



What happens to inorganic nitrogen species during conductive diamond electrochemical oxidation of real wastewater?



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ABSTRACT

This work describes the oxidation of caffeine, metoprolol, SMX and progesterone in real wastewater in terms of inorganic nitrogen speciation and help clarify the mechanisms that affect inorganic nitrogen species as final products. In synthetic solutions containing ammonium or nitrate ions, it has been confirmed that reduction of nitrates is a very favored process while oxidation of ammonium is negligible. Role of chloride is demonstrated to be important in the formation of chloramines, as well. These results allow the clarification of the production of nitrates as main products of the oxidation of organic chemicals and the occurrence of ammonium and chloramines in the reaction media, as well as the depletion of nitrogen by gaseous nitrogen production. Results are of a great relevance to interpret the mechanisms proposed in the literature for the treatment of organic wastes by conductive diamond electrochemical oxidation.

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1. Introduction

Many anthropogenic chemicals contained in wastewater, commonly known as Persistent Organic Pollutants (POPs), are not efficiently removed by the conventional treatments typically applied in industrial and Municipal Wastewater Treatment Plants (MWTP) [1–4]. Consequently, they enter into the environment, being detected in ground and surface water. They are typically associated with serious damages not only in environment but also in human health. Specifically, these compounds can affect endocrine, immunologic and neurologic systems, and they may cause various types of cancers and they are even associated with low intelligence quotient in children [5–7].

Many authors have studied different technologies for an efficient removal of POPs from wastewater. In this context, Conductive Diamond Electrochemical Oxidation (CDEO) is considered as a good alternative for their treatment, as many other Advance Oxidation Processes [8–12]. From the viewpoint of carbon, typical degradation of these POPs proceeds through the breakage of the aromatic rings, formation of carboxylic acids and ends with the mineralization to carbon dioxide [13–15]. However, despite the large number of papers published, there is less information regarding nitrogen evolution during oxidation processes and this information could be very useful in the design of full-scale environmental applications. In particular, to the authors' knowledge, there is no general information about the final products formed and, in most papers, the formation of ammonium and nitrate ions are reported, without giving a clear description of the oxidation mechanisms.

Another important point regarding the treatment of POPs is the fact that most studies are focused on the treatment of synthetic wastewater. Although the characteristics of the synthetic wastewater prepared tried to be similar to those of real wastewater, there are important variables not accounted with this simplified wastes that can affect the performance of the evaluated technology [16–18]. Because of that, there is an increasing number of manuscripts dealing with the evaluation of the treatment of real wastewater spiked with a specific concentration of POP (the pollutant concentration is increased by adding an extra concentration of the compound) [19–22].

With this background, the aim of this research work is to study the degradation of four pollutants from real wastewater by CDEO (shown in Table 1) paying attention to the nitrogen species formed during the treatment (nitrate, ammonium and chloramines), in order to study the main oxidation mechanisms related to this process and to increase the knowledge about nitrogen speciation during the electrooxidation process.

To do this, treated wastewater from the secondary treatment of a MWTP are spiked with 100 mg dm⁻³ of POP (the pollutant is spiked on the wastewater) in order to account with the effect of the wastewater matrix. Production of nitrogen inorganic species is monitored and compared to that obtained in the treatment of synthetic solutions.

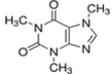
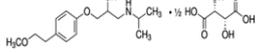
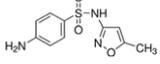
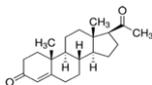
2. Materials and methods

2.1. Chemicals

Caffeine, metoprolol tartrate (2:1) salt, progesterone and sulfamethoxazole (SMX) were of analytical grade (>99.0% purity) and supplied by Sigma-Aldrich Laborchemikalien GmbH (Steinheim, Germany). The

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Table 1
Molecular formula, molecular structure and chemical family of POPs studied.

POP	Molecular formula	Molecular structure	Chemical family
Caffeine	C ₈ H ₁₀ N ₄ O ₂		Stimulant
Metoprolol	(C ₁₅ H ₂₅ NO ₃) ₂ ·C ₄ H ₆ O ₆		β-Blocker
Sulfamethoxazole	C ₁₀ H ₁₁ N ₃ O ₃ S		Antibiotic
Progesterone	C ₂₁ H ₃₀ O ₂		Hormone

anhydrous sodium sulfate was of analytical grade and purchased from Fluka. Sulfuric acid and sodium hydroxide, which were used to adjust the pH of the solution, were of analytical grade and supplied by Panreac Química S.A. (Barcelona, Spain).

2.2. Real wastewater

Real effluents were collected from secondary treatment of a Municipal Wastewater Treatment Plant (MWTP) located in Ciudad Real (Spain). An exhaustive characterization of these effluents was conducted, as reported elsewhere [23].

2.3. Analytical procedures

The carbon concentration was monitored using a Multi N/C 3100 Analytik Jena TOC analyzer. Measurements of pH and conductivity were conducted with an InoLab WTW pH-meter and a GLP Crison conductivity meter, respectively. The concentration of the persistent pollutants and the generated intermediates were measured by HPLC–UV (Agilent 1100 series), as reported elsewhere [9,24–26]. Ionic species were measured by ion chromatography using a Shimadzu LC-20A, as reported elsewhere [27]. Inorganic chloramines were measured following the procedure described by Cotillas et al. [27].

2.4. Electrochemical cells

The electrolyses were conducted in a non-divided compartment electrochemical flow cell working under batch-operation mode [28]. A Conductive Diamond Electrode (p-Si-Boron Doped Diamond) was used as the anode and stainless steel (AISI 304) as the cathode. Both electrodes were circular (100 mm in diameter) and had a geometric area of 78 cm² and an electrode gap of 9 mm. The wastewater was stored in a glass tank and circulated through the electrolytic cell by means of a centrifugal pump (flow rate 21.4 dm³ h⁻¹), as reported elsewhere [28].

3. Results and discussion

Fig. 1 shows the profiles of N ionic species (NO₃⁻, NH₄⁺ and chloramines) measured during the electrochemical oxidation of synthetic solutions prepared with the typical concentrations of NO₃⁻, Cl⁻, SO₄²⁻ and/or NH₄⁺ that can be found in real wastewater (see Figure caption). In order to do this, two solutions have been prepared, one with NO₃⁻ and without NH₄⁺ (used for Experiment 1) and the other with NH₄⁺ but without NO₃⁻ (used for Experiment 2). The applied current density in both tests was 15 mA cm⁻². Results are shown in mg N dm⁻³ units for a better comparison.

As it can be observed, in Experiment 1 (full symbols), nitrate concentration decreases significantly during the test. Initially, this can be explained in terms of the reduction of this species to form ammonium [29,30]. However, the concentration of ammonium formed is only 1.5 mg dm⁻³ and it should be higher according to the removal of nitrate observed. The only way to explain this result is by accounting the formation of chloramines by reaction between ammonium and hypochlorite (electrogenerated by oxidation of chloride), as it is pointed out in Eqs. (1) to (3) (break-point chlorination) [31–34]. As it is known, these species are very reactive and the process entails the formation of nitrogen gas as the later stage.



This behavior is also observed in Experiment 2 (empty symbols), observing also the formation of chloramines. In this case, it is important to point out that the ammonium concentration decreases only to a constant value of 4.5 mg dm⁻³ and these results can be easily explained in terms of the lower concentration of available hypochlorite: there is not enough hypochlorite ready to react with ammonium, because it is oxidized to chlorate and perchlorate [35,36]. In fact, high concentrations of these compounds were found during both experiments. On the other

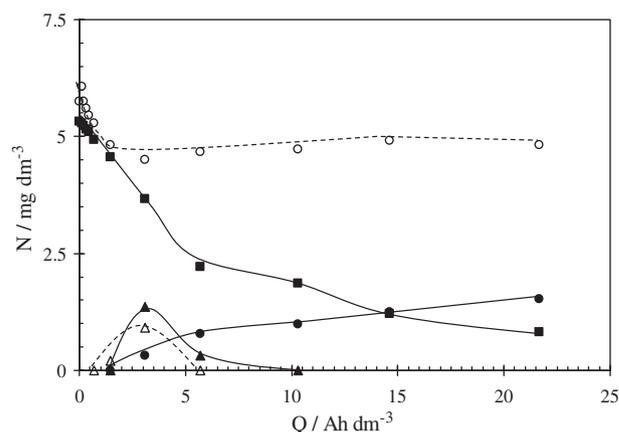


Fig. 1. Nitrate (■), ammonium (●) and chloramines (▲) profiles observed in the treatment of synthetic solutions by CDEO. Full symbols: Experiment 1 ([NaNO₃]₀ = 34.3 mg dm⁻³, [NaCl]₀ = 296.6 mg dm⁻³, [Na₂SO₄]₀ = 384.6 mg dm⁻³). Empty symbols: Experiment 2 ([NH₄]₀ = 82.3 mg dm⁻³, [NaCl]₀ = 296.6 mg dm⁻³, [Na₂SO₄]₀ = 282.5 mg dm⁻³). Operating conditions: j = 15 mA cm⁻².

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