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In this work, the transformation of urine into nutrients using electrolytic oxidation in a single-compartment electrochemical cell in galvanostatic mode was investigated. The electrolytic oxidation was performed using thin film anode materials: boron-doped diamond (BDD) and dimensionally stable anodes (DSA). The transformation of urine into nutrients was confirmed by the release of nitrate (NO3?) and ammonium (NH4+) ions during electrolytic treatment of synthetic urine aqueous solutions. The removal of chemical oxygen demand (COD) and total organic carbon (TOC) during electrolytic treatment confirmed the conversion of organic pollutants into biocompatible substances. Higher amounts of NO3? and NH4+ were released by electrolytic oxidation using BDD compared to DSA anodes. The removal of COD and TOC was faster using BDD anodes at different current densities. Active chlorine and chloramines were formed during electrolytic treatment, which is advantageous to deactivate any pathogenic microorganisms. Larger quantities of active chlorine and chloramines were measured with DSA anodes. The control of chlorine by-products to concentrations lower than the regulations require can be possible by lowering the current density to values smaller than 20 mA/cm2. Electrolytic oxidation using BDD or DSA thin film anodes seems to be a sustainable method capable of transforming urine into nutrients, removing organic pollution, and deactivating pathogens.

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Electrolytic Oxidation as a Sustainable Method to Transform Urine into Nutrients

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Abstract: In this work, the transformation of urine into nutrients using electrolytic oxidation in a single-compartment electrochemical cell in galvanostatic mode was investigated. The electrolytic oxidation was performed using thin film anode materials: boron-doped diamond (BDD) and dimensionally stable anodes (DSA). The transformation of urine into nutrients was confirmed by the release of nitrate (NO_3^-) and ammonium (NH_4^+) ions during electrolytic treatment of synthetic urine aqueous solutions. The removal of chemical oxygen demand (COD) and total organic carbon (TOC) during electrolytic treatment confirmed the conversion of organic pollutants into biocompatible substances. Higher amounts of NO_3^- and NH_4^+ were released by electrolytic oxidation using BDD compared to DSA anodes. The removal of COD and TOC was faster using BDD anodes at different current densities. Active chlorine and chloramines were formed during electrolytic treatment, which is advantageous to deactivate any pathogenic microorganisms. Larger quantities of active chlorine and chloramines were measured with DSA anodes. The control of chlorine by-products to concentrations lower than the regulations require can be possible by lowering the current density to values smaller than 20 mA/cm^2. Electrolytic oxidation using BDD or DSA thin film anodes seems to be a sustainable method capable of transforming urine into nutrients, removing organic pollution, and deactivating pathogens.

Keywords: electrolytic oxidation; thin film anode materials; urine; nutrients; degradation

1. Introduction

Human urine is an extremely complex liquid with variable chemical composition. Urine chemical composition can change over time and between different people depending on numerous factors such as physical activity, diet, and climate [1–5]. Urine is an aqueous medium containing both organic and inorganic components. Urea, creatinine, uric acid, vitamins, hormones, nutrients (N, P, and K), chloride, and trace metals are some of the components excreted in urine [5–8]. Many studies have attempted to find a method to take advantage of the richness of urine in regards to macro and micronutrients and transform it into natural fertilizers that can be used in agricultural production [4,9–11]. However, the hormones and pharmaceuticals excreted with urine as micro-pollutants can bioaccumulate in plants and be transferred to the food chain, which causes high risks to human health [12–14]. Furthermore, urine can contain pathogenic organisms as disease-carriers that can multiply in the soil and contaminate the food web [12,15]. The reuse of insufficiently treated human and animal urine in agriculture may result in transmission of pathogens [5,9,15,16]. Therefore, it is vital to develop a treatment method capable of removing the micropollutants, killing the pathogens, and transforming urine into a valuable fluid rich in nutrients that can be recycled in landscaping and agriculture.

Recently, electrochemical advanced oxidation processes (EAOPs) have attracted more and more attention as compatible techniques for the destruction of toxic and persistent organic pollutants in wastewater [17–19]. These processes are based on the generation of strong oxidants, such as hydroxyl radicals, directly on the anode surface [20–22]. These radicals are powerful oxidizing agents that are highly reactive, non-selective and capable of destroying recalcitrant organics and converting them into CO_2, H_2O and other inorganic ions, or partially transforming them into easily biodegradable compounds [23–29]. Dimensionally stable anodes (DSA) and boron-doped diamond (BDD) electrodes have largely been investigated as thin film active anodic materials in electrolytic processes for water and wastewater treatment [30–35]. These anode materials present excellent electrochemical stability in harsh environments, high efficiency in the production of strong oxidants, and long-lasting disinfecting action [33–35]. DSA anodes are unique in producing active chloride by the electro-oxidation of chlorides in water at low voltage compared to other materials [36,37]. BDD anodes are characterized by much larger O_2 evolution over-potential, enabling the production of a large amount of hydroxyl radicals from water discharge, which are weakly adsorbed on the surface of the anode (Equation (1)) [30].

$$\mathrm{BDD} + \mathrm{H_2O} \rightarrow \mathrm{BDD(HO^{\bullet})} + \mathrm{H^+} + 1\mathrm{e} \quad (1)$$

In addition, BDD anodes have a large electrochemical window that facilitates the electro-oxidation of salts in water to produce strong oxidants (persulfates) and disinfectants (hypochlorites and chloramines) [38–40]. Several authors have investigated the treatment of urine using BDD and DSA anodes [32–34,38–40]. These investigations resulted in the degradation of organic content, with a minor focus on the final products obtained at the end of the treatment and the recycling of the treated urine wastewater [33,34,39].

The goal of this work was to transform synthetic urine into macro and micronutrients by electrolytic oxidation using DSA and BDD thin film electrodes. We aimed to evaluate the effects of the principal parameters such as current density, flow rate, and temperature on the kinetics and performance of electrolytic oxidation using BDD and DSA anodes during electrolytic treatment of urine. To do this, chemical oxygen demand (COD) and total organic carbon (TOC) were monitored during the electrolytic oxidation. The amounts of macro and micronutrients were measured during and at the end of electrolytic treatment. Furthermore, the analysis of undesirable oxidation products (chlorates and perchlorates) was performed in order to determine the toxicity of the treated urine effluent.

2. Materials and Methods

2.1. Synthetic Urine Composition

The synthetic urine was prepared by dissolving all the components in the concentrations illustrated in Table 1. The prepared urine has a representative composition of human urine described in the literature [1,9]. This liquid effluent is characterized by high organic content with an initial TOC of about 750 mg C/L. It is rich in nitrogen (1650 mg N/L) and contains the major macronutrients (potassium, phosphorus, magnesium, calcium, sulfur) and some micronutrients.

Table 1. Composition of synthetic urine and its physicochemical parameters.

Component	Parameter
Urea (CH_4N_2O)	3333.3 mg/L
Uric acid ($C_5H_4N_4O_3$)	50.0 mg/L
Creatinine ($C_4H_7N_3O$)	166.7 mg/L
Potassium (K^+)	1000.0
Sodium (Na^+)	166.7 mg/L
Ammonium (NH_4^+)	25.0 mg/L
Magnesium (Mg^{2+})	16.7 mg/L
Calcium (Ca^{2+})	25.0 mg/L
Chloride (Cl^-)	1000.0 mg/L
Phosphate (PO_4^{3-})	25.0 mg/L
Sulfate (SO_4^{2-})	300.0 mg/L
Carbonates (CO_3^-)	166.7 mg/L
TOC	750 mg C/L
COD	825 mg O_2/L
pH	5.5
Conductivity	6.5 mS/cm

2.2. Chemicals

The organic chemicals (urea, uric acid, and creatinine) were purchased from Sigma Aldrich (with purity >99.0%). Analytical grade inorganic salts, H_2SO_4 and NaOH were obtained from VWR. Synthetic urine solutions were made by dissolving the components in deionized water prepared by a Millipore system with resistivity ≥18.2 MΩ cm at 25 °C.

2.3. Analytical Methods

An InoLab WTW pH-meter (Thermo Fisher Scientific, Stockholm, Sweeden) and a GLP 31 Crison conductimeter (Crison Instruments SA, Barcelona, Spain) were used to measure the pH and conductivity. All samples withdrawn from electrolyzed urine at the desired times underwent a filtration through 0.2 µm membrane filters (Whatman®membrane filters nylon, Merck, Darmstadt, Germany) before they were sent for analysis. TOC content was measured by catalytic high temperature oxidation/combustion (up to 950 °C) using a TOC analyzer (Multi N/C 3100 Analytik Jena, Jena, Germany). COD was analyzed by the spectrophotometric method using the standard method [41]. Two milliliters of the electrolyzed solution were mixed with an oxidizing solution (purchased from Merck (Spectroquant®®), Darmstadt, Germany) in a glass tube (the chloride content did not affect the COD measurement as it was less than 2 g/L). The speciation of chlorine anions (Cl^-, ClO^-, ClO_2^-, ClO_3^-, and ClO_4^-) were performed by ion chromatography using a Shimadzu LC-20A chromatograph (Shimadzu Corporation, Kyoto, Japan) equipped with a Shodex IC I-524A column (Shimadzu Corporation, Kyoto, Japan). Phthalic acid (2.5 mM) at pH 4.0 was the mobile phase at 1.0 mL/min flow rate. The other inorganic anions (NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}) were monitored using the same ion chromatograph (column, Shodex IC YK-421 Shimadzu Corporation, Kyoto, Japan) with a mobile phase of 5.0 mM tartaric, 1.0 mM dipicolinic acid and 24.3 mM boric acid at a flow rate of 1.0 mL/min. Ammonium ions were analyzed by an ion-selective electrode for ammonium ion (ELIT 8051 PVC membrane, NICO2000 Ltd, UK). The determination of hypochlorite was done by titration with As_2O_3 in 2 M NaOH. Inorganic chloramines measured by the DPD colorimetric method was conducted using Shimadzu spectrophotometer UV-2400PC (Shimadzu Corporation, Kyoto, Japan) as described in the literature [42].

2.4. Electrolytic Treatment

A single compartment electrochemical flow cell working in batch-operation mode was used to perform all of the electrolytic experiments (see Figure 1). BDD anodes were purchased from Adamant Technologies (Neuchatel, Switzerland). They were fabricated by the hot filament chemical vapor deposition (HF CVD) technique of a boron-doped diamond thin film deposited on single-crystal p-type Si (100) substrates (0.1 Ω cm Siltronix) as described elsewhere [43]. DSA$^{®®}$ O_2 evolution anodes were obtained from DeNora, Italy and were fabricated by coating titanium sheet (3 mm thickness) with thin and impervious layers of mixed metal oxide (IrO_2–RuO_2) (5–10 μm thickness). Stainless steel (AISI 304) was used as the cathode material for all electrolytic tests.

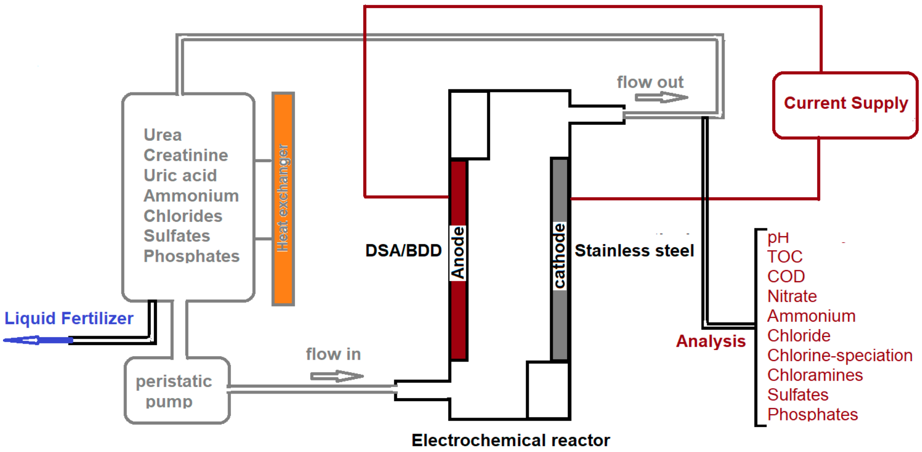

Figure 1. Experimental setup and procedures used during electrolytic treatment.

The circular electrodes (100 mm diameter) had a geometric area of 78 cm^2 and were separated from each other by 9 mm. A centrifugal pump was employed to circulate the electrolyte stored in a glass tank (600 mL) through the electrolytic cell at variable flow rates. The temperature was maintained at the desired value using a thermostatic bath. The electrolytic experiments were performed under galvanostatic mode (constant current density). The electrodes were connected to a digital dc power supply (Monacor PS-430, Monacor International GmbH & Co., Bremen, Germany) providing current and voltage in the ranges 0−30 A and 0−20 V. No variation in cell voltage was observed during electrochemical oxidation indicating that BDD or DSA did not undergo appreciable deterioration or passivation phenomena.

3. Results and Discussion

Many studies have indicated that the current density is a very important experimental parameter in all electrochemical processes [44–46]. Electrolytic oxidation performance is strongly dependent on the chemical stability and electrochemical activity of the anode material. An adequate anode material should be capable of generating strong oxidizing agents such as HO radicals from water discharge on the surface of anode and other oxidants to mediate the oxidation/degradation of pollutants in solution [44–46].

Figure 2 shows the changes of COD and TOC with the specific electric charge (Q, Ah/L) during galvanostatic electrolyses of synthetic urine using both BDD and DSA at different values of current density. Both parameters, COD and TOC, undergo a rapid decrease with Q, as the treatment began in a similar way for both BDD and DSA anodes. An exponential decline of COD and TOC with Q was observed at different current densities. The increase in the current density from 20 mA/cm^2 to 100 mA/cm^2 led to lower performance in terms of COD and TOC removal, since a higher Q was needed to accomplish 90% COD and TOC removal for both anode materials. The changes of COD with Q has an exponential trend, indicating that mass transfer is controlling the overall process for the range of 20–100 mA/cm^2 current density for both DSA and BDD. These results are in agreement with the literature [29,47,48] and it can be explained by mass transfer limitation and the competition of secondary reactions of oxygen evolution and salt oxidation electroactive species at higher current densities. It is important to note that both anode materials have shown similar performance in removing COD from synthetic urine, whereas the BDD anode was more effective than DSA in terms of TOC removal.

Taking into consideration that any decay in TOC content is indicative of mineralization of organic carbon (transformation of organic carbon into CO_2) contained in wastewater, it can be concluded that BDD has greater potentiality to achieve the complete removal of all toxic and bioresistant pollutant excreted with urine. In addition, the similar electrochemical behavior of both anodes in declining COD concentration indicates that BDD and DSA are capable of improving the biodegradability and reducing the toxicity of synthetic urine. The higher performance of BDD compared to DSA is mainly due to its larger electrochemical window enabling direct and mediated oxidation of the urine components and their intermediates [33,35,49]. Although small differences in the performance of BDD and DSA were observed, both anodes were efficient in decontaminating urine and enriching the composition of the treated effluent with biocompatible products through the electrolytic conversion of the major part of the organic fraction (more than 90%) into inorganic species. Further details related to the nature and the amount of the final products are desirable to determine the usefulness of the treated urine as liquid fertilizer in agriculture and horticulture applications.

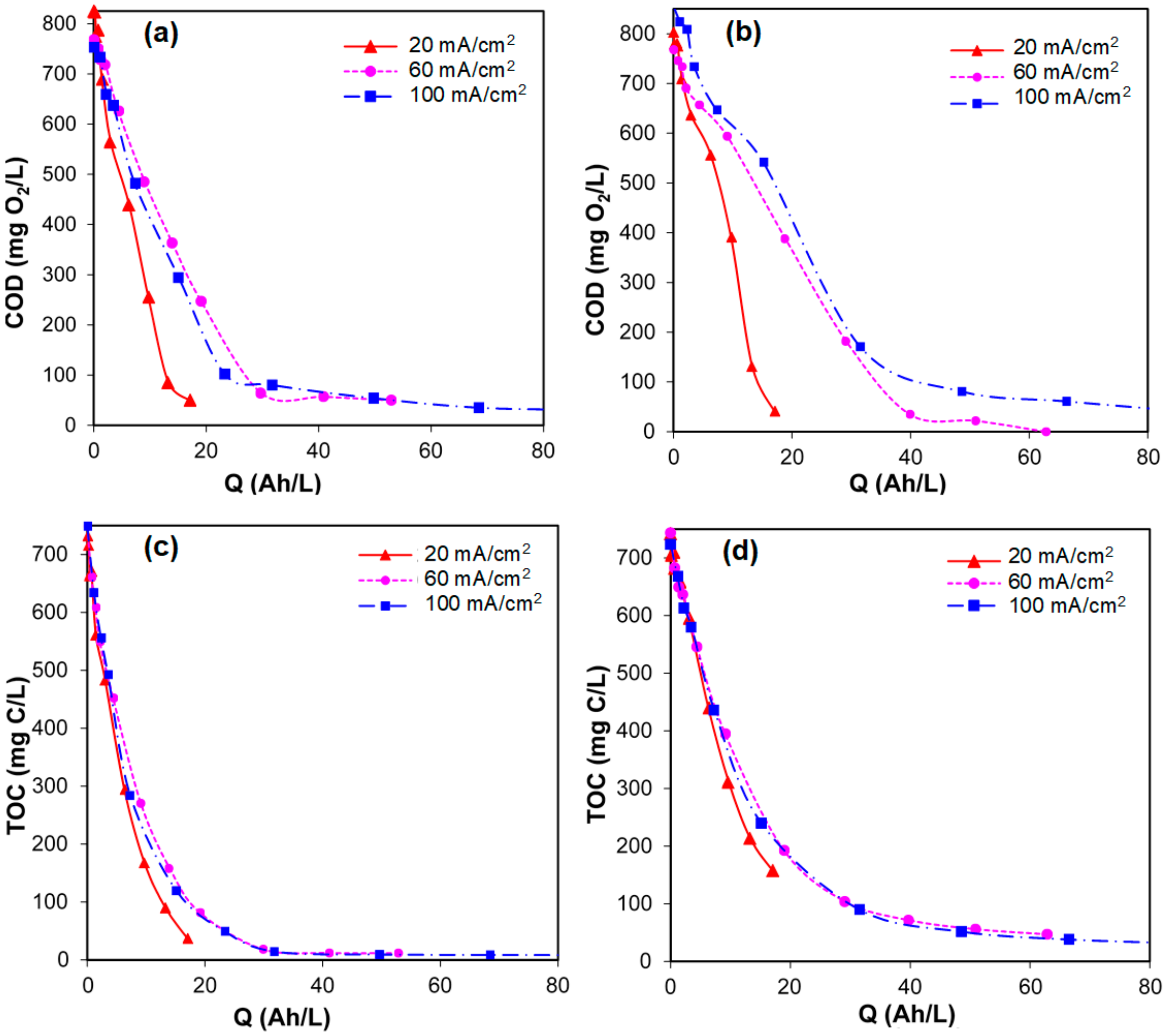

Figure 2. Changes of COD (**a**,**b**) and TOC (**c**,**d**) with the specific electric charge during electrolytic treatment of synthetic urine of pH 5.5 at room temperature (25 °C) using BDD (**a**,**c**) and DSA (**b**,**d**) anodes and a stainless steel cathode with a flow rate of 800 mL/min at different current densities: (▲) 20 mA/cm^2, (●) 60 mA/cm^2, and (■) 100 mA/cm^2.

Figure 3 presents the changes of TOC and pseudo-first order behavior ($LnTOC_0/TOC_t$) with the specific charge Q (Ah/L) during the electrolytic treatment of synthetic urine in undivided (one-compartment) and divided cells (two-compartment) using BDD and DSA anodes. Divided cells achieved higher TOC removals (Figure 3a) and better kinetics (Figure 3b) than undivided cells for both BDD and DSA anodes at the same operational conditions. The overall more efficient electrolytic treatment in divided cells can be due to a greater contribution of the electrogenerated oxidizing agents blocked by the membrane to transfer to the cathode and be reduced. However, a 2–3 fold higher voltage was measured with divided cells indicating that higher energy consumption is needed to reach similar TOC removals. The separation of anodic and cathodic compartments improved the efficiency of the electrolytic process, while the costs are at risk of increasing greatly considering the additional cost of the replacement of the separation membrane and the higher energy consumption. A more detailed study is needed to evaluate if the gain in the treatment efficiency is beneficial in terms of costs for the whole process.

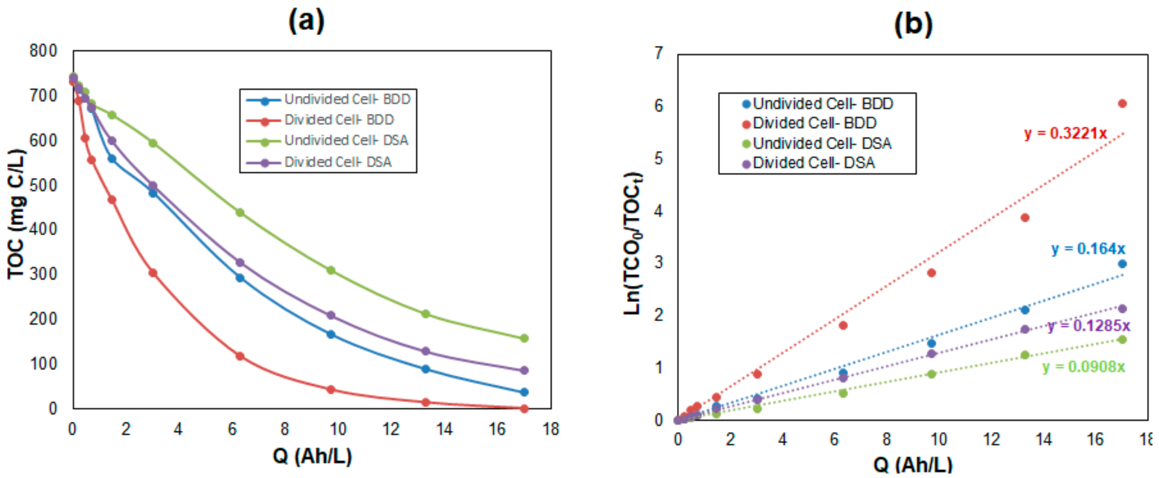

Figure 3. (**a**) Changes of TOC, and (**b**) First-order prediction with the specific electric charge during electrolytic treatment of synthetic urine at pH 5.5 using BDD and DSA anodes and a stainless steel cathode at 20 mA/cm^2 with a flow rate of 800 mL/min in undivided and divided cells.

Figure 4 presents the effects of flow rate and temperature on the changes of TOC with Q during the electrolytic treatment of synthetic urine using a BDD anode at a current density of 20 mA/cm^2. It is clear that the flow rate in the range 800–1250 mL/min did not have an effect on the TOC trend and the curves of TOC with Q overlapped.

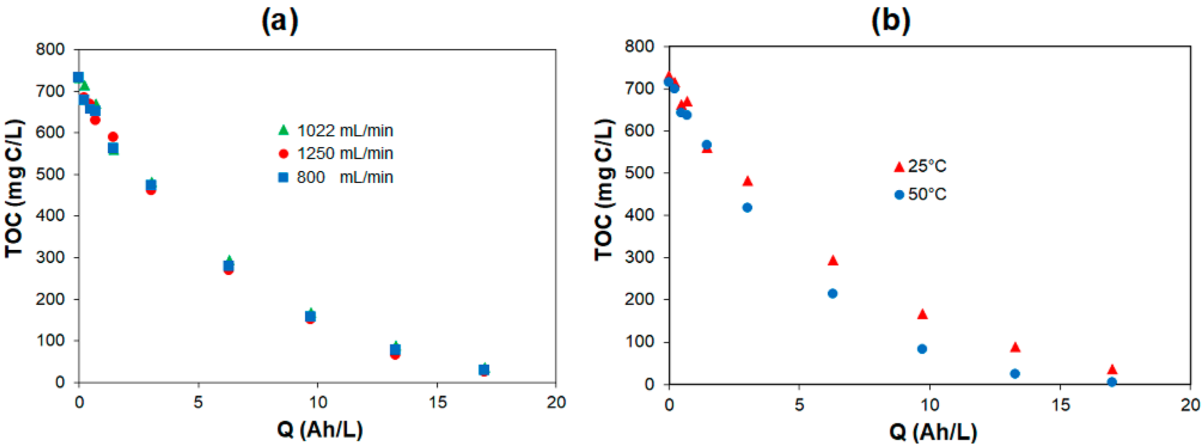

Figure 4. Effects of (**a**) flow rate and (**b**) temperature on the changes of TOC with the specific electric charge during electrolytic treatment of synthetic urine at pH 5.5 using a BDD anode and stainless steel cathode at different 20 mA/cm^2.

This indicates that mass transfer kinetics is not affected by the flow rate in the range studied. However, it seems that the temperature showed a more rapid and efficient TOC removal at 50 °C than 25 °C, especially in the final stages of the electrolytic treatment. The remarkable effect of temperature at the final stage of the electrolytic treatment indicates that the removal of organic matter (TOC) is performed by mediated oxidation in solution rather than at the surface of BDD when the mass transfer is controlling the kinetics of the process.

Figure 5 shows the change of pH with Q during electrolytic treatment of synthetic urine (initial pH = 5.5) using BDD and DSA anodes at different current densities. A remarkable difference in pH change was observed between BDD and DSA anodes. The pH decreased from 5.6 to 2.0, and then it remained unchanged at pH 2.0 for Q > 20 Ah dm^{-3} during the electrolytic treatment using the BDD anode. However, after a decrease from 5.6 to around 3.0 at the beginning of the treatment, the pH increased to stabilize to a value between 8.0 and 9.0 depending on the current density when DSA was used as the anode material.

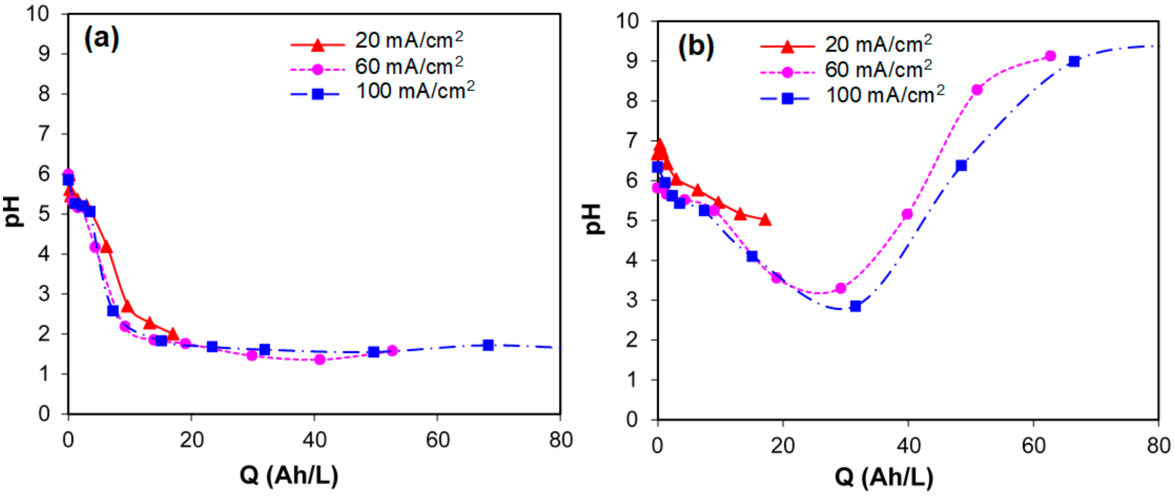

Figure 5. Changes of pH with the specific electric charge during electrolytic treatment of synthetic urine at pH 5.5 and at room temperature (25 °C) using BDD **(a)** and DSA **(b)** anodes and a stainless steel cathode with a flow rate of 800 mL/min at different values of applied current densities: (▲) 20 mA/cm^2, (●) 60 mA/cm^2, and (■) 100 mA/cm^2.

The change of pH in a one-compartment cell is the result of the acid-base reactions that occur on the surface of the anode and cathode and in solution. The formation of CO_2, carboxylic acids and other inorganic ions by oxidation of organic components liberates protons in water, acidifying the medium; however, if only these reactions contribute to the changes of pH during electrolytic treatment of urine, no differences would be observed between BDD and DSA anodes. Furthermore, the reactions of electro-generation of hydroxyl radicals and oxygen and hydrogen evolution from water discharge at the surface of BDD and DSA anodes involves protons (Equations (2)–(4)) during the electrolytic treatment:

$$H_2O \rightarrow HO^\bullet + H^+ + 1e \tag{2}$$

$$2H_2O \rightarrow O_2 + 4\,H^+ + 4e \tag{3}$$

$$2H_2O\ + 2\,e \rightarrow H_2 + 2\,OH^- \tag{4}$$

The reaction of oxygen evolution, which liberates extra protons, is more important at the BDD anode than DSA. This reaction becomes predominant at high current densities retaining a pH of 2.0 until the end of the electrolytic treatment with BDD. The increase of pH at the end of electrolytic treatment using DSA (at high current densities) indicates that hydrogen evolution is predominant, favoring the formation of basic/alkaline species. The analysis of final inorganic products can improve our understanding about the observed difference of pH changes between BDD and DSA anodes.

Figure 6 shows the changes of NO_3^- and NH_4^+ concentrations with Q during electrolytic treatment of synthetic urine using BDD and DSA anodes at different current densities. Nitrate and ammonium ions were formed from the beginning of the treatment for BDD and DSA anodes. Higher amounts of ammonium than nitrate were measured at the end of the treatment, regardless of current density (20, 60, or 100 mA cm^{-2}) and nature of the anode (BDD or DSA).

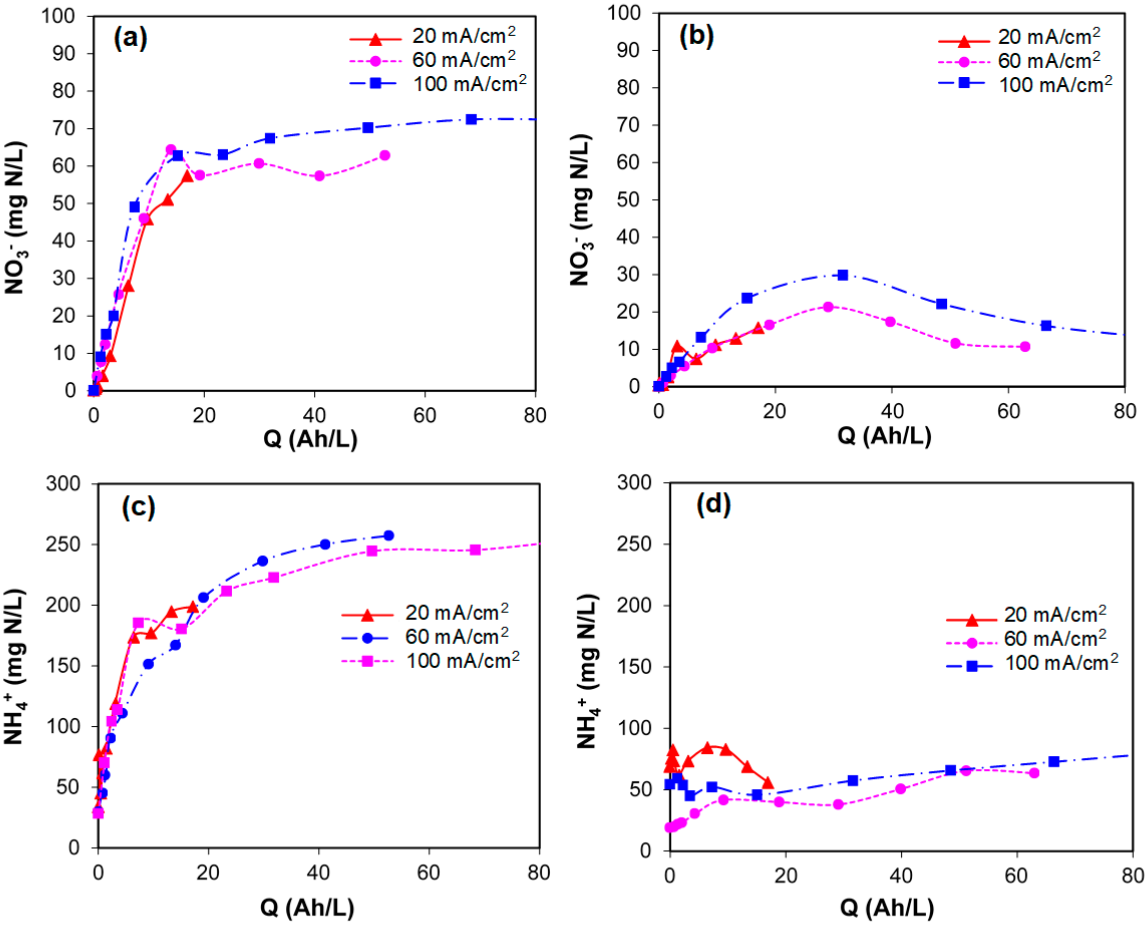

Figure 6. Changes in the concentration of nitrates (**a**,**b**) and ammonium (**c**,**d**) ions with the specific electric charge during electrolytic treatment of synthetic urine at pH = 5.5 and at room temperature (25 °C) using BDD (**a**,**c**) and DSA (**b**,**d**) anodes and a stainless steel cathode with a flow rate of 800 mL/min at different current densities: (▲) 20 mA/cm^2, (●) 60 mA/cm^2, and (■) 100 mA/cm$^{2.}$

Even the concentrations of NO_3^- and NH_4^+ ions exhibited similar trends for BDD and DSA (a rapid increase with Q to reach a maximum value around 20 Ah dm^{-3}, followed by a plateau after 20 Ah dm^{-3}); larger amounts were measured with BDD than DSA. The maximum NO_3^- concentrations measured at the end of electrolytic treatment were 70 and 30 mg N/L for BDD and DSA, respectively. The highest NH_4^+ concentrations were 250 mg N/L and 50 mg N/L at the end of electrolytic treatment. It is remarkable that current density did not have a significant effect on the concentrations of NH_4^+ and NO_3^- at the end of the electrolytic treatment, which is in good agreement with the results of TOC and COD. The higher amounts of ammonium than nitrate ions can be explained by the reduction of NO_3^- ions (formed by oxidative release of organic nitrogen) in solution or at the cathode to NH_3/NH_4^+. The higher amounts of NH_4^+ measured with BDD compared to DSA can be correlated with the pH changes (Figure 5) that favor the formation of NH_4^+ in the case of BDD (acidic medium) and NH_3 in the case of DSA (alkaline medium).

Furthermore, taking into account the initial concentration of organic nitrogen (≈1650 mg N/L) and the almost complete mineralization of the organic carbon (confirmed by the results of TOC in Figure 2), the amounts of ammonium and nitrate (in mg N/L) were surprisingly much lower than the initial organic nitrogen in all conditions. This indicates that the major part of organic nitrogen was transformed to molecular and/or volatile forms (NH_3, NO_x, N_2, and chloramines) at the end of the electrolytic treatment with BDD or DSA. However, the amounts of NO_3^- and NH_4^+ measured at the end of the treatment are sufficient to supply nitrogen as a plant nutrient in short (nitrate) and long (ammonium) terms in agriculture or landscaping applications [50–52].

On the other hand, urine contains, in addition to the organic fraction, chlorides, sulfates, and phosphates. The literature review demonstrates that BDD and DSA are able to oxidize these anions and transform them into strong oxidants offering an additional route to transform the organic fraction into minerals and valuable products that are safely recycled in the ecosystem [53–56]. A careful analysis of the production of the strong oxidants from chlorides, sulfates and phosphates is mandatory to control the quality of the treated urine because excessive amounts would have negative effects and render the treated urine non-useful as enriched-liquid fertilizer. The changes of chloride and hypochlorite concentrations (in mg Cl/L) during electrolytic treatment of urine using BDD and DSA anodes at different current densities are shown in Figure 7.

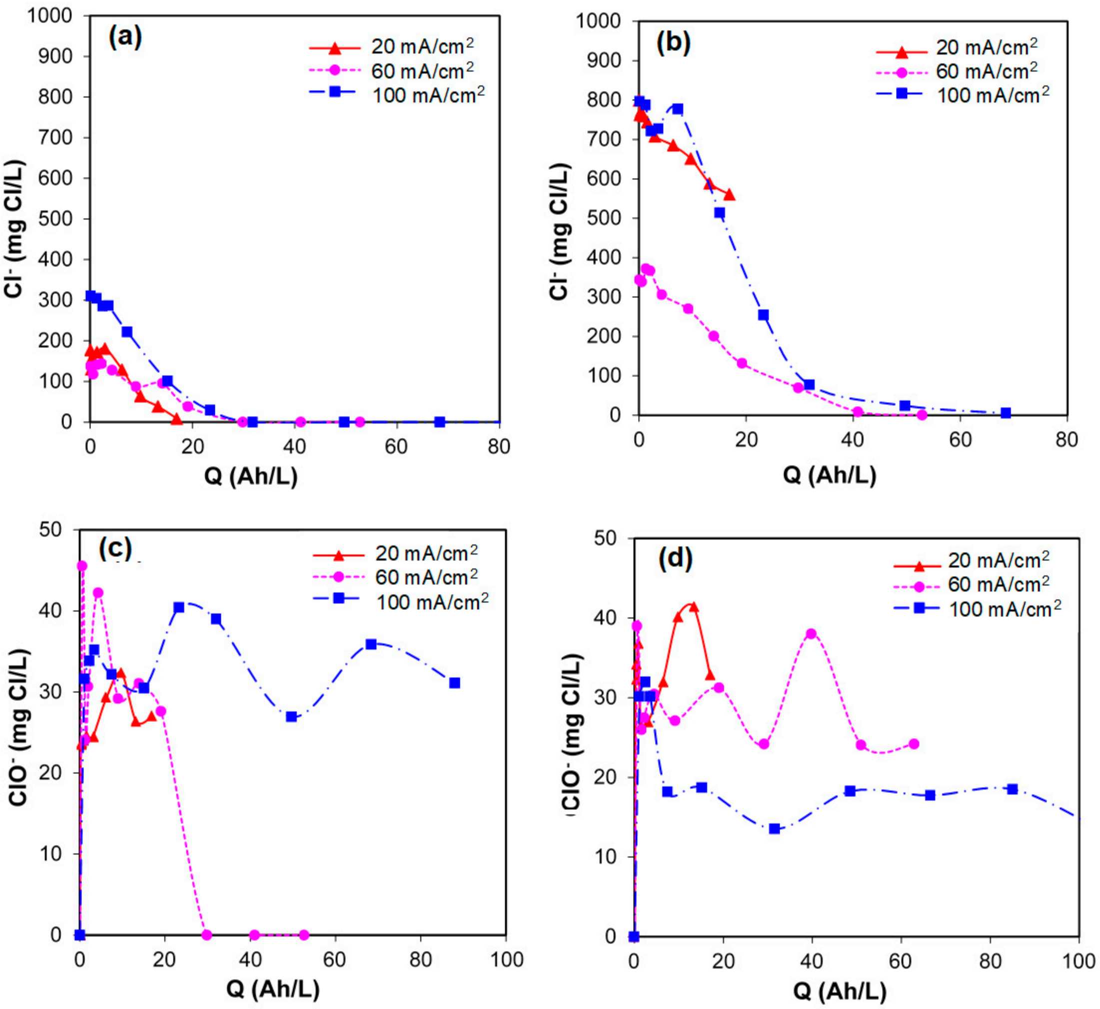

Figure 7. Changes in concentrations of (**a**,**b**) chlorides (Cl^-) and (**c**,**d**) hypochlorite (ClO^-) with the specific electric charge during electrolytic treatment of synthetic urine at pH = 5.5 and at room temperature (25 °C) using BDD (**a**,**c**) and DSA (**b**,**d**) anodes and a stainless steel cathode with a flow rate of 800 mL/min at different current densities: (▲) 20 mA/cm², (●) 60 mA/cm², and (■) 100 mA/cm².

Chlorides concentration started to decay from the beginning of the treatment, at the same time, hypochlorites concentration increased. BDD achieved a complete depletion of chlorides for all the current densities at 20–30 Ah/L, whereas DSA achieved the total depletion of chlorides only for current densities higher than 20 Ah/L and after consumption of 40 Ah/L. Similar amounts of hypochlorites (40–50 mg Cl/L) were measured at the end of the treatment, regardless of current density and nature of the anode (DSA or BDD).

It is well-documented that BDD and DSA are capable of oxidizing chlorides into hypochlorites (or hypochlorous acid) directly at the surface of the anode or by the electro-generated hydroxyl radicals [38,49,57]. The production of hypochlorites during the treatment of urine is important because they are known by their disinfectant action, which deactivates/kills most of the pathogenic bacteria and participates in the partial degradation of organic pollutants. However, considering the initial amount of chlorides (1000 mg Cl/L), it seems that the amounts of hypochlorites are very low compared to the stoichiometric amount. The results of Figure 8a,b confirmed the quick transformation of hypochlorites into chlorates during the electrolytic treatment of synthetic urine with BDD and DSA. The amount of chlorates formed depends largely on the current density for both anodes. At 20 mA/cm^2, the amounts of chlorates were 312 mg Cl/L and 16 mg Cl/L (after consumption of 20 Ah/L) for BDD and DSA, respectively.

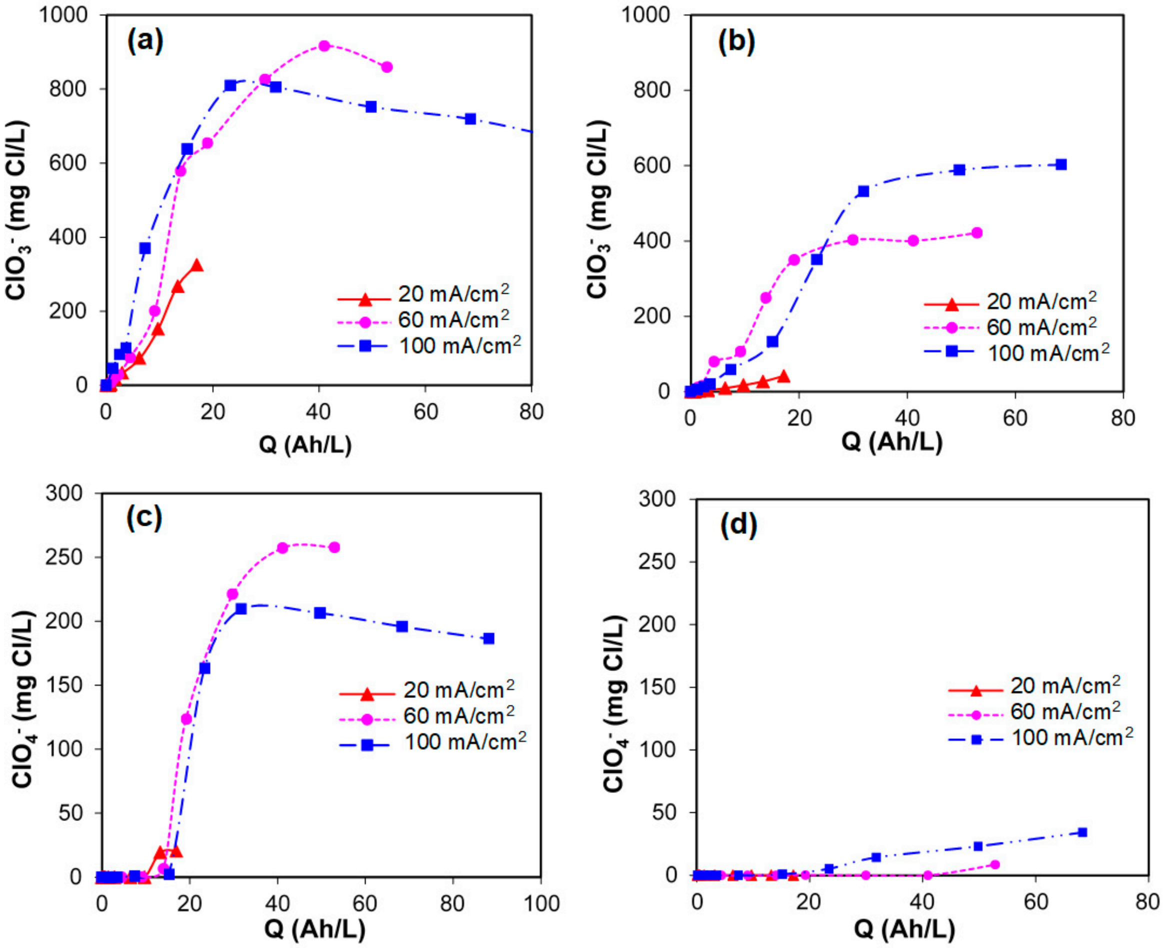

Figure 8. Changes in the concentrations of (**a**,**b**) chlorates (ClO_3^-) and (**c**,**d**) perchlorate (ClO_4^-) formed with the specific electric charge during electrolytic treatment of synthetic urine at pH = 5.5 and at room temperature (25 °C) using BDD (**a**,**c**) and DSA (**b**,**d**) anodes and a stainless steel cathode with a flow rate of 800 mL/min at different current densities: (▲) 20 mA/cm^2, (●) 60 mA/cm^2, and (■) 100 mA/cm$^{2.}$

For current densities higher than 20 mA/cm^2, a massive production of chlorates occurred reaching 800 mg Cl/L and 600 mg Cl/L for BDD and DSA, respectively. The higher amounts of chlorates formed with BDD than DSA can be due to a greater contribution of hydroxyl radicals in the oxidation of hypochlorites. This also explains the higher perchlorates concentration measured at the end of the treatment of synthetic urine by BDD (see Figure 8c,d). It should be noted that chlorates and perchlorates are classified as toxic substances and their concentrations are regulated by several environmental agencies over the world [58–60]. The production of chlorates and perchlorates during electrolytic treatment of synthetic urine by BDD and DSA anodes hinders any technical applications. However, the control of the current density can play an important role in overcoming this obstacle because lowering the current density to values ≤20 mA/cm^2 with DSA anodes produces very low amounts of chlorates and perchlorates, which fits the regulations. Table 2 illustrates the concentrations of chlorates and perchlorates measured at the end of the electrolytic treatment of synthetic urine at pH 5.5 and at 20 mA/cm^2 under different flow rates. The amounts of chlorates and perchlorates decreased with the increase of flow rate indicating that the formation rate of chlorates and perchlorates decreases with lower residence times [61,62].

Table 2. Effect of the flow rate on the concentrations of chlorates and perchlorates formed during the electrolytic treatment of synthetic urine at pH 5.5 using BDD and DSA anodes and a stainless steel cathode at 20 mA/cm^2 after the consumption of 17 Ah/L.

Flow Rate (mL/min)	**Chlorates (mg Cl/L)**		**Perchlorates (mg Cl/L)**	
	BDD	**DSA**	**BDD**	**DSA**
800	325.4	41.1	20.5	0.1
1250	198.9	15.9	8.3	ND
1780	84.2	5.2	1.2	ND

Based on the results of chlorine speciation, the BDD anode seems to be inadequate material for the transformation of urine to liquid fertilizer without any further treatment. Although it showed higher efficiency in terms of TOC and COD removal, it produced large amounts of chlorine hazardous by-products. In addition to oxychlorine species (ClO^-, ClO_3^-, ClO_4^-), chloramines (NH_xCl_y) were also identified as inorganic intermediates during the electrolytic treatment of synthetic urine. Figure 9 presents the changes of chloramines concentration with Q during the electrolytic treatment of synthetic urine using BDD and DSA anodes at different current densities. As can be seen, chloramines started to form gradually from the beginning of the treatment to reach a maximum at around 20 Ah/L, then decayed with Q to disappear at the end of the treatment. The higher amounts of chloramines reached with DSA than BDD can be due to basic pH conditions, which favors their formation [63,64]. The disappearance of chloramines at the end of the treatment is mainly due to their high volatility. Nevertheless, they can participate in deactivating the microorganisms contained in urine.

Phosphate concentrations did not change with Q during the electrolytic treatment of synthetic urine DSA anodes at different current densities. With the BDD anode, phosphates concentration decreased with Q to reach a minimum at around 10 Ah/L, after that it increased and then stabilized at its initial value. This can be due to the formation of peroxomonophosphate (PO_5^{2-}) and peroxodiphosphate ($P_2O_8^{2-}$) by oxidation of phosphates at the BDD anode and/or with hydroxyl radicals [65,66]. Peroxomono- and diphospahtes are unstable when the pH is acid and they decompose to regenerate phosphates (this is what happened in the case of BDD). The amount of phosphates measured at the end of the treatment with DSA and BDD is sufficient to supply phosphorus in liquid form in the case of the treated urine being used in irrigation.

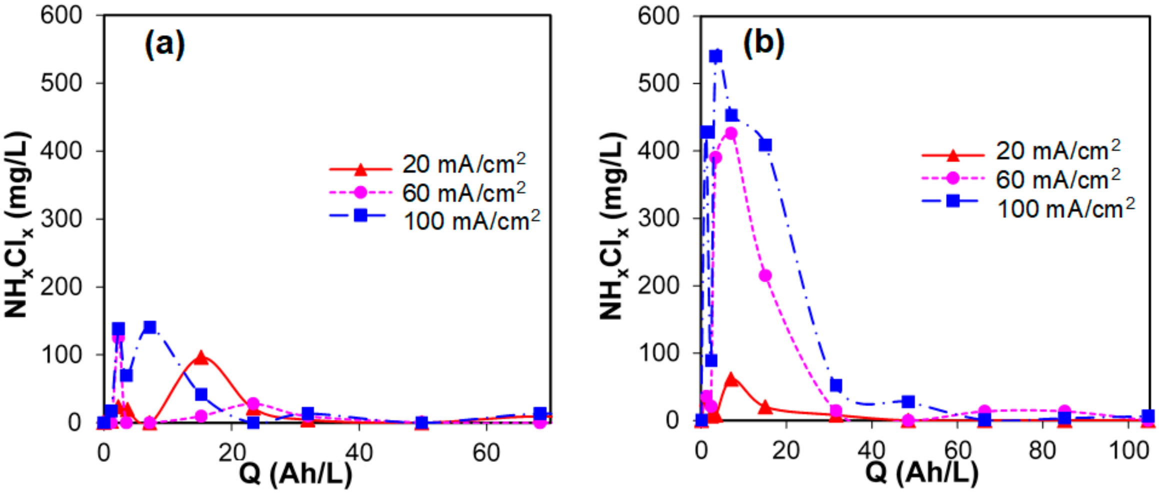

Figure 9. Changes in the concentration of chloramines with the specific electric charge during electrolytic treatment of synthetic urine at pH = 5.5 and at room temperature (25 °C) using BDD (**a**) and DSA (**b**) anodes and a stainless steel cathode with a flow rate of 800 mL/min at different current densities: (▲) 20 mA/cm^2, (●) 60 mA/cm^2, and (■) 100 mA/cm^2.

4. Conclusions

The main conclusions extracted from this work can be summarized as follows:

- Electrolytic oxidation using BDD and DSA anodes achieved the almost complete mineralization of the organic carbon initially contained in synthetic urine, regardless of the current density, flow rate, and temperature. Higher current densities were less efficient because the oxygen evolution becomes competitive with the degradation of organic pollution.
- Nitrates, ammonium, and other volatile nitrogen forms were released during the electrolytic treatment of synthetic urine. Higher amounts of inorganic nitrogen were produced with BDD anodes than DSA. This is in good correlation with the pH changes observed during the electrolytic treatment with BDD (acid pH) and DSA (basic pH).
- Chlorides were transformed into hypochlorites that rapidly react with ammonium and/or ammonia to form chloramines. The formation of these species during the electrolytic treatment is very important because they deactivate the microorganisms and kill the pathogens.
- Chlorates and perchlorates can be formed at high current densities with BDD and DSA. The control of the current density can avoid the formation of these toxic and hazardous chlorine species especially when DSA is used as an anode material.
- Phosphates are affected by the pH of the medium and the nature of the anode material. The amount of phosphates measured at the end of the treatment provides the needed amount of phosphorus in liquid form, facilitating its assimilation by plants.
- Electrolytic oxidation using DSA or BDD anodes at low current densities (≤20 mA/cm^2) seems promising as a sustainable method to transform urine into a liquid fertilizer rich in nitrogen, phosphorus, and other micronutrients (potassium, sodium, calcium, etc.) free of hazardous substances. This liquid fertilizer is safe to be used as it is or after dilution in gardening, landscaping, and agriculture to supply the plants with the needed nutrients.

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