

Treatment of Synthetic Urine by Electrochemical Oxidation using Conductive-Diamond Anodes

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Abstract

In this work, the electrochemical oxidation of synthetic urine by anodic oxidation using boron-doped diamond (BDD) as anode and stainless steel as cathode was investigated. Results show that complete depletion of COD and TOC can be attained regardless of the current density applied in the range 20 - 100 mA cm⁻². Oxalic and oxamic acids, and, in lower concentrations, creatol and guanidine were identified as the main intermediates. Chloride ions play a very important role as mediators and contribute not only to obtain a high efficiency in the removal of the organics but also to obtain an efficient removal of nitrogen by the transformation of the various raw nitrogen species into gaseous nitrogen through chloramine formation. Main drawback of the technology is the formation of chlorates and perchlorates as final chlorine products. The increase of current density from 20 mA cm⁻² to 60 mA cm⁻² led to an increase in the rate of COD and TOC removals although the process becomes less efficient in terms of energy consumption (removals of COD and TOC after applying 18 Ah dm⁻³ were

93.94 and 94.94%, respectively at 20 mA cm⁻² and 89.17 and 86.72%, respectively, at 60 mA cm⁻²).

The most efficient conditions are low current densities and high temperature reaching total mineralization at an applied charge as low as 20 kWh m⁻³. This result confirmed that the electrolysis using diamond anodes is a very interesting technology for the treatment of urine.

Keys words: Synthetic urine, Anodic oxidation, Boron-doped diamond anodes, Hydroxyl radicals, Mineralization.

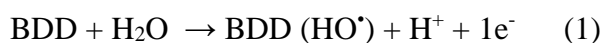
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1. Introduction.

Urine can be considered as a special type of wastewater with very complex chemical composition. This composition has been studied by many researchers, showing that it depends on time of day, diet, climate, physical activity and body size (Heinonen-Tanski et al. 2007). The means of inorganic compounds are nitrogen, phosphorus and potassium. The organic fraction contains many substances such as vitamins, hormones, organic acids and especially urea, uric acid and creatinine. The urine is the fraction of domestic wastewater that contains the major part of plants nutrient with approximately 80% of nitrogen, 55% of phosphorus and 60% of potassium and very low metals content (Vinneras et al. 2006), being considered as natural resource of nutrients. However, the reuse of this wastewater as a fertilizer may result in transmission of pathogens such as *Leptospira interrogans*, *Salmonella typhi*, *Salmonella paratyphi* and *Schistosoma haematobium* (Heinonen-Tanski et al. 2007) (Blum & Feachem 1983, Höglund et al. 2002). This may produce many diseases such as cholera and typhoid fever leptospirosis, paratyphoid fever (Hanjra et al. 2012, Shuval et al. 1997). For this reason, it is necessary to treat the urine wastewater before any reuse because it has been demonstrated (Höglund et al. 2002) that pathogens can survive in urine during very long periods.

The literature indicated that advanced oxidation processes AOPs are the best technologies to mineralize persistent and bio-resistant organic pollutants in water and wastewater such as photographic and agro-industrial wastewaters (Ahmed et al. 2011, Bensalah et al. 2013) in which total mineralization can be attained. The great effectiveness of AOPs is due to the production of the hydroxyl radicals (HO^\bullet). Hydroxyl radicals which are non-selective, and very powerful oxidants ($E^\circ = 2.80 \text{ V/NHE}$), react very quickly with the organic pollutants to mineralize them in CO_2 , H_2O and inorganic ions (Elahmadi et al. 2009, Oturan et al. 2011) or at least transform into biodegradable compounds. Recently, electrochemical methods which

may be easily coupled with green chemical technologies become good candidates to replace conventional methods for the destruction or removal of bio-refractory organics in water. In particular, anodic oxidation is increasingly taking attention for its high efficiency and low costs, especially when combined with renewable energy sources like wind and solar sources, in removing persistent organic pollutants from water and wastewater. The effectiveness of anodic oxidation is mainly related to the innovation of new anode materials capable of generating large quantities of strong oxidizing agents such as hydroxyl radicals HO[•] which are weakly adsorbed on the surface of the anode. Boron-doped diamond (BDD) anodes developed in last decade, exhibits high efficiency and excellent compatibility to degrade variety organic of pollutants, reaching efficiencies close to 100% when mass transfer is not limiting the rate of the processes (Sires et al. 2006) (Guinea et al. 2009a). BDD electrode has much larger O₂ evolution over potential enabling the production of large amounts of hydroxyl radicals on the surface by water oxidation (Eq.1) (Guinea et al. 2008, Lacasa et al. 2012a, Panizza & Cerisola 2008, Zhou et al. 2011).



Recently it has been studied the treatment of human urine by electrochemical methods (Raut et al. 2013) showing their ability to completely disinfect synthetic urine spiked with *Escherichia coli* using boron-doped diamond electrode. The aim of this work was to study the electrochemical treatment of synthetic urine using BDD anodes. Furthermore, the influence of the main operation parameters such as current density and temperature on the performance of oxidation and mineralization of synthetic urine with BDD anodes was investigated. The efficiency of the electrochemical process was followed by different analytical methods including total organic carbon (TOC), chemical oxygen demand (COD), pH, conductivity. The formation of organic intermediates and the decay of initial products were performed with

high performance liquid chromatography (HPLC). Ion chromatography was used to identify and quantify inorganic ions formed during galvanostatic electrolyses.

2. Materials and methods

2.1. Chemicals. The synthetic urine solutions were prepared by dissolving urea 3.333 g/L ($\text{CH}_4\text{N}_2\text{O}$), 0.050 g/L uric acid ($\text{C}_5\text{H}_4\text{N}_4\text{O}_3$) and 0.166 g/L creatinine ($\text{C}_4\text{H}_7\text{N}_3\text{O}$). Salts were also dissolved to obtain 1 g/L chloride (Cl^-), 1 g/L potassium (K^+), 0.025 g/L phosphate (PO_4^{3-}), 0.3 g/L sulfate (SO_4^{2-}), 0.025 g/L calcium (Ca^{2+}), 0.016 g/L magnesium (Mg^{2+}), 0.166 g/L sodium (Na^+), 0.025 g/L ammonium (NH_4^+), and 0.166 g/L carbonates (CO_3^-). Urea ($\text{CH}_4\text{N}_2\text{O}$), uric acid ($\text{C}_5\text{H}_4\text{N}_4\text{O}_3$) and creatinine ($\text{C}_4\text{H}_7\text{N}_3\text{O}$) were analytical grade (>99.0% purity), purchased from Sigma-Aldrich. Sulfuric acid utilized to adjust the initial pH from 8.0 to 5.6 were analytical grade purchased from Merck. The other chemicals were analytical grade purchased from Fluka. All solutions were prepared with high-purity water obtained from a Millipore Milli-Q system, with resistivity $>18 \text{ M}\Omega \text{ cm}^{-1}$ at $25 \text{ }^\circ\text{C}$.

2.2. Analytical methods. The total organic carbon (TOC) and total nitrogen (TN) were monitored with a Multi N/C 3100 Analytik Jena TOC analyzer. Chlorine species (Cl^- , ClO_3^- , and ClO_4^-) were measured by ion chromatography using a Shimadzu LC-20A equipped with Shodex IC I-524A column. The mobile phase was 2.5 mM phthalic acid at pH 4.0 with a flow rate of 1.0 ml min^{-1} . The formation of inorganic ions (nitrate, nitrite, NH_4^+ , sulphate, phosphate) was determined by the same ion chromatograph (column, Shodex IC YK-421) with a mobile phase 5.0 mM tartaric, 1.0 mM dipicolinic acid and 24.3 mM boric acid at flow rate of 1.0 ml min^{-1} . The determination of hypochlorite was carried out by titration with As_2O_3 in NaOH 2 M. The concentrations of urine and intermediates generated were identified by HPLC–UV (Agilent 1100 series). The column temperature was $25 \text{ }^\circ\text{C}$. Volume injection was set to $20 \text{ }\mu\text{L}$. The analytical column used was Phenomenex Gemini $5 \text{ }\mu\text{m}$ C18. The

detection wavelength of HPLC–UV was performed at 291 nm. A lineal gradient chromatographic elution was used by initially running 10% of Solvent B ascending to 100% in 40 min. Solvent A was composed by 25 mM of formic acid water solution and Solvent B was acetonitrile. Samples taken from electrolyzed solutions were filtered with 0.20 μm Nylon filters before analysis. Inorganic chloramines measured by the DPD colorimetric method was conducted using Shimadzu spectrophotometer UV-2400PC as previously described in the literature (Cotillas et al. 2013). Chemical oxygen demand (COD) was monitored by sampling 2 mL of the electrolyzed solution at certain time intervals. These samples were mixed in a glass tube filled with an oxidizing solution purchased from Merck (Spectroquant®) ($[\text{Cl}^-]$ in samples was kept below 2 g L⁻¹, as recommended). UV-vis spectra were obtained using a Shimadzu UV-1603 spectrophotometer in 1 cm quartz cells. The solution pH and conductivity were measured with an InoLab WTW pH-meter and a GLP 31 Crison conductimeter, respectively.

2.3. Electrochemical set up. The electrochemical experiments were carried out in a single compartment electrochemical flow cell (Fig.1) working under a batch-operation mode (Canizares et al. 2005). Two types of electrodes were used: Diamond-based material (p-Si–boron-doped diamond) as anode and stainless steel (AISI 304) as cathode. Boron-doped diamond (BDD) 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), (Si substrate; 2 mm thickness; 100 m Ω cm resistivity; 500 ppm boron concentration; 2.62 μm CDE-film thickness; 115 CDE-film Raman sp^3/sp^2). Both electrodes were circular (100 mm diameter) with a geometric area of 78 cm² and an electrode gap of 9 mm.

2.4. Experimental procedures. Lab-scale electrolyses were carried out under galvanostatic conditions. The volume of wastewater was 600 mL. The pH was adjusted about 5.6 with

sulfuric acid. The current density applied ranged from 20 to 100 mA cm⁻². The cell voltage did not vary during electrolysis indicating that conductive-diamond layers did not undergo appreciable deterioration or passivation phenomena. The wastewater was stored in a glass tank and circulated through the electrolytic cell by means of a centrifugal pump (at different flow rate). A heat exchanger coupled with a controlled thermostatic bath (Digiterm 100, JP Selecta) was used to maintain the temperature at the desired set point (25 °C). At certain time intervals, samples of 20 mL volume were taken from the solution and filtered through 0.20 µm Nylon filters and analyzed for ions, TOC, TN, target compounds and intermediates, and UV-vis.

3. Results and discussion

BDD anodes have been successfully used to treat domestic and industrial wastewater (Martinez-Huitle & Ferro 2006), to produce strong oxidants (Cano et al. 2012), and to analyze different organic and inorganic species (Svorc et al. 2014). Likewise, several researchers (Bensalah et al. 2013, Marselli et al. 2003, Michaud et al. 2000, Serrano et al. 2002) have indicated that strong oxidants can be produced at the surface of BDD anodes by anodic oxidation of water during the electrolysis of wastewater and the nature of supporting electrolyte and current density have a strong influence on this production. The production of these strong oxidants on BDD anodes plays an important role in the overall electrochemical process and affects largely the efficiency of the BDD-anodic oxidation. Because urine contains many ionic inorganic species dissolved, it is then necessary to study the effects of operating conditions on the efficiency of urine treatment by electrochemical oxidation using BDD anodes. Literature indicated that the current density is the most important operation parameter to be optimized in all electrochemical processes in order to reach high current

efficiencies (Bensalah et al. 2013, Brillas et al. 2009, Lacasa et al. 2013, Oturan et al. 2011) (Panizza & Cerisola 2005, Zhou et al. 2011). For this reason, in this work to study the effect of current density on the oxidative degradation of urine, galvanostatic electrolyses of the synthetic urine were carried out at different current densities of 20, 60 and 100 mA cm⁻² keeping the other operating parameters unchanged (pH, temperature, organic and inorganic load).

3.1 Removal of TOC and COD

Figure 2 shows (in semi-logarithmic plot) the changes in TOC and COD with the electric charge applied, during the electrochemical oxidation of synthetic urine with BDD anodes at the three different current densities assessed. As experiments were carried out galvanostatically, changes with the electric charge applied time and with current charge for both parameters follow the same fashion, because electric charge applied and reaction time is proportional. As it can be observed, linear trends are obtained for the decay of both parameters (COD and TOC) during electrolyses for all values of current density tested, indicating that results fit a first order kinetic decay kinetics. As it is known, this type of kinetic behavior is characteristic not only of mass transport controlled electrochemical processes but also of mediated electrochemical processes. As it can be seen, the TOC and COD have a rapid decrease from 731 to 37 mgC dm⁻³ and from 825 to 50 mg O₂ dm⁻³ respectively during electrolysis of synthetic urine using BDD anodes at 20 Ah dm⁻³ and room temperature. The decrease in TOC content indicates the mineralization of synthetic urine by anodic oxidation (transformation of organic matter into carbon dioxide CO₂), while a decrease in the COD is related to the change in the chemical species during the treatment. These results indicate that the complete removal of urine synthetic by anodic oxidation with BDD anodes was observed after 300 min for all current densities. Then, an almost complete depletion of TOC and COD is attained at larger Q regardless of the current density applied. The harsh

oxidation conditions that should account for this efficient removal (especially, if compared with other electrodes) is explained in the literature (Haidar et al. 2013, Marselli et al. 2003) (Oturán et al. 2011, Panizza & Cerisola 2005, Zhou et al. 2011) by the production of higher amount of hydroxyl radicals (HO^\bullet) generated from oxidation of water at the surface of BDD anodes (Eq. 1).

Likewise, in the treatment of urine and due to the very large amount of chlorides, it can also be explained by the generation of hypochlorite ions by the oxidation of chloride during the anodic oxidation of synthetic urine using BDD anode materials. To better observe this influence of the supporting media and current density, and taking into account the linear trend observed in the COD vs. Q plot, data COD vs t of each test were fitted to a first order decay kinetic. First order kinetic constants and maximum efficiency for the removal of TOC and COD during the electrochemical treatment of synthetic urine with BDD anodes are summarized in Table 1. Concerning the kinetic aspect, this table shows that the increase of current density increases the degradation rate constant, while temperature seems to have a lower positive influence on the degradation rate, but still appreciable. Anyhow, this increase may suggest the significance of mediated processes in the overall oxidation of urine. As it is known, these processes are largely influenced by temperature, and chlorine and other oxidants could have advantage of this temperature increase, improving the organic degradation rate by more than 30%.

The last column of the table 1 is a good agreement with previous results for the efficiency of TOC and COD removal during the electrolyses indicating that the anodic oxidation using BDD anode is a good choice for the successful treatment of a great variety of pollutants with efficiencies expressed in terms of mg pollutant/Ah much higher than obtained with other anodes (Brillas et al. 2004, Canizares et al. 2005, Canizares et al. 2007, Canizares et al. 2008, Faouzi et al. 2006, Guinea et al. 2008, Guinea et al. 2009b, Martinez-Huitle & Brillas 2009,

Martinez-Huitle & Ferro 2006, Panizza & Cerisola 2007, 2008, 2009, Polcaro et al. 2004, Polcaro et al. 2005, Polcaro et al. 2007, Sires et al. 2006). These high efficiencies are explained in terms of the significant role played by mediated processes. However, in spite of the important role of mediated electrolysis, the process is also strongly influenced by mass transfer limitations, because the higher the current density the lower is the efficiency. Therefore, the most efficient conditions for this treatment are low current densities (which are associated with low diffusion limitations) at high temperature (which can be associated with an enhanced mediated oxidation), which attain total removal of organics at an applied current charge as low as 20 Ah dm^{-3} . This is a very important result, because this means that costs for the complete treatment of urine could be lower than 100 kWh m^{-3} if a typical cell potential of 5.0 V is supposed, converting electrolysis into a very promising technology for this application in terms of energy consumption.

3.2 Changes of pH and conductivity

Figure 3 shows the changes of pH and conductivity of the electrolyte as a function of specific electric charge during the electrolyses at different current densities. It can be observed that the pH has a rapid decrease from $\text{pH} \approx 6.0$ to $\text{pH} \approx 1.8 - 2.0$ at the beginning of the experiments and then it is kept almost constant until the end of treatment. This strongly acidic pH is expected to have an important role in the speciation of the intermediates and, as a key point, it helps to prevent the volatilization of ammonia during the electrolysis (Lacasa et al. 2011a, 2012a, Lacasa et al. 2012b). The increase observed in the conductivity may be explained by the release of inorganic species during the mineralization of the organic pollutants and also by the drastic change in the pH.

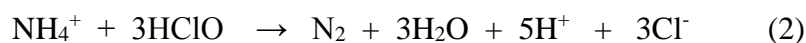
3.3 Formation of soluble phosphate and sulfate

The mineralization of organic matter by electrochemical processes involves the transformation of organic matter into carbon dioxide and inorganic ions. The most important ions that are expected to be formed during mineralization are nitrates, nitrites, ammonium, chlorides, sulfates, and phosphates (Dirany et al. 2010, Haidar et al. 2013, Sires et al. 2008). In this work, ionic chromatography analyses confirmed the presence of sulfates, phosphates, nitrates, ammonium and different species of chlorine and it also proved the absence of nitrites. Figure 4 shows the changes in the concentration of soluble phosphate (a) and sulfate (b) during the electrolyses of synthetic urine with BDD anodes. The changes on the concentration of soluble phosphates are mainly due to the pH changes during electrolyses (Lacasa et al. 2011b). This can be explained in terms of the dependence of acid-base and solubility properties of this inorganic species on pH. Contrarily, the concentration of sulfates is not influenced by pH and it is almost kept constant at the same value during the electrolysis of synthetic urine with BDD anodes.

3.4 Nitrogen speciation

Figure 5 shows the changes of the concentration of nitrogen speciation (nitrates, ammonium and nitrites) as a function of specific electric charge during the electrolyses. As it is shown, the production of nitrate and ammonium is observed from the beginning of tests. The concentration of nitrate and ammonium undergoes a linear increase and then reaches a plateau until the end of treatment. A very important observation is that large differences are obtained between the measured concentrations of nitrogen and the concentration expected. In this treatment, the initial concentration of nitrogen in the synthetic urine is very high (around 1634 ppm) and this nitrogen is mostly associated with urea in raw synthetic urine (>95%) being the rest free ammonium ion (20 mg/dm^{-3}) and organic nitrogen (associated with creatinine and uric acid). At the conclusion of treatment tests, the concentration of nitrate reaches about 57

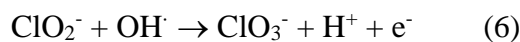
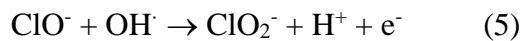
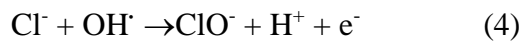
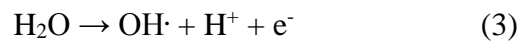
mgN /L, 62 mgN /L and 72 mgN /L, the concentration of ammonium attains about 198 mgN /L, 257 mgN /L and 255 mgN /L and organic species are depleted, respectively, at current densities of 20 mA/cm², 60 mA/cm² and 100 mA/cm². These results indicate that the concentrations of nitrogen measured are far away from those contained in the initial synthetic urine. At this point, it is important to realize that nitrate is known to be easily transformed into ammonium ions in single compartment electrochemical cells as previously reported in the literature by reduction on the cathode surface (Lacasa et al. 2011a, 2012a, Lacasa et al. 2012b). In addition the lower concentrations measured in comparison to those expected can be explained by the formation of volatile nitrogenous species, in particular gaseous nitrogen, by oxidation of ammonia with hypochlorite (eq. 2) as it will be explained later on, when the role of chlorinated species will be discussed. Hence, electrolysis becomes a very interesting technology not only for organic depletion but also for nitrogen removal in this type of wastewater.



3.5 Formation of chlorine species

Figure 6 shows the changes in the concentration of the chlorine species during the electrolyses. Synthetic urine contains large concentration of chlorine species which are expected to be transformed into a variety of species during the anodic oxidation on BDD anodes such as chloride, chloramines, hypochlorite, chlorate, and perchlorates. As it can be seen in Fig. 6, the concentration of chlorides decreased rapidly during electrolyses and they are completely removed at the conclusion of treatment, being completely transformed into hypochlorite (ClO⁻), chlorate (ClO₃⁻) and perchlorates (ClO₄⁻). This transformation is known to develop either by direct anodic oxidation on BDD anodes (only the formation of

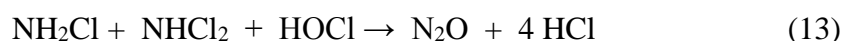
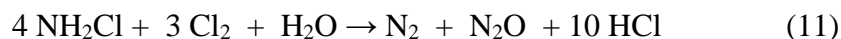
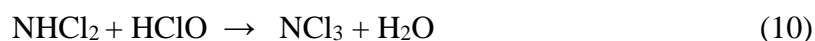
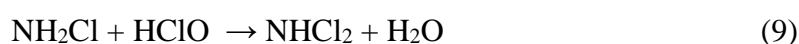
hypochlorite) and by the participation of hydroxyl radicals generated on the anode surface during anodic oxidation process (in this case hypochlorite, chlorate and perchlorate may be formed) as it is shown in eqs. 3 to 7 (chlorite is unstable and rapidly disproportionate to chloride and chlorate)(Feng et al. 2013, Panizza & Cerisola 2009, Randazzo et al. 2011, Sanchez-Carretero et al. 2011). At this point, it is worth taking into account occurrence of chlorate and perchlorate is undesirable and becomes the main drawback of this application of the electrochemical technology in urine treatment. Hence further research should be carried out to prevent the oxidation of hypochlorite by hydroxyl radical taking into account the hazardousness of chlorates and perchlorates. The occurrence of these species has been largely reported in other wastewater treatments carried out with diamond anodes and even in disinfection of water and reclaimed wastewater and currently it is a major concern for the use of diamond electrolysis in many applications (Bergmann et al. 2014, Greer et al. 2002).



A key point for this expected future research seems to be that just in the moment in which chloramines start decaying, chlorates are produced massively, in particular in the experiments carried out at 60 and 100 mA cm⁻². For the lowest current density production is smaller and this fact indicates that gaseous chlorine is being produced and dispersed. This means that prevention of the formation of chlorates or perchlorates may be obtained by the addition of an inhibitor (reductant agent) in this part of the treatment or by depleting Cl₂ (in equilibrium with hypochlorite) by gas stripping during the treatment. However, this possibility of removal is

only a hypothesis and it should be studied carefully because hypochlorite has a very important role and conditions have to be optimized. Under no prevention conditions, Figure 6 (Inset) shows that the oxidation of chlorides into hypochlorite, chlorate and perchlorate ions is complete.

Role of hypochlorite is very important because the presence of high concentration of hypochlorite by oxidation of chlorides is a key to facilitate the mineralization of synthetic urine and the removal of the associated nitrogen in the form of gaseous nitrogen. Regarding the removal of nitrogen, in a previous work, it was showed that the both formations of ammonium (by cathodic nitrate reduction) and hypochlorite (by anodic oxidation) during electrolyses develop at a high rate in electrochemical processes (Lacasa et al. 2011a, 2012a). The chloramines were formed by the chemical reaction between the ammonium ions and the hypochlorite ions according to equation (3) which develops in the bulk. Monochloramine, dichloramine and trichloramine and gaseous nitrogen (not only dinitrogen but also nitrogen oxides in very low concentrations) are expected to be produced successively in the bulk during the electrolysis by the reactions (Eq. 8-14) (Lacasa et al. 2012b).



The low concentrations of chloramines monitored can be explained taking into account their role as intermediates and they suggest that the very important shifting of the reaction set

towards the formation of gaseous nitrogen (Reyter et al. 2010, Vlyssides et al. 2002) and hence the validity of this technology for the removal not only of organic pollutant but also of nitrogen in urine. Once clarified the role of inorganic species, it is interesting to focus on organics.

3.6 Changes in the raw species and organic intermediates

As in many other electrochemical processes, the oxidative degradation of synthetic urine by the anodic oxidation is accompanied by the formation of organic intermediates, and sometimes they could be even more hazardous than the initial product. For this reason, it is very important to identify the intermediates and this work was carried by reversed phase HPLC analyses. Results are shown in Figure 7. In fact, uric acid, urea and creatinine (raw species) are depleted very rapidly and transformed sequentially into aromatic species and carboxylic acid species, being the primary intermediates detected oxalic acid, creatol, oxamic acid and guanidine. All these species are depleted at the conclusion of the treatment and they show a very low relevance in terms of chromatographic area. At this point, it is important to take in mind that no chlorinated organic species were detected at significant concentrations (within the detection limits of the HPLC and standard checked) indicating that occurrence of these compounds is not a drawback which could be associated with this electrochemical technology. These results are in very good agreement with that found by the previous works in which the electrolysis of compounds contained in urine were studied (Antoniou et al. 2009, Calza et al. 2005) and make electrochemical oxidation with diamond anodes a very interesting technology for the treatment of urine.

4. Conclusion

From this work, the following conclusions can be drawn:

- The anodic oxidation with boron-doped diamond (BDD) anodes is an effective technology to eliminate organic content of synthetic urine and it can also efficiently remove nitrogen and chlorine.
- Complete depletion of COD and TOC can be obtained regardless of current density applied. Organic carbon is transformed into carbon dioxide CO_2 , being oxalic acid, creatol, oxamic acid and guanidine the main organic intermediates formed. Moreover, the production of ammonium and nitrates was observed during the electrolyses but these concentrations are far away from those contained in the initial sample because gaseous nitrogen is the primary product of the electrolytic process. This production is carried out via formation of chloramines, produced by chemical reaction between ammonium and hypochlorite.
- The chlorine present in urine is completely released in the form of chloride, which is rapidly oxidized to hypochlorite (ClO^-), chlorate (ClO_3^-) and perchlorate (ClO_4^-) during the treatment on BDD anodes. An important formation of chloramines was obtained as intermediates in the production of gaseous nitrogen, as well. Further research should be carried out to prevent the oxidation of hypochlorite taking into account the hazardousness of chlorates and perchlorates which behaves as an important drawback of the technology.
- The most efficient conditions are low current densities and high temperature, which attains total removal at an applied charge as low as 20 Ah dm^{-3} . This low current density requirement makes that electrolysis with the BDD anodes can be successfully used to treat the aqueous solution of synthetic urine at a reasonable cost.
- The highest efficiency of anodic oxidation using BDD anodes can be explained by the contribution of direct and indirect oxidation ways in the mechanism of degradation of synthetic urine. This includes: 1) oxidation via hydroxyl radicals electrogenerated

from water discharge on the surface of BDD anodes, 2) direct oxidation of synthetic urine and its intermediates on the surface of BDD anodes, and 3) mediated oxidation with chlorine species electrogenerated from anodic oxidation of chloride ions.

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Figures Captions

Figure 1. The experimental set-up used in this work.

Figure 2. Oxidation progress and mineralization during electrolyses of synthetic urine with BDD anodes at different current densities and temperatures ▲ 20 mA cm⁻², 25°C; ● 60 mA cm⁻², 25°C; ■ 100 mA cm⁻², 25°C; ◆ 20 mA cm⁻², 50°C

Figure 3. Changes in the pH (full points) and conductivity (empty points) of the electrolyte during the electrolyses of synthetic urine with BDD anodes ▲ 20 mA cm⁻², 25°C; ● 60 mA cm⁻², 25°C; ■ 100 mA cm⁻², 25°C; ◆ 20 mA cm⁻², 50°C.

Figure 4. Changes in the concentration of soluble phosphate (full points) and sulfate (empty points) during the electrolyses of synthetic urine with BDD anodes ▲ 20 mA cm⁻², 25°C; ● 60 mA cm⁻², 25°C; ■ 100 mA cm⁻², 25°C; ◆ 20 mA cm⁻², 50°C.

Figure 5. Speciation of nitrogen during the electrolyses of synthetic urine with BDD anodes ▲ 20 mA cm⁻², 25°C; ● 60 mA cm⁻², 25°C; ■ 100 mA cm⁻², 25°C. Black points: nitrates, White points: ammonium, Grey points: nitrites

Figure 6. Speciation of chlorine during the electrolyses of synthetic urine ▲ 20 mA cm⁻², 25°C; ● 60 mA cm⁻², 25°C; ■ DDB 100 mA cm⁻², 25°C. Black points: chloride, white points: chloramines. Inset: Black point: hypochlorite, white points: chlorate, grey points: perchlorates.

Figure 7. Oxidation progress during the electrolyses of synthetic urine with BDD anodes at 20 mA cm⁻², raw matters: ▲ uric acid; ● urea; ■ creatinine. Inset: reaction intermediates: ▲ unknown 1; ● unknown 2; ■ unknown 3; ◆ oxalic acid; △ creatol; ○ oxamic acid; □ guanidine

Table

Table 1. Kinetic constants and maximum efficiency for the removal of TOC and COD during the electrochemical treatment of synthetic urine with BDD anodes.

j (mA cm ⁻²)	Temperature (°C)	K(h ⁻¹)		maximum efficiency (mg/Ah)	
		TOC	COD	TOC	COD
20	25	0.37	0.36	125.07	130.32
	50	0.78	0.52	205.25	180.72
60	25	1.24	0.85	87.29	62.32
100	25	0.61	0.50	83.70	60.88

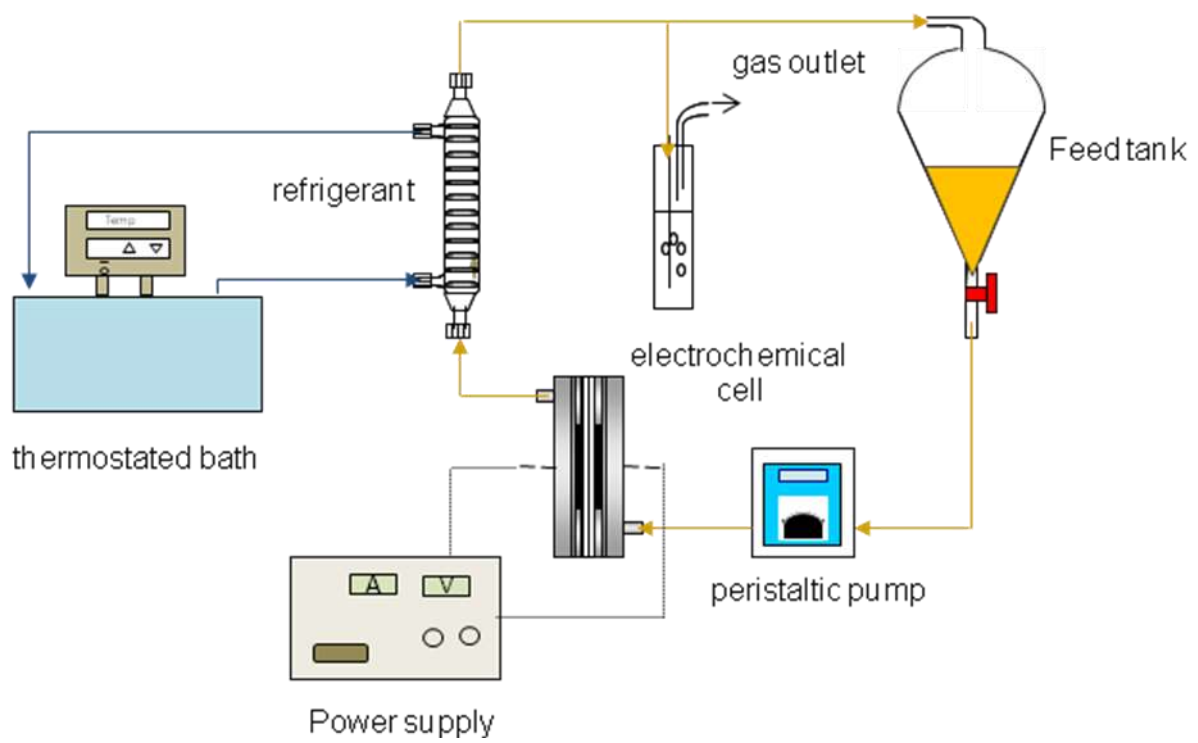


Figure 1

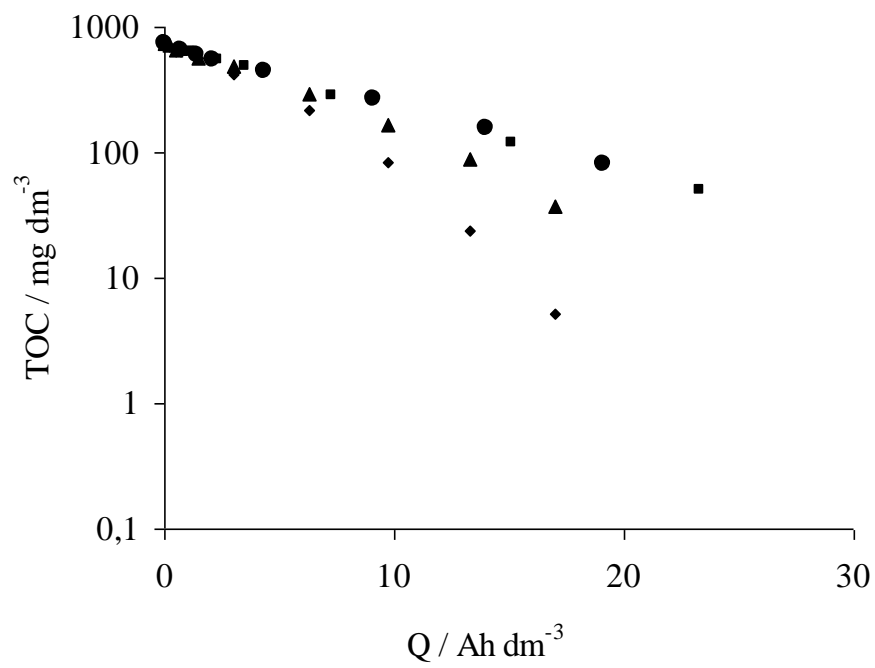
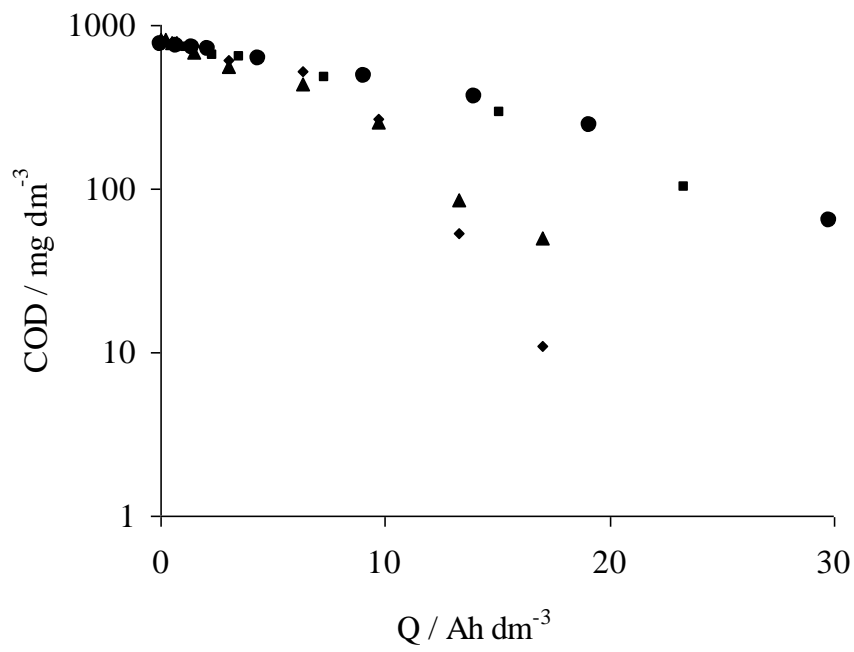


Figure 2

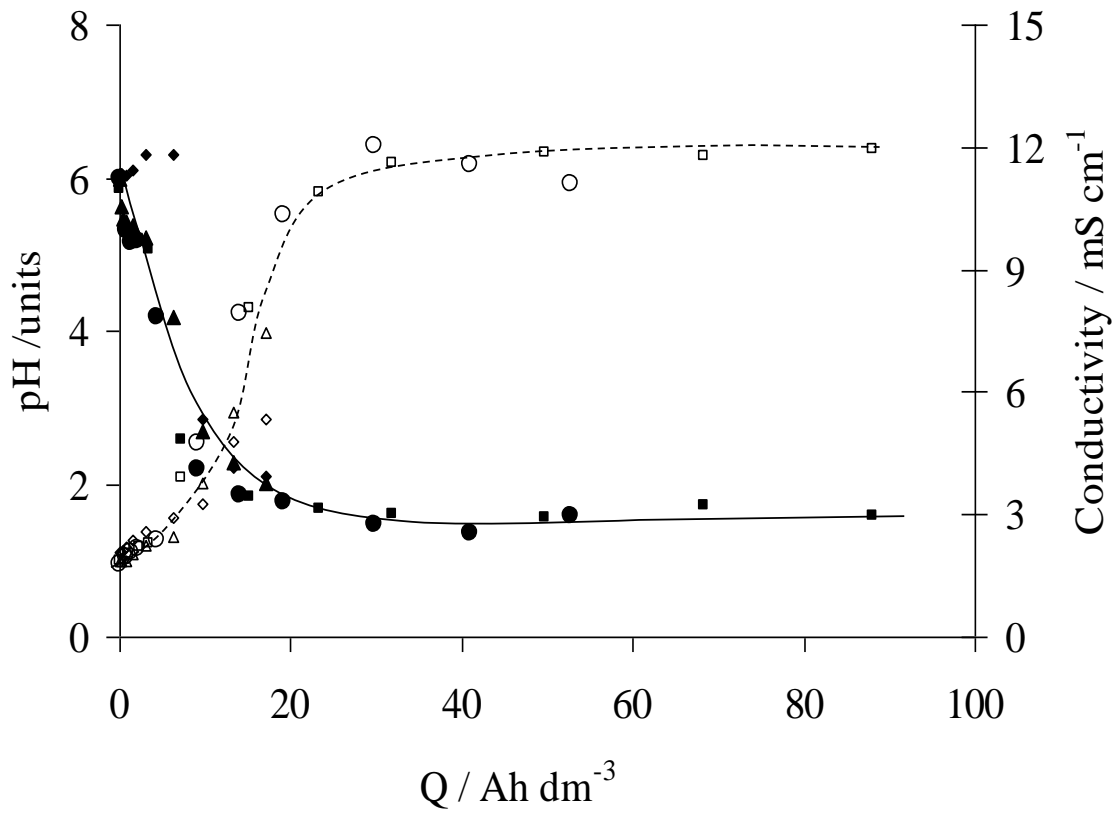


Figure 3

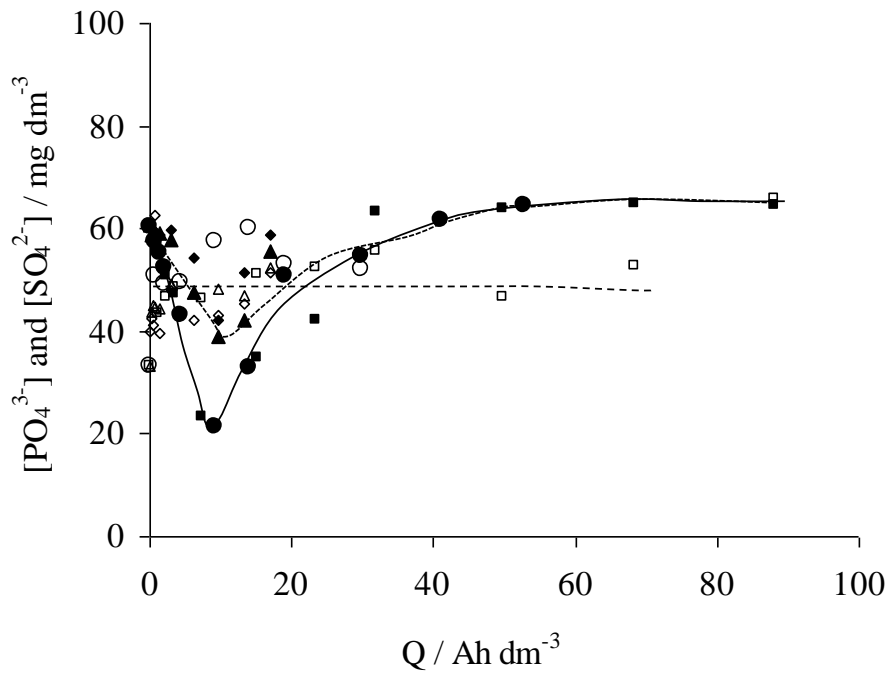


Figure 4

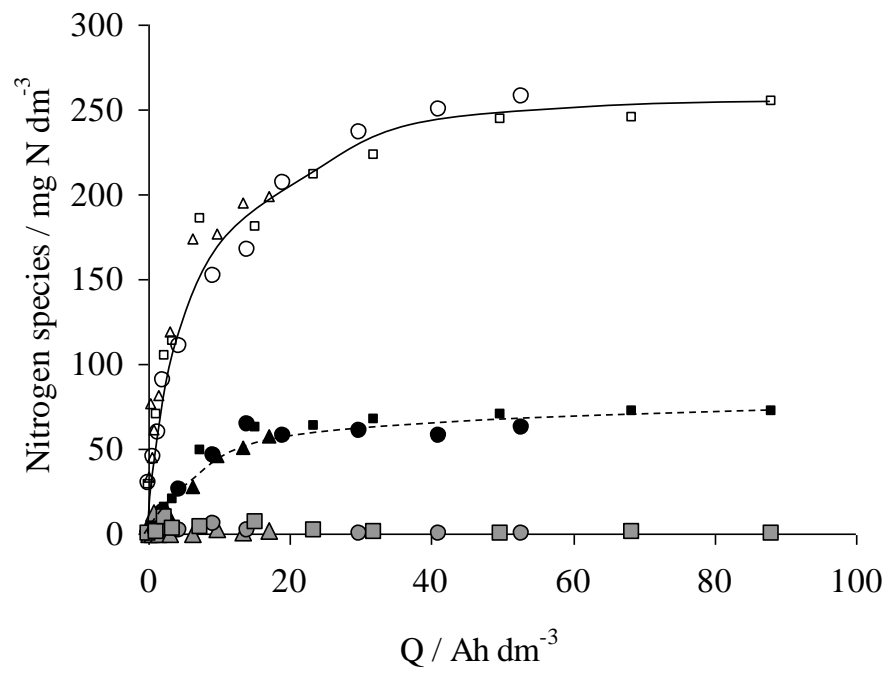


Figure 5

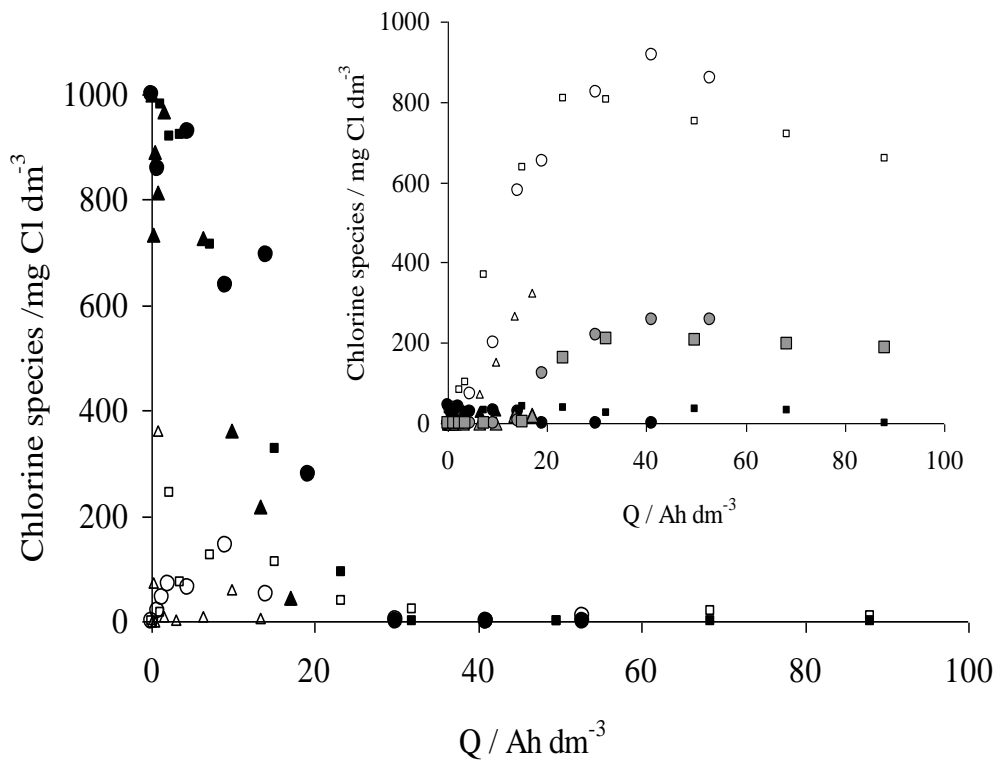


Figure 6

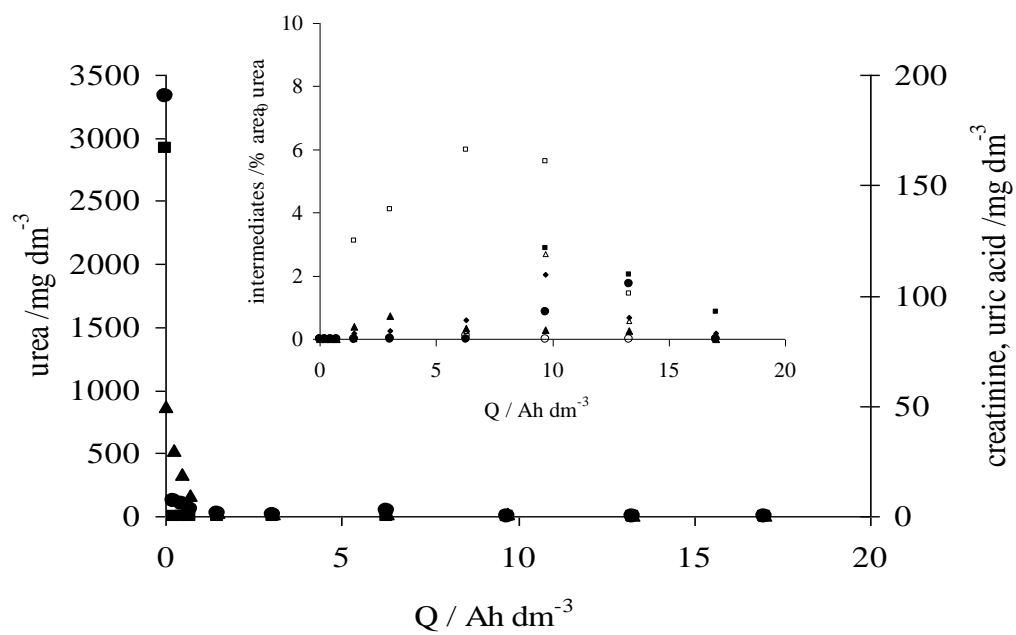


Figure 7