixes was assessed. The oxidation of actual wastewater intensified with caffeine (from 1 to 100 mg L^{-1}) was studied, paying particular attention to the influence of the initial load of caffeine and the differences observed during the treatment of caffeine in synthetic wastewater. The results showed that CDEO is a technology that is capable of efficiently degrading this compound even at very low concentrations and that it can even be completely depleted. Profiles of the ionic species of S (SO_4^{2-}), N (NH_4^+, NO_3^-) and Cl (ClO^-, ClO_3^- and ClO_4^-) were monitored and explained for plausible oxidation mechanisms. It was observed that the efficiency achieved is higher in the treatment of real wastewater than in the oxidation of synthetic wastewater because of the contribution of electrogenerated oxidant species such as hypochlorite. The formation of chlorate and perchlorate during electrochemical processes was observed, and a combined strategy to prevent this important drawback was successfully tested based on the application of low current densities with the simultaneous dosing of hydrogen peroxide.

Key Words: Electrochemical oxidation, Boron Doped Diamond, persistent pollutant, real wastewater, caffeine

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Highlights

- CDEO shows a high efficiency in the removal of caffeine in urban wastewater.
- The presence of electrogenerated oxidants increases the efficiency in real medium.
- The N atoms present in the molecule of caffeine are oxidized to nitrate.
- Ammonium and hypochlorite can react to form chloramines.
- Operation mode must be modified to minimize the formation of chlorate and perchlorate.

1. Introduction

Persistent Organic Pollutants (POPs) are chemicals that possess a combination of physical and chemical properties that allow them to resist biodegradation and accumulate in the environment (Fitzgerald and Wikoff, 2014).

Recently, POPs have been detected in ground and drinking water, indicating that the conventional treatments performed in Municipal Wastewater Treatment Plants (MWTP) failed to completely remove them from the wastewater. In fact, recent studies have shown that biological treatment cannot completely degrade these compounds (Kim et al., 2014; Maeng et al., 2011) and as a consequence they are accumulated in the environment. Exposure to these compounds may have unpredictable consequences in aquatic environments and on public health (Lintelmann et al., 2003; Esplugas et al., 2007; Bachman et al., 2014; Pestana et al., 2014). Thus, an intensive research effort is needed to develop new technologies that can handle this environmental issue; currently, a great deal of research is particularly focused on the search for cost-effective technologies to effectively degrade POPs contained in wastewater, which is the primary source of the occurrence of these chemicals in the environment (Daughton, 2001; Lishman et al., 2006; Caliman and Gavrilescu, 2009; Giri et al., 2010; Martín de Vidales et al., 2012a; Martín de Vidales et al., 2012b, c; Tijani et al., 2013). Currently, Advanced Oxidation Processes (AOPs) are the most reliable technologies (Sirés et al., 2014). One promising AOP is Conductive Diamond Electrochemical Oxidation (CDEO). Typically, these processes have been studied for the treatment of synthetic wastewater, with initial concentrations of POPs on the order of mg L^{-1} in a synthetic matrix, to evaluate the feasibility of the process and obtain information about the oxidation mechanisms. However, a key step in the scaleup of this electrochemical technology is its study under conditions (e.g., pollutant concentration and water composition) that are similar to those of real effluents.

A wide range of variables may influence the performance of wastewater treatment. In the case of electro-oxidation, inorganic salts present in the medium can play an important role in the oxidation mechanisms of POP degradation (Serrano et al., 2002; Wang and Farrell, 2004; Murata et al., 2008; Polcaro et al., 2008; Bergmann et al., 2009). Even trace concentrations of elements, such as Fe, Mg or Co, are reported to influence wastewater treatments (Hermosilla et al., 2015). In addition, the oxidation of the target molecule (i.e., the POP to be degraded) is normally in competition with other organics and inorganics that are present in the aqueous matrix, which adds extra difficulty to the removal process. Therefore, experiments in synthetic medium need to be understood as a preliminary stage in the investigation of new processes because it is difficult to reproduce real conditions.

As mentioned above, one of the primary routes of pollutant occurrence in the environment is the discharge of insufficiently treated wastewater from industrial facilities or Municipal Wastewater Treatment Plants (MWTP) (Indermuhle et al., 2013). With this in mind, different studies aimed at degrading POPs by means of AOPs have been conducted on real effluents from MWTPs or industrial activities, although the application of CDEO is scarce. A common procedure is to intensify the wastewater, that is, to increase the POP concentration by adding an extra concentration of the compound, which helps in monitoring its degradation. This way, the analysis of the process becomes much simpler from an experimental point of view (Klamerth et al., 2010; Antoniou et al., 2013; Lee et al., 2013; Espejo et al., 2014; Miralles-Cuevas et al., 2014; Muz et al., 2014; Pešoutová et al., 2014) and oxidation mechanims can be discussed.

This work focuses on the treatment of real wastewater coming from a secondary reactor of a MWTP intensified with caffeine (1-100 mg L^{-1} of caffeine was added to wastewater) by using CDEO. Caffeine ($C_8H_{10}N_4O_2$) is an alkaloid belonging to methylxanthine family which acts as a central nervous system (CNS) stimulant, temporarily warding off drowsiness and restoring alertness. It is the world's most widely consumed legal psychoactive substance and thus, it can be presence in relatively high concentration in domestic wastewater (Lovett, 2005). Likewise, MWTF cannot degrade caffeine efficiently and it is also refractory to others well-known AOPs (Broséus et al., 2009; Rosal et al., 2009; Klamerth et al., 2010). For all these reason, this pollutant was chosen as a POP model. Besides caffeine degradation, in this work it is also evaluated the role of side reactions of other species (such as ionic species) present in the wastewater.

2. Materials and methods

2.1. Chemicals

The caffeine ($C_8H_{10}N_4O_2$) was analytical grade (> 99.0 % purity) and supplied by Sigma-Aldrich Laborchemikalien GmbH (Steinheim, Germany). The anhydrous sodium sulfate was analytical grade and purchased from Fluka. Sulfuric acid and sodium hydroxide, which were used to adjust the pH of the solution, were analytical grade and supplied by Panreac Química S.A. (Barcelona, Spain). Hydrogen peroxide (33 % w/v) was also supplied by Panreac Química S.A. (Barcelona, Spain).

2.2. Real wastewater

Real effluents were collected from secondary treatment of a MWTP located in Ciudad Real (Spain). An exhaustive characterization of these effluents was conducted, and the characteristics are shown in Table 1. It is important to note the low concentration of organic mass (TOC ≈ 13 mg L^{-1}) and the relatively high concentration of chloride and sulfate, which were above 110 and 80 mg L^{-1}, respectively.

2.3. Analytical procedures

The carbon concentration was monitored using a Multi N/C 3100 Analytik Jena TOC analyzer. Measurements of pH and conductivity were conducted with an InoLab WTW pH-meter and a GLP Crison conductimeter, respectively. Hydrogen peroxide was measured according with Eisenberg (1943).

The concentrations of caffeine and the generated intermediates were measured by HPLC–UV (Agilent 1100 series), and a 205 nm detection wavelength was used. The column temperature was 25 °C. The volume injection was set at 20 μL, and a Phenomenex Gemini 5 μm C18 analytical column was used. Solvent A was composed of 25 mM of a formic acid water solution, and Solvent B was acetonitrile. A linear gradient chromatographic elution was obtained by initially running 10 % of Solvent B and ascending to 100 % in 40 min. The samples extracted from the electrolyzed solutions were filtered with 0.20 μm Nylon filters before analysis.

Ionic species (NH_4^+, NO_3^-, NO_2^-, SO_4^{2-}, Cl^-, ClO_2^-, ClO_3^-, and ClO_4^-) were measured by ion chromatography using a Shimadzu LC-20A equipped with a Shodex IC I-524A column (anionic species) or Shodex IC YK-421 column (cationic species); mobile phase, 2.5 mM phthalic acid at pH 4.0; flow rate, $1 \cdot 10^{-3}$ dm^3 min^{-1} (concentration accuracy: ± 0.5 %). The peak corresponding to hypochlorite interferes with the peak of chloride; therefore, the determination of hypochlorite was conducted by titration with 0.001 M

As_2O_3 in 2.0 M NaOH. This method consists of a redox determination to selectively quantify the hypochlorite concentration. In particular, it is based on the redox reaction between the hypochlorite and arsenite. Hypochlorite is reduced to chloride by the continuous addition of arsenite, which is oxidized to arsenate. Pretreatment of the samples consists of the addition of $2 \cdot 10^{-3}$ dm^3 of NaOH (2 M) to increase the pH.

2.4. Electrochemical cells

The electrolyses were conducted in a compartment electrochemical flow cell working under batch-operation mode (Cañizares et al., 2005). A Conductive Diamond Electrode (p-Si-Boron Doped Diamond) was used as the anode and stainless steel (AISI 304) as the cathode. Both electrodes were circular (100 mm in diameter) and had a geometric area of 78 cm^2 and an electrode gap of 9 mm. The Boron Doped Diamond films were provided by Adamant Technologies (Neuchatel, Switzerland) and synthesized by the hot filament chemical vapor deposition technique (HF CVD) on single-crystal p-type Si <100> wafers (0.1 Ω cm, Siltronix).

2.5. Experimental procedures

The wastewater was stored in a glass tank and circulated through the electrolytic cell by means of a centrifugal pump (flow rate 21.4 dm^3 h^{-1}). The mass transfer coefficient (K_m) of the electrochemical cell within the fluid dynamic conditions used (21.4 dm^3 h^{-1}, 298 K) was $8 \cdot 10^{-6}$ m s^{-1} and was calculated using a standard $Fe(CN)_6^{3+}$/ $Fe(CN)_6^{2+}$ current limit test (Cañizares et al., 2006). A heat exchanger coupled with a controlled thermostatic bath (Digiterm 100, JP Selecta, Barcelona, Spain) was used to maintain the temperature at the desired set point (25 °C). A dosing system is also coupled to dose hydrogen peroxide with a mass flow ranging from 0.15 to 4.95 mg min^{-1}. The cell voltage did not vary during electrolysis, indicating that the conductive diamond layers did not undergo appreciable deterioration or a passivation phenomenon. Prior to use in galvanostatic electrolysis assays, the electrode was polarized for 10 min using a 0.035 M Na_2SO_4 solution at 30 mA cm^{-2} to remove impurities from the electrode surface.

3. Results and discussion

Figure 1 shows the TOC (part a) and caffeine (part b) profiles obtained during the treatment of wastewater samples coming from the secondary treatment of a MWTP intensified with caffeine (1-100 mg L^{-1} of caffeine as the initial concentration) by CDEO (semi-logarithmic scale is used in Figure 1b for a better comparison). The applied current density was 15 mA cm^{-2}. For comparative purposes, the profiles obtained during the CDEO of real wastewater without caffeine intensification and during the CDEO of synthetic wastewater polluted with 100 mg L^{-1} of caffeine in sulfate media are shown.

As expected, in every case, the electric current charge required for the total removal increases with the initial organic load. Additionally, it is important to note the higher efficiency of the process in real wastewater compared with the experiments conducted in synthetic medium with Na_2SO_4 as the supporting electrolyte.

Regarding the degradation of caffeine (part b), it seems to be again more efficient in real wastewater than in the synthetic medium, and, as expected, the applied electric charge necessary to achieve the complete removal of the compound also depends on the initial concentration of the pollutant: 16, 3.5, and 0.4 Ah L^{-1} are necessary for the removal of 100, 10 and 1 mg L^{-1} of caffeine, respectively. These electric charges are significantly lower than those required to attain complete mineralization, indicating the formation of reaction intermediates in the oxidation process. The HPLC analysis shows only one relevant peak, which could be associated with the degradation of caffeine (peak not contained in the initial matrix samples) and was identified as 1,7-dimethyl-1H-purine-2,6 (3H,7H) dione ($C_7H_8N_4O_2$) (Indermuhle et al., 2013). This compound behaved as an intermediate, and its complete degradation was achieved for electrical charges below 6 Ah L^{-1}. It is in accordance to the caffeine-oxidation pathways proposed in a previous work (Indermuhle et al., 2013). In addition, it was observed that the pH decreased at the end of the experiments conducted with real wastewater, which is the opposite of that observed in the case of the sulfate medium, where the final value is close to neutrality. This fact can be explained in terms of the complexity of the aqueous matrix and may be related to the formation and accumulation of intermediate acid species as a consequence of the oxidation of the organic compounds present in the real wastewater (Cañzares et al., 2003) or to the very important role of chlorides in the treatment of real wastewater, as previously noted (Rajkumar et al., 2007; Song et al., 2010; Madsen et al., 2015).

The concentration of some ionic species was also monitored during the experiments. Figures 2, 3 and 4 show the evolution of ionic species of S (SO_2^{4-}), Cl (ClO^-, ClO_3^- and ClO_4^-) and N (NH^{4+} and NO_3^-) in the reaction medium during the different treatments. The concentrations are shown in elemental units.

It is important to consider the variability of the wastewater under study. To avoid effects associated with the ageing of wastewater, it was decided to treat only fresh wastewater. As a consequence, the initial concentrations of the ionic species varied between the different experiments. In fact, the two wastewater samples used in the experiment without caffeine and with 10 mg L^{-1} of this compound had significantly higher initial ammonium concentration (Figure 4) than the other samples.

As observed in Figure 2, there are no significant variations in the sulfate concentrations during the electrolyses. As reported in the literature (Serrano et al., 2002; Cañizares et al., 2005; Cañizares et al., 2009), during the electrochemical oxidation of wastewater with a high concentration of sulfate, the generation of peroxodisulfate is expected (Eq. 1).

$$2\ SO_4^{2-} \rightarrow S_2O_8^{2-} + 2\ e^- \qquad [1]$$

This species has a high oxidizing power, and its decomposition can lead to H_2O_2 and other oxidants, which can chemically oxidize organic species. The constant profile of sulfate concentration observed during the experiments may be explained as follows:

- The electrochemical formation of peroxodisulfate from sulfate is not favored under the experimental conditions that were used (15 mA cm^{-2}). In fact, the application of current densities greater than 120 mA cm^{-2} (cell potential of 9.4 V) for the massive generation of this oxidative species is suggested (Cañizares et al., 2009).
- Pseudostationary responses: the consumption (oxidation to persulfate) and formation (reduction of persulfate) rates of the sulfate ion become comparable, which may be explained by the great oxidation capacity of persulfate ions, particularly when they are activated with other oxidants in bulk (Souza et al., 2013; Vidales et al., 2014).
- The oxidative competition by hydroxyl radicals between the formation of active chlorine species and persulfate (Bezerra Rocha et al., 2014).

Another important aspect is the evolution of chlorine oxidant species during electrolyses. As confirmed in Figure 3a, the oxidation of chloride may result in the formation of hypochlorite (Eqs. 2 to 4):

$$2\ Cl^- \rightarrow Cl_2 + 2e^- \qquad [2]$$

$$Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+ \qquad [3]$$

$$HClO \leftrightarrow ClO^- + H^+ \qquad [4]$$

Hypochlorite is an intermediate, and its oxidation can lead to the formation of different by-products, such as chlorite (ClO_2^-) and chlorate (ClO_3^-), via direct oxidation (Eqs. 5 to 8) or mediated by the oxidation of hydroxyl radicals (Eqs. 9 and 10) (Vacca et al., 2013):

$$2\ ClO^- \rightarrow ClO_2^- + Cl^- \qquad [5]$$

$$ClO^- + ClO_2^- \rightarrow ClO_3^- + Cl^- \qquad [6]$$

$$ClO^- + H_2O \rightarrow ClO_2^- + 2\ H^+ \qquad [7]$$

$$ClO_2^- + H_2O \rightarrow ClO_3^- + 2\ H^+ \qquad [8]$$

$$ClO^- + {}^\bullet OH \rightarrow ClO_2^- + H^+ + e^- \qquad [9]$$

$$ClO_2^- + {}^\bullet OH \rightarrow ClO_3^- + H^+ + e^- \qquad [10]$$

As Figure 3a shows, the hypochlorite concentration follows a typical profile of a reaction intermediate, with a maximum concentration value for electric charges of approximately 1-2 Ah L^{-1}, except for the experiment conducted with non-intensified water, where hypochlorite begins to disappear at higher electric charges (5.3 Ah L^{-1}). Chlorite is a very unstable species, which explains why it cannot be detected in the reaction media. However, chlorate accumulation begins at the same time as the disappearance of hypochlorite and attains its maximum concentration at around approximately 4 Ah L^{-1}.

From this point forward, the concentration of perchlorate begins to increase to achieve a stable value of approximately 150 mg L^{-1}.

According to the literature, the formation of perchlorate can be explained in terms of the decomposition of chlorate (Eq. 11) and/or the reaction between hydroxyl radicals and chlorate (Eq. 12). The first option is possible from the thermodynamic point of view; however, the reaction is not kinetically favored. For this reason, the second option is most probable as it has been proposed in a previous manuscript regarding the electrochemistry of chlorine with conductive diamond anodes (Sánchez-Carretero et al., 2011).

$$2\,ClO_3^- \rightarrow ClO_4^- + Cl^- \qquad [11]$$

$$ClO_3^- + {}^\bullet OH \rightarrow ClO_4^- + H^+ + e^- \qquad [12]$$

An important consideration is the hazard risk of chlorate and perchlorate formation in the aqueous medium given their toxicity. These compounds are thermodynamically stronger oxidants than hypochlorite is. However, they react slowly with organics at room temperature. Therefore, its contribution to organic mass degradation is expected to be negligible.

Concerning the ionic species of nitrogen (Figure 4), it was observed that the ammonium concentration (part a) slightly decreases during the experiments. This decrease is moderately higher in the experiment conducted with wastewater without intensification. On the contrary, the variation of nitrate in the medium (part b) is very significant. It is widely known that the oxidation of ammonium to nitrate is not favored because the positive charge of the ammonium ion prevents its approach to the anodic surface (which is also positively charged) and because direct contact is a necessary requisite for electronic transference (Jafvert and Valentine, 1992; Lee et al., 2002; Li et al., 2009; Lacasa et al., 2011). This result indicates that the increase in nitrate concentration may be related to the oxidation of the nitrogen contained in the molecule of caffeine (28.87 mg L^{-1} of N per 100 mg L^{-1}) and to the release of oxidized nitro-species by the rupture of the caffeine molecule. In this point, it was checked that the increase in nitrate concentration is directly related to the initial concentration of caffeine that is present in the reaction medium.

From a specific electric charge, the nitrate concentration decreases, this suggests that this anion is somehow reacting. According to previous studies (Tenne et al., 1993; Lacasa et al., 2011), nitrate is easily reduced to ammonium on cathodes, also for stainless steel. However, this decrease in the concentration of nitrate does not correspond to an increase in the concentration of ammonium (part a). This fact can be explained in terms of the reactivity between ammonium and hypochlorite (break-point chlorination) (Liu et al., 2009; Kapałka et al., 2010; Lacasa et al., 2012), which prevents the accumulation of ammonium in the media. The slight decrease in ammonium concentration indicates that the kinetic of the formation is slightly slower than that of disappearance.

Based on these results, the oxidation of persistent pollutants in real wastewater is heavily influenced by the mediated oxidation processes. Apart from the reaction of degradation of the pollutant, the electrons that are supplied with an applied electric charge are also involved in a series of side chemical and electrochemical reactions where inorganic species are implied. This behavior can affect the evaluated process efficiency. In fact, efficiency increases in the real medium because generated species can promote the degradation process. Hypochlorite formation from chlorine seems to be the reason behind the improvement in caffeine removal observed in real wastewater. This oxidant can easily and effectively react with caffeine, forming intermediates that will be subsequently oxidized to CO_2. In fact, in the non-intensified experiment, the concentration of hypochlorite was higher, and it took longer to completely disappear (Figure 3). This result means that in the rest of the experiments, caffeine and hypochlorite are reacting.

At this point, to demonstrate that the presence of hypochlorite in the medium improves the degradation of the organic mass, Figure 5 shows the percentage of TOC removal attained with the application of 2, 10 and 20 Ah L^{-1}, when the treatment of wastewater polluted with caffeine (100 mg L^{-1}) is conducted in different media (synthetic with Na_2SO_4 as the electrolyte at 15 mA cm^{-2}, synthetic with NaCl as the electrolyte at 30 mA cm^{-2} or real at 15 mA cm^{-2}). In general, in synthetic wastewater, higher process efficiency can be observed when NaCl is used as the supporting electrolyte, and in real wastewater, the process efficiency is even higher because of the joint contribution of hypochlorite and other oxidant agents present in the real water for the oxidation of organic mass.

The results shown in this paper noted one of the main drawbacks of the application of CDEO to the treatment of real wastewater: the formation of undesired byproducts such as chlorate and perchlorate. In fact, regulation is very strict with respect to the presence of chlorate and perchlorate in water and wastewater. Chloride is a typical anion in wastewater because it is typically contained in the wastewater supply and because urine is highly loaded with this anion. Thus, for the real application, preventing or at least reducing their formation is a matter of the utmost importance. With this in mind, two strategies were combined in this work: (1) the applied current density has been decreased to minimize the formation of chlorine species in the high-oxidation state, and (2) hydrogen peroxide has been dosed during the treatment to react with the electrogenerated hypochlorite.

Electrolysis experiments with an external dosage of hydrogen peroxide (0, 0.15 y 4.95 mg min^{-1}) were conducted for the treatment of wastewater polluted with 100 mg L^{-1} of caffeine by applying a current density of 5 and 15 mA cm^{-2}. Unfortunately, TOC concentration could not be monitored during these electrolyses because hydrogen peroxide interferes with the analytical technique, leading to erroneous mineralization values for the organic load. Figure 6 shows the caffeine concentration profiles (part a) and the variation of the concentration of chlorate (part b) and perchlorate (part c) during the electrochemical oxidation essays.

As can be observed, the process efficiency decreases with the presence of hydrogen peroxide in the reaction medium, regardless of the concentration of dosed H_2O_2 (at least within the concentration range evaluated). This behavior suggests that in presence of H_2O_2, mediated oxidation of the caffeine molecule by H_2O_2 does not occur (or at least, it is not a predominant oxidation mechanism), indicating that H_2O_2 reacts rapidly with other species that are present in the reaction medium. Likewise, in presence of H_2O_2, hypochlorite-mediated oxidation of the caffeine molecule takes place in less extension, either because of hypochlorite is not generated or because it reacts rapidly with other species.

According to the literature (Crump et al., 1998; Cotillas et al., 2015), hydrogen peroxide may act as an oxidant or reactant, depending on the composition of the reaction medium. Thus, H_2O_2 can react with hypochlorite to form chloride (Eq. 13) and with chlorate to form chlorine dioxide (Eq. 14). This could explain the lower process efficiency and the concentration profiles of the chlorine species obtained.

$$ClO^- + H_2O_2 \rightarrow Cl^- + 3/2\ O_2 + 2\ H^+ + 2\ e^- \qquad [13]$$

$$2\ H^+ + 2\ ClO_3^- + H_2O_2 \rightarrow 2\ ClO_2 + 2\ H_2O + O_2 \qquad [14]$$

Regarding the chlorate concentration (part b of the figure), it is significantly lower when H_2O_2 is present in the reaction medium. In addition, the formation of perchlorate is drastically inhibited when low current densities are applied.

On the other hand, if the experiments conducted with a dosage of 0.15 mg min^{-1} of H_2O_2 and a different applied current density (5 and 15 mA cm^{-2}) are compared, it can be observed that process efficiency decreases with the applied current density. In addition, a decrease in the current density reduces the formation of chlorine species in a high oxidation state (chlorate and perchlorate). Chlorate and perchlorate are oxidant agents that are kinetically slower than hypochlorite at room temperature. This could explain the lower efficiency observed at 15 mA cm^{-2}. For this reason, a reduction of the current density is also an interesting option to fulfill the regulations in terms of chlorate and perchlorate concentration.

These results demonstrate that electrochemical oxidation is a capable technology for the treatment of wastewater with chlorides and is promising for the removal of POPs, even in complex matrixes such as real wastewater. Therefore, using this technology creates the possibility of performing wastewater treatments by CDEO in industrial and municipal plants with a low formation of chlorine species at a high oxidation state (chlorate and perchlorate). However, a more exhaustive study is necessary to establish the optimal applied current density values and hydrogen peroxide concentrations, which would ensure the inhibition of high-oxidation-state chlorine by-products formation and would not significantly reduce the degradation process efficiency.

4. Conclusions

From this work, the following conclusions can be drawn:

- Treatment of real wastewater intensified with different concentrations of caffeine (1-100 mg L^{-1}) has demonstrated the high efficiency of Conductive Diamond Electrochemical Oxidation for use in the degradation of persistent pollutants. The efficiency achieved is even higher in real systems compared with a synthetic medium, which is due to the contribution of electrogenerated oxidant species such as hypochlorite.
- The evolution of the ionic species of N, S and Cl was monitored. Sulfate was nearly constant throughout all of the experiments. Variations in ammonium and nitrate were primarily due to the N atoms present in the molecule of caffeine, which are oxidized to nitrate, and to the reaction between ammonium and hypochlorite to form chloramines.
- The formation of chlorate and perchlorate during electrochemical processes may be minimized by decreasing the current density and/or dosing hydrogen peroxide into the reaction medium. This finding creates the possibility of treating wastewater with a high concentration of chlorides by means of CDEO. However, further experiments are needed to determine the optimal value at which the formation of these species would be avoided and the efficiency would not be significantly affected.

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Figure and Table Captions

Table 1. Characteristics of the secondary treatment effluent.

Figure 1. The influence of the initial POP concentration on TOC (a) and caffeine (b) removal in the treatment of real wastewater polluted with caffeine by CDEO. Operational

conditions: j = 15 mA cm^{-2}. Real wastewater: filled symbols. Synthetic wastewater: empty symbols (supporting electrolyte: Na_2SO_4, 0.035 M). (■) 100 mg L^{-1}, (▲) 10 mg L^{-1}, (●) 1 mg L^{-1}, and (♦) 0 mg L^{-1}.

Figure 2. The influence of the initial concentration of caffeine on sulfate profiles in the treatment of real wastewater by CDEO. Operational conditions: j= 15 mA cm^{-2}. (■) 100 mg L^{-1}, (▲) 10 mg L^{-1}, (●) 1 mg L^{-1}, and (♦) 0 mg L^{-1}.

Figure 3. The influence of the initial concentration of caffeine on ammonium (a) and nitrate (b) profiles in the treatment of real wastewater by CDEO. Operational conditions: j= 15 mA cm^{-2}. (■) 100 mg L^{-1}, (▲) 10 mg L^{-1}, (●) 1 mg L^{-1}, and (♦) 0 mg L^{-1}.

Figure 4. The influence of the initial concentration of caffeine on hypochlorite (a), chlorate (b) and perchlorate (c) profiles in the treatment of real wastewater by CDEO. Operational conditions: j= 15 mA cm^{-2}. (■) 100 mg L^{-1}, (▲) 10 mg L^{-1}, (●) 1 mg L^{-1}, and (♦) 0 mg L^{-1}.

Figure 5. The influence of the reaction medium on the percentage of TOC removal with the application of different electric charges. The synthetic medium with Na_2SO_4 as an electrolyte: [Caffeine]$_0$= 100 mg L^{-1}, 0.035 M Na_2SO_4, j= 15 mA cm^{-2}. The synthetic medium with NaCl as the electrolyte: [Caffeine]$_0$= 100 mg L^{-1}, 0.035 M NaCl, j= 30 mA cm^{-2}. Real medium: [Caffeine]$_0$= 100 mg L^{-1}, j= 15 mA cm^{-2}.

Figure 6. The influence of the concentration of dosed H_2O_2 on the degradation of caffeine (a) and the formation of chlorate (b) and perchlorate (c) during the treatment of real

wastewater by CDEO. Operational conditions: [Caffeine]$_0$= 100 mg L^{-1}, $Q_{H_2O_2}$= 0.3 mL min^{-1}. (■) 0 mg L^{-1}, j= 5 mA cm^{-2} (∆) 4.95 mg min^{-1}, j= 5 mA cm^{-2} (▲) 0.15 mg min^{-1}, j= 5 mA cm^{-2}, (□) 0.15 mg min^{-1}, j= 15 mA cm^{-2}.

Table 1.

Parameter	**Value**
Cl^- (mg Cl L^{-1})	110-180
NO_3^- (mg N L^{-1})	3-12
SO_4^{2-} (mg S L^{-1})	80-105
NH_4^+ (mg N L^{-1})	10-28
Turbidity (NTU)	10-11
TSS (mg L^{-1})	7-10
TOC (mg L^{-1})	12-14
COD (mg O_2 L^{-1})	35-42

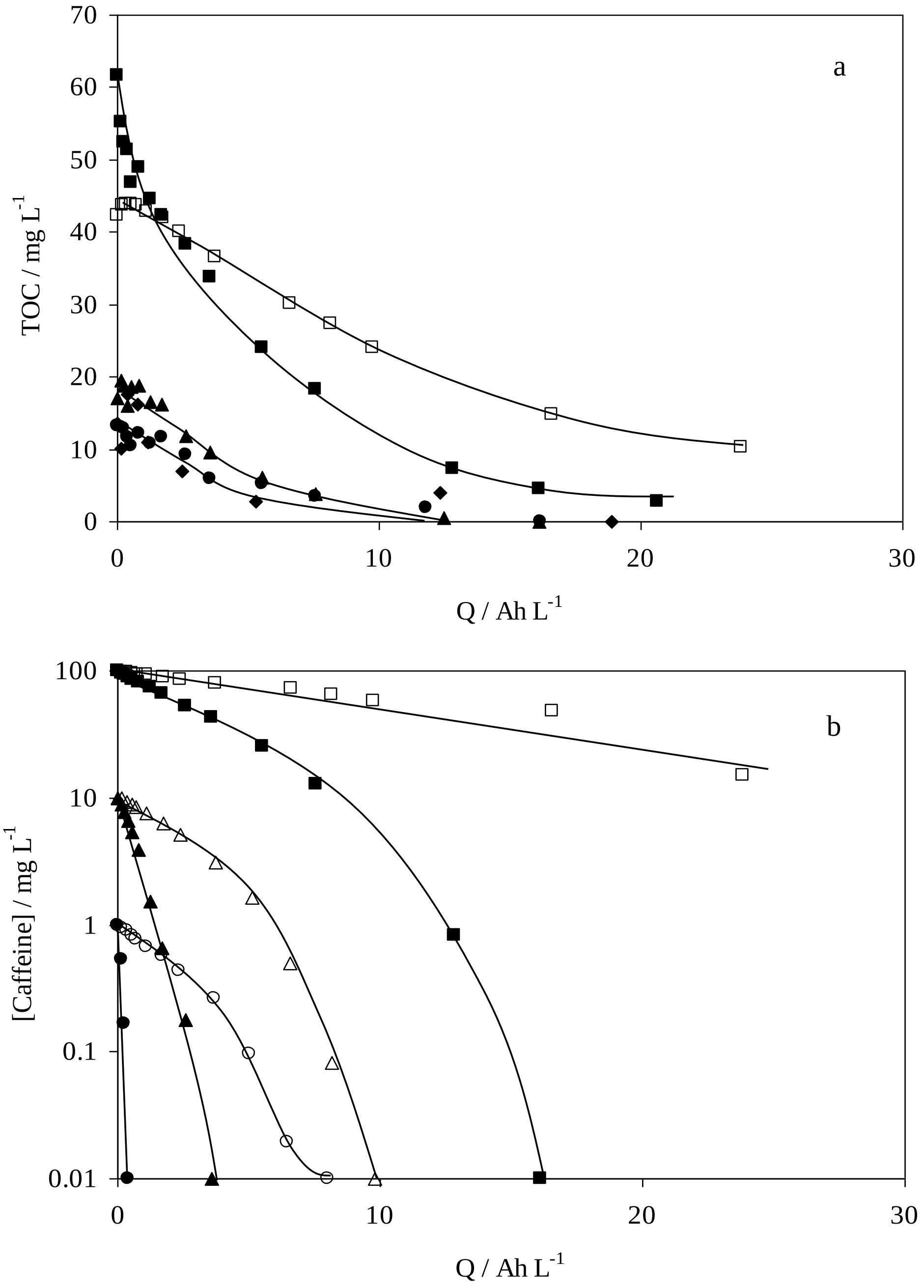
a
TOC / mg L^{-1}
0
10
20
30
40
50
60
70
Q / Ah L^{-1}
0
10
20
30
b
[Caffeine] / mg L^{-1}
0.01
0.1
1
10
100
Q / Ah L^{-1}
0
10
20
30

Figure 1

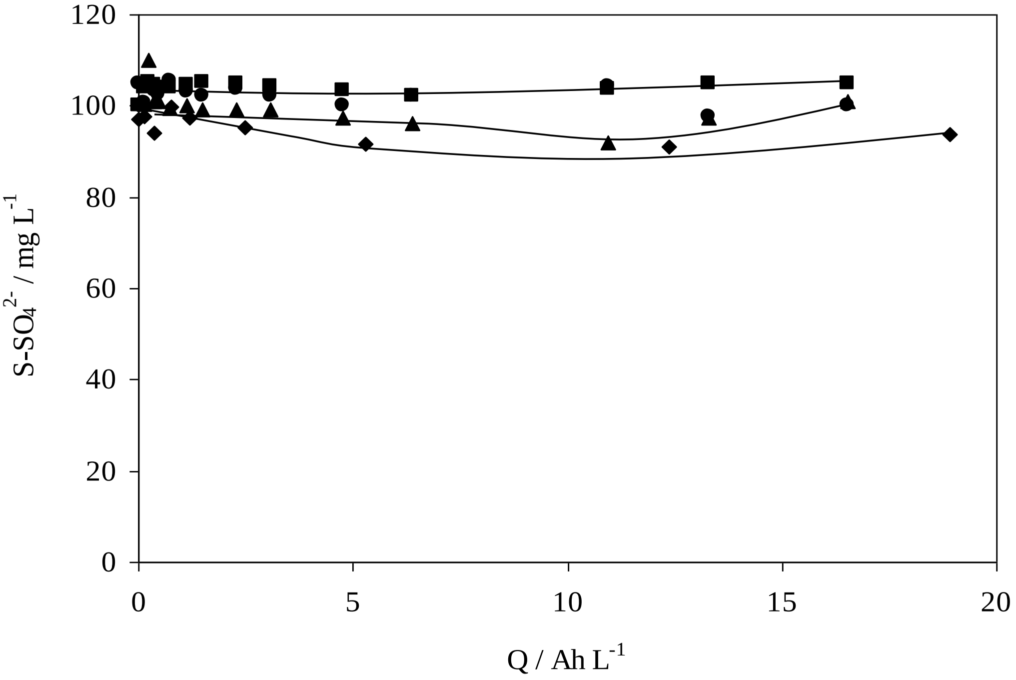

Figure 2

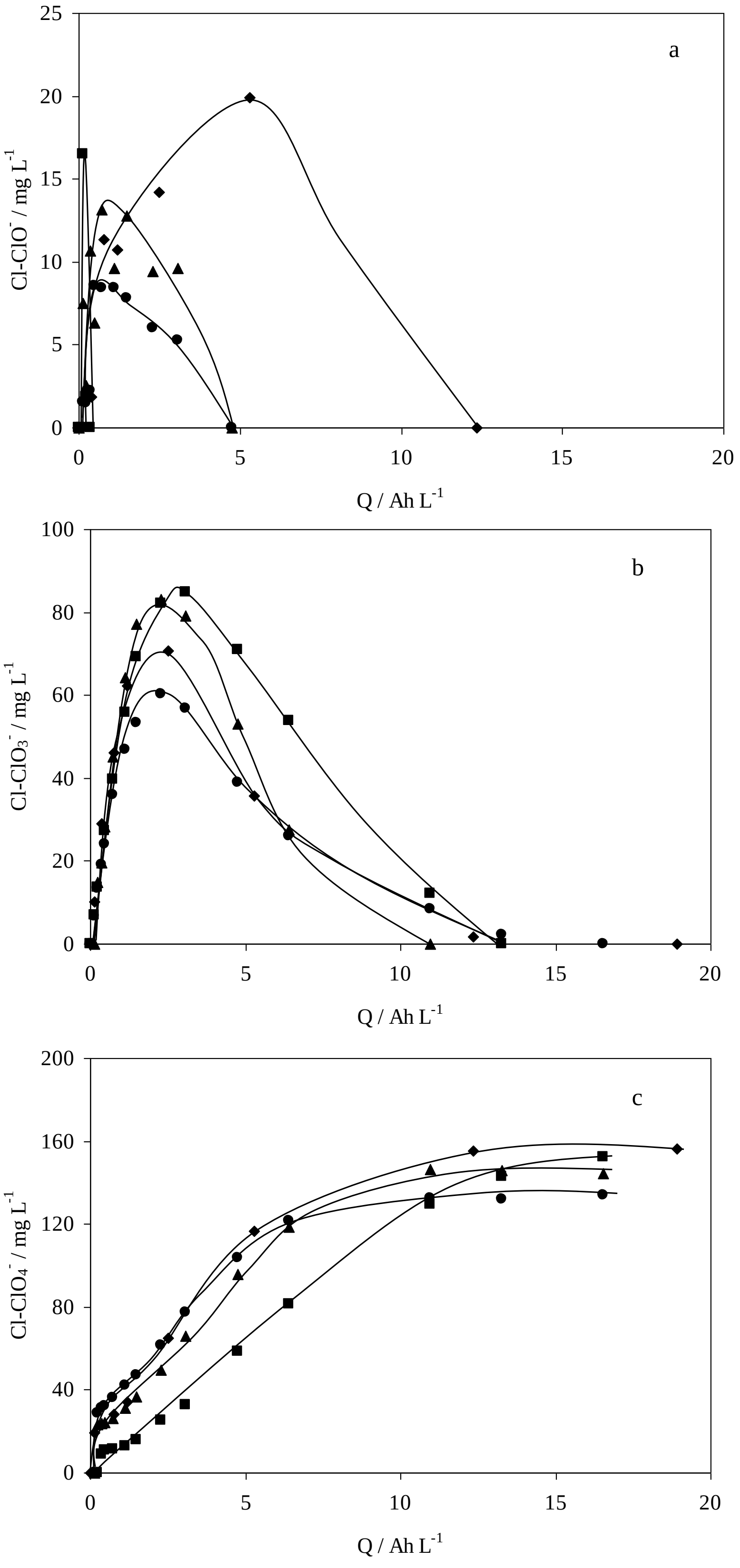
a
Cl-ClO$^-$ / mg L^{-1}
0
5
10
15
20
25
Q / Ah L^{-1}
0
5
10
15
20
b
Cl-ClO$_3^-$ / mg L^{-1}
0
20
40
60
80
100
Q / Ah L^{-1}
0
5
10
15
20
c
Cl-ClO$_4^-$ / mg L^{-1}
0
40
80
120
160
200
Q / Ah L^{-1}
0
5
10
15
20

Figure 3

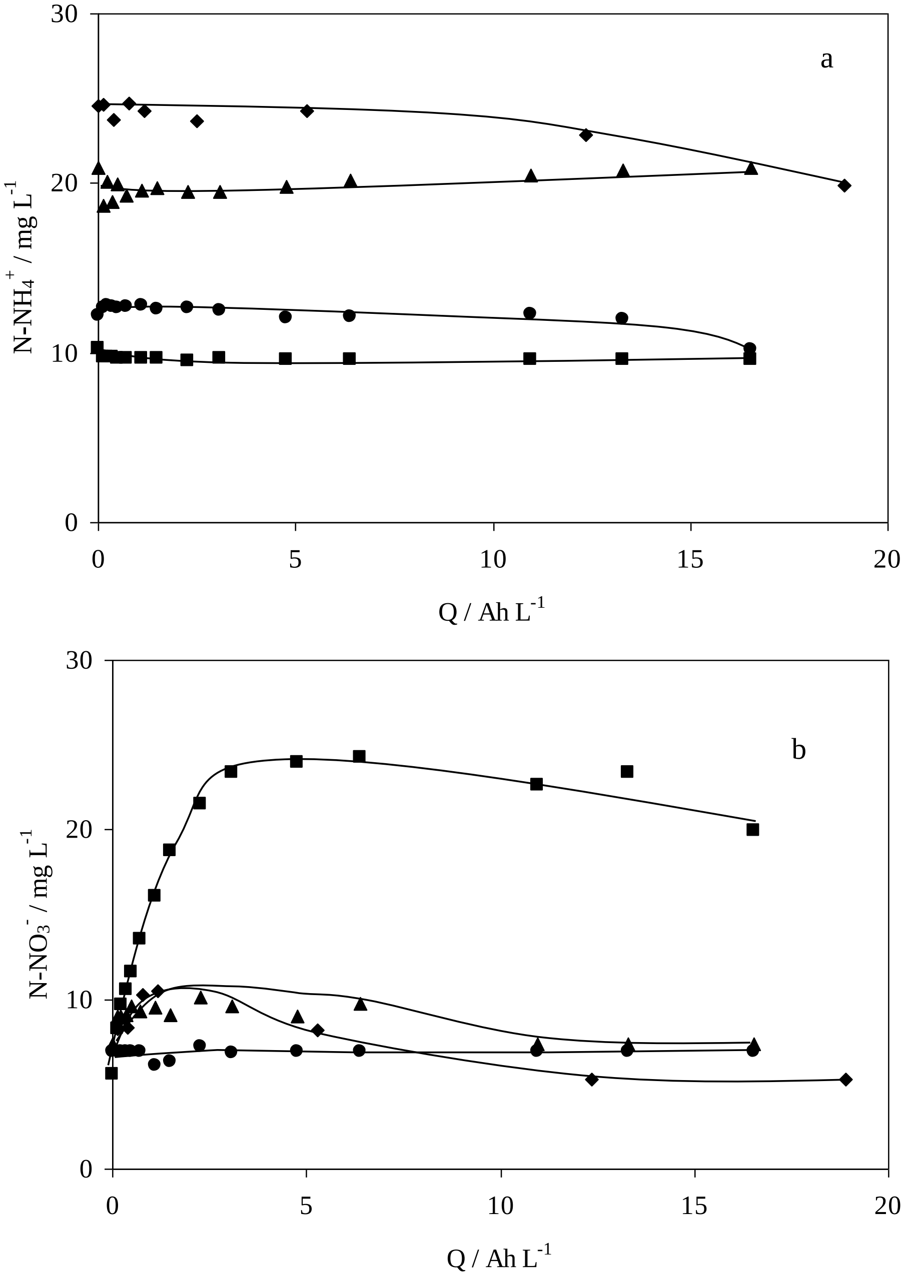
a
N-NH$_4^+$ / mg L^{-1}
0
10
20
30
0
5
10
15
20
Q / Ah L^{-1}
b
N-NO$_3^-$ / mg L^{-1}
0
10
20
30
0
5
10
15
20
Q / Ah L^{-1}

Figure 4

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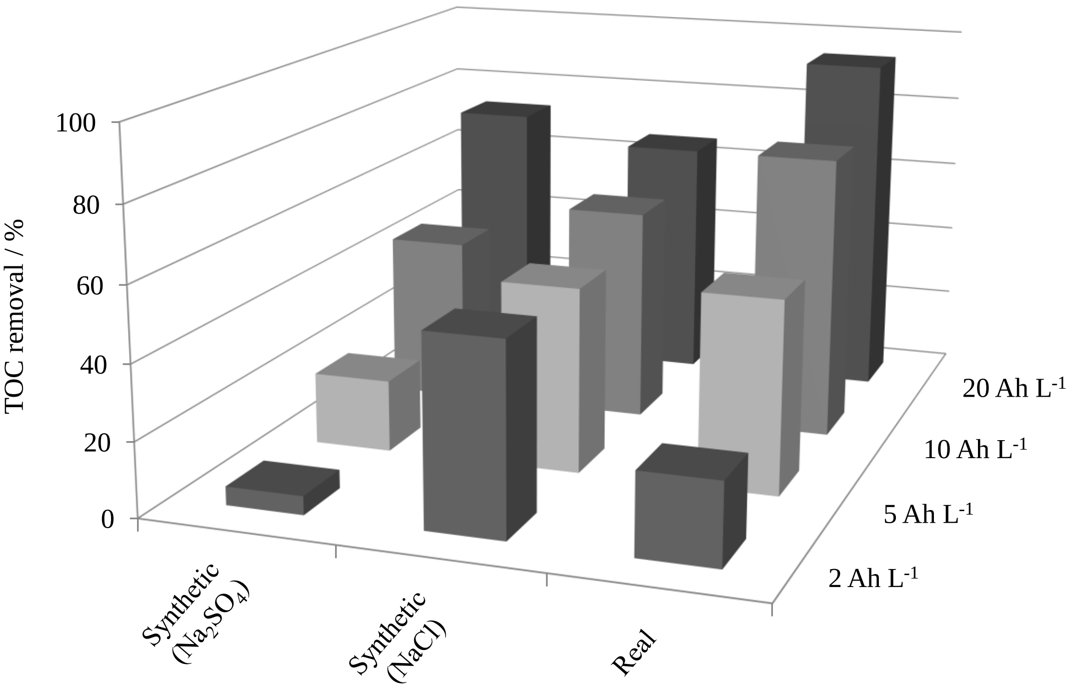

659 **Figure 5**

660

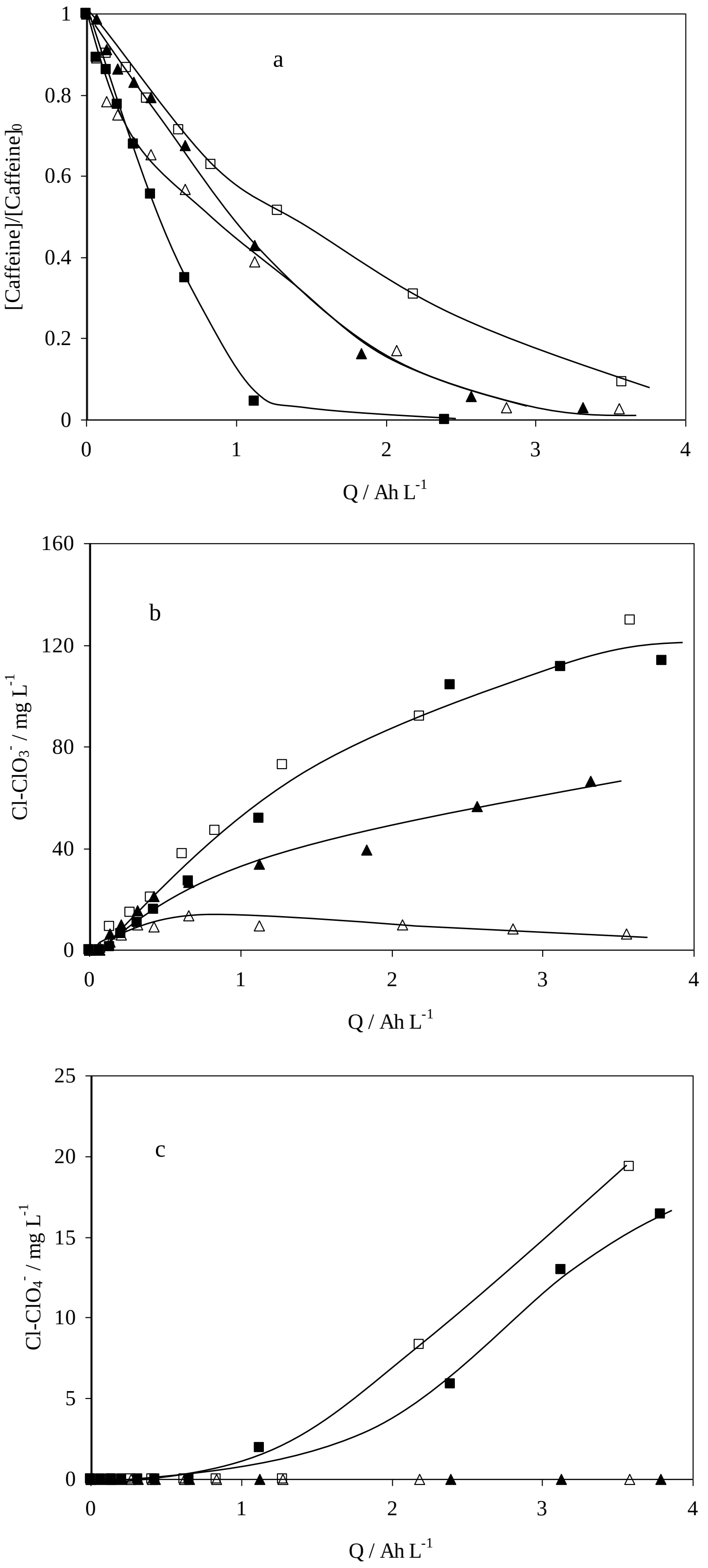
a
[Caffeine]/[Caffeine]$_0$
1
0.8
0.6
0.4
0.2
0
0
1
2
3
4
Q / Ah L^{-1}
b
Cl-ClO$_3^-$ / mg L^{-1}
160
120
80
40
0
0
1
2
3
4
Q / Ah L^{-1}
c
Cl-ClO$_4^-$ / mg L^{-1}
25
20
15
10
5
0
0
1
2
3
4
Q / Ah L^{-1}

Figure 6