**Towards the scale-up of electrolysis with diamond anodes: Effect of stacking on
the electrochemical oxidation of 2,4 D**

F. L. Souza¹, C. Saéz², M. R. V. Lanza¹, P. Cañizares², M. A. Rodrigo^{2*}

⁽¹⁾ Instituto de Química de São Carlos, Universidade de São Paulo, P.O. Box 780, CEP
13560-970, São Carlos, SP, Brazil

⁽²⁾ Department of Chemical Engineering, Faculty of Chemical Sciences & Technologies,
Universidad de Castilla - La Mancha, Campus Universitario s/n, 13071 Ciudad Real,
Spain

*Corresponding author

Tel: (+34)902204100 ext. 3411

Fax: (+34)926295256

e-mail: manuel.rodrigo@uclm.es

Abstract

BACKGROUND: In recent years, the application of electrochemical wastewater treatment processes has proven to be very efficient in the removal of recalcitrant organic compounds. However, the scale-up of the boron-doped diamond (BDD) anode system for industrial applications has not been sufficiently evaluated. This study assesses the effect of increasing the number of compartments in the same electrochemical module (DiaCell® 1001) on the treatment of synthetic wastewater with pesticide 2,4-D and chlorides. This commercial module can be considered to be a stack of cells, in which the number of single cells varies from 2 to 10 and the anode areas range from 140 – 700 cm².

RESULTS: The results of the study demonstrate that an increase in the number of cells and a decrease in the resulting current density at the same current intensity caused an increase in the removal and mineralisation rates. Complete mineralisation was attained in all tested configurations. The production of hazardous species, such as chlorates and perchlorates, are also affected by the number of stacked cells, which causes them to be positioned lower in the stack due to the large number of cells.

CONCLUSIONS: No distinct differences in electrochemical efficiency are observed among the different tested configurations. However, a distinct improvement in the energy efficiency (g kWh⁻¹) with an increase in the number of stacked cells is observed due to the reduced stack potential caused by applying the same current intensity to the stack with the higher number of cells.

Keywords

Scale-up, stack, cell, BDD, electrolysis, chloro species, herbicide

Highlights

- 39 - Stacking of single cells has a significant influence on the electrolytic results
40 obtained in the treatment of wastewater
- 41 - At the same intensity, the superior performance of stacks with several cells can
42 be explained by the lower current density
- 43 - The larger is the number of cells, the lower is the required applied electric charge
44 to attain complete oxidation of pollutants.
- 45 - The process conditions in electrolysis with diamond are very harsh; only small
46 concentrations of intermediates were obtained.
- 47 - Although the electric current efficiency is similar for different compartments, the
48 maximum energy required to oxidised chlorides was obtained with 6
49 compartment.

50

51

Introduction

In recent years, numerous publications have demonstrated the efficiency of electrochemical treatments with diamond anodes for the destruction of bio-refractory organic pollutants. These materials possess excellent properties, such as higher chemical and electrochemical stability, robustness, weak electrode fouling and long service life¹. They are known for their ability to generate large quantities of hydroxyl radicals, are weakly adsorbed and are responsible for the strong oxidation of contaminants present in solution³. In addition to hydroxyl radicals, the formation of ozone and hydrogen peroxide and the production of peroxyanions in the presence of sulfate, phosphate or carbonate has been documented⁴⁻⁷. In the presence of chloride, chlorine gas (Cl_2) can be formed on an anode by direct electro-oxidation. Hypochlorite (ClO^-) can be produced by a disproportionation reaction of chlorine with OH^- formed on the cathode. Both gases are powerful oxidising agents. In addition, the action of hydroxyl radical can also promote the oxidation of hypochlorite to chlorate and perchlorate, which are harmful to human health and the environment. In this case, the results of the treatment must be carefully assessed as the occurrence of these species may prevent the use of this technology^{5, 8, 9}.

These characteristics enhance the prevalence of this technology due to its significant potential for wastewater treatment processes, which requires additional studies. The majority of published studies have focused on the influence of operating conditions, the effect of supporting electrolytes on the intermediates and final products formed during the electrolytic process and the efficiency of the process. The next research challenge is the scale-up of the electrochemical cell to verify the process performance at pilot and industrial scales. Scale-up suggests not only the operation of large plants but also the development of new, efficient, competitive and environmentally friendly technologies¹⁰.

For this reason, it is important to understand the effects of the design cell, the phase transport phenomena and the kinetics reaction.

Currently, mixed tanks and simple flow pass cells have been the most applied reactors to study wastewater treatment^{11, 12}. Typical mass transfer coefficients in these cells range from 10^{-6} to 10^{-4} m s⁻¹. The lowest values are typically associated with mixed-tank laboratory-fabricated cells. The highest values are typically associated with commercial cells with a proper cell design, in which aspects such as the design of turbulence promoters, spacers, and construction details of the inlet and outlet of the cell are considered^{9, 13-15}. In addition to factors that influence mass transport, connections of electrodes to wires and other construction details, a suitable and uniform current density distribution may increase the efficiency of the electric current and minimise the ohmic drop, which are directly related to the economy of the process via the minimisation of the resulting cell voltage. Thus, numerous parameters may improve the performance of the total process¹⁶⁻¹⁸ and laboratory-fabricated cells. The majority of the cases presented in the literature do not consider (or scarcely consider) these points. Other details such as heat dissipation or gas stripping are never considered in studies about wastewater treatment but are worthy of attention. The commercial cells in studies about wastewater treatment have been designed for other applications (typically electrosynthesis); therefore, special considerations of wastewater treatment are sometimes disregarded. Three relevant cells are typically discussed in studies about the electrolysis of wastewater: the ELECTROCELL (ElectroCell A/S, Denmark)¹⁹, the FC01-LC (formerly ICI Chemicals and Polymers Ltd.; currently INEOS Chlor-chemicals, UK)²⁰⁻²² and the DIACELL (formerly ADAMANT TECH; currently WaterDiam, Switzerland)²³. The first two cells were designed for the chlor-alkali process and have to be adapted (or at least applied in different conditions) for application in studies about wastewater treatment.

Only the DIACELL was specifically designed for environmental applications; minimal attention has been given to its engineering details in the scientific literature. Note that this cell was initially designed for implementing the diamond electrode. It has been typically commercialised; thus, the majority of the relevant studies it assess the outstanding performance of diamond instead of the performance of the cell. Few studies have reported applications in the wastewater treatment of commercial cells with an active area of diamond electrodes larger than 100 cm². Zhu's group ^{17, 24} assessed the scale-up from 24 cm² to 2904 cm² in an anodic area (121 times) for the electrochemical oxidation of wastewater that contains phenol, in continuous mode and batch mode. The results demonstrated that an equivalent performance could be attained for both systems if parameters such as retention time, current density, initial Chemical Oxygen Demand (COD), and conductivity conditions were properly controlled. Similarly, Urtiaga's group ^{25, 26} examined the removal of tetrahydrofuran (THF) from industrial wastewater using a commercial cell with BDD electrodes with anodic area of 140 cm² and tested the scale-up to 2800 cm². Complete removal of COD was attained in both the laboratory test and the pilot test and the depletion rates were validated in the scale-up experiments. Both studies are very important as they demonstrate the viability of scaling-up of this environmental remediation technology. They also noted that additional studies should be performed to understand the parameters required for proper scale-up. In this context, information about the effect of stacking single electrochemical cells on the results obtained during the electrolysis of wastewater is lacking. Stacking is a very important part of the scale-up as it helps to determine the real configuration of cells in actual applications. This manuscript aims to assess the effect of an increase in the number of compartments in the same electrochemical module (DiaCell® 1001) on the results of the treatment of synthetic wastewater that contains pesticide 2,4-D and chlorides. This

module can be considered to be a stack of single DiaCells, in which the number of single cells vary from 1 to 10. Two major reactions are expected to be developed: the depletion of the pesticide and the generation of the perchlorates by the oxidation of chlorides. The objective is not the optimisation of the environmental remediation process (in such an application, the production of perchlorate should be prevented and diamond is not the best choice for an anode) but increased knowledge about the scale-up of this type of process, which offers the following advantages:

- (i) the simultaneous occurrence of both reactions during the electrolysis of synthetic wastewater and
- (ii) chlorates and perchlorates behave as inert species with respect to the organics contained in the wastewater; thus, they should be considered.

The herbicide 2,4- dichlorophenoxyacetic acid (2,4-D) was selected as the compound model as 2, 4 D is extensively employed in agriculture and in many commercial products and its electrochemical oxidation has been previously investigated ^{6, 27}. This organic pollutant is considered to be toxic and is commonly detected into wastewater.

Materials and Methods

Experimental setup

Electrolysis was conducted in a DiaCell® 1001 supplied by Adamant Technologies (Switzerland). The DiaCell® is a module with 1-10 compartments equipped with BDD electrodes as anodes and five stainless steel plates; each plate serves as a common cathode for two parallel BDD anodes (Fig. 1). In each compartment, a pair of Si/BDD and stainless steel electrodes with an active surface of 70 cm² behaves as a unit cell. The interelectrode gap is 3 mm. The coatings of the BDD electrodes had a boron concentration

of 500 ppm and the ratio sp^3/sp^2 of approximately 150. The resistivity of the Si wafers was 100 m Ω cm, and the thicknesses of the BDD coatings ranged from 2-3 μ m. Mass transfer coefficients have been determined using the ferro-ferricyanide test for the different stacks studied for the DIACELL ® 1001 at the flowrate used in the experiments, obtaining values of within the range 2.16 to 7.16 10⁻⁶ m s⁻¹.

Analysis procedures and methods

In this study, a jacketed tank with a volume of 1.2 dm³ was employed as an auxiliary reservoir of the electrochemical stack. The experiments were performed in recirculated batch mode by a peristaltic pump at a constant flow rate of 26.4 dm³ h⁻¹. A controlled thermostatic bath was used to maintain the temperature in the jacket at 25 °C. The electrolyses were galvanostatically performed (external current of 10 A was applied by a DC power supply). Prior to the electrolysis assays, the BDD electrodes were cleaned for 10 min in a 1 M Na₂SO₄ solution at 15 mA cm⁻². The wastewater consists of a solution of 100 mg dm⁻³ 2,4-dichlorophenoxyacetic acid (2,4-D) at a natural pH. NaCl served as the supporting electrolyte (3.0 g dm⁻³).

All samples extracted from the electrolysed solutions were filtered with 0.45 μ m nylon filters from Whatman prior to analysis. The quantitative analysis of 2,4-D and its organic intermediates were followed by reversed-phase chromatography, Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD). The high performance liquid chromatography system Agilent 1100 was equipped with an UV detector (280 nm) and column Phenomenex Gemini 5 μ m C18. The analytical conditions were as follows: a mobile phase that consisted of 60 % acetonitrile and 40 % water to 2 % acetic acid with a flow rate of 0.4 cm³ min⁻¹, an oven temperature of 25 °C, and volume injection of 20 μ L. The TOC concentration was monitored using a Multi N/C 3100 Analytik Jena

analyser. The measurements of pH were performed with an InoLab WTW pH-metre. The Chemical Oxygen Demand (COD) was monitored using a HACH DR200 analyser.

The chlorine species (Cl^- , ClO_3^- and ClO_4^-) were determined by ion chromatography using a Metrohm 7330 IC Separation Centre coupled with a 752 pump unit and a 732 IC detector. A Metrosep A Supp 4 column was employed. The mobile phase consisted of 1.8 mM Na_2CO_3 and 1.7 mM NaHCO_3 with a flow rate of 1.0 ml min^{-1} .

The current efficiency (CE) was calculated with Equation 1, where COD_t and $\text{COD}_{t+\Delta t}$ correspond to the organic load (g dm^{-3}) at a certain time t (s) and $t+\Delta t$, respectively, F is the Faraday constant (96485 C mol^{-1}), V (dm^3) is the volume of the electrolysed solution, and I (A) is the applied electric current.

$$CE = \frac{[(\text{COD})_t - (\text{COD})_{t+\Delta t}]FV}{8I\Delta t} \quad (1)$$

The specific energy consumption (w , kW h m^{-3}) was calculated by Equation 2, where U is the cell potential (V):

$$w = \frac{UIt}{V} \quad (2)$$

Results and discussion

Figure 2 shows the value of the cell voltage in each experiment and the applied current density during the electrolyses of the synthetic wastewater with the different cell configurations and a current of 10 A. As the experiments were conducted with a constant intensity regardless of the number of cell compartments, the current density decreases as the number of compartments increases; this reduction causes a decrease in the resulting total cell potential, which is explained in terms of a smaller ohmic loss. Almost a constant

cell voltage was maintained during the tests, which indicates no deterioration of the electrode materials or formation of fouling.

Figure 3 shows the effect of the number of cells of the stack on the depletion of 2,4-D and the percentage of TOC removal. Mineralisation is attained in all tests regardless of the number of compartments in the electrochemical cell and the current density. However, the higher is the number of compartments (and the lower is the resulting applied current density), the more efficient and faster is the depletion of 2,4-D and its conversion to carbon dioxide. The total concentration of the intermediates (calculated by the addition of the chromatographic area of peaks) is very low, as shown in Figure 3b; it is not dependent on the number of single cells contained in the stack and the applied current density. Note that chromatographic areas less than 200 units are considered to be noise by the analytical device; thus, the concentration of detected intermediates limit the detection of the equipment. This result indicates that electrolytic oxidation of 2,4-D produces harsh conditions in the reaction media, which minimise the production of intermediates for very low concentrations of pollutant. Thus, the electrolytic stack may behave as a cold incinerator.

Plots in semi-logarithmic scale of the TOC vs time during the experiments result in distinct straight lines for each test, with regression coefficients greater than 0.98. Mineralisation during the electrolysis of 2,4-D corresponds to a first-order kinetic. This type of kinetic behaviour has been explained in the literature in terms of a mass transfer control of the rate of mineralisation (if the constant is equal to the mass transfer coefficient for the relevant Re number) or by the effect of mediated oxidation (if oxidants are efficiently produced during the electrolysis)²⁸⁻³⁰. Both explanations are important in this

study as the concentration of 2,4-D is very low and chlorine that is electrolytically produced (and also hypochlorite formed by its disproportionation after dissolution) is known to be a suitable oxidant for organics such as 2,4-D³¹. Figure 4 shows the obtained values for the pseudo-first kinetic constant. An increase in the number of compartments and a decrease in the applied current density are observed.

This is clearly observed in Figure 5 in which it can be observed that the energy efficiency in the mineralization (expressed in g kWh⁻¹ and calculated by dividing the change in the TOC according to a mass balance by the specific energy consumption calculated by Eq. 2) decreases at higher current densities as the amount of carbon mineralised by each energy unit decreases as the j increases (lower number of cells in the stack). The efficiency of the oxidation in terms of COD (expressed as a percentage of the electric current used in the oxidation of COD according to eq. 1) is constant in the complete range of j . Note that the COD measurement was not very accurate due to the low concentration of organics and high concentration of chlorides.

The synthetic wastewater in this study contained a large amount of chlorides. The application of diamond electrodes is not recommended for a system with a large concentration of chlorides as the final oxidation product obtained during electrolysis consists of perchlorates instead of chlorine (and hypochlorite). As these species are known to be hazardous to the environment and to human health, their production should be prevented⁵. However, the use of this supporting electrolyte was considered due to the inert behaviour of chlorates and perchlorates in the oxidation of 2,4-D. This inerticity facilitates the use of the same experiment to simultaneously evaluate the effect of the almost direct electrochemical oxidation of an organic pollutant and the potential effect of a mediator in the reaction system.

Figure 6 shows the changes in the concentrations of chloride and perchlorate during the electrolysis. Figure 7 shows the changes in the two main intermediates: chlorine /hypochlorite (calculated by mass balance to account for the stripped amounts of chlorine) and chlorate.

Chloride is completely depleted during the experiments. Its concentration does not change in an exponential manner as expected according to previous studies but it exhibits a strange shape, which can be associated with the resulting current density in the cell ⁵. Removal increases for the cells with two and three compartments and decreases for the cells with four and five compartments. Similarly, the concentration of perchlorate at the end of the experiment was higher in the cells with the lower number of compartments (and the higher current density). This finding can be explained in terms of the formed intermediates. Chloride/hypochlorite is formed in higher amounts at high current densities and subsequently stripped from the system. This results explains the lower production of chlorates in these conditions, which is the main species formed in the cells that contain a large number of compartments.

As shown in Figure 8, a constant electric current efficiency is maintained during the experiments if the electrons required to form the different products are considered (two electrons for every molecule chlorine that is produced, six electrons for every chlorate that is produced and eight electrons for every perchlorate that is produced). However, the minimum energy required to oxidised chlorides is distinct for six compartments (maximum energy efficiency); only the conditions in which the production of large quantities of chlorine are promoted.

Conclusions

The following conclusions are formed:

- The different arrangements investigated in this study (that contain different number of single cells stacked into a module) showed that an increased number of cells can improve the performance of the wastewater treatment process in terms of galvanostatic operation at the same current intensity. The higher is the number of compartments, the more efficient is the depletion of 2,4-D and its conversion into carbon dioxide with an almost negligible formation of intermediates.
- Kinetic improvement by increasing the number of cells in the stack can be explained by the lower resulting current densities. This improvement can be explained by the diffusion control of the rate of the electrochemical process due to the low concentration of pollutants.
- The presence of chloride ions causes the production of undesired secondary species, such as chlorates and perchlorates. The concentration of these hazardous species is minimised in stacks that contain a large number of single cells due to the reduction in the current density.
- Regarding the oxidation of chloride, the electric current efficiency seems to be dependent on the production of gas chlorine instead of the number of stacked single cells. The setup with six compartments produces a maximum energy efficiency.

Acknowledgements

The authors acknowledge funding support from the EU and Spanish Government via the MINECO Project CTM2013-45612-R, FEDER 2007-2013 PP201010 (Planta Piloto de Estación de Estación de Regeneración de Aguas Depuradas) and INNOCAMPUS. The Brazil government grant 2014/02580-7 and the São Paulo Research Foundation (FAPESP) are gratefully acknowledged.

- 295 1. Rodrigo MA, Cañizares P, Sánchez-Carretero A and Sáez C, Use of conductive-diamond
296 electrochemical oxidation for wastewater treatment. *Catalysis Today* **151**:173-177
297 (2010).
- 298 2. Panizza M and Cerisola G, Application of diamond electrodes to electrochemical
299 processes. *Electrochimica Acta* **51**:191-199 (2005).
- 300 3. Marselli B, Garcia-Gomez J, Michaud PA, Rodrigo MA and Comninellis C,
301 Electrogeneration of Hydroxyl Radicals on Boron-Doped Diamond Electrodes. *Journal of*
302 *The Electrochemical Society* **150**:D79 (2003).
- 303 4. Cañizares P, Sáez C, Sánchez-Carretero A and Rodrigo MA, Synthesis of novel oxidants
304 by electrochemical technology. *Journal of Applied Electrochemistry* **39**:2143-2149
305 (2009).
- 306 5. Sánchez-Carretero A, Sáez C, Cañizares P and Rodrigo MA, Electrochemical production
307 of perchlorates using conductive diamond electrolyses. *Chemical Engineering Journal*
308 **166**:710-714 (2011).
- 309 6. Fontmorin J-M, Huguet S, Fourcade F, Geneste F, Floner D and Amrane A,
310 Electrochemical oxidation of 2,4-Dichlorophenoxyacetic acid: Analysis of by-products
311 and improvement of the biodegradability. *Chemical Engineering Journal* **195-196**:208-
312 217 (2012).
- 313 7. Serrano K, Michaud PA, Comninellis C and Savall A, Electrochemical preparation of
314 peroxodisulfuric acid using boron doped diamond thin film electrodes. *Electrochimica*
315 *Acta* **48**:431-436 (2002).
- 316 8. Bergmann MEH, Rollin J and Iourtchouk T, The occurrence of perchlorate during drinking
317 water electrolysis using BDD anodes. *Electrochimica Acta* **54**:2102-2107 (2009).
- 318 9. Vacca A, Mascia M, Palmas S and Da Pozzo A, Electrochemical treatment of water
319 containing chlorides under non-ideal flow conditions with BDD anodes. *Journal of*
320 *Applied Electrochemistry* **41**:1087-1097 (2011).
- 321 10. Paludetto GDR, Scale up of chemical reactors. *Catalysis Today* **34**:483-533 (1997).
- 322 11. Zhao X, Qu J, Liu H, Wang C, Xiao S, Liu R, Liu P, Lan H and Hu C, Photoelectrochemical
323 treatment of landfill leachate in a continuous flow reactor. *Bioresource technology*
324 **101**:865-869 (2010).
- 325 12. Ramírez C, Saldaña A, Hernández B, Acero R, Guerra R, Garcia-Segura S, Brillas E and
326 Peralta-Hernández JM, Electrochemical oxidation of methyl orange azo dye at pilot flow
327 plant using BDD technology. *Journal of Industrial and Engineering Chemistry* **19**:571-579
328 (2013).
- 329 13. Zhao G, Shen S, Li M, Wu M, Cao T and Li D, The mechanism and kinetics of ultrasound-
330 enhanced electrochemical oxidation of phenol on boron-doped diamond and Pt
331 electrodes. *Chemosphere* **73**:1407-1413 (2008).
- 332 14. Zhao G, Gao J, Shen S, Liu M, Li D, Wu M and Lei Y, Ultrasound enhanced electrochemical
333 oxidation of phenol and phthalic acid on boron-doped diamond electrode. *Journal of*
334 *hazardous materials* **172**:1076-1081 (2009).
- 335 15. de Souza F, Sáez C, Cañizares P, de Motheo A and Rodrigo M, Electrochemical removal
336 of dimethyl phthalate with diamond anodes. *Journal of Chemical Technology &*
337 *Biotechnology* **89**:282-289 (2014).
- 338 16. Wang L, Hu Y, Li P, Zhang Y, Yan Q and Zhao Y, Electrochemical treatment of industrial
339 wastewater using a novel layer-upon-layer bipolar electrode system (nLBPEs). *Chemical*
340 *Engineering Journal* **215-216**:157-161 (2013).
- 341 17. Zhu X, Ni J, Wei J and Chen P, Scale-up of B-doped diamond anode system for
342 electrochemical oxidation of phenol simulated wastewater in batch mode.
343 *Electrochimica Acta* **56**:9439-9447 (2011).

18. Souza FL, Sáez C, Lanza MRV, Cañizares P and Rodrigo MA, Is it worth the use of bipolar electrodes in electrolytic wastewater treatment processes? *Chemical Engineering Journal* **264**:310-315 (2015).
19. Bengoa C, Montiller A, Legentilhomme P and Legrand J, Flow visualization and modelling of a filter-press type electrochemical reactor. *Journal of Applied Electrochemistry* **27**:1313-1322 (1997).
20. Cruz-Díaz MR, Rivero EP, Almazán-Ruiz FJ, Torres-Mendoza Á and González I, Design of a new FM01-LC reactor in parallel plate configuration using numerical simulation and experimental validation with residence time distribution (RTD). *Chemical Engineering and Processing: Process Intensification* **85**:145-154 (2014).
21. Pérez T, Ponce de León C, Walsh FC and Nava JL, Simulation of current distribution along a planar electrode under turbulent flow conditions in a laboratory filter-press flow cell. *Electrochimica Acta* **154**:352-360 (2015).
22. Terrazas-Rodríguez JE, Gutiérrez-Granados S, Alatorre-Ordaz MA, Ponce de León C and Walsh FC, A comparison of the electrochemical recovery of palladium using a parallel flat plate flow-by reactor and a rotating cylinder electrode reactor. *Electrochimica Acta* **56**:9357-9363 (2011).
23. Abdessamad N, Akrouit H, Hamdaoui G, Elghniji K, Ksibi M and Bousselmi L, Evaluation of the efficiency of monopolar and bipolar BDD electrodes for electrochemical oxidation of anthraquinone textile synthetic effluent for reuse. *Chemosphere* **93**:1309-1316 (2013).
24. Zhu X, Ni J, Wei J, Xing X, Li H and Jiang Y, Scale-up of BDD anode system for electrochemical oxidation of phenol simulated wastewater in continuous mode. *Journal of hazardous materials* **184**:493-498 (2010).
25. Urtiaga A, Fernandez-Castro P, Gómez P and Ortiz I, Remediation of wastewaters containing tetrahydrofuran. Study of the electrochemical mineralization on BDD electrodes. *Chemical Engineering Journal* **239**:341-350 (2014).
26. Urtiaga A, Gómez P, Arruti A and Ortiz I, Electrochemical removal of tetrahydrofuran from industrial wastewaters: anode selection and process scale-up. *Journal of Chemical Technology & Biotechnology* **89**:1243-1250 (2014).
27. Brillas E, Banos MA, Skoumal M, Cabot PL, Garrido JA and Rodriguez RM, Degradation of the herbicide 2,4-DP by anodic oxidation, electro-Fenton and photoelectro-Fenton using platinum and boron-doped diamond anodes. *Chemosphere* **68**:199-209 (2007).
28. Souza FL, Sáez C, Cañizares P, Motheo AJ and Rodrigo MA, Sonoelectrolysis of Wastewaters Polluted with Dimethyl Phthalate. *Industrial & Engineering Chemistry Research* **52**:9674-9682 (2013).
29. Mascia M, Vacca A, Palmas S and Polcaro AM, Kinetics of the electrochemical oxidation of organic compounds at BDD anodes: modelling of surface reactions. *Journal of Applied Electrochemistry* **37**:71-76 (2006).
30. Souza FL, Sáez C, Cañizares P, Motheo AJ and Rodrigo MA, Coupling photo and sono technologies to improve efficiencies in conductive diamond electrochemical oxidation. *Applied Catalysis B: Environmental* **144**:121-128 (2014).
31. Aquino JM, Rodrigo MA, Rocha-Filho RC, Sáez C and Cañizares P, Influence of the supporting electrolyte on the electrolyses of dyes with conductive-diamond anodes. *Chemical Engineering Journal* **184**:221-227 (2012).

Figure captions

Figure 1. a) Schematic of the Diacell equipped with ten single cells and b) photographic image of DiaCell® 1001

~~**Figure 2. a) Changes in the cell voltage during the electrochemical oxidation of a synthetic wastewater with a Diacell® equipped with (▼) 1 compartment; (▲) 2 compartments; (●) 3 compartments; (■) 4 compartments; (x) 5 compartments. b) Influence of the number of compartments on the applied current density (Δ) and cell voltage (▲). Current intensity: 10 A.**~~

Figure 3. Changes in the concentration of 2,4-D (full points), intermediates (Grey points) and TOC removal (empty points) during the electrolysis of synthetic wastewater using a Diacell® equipped with (▲, Δ) 2 cells; (■, □) 4 cells; (●, ○) 6 cells; (◆, ◇) 8 cells; (x, *) 10 cells.

Figure 4. Influence of the number of compartments in the cell in the kinetic constants of the mineralisation of 2,4-D when a constant current intensity of 10 A is applied.

Figure 5. Influence of the resulting current density on the mineralisation energy consumption and on the current efficiency for the mineralisation of 2,4-D ($Q = 8.31 \text{ Ah dm}^{-3}$ for TOC and 2.1 Ah dm^{-3} for COD).

Figure 6. Changes in the concentration of chlorides (full points) and perchlorates (empty points) during the electrolysis of the synthetic wastewater with a Diacell® equipped with (▲, Δ) 2 cells; (■, □) 4 cells; (●, ○) 6 cells; (◆, ◇) 8 cells; and (x, *) 10 cells.

Figure 7. Changes in the concentration of chlorates (full points) and chlorine/hypochlorite (empty points) during the electrolysis of the synthetic wastewater

413 with a Diacell[®] equipped with (▲, △) 2 cells; (■, □) 4 cells ; (●, ○) 6 cells; (◆, ◇) 8
414 cells; (x, *) 10 cells.

415 **Figure 8.** Influence of the resulting current density on the mineralisation energy
416 consumption and on the current efficiency for the oxidation of chloride ($Q=17.31 \text{ Ah dm}^{-3}$).
417 ³).

418

419

420

421

422

423

424

425

Figure 1

429

430

431

Figure 2

Figure 3

Figure 4

437

438

439

Figure 5

440

441

442

443

444

Figure 6

Figure 7

448

449

450

Figure 8

451

452