Research Article

Electrochemical Oxidation of Ethinylestradiol on a Commercial Ti/Ru_{0.3} Ti_{0.7}O₂ DSA Electrode

Karla M. Vieira,¹ Clésia C. Nascentes,² Artur J. Motheo,³ and Rodinei Augusti²

¹ Department of Exact and Applied Sciences, Federal University of Ouro Preto, Loanda, 35931-008 João Monlevade, MG, Brazil

² Department of Chemistry, Federal University of Minas Gerais, Pampulha, 31270-901 Belo Horizonte, MG, Brazil

³ Institute of Chemistry of São Carlos, University of São Paulo, P.O. Box 780, 13560-970 São Carlos, SP, Brazil

Correspondence should be addressed to Rodinei Augusti; augusti.rodinei@gmail.com

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The electrochemical oxidation of the hormone ethinylestradiol in an aqueous-methanolic medium by the application of a constant current of 40 mA cm⁻² in a flow cell with a commercial Ti/Ru_{0.3} Ti_{0.7}O₂ electrode was evaluated. The effect caused by the use of NaCl as a support electrolyte was also investigated. Hence, HPLC-UV analyses revealed that ethinylestradiol was almost totally consumed after a 60 min reaction time in the presence of NaCl. Conversely, much lower degradation rates were obtained when NaCl was not employed. Moreover, direct infusion ESI-MS and GC-MS analysis revealed that apparently no degradation products had been formed under these conditions. Hence, this study clearly demonstrated that such electrochemical treatment can be efficiently used to promote the complete degradation (and probably mineralization) of the hormone ethinylestradiol.

1. Introduction

It has been profusely reported that several pharmaceuticals, including the endocrine disrupting compounds (EDCs), are directly released into water bodies, such as rivers and lakes, thus representing a serious risk to the natural ecosystems [1]. These substances, which cannot be completely eliminated by the conventional treatment procedures, have been detected in drinking water and are potentially dangerous to the human health [1–3].

The presence of estrogens in the effluents of sewage treatment plants has been reported in many countries [4]. Ethinylestradiol (Figure 1), a synthetic steroidal estrogen, is a common component widely used as the active principle of many contraceptive agents and therapy drugs. The occurrence of estrogen hormones in natural systems, such as surface waters, soils, and sediments, has become a subject of major concern. Many problems, for instance the feminization of male fishes, the lower sperm counts in adult males, and an increasing incidence of cancer, have been related to the existence of these hormones in natural waters [4].

Advanced oxidative processes (AOPs) have been widely applied for the disinfection (elimination of undesired

micropollutants) from drinking and waste waters [5, 6]. Ozone, chlorine, and chlorine dioxide are the most used reactants for such purpose. In AOPs, hydroxyl radicals, very reactive species that ultimately account for the oxidation of target compounds, are secondary oxidants that can be produced *in situ* by the decomposition of ozone or mainly from combined systems as Fenton, UV/H₂O₂, and UV/TiO₂ [7, 8].

The interest in using electrochemical techniques to deplete organic compounds has enormously increased in the last years due to the following advantageous features of such methods: the catalytic electrode is immobilized (thus reducing the need to separate the catalyst from the reaction mixture); the variables (i.e., current and potential) are easily controlled facilitating automation; the equipments required are of low cost; and the electrochemical cells are easily adapted for use in flow systems [9, 10].

In electrochemical studies the choice of the electrode material is very important. Dimensionally stable anode (DSA) materials have been widely used in the chloro-alkali industry and, more recently, in studies of organic oxidations and waste treatment [11–13]. DSAs are attractive for use in treatment systems as they present relatively long lifetimes and do not necessarily undergo the same poisoning phenomena

FIGURE 1: Chemical structure of the synthetic hormone ethinylestradiol.

associated with traditional electrode materials such as Pt. The most common DSA is the commercially available $\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$.

In the electrochemical processes an important factor is the effluent conductivity. Hence, the higher the conductivity (and thus the lower the resistivity), the higher the current efficiency across the electrochemical cell. Usually, salts are added to the effluent (especially NaCl) in order to increase conductivity. The addition of NaCl can be beneficial as powerful oxidizing agents are formed: chlorine gas (Cl_2) (see (1)) and hypochlorite (OCl^-) (see (2)) [9, 11]. Chlorine gas is formed at the anode according to

The subsequent reaction of Cl_2 with OH^- formed at the cathode yields hypochlorite (OCl^-):

On the other hand, there is a noticeable concern that the application of the usual procedures for water disinfection can yield highly toxic organic species [5], potentially more harmful than the own precursors [14, 15]. The identification of such sort of by-products is therefore an important task that must be accomplished in order to evaluate the overall performance of a given treatment process [15].

For the characterization of by-products resulting from the degradation of pharmaceuticals (and other emerging pollutants) in aqueous medium, different mass spectrometry approaches have been used [16, 17]. For such intent, electrospray ionization mass spectrometry (ESI-MS) and gas chromatography coupled to mass spectrometry (GC-MS) are the techniques of primary choice. ESI-MS, because of its appealing and unique attributes, has rapidly become an alternative approach to be used in the monitoring of an increasing number of relevant environmental processes [18–25]. Conversely, GC-MS is frequently employed for the detection and characterization of by-products with a nonpolar nature [16, 17].

In the present work, the feasibility of an oxidative electrochemical process, which makes use of a commercial $\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ anode, to degrade the hormone ethinylestradiol (Figure 1) in an aqueous-methanolic solution was investigated. The effect of NaCl (support electrolyte) on the

performance of the process is also evaluated. Whereas high performance liquid chromatography with an UV detector (HPLC-UV) is used to track the substratum consumption, ESI-MS and GC-MS techniques are applied to detect (and expectantly characterize) residual organic compounds (by-products) possibly formed in solution.

2. Experimental

2.1. Electrochemical Reactor. A single-compartment filter-press cell was used with a commercial $\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ plate (De Nora, Brazil) as the working electrode (anode). This electrode and a stainless steel cathode, both with geometric areas of 14 cm^2 , were exposed to the work solution. The reactor was mounted by positioning the electrodes between the Viton and Teflon spacers (with variable thickness, Figure 2).

2.2. Electrochemical Degradation. For each experiment, 250 mL of a solution of ethinylestradiol (100 mg L^{-1} in water/methanol 7:3 v/v) were transferred to the reservoir. The very high concentration of the ethinylestradiol solution (100 mg L^{-1}), much superior than those typically found in environmental samples, was chosen to facilitate the detection of possible by-products formed under these conditions. Given the very low solubility of ethinylestradiol in water, a solution of water/methanol 7:3 v/v was employed as solvent to assure the total solubilization of the analyte. The solution pH was adjusted to 2 by dropping HCl 0.1 mol L^{-1} . The assays were conducted by applying a constant current of 40 mA cm^{-2} and by using a potentiostat/galvanostat (Autolab, model SPGSTAT). In the assays that made use of NaCl as a support electrolyte, the salt concentration was 250 mg L^{-1} (such concentration was employed following the recommendations of the Brazilian Council of Environment, CONAMA). Aliquots were taken from the reaction vessel at reaction times of 0, 30, 60, 90, and 120 min (5 mL of the first and last aliquots and 2 mL of the other ones). Ethinylestradiol (Organon 98%) and NaCl (Merck, Darmstadt, Germany) were used without further purification.

2.3. HPLC-UV Monitoring. HPLC-UV measurements were performed on an SPD-M10A VP instrument (Shimadzu, Kyoto, Japan) using a Hypersil C18 column (250 mm long, 4.6 mm i.d., $5\text{ }\mu\text{m}$ particle size) and acetonitrile/ H_2O (1:1) as mobile phase. The isocratic elution was maintained at a flow rate of 1 mL min^{-1} during the 10 min run. The injection volume was $20\text{ }\mu\text{L}$ and UV detector set to operate at 210 and 280 nm.

2.4. ESI-MS Monitoring. The ESI-MS analyses were conducted on an LCQ Fleet (Thermo Scientific, San Jose, CA) mass spectrometer with an electrospray ionization (ESI) source and operating in the negative ion mode. Mass spectra were obtained as an average of 50 scans, with each one requiring 0.2 s. The withdrawn aliquots were directly injected into the ESI source at a flow rate of $25\text{ }\mu\text{L min}^{-1}$ by using a $500\text{ }\mu\text{L}$ -microsyringe (Hamilton, Reno, NV). ESI source

FIGURE 2: Schematic representation of the electrochemical flow cell used in the present study.

FIGURE 3: Normalized concentration (C/C_0) of ethinylestradiol as function of time. The initial solution of ethinylestradiol (100 mg L^{-1} in water/methanol 7:3 v/v at pH 2 and in the presence or absence of NaCl 250 mg L^{-1}) was submitted to the electrochemical treatment and the aliquots analyzed by HPLC-UV.

conditions were as follows: heated capillary temperature of 285°C , sheath gas (N_2) flow rate at 20 (arbitrary units), spray voltage of 5.0 kV, capillary voltage of -38 V , and tube lens offset voltage of -110 V .

2.5. GC-MS Monitoring. For the GC-MS analyses, two extraction methods were evaluated: liquid-liquid extraction (LLE) and solid phase microextraction (SPME). The liquid-liquid extraction (LLE) was performed by mixing 0.5 mL of the collected aliquot and 0.5 mL of dichloromethane (Tedia, Fairfield, USA) followed by vortex stirring (Phoenix, Araraquara, Brazil) for 30 seconds. The organic phase was isolated and the aqueous layer submitted to the same extraction procedure for two more times. The organic extracts were combined and the solvent evaporated. To the resulting

solvent-free material, 1 mL of dichloromethane was then added.

The SPME extraction was conducted by employing manual holders with the CAR/PDMS (carboxen/polydimethylsiloxane) or DVB/CAR/PDMS (divinylbenzene/carboxen/polydimethylsiloxane) fibers (purchased from Supelco, Bellefonte, PA, USA). Prior to use, the fibers were conditioned following the manufacturer's instructions. The fibers were directly inserted into the solutions (prepared by diluting the collected aliquots 100 times with Milli-Q water) for 10 min at ambient temperature (25°C) and then introduced into the GC inlet.

GC-MS analysis was conducted on a chromatograph (Trace GC Ultra) coupled to an ion trap mass spectrometer (POLARIS Q) (Thermo Electron, San Jose, CA). An HP-5MS (Agilent, Santa Clara, CA) capillary column ($30 \text{ m} \times 0.25 \text{ mm id} \times 0.25 \mu\text{m film}$) containing 5% diphenyl and 95% dimethylpolysiloxane was used. The inlet was adjusted to operate in the splitless mode for 2 min under a temperature of 250°C . The oven temperature program was as follows: 120°C (holding time: 2 min) with an increment of $10^\circ\text{C min}^{-1}$ up to 290°C (holding time: 5 min) and finishing with an increase of $10^\circ\text{C min}^{-1}$ up to 300°C for 2 minutes. The total run time was 27 minutes and helium was used as carrier gas at a constant flow of 1.5 mL min^{-1} . The following parameters were used while operating the mass spectrometer: electron ionization at 70 eV, full scan mode with a mass range of 50–400, and a source temperature of 200°C .

3. Results and Discussion

3.1. HPLC-UV Monitoring. To determine the time-dependence of depletion of ethinylestradiol by the electrochemical process, aliquots were successively withdrawn from the reaction vessel and analyzed by HPLC-UV. Figure 3 shows the normalized concentration of ethinylestradiol as a function of time in the absence and presence of NaCl, used as a support electrolyte at 250 mg L^{-1} . These results remarkably

FIGURE 4: ESI(-)-MS monitoring of the electrochemical treatment of a solution of ethinylestradiol (100 mg L^{-1} in water/methanol 7 : 3 v/v at pH 2 and in the presence of NaCl 250 mg L^{-1}). Aliquots were withdrawn at the following reaction times: (a) 0 min; (b) 60 min; (c) 120 min. Note that the intensity of the anion of m/z 295 (deprotonated ethinylestradiol) decreases as a function of reaction time.

demonstrate the great efficiency of the electrochemical process because a high degradation rate (90%) was achieved after 60 min reaction time. As expected, in the absence of NaCl the degradation rate dropped to only 30% after identical time. The addition of an electrolyte to the reaction mixture, a practice usually adopted [5, 6, 10] to improve the solution conductivity (the initial solution of ethinylestradiol at pH 2 displayed a conductivity of only 2.42 mS cm^{-1}) and thus the overall process efficiency, allows the *in situ* formation of oxidizing species (as the ones represented in (2)) that ultimately promote the degradation of the target compound. Similar results were described by Malpass and coworkers [11] that reported high degradation rates in the electrooxidation of dyes in aqueous solution upon the addition of NaCl. The authors achieved a complete solution discoloration and 58% of TOC (Total Organic Removal) removal. Other works also reported the successful application of such electrochemical process for the degradation/mineralization of dyes and pesticides [5, 6, 9–11].

3.2. ESI-MS Monitoring. The electrochemical degradation of ethinylestradiol was continuously monitored by direct infusion electrospray ionization mass spectrometry. This technique has been successfully employed in the determination of degradation by-products [18–22, 26, 27]. Figure 4 displays representative ESI mass spectra in the negative ion mode, ESI(-)-MS, of the aliquots withdrawn after reaction times of 0, 60, and 120 min in the presence of NaCl (250 mg L^{-1}). Figure 4(a) shows the mass spectrum of the initial solution which displays an intense anion of m/z 295, corresponding to $[1 - \text{H}]^-$ (the deprotonated form of ethinylestradiol). The $[1 - \text{H}]^-$ anion decreases continuously and disappears after 30 min reaction time (Figures 4(b) and 4(c)). Other anions, of m/z 261, 339, 403, 545, 687, and 829, are also detected in all the ESI(-)-MS. The presence of such anions in the ESI(-)-MS of the initial solution (Figure 4(a)) indicates, therefore, that

their origin is likely due to the presence of impurities in the reaction vessel or instrumental system rather than a possible formation of degradation products (expected to occur under these conditions).

Figure 5 displays the ESI(-)-MS of the aliquots of the reaction conducted in the absence of NaCl. Note that after successive reaction times (Figures 5(a)–5(c)) the anion of m/z 295 (the deprotonated form of ethinylestradiol) remains roughly unaltered thus indicating that the hormone seems to not undergo degradation. Once more, the appearance of different anions, which could indicate the presence of degradation products in the reaction solution, was not verified. These results thus confirm that the presence of NaCl strongly affects the performance of such electrochemical process.

3.3. GC-MS Monitoring. GC-MS analyses were performed in an attempt to identify non-polar (and possibly chlorinated) degradation products. Two extraction methods were applied: SPME (solid phase micro extraction) and LLE (liquid-liquid extraction). In the SPME procedure, two fibers with distinct polarities were evaluated: divinylbenzene/carboxen (DVB/CAR) and divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS). In spite of these distinct characteristics, both fibers produced quite similar results. Figures 6(a) and 6(b) show, respectively, the chromatograms, obtained by the use of the DVB/CAR/PDMS fiber, of the initial solution and of the aliquot withdrawn after 120 min (reaction conducted in the presence of NaCl 250 mg L^{-1}). Note that the chromatographic peaks related to ethinylestradiol (its EI 70 eV mass spectrum is shown as an insert in Figure 6(a)) and estrone (resulting from a slow loss of acetylene from ethinylestradiol), which eluted at retention times of ca. 19.8 and 18.9 min, respectively, completely disappeared after 120 min of the electrochemical treatment. Note also the clear absence of other peaks that could indicate the formation of degradation products. The chromatograms

FIGURE 5: ESI(-)-MS monitoring of the electrochemical treatment of a solution of ethinylestradiol (100 mg L^{-1} in water/methanol 7:3 v/v at pH 2 with no addition of NaCl 250 mg L^{-1}). Aliquots were withdrawn at the following reaction times: (a) 0 min; (b) 60 min; (c) 120 min. Note that the intensity of the anion of m/z 295 (deprotonated ethinylestradiol) stays practically constant as the reaction proceeds.

FIGURE 6: Chromatograms (GC-MS) obtained upon the SPME extraction (DVB/CAR/PDMS fiber) of a solution of ethinylestradiol (100 mg L^{-1} in water/methanol 7:3 v/v at pH 2 with addition of NaCl 250 mg L^{-1}) submitted to the electrochemical treatment. Aliquots were withdrawn at the following reaction times: (a) 0 min; (b) 120 min.

resulting from the liquid-liquid extraction procedure (not shown) revealed that the intensity of the ethinylestradiol peak decreased continuously as the reaction proceeded. Also in this case, no degradation products could be observed.

Other process to ethinylestradiol degradation has been proposed in the literature. For instance, Zhang and coworkers [28] investigated the degradation of ethinylestradiol via ultraviolet (UV) photolysis and $\text{UV}/\text{H}_2\text{O}_2$ process. Using the last process, more than 90% of the hormone was removed in 20 min. In another work [29], an electrochemical process was employed to ethinylestradiol degradation and the authors verified that the initial concentration decay 96.5% in 15 min. However, in these works no monitoring of the by-products possibly formed during the degradation process was performed.

4. Conclusions

The results presented herein demonstrated the high efficiency of the electrochemical treatment that employs the commercial $\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ anode in promoting the degradation of the hormone ethinylestradiol in an aqueous-methanolic

solution. It was also verified that the use of NaCl (a support electrolyte at 250 mg L^{-1}) dramatically improves the process performance, with a degradation rate higher than 90% after a reaction time of 60 min. The analytical techniques employed herein, that is, GC-MS (via two extraction procedures: LLE and SPME) and direct infusion ESI-MS, indicated that the depletion of the hormone did not lead to a concomitant formation of degradation products. These results thus evidenced that the electrochemical treatment caused the mineralization of ethinylestradiol (TOC measurements could not be executed as the initial ethinylestradiol solution was prepared by using methanol as one of the solvents). Finally, it can be envisaged that such methodology can be potentially applied to the treatment of water contaminated with other sorts of organic pollutants.

Conflict of Interests

The authors state that there is no a direct financial relation with the commercial identities mentioned in the paper (manufacturer of the $\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ DSA electrode) that might lead to conflict of interests.

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References

- [1] X. Zhang, P. Chen, F. Wu, N. Deng, J. Liu, and T. Fang, "Degradation of 17 α -ethinylestradiol in aqueous solution by ozonation," *Journal of Hazardous Materials*, vol. 133, no. 1-3, pp. 291-298, 2006.
- [2] M. Farré, S. Pérez, L. Kantiani, and D. Barceló, "Fate and toxicity of emerging pollutants, their metabolites and transformation products in the aquatic environment," *Trends in Analytical Chemistry*, vol. 27, pp. 991-1007, 2008.
- [3] D. W. Kolpin, E. T. Furlong, M. T. Meyer et al., "Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: a national reconnaissance," *Environmental Science and Technology*, vol. 36, no. 6, pp. 1202-1211, 2002.
- [4] R. P. S. Suri, M. Nayak, U. Devaiah, and E. Helmig, "Ultrasound assisted destruction of estrogen hormones in aqueous solution: effect of power density, power intensity and reactor configuration," *Journal of Hazardous Materials*, vol. 146, no. 3, pp. 472-478, 2007.
- [5] G. R. P. Malpass, D. W. Miwa, S. A. S. Machado, and A. J. Motheo, "Decolourisation of real textile waste using electrochemical techniques: effect of electrode composition," *Journal of Hazardous Materials*, vol. 156, no. 1-3, pp. 170-177, 2008.
- [6] M. Catanho, G. R. P. Malpass, and A. J. Motheo, "Photoelectrochemical treatment of the dye reactive red 198 using DSA electrodes," *Applied Catalysis B*, vol. 62, no. 3-4, pp. 193-200, 2006.
- [7] R. Broséus, S. Vincent, K. Aboulfadl et al., "Ozone oxidation of pharmaceuticals, endocrine disruptors and pesticides during drinking water treatment," *Water Research*, vol. 43, no. 18, pp. 4707-4717, 2009.
- [8] M. N. Chong, B. Jin, C. W. K. Chow, and C. Saint, "Recent developments in photocatalytic water treatment technology: a review," *Water Research*, vol. 44, no. 10, pp. 2997-3027, 2010.
- [9] G. R. P. Malpass, D. W. Miwa, S. A. S. Machado, P. Olivi, and A. J. Motheo, "Oxidation of the pesticide atrazine at DSA electrodes," *Journal of Hazardous Materials*, vol. 137, no. 1, pp. 565-572, 2006.
- [10] G. R. P. Malpass, D. W. Miwa, A. C. P. Miwa, S. A. S. Machado, and A. J. Motheo, "Photo-assisted electrochemical oxidation of atrazine on a commercial Ti/Ru_{0.3}Ti_{0.7}O₂ DSA electrode," *Environmental Science and Technology*, vol. 41, no. 20, pp. 7120-7125, 2007.
- [11] G. R. P. Malpass, D. W. Miwa, D. A. Mortari, S. A. S. Machado, and A. J. Motheo, "Decolorisation of real textile waste using electrochemical techniques: effect of the chloride concentration," *Water Research*, vol. 41, no. 13, pp. 2969-2977, 2007.
- [12] G. R. P. Malpass and A. J. Motheo, "Screening process for activity determination of conductive oxide electrodes for organic oxidation," *Journal of the Brazilian Chemical Society*, vol. 19, no. 4, pp. 672-678, 2008.
- [13] A. P. Buzzini, D. W. Miwa, A. J. Motheo, and E. C. Pires, "Use of electrochemical oxidation process as post-treatment for the effluents of a UASB reactor treating cellulose pulp mill wastewater," *Water Science and Technology*, vol. 54, no. 2, pp. 207-213, 2006.
- [14] M. Catanho, G. R. P. Malpass, and A. J. Motheo, "Evaluation of electrochemical and photoelectrochemical methods for the degradation of three textile dyes," *Química Nova*, vol. 29, no. 5, pp. 983-989, 2006.
- [15] W. F. Jardim, S. G. Moraes, and M. M. K. Takiyama, "Photocatalytic degradation of aromatic chlorinated compounds using TiO₂: toxicity of intermediates," *Water Research*, vol. 31, no. 7, pp. 1728-1732, 1997.
- [16] J. Radjenović, M. Petrović, and D. Barceló, "Complementary mass spectrometry and bioassays for evaluating pharmaceutical-transformation products in treatment of drinking water and wastewater," *Trends in Analytical Chemistry*, vol. 28, no. 5, pp. 562-580, 2009.
- [17] S. Pérez and D. Barceló, "Applications of LC-MS to quantitation and evaluation of the environmental fate of chiral drugs and their metabolites," *Trends in Analytical Chemistry*, vol. 27, pp. 836-846, 2008.
- [18] I. Dalmázio, A. P. F. M. de Urzedo, T. M. A. Alves et al., "Electrospray ionization mass spectrometry monitoring of indigo carmine degradation by advanced oxidative processes," *Journal of Mass Spectrometry*, vol. 42, no. 10, pp. 1273-1278, 2007.
- [19] A. P. F. M. de Urzedo, M. E. R. Diniz, C. C. Nascentes, R. R. Catharino, M. N. Eberlin, and R. Augusti, "Photolytic degradation of the insecticide thiamethoxam in aqueous medium monitored by direct infusion electrospray ionization mass spectrometry," *Journal of Mass Spectrometry*, vol. 42, no. 10, pp. 1319-1325, 2007.
- [20] A. P. F. M. de Urzedo, C. C. Nascentes, M. E. R. Diniz, R. R. Catharino, M. N. Eberlin, and R. Augusti, "Indigo Carmine degradation by hypochlorite in aqueous medium monitored by electrospray ionization mass spectrometry," *Rapid Communications in Mass Spectrometry*, vol. 21, no. 12, pp. 1893-1899, 2007.
- [21] M. H. Florêncio, E. Pires, A. L. Castro, M. R. Nunes, C. Borges, and F. M. Costa, "Photodegradation of diquat and paraquat in aqueous solutions by titanium dioxide: evolution of degradation reactions and identification of intermediates," *Chemosphere*, vol. 55, no. 3, pp. 345-355, 2004.
- [22] T. F. Hess, T. S. Renn, R. J. Watts, and A. J. Paszczyński, "Studies on nitroaromatic compound degradation in modified Fenton reactions by electrospray ionization tandem mass spectrometry (ESI-MS-MS)," *Analyst*, vol. 128, no. 2, pp. 156-160, 2003.
- [23] R. P. Lopes, A. P. F. M. de Urzedo, C. C. Nascentes, and R. Augusti, "Degradation of the insecticides thiamethoxam and imidacloprid by zero-valent metals exposed to ultrasonic irradiation in water medium: electrospray ionization mass spectrometry monitoring," *Rapid Communications in Mass Spectrometry*, vol. 22, no. 22, pp. 3472-3480, 2008.
- [24] P. Madeira, M. R. Nunes, C. Borges, F. M. A. Costa, and M. H. Florêncio, "Benzidine photodegradation: a mass spectrometry and UV spectroscopy combined study," *Rapid Communications in Mass Spectrometry*, vol. 19, no. 14, pp. 2015-2020, 2005.
- [25] L. S. Santos, I. Dalmázio, M. N. Eberlin, M. Claeys, and R. Augusti, "Mimicking the atmospheric OH-radical-mediated photooxidation of isoprene: formation of cloud-condensation nuclei polyols monitored by electrospray ionization mass spectrometry," *Rapid Communications in Mass Spectrometry*, vol. 20, no. 14, pp. 2104-2108, 2006.
- [26] I. Dalmázio, L. S. Santos, R. P. Lopes, M. N. Eberlin, and R. Augusti, "Advanced oxidation of caffeine in water: on-line and real-time monitoring by electrospray ionization mass spectrometry," *Environmental Science and Technology*, vol. 39, no. 16, pp. 5982-5988, 2005.

- [27] F. C. C. Moura, M. H. Araujo, I. Dalmázio et al., "Investigation of reaction mechanisms by electrospray ionization mass spectrometry: characterization of intermediates in the degradation of phenol by a novel iron/magnetite/hydrogen peroxide heterogeneous oxidation system," *Rapid Communications in Mass Spectrometry*, vol. 20, no. 12, pp. 1859–1863, 2006.
- [28] Z. Zhang, Y. Feng, Y. Liu, Q. Sun, P. Gao, and N. Ren, "Kinetic degradation model and estrogenicity changes of EE₂ (17 α -ethinylestradiol) in aqueous solution by UV and UV/H₂O₂ technology," *Journal of Hazardous Materials*, vol. 181, no. 1–3, pp. 1127–1133, 2010.
- [29] Y. Feng, C. Wang, J. Liu, and Z. Zhang, "Electrochemical degradation of 17-alpha-ethinylestradiol (EE₂) and estrogenic activity changes," *Journal of Environmental Monitoring*, vol. 12, no. 2, pp. 404–408, 2010.