# The contribution of mediated oxidation mechanisms in the electrolytic degradation of cyanuric acid using diamond anodes

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## ARTICLE INFO

## ABSTRACT

In this work, the contribution of mediated oxidation mechanisms in the electrolytic degradation of cyanuric acid using boron-doped diamond (BDD) anodes was investigated in different electrolytes. A complete mineralization of cyanuric acid was obtained in NaCl; however lower degrees of mineralization of 70% and 40% were obtained in $Na_2SO_4$ and $NaClO_4$, respectively. This can be explained by the nature of the oxidants electrogenerated in each electrolyte. It is clear that the contribution of active chlorine ($Cl_2$, HClO, $ClO^-$) electrogenerated from oxidation of chlorides on BDD is much more important in the electrolytic degradation of cyanuric acid than the persulfate and hydroxyl radicals produced by electro-oxidation of sulfate and water on BDD anodes. This could be explained by the high affinity of active chlorine towards nitrogen compounds. No organic intermediates were detected during the electrolytic degradation of cyanuric acid in any the electrolytes, which can be explained by their immediate depletion by hydroxyl radicals produced on the BDD surface. Nitrates and ammonium were the final products of electrolytic degradation of cyanuric acid on BDD anodes in all electrolytes. In addition, small amounts of chloramines were formed in the chloride medium. Low current density ($\leq 10$ mA/cm$^2$) and neutral medium (pH in the range 6–9) should be used for high efficiency electrolytic degradation and negligible formation of hazardous chlorate and perchlorate.

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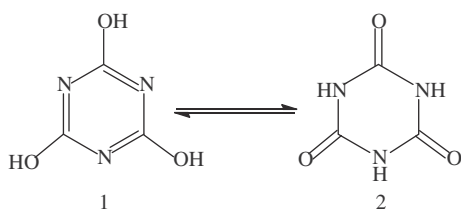Published by Elsevier B.V.

## Introduction

Cyanuric acid (2,4,6-trihydroxy-1,3,5-triazine) is an important industrial product widely used as an ingredient in the production of industrial cleansers, fire retardants, scouring powders, household bleaches, and automatic dishwasher components (Miao et al., 2009). It is also widely used as a stabilizer in swimming pools to prevent the destruction of chlorine by solar irradiation (Yu et al., 2009). Cyanuric acid is in equilibrium with its tautomeric form known as isocyanuric acid (the term cyanuric acid is often used for the two tautomers) (see Fig. 1).

The measured pKa values of cyanuric acid are 6.9, 11.4, and 13.5. The trianion is best described by the fully deprotonated form of cyanuric acid. It is highly polar and hydrophilic due to the presence of hydroxide groups in the structure, and fairly stable under many environmental conditions (Stipicevic et al., 2013; Tetzlaff and Jenks, 1999).

It has been reported in the literature (Tetzlaff and Jenks, 1999; Oh and Jenks, 2004; Garcia-Lopez et al., 2007; Dbira et al., 2014) that cyanuric acid is resistant to oxidation by hydroxyl radicals. Dbira et al. (2014) showed that no degradation of cyanuric acid was obtained by hydroxyl radicals generated

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**Fig. 1 – Chemical structure of cyanuric acid tautomers: (1) cyanuric acid, (2) isocyanuric acid.**

during the photo-Fenton process and no nitrate ions and no carbon dioxide are formed for long-period irradiation experiments during degradation of atrazine herbicides. In addition, Watanabe et al. (2005) showed that no degradation was obtained during treatment of cyanuric acid with Fenton's reagent and UV/TiO$_2$ photolysis. These results can be explained by the fact that the carbon atoms contained in cyanuric acid are in a higher oxidation state (+IV), formally at the same oxidation state as in CO$_2$, and consequently oxidation of the carbon contained in cyanuric acid by oxidation processes is not possible. The degradation of cyanuric acid seems to be possible only through the oxidization of the nitrogen of the triazine ring. Urea, where carbon exists in oxidation state +IV, has been completely degraded by advanced oxidation processes. Tetzlaff and Jenks (1999) showed that the resistance of cyanuric acid to degradation by advanced oxidation processes is not simply due to the oxidation state of carbon, but the reversibility of substitution reactions of OH groups by hydroxyl radicals HO. might explain the unique properties of cyanuric acid. In addition, several authors reported the formation of cyanuric acid as a final product of microbial degradation, chemical or photo-oxidation of s-triazine herbicides. Thus, it is necessary to find a suitable technology that allows depletion of cyanuric acid.

Recently, electrochemical advanced oxidation processes (EAOPs) have been efficiently used to remove cyanuric acid and s-triazine herbicides from water (Malpass et al., 2013; Oturan et al., 2012; Polcaro et al., 2005; Borras et al., 2010; Balci et al., 2009). In particular, electrochemical oxidation on boron doped diamond (BDD) anodes achieved complete mineralization of cyanuric acid. The high efficiency of electrochemical oxidation on BDD anodes is mainly explained by the synergetic effects of (1) the direct electro-oxidation on the surface of anode, (2) the oxidation by means of hydroxyl radicals in a region close to the electrode surface, and (3) the oxidation mediated by oxidants electrogenerated on the BDD surface from the electrolyte salts in the bulk solution. The importance of the contribution of each pathway in the overall efficiency of electrochemical oxidation on the BDD anode is still ambiguous, and the role of the oxidants electrogenerated on the BDD anode from the oxidation of supporting electrolytes has not been well investigated. Thus, the aim of the present work is to investigate the role of mediated oxidation mechanisms in the degradation of cyanuric acid by electrochemical oxidation using BDD anodes. Cyanuric acid was selected for study in this work because it is well documented that hydroxyl radicals are

inefficient at degrading it (Dbira et al., 2014; Tetzlaff and Jenks, 1999; Watanabe et al., 2005). Consequently, any degradation observed at the beginning of the treatment of cyanuric acid aqueous solutions can be attributed to either direct oxidation on the surface of the BDD anode or mediated oxidation by oxidants electrogenerated from the oxidation of electrolyte salts at BDD anodes. To do this, the electrochemical oxidation of cyanuric acid aqueous solutions was carried out in different supporting media in order to increase the understanding of the role of mediated oxidation on the degradation process. The effects of some experimental parameters including current density, initial pH, and initial concentration of cyanuric acid on the efficiency of the degradation of cyanuric acid by electrochemical oxidation on BDD anodes were also evaluated.

# 1. Materials and methods

## 1.1. Chemicals

Cyanuric acid was purchased from Fluka. The other chemicals such as NaCl, NaClO$_4$, and Na$_2$SO$_4$ were of analytical grade and were purchased from Sigma-Aldrich. All solutions were prepared with deionized water with 18 MΩ/cm resistivity from a Milli-Q™ system. The initial pH was adjusted to the appropriate value with analytical grade sulfuric acid and or sodium hydroxide, both purchased from Acros.
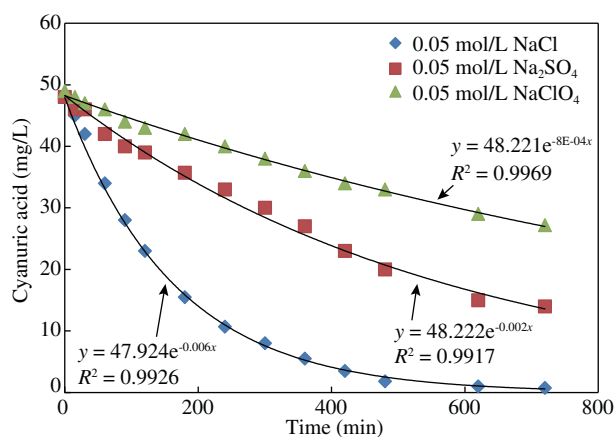
## 1.2. Analytical methods

The chromatographic analyses of cyanuric acid were performed using isocratic conditions on a Shimadzu high performance liquid chromatography (HPLC) system (model LC-10AD VP, Shimadzu, USA) with a reverse-phase column (C18, Supelco) coupled with a L-7455 photodiode array detector selected at the wavelength of 213 nm. The mobile phase consisted of 93:7 (V/V) phosphate buffer/methanol at flow rate of 0.8 mL/min at 30°C. The phosphate buffer of pH 7.3 was composed of 0.00625 mol/L NaH$_2$PO$_4$ and 0.0125 mol/L Na$_2$HPO$_4$. The total organic carbon (TOC), total nitrogen (TN), total Kjeldahl nitrogen (TKN), and nitrate–nitrite nitrogen (NN) were monitored with a TOC/TN analyzer (Formacs$^{HT-I}$ TOC/TN analyzer, Skalar, Netherlands) The formation of inorganic ions (nitrate, nitrite, chloride, hypochlorite) was determined using ion chromatography (Dionex ICS 2000 ion chromatograph, Thermo Scientific™ Dionex™ products, USA) equipped with an AS autosampler, Ion Pac AG 19 (4 mm × 50 mm) guard column, Ion Pac AS 19 (4 mm × 250 mm) analytical column, ASRS 300 mm–4 mm suppressor, DS6 conductimetric cell and an EGC eluent generator. The mobile phase was 20 mmol/L aqueous solution of potassium hydroxide KOH prepared by dilution of 1 mol/L aqueous solution of KOH. Ammonium ion analysis was performed using ion selective electrode (Ion-Selective Electrodes NH4-BTA, Vernier, USA). Measurement of inorganic chloramines was conducted by the DPD colorimetric method 4500-Cl G (APHA, 2005) (test kit and pocket colorimeter, HACH, USA).

### 1.3. Electrochemical experiments

The electrochemical experiments were carried out in a single-compartment cylindrical electrochemical cell with a double jacket in which water is circulated to maintain the solution temperature at room temperature. Parallel rectangular electrodes with a geometric area of 30 cm$^2$ and an inter-electrode gap of 1 cm were used. BDD and Pt electrodes were used as anodes, while a stainless steel (AISI 304) was the cathode material. BDD films were provided by CSEM (Neuchatel, Switzerland) and synthesized by the hot filament chemical vapor deposition technique (HF CVD) on single-crystal p-type Si (100) wafers (0.1 V cm Siltronise). Prior to use in electrolysis, the BDD electrode was polarized for 10 min in a 0.05 mol/L H$_2$SO$_4$ solution at 20 mA cm$^2$ to remove any impurities from its surface. Platinum sheet of 99.99% purity from Advent Research Materials (Oxford, England, UK) was also used as an anode material in this work. Electrolyses were carried out in galvanostatic mode under constant stirring with a Teflon-coated magnetic bar at 300 r/min. The electrodes were connected to a digital DC power supply with galvanostatic operational options (Monacor PS-430) providing current and voltage in the range of 0–30 Å and 0–20 V. A fixed current intensity in the range 30–1200 mA was applied from the power supply during electrolysis and the cell voltage was recorded using a potentiometer (Micronal B474 potentiometer, Brazil). At designated time intervals, samples were taken from the solution and then filtered by 0.45-μm membrane for analysis.
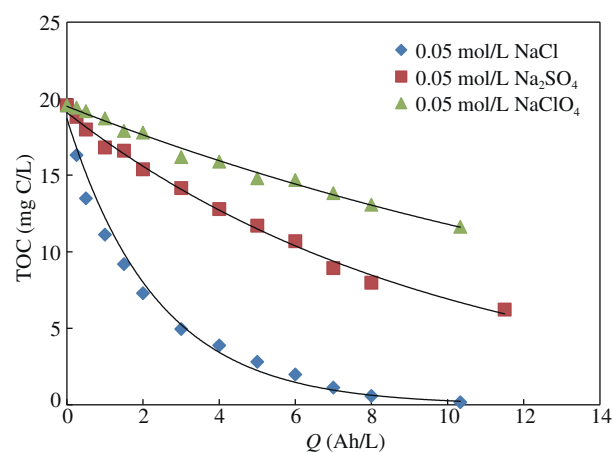
## 2. Results and discussion

Fig. 2 presents the changes in cyanuric acid concentrations with time during the electrochemical oxidation of 50 mg/L cyanuric acid on a BDD anode at a constant current density $j = 20$ mA/cm$^2$ in different electrolyte solutions (NaCl, Na$_2$SO$_4$, and NaClO$_4$). An exponential decline in cyanuric acid concentration with time was observed in all the electrolyte solutions, indicating pseudo-first order kinetics for the electrochemical degradation process. The pseudo-first order rates of cyanuric acid degradation were 0.006, 0.002, and 0.0008/min in 0.05 mol/L NaCl, Na$_2$SO$_4$, and NaClO$_4$, respectively. Cyanuric acid could be depleted completely within 12 hr' electrolysis in 0.05 mol/L NaCl, while in the same period of time only 70% and 40% of cyanuric acid were removed in Na$_2$SO$_4$ and NaClO$_4$, respectively. It is obvious that the degradation of cyanuric acid was more rapid and more efficient in the presence of NaCl, which is in agreement with the results reported by other authors during the degradation of s-triazine herbicides (Malpass et al., 2013; Oturan, 2000; Polcaro et al., 2005; Borras et al., 2010; Balci et al., 2009). Fig. 3 presents the results of mineralization of cyanuric acid in terms of TOC changes, with specific electrical charge in Ah/L, during the same experiments. As can be observed, a decline in TOC was observed in all the electrolytes, indicating that the triazine ring was gradually opened and mineralization of organic carbon into CO$_2$ took place during the electrolysis. The TOC removal was more efficient in NaCl than in Na$_2$SO$_4$ and NaClO$_4$. The electrolysis of cyanuric acid in Na$_2$SO$_4$ was more efficient than that in NaClO$_4$. Almost complete mineralization of cyanuric acid was achieved in NaCl after consumption of 12 Ah/L; however, for the same specific electrical charge, the electrolyses of cyanuric acid in Na$_2$SO$_4$ and NaClO$_4$ achieved 70% and 40% TOC removal, respectively. It is remarkable that the percentage of decreases for cyanuric acid and TOC removals were the same for all the electrolytes. These results indicate that the intermediates of degradation of cyanuric acid are easier to degrade by electrochemical oxidation on BDD anodes than cyanuric acid itself, and that they are immediately mineralized once they are formed. This is in agreement with the results of Polcaro et al. (2005), reporting that no degradation intermediates were detected during the electrochemical oxidation of cyanuric acid on BDD anodes.



Fig. 2 – Influence of supporting electrolyte on the degradation of cyanuric acid during galvanostatic electrolyses on boron-doped diamond (BDD) anode. Experimental conditions: 50 mg/L cyanuric acid, $j = 20$ mA/cm$^2$, pH = 6.0, temperature = 25°C, 300 r/min.
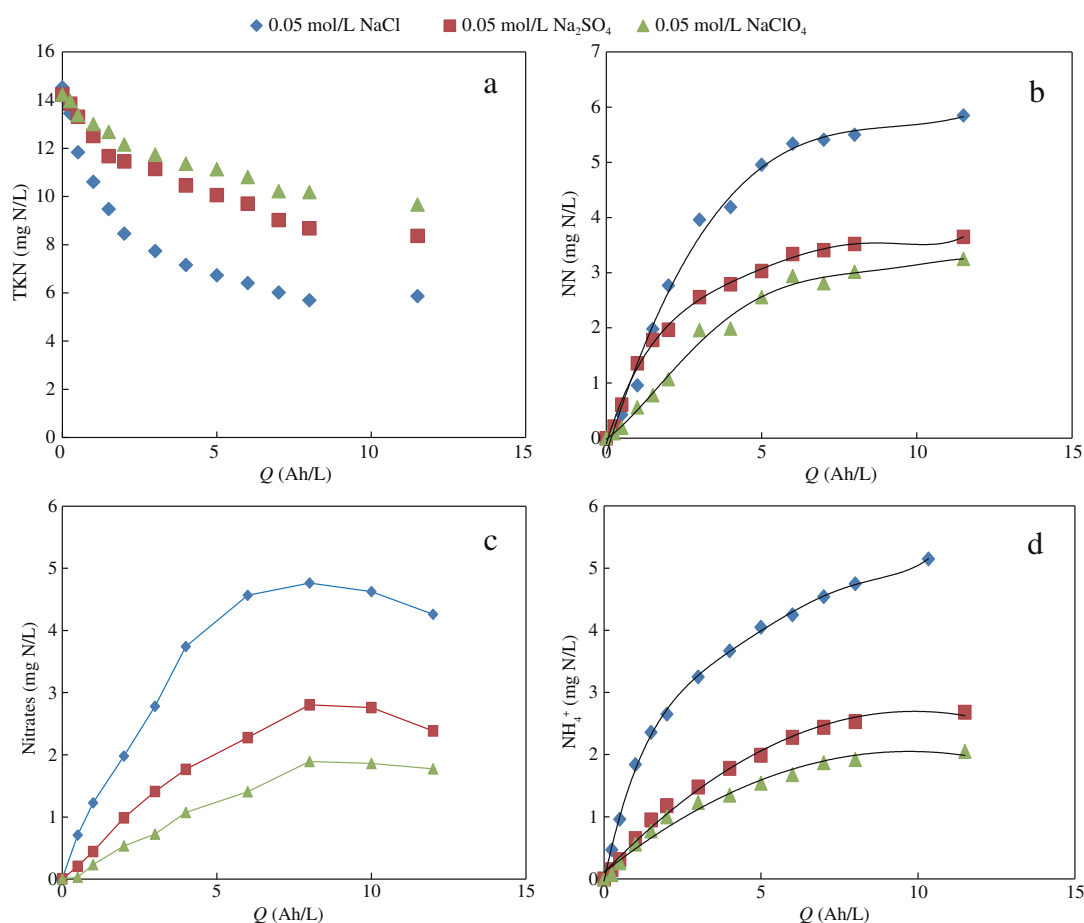


Fig. 3 – Influence of supporting electrolyte on the mineralization of cyanuric acid during galvanostatic electrolyses on BDD anode. Experimental conditions: 50 mg/L cyanuric acid, $j = 20$ mA/cm$^2$, pH = 6.0, temperature = 25°C, 300 r/min.

To obtain more details about the degradation of cyanuric acid by electrochemical oxidation on BDD anodes, additional chemical analyses were also conducted. Fig. 4 presents the changes in TKN, NN, nitrates, and ammonium (all in mg N/L) during galvanostatic electrolysis of 50 mg/L cyanuric acid at 20 mA/cm$^2$ in 0.05 mol/L NaCl, Na$_2$SO$_4$ and NaClO$_4$. TKN content (organic nitrogen and ammonia/ammonium nitrogen) decreased from the beginning of electrolysis in all electrolyte solutions, and then it remained unchanged after the consumption of 7.5 Ah/L (Fig. 4a). The decline in TKN was also more efficient in NaCl than in the other electrolytes, confirming the results for TOC. TKN decay at the beginning of electrolysis was very similar in Na$_2$SO$_4$ and NaClO$_4$. After the consumption of 12 Ah/L, TKN content decreased from 14.3 mg N/L to 5.8, 8.4, and 9.6 mg N/L in NaCl, Na$_2$SO$_4$, and NaClO$_4$ solutions, respectively. The decay of TKN during electrolysis confirms the opening of the triazine ring and shows that part of the organic nitrogen was oxidized to higher oxidation states. On the other hand, NN nitrogen showed a progressive increase from the beginning of electrolysis to reach a plateau at the end (Fig. 4b). A higher amount of NN nitrogen was formed in NaCl than in the other electrolytes, demonstrating that harsher oxidation of cyanuric acid

occurred in NaCl. NN nitrogen concentrations measured at 12 Ah/L were 5.85, 3.65, and 3.25 mg N/L in NaCl, Na$_2$SO$_4$ and NaClO$_4$, respectively. These results reveal that the organic nitrogen initially contained in cyanuric acid was partially transformed into NN nitrogen during electrochemical oxidation on the BDD anode. More details about the forms of inorganic nitrogen formed can be obtained from the analysis of nitrates by ion chromatography. Nitrate concentration increased to reach a maximum after consumption of 7.5 Ah/L and then started to decline after that point in all electrolytes. A maximum amount of nitrate of 4.8 mg N/L was measured in NaCl, while 2.8 and 1.9 mg N/L were measured in Na$_2$SO$_4$ and NaClO$_4$. Based on the results of NN nitrogen and ion chromatography analyses, the major part of NN nitrogen was in the form of nitrates; however small amounts of nitrites could be calculated from mass balance. The decrease of nitrate concentrations can be explained by its chemical or electrochemical reduction to less oxidized forms (NO$_2^-$, NH$_3$, NH$_4^+$) as mentioned in other studies (Dbira et al., 2015a, 2015b; De Araujo and Martínez-Huitle, 2015; Hu et al., 2009; Xiao et al., 2009).

Taking into account the results of TOC, TKN, NN and nitrates, it is clear that the organic nitrogen was not completely



**Fig. 4 – Influence of supporting electrolyte on the changes with time of (a) total Kjeldahl nitrogen (TKN), (b) nitrate–nitrite nitrogen (NN), (c) nitrates, and (d) ammonium during galvanostatic electrolyses on BDD anode. Experimental conditions: 50 mg/L cyanuric acid, j = 20 mA/cm$^2$, pH = 6.0, temperature = 25°C, 300 r/min.**

transformed into nitrates and nitrites. The difference can be explained by the formation of ammonium and other volatile nitrogen species. Fig. 4d shows the changes of concentration of ammonium measured during electrolyses in the three different electrolytes. As it can observed, ammonium ions were formed during electrolytic degradation of cyanuric acid, indicating that part of the TKN was in the form of ammonium ions. The concentration of ammonium ions increased at the beginning of electrolysis to reach a plateau at 5.2, 2.7, and 2.0 mg N/L in NaCl, $Na_2SO_4$, and $NaClO_4$ solutions, respectively. Based on the mass balance equation for nitrogen (VN = $TKN_0$ – ($NN_t$ + $TKN_t$), with VN representing the volatile nitrogen, $TKN_0$ is the initial TKN, and $NN_t$ and $TKN_t$ are NN and TKN at an time t, respectively), it was found that 3.0, 2.2, and 1.3 mg N/L escaped from the solution as volatile nitrogen species ($NH_3$, $NH_2Cl$, $NHCl_2$, $NCl_3$, $N_2$, and $NO_x$).
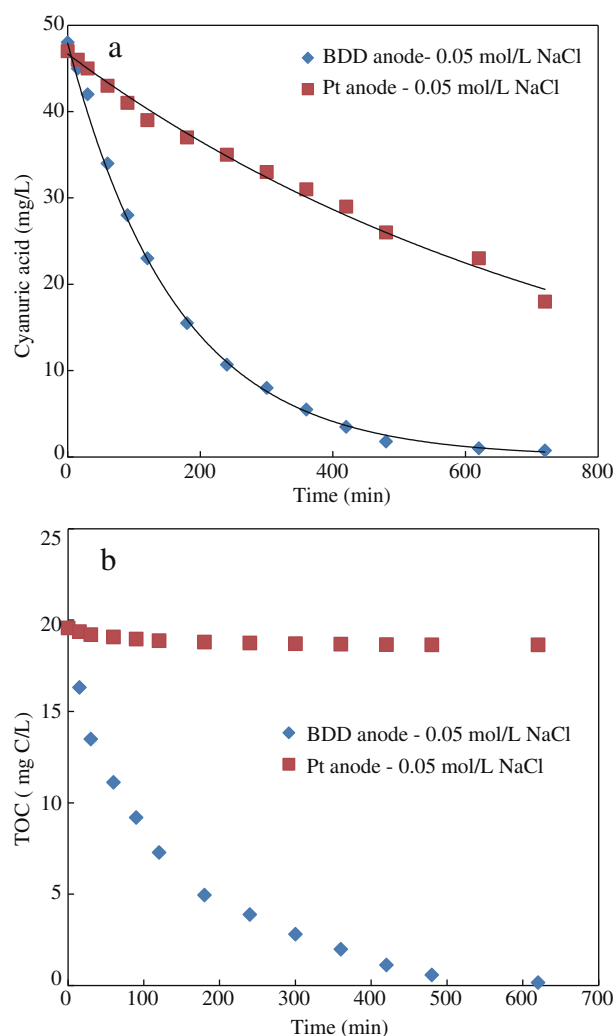
The results of electrolytic degradation and mineralization of cyanuric acid on the BDD anode show an important influence by the supporting electrolyte on the kinetics and efficiency of the electrochemical process. This can be explained by the nature of oxidants electrogenerated in each electrolyte. It is well-known that during electrolysis on the BBD anode, an important production of hydroxyl radicals takes place in the vicinity of the BDD surface (Marselli et al., 2003; Michaud et al., 2003; Oturan, 2000; Oturan et al., 2001; Bensalah et al., 2005) which is common for all electrolytic solutions. No additional oxidants can be electrogenerated in the presence of perchlorates ($NaClO_4$). However, in addition to hydroxyl radicals, chlorine gas ($Cl_2$), hypochlorous acid (HClO), and hypochlorite ($ClO^-$) can be produced from the oxidation of chlorides on BDD anodes (Ferro et al., 2000, Martinez-Huitle et al., 2005; Xiao et al., 2009), and persulfate ($S_2O_8^{2-}$) can be generated by oxidation of sulfate ions ($SO_4^{2-}$) at BDD anodes (Serrano et al., 2002; Michaud et al., 2001).

The mechanism of degradation of cyanuric acid involves several oxidation pathways: (1) direct oxidation on the surface of the BDD anode, (2) indirect oxidation by hydroxyl radicals in a region very close to the BDD surface, and (3) mediated oxidation in the bulk of solution by means of the oxidants electrogenerated from the oxidation of support electrolyte on the BDD anode. Although hydroxyl radicals are more powerful than the oxidants electrogenerated during electrolysis on the BDD anode in the presence of NaCl and $Na_2SO_4$, the kinetics and efficiency of degradation and mineralization of cyanuric acid were poorer in the presence of $NaClO_4$, which was unexpected. It is important to consider that hydroxyl radicals formed in solution by Fenton, $UV/H_2O_2$, $UV/TiO_2$, and electro-Fenton were not efficient at degrading cyanuric acid, as reported in the literature by several researchers (Dbira et al., 2014; Garcia-Lopez et al., 2007; Oh and Jenks, 2004; Tetzlaff and Jenks, 1999; Watanabe et al., 2005). Accordingly, it seems that the contribution of hydroxyl radicals in the first step of degradation of cyanuric acid (triazine ring opening) is minor and limited to a region very close to the BDD anode, where cyanuric acid can be adsorbed on the surface, and then its oxidation can occur directly by electron transfer or via hydroxyl radicals. In this case a competition between direct oxidation of cyanuric acid and hydroxyl radical production can take place on the BDD surface. In this case the kinetics is governed by mass transfer, which makes the degradation very

slow. However, the contribution of hydroxyl radicals becomes very effective in the oxidation of intermediates produced by triazine ring opening, as confirmed by the percentage decreases in cyanuric acid concentration and TOC removal obtained in all electrolytes being the same.
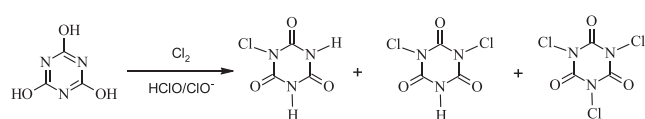
It was expected that the degradation of cyanuric acid in $Na_2SO_4$ electrolyte would be more efficient than in NaCl electrolyte because persulfate ions are stronger oxidants than active chlorine. However, the experimental results showed that the electrolytic degradation and mineralization of cyanuric acid on the BDD anode was slower and less efficient in $Na_2SO_4$ electrolyte than in NaCl electrolyte. It is clear that the contribution of active chlorine ($Cl_2$, HClO, $ClO^-$) in the electrolytic degradation of cyanuric acid is much more important than that of persulfate and hydroxyl radicals. This could be explained by the high affinity of active chlorine towards nitrogen compounds (Hu et al., 2009; Perez et al., 2012; Varghese et al., 2007; Wojtowicz, 2001; Xiao et al., 2009). This result is in good agreement with those reported in the literature, indicating that hypochlorite ions can be used very effectively to eliminate cyanuric acid from water (Carlson, 1978; Wojtowicz, 2001). Furthermore, the contribution of persulfate in the first steps of the degradation of cyanuric acid is more important than that of hydroxyl radicals. This can be explained by the high stability of persulfate ions, which makes them react with cyanuric acid and its degradation intermediates in the bulk of the solution for longer contact times. From these results, it can be concluded that the contribution of mediated oxidation via the inorganic oxidant pathway on the degradation and mineralization of cyanuric is much more important than direct oxidation on the BDD surface and degradation by hydroxyl radicals in the vicinity of the BDD anode. It should be noted that other studies related to the electrolytic degradation of organic pollutants (phenols, dyes, carboxylic acids, etc.) on BDD anodes showed opposite results (Bensalah et al., 2012; Canizares et al., 2007; Guinea et al., 2008; Indermuhle et al., 2013; Louhichi et al., 2008; Martin de Vidales et al., 2012). Cyanuric acid represents a particular case where the electrolytic degradation is more efficient in NaCl electrolyte than in other electrolytes because of its exceptional tautomeric chemical structure and its high reactivity with active chlorine.

To confirm these suppositions, additional experiments were conducted using a Pt anode instead of a BDD anode. Fig. 5 presents the changes of cyanuric acid and TOC with time during the electrochemical oxidation of 50 mg/L cyanuric acid on BDD and Pt anodes at a constant current density j = 20 mA/cm$^2$ in the presence of 0.05 mol/L NaCl. As can be observed, cyanuric acid was decreased using both BDD and Pt anodes, but more rapid degradation was observed on the BDD anode. However, no mineralization was observed on the Pt anode, while almost total mineralization was achieved on the BDD anode. It should be noted that no cyanuric acid degradation was observed in the other electrolytes. The degradation of cyanuric acid during electrochemical oxidation on the Pt anode can be due to its chemical oxidation by active chlorine species (chlorine, hypochlorous acid/hypochlorite) generated in the medium by oxidation of chloride ions at the Pt surface, into chlorinated organic compounds (mono-, di- and tri-chloroisocyanuric acids). This was supported by

Fig. 6 – Influence of initial pH on nitrate release during galvanostatic electrolyses of cyanuric acid on BDD anode. Experimental conditions: 50 mg/L cyanuric acid, 0.05 mol/L NaCl, j = 20 mA/cm², temperature = 25°C, 300 r/min.
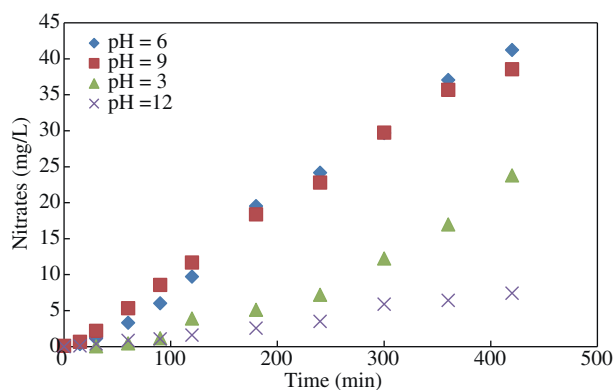


**Fig. 5 – Changes of (a) cyanuric acid concentration, and (b) total organic carbon (TOC) with time during galvanostatic electrolyses of cyanuric acid using BDD and Pt anodes. Experimental conditions: 50 mg/L cyanuric acid, 0.05 mol/L NaCl, j = 20 mA/cm², temperature = 25°C, 300 r/min.**

Huthmacher and Most (2000), who reported that chlorine reacts with cyanuric acid in water to form di and tri-chloroisocyanuric acids in neutral and alkaline conditions. These intermediates can undergo oxidative triazine ring opening by hydroxyl radicals; but active chlorine cannot degrade them further.



From these results, it is obvious that the use of chloride medium is the best choice to achieve higher efficiency electrolytic degradation of cyanuric acid on BDD anodes. Certain experimental parameters including initial pH and current

density should be optimized in order to maximize the efficiency of the electrochemical process. The highest mineralization degrees in terms of nitrate release during galvanostatic electrolysis (j = 10 mA/cm²) of 50 mg/L cyanuric acid in 0.05 mol/L NaCl were obtained in a pH range between 6 and 9 as shown in Fig. 6. After 5 h electrolysis, similar nitrate concentrations (29.5 and 29.7 mg/L) were released for pH 6 and 9; however a lower concentration was measured at pH 3 (23.8 mg/L); and it did not exceed 6 mg/L at pH 12. This can be due to the nature of the reactive forms present in the medium that are pH-dependent. This can be explained as follows:
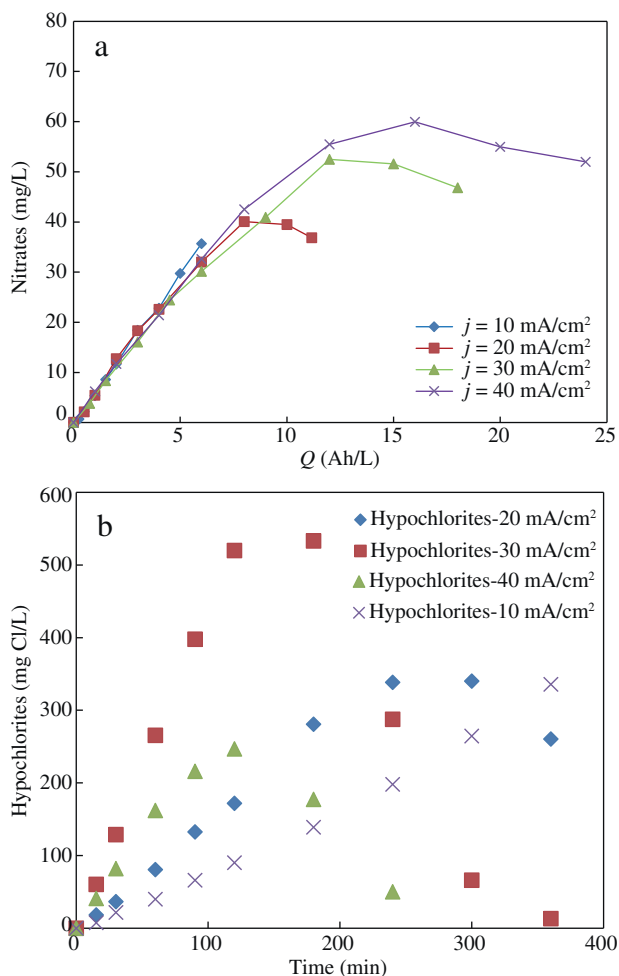
In chloride media, active chlorine species ($Cl_2$, HClO and $ClO^-$) are electrogenerated by oxidation of $Cl^-$ on the BDD anode as given by the following Eqs. ((1)–(3)):

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{1}$$

$$Cl_2 + H_2O \rightarrow HOCl + HCl \tag{2}$$

$$HClO \rightleftharpoons ClO^- + H^+. \tag{3}$$

HClO is predominant for pH between 3 and 8; while $ClO^-$ is predominant for pH higher than 8. The mediated oxidation of cyanuric acid and its intermediates with active chlorine species is expected to be more efficient in neutral rather than in alkaline media because of the higher standard potential of HClO (E° = 1.73 V) than $ClO^-$ (E° = 1.13 V).

In addition, in neutral to slightly acidic solution, the tautomeric form known as isocyanuric acid is predominant over cyanuric acid (Wojtowicz, 2001). Isocyanuric acid has more affinity towards active chlorine than cyanuric acid due to the presence of an amine group.
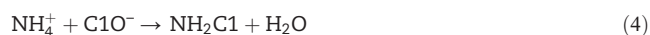
Fig. 7 presents the effect of current density on the mineralization of cyanuric acid (50 mg/L) at pH 6 in terms of nitrate release and the production of hypochlorite. The profiles of nitrate concentration with specific electrical charge

Fig. 7 – Influence of current density on (a) nitrate release and (b) hypochlorite formation during galvanostatic electrolyses of cyanuric acid on BDD anode. Experimental conditions: 50 mg/L cyanuric acid, 0.05 mol/L NaCl, pH = 6, temperature = 25°C, 300 r/min.
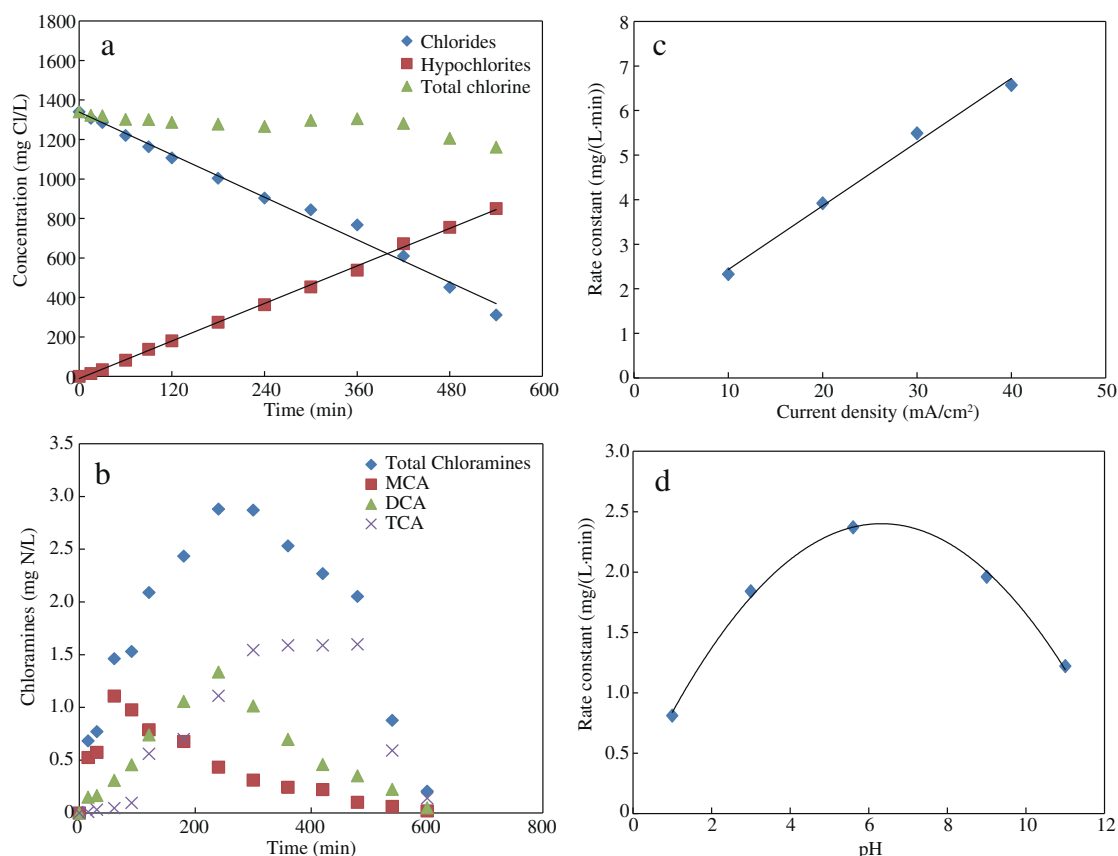
started to decline, indicating possible oxidation of hypochlorite to chlorate and perchlorate as mentioned by other researchers (Bensalah and Abdel-Wahab, 2013; Bergmann et al., 2014; Dbira et al., 2015a, 2015b). From an environmental point of view, these species are hazardous byproducts, and their production can limit the utilization of this electrochemical method (Greer et al., 2002). Fig. 8a shows that at 10 mA/cm$^2$, the BDD anode transformed chloride equivalently into hypochlorite without formation of chlorate and perchlorate, based on mass balance. Current density and initial pH affected the rate of oxidation of chloride at the BDD anode. The rate of oxidation of chloride increased linearly with the current density as shown in Fig. 8c. The rate of oxidation of chloride was more rapid in neutral media than acidic or alkaline media (Fig. 8d). In addition, the electrolytic degradation of cyanuric acid at 10 mA/cm$^2$ produced chloramines (monochloramine (MCA), dichloramine (DCA) and trichloramine (TCA)) (Fig. 8b). MCA, DCA, and TCA concentrations increased to reach a maximum and then declined to zero at the end of electrolysis. This is expected because the reaction of hypochlorite with ammonium ions can lead to the formation of $NH_2Cl$, $NHCl_2$ and $NCl_3$ given by the following Eqs. ((4)–(6)) (Lacasa et al., 2012, 2013):

$$NH_4^+ + C1O^- \rightarrow NH_2C1 + H_2O \tag{4}$$

$$NH_2C1 + C1O^- \rightarrow NHC1_2 + H_2O \tag{5}$$

$$NHC1_2 + C1O^- \rightarrow NC1_3 + H_2O. \tag{6}$$

A current density of 10 mA/cm$^2$ or lower should be a good choice for the electrolytic degradation of cyanuric acid using the BDD anode because of it gives similar efficiency to higher current densities in terms of nitrate release, and negligible amounts of chlorate and perchlorate can be formed.

for different current densities in the range 10–40 mA/cm$^2$ overlapped each other from the beginning of electrolysis till 7.5 Å h/L (Fig. 7a). The current density did not have a significant effect on the efficiency of electrolytic degradation of cyanuric acid. This can be explained by the mass-transfer kinetic limitations of the whole electrochemical process. It also confirms the important contribution of mediated oxidation in the overall efficiency of electrolytic degradation of cyanuric acid on the BDD anode. However, current density has an important effect on the production of hypochlorite as shown in Fig. 7b. At the beginning of electrolysis, a linear increase of the hypochlorite concentration with time was observed for all the current densities studied. The increase of current density increases the rate of production of hypochlorite (considering only 120 min of electrolysis, where linearity was observed) from 0.74 mg/(L·min) for 10 mA/cm$^2$ to 1.43, 2.28, and 4.37 mg/(L·min) for 20, 30, and 40 mA/cm$^2$, respectively. For current densities higher than 10 mA/cm$^2$, the hypochlorite concentration reached a maximum and then

## 3. Conclusions

The results obtained in this work proved the important contribution of mediated oxidation with strong inorganic oxidants electrogenerated by the oxidation of supporting electrolyte on the BDD anode in the overall mechanism of electrolytic degradation of cyanuric acid. The electrolytic degradation and mineralization of cyanuric acid using a BDD anode was more rapid and efficient in NaCl than in $Na_2SO_4$ and $NaClO_4$ solutions. This can be explained by the high affinity of active chlorine towards cyanuric acid and nitrogen species. However, the mineralization of degradation intermediates was immediate and highly efficient in all electrolytes. The most highly efficient electrolytic degradation of cyanuric acid on the BDD anode was obtained with low current density and in a neutral medium. These results are promising for the development of electrochemical pilot plants using the BDD anode in a chloride medium for wastewater treatment.

**Fig. 8 – Changes of (a) chlorine speciation, and (b) chloramines with time, and changes of rate constant of chloride oxidation with (c) current density, and (d) initial pH during galvanostatic electrolyses of cyanuric acid on BDD anode. Experimental conditions: 50 mg/L cyanuric acid, 0.05 mol/L NaCl, pH = 6, j = 10 mA/cm$^2$, temperature = 25°C, 300 r/min.**

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