



Conductive diamond electrochemical oxidation of caffeine-intensified biologically treated urban wastewater



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HIGHLIGHTS

- CDEO shows a high efficiency in the removal of caffeine in urban wastewater.
- The presence of electrogenerated oxidants increases the efficiency in real medium.
- The N atoms present in the molecule of caffeine are oxidized to nitrate.
- Ammonium and hypochlorite can react to form chloramines.
- Operation mode must be modified to minimize the formation of chlorate and perchlorate.

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ABSTRACT

In this work, the usefulness of Conductive Diamond Electrochemical Oxidation (CDEO) to degrade caffeine in real urban wastewater matrixes was assessed. The oxidation of actual wastewater intensified with caffeine (from 1 to 100 mg L⁻¹) was studied, paying particular attention to the influence of the initial load of caffeine and the differences observed during the treatment of caffeine in synthetic wastewater. The results showed that CDEO is a technology that is capable of efficiently degrading this compound even at very low concentrations and that it can even be completely depleted. Profiles of the ionic species of S (SO₄²⁻), N (NH₄⁺, NO₃⁻) and Cl (ClO⁻, ClO₂⁻ and ClO₄⁻) were monitored and explained for plausible oxidation mechanisms. It was observed that the efficiency achieved is higher in the treatment of real wastewater than in the oxidation of synthetic wastewater because of the contribution of electrogenerated oxidant species such as hypochlorite. The formation of chlorate and perchlorate during electrochemical processes was observed, and a combined strategy to prevent this important drawback was successfully tested based on the application of low current densities with the simultaneous dosing of hydrogen peroxide.

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1. Introduction

Persistent Organic Pollutants (POPs) are chemicals that possess a combination of physical and chemical properties that allow them to resist biodegradation and accumulate in the environment (Fitzgerald and Wikoff, 2014).

Recently, POPs have been detected in ground and drinking water, indicating that the conventional treatments performed in Municipal Wastewater Treatment Plants (MWTP) failed to completely remove them from the wastewater. In fact, recent studies have shown that biological treatment cannot completely degrade these compounds (Kim et al., 2014; Maeng et al., 2011) and as a consequence they are accumulated in the environment. Exposure to these compounds may have unpredictable consequences in

aquatic environments and on public health (Lintelmann et al., 2003; Esplugas et al., 2007; Bachman et al., 2014; Pestana et al., 2014). Thus, an intensive research effort is needed to develop new technologies that can handle this environmental issue; currently, a great deal of research is particularly focused on the search for cost-effective technologies to effectively degrade POPs contained in wastewater, which is the primary source of the occurrence of these chemicals in the environment (Daughton, 2001; Lishman et al., 2006; Caliman and Gavrilescu, 2009; Giri et al., 2010; Martín de Vidales et al., 2012a,b,c; Tijani et al., 2013). Currently, Advanced Oxidation Processes (AOPs) are the most reliable technologies (Sirés et al., 2014). One promising AOP is Conductive Diamond Electrochemical Oxidation (CDEO). Typically, these processes have been studied for the treatment of synthetic wastewater, with initial concentrations of POPs on the order of mg L⁻¹ in a synthetic matrix, to evaluate the feasibility of the process and obtain information about the oxidation mechanisms. However, a key step

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in the scale-up of this electrochemical technology is its study under conditions (e.g., pollutant concentration and water composition) that are similar to those of real effluents.

A wide range of variables may influence the performance of wastewater treatment. In the case of electro-oxidation, inorganic salts present in the medium can play an important role in the oxidation mechanisms of POP degradation (Serrano et al., 2002; Wang and Farrell, 2004; Murata et al., 2008; Polcaro et al., 2008; Bergmann et al., 2009). Even trace concentrations of elements, such as Fe, Mg or Co, are reported to influence wastewater treatments (Hermosilla et al., 2015). In addition, the oxidation of the target molecule (i.e., the POP to be degraded) is normally in competition with other organics and inorganics that are present in the aqueous matrix, which adds extra difficulty to the removal process. Therefore, experiments in synthetic medium need to be understood as a preliminary stage in the investigation of new processes because it is difficult to reproduce real conditions.

As mentioned above, one of the primary routes of pollutant occurrence in the environment is the discharge of insufficiently treated wastewater from industrial facilities or Municipal Wastewater Treatment Plants (MWTP) (Indermuhle et al., 2013). With this in mind, different studies aimed at degrading POPs by means of AOPs have been conducted on real effluents from MWTPs or industrial activities, although the application of CDEO is scarce. A common procedure is to intensify the wastewater, that is, to increase the POP concentration by adding an extra concentration of the compound, which helps in monitoring its degradation. This way, the analysis of the process becomes much simpler from an experimental point of view (Klamerth et al., 2010; Antoniou et al., 2013; Lee et al., 2013; Espejo et al., 2014; Miralles-Cuevas et al., 2014; Muz et al., 2014; Pešoutová et al., 2014) and oxidation mechanism can be discussed.

This work focuses on the treatment of real wastewater coming from a secondary reactor of a MWTP intensified with caffeine (1–100 mg L⁻¹ of caffeine was added to wastewater) by using CDEO. Caffeine (C₈H₁₀N₄O₂) is an alkaloid belonging to methylxanthine family which acts as a central nervous system (CNS) stimulant, temporarily warding off drowsiness and restoring alertness. It is the world's most widely consumed legal psychoactive substance and thus, it can be present in relatively high concentration in domestic wastewater (Lovett, 2005). Likewise, MWTF cannot degrade caffeine efficiently and it is also refractory to others well-known AOPs (Broséus et al., 2009; Rosal et al., 2009; Klamerth et al., 2010). For all these reason, this pollutant was chosen as a POP model. Besides caffeine degradation, in this work it is also evaluated the role of side reactions of other species (such as ionic species) present in the wastewater.

2. Materials and methods

2.1. Chemicals

The caffeine (C₈H₁₀N₄O₂) was 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). Hydrogen peroxide (33% w/v) was also supplied by Panreac Química S.A. (Barcelona, Spain).

2.2. Real wastewater

Real effluents were collected from secondary treatment of a MWTP located in Ciudad Real (Spain). An exhaustive

characterization of these effluents was conducted, and the characteristics are shown in Table 1. It is important to note the low concentration of organic mass (TOC ≈ 13 mg L⁻¹) and the relatively high concentration of chloride and sulfate, which were above 110 and 80 mg L⁻¹, respectively.

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 conductometer, respectively. Hydrogen peroxide was measured according with Eisenberg (1943).

The concentrations of caffeine and the generated intermediates were measured by HPLC–UV (Agilent 1100 series), and a 205 nm detection wavelength was used. The column temperature was 25 °C. The volume injection was set at 20 μL, and a Phenomenex Gemini 5 μm C18 analytical column was used. Solvent A was composed of 25 mM of a formic acid water solution, and Solvent B was acetonitrile. A linear gradient chromatographic elution was obtained by initially running 10% of Solvent B and ascending to 100% in 40 min. The samples extracted from the electrolyzed solutions were filtered with 0.20 μm Nylon filters before analysis.

Ionic species (NH₄⁺, NO₃⁻, NO₂⁻, SO₄²⁻, Cl⁻, ClO₂⁻, ClO₃⁻, and ClO₄⁻) were measured by ion chromatography using a Shimadzu LC-20A equipped with a Shodex IC I-524A column (anionic species) or Shodex IC YK-421 column (cationic species); mobile phase, 2.5 mM phthalic acid at pH 4.0; flow rate, 1 · 10⁻³ dm³ min⁻¹ (concentration accuracy: ±0.5%). The peak corresponding to hypochlorite interferes with the peak of chloride; therefore, the determination of hypochlorite was conducted by titration with 0.001 M As₂O₃ in 2.0 M NaOH. This method consists of a redox determination to selectively quantify the hypochlorite concentration. In particular, it is based on the redox reaction between the hypochlorite and arsenite. Hypochlorite is reduced to chloride by the continuous addition of arsenite, which is oxidized to arsenate. Pretreatment of the samples consists of the addition of 2 · 10⁻³ dm³ of NaOH (2 M) to increase the pH.

2.4. Electrochemical cells

The electrolyses were conducted in a compartment electrochemical flow cell working under batch-operation mode (Cañizares et al., 2005). 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 Boron Doped Diamond 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).

Table 1
Characteristics of the secondary treatment effluent.

Parameter	Value
Cl ⁻ (mg Cl L ⁻¹)	110–180
NO ₃ ⁻ (mg N L ⁻¹)	3–12
SO ₄ ²⁻ (mg S L ⁻¹)	80–105
NH ₄ ⁺ (mg N L ⁻¹)	10–28
Turbidity (NTU)	10–11
TSS (mg L ⁻¹)	7–10
TOC (mg L ⁻¹)	12–14
COD (mg O ₂ L ⁻¹)	35–42

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