



# Is it really important the addition of salts for the electrolysis of soil washing effluents?



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## ABSTRACT

The addition of salts is a common practice in the studies reported in literature for the electrochemical degradation of many types of organics contained in wastewater. Often, this addition is explained in terms of the high concentration of salts that some industrial effluents may contain. However, even in studies focused on the treatment of real wastewater, the addition of extra amount of salts is a common practice. As a consequence, after the electrochemical treatment, the effluent is polluted with salts which become non-hazardous but persistent inorganic pollution. In this work, it is compared the electrolysis of a model pollutant, the pesticide clopyralid, in a realistic matrix obtained by soil washing of spiked soil and in two synthetic electrolyte matrixes with typical concentrations of the two salts more frequently used in electrochemical oxidation of water and wastewater (sodium chloride and sulfate). Results point out that it is possible to attain the complete removal of pesticide and organic intermediates when applying current densities within the range 10–100 mA cm<sup>-2</sup> with BDD anodes in the realistic effluent and that no important differences arise with the addition of extra electrolyte salts. Obviously, the type of electrolyte influences the production of different oxidant species which, in turn, contributes to the degradation of the clopyralid pesticide in a different way and with different energy efficiency. However, for soil washing effluents, it is not necessary to add large amounts of salts for pesticide removal and the electrolysis of the raw soil washing waste, with a conductivity of only 1 mS cm<sup>-1</sup>, was found to attain even a better performance than those of two synthetic wastewaters in which the concentration of salts was over 3,000 mg dm<sup>-3</sup>.

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## 1. Introduction

In recent years, Conductive-Diamond Electrochemical Oxidation (CDEO) has become an excellent alternative to conventional wastewater treatments [1,2]. It has been evaluated in the treatment of wastewater polluted with several compounds, for which conventional processes are unable to attain a complete mineralization of the organic matter [3–7]. Specifically, this technology has been proven efficient in the removal of different organics such as pharmaceuticals [8–10], pesticides [11,12] and hormones [13]. In addition, it has been tested as a proper

technology for disinfection [5,14,15] and also for the synthesis of novel oxidants [16–19].

CDEO presents many advantages over conventional wastewater treatments, being the most important that it is environmentally-friendly (because the electron in the main reagent used and it is not required the addition of chemicals during this process), and that it operates at mild conditions (room temperature and atmospheric pressure) [4,20,21].

Most of the research works carried out about wastewater treatment with diamond anodes are focused on the removal of pollutants from synthetic wastewater [11]. The final aim is to check if target pollutants can be mineralized or at least degraded to a point for which their reduced hazardousness allows to combine the electrolysis with a cheaper treatment, such as the bio-oxidation. During these studies, very high concentrations of salts are added as supporting electrolyte in order to increase the ionic conductivity [22,23] and hence, to decrease the resulting cell

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voltage at which the electrolyses are carried out. Often, this addition is explained in terms of the high concentration of salts that some industrial effluents may contain. However, even in studies focused on the treatment of real wastewater, the addition of extra amount of salts is a common practice [24]. As a result, the physical-chemical properties of the resulting wastewater are typically very different in comparison with those of actual effluents and, therefore, conclusions cannot always be extrapolated to real examples, increasing the difficulty of the later scale-up procedures needed for the application of the technology at the full-scale. Another advantage looked for with the addition of salts to synthetic or real effluents is the promotion of mediated electrolysis mechanisms that enhance the efficiency of the overall process. It is well-known the formation of oxidants like peroxosalts, ozone and hydrogen peroxide on the surface of the diamond electrodes during electrolysis [25,26] and, currently, combination of CDEO with ultrasound or UV light irradiation is a topic of the major interest, because these technologies can help to transform these oxidants into very powerful radicals, which enhance hugely the mineralization of the pollutants contained in the bulk [5,27].

However, despite the good features attained with the addition of salts to wastewater, there are many important drawbacks. The most important is that salts become in fact a new pollutant, typically with a lower hazardousness than the organic pollutant contained in the raw wastewater, but with a larger persistence, because most of them remained in the effluent after the treatment. At this point, it is important to remind that there are no treatments to decrease their concentration but just treatments like electro-dialysis that allows to split up the effluent into a salty and non-salty streams. In addition, the improvement in the efficiency obtained with the extra salts addition turns into a problem when oxidation products formed becomes more hazardous than the raw pollutants contained in wastewater. This is a typical and well-known outcome when chloride salts are added to wastewater, which was a common practice in most of the research papers focused on electrolysis during the eighties and nineties of the last century and that now, fortunately, it is less frequently found, because of the great alarm caused by organochlorinated species [28,29]. Hence, it is not clear at all the benefit to the environment of this salt addition and electrochemical technology has to determine ways to avoid or at least minimize this practice.

With this background, the main aim of the present work is to evaluate if the conclusions drawn in electrochemical treatment of these synthetic salty media is really representative of the conclusions that can be found in the treatment of a more realistic matrix. To do this, the electrolysis of a soil washing effluent (SWE) polluted with pesticide clopyralid ( $C_6H_3Cl_2NO_2$ ) is compared to the electrolyses of synthetic wastewater made with the same concentration of clopyralid and with the two more commonly studied electrolytes in the literature: sodium chloride (synthetic wastewater 1) and sodium sulfate (synthetic wastewater 2). Hence, one of the matrixes tested corresponds to a formulation based on the real characteristics of the water supply of our region (area of La Mancha, Spain), with a conductivity of  $1,030 \mu S cm^{-1}$ . The other two correspond to synthetic solutions of the herbicide containing only one salt (chloride or sulfate), in a much higher concentration ( $3,000 mg dm^{-3}$ ), within the same range of the use in most of the studies found in the literature about electrolysis of wastewater and hence with an ionic conductivity more than 4 times higher. On the other hand, because electrolysis with diamond may have two rather different behaviors depending on the conditions applied [30], in this work the comparison was carried out at two extreme current density conditions: 10 and  $100 mA cm^{-2}$ . In the first, the oxidation is expected to be softer than in the second and, hence, the contribution of oxidants electrogenerated on the anode (including hydroxyl radicals) is expected to be less relevant than

in the second, were the typical harsh oxidation conditions applied in electrolysis with diamond anodes are tested.

## 2. Experimental

### 2.1. Chemicals

Clopyralid (3,6-Dichloro-pyridine-2-carboxylic acid), sodium sulfate, sodium chloride, sodium nitrate, magnesium sulfate, potassium iodide and calcium carbonate (Sigma-Aldrich, Spain) were analytical grade and used as received. Methanol HPLC grade and formic acid (Sigma-Aldrich, Spain) were used for the mobile phase. Double deionized water (Millipore Milli-Q system, resistivity:  $18.2 M\Omega cm$  at  $25^\circ C$ ) was used to prepare all solutions.

### 2.2. Analytical techniques

The concentration of pesticide was followed by reversed-phase chromatography and measurement of Total Organic Carbon (TOC). The chromatography system was an Agilent 1200 series coupled a DAD detector. A ZORBAX Eclipse Plus C18 analytical column was used. The mobile phase consisted of 30% methanol/70% water with 0.1% of formic acid (flow rate:  $0.8 cm^3 min^{-1}$ ). The DAD detection wavelength was 280 nm, the temperature was maintained  $25^\circ C$  and the injection volume was  $20 \mu L$ . The TOC concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer. The concentration of oxidants was measured iodometrically by titration with thiosulphate in acidic media. This method quantifies all oxidants capable to oxidize iodide ( $I^-$ ) to iodate ( $IO_3^-$ ) [31].

Organic by-products generated during the degradation of clopyralid were extracted with ethyl acetate (ratio pollutant/solvent: 0.6 w/w) and then, both phases were stirred using a vortex mixer during 5 minutes. Next, samples were centrifuged during 15 minutes at 4,000 rpm. The organic phase was analyzed by GC-MS using a Thermo Scientific DSQ II Series Single Quadrupole GC-MS with a NIST05-MS library. The column was a polar TR-WAXMS ( $30 m \times 0.25 mm \times 0.25 \mu m$ ). The temperature ramp was  $70^\circ C$  for 1 min,  $30^\circ C min^{-1}$  up to  $300^\circ C$  and hold time 5 minutes. The inlet, source and transfer line temperatures were 250, 200 and  $300^\circ C$ , respectively.

The current efficiency ( $\eta$ ) was calculated with equation (1) where  $C_j$  is the concentration of clopyralid (in  $mg dm^{-3}$ ),  $V$  is the volume of the electrolyte ( $dm^3$ ),  $n$  is the number of electrons ( $mmol e^-/mmol$  clopyralid),  $F$  is the Faraday constant ( $96,487 C mol^{-1}$ ),  $I$  is the current intensity (A),  $t$  is the operation time in seconds (s) and  $M$  is the molecular weight of clopyralid ( $192 mg mmol^{-1}$ ).

$$\eta = \frac{C_j \cdot V \cdot n \cdot F}{I \cdot t \cdot M} \cdot 100 \quad (1)$$

### 2.3. Electrochemical cell

Electrolyses were carried out in a single compartment electrochemical flow cell ( $50 dm^3 h^{-1}$ ). Boron doped diamond (BDD) (WaterDiam, Switzerland) was used as anode and cathode. The electrodes were circular with a geometric area of  $78 cm^2$ , boron concentration of  $500 mg dm^{-3}$ , a thickness of  $2.72 \mu m$ ,  $sp^3/sp^2$  ratio of 220 and p-Si as support. The electrode gap between anode and cathode was 3 mm. The electric current was provided by a Delta Electronika ES030-10 power supply (0–30 V, 0–10 A). The current density applied was in the range  $10$ – $100 mA cm^{-2}$ . The temperature was maintained at  $25^\circ C$  using a thermostated bath.

Synthetic wastewaters 1 and 2 (SWW1 and SWW2) consisted of a solution ( $1 dm^3$ ) containing  $100 mg dm^{-3}$  of pesticide and  $3,000 mg dm^{-3}$  of supporting electrolyte (NaCl,  $Na_2SO_4$ ). Soil

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