



Electrooxidation of Ceftriaxone in Its Commercial Formulation on Boron Doped Diamond Anode

G.C. Quand-Meme¹, A.F. Thiery Auguste¹, L.E. Marie Hélène¹, B. Mohamed¹, S.S. Placide¹, I. Sanogo², L. Ouattara^{1,*}

¹The Chemical Physics Laboratory, UFR SSMT, University Félix Houphouët-Boigny of Cocody, Abidjan, 22 BP 582 Abidjan 22, Ivory Coast.

²University Hospital Center of Treichville (CHU of Treichville), Abidjan, 01 BP V3 Abidjan 01, Ivory Coast.

ARTICLE DETAILS

Article history:

Received 20 May 2016

Accepted 29 May 2016

Available online 08 June 2016

Keywords:

Ceftriaxone

Boron Doped Diamond

Chemical Oxygen Demand

Oxidation

ABSTRACT

The degradation of ceftriaxone (CTX) has been studied by the electrochemical oxidation processes in an ideally stirred batch reactor using a boron-doped diamond (BDD) as the anode. The mineralization of CTX was investigated by UV-vis measurements and chemical oxygen demand (COD) analysis. The removal efficiency was studied as a function of several operational variables, such as current densities, initial CTX concentration, initial pH values and inorganic ions. It was found that BDD electrode exhibited good mineralization capability of CTX in neutral conditions at a current density of 100 mAcm⁻². That oxidation is mainly caused by hydroxyl radicals produced through water discharge at BDD surface in aqueous solution of potassium perchlorate. In presence of nitrate, no improvement of the CTX removal was observed but in presence of phosphate and chloride ions, CTX removal yield was enhanced. That enhancement was explained to be due by the involvement of in situ produced reactive (oxidative) species such as chlorine and phosphate radicals in the oxidation of the organic compound in the bulk of the solution.

1. Introduction

The presence of the pharmaceutical compounds, namely antibiotics, in the ecosystem was known for almost 30 years. Unfortunately, the unused overtime drugs such as antibiotics including human and veterinary medical compounds are released into environment continuously. A small part of unused or expired drugs is gathered to be incinerated. However a large part, in the form of original drugs or metabolites, is discarded to waste disposal site or flushed down via toilet into municipal sewer in excrement. Pharmaceuticals in general and specifically antibiotics attracted much attention as potential bioactive chemicals in the environment [1-3]. Antibiotics are frequently used to treat human, animal diseases but their antibacterial nature does not allow their effective removal in conventional wastewater treatment processes [4]. And so antibiotics and their metabolites persist in the environment because of their incomplete elimination in sewage treatment plants with 60-90% of the parent molecules which are still present after biodegradation steps [5]. Among antibiotics, ceftriaxone (CTX) is a broad spectrum third generation cephalosporin which is prescribed for the treatment of several infectious diseases [6-10]. The treatment of waters containing antibiotics such as CTX is not easy due to its non-biodegradable character. Due to such reason and because of the fact that in Côte d'Ivoire, especially in the teaching hospital of Treichville, it has been obtained from a survey undertaken that ceftriaxone is one of the most prescribed pharmaceuticals, and because of the fact that the hospital wastewaters are released in the environment without any treatment, our attention was focused on such a drug in order to develop techniques for its elimination. By our knowledge, it is worth noting that studies undertaken on ceftriaxone are very scarce. Most of the works dealing with ceftriaxone were focused on their characterization, determination [11, 12] and few studies (scarce) have been performed on their oxidation [13, 14]. Various techniques such as physicochemical methods, ozonation, electrochemical, Fenton, and photo-Fenton have been tested for organics oxidation like phenol, carboxylic acid, azo dyes but no much work has been performed for antibiotic oxidation especially ceftriaxone. Amid the techniques mentioned above, electrochemical techniques appears to be a very promising solution for the treatment of

pharmaceuticals [15, 16]. Anodic oxidation is one of the most common electrochemical processes for the remediation of waters containing organic pollutants [17, 18]. For such a method, electrode materials play an important role since the electrochemical oxidation could proceed via various reaction routes such as via direct electron transfer to the anode and/or mediated oxidation with OH[•] or other oxidative species formed from water or other species discharge at the anode surface at high current in case of indirect organics oxidation. The best anodes for this procedure are non-active boron doped diamond (BDD) thin-film electrodes because they interact very weakly with physisorbed BDD(OH[•]) and promote a much greater O₂-overpotential than other conventional anodes like Pt, DSA (dimensionally stable anode) and PbO₂ [19, 20]. Electrochemical oxidation with BDD presents advantages from the point of view of efficiency, stability, cost performance in comparison with other electrodes and methods because of its technologically important properties such as inert surface with low adsorption, remarkable corrosion stability even in strongly acidic media and extremely high O₂-evolution overvoltage.

In this study, BDD was used as anode to evaluate the elimination of CTX in water. The effect of various oxidation parameters has been investigated to study the CTX oxidation on the BDD electrode. Spectrophotometric measurements have been carried out for the evaluation of the removal rate of intermediates that could be produced.

2. Experimental Methods

2.1 Electrode Preparation

Boron doped diamond (BDD) electrodes were prepared by hot-filament chemical vapor deposition (HF-CVD) on low resistivity (1-3 mΩcm) p-Si wafers (siltronix, diameter 10 cm, thickness 0.5 mm). The process gas was a mixture of 1 % CH₄ in H₂ containing trimethylboron. Film growth occurred at a rate of 0.24 μm h⁻¹. The film thickness was about 1 μm. The Scanning Electron Microscopic (SEM) image of the BDD electrode was carried out with a JEOL LJMS-6300-F instrument.

2.2 Chemicals

Ceftriaxone was purchased from a pharmacy in Abidjan. All chemicals used in the experiments were reagent grade or higher and were used as received without any further purification. Potassium perchlorate (KClO₄), perchloric acid (HClO₄), potassium hydroxide (KOH), potassium nitrate

*Corresponding Author

Email Address: ouatlassine@yahoo.fr (Lassiné Ouattara)

(KNO₃), potassium chloride (KCl), potassium dihydrogen phosphate (KH₂PO₄) were obtained from Fluka. Solutions were prepared with distilled water and the pH value was adjusted by HClO₄ and KOH.

2.3 Bulk Electrolysis

For the bulk electrolysis of ceftriaxone in potassium perchlorate solution, an undivided reactor has been used under a galvanostatic regime. The system worked under a batch operation mode. The simulated wastewater was fed with a peristaltic pump into the electrochemical reactor at a flow rate of 2.08 mLs⁻¹. All the electrolysis were conducted at room temperature in an open, cylindrical and undivided glass cell of 250 mL capacity with magnetic stirring. The anode used for the electrolysis was a boron doped diamond electrode (BDD) and the cathode was a titanium plate. The exposed electrode surface area with the solution was about 16 cm².

3. Results and Discussion

3.1 Physical Characterization of the Boron Doped Diamond (BDD) Electrode

Fig. 1 shows the scanning electron microscopic image of the boron doped diamond electrode.

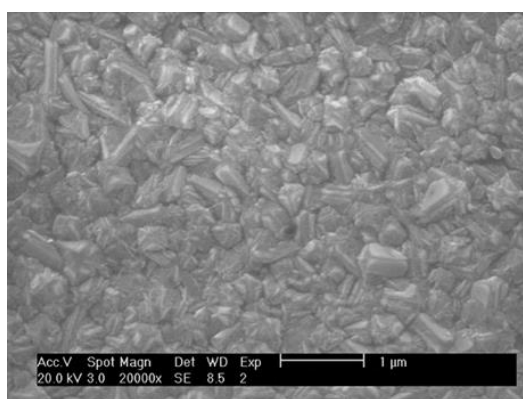


Fig. 1 Scanning electron micrograph of boron doped diamond

That image indicates that BDD presents a polycrystalline structure. The morphological grains sizes are ranging between 0.3 and 0.6 μm. The grains are heavily twinned. At the bottom of the diamond grains, a relative dark space was observed especially at grains boundary which can be related probably to graphitic carbon (Csp²) formed during the BDD preparation.

3.2 Electrochemical Degradation Kinetics of Ceftriaxone (CTX)

The effect of applied current density (20–100 mAcm⁻²), initial concentration of ceftriaxone (0.5–2 gL⁻¹), inorganic ions (concentration of Cl⁻, NO₃⁻, H₂PO₄⁻) and initial pH (2, 7 and 10) on the decay kinetics of CTX solution using the BDD anode are shown in Figs. 2–4.

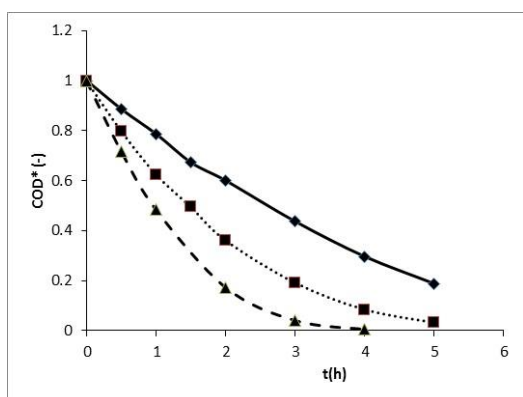
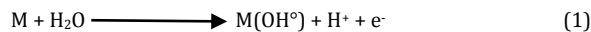


Fig. 2 Effect of current density on COD removal vs electrolysis time for the degradation of 250 mL of 1 gL⁻¹ ceftriaxone in KClO₄ 0.1 M of pH 7.0 at 25 °C. (a: 20 mAcm⁻²; b: 50 mAcm⁻²; c: 100 mAcm⁻²). In the inset: plot of ln(COD) versus electrolysis time. Anode: BDD, cathode: Titanium plate, T = 25 °C. Q = 2.08 mLs⁻¹.

3.2.1 Effect of Applied Current Density

Fig. 2 shows the effect of the applied current density on the degradation of 1 gL⁻¹ CTX. The applied current density *j* is the main key factor governing the effectiveness of the Anodic Oxidation (AO). To assess the effect of this

experimental variable, *j* values ranging between 20 and 100 mAcm⁻² were applied to the AO treatment of a 1 gL⁻¹ ceftriaxone solution of pH 7.0 in the BDD cell for 5 h. The corresponding COD abatement presented in Fig. 2 highlights an increasing degradation rate of CTX with rising *j*, reaching 81%, 92% and 99% mineralization at the end of electrolysis at 20, 50 and 100 mAcm⁻², respectively, with corresponding consumed charge *Q_c* values of 7.44 AhL⁻¹, 18.60 AhL⁻¹ and 28.44 AhL⁻¹. The higher CTX degradation rate and mineralization degree reached at higher *j* can be due to the acceleration of water oxidation from reaction (Eq.1):



Plotting the logarithm of the chemical oxidation demand versus the electrolysis time, a straight line was obtained (inset of Fig. 2) indicating that in the working conditions, the chemical oxygen demand decay follows a pseudo first order kinetic with a constant of 1.07 h⁻¹.

3.2.2 Effect of Initial pH Value

The initial pH is of crucial importance for the electrochemical oxidation process, which may affect the structure of organic matter or coexisting ions. Thus, in order to make this study reach more extensive application prospect in actual wastewater, the influence of initial pH was determined over a wide pH range by adjusting the pH of the medium to 2.0, 7.0 and 10.0 before electrolysis, and no buffer was used in this part of experiment. The results are shown in Fig. 3. It is obtained that CTX solutions with lower initial pH had slightly higher oxidation rate than those of the CTX solutions with higher pH, indicating that the oxidation process was more favorable in acidic solution. The total degradation is attained after 3 h of electrolysis independently of pH.

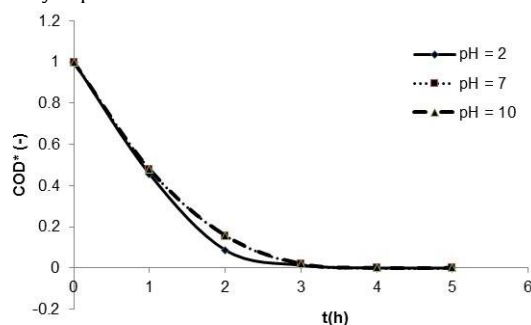


Fig. 3 Effect of pH on COD removal vs electrolysis time for degradation of 250 mL of 1000 mg/L ceftriaxone in KClO₄ 0.1 M at 25 °C. Anode: BDD, cathode: Titanium plate, flow rate Q = 2.08 mLs⁻¹

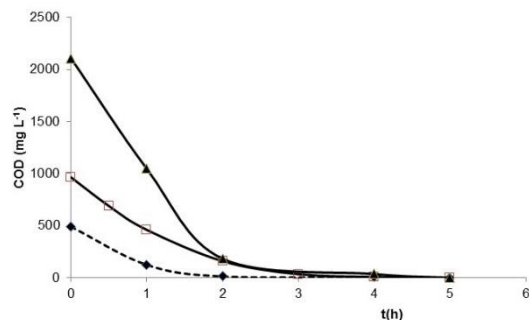


Fig. 4 Effect of initial concentration of CTX (a: 0.5 gL⁻¹; b: 1 gL⁻¹; c: 2 gL⁻¹) on COD removal vs electrolysis time for degradation of 250 mL at 100 mAcm⁻² in KClO₄ 0.1 M of pH 7.0 at 26 °C. Anode: BDD, cathode: Titanium plate, T = 25 °C. Q = 2.08 mLs⁻¹

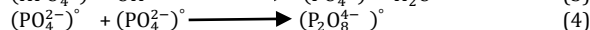
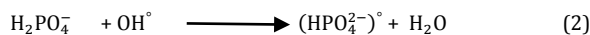
3.2.3 Effect of Initial CTX Concentration

Due to the fact that the hospital wastewaters usually contain different concentrations of pharmaceutical compounds, it is very important to investigate the effect of the initial concentration of ceftriaxone on the performance of the electrochemical oxidation process from a practical point of view. For that, a solution of ceftriaxone of 0.5 gL⁻¹, 1 gL⁻¹ and 2 gL⁻¹ at pH 7 was electrolyzed under 100 mAcm⁻² using BDD anode. The initial pH of the three solutions decreases with time to remain practically constant up to a final value of 1.3. The obtained result is depicted in Fig. 4. That result indicates that in the course of the electrolysis, ceftriaxone oxidation leads to intermediates presenting an acidic character [12, 21]. That result is in accordance to that of other authors where an antibiotic such as oxacillin was oxidized on Ti/IrO₂ electrode [14]. The mineralization rate of ceftriaxone decreases quickly as the initial

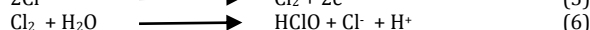
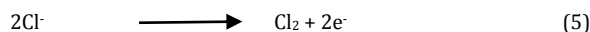
concentration of the ceftriaxone solution increases. Martinez-Huitle and Ferro [20, 22] claimed that the oxidation reaction that occurs on the electrode surface are mediated by hydroxyl radicals, thus, due to the mass transfer control, it could be assumed that the effect of the concentration of organic matter could not be ignored. At low initial concentration, the electrochemical reaction is faster than diffusion i.e. the process is diffusion controlled for very low ceftriaxone concentration. As shown in Fig. 4, CTX disappeared almost completely in 120 min of electrolysis for an initial concentration of 0.5 gL⁻¹. After a quantity of electricity of $Q_c = 13.61 \text{ AhL}^{-1}$ is passed, COD was reduced to reach 98%, 82% and 91% for 0.5, 1 and 2 gL⁻¹ respectively.

3.2.4 Effect of Inorganic Ions

In order to investigate the influence of the inorganic ions on the degradation kinetics and mineralization efficiency of ceftriaxone aqueous solutions, the experiments were performed in neutral medium (pH 7) containing different inorganic ions Cl⁻, NO₃⁻ and phosphate ions H₂PO₄⁻. It is worth noting that at pH around 7, both HPO₄²⁻ and H₂PO₄⁻ forms are present in the electrolysis solution with almost the same concentration buffering the solution. The obtained results were presented in Fig. 5. The degradation rate of ceftriaxone in the presence of NO₃⁻ is similar to that obtained without these ions until 3h of electrolysis. As can be seen from Fig. 5, the complete degradation of ceftriaxone took place after 180, 240, 300 min and 120 min of electrolysis in presence of phosphate ions, in absence of ions, in presence of NO₃⁻ and in presence of chlorides respectively. Plots of the logarithm of the chemical oxidation demand versus the electrolysis time realized in presence and in absence of inorganic ions used in this work showed straight lines with kinetic constant of 1.76 h⁻¹ (R²=1); 0.98 h⁻¹ (R²=0.99); 1.20 h⁻¹ (R²=0.98); 1.07 h⁻¹ (R²=0.98) for Cl⁻, NO₃⁻ and H₂PO₄⁻ ions and in absence of ions respectively. In order to compare the COD removal values of these systems, we performed the COD analysis at 120 min of electrolysis and calculated the corresponding current efficiency CE% values. After 120 min of electrolysis, the degradation of ceftriaxone reaches 82.8%, 100%, 82.6% and 90.1% of COD removal with 21.6%, 26.2%, 21.6% and 23.6% current efficiency respectively in absence and in presence of chloride ions, nitrates ions and phosphate ions respectively. In this experimental condition, it is obtained that the mineralization rate of ceftriaxone in presence of the inorganic ions investigated increases in the following order: Cl⁻ > H₂PO₄⁻ > NO₃⁻ ≈ absence of additional inorganic ions. That observation is positively correlated with the kinetic constant determined above. In all cases, current efficiencies are almost the same indicating that independently of the composition of the electrolysis solution in term of additional ions only 21.6–23.6% part of the current applied is really involved in the degradation of ceftriaxone. The other part of current could intervene in the production of reactive species that could participate in the oxidation process and/or in the production of undesirable side reactions. From this result, it appears that chlorides have a very important effect on the degradation kinetic of ceftriaxone. In case of phosphate ions, a slight increase of the ceftriaxone degradation yield was observed and in case of nitrate, no improvement of ceftriaxone degradation yield was observed when results are compared to situation where no additional ions were used. The improvement observed in presence of phosphate ions could result from the participation of phosphate radicals that are produced in situ by many reactions routes. They can be produced directly on the electrode surface by direct reaction or through the reaction between hydroxyl radicals and the phosphate ions (Eqs. 2–4). In some works, it has been indicated that the produced radicals are less reactive than hydroxyl radicals meanwhile the phosphate radicals diffuse in the bulk of the solution and can oxidize in a chemical way the organic compound, ceftriaxone [22, 23].



These reactive species can also react with the organics and contribute in enhancing the degradation yield of ceftriaxone leading to its mineralization. The very fast degradation kinetics in the case of Cl⁻ can be explained by parallel degradation reaction in the solution phase via indirectly formed reactive species. The chloride ions were oxidized to chlorine gas (Cl₂) at BDD anode (Eq. 5), which reacts with water to form hypochlorite (ClO⁻) ions (Eq. 6):



In the course of the experiment, odor of hypochlorite was spread in the laboratory confirming such mechanism. The formed chlorine gas, a strong

chlorination agent, and hypochlorite ions can react with ceftriaxone to form chlorinated by-products.

During the electrolysis, the absorbance of the samples withdrawn from the simulated wastewater tank was recorded. The result is shown in Fig. 6. One observed in Fig. 6 that during the first 0.5 h, an increase of the absorbance is observed and reached a maximum. That could be due to the production of intermediates which absorb at the same wavelength as ceftriaxone. During the electrolysis, a decrease of the absorbance is observed until total degradation is obtained after almost 3 h of electrolysis and the colour of the solution was followed. From a colourless solution at 0 h, solution became red after 0.5 h of electrolysis and as the electrolysis is running that colour intensity decreases to be almost colourless after 3 h of electrolysis and totally colourless after 5 h of electrolysis (Fig. 7). In fact, the change of the solution colour from colourless to red during the electrolysis could be due to the production of intermediates which absorbed at the wavelength around 520 nm. The decrease of the absorbance after 0.5 h (inset of Fig. 6) and the decrease in the intensity of the colour of the solution (Fig. 7) can result from the oxidation (removal) of the produced intermediates.

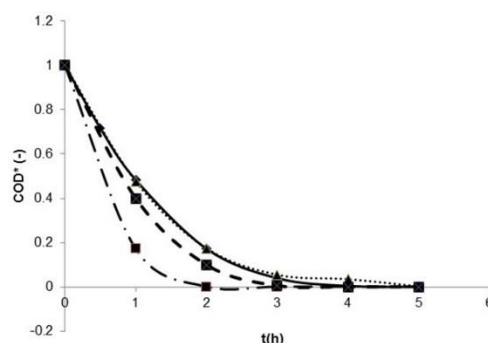


Fig. 5 Effect of inorganic ions on COD removal vs electrolysis time for degradation of 250 mL of CTX 1000 mgL⁻¹ at 100 mAcm⁻² in KClO₄ 0.1 M of pH 7.0 at 25 °C. (a: CTX 1 gL⁻¹; b: CTX 1 gL⁻¹ + 50 mM KCl; c: CTX 1 gL⁻¹ + 50 mM NaNO₃; d: CTX 1 gL⁻¹ + 50 mM KH₂PO₄) Anode: BDD, cathode: Titanium plate, Q = 2.08 mLs⁻¹

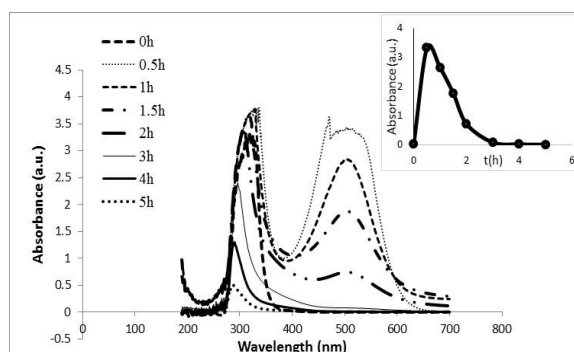


Fig. 6 Absorption spectra of ceftriaxone samples during ceftriaxone electrolysis at 50 mA cm⁻² on BDD electrode. Inset: absorbance at 520 nm versus electrolysis time



Fig. 7 Photo of the solution withdrawn from the wastewater tank during electrolysis (from left to right : t = 0 h; 0.5 h; 1 h; 1.5 h; 2 h; 3 h; 4 h; 5 h)

4. Conclusion

From this work, it has been pointed out that the boron doped diamond (BDD) electrode presents a polycrystalline structure with well defined diamond grains with graphitic carbon (Csp²) at the diamond grain boundaries. It has been demonstrated that anodic oxidation of ceftriaxone with BDD is a very effective method for its degradation reaching its mineralization in aqueous medium. The degradation of ceftriaxone led to intermediates which undergo further degradation until total

mineralization of parent organic compound (ceftriaxone) and produced intermediates occurs. That oxidation occurs on BDD electrode in potassium perchlorate solution via the involvement of hydroxyl radicals. Addition of inorganic ions to the solution has indicated that chloride and phosphate ions contributed in the enhancement of the degradation yield of ceftriaxone through the involvement of oxidative species (radicals) produced. The presence of nitrate did not contribute in increasing the ceftriaxone degradation yield.

Acknowledgements

We greatly thank the Swiss National Funds for its financial support that allowed this work to be carried out. Our Team has received part of the grant IZ01Z0_146919 for that work. We also thank Prof. Cesar Pulgarin at the Swiss Federal Institute of Lausanne (Switzerland) and Prof. Ricardo Torres at the University of Antioquia (Colombia) for their help in that work. We also thank Prof. Bakayoko-Ly Ramata, the President of the University Felix Houphouet-Boigny for her help in the realization of that work.

References

- [1] K. Kümmerer, The presence of pharmaceuticals in the environment due to human use – present knowledge and future challenges, *J. Environ. Manage.* 90 (2009) 2354–66.
- [2] S. Esplugas, D.M. Bila, L.G.T. Krause, M. Dezotti, Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents, *J. Hazard Mater.* 149 (2007) 631–642.
- [3] L. Lissemore, C. Hao, P. Yang, P.K. Sibley, An exposure assessment for selected pharmaceuticals within a watershed in Southern Ontario, *Chemosphere* 64 (2000) 717–729.
- [4] K.D. Brown, J. Kulis, B. Thomson, T.H. Chapman, D.B. Mawhinney, Occurrence of antibiotics in hospital, residential, and dairy effluent, municipal wastewater, and the Rio Grande in New Mexico, *Sci. Total Environ.* 366 (2006) 772–783.
- [5] V. Homem, L. Santos, Degradation and removal methods of antibiotics from aqueous matrices - A review, *J. Environ. Manage.* 92(10) (2011) 2304–2347.
- [6] H.P. Lambert, F. O'Grady, *Antibiotics and chemotherapy*, 6th Ed., Churchill Livingstone, Edinburgh, 1992.
- [7] A. Mazza, Ceftriaxone as short-term antibiotic prophylaxis in orthopedic surgery: a cost-benefit analysis involving 808 patients, *J. Chemother.* 12 (2000) 29–33.
- [8] S.L. Kaplan, Serious pediatric infections, *Am. J. Med.* 88 (1990) 18–24.
- [9] W. Zhao, Y. Zhang, Q. Li, Indirect spectrophotometric determination of sodium ceftriaxone with n-propyl alcohol-ammonium sulfate–water system by extraction flotation of copper(II), *Clinica Chimica* 391 (2008) 80–84.
- [10] I.A. Balcioglu, M. Öther, Treatment of pharmaceutical wastewater containing antibiotics by O₃ and O₃/H₂O₂ processes, *Chemosphere* 50 (2003) 85–95.
- [11] E. Brillas, I. Sires, C. Arias, P.L. Cabot, F. Cantellas, R.M. Rodriguez, J.A. Garrido, Mineralization of paracetamol in aqueous medium by anodic oxidation with a boron-doped diamond electrode, *Chemosphere* 58 (2005) 399–406.
- [12] I. Sires, J.A. Garrido, R.M. Rodriguez, P.L. Cabot, F. Cantellas, C. Arias, E. Brillas, Electrochemical degradation of paracetamol from water by catalytic action of Fe²⁺, Cu²⁺, and UVA light on electrogenerated hydrogen peroxide, *J. Electrochem. Soc.* 153 (2006) 1–9.
- [13] X. Guo, L. Dong, W. Jiafeng, Y. Xiujuan, Preparation and electrochemical property of TiO₂/Nano-graphite composite anode for electro-catalytic degradation of ceftriaxone sodium, *Electrochim. Acta* 180 (2015) 957–964.
- [14] A.L. Giraldo, E.D. Erazo-Erazo, O.A. Flórez-Acosta, E.A. Serna-Galvis, R.A. Torres-Palma, Degradation of the antibiotic oxacillin in water by anodic oxidation with Ti/IrO₂ anodes: Evaluation of degradation routes, organic by-products and effects of water matrix components, *Chem. Eng. J.* 279 (2015) 103–114.
- [15] G.B. Tissot, A. Anglada, P. Dimitriou-Christidis, L. Rossi, J. Samuel Arey, Ch. Comninellis, Kinetic experiments of electrochemical oxidation of iohexol on BDD electrodes for wastewater treatment, *Electrochem. Commun.* 23 (2012) 48–51.
- [16] C.Q.M. Gnamba, F.T.A. Appia, E.M.H. Loba, I. Sanogo, L. Ouattara, Electrochemical oxidation of amoxicillin in its pharmaceutical formulation at boron doped diamond (BDD) electrode, *J. Electrochem. Sci. Eng.* 5(2) (2015) 129–143.
- [17] C. Indermuhle, M.J. Martín de Vidales, C. Sáez, J. Robles, P. Cañizares, J.F. García-Reyes, et al, Degradation of caffeine by conductive diamond electrochemical oxidation, *Chemosphere* 93(9) (2013) 1720–1725.
- [18] B. Boye, E. Brillas, B. Marselli, P.A. Michaud, Ch. Comninellis, G. Farnia, G. Sándonà, Electrochemical incineration of chloromethylphenoxy herbicides in acid medium by anodic oxidation with boron-doped diamond electrode, *Electrochim. Acta* 51(14) (2006) 2872–2880.
- [19] Q. Dai, J. Zhou, M. Weng, X. Luo, D. Feng, J. Chen, Electrochemical oxidation metronidazole with Co modified PbO₂ electrode: Degradation and mechanism, *Sep. Purif. Technol.* 166 (2016) 109–116.
- [20] D.O. Martire, M.C. Gonzalez, Aqueous phase kinetic studies involving intermediates of environmental interest: phosphate radicals and their reactions with substituted benzenes, *Prog. React. Kinet. Mec.* 26 (2001) 201–218.
- [21] C.A. Martinez-Huitle, S. Ferro, Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes, *Chem. Soc. Rev.* 35 (2006) 1324–1340.
- [22] P. cañizares, J. Garcia-Gomez, C. saez, M. A. Rodrigo, Electrochemical oxidation of several chlorophenols on diamond electrode: Part I: reaction mechanism, *J. Appl. Electrochem.* 33 (2003) 917–927.
- [23] A. Sánchez-Carretero, C. saez, P. cañizares, M.A. Rodrigo, *Characterization and application*, Wiley, New jersey, 2011.