



## Degradation of caffeine by conductive diamond electrochemical oxidation



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### HIGHLIGHTS

- Electrochemical and sonoelectrochemical oxidation of caffeine was investigated in wastewater.
- Intermediates was identified by liquid chromatography-time of flight-mass spectrometry.
- Effects of initial concentration, current density and supporting electrolyte on the efficiency are assessed.

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### ABSTRACT

The use of Conductive-Diamond Electrochemical Oxidation (CDEO) and Sonoelectrochemical Oxidation (CDSEO) has been evaluated for the removal of caffeine of wastewater. Effects of initial concentration, current density and supporting electrolyte on the process efficiency are assessed. Results show that caffeine is very efficiently removed with CDEO and that depletion of caffeine has two stages depending on its concentration. At low concentrations, opposite to what it is expected in a mass-transfer controlled process, the efficiency increases with current density very significantly, suggesting a very important role of mediated oxidation processes on the removal of caffeine. In addition, the removal of caffeine is faster than TOC, indicating the formation of reaction intermediates. The number and relative abundance of them depend on the operating conditions and supporting electrolyte used. In chloride media, removal of caffeine is faster and more efficiently, although the occurrence of more intermediates takes place. CDSEO does not increase the efficiency of caffeine removal, but it affects to the formation of intermediates. A detailed characterization of intermediates by liquid chromatography time-of-flight mass spectrometry seems to indicate that the degradation of caffeine by CDEO follows an oxidation pathway similar to mechanism proposed by other advanced oxidation processes.

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### 1. Introduction

Occurrence of Persistent Organic Pollutants (POPs) in the aquatic environment is a well-known environmental issue (Esplugas et al., 2007). It is caused by discharges of industrial or household activities, and the magnitude of the problem is raised because conventional treatments in Municipal Wastewater Treatment Facilities (MWTF) are not very efficient for their removal. Low concentrations of these pollutants can lead to toxic effects, affecting the endocrine system. Hence they become a potential risk for the human health (Lintelman et al., 2003).

Caffeine (C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>) is an alkaloid belonging to methylxanthine family. In humans, caffeine acts as a central nervous system (CNS)

stimulant, temporarily warding off drowsiness and restoring alertness. It is present in cola drinks, coffee, tea and energy drinks. This drug is highly consumed and, for example, in high-developed countries, 90% of adults consume caffeine daily. Caffeine is the world's most widely consumed psychoactive substance (Lovett, 2005) but, unlike many other psychoactive substances, it is legal. Therefore, there is an important occurrence of this pollutant not only into some industrial effluents but also into domestic wastewaters.

Because conventional treatments of MWTF cannot degrade caffeine efficiently, it is necessary to look for alternatives. Advanced Oxidation Processes (AOPs) seem to be very promising, although many other alternatives have been proposed in the recent years such as microbial and enzymatic methods (Gokulakrishnan et al., 2005). Among AOPs, ozonation (Broséus et al., 2009; Rosal et al., 2009), photo-Fenton (Klamerth et al., 2010), neutral photo-Fenton (Bernabeu et al., 2011) have been studied for the degradation of

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caffeine. However, results encourage looking for better alternatives. Specifically, the degradation by ozonation is slow and many reaction intermediates and transformation products are found, photo-Fenton cannot degrade this compound completely and it has to be significantly optimized to determine its real applicability.

Conductive-Diamond Electrochemical Oxidation (CDEO) is considered as a good alternative for the treatment of POPs (Polcaro et al., 2005; Sirés et al., 2006; Cañizares et al., 2007, 2008; Guinea et al., 2008; Panizza et al., 2008; Mascia et al., 2010; Martín de Vidales et al., 2012a,b,c). The main drawback is the low efficiency, usually explained by a mass transfer control of the oxidation rate. Coupling ultrasounds (US) with CDEO into a sonoelectrolytic process (Conductive-Diamond Sonoelectrochemical Oxidation, CDSEO) is expected to produce a great improvement in the results (Martín de Vidales et al., 2012d). Ultrasounds are expected to improve the mass transfer coefficient and to promote the decomposition of water producing hydroxyl radicals.

The goal of this work is to study if CDEO and CDSEO are proper technologies to remove efficiently caffeine from wastewaters. The influence of the principal parameters of oxidation will be evaluated, such as initial concentration of the pollutant, current density applied or electrolyte supporting nature. Thus, the system features and the mechanism of the process will be assessed.

## 2. Materials and methods

### 2.1. Chemicals

Caffeine ( $C_8H_{10}N_4O_2$ ) was analytical grade (>99.0% purity), supplied by Sigma-Aldrich Laborchemikalien GmbH (Steinheim, Germany). Anhydrous sodium sulphate and sodium chloride used as supporting electrolyte were analytical grade purchased from Fluka. All solutions were prepared with high-purity water obtained from a Millipore Milli-Q system, with resistivity >18 M $\Omega$  cm at 25 °C.

### 2.2. Analytical procedures

The carbon concentration was monitored using a Multi N/C 3100 Analytik Jena TOC analyzer. Measurements of pH and conductivity were carried out with an InoLab WTW pH-meter and a GLP 31 Crison conductimeter, respectively.

The concentrations of the caffeine and intermediates generated were measured by both HPLC–UV (Agilent 1100 series) and HPLC–TOFMS (Agilent series 1200 coupled with Agilent 6220 accurate mass TOF). In the case of using HPLC–UV, the detection wavelength used was 205 nm. The column temperature was 25 °C. Volume injection was set to 20  $\mu$ L. The analytical column used was Phenomenex Gemini 5  $\mu$ m C18. Solvent A was composed by 25 mM of formic acid water solution and Solvent B was acetonitrile. A linear gradient chromatographic elution was obtained by initially running 10% of Solvent B ascending to 100% in 40 min. Samples extracted from electrolyzed solutions were filtered with 0.20  $\mu$ m Nylon filters before analysis.

HPLC–TOFMS technique has been used to identify the intermediates formed. In this case, the HPLC system (consisting of vacuum degasser, autosampler and a binary pump) (Agilent series 1200, Agilent Technologies, Santa Clara, CA) is equipped with a reversed-phase XDB-C18 analytical column of 4.6 mm  $\times$  100 mm and 1.8  $\mu$ m particle size (Agilent Technologies, Santa Clara, CA). A sample volume of 20  $\mu$ L was injected in each run. Mobile phases were water with 0.1% formic acid (A) and acetonitrile (B). The chromatographic method was performed with the same conditions as the HPLC–UV analysis. The HPLC system was connected to a time-of-flight mass spectrometer (Agilent 6220 accurate mass TOF, Agilent Technologies, Santa Clara, CA) equipped with an electrospray interface oper-

ating in positive and negative ion mode, using the following operation parameters: capillary voltage, 4000 V; nebulizer pressure, 40 psig; drying gas flow rate, 9.0 dm<sup>3</sup> min<sup>-1</sup>; gas temperature, 325 °C; skimmer voltage, 65 V; octapole 1 rf, 250 V; fragmentor voltage, 190 and 230 V (in-source CID fragmentation). LC–MS accurate mass spectra were recorded across the range of 50–1000  $m/z$  in positive ion mode and 50–1100 in negative ion mode. The instrument performed the internal mass calibration automatically using a dual-nebulizer electrospray source with an automated calibrate delivery system, which introduces the flow from the outlet of the chromatograph together with a low flow (approximately 45 mm<sup>3</sup> min<sup>-1</sup>) of a calibrating solution that contains the internal reference masses TFANH<sub>4</sub> (ammonium trifluoroacetate, C<sub>2</sub>O<sub>2</sub>F<sub>3</sub>NH<sub>4</sub>, at  $m/z$  112.985587 in negative ion mode), purine (C<sub>5</sub>H<sub>4</sub>N<sub>4</sub>, at  $m/z$  121.050873, in positive ion mode) and HP-0921 [hexakis-(1*H*,1*H*,3*H*-tetrafluoropropoxy) phosphazine, C<sub>18</sub>H<sub>18</sub>O<sub>6</sub>N<sub>3</sub>P<sub>3</sub>F<sub>24</sub>, at  $m/z$  922.009798 in positive ion mode and 1033.988109 in negative mode]. The instrument provided a typical resolution higher than 10000 on the 118  $m/z$  and higher than 18000 on the 1522  $m/z$ . The full scan data were recorded with Agilent Mass Hunter Data Acquisition software (version B.04.00) and processed with Agilent Mass Hunter Qualitative Analysis software (version B.04.00).

### 2.3. Electrochemical cells

The electrochemical oxidation assays of caffeine were carried out in a single compartment electrochemical flow cell working under a batch-operation mode (Cañizares et al., 2005). Diamond-based material (p-Si–boron-doped diamond) was used as anode and stainless steel (AISI 304) as cathode. Both electrodes were circular (100 mm diameter) with a geometric area of 78 cm<sup>2</sup> and an electrode gap of 9 mm. Boron-doped diamond films were provided by Adamant Technologies (Neuchatel, Switzerland) and synthesized by the hot filament chemical vapour deposition technique (HF CVD) on single-crystal p-type Si (100) wafers (0.1  $\Omega$  cm, Siltronix).

The ultrasound generator was a UP200S (Hielscher Ultrasonics GmbH, Germany) equipped with a titanium glass horn of 40 mm diameter, length 100 mm, emitting 24 kHz and maximum ultrasonic power 200 W. The output can be continuous or pulsed with varying percentage of cycle duty ranging from 10% to 100%.

### 2.4. Experimental procedures

Lab-scale electrolyses of 600 cm<sup>3</sup> of wastewater were carried out under galvanostatic conditions. The concentration of caffeine was ranged from 0.1 to 100 ppm, and 0.035 M Na<sub>2</sub>SO<sub>4</sub> or NaCl was used as supporting electrolyte. The current density employed ranged from 15 to 100 mA cm<sup>-2</sup>. The cell voltage did not vary during each electrolysis indicating that conductive-diamond layers did not undergo appreciable deterioration or passivation phenomena. Prior to use in galvanostatic electrolysis assays, the electrode was polarized during 10 min in a 0.035 M Na<sub>2</sub>SO<sub>4</sub> solution at 15 mA cm<sup>-2</sup> to remove any kind of impurity from its surface. The wastewater was stored in a glass tank and circulated through the electrolytic cell by means of a centrifugal pump (flow rate 21.4 dm<sup>3</sup> h<sup>-1</sup>). A heat exchanger coupled with a controlled thermostatic bath (Digiterm 100, JP Selecta, Barcelona, Spain) was used to maintain the temperature at the desired set point (25 °C).

## 3. Results and discussion

### 3.1. Conductive-diamond electrochemical oxidation

Fig. 1 shows the changes with the applied current in the concentration of caffeine during electrolyses with conductive diamond

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