



# Coupling ultraviolet light and ultrasound irradiation with Conductive-Diamond Electrochemical Oxidation for the removal of progesterone



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## ABSTRACT

This work focusses on the improvement of the efficiency of Conductive Diamond Electrochemical Oxidation (CDEO) by coupling US and UV irradiation in the degradation of progesterone from wastewater. Results show that CDEO is a promising technology for the degradation of progesterone, just the opposite of that observed for single sonolysis and photolysis technologies, which only entail a slight removal of progesterone and nil mineralization. Coupling UV light and US irradiations with CDEO seems to have a very positive effect, improving results obtained by single CDEO very significantly. Conductive Diamond Sono Electrochemical Oxidation (CDSEO) mainly seems to improve the transfer of pollutants to the conductive-diamond surface, while Conductive Diamond Photo Electrochemical Oxidation (CDPEO) seems to promote the formation of radicals from oxidants produced electrochemically. Soft oxidation conditions are obtained with the single application of both irradiation technologies, whereas an efficient mineralization is attained with CDEO, CDSEO, CDPEO and Conductive Diamond Sono-Photo Electrochemical Oxidation (CDSPEO). However, the high energy demands of US irradiation technologies advises against the use of CDSEO and CDSPEO.

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## 1. Introduction

During the recent years, many studies have demonstrated that conductive diamond electrochemical oxidation (CDEO) is a very robust and effective technology for the treatment of wastewaters polluted with a great variety of organic pollutants [1–13]. In fact, it can get the complete mineralization of the organic load without the formation of refractory compounds and it can also attain current efficiencies of 100% in the treatment of highly concentrated wastewaters (1,500–20,000 mg COD dm<sup>-3</sup>). However, in the treatment of diluted wastewaters (below 1,500 mg COD dm<sup>-3</sup>), electrolyses may be controlled by the mass transfer rate of pollutant from the bulk to the anode surface and thus, the current efficiency decreases linearly with COD concentration [14]. This is what used to be observed in the treatment of wastewaters polluted with persistent organic pollutants (POPs), in which these species are typically found at very low concentrations because of their low solubility.

The harsh oxidation conditions attained with CDEO is usually explained in terms of the oxidation mechanisms involved in the process. It is well documented [15] that besides direct electrooxidation on the surface and oxidation by means of hydroxyl radicals in a region close to the electrode surface, the oxidation mediated by other oxidants electrogenerated on the diamond surface from the electrolyte salts should be taken into account, as it can counterpart the mechanisms of oxidation in this kind of electrochemical technology, and it contributes to increase the global oxidation efficiency [16]. However, recent studies have shown that the oxidation efficiency of the oxidants produced electrochemically is much more significant than that show by commercial oxidants [17]. This fact seems to point out that it is necessary the activation of these oxidants to promote the mediated oxidation. This activation can be carried out by chemical reactions or by irradiation of ultrasound or ultraviolet-light (UV) [18–31].

Recent studies coupling ultrasounds to CDEO (Conductive-Diamond Sono Electrochemical Oxidation, CDSEO) have shown that process efficiency can be also increased because of the improvement of the mass transfer, promotion of the decomposition of water producing hydroxyl radicals, formation of new radical species and components and the electrohydraulic cavitations, growth and

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cyclical collapse of gas bubbles [18–24]. These changes are complementary and even synergistic with those taking place during electrolyses, resulting in very effective processes.

On the other hand, it has been also demonstrated that coupling UV irradiation to CDEO (Conductive–Diamond Photo Electrochemical Oxidation, CDPEO) leads to a synergistic effect explained either by heterogeneous (external bias contribute to a decrease in the electron-hole pair recombination process and the UV-photons reaching the electrode surface form excited radicals) and/or homogenous (photo activation of electrochemically generated reactive species) catalytic processes [25–31].

Progesterone have been often selected as model of POPs and its removal from waters and wastewaters has been studied by oxidation with potassium permanganate [32], ozonation [33,34], photocatalysis [35], or solar photo-Fenton [36] but, to the authors' knowledge, not a study has been made till now coupling UV and US irradiation technologies with CDEO. A previous work of our group [37] clarified the mechanisms and performance of CDEO in the removal of progesterone. In that paper, different parameters, such as current density, initial concentration of pollutant or nature of the supporting electrolyte were studied.

Thus, this work focuses on the improvement of the process efficiency by coupling US and UV irradiation to CDEO in the degradation of progesterone from wastewaters. Thus, the treatment of wastewaters polluted with this compound is studied by CDEO, sonolysis, photolysis, CDSEO, CDPEO and Conductive Diamond Sono-Photo Electrochemical Oxidation (CDSPEO). Results will be discussed at the light of the influence of the operating conditions on mineralization and reaction intermediates formation.

## 2. Experimental

### 2.1. Chemicals

Water-Soluble Progesterone (WSP) or Progesterone/2-hydroxypropyl- $\beta$ -cyclodextrin (7/93), where 2-hydroxypropyl- $\beta$ -cyclodextrin is a stabilising agent [38]. This compound was supplied by Sigma-Aldrich Laborchemikalien GmbH (Steinheim, Germany). Anhydrous sodium sulphate, used as supporting electrolyte, was 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. Sulphuric acid and sodium hydroxide used to adjust the solution pH were analytical grade and supplied by Panreac Química S.A. (Barcelona, Spain).

### 2.2. Analytical procedures

The Total Organic Carbon concentration was monitored using a Multi N/C 3100 Analytik Jena 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 compounds were quantified by HPLC (Agilent 1100 series). The detection wavelength used to detect progesterone was 248 nm. The column temperature was 25 °C. Volume injection was set to 50  $\mu$ 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. Moreover, the acids intermediates formed during the experiments were detected with a detection wavelength of 190 nm. The ion exchange column used was SUPELCOGELTM H Carbohydrate Columns from Sigma-Aldrich and dilute H<sub>3</sub>PO<sub>4</sub> (0.022 M) was employed as the

solvent. The retention times of 2-hydroxypropyl- $\beta$ -cyclodextrin, oxalic and formic carboxylic acids were 27.2, 9.3 and 19.5 minutes, respectively.

### 2.3. Electrochemical cells

Electrolyses were carried out in a single compartment electrochemical flow cell working under a batch-operation mode [39]. Conductive–Diamond Electrodes (p-Si–boron-doped diamond) were used as anode and a 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 horn 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 of 200 W. The output can be continuous or pulsed with varying percentage of cycle duty ranging from 10 to 100%.

The ultraviolet lamp was a Filtered Lamp Vilber Lourmat VL-215.MC with a power of 4 W. The wavelength used was 254 nm (UV-C).

### 2.4. Experimental procedures

Bench-scale electrolyses of 1000 cm<sup>3</sup> of wastewater were carried out under galvanostatic conditions. The current density employed was 30 mA cm<sup>-2</sup>. Na<sub>2</sub>SO<sub>4</sub> is used as supporting electrolyte (0.035 M) to ensure a minimum conductivity of 4.7 mS cm<sup>-1</sup>. In all cases, initial pH was 4.

The cell voltage did not vary during electrolysis, indicating that conductive-diamond layers did not under go 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

Fig. 1 shows the changes in the concentration of progesterone (part a) and TOC (part b) during the treatment of synthetic wastewater polluted with 100 mg dm<sup>-3</sup>, using different technologies (semi-logarithmic scale is used for a better comparison). Operation conditions of each experiment are detailed in the Figure caption.

Regarding oxidation of the progesterone molecule (part a of Fig. 1), an efficient degradation can be observed when single CDEO is used, just the opposite of that observed for single sonolysis and photolysis technologies, which only entail a slight removal of progesterone. On the contrary, coupling UV light and US irradiations with CDEO seems to have a positive effect, improving results obtained by single CDEO. Anyhow, enhancement observed seems to be different in both combined technologies. CDSEO enhancement is observed only for reaction times higher than 200 minutes, just when the mass transfer control limitations should be more important for the single CDEO technology (according to the concentration of pollutants which is diminished in one fold at this time). Hence, it could be suggested that this mechanical irradiation should improve the turbulence of the electrolyte and, consequently, the transfer of

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