
Irradiated electrochemical processes for the removal of persistent organic pollutants from waters

C. Sáez*, M.J. Martín de Vidales, P. Cañizares, S. Cotillas, J. Llanos, J.F. Pérez and M.A. Rodrigo

Department of Chemical Engineering. Faculty of Chemical Sciences and Technologies, University of Castilla - La Mancha. Avenida Camilo José Cela 12, 13005 Ciudad Real, Spain

*Corresponding author: cristina.saez@uclm.es

1. Introduction

Recently, regulations for the control of occurrence of Persistent Organic Pollutants (POPs) on wastewater are considered as an important topic. These compounds have been found in surface, ground and drinking waters, because conventional treatments of wastewater treatment plants are not able to remove them completely. Thus, it is necessary to look for a suitable technology for the removal of POPs from waters and wastewaters efficiently. In the recent years, many works have demonstrated the efficiency and robustness of the application of Conductive-Diamond Electrochemical Oxidation (CDEO) for the treatment of wastewaters contained refractory organic compounds (Brillas et al., 2004, Boye et al., 2006, Cañizares et al., 2006, Cañizares et al., 2008, Brillas et al., 2010, Wang and Li, 2012, Abdessamad et al., 2013, Daskalaki et al., 2013). However, in the treatment of diluted wastewaters (below 1,500 mg COD dm⁻³), 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 (Comminellis and Pulgarin, 1991). This is what used to be observed in the treatment of wastewaters polluted with POPs (Robles-Molina et al., 2012, Martín de Vidales et al., 2012a, 2012b, 2012c, 2013, Indermuhle et al., 2013), in which these species are typically found at very low concentrations because of their low solubility.

The high efficiency of CDEO is achieved thanks to the great chemical and electrochemical stability of diamond electrodes, the high overpotential for water electrolysis and, mainly, the special properties to generate other oxidants like, persulphates, peroxophosphates, oxochlorinated anions and hydrogen peroxide (Cañizares et al., 2009, Sánchez-Carretero et al., 2011). However, recent studies show 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 technologies (Souza et al., 2014, Martín de Vidales et al., 2014). In this way, several authors (Pinhedo et al., 2005, Osugi et al., 2005, Socha et al., 2007, Freitas et al., 2011) propose that the combination of photo and electrolysis technologies leads to a synergistic effect due to photoactivation of electrochemically generated reactive species, increasing also the yield by photolysis (Catanho et al., 2006, Socha et al., 2006). On the other hand, ultrasound irradiation is an effective technology to increase mass transport and to produce important changes in the chemical composition of the electrolyte because of the ultrasonic cavitation phenomenon, which takes advantage of the high pressure and temperature produced during the implosive collapse of bubbles irradiated with the ultrasound to form new radical species and components (Lorimer et al., 2004, Sánchez-Carretero et al., 2010).

Some examples of POPs are caffeine (C₈H₁₀N₄O₂) and triclosan (C₁₂H₇Cl₃O₂), identified as stimulant and pesticide, respectively. Their removals from waters and wastewaters has been studied by ozonation (Broséus et al., 2009, Rosal et al., 2009), electroFenton (Sirés et al., 2007), or CDEO (Wang and Farrell, 2004, Martín de Vidales et al., 2013, Indermuhle et al., 2013) but, to the authors' knowledge, very few works have been made till now coupling UV and US irradiation technologies with CDEO. Thus, the goal of this work is to couple US and UV irradiations to CDEO in order to improve the degradation of these persistent pollutants from waters. Thus, the efficiency of different technologies (CDEO, sonolysis, photolysis, CDSEO,

CDPEO and Conductive Diamond Sono-Photo Electrochemical Oxidation, CDSPEO) is also compared, observing the influence of the technology applied in the degradation rate and the mechanism of oxidation.

2. Materials and methods

2.1. Chemicals

Caffeine (analytical grade, > 99% purity) and triclosan were 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 Ω 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 pollutants, intermediates and final products were quantified by HPLC (Agilent 1100 series). The detection wavelength used to detect POPs depends on the compound (caffeine: 205 nm, triclosan: 280 nm). The column temperature was 25 °C. Volume injection was set to 50 μ L. The analytical column used was Phenomenex Gemini 5 μ 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 μ 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 H₃PO₄ (0.022 M) was employed as the solvent.

2.3. Electrochemical cells

Electrolyses were carried out in a single compartment electrochemical flow cell working under a batch-operation mode (Cañizares et al., 2005). 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 cm² 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 Ω 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 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 cm³ of wastewater were carried out under galvanostatic conditions. The current density employed was 30 mA cm⁻², and the pollutant concentration was 100 mg dm⁻³. Due to the low solubility of triclosan in aqueous solution, methanol is used as solubilizing agent (37% v/v) (Martín de Vidales et al., 2013).

The cell voltage did not vary during 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 Na₂SO₄ solution at 15 mA cm⁻² 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 dm³ h⁻¹). 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

Figure 1 shows the concentration profiles of caffeine (part a) and triclosan (part b) during the treatment by different irradiated and electrochemical technologies of synthetic wastewater containing 100 mg dm^{-3} of these compounds. Na_2SO_4 is used as supporting electrolyte (0.035 M) in all cases. Semi-logarithmic scale is used for a better comparison.

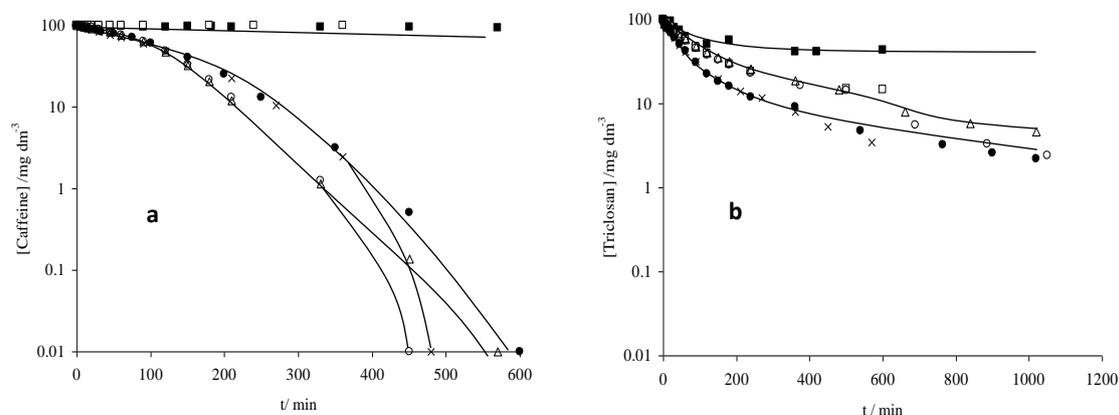
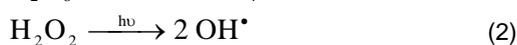
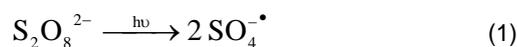


Figure 1: Caffeine (a) and triclosan (b) concentration profiles for the experiments made by CDEO (Δ), sonolysis (\blacksquare), photolysis (\square), CDSEO (\circ), CDPEO (\bullet) and CDSPEO (\times). $[\text{Pollutant}]_0: 100 \text{ mg dm}^{-3}$, $j: 30 \text{ mA cm}^{-2}$, $0.035 \text{ M Na}_2\text{SO}_4$. Ultrasound wave: continuous mode/200 W. Ultraviolet light: 254 nm/4 W.

As it can be observed, the experimental behavior of both POPs is significantly different and the reaction time required for the degradation of triclosan is higher than that to decrease the concentration of caffeine to the detection limit of the chromatographic technique used (HPLC; 0.01 mg dm^{-3}). In this point, it is important to point out that methanol is added as solubilizing agent to triclosan solutions and that it can compete with triclosan for being oxidized. This fact can explain the longer time required to attain the total removal of triclosan. In general, electrochemical processes seem to be more efficient than irradiated technology, although the effect of photolysis and sonolysis techniques shows a marked influence with the nature of the POPs studied. Thus, in Figure 1a it can be observed that sonolysis and photolysis processes only achieve a slight degradation of caffeine (around 10 and 1 % of removal, respectively), whereas in the case of triclosan solution (Figure 1b), irradiated technologies are able to attain percentage removals higher than 60 %. In fact, it can be pointed out that photolysis degrades around 85 % of the initial concentration of triclosan.

In both cases, the use of electrochemical technologies show good results (percentage removals above 90%), but the effect of combining CDEO with irradiated techniques is not clear and again depends on the nature of the pollutant. Coupling UV light and US irradiations with CDEO seems to have a positive effect in the triclosan degradation, improving results obtained by single CDEO, but it seems to have a negative effect in the degradation of caffeine, except when the concentration of caffeine is very low and the mass transfer controls single CDEO technology. In this case, US mechanical irradiation should improve the turbulence of the electrolyte and, consequently, the transfer of pollutants to the conductive-diamond surface.

On the other hand, the effect of UV irradiation is related to activation of radicals in the reaction media. In fact, CDEO of wastes containing sulfates is known to produce peroxosulfates and it is also reported the formation of ozone and hydrogen peroxide. In this point, light irradiation is known to promote the production of sulfate radical from persulfate (Eq. 1) and to improve the production of hydroxyl radicals according to eqs. 2 and 3 (Lin et al., 2011, Shih et al., 2012).



These radicals are very reactive, and at the light of the obtained results, they may react easily with triclosan molecule (Catanho et al., 2006, Socha et al., 2006). The antagonistic effect observed in the case of caffeine may be explained in terms of an excessive formation of radicals which, instead of oxidizing caffeine, combine among them to form more stable and less aggressive oxidants or decompose forming oxygen (Souza et al., 2014).

Figure 2 shows the TOC removal for the studies of degradation of caffeine (a) and triclosan (b) by the different technologies used.

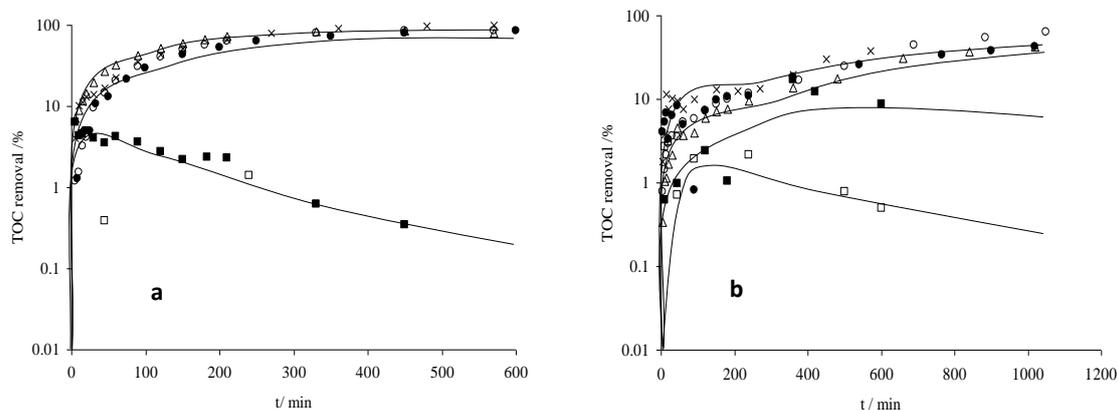


Figure 2: TOC removal for the experiments of degradation of caffeine (a) and triclosan (b) by CDEO (Δ), sonolysis (\blacksquare), photolysis (\square), CDSEO (\circ), CDPEO (\bullet) and CDSPEO (\times). [Pollutant] $_0$: 100 mg dm $^{-3}$, j: 30 mA cm $^{-2}$, 0.035 M Na $_2$ SO $_4$. Ultrasound wave: continuous mode/200 W. Ultraviolet light: 254 nm/4 W.

As it was expected, no mineralization of caffeine solutions is attained by single sonolysis or photolysis processes. Opposite, single CDEO obtains an efficient mineralization but the use of UV or US irradiation simultaneously with the electrolysis does not improve the mineralization rate. The smaller differences observed between caffeine and TOC removals can be explained in terms of the formation reaction intermediates during the different processes which entail a slower removal of TOC than of pollutant.

On the other hand, the mineralization percentage attained during the treatment of triclosan wastes is significantly lower than triclosan percentage removal independently of the technology used. This fact means that the mineralization of methanol added is slow and the effect of oxidants on its removal should be smaller. On the contrary of that observed in Figure 1b, coupling US irradiation to CDEO shows a higher effect in TOC removal than the combined use of UV irradiation and CDEO.

Experimental results shown in Fig. 1 fit straight lines during the first stages of the process regardless of the treatment technology. This means that they can be modeled with a pseudo-first order kinetic approach (eq. 4) that depends on the concentration of oxidants produced on the anodic surface and/or in the bulk. This approach has been proposed and applied successfully in previous works for CDEO of POPs (Polcaro y col., 1999, Martín de Vidales y col., 2012a, 2012b y 2012c).

$$r = k' [\text{Oxidant agents}][\text{Pollutant}] = K [\text{Pollutant}] \quad (4)$$

Fig. 3 shows the first order kinetic constants calculated in terms of pollutant for the experiments shown in Fig. 1. This Figure also compares these values with the values calculated by the addition of the different single technologies. The effect of the combination is greater than the addition of the effects of the single technologies, mainly in the treatment of wastewater containing triclosan. This synergistic effect is higher for the case of the combined UV light irradiation. Hence, irradiations of UV or US have a positive effect on triclosan results although this does not mean a greater efficiency.

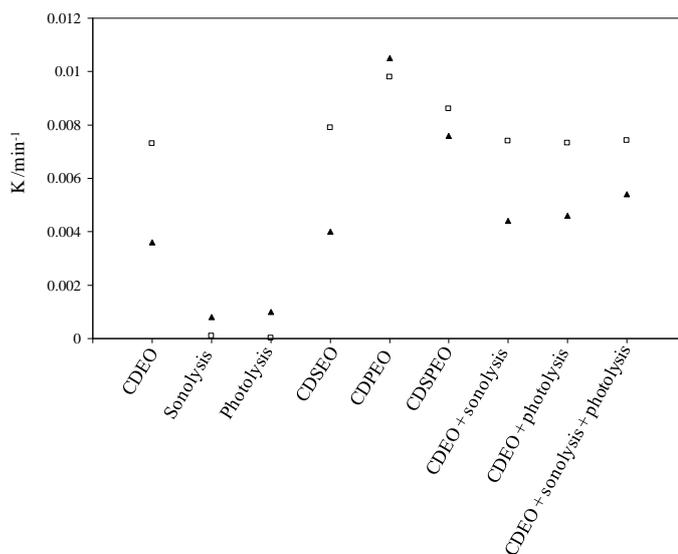


Figure 3: Kinetic constants calculated for the different processes and comparison with the values calculated by the addition of the different single contributions. Caffeine (□), triclosan (▲).

4. Conclusions

Electrochemical oxidation with conductive-diamond anode is a suitable technology to attain efficient degradation of caffeine and triclosan. Single sonolysis and photolysis technologies only entail removal of triclosan but nil removal of caffeine and mineralization. Synergistic effects of irradiating UV light are clearly observed in the oxidation rate, due to the promotion of the formation of radicals in the bulk solution from oxidants produced electrochemically. US irradiation contributes to improve mass transfer to the conductive-diamond surface during the last stages of the process.

Acknowledgements

The authors acknowledge funding support from the Spanish Government (CTM2013-45612-R). The FPU scholarship of María Jose Martín de Vidales is also gratefully acknowledged. Financial support of the Spanish government and EU through project FEDER 2007-2013 PP201010 (Planta Piloto de Estación de Estación de Regeneración de Aguas Depuradas) is gratefully acknowledged.

References

- Abdessamad, N., Akrouf, H., Hamdaoui, G., Elghniji, K., Ksibi, M., Bousseml, L., 2013, Evaluation of the efficiency of monopolar and bipolar BDD electrodes for electrochemical oxidation of anthraquinone textile synthetic effluent for reuse. *Chemosphere* 93, 1309-1316.
- Boye, B., Brillas, E., Marselli, B., Michaud, P.A., Comninellis, Ch., Farnia, G., Sandonà, G., 2006, Electrochemical incineration of chloromethylphenoxy herbicides in acid medium by anodic oxidation with boron-doped diamond electrode, *Electrochim. Acta* 51, 2872-2880.
- Brillas, E., Boye, B., Sirés, I., Garrido, J.A., Rodríguez, R.M., Arias, C., Cabot, P.L., Comninellis, C., 2004, Electrochemical destruction of chlorophenoxy herbicides by anodic oxidation and electro-Fenton using a boron-doped diamond electrode, *Electrochim. Acta* 49, 4487-4496.
- Brillas, E., Garcia-Segura, S., Skoumal, M., Arias, C., 2010, Electrochemical incineration of diclofenac in neutral aqueous medium by anodic oxidation using Pt and boron-doped diamond anodes, *Chemosphere* 79, 605-612.
- Broséus, R., Vincent, S., Aboulfadl, K., Daneshvar, A., Sauvé, S., Barbeau, B., Prévost, M., 2009, Ozone oxidation of pharmaceuticals, endocrine disruptors and pesticides during drinking water treatment, *Water Res.* 43, 4707-4717.
- Cañizares, P., Lobato, J., Paz, R., Rodrigo, M.A., Sáez, C., 2005, Electrochemical oxidation of phenolic wastes with boron-doped diamond anodes, *Water Res.* 39, 2687-2705.

- Cañizares, P., Paz, R., Lobato, J., Saez, C., Rodrigo, M.A., 2006, Electrochemical treatment of the effluent of a fine chemical manufacturing plant. *J. Hazard. Mater.* 138, 173-181.
- Cañizares, P., Paz, R., Sáez, C., Rodrigo, M.A., 2008, Electrochemical oxidation of alcohols and carboxylic acids with diamond anodes: A comparison with other advanced oxidation processes, *Electrochim. Acta* 53, 2144-2153.
- Cañizares, P., Sáez, C., Sánchez-Carretero, A., Rodrigo, M.A., 2009, Synthesis of novel oxidants by electrochemical technology, *J. Appl. Electrochem.* 39, 2143-2149.
- Catanho, M., Malpass, G.R.P., Motheo, A.J., 2006, Photoelectrochemical treatment of the dye reactive red 198 using DSA® electrodes, *Appl. Catal., B.* 62, 193-200.
- Daskalaki, V.M., Marakas, H., Mantzavinos, D., Katsaounis, A., Gikas, P., 2013, Use of seawater for the boron-doped diamond electrochemical treatment of diluted vinasse wastewater. *Water Sci. Technol.* 68, 2344-2350.
- Freitas, A.M., Sirtori, C., Peralta-Zamora, P., 2011, Photoelectrocatalytic degradation of camphor on TiO₂/RuO₂ electrodes, *Environ. Chem. Lett.* 9, 97-102.
- Indermuhle, C., Martín de Vidales, M.J., Sáez, C., Robles, J., Cañizares, P., García-Reyes, J.F., Molina-Díaz, A., Comninellis, C., Rodrigo, M.A., 2013, Degradation of caffeine by conductive diamond electrochemical oxidation, *Chemosphere* 93, 1720-1725.
- Lin, Y.T., Liang, C., Chen, J.H., 2011, Feasibility study of ultraviolet activated persulfate oxidation of phenol, *Chemosphere* 82, 1168-1172.
- Lorimer, J.P., Mason, T.J., Plattes, M., Phull, S.S., Iniesta, J., Walton, D.J., 2004, Sonovoltammetric studies on copper in buffered alkaline solution, *Ultrason. Sonochem.* 11, 223-226.
- Martín de Vidales, M.J., Barba, S., Sáez, C., Cañizares, P., Rodrigo, M.A., 2014, Coupling ultraviolet light and ultrasound irradiation with Conductive-Diamond Electrochemical Oxidation for the removal of progesterone, *Electrochim. Acta* in press, 10.1016/j.electacta.2014.02.118.
- Martín de Vidales, M.J., Robles-Molina, J., Domínguez-Romero, J.C., Cañizares, P., Sáez, C., Molina-Díaz, A., Rodrigo, M.A., 2012b, Removal of sulfamethoxazole from waters and wastewaters by conductive-diamond electrochemical oxidation, *J. Chem. Technol. Biotechnol.* 87, 1441-1449.
- Martín de Vidales, M.J., Sáez, C., Cañizares, P., Rodrigo, M.A., 2013, Removal of triclosan by conductive-diamond electrolysis and sonoelectrolysis, *J. Chem. Technol. Biotechnol.* 88, 823-828.
- Martín de Vidales, M.J., Sáez, C., Cañizares, P., Rodrigo, M.A., 2012a, Metoprolol abatement from wastewaters by electrochemical oxidation with boron doped diamond anodes, *J. Chem. Technol. Biotechnol.* 87, 225-231.
- Martín de Vidales, M.J., Sáez, C., Cañizares, P., Rodrigo, M.A., 2012c, Electrolysis of progesterone with conductive-diamond electrodes, *J. Chem. Technol. Biotechnol.* 87, 1173-1178.
- Osugi, M.E., Umbuzeiro, G.A., Anderson, M.A., Zanoni, M.V.B., 2005, Degradation of metallophthalocyanine dye by combined processes of electrochemistry and photoelectrochemistry, *Electrochim. Acta* 50, 5261-5269.
- Pinhedo, L., Pelegrini, R., Bertazzoli, R., Motheo, A.J., 2005, Photoelectrochemical degradation of humic acid on a (TiO₂)_{0.7}(RuO₂)_{0.3} dimensionally stable anode, *Appl. Catal., B* 57, 75-81.
- Robles-Molina, J., Martín de Vidales, M.J., García-Reyes, J.F., Cañizares, P., Sáez, C., Rodrigo, M.A., Molina-Díaz, A., 2012, Conductive-diamond electrochemical oxidation of chlorpyrifos in wastewater and identification of its main degradation products by LC-TOFMS, *Chemosphere* 89, 1169-1176.
- Rosal, R., Rodríguez, A., Perdigón-Melón, J.A., Petre, A., García-Calvo, E., Gómez, M.J., Agüera, A., Fernández-Alba, A.R., 2009, Degradation of caffeine and identification of the transformation products generated by ozonation, *Chemosphere* 74, 825-831.
- Sánchez-Carretero, A., Rodrigo, M.A., Cañizares, P., Sáez, C., 2010, Electrochemical synthesis of ferrate in presence of ultrasound using boron doped diamond anodes, *Electrochem. Commun.* 12, 644-646.
- Sánchez-Carretero, A., Sáez, C., Cañizares, P., Rodrigo, M.A., 2011, Production of Strong Oxidizing Substances with BDD Anodes, *Synthetic Diamond Films: Preparation, Electrochemistry, Characterization, and Applications* 15, 281-310.
- Shih, Y.J., Putra, W.N., Huang, Y.H., Tsai, J.C., 2012, Mineralization and defluorization of 2,2,3,3-tetrafluoro-1-propanol (TFP) by UV/persulfate oxidation and sequential adsorption, *Chemosphere* 89, 1262-1266.
- Sirés, I., Oturan, N., Oturan, M.A., Rodríguez, R.M., Garrido, J.A., Brillas, E., 2007, Electro-Fenton degradation of antimicrobials triclosan and triclocarban, *Electrochimica Acta* 52, 5493-5503.
- Socha, A., Sochocka, E., Podsiadły, R., Sokołowska, J., 2006, Electrochemical and photoelectrochemical degradation of direct dyes, *Color. Technol.* 122, 207-212.
- Socha, A., Sochocka, E., Podsiadły, R., Sokołowska, J., 2007, Electrochemical and photoelectrochemical treatment of C.I. Acid Violet 1, *Dyes Pigment.* 73, 390-393.

- Souza, F.L., Sáez, C., Cañizares, P., Motheo, A.J., Rodrigo, M.A., 2014, Coupling photo and sono technologies to improve efficiencies in conductive diamond electrochemical oxidation. *Appl. Catal., B: Environmental*, 144, 121-128.
- Wang, J., Farrell, J., 2004, Electrochemical Inactivation of Triclosan with Boron Doped Diamond Film Electrodes, *Environ. Sci. Technol.* 38, 5232-5237.
- Wang, J., Li, X., 2012, Electrochemical treatment of wastewater containing chlorophenols using boron-doped diamond film electrodes, *Advanced Materials Research* 356-360, 1418-1422.