What happens to inorganic nitrogen species during Conductive Diamond

Electrochemical Oxidation of real wastewater?

María J. Martín de Viales, María Millán, Cristina Sáez*, Pablo Cañizares, Manuel A. Rodrigo

Chemical Engineering Department, University of Castilla-La Mancha, Enrique Costa Novella Building. Av. Camilo José Cela nº 12, 13071 Ciudad Real, Spain

Abstract

This work describes the oxidation of caffeine, metoprolol, SMX and progesterone in real wastewater in terms of inorganic nitrogen speciation and help to clarify the mechanisms that affect inorganic nitrogen species as final products. In synthetic solutions containing ammonium or nitrates 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 to clarify the production of nitrates as main product 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.

Key Words: Electrochemical oxidation, persistent pollutant, real wastewater, Nitrate, Diamond.

*Corresponding author: Tel.: +34 902204100 ext. 6708; Fax: +34 926295256; e-mail: Cristina.Saez@uclm.es

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 to 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 to 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.

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

POP	Molecular formula	Molecular structure	Chemical family
Caffeine	$C_8H_{10}N_4O_2$		Stimulant
Metoprolol	$(C_{15}H_{25}NO_3)_2 \cdot C_4H_6O_6$		β -blocker
Sulfamethoxazole	$C_{10}H_{11}N_3O_3S$		Antibiotic
Progesterone	$C_{21}H_{30}O_2$		Hormone

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 analytical grade (> 99.0 % purity) and supplied by Sigma-Aldrich Laborchemikalien GmbH (Steinheim, Germany). The anhydrous sodium sulfate was analytical grade and purchased from Fluka. Sulfuric acid and sodium hydroxide, which were used to adjust the pH of the solution, were analytical grade and supplied by Panreac Química S.A. (Barcelona, Spain).

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, 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 conductimeter, 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 $21.4 \text{ dm}^3 \text{ h}^{-1}$),
reported elsewhere [28].

3. Results and discussion

Figure 1 shows the profiles of N ionic species (NO_3^- , NH_4^+ and chloramines) measured during the electrochemical oxidation of synthetic solutions prepared with the typical concentrations of NO_3^- , Cl^- , SO_4^{2-} and/or NH_4^+ that can be found in real wastewater (see Figure caption). In order to do this, two solutions have been prepared, one with NO_3^- and without NH_4^+ (used for Experiment 1) and other with NH_4^+ but without NO_3^- (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.

Figure 1. Nitrate (■), ammonium (●) and chloramines (▲) profiles observed in the treatment of synthetic solutions by CDEO. Full symbols: Experiment 1 ($[\text{NaNO}_3]_0 = 34.3 \text{ mg dm}^{-3}$, $[\text{NaCl}]_0 = 296.6 \text{ mg dm}^{-3}$, $[\text{Na}_2\text{SO}_4]_0 = 384.6 \text{ mg dm}^{-3}$). Empty symbols: Experiment 2 ($[(\text{NH}_4)_2\text{SO}_4]_0 = 82.3 \text{ mg dm}^{-3}$, $[\text{NaCl}]_0 = 296.6 \text{ mg dm}^{-3}$, $[\text{Na}_2\text{SO}_4]_0 = 282.5 \text{ mg dm}^{-3}$). Operating conditions: $j = 15 \text{ mA cm}^{-2}$.

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 Eq. 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 this 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 hand, in this experiment the formation of nitrate is not observed because ammonium has a positive charge and its oxidation is not favored (the anodic surface has also positive charge), as it has been demonstrated in previous studies [29, 37, 38]. Hence, from both test it can be concluded that in CDEO processes, ammonium can be produced from nitrate but not the opposite and that chloramines have an important role which has to be explained in terms of the concentration of chloride.

Knowing that, a real wastewater coming from the secondary treatment of a MWTP have been spiked with 100 mg dm^{-3} of caffeine, metoprolol, SMX or progesterone, in order to study the influence of the production of nitrogen inorganic species by CDEO. Real matrix used contains significant concentrations of ammonium and nitrates and progesterone was used as a reference test because this molecule does not contain nitrogen atoms. The applied current density was also 15 mA cm^{-2} (as in the tests shown in Figure 1). Figure 2 shows the evolution of ionic species of N (NH_4^+ and NO_3^-) during the experiments carried out (the variability exhibited by the real matrix influences on the initial concentration of the ionic species).

Figure 2. Ammonium (full symbols) and nitrate (empty symbols) profiles observed in the treatment of real wastewater polluted with POPs by CDEO. Operating conditions: $[\text{POP}]_0 = 100 \text{ mg dm}^{-3}$, $j = 15 \text{ mA cm}^{-2}$. (■) Caffeine, (●) metoprolol, (▲) SMX, (◆) progesterone.

Regarding the profile of nitrate concentration (empty symbols), it increases during the studies carried out with caffeine, metoprolol and SMX, while it can be considered constant for progesterone. The oxidation of ammonium to form nitrate is not favored due

to the positive charge of this ion [29, 37, 38], as previously discussed. Thus, the increase of the concentration of nitrate may be related to the oxidation of nitrogen atoms contained in the molecule of the pollutant and the release of oxidized nitro-species after its rupture. In fact, the maximum concentration of nitrate is directly proportional to the concentration of N in each molecule (the concentration of N per 100 mg dm⁻³ of molecule is: 28.87 mg N dm⁻³, 16.60 mg N dm⁻³, 4.09 mg N dm⁻³ and 0 mg N dm⁻³ for caffeine, SMX, metoprolol and progesterone, respectively). This is an important observation, because if the formation of nitrate by oxidation of ammonium is very complicated, as Figure 1 shows, it is possible starting from nitrogenous organic molecules. Thus, it is provided a clear evidence of the release of nitrate in the treatment of real wastewater polluted with nitrogenous organic molecules by electrochemical oxidation. Similar behaviour was observed by Oliviero et al., [39] and Berger et al., [40] in the oxidation of nitrogen-containing organic compounds by other technologies. The initial increase of the nitrate concentration is followed by a slight decrease. The explication for this behaviour might be in the reduction of nitrate to ammonium [29, 30, 41]. However, the increase in the concentration of ammonium is very slight. This can be explained considering the formation of chloramines (disappearance of ammonium) which seems to be faster than the reduction of nitrate (formation of ammonium) [31, 32, 42].

4. Conclusions

From this work, the following conclusions can be drawn:

- The electrochemical oxidation of synthetic solutions prepared with typical concentrations of inorganic species has demonstrated that nitrate can be reduced on the cathodic surface to form ammonium, which can react with hypochlorite (electrogenerated by oxidation of chloride) to form chloramines. However, the

oxidation of ammonium to nitrate is not favored due to the positive charge of this ion that prevents its contact with the anodic surface and thus its direct oxidation.

- The treatment of urban wastewater spiked with a nitrogen-containing persistent pollutant has revealed that it is possible the generation of nitrate by the oxidation of nitrogen atoms contained in the molecule of the pollutant and the release of oxidized nitro-species after its rupture. Presence of ammonium and chloramines can be explained by cathodic reduction of nitrates and reactivity with hypochlorite.

Acknowledgements

The authors acknowledge funding support from the Spanish Government and JCCM (Junta de Comunidades de Castilla-La Mancha) through the Projects CTM2013-45612-R and PEII-2014-039-P.

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