Research Article

Electrochemical degradation of triketone herbicides and identification of their main degradation products[†]

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Abstract

The aim of this paper was the development and optimization of an electrochemical method for the degradation of two triketone herbicides, mesotrione and sulcotrione, in a two-electrode undivided electrochemical cell equipped with commercially available, non-modified, electrode materials. The electrochemical parameters studied included five different electrode systems (Zr/Pt, Pd/Pt, C/Pt, Nb/Pt and Ti/Pt), current densities (27.66, 55.33, …, 110.66 mA·cm^{-2}) and pH values (3, 7 and 9) in 0.05 M sodium sulfate as supporting electrolyte. The electrical energy consumption and chemical oxygen demand were calculated for optimal conditions. The degradation efficiency was determined by high performance liquid chromatography equipped with a diode array detector, while the degradation products for both pesticides were identified and compared by UHPLC-mass spectrometry. The results could lead to an accurate estimate of their effect on the environment. A real water sample was used to study the influence of organic matter on pesticide degradation. Based on the results obtained the electrochemical treatment could be used for the successful removal of triketone herbicides from contaminated water.

1. Introduction

Agricultural industry inevitably depends on the pesticide usage. A large number of active components in pesticide formulations has been registered and present on the market for pest control purposes [1]. There is a big concern about the environmental impact of excessive pesticide usage. Pesticides in the environment can migrate from treated fields to air, other land, and water [2]. Their removal from water effluents is the subject of environmental remediation and has attracted many researchers [3].

Mesotrione and sulcotrione are members of the triketone group of herbicides which originates from the phytotoxin of the bottlebrush plant *Callistemon citrinus* [4, 5]. Mesotrione is used in maize crops for the control of broadleaf plants and grass weeds [6]. Sulcotrione is also used in maize crops against barnyard grass and dicotyledonous weeds [7]. Typical concentrations of mesotrione range from 100 to 224 g·ha^{-1} when applied as a pre-emergent and from 70 to 150 g·ha^{-1} as a post-emergent herbicide [6].

Many classical processes have been used for the treatment of effluent water. They include physical (e.g. adsorption [8], membrane separation [9]), chemical (e.g. oxidation [3], coagulation [10]), biological methods [11] and their combinations. Each of these treatments has advantages and disadvantages. For example, chemical treatments may cause additional pollution due to the usage of chemical agents [12] while biological treatments can be limited due to the toxicity of degradation by-products. Electrochemical processes are today a viable alternative to classic methods employed in the treatment of effluent water which contains organic contaminants. Electrochemical degradation uses the electron as the principal reagent, and the reactions occur between the pollutant and the electrode surface or by synergism with the oxidant species which are generated *in situ*. The application of the electrochemical technology avoids the necessity of modifying the effluent after processing (no need for filtration, removal of catalysts…) [13]. So far, electrochemical methods have been successfully utilized for the purification of olive oil wastewater, domestic sewage, landfill leachate, tannery wastes, and textile wastes [14]. They are environmentally friendly and do not form new toxic wastes. Boron doped diamond electrodes are one of the best electrodes for electrochemical treatment, but they are more expensive compared to other electrodes and require pretreatment prior to use. A continuous usage may cause changes at the electrode surface which needs to be renewed periodically, making the whole treatment more expensive [15]. The goal of this work is to develop an electrochemical treatment with commercially available, cheap, non-modified electrode materials.

Some related papers on analytical methods for pesticides, together with those on pesticide retention/liberation from soils and the pollution of water resources and the food chain could be found in the literature [16--20].

Triketone herbicides, mesotrione and sulcotrione (Fig. 1), were degraded by microbial degradation [21--23] and different advanced oxidation processes [3, 7, 24, 25]. Methods for electrochemical determination of mesotrione can be found in the literature [26--28] but there were no reports on electrochemical degradation.

The aim of this study was the development and optimization of electrochemical degradation of triketone herbicides, mesotrione and sulcotrione, in an undivided two-electrode electrochemical cell with commercially available electrode materials. The overall performance of the electrochemical process is determined by the parameters that need to be optimized to obtain an effective and economic removal of pollutants. These parameters include:

electrode material, electrode potential and current density, cell design and electrolysis medium. The electrode material should be stable in electrolysis medium, cheap, and exhibit high activity toward organic oxidation and low activity toward secondary reactions (hydrogen and oxygen evolution). The current density determines the overall efficiency of the treatment and controls reactions rates on electrodes [29]. The optimization of the electrochemical degradation included five electrode systems with different electrode materials (Zr/Pt, Pd/Pt, C/Pt, Nb/Pt and Ti/Pt), current densities (27.66, 55.33, and 110.66 mA·cm^{-2}), and pH values (3, 7, and 9) in 0.05 M sodium sulfate as supporting electrolyte. Electrical energy consumption and chemical oxygen demand (COD) were determined. For the evaluation of the efficiency of the electrochemical system the remaining pesticides concentration was determined by high performance liquid chromatography equipped with a diode array detector (HPLC-DAD). When the optimization of the electrochemical treatment for mesotrione was complete, sulcotrione was degraded under the same conditions. The next step was the identification of aliphatic and aromatic degradation products of both pesticides by high performance liquid chromatography combined with mass spectrometry (UHPLC-MS). In a separate experiment, the influence of organic matter from real water on electrochemical degradation was studied.

2. Materials and methods

2.1 Chemicals

Mesotrione (Syngenta, technical grade, 97%) and sulcotrione (Makhteshim Agan, technical grade, 96.4%) were obtained from the Institute for Plant Protection, Belgrade. In all degradation experiments the pesticide concentration was 100 ppm. Sodium sulfate (Merck, p.a.) was used as supporting electrolyte. The solution pH was set with a pH meter (Microcomputer pH-Vision 6071 Jenco Electronics, Taiwan). For the pH adjustment, sulfuric acid and sodium hydroxide (Carlo Erba, Italy) were used. For HPLC and HPLC-MS, acetonitrile (Sigma Aldrich, HPLC grade; Merck, MS grade) and formic acid were used (Fluka, analytical HPLC grade; Merck, MS grade). All solutions were prepared using double distilled water, except the solutions for HPLC analysis (HPLC grade water, Sigma Aldrich) and HPLC-MS (Ultrapure water, Thermo Fisher, TKA MicroPure water purification system, 0.055 µS·cm^{-1}). Syringe filters (13 mm, PTFE membrane 0.45 µm) were purchased from Supelco (Bellefonte, PA, USA).

2.2 Analytical procedures

Chromatographic separations were performed using HPLC (Dionex Ultimate 3000, Thermo Fisher) with photodiode array detection on a Hypersil Gold aQ C18 analytical column (150 mm × 3 mm, 3 µm) at 40°C. The mobile phase consisted of water (0.1% formic acid) as component A and acetonitrile as component B. The chromatographic elution was conducted at a flow rate of 0.4 mL·min^{-1} in gradient mode: 5--50% B in 10 min, 50% B in 6 min. The injection volume was 20 µL. The detector was set at 240 nm. Data analysis was handled by software Chromeleon, 6.8 (Thermo Fisher Scientific, Bremen, Germany).

The identification of the degradation products was done by UHPLC–MS (Orbitrap^{TM}, Thermo Fisher). The analytical column used for separation was a Syncronis C18 column (100 × 2.1 mm, 1.7 µm particle size, Thermo Fisher Scientific). The mobile phase and elution program were the same as for HPLC method described above. The injection volume for all samples was 10 µL, and the flow rate was 400 µL·min^{-1}. The UHPLC system was coupled

to a linear ion trap-Orbitrap^{TM} hybrid mass spectrometer (LTQ OrbiTrap MS) equipped with a heated-electrospray ionization probe (HESI-II, Thermo Fisher Scientific, Bremen, Germany). The mass spectrometer was operated in negative mode. Parameters of the ion source were as follows: source voltage 4.5 kV, capillary voltage –40 V, tube lens voltage –80 V, capillary temperature 300 °C, sheath and auxiliary gas flow (N_2) 35 and 7 (arbitrary units). MS spectra were acquired by full range acquisition covering 50–900 *m/z*. For fragmentation study, a data dependent scan was performed by deploying the collision-induced dissociation (CID). The normalized collision energy of the CID cell was set at 40 eV.

Chemical oxygen demand (COD) was determined by standard method (ISO 6060, 1989) [30].

2.3 Electrochemical systems

All electrolytic experiments were performed in an open, undivided and thermo-stated two-electrode cylindrical glass cell (height 80 mm, inner radius 20 mm). During the electrochemical degradation the uniform nature of the medium was kept using a magnetic stirrer. Sodium sulfate served as the supporting electrolyte to induce electrochemical degradation. The total volume of the pesticide solution in the electrochemical cell with a condenser was 100 mL. Experiments were carried out with several electrodes. Five electrodes which showed the best efficiencies were chosen for further study: Zr, Pd, graphite, Ti, Nb and Fisher Pt electrode. They were checked for leaching using inductively coupled plasma optical emission spectrometry. Graphite was chosen as electrode material as it is a widely available, inexpensive material. It is used in electro-analytical chemistry due to the specific surface area. There was interest to compare its effectiveness in the electrochemical degradation treatment with metal electrode materials. Electrodes were supplied from a copper mining and smelting complex located in Bor, Serbia. The purity of the electrode material was 99.99%. Electrodes were used without previous preparation. The idea of this study was to use commercially available electrode materials. The total effective area of all electrodes was 1.81 cm^2 while the Fisher platinum electrode was 25 cm^2. Experiments were carried out under galvanostatic conditions by applying a constant current density supplied with an adjustable DC power supply PS3010 (0-32VDC, 0-10A) E – HQ^{TM}. High voltages were applied to the electrochemical cell for the simultaneous oxidation of pesticides and water, thus maintaining electrode activity. In the experiments 100 mL of pesticide aqueous solution was dissolved in 0.05 M sodium sulfate. The concentration of the pesticide was 100 mg·L^{-1}. The pesticide solution was transferred to the electrochemical cell and an appropriate current density was applied. Aliquots (1 mL) of the reaction mixture were taken every 10 min during the experiment and analyzed by HPLC. All experiments were performed in triplicate.

2.4 Real water (Danube water)

Water samples were collected on the 15th November 2013 from the Danube River near Belgrade, Serbia. Samples were taken from the middle of the river below the water surface, collected in glass bottles, filtered through 0.45 μm cellulose filters, cooled to 4°C and kept refrigerated away from light until analysis (EPA 200.7). Water parameters were: pH 8.2; temperature 10.6°C, conductivity 412 μS·cm^{-1}; O_2 12.09 mg·L^{-1}; COD 4.8 mg·L^{-1}; NO_3^- 1.40 mg·L^{-1}; NO_2^- 0.012 mg·L^{-1}; NH_4^+ 0.02 mg·L^{-1} (according to the analysis performed by the Agency for Environmental

Protection, Republic of Serbia, www.sepa.gov.rs/). The degradation of mesotrione dissolved in Danube water samples was performed in the same way as described in Section 2.3.

3. Results and Discussion

3.1 Optimization of electrochemical parameters

From an electrochemical point of view the choice of the electrode material is of fundamental importance. According to the Comninellis's active/non-active electrode mechanism the use of different electrode materials could change the oxidation pathway by creating different oxidizing species. The degradation mechanism of organic matter involves the initial discharge of water at the anodic surface (M) producing hydroxyl radicals (OH$^{\bullet}$) [31]:

$$\text{(1)}$$

Hydroxyl radicals then react with organic substances:

$$\text{(2)}$$

Five different electrode systems Zr/Pt, Pd/Pt, C/Pt, Ti/Pt and Nb/Pt were studied at a current density of 55.33 mA·cm^{-2} on various pH values (3, 7 and 9) in order to optimize mesotrione degradation (Fig. 2). The degradation efficiency was calculated from the peak area.

The pH is an important factor that affects the performance of the electrochemical process. For all three examined pH values (3, 7 and 9) the electrode system Ti/Pt was the most efficient for mesotrione degradation (Fig. 2). After the electrochemical treatment the pH value of the solution remained almost the same under acidic and neutral conditions while it decreased under alkaline conditions. The highest mesotrione removal in the system Ti/Pt was at pH 3. Complete mesotrione removal was achieved after 60 min. At pH 7 it was after 70 min and at pH 9 after 80 min of electrolysis. Optimal conditions for the mesotrione electrochemical degradation were the electrode system Ti/Pt and pH 3. This could be explained by the protonated form of mesotrione in acidic solution, pH 3 (pK_a 3.12), and a higher solution conductivity. Average degradation efficiencies for different electrochemical systems and standard deviations are shown in Supporting Information Table S1.

When the electrode material and pH value were optimized the next step in the experiments was the optimization of the current value. Current is an important parameter in electrochemical experiments. An increased current value will increase the generation of hydroxyl radicals as indirect oxidants. On the other hand, an increased current gives a higher probability for side reactions on the electrodes. Different current densities (27.66, 55.33, 110.66 mA·cm^{-2}) were applied in the electrochemical cell in order to study its influence on mesotrione degradation. The degradation efficiency increased with the increase of the current (Fig. 3). The highest mesotrione removal rate was obtained at 110.66 mA·cm^{-2} and the degradation was complete after 50 min of electrolysis. Electrolysis with 55.33 mA·cm^{-2} was slightly less effective (60 min for complete removal) while 27.66 mA·cm^{-2} was the least effective (66.66% pesticide removal for 80 min of electrolysis). A further increase in the current density to >110.66 mA·cm^{-2} did not result in a significant acceleration of the process due to side reactions on both electrodes.

Electrochemical degradations are energy intense processes and the major economic problem is the consumption of electric energy. The electric energy consumption required for the degradation of mesotrione solution (Table 1) for different current values could be calculated by Eq. (3):

1

(3)

where E is the electric energy consumption (kWh), V is the voltage (V), I the current value (A), t_E the electrolysis time and V_S the volume of treated pesticide solution (m^3).

Electric energy consumption values for the electrode system Ti/Pt are given in Table 1. The electrolysis time in Table 1 is the time needed for complete pesticide removal for a given current value. The minimum of the energy consumption for the electrochemical treatment (1 h) was obtained with 55.33 mA·cm^{-2} (1.5 kWh m^{-3}). The complete mesotrione degradation with 110.66 mA·cm^{-2} required less time (0.83 h) but the energy consumption was higher (3.32 kWh·m^{-3}) as the higher current value lead to a higher production of hydrogen and oxygen at the electrodes.

Based on the results from Table 1 the optimal current value was chosen to be 55.33 mA·cm^{-2} and was used in further experiments.

Optimal electrochemical parameters for mesotrione degradation were: electrode material Ti/Pt, pH 3, current 55.33 mA·cm^{-2}. The degradation of another member of the triketone group, sulcotrione, was performed under optimal conditions. With a pK_a value of 3.13 sulcotrione is expected to behave in a similar manner at optimal pH 3.

3.2 Analysis of COD

In order to follow the mesotrione and sulcotrione degradation under optimal conditions (system Ti/Pt, pH 3, 55.33 mA·cm^{-2}) the COD values were determined for solutions before degradation as well as after 50 and 100 min of degradation. As expected, the COD removal increased with the electrolysis time. After 50 min of treatment an almost complete degradation of both pesticides was achieved, but the COD removal efficiency was only 33 and 37% for mesotrione and sulcotrione, respectively. In order to achieve a higher COD removal it was necessary to increase the treatment time. After 100 min of electrolysis the COD removal increased (51 and 50%, respectively), indicating that after the complete pesticide removal in the electrochemical cell their products were also degraded. A good correlation between pesticide removal and COD removal of mesotrione and sulcotrione was found due to their similar structure (Table 2).

3.3 UHPLC-MS

In order to characterize the by-products of mesotrione and sulcotrione, the electrochemical degradation under optimal conditions UHPLC-MS was employed. Samples were collected from the electrolyte medium and analyzed. The degradation products were identified according to corresponding spectral characteristics: mass spectra, accurate mass and characteristic fragmentation. Structures of all identified products are shown in Fig. 4, while their molecular formulas, double bond equivalent, theoretical and experimental masses along with mass accuracy (Δm) expressed in ppm are shown in Tables 3 and 4. The mass accuracy was calculated from Eq. (4):

(4)

In Tables 3 and 4, the compounds were arranged and marked with the increase of retention time. Mesotrione degradation products were marked with M, while the sulcotrione degradation products were marked with S.

The structure of triketone pesticides can be divided into two parts: the benzoyl part and the cyclohexanedione part.

Each part can be viewed separately because they have different roles in the herbicidal activity. The benzoyl part is responsible for the herbicidal activity. Both substituents are favored to be electron-withdrawing groups in order to decrease the pK_a value and increase herbicidal activity [4]. The aim of adding substituents on the dione part is blocking the plant metabolism. This contributes to a greater herbicidal activity as the plants tend to remove herbicide molecules from the system. The substituents on the dione part determine the types of the grass that the herbicide affects [6].

In the MS study five degradation products were identified for both pesticides. There were three common degradation products for both pesticides, two aliphatic acids, 3-hydroxy-hexanedioic acid (M_1, S_1), glutaric acid (M_2, S_2), and one aromatic product, 2-hydroxy-4-methylsulfonylbenzoic acid (M_4, S_3). The remaining two compounds for the mesotrione solution were 2-nitro-4-methylsulfonylbenzoic acid (M_3) and 2-nitro-benzoic acid (M_5). Two compounds found in the sulcotrione solution were analogue to mesotrione compounds: 2-chloro-4-methylsulfonylbenzoic acid (S_4) and 2-chloro-benzoic acid (S_5).

On the basis of identified products it could be concluded that the degradation started with the bond cleavage between cyclohexanedione and the third carbonyl group. This was also the mechanism for mesotrione and sulcotrione degradation using advanced oxidation processes (AOPs) (Fenton, photocatalytic degradation, ozonization and plasma discharge) [7]. Electrochemical degradation destroyed the dione structure in these pesticides and two identified aliphatic acids were formed: 3-hydroxy-hexanedioic acid (M_1, S_1) and glutaric acid (M_2, S_2). The benzene ring remained untouched and aromatic products containing benzene rings were identified. A small drop in COD (Table 2) also confirmed these results. The product 2-hydroxy-4-methylsulfonylbenzoic acid (M_4, S_3) which was common for both pesticides indicated the replacement of $-NO_2$ and $-Cl$ groups with $-OH$ groups. It was also interesting to detect the degradation products 2-nitro-benzoic acid (M_5) and 2-chloro-benzoic acid (S_5) which indicated the cleavage of the methylsulfonyl group from the benzene ring in both pesticides. The evolution of different degradation products with time confirmed the advantage of electrochemical methods. The products generated at the beginning of the treatment were further degraded. This was confirmed with COD removal, which was about 30% after 50 min and 50% after 100 min of treatment. These degradation products were not identified in AOP degradations of triketone herbicides and it means that these products were formed only in electrochemical degradation [7].

In base peak chromatograms (Fig. 4) for both pesticides the first dominant peak at 1.21 min is sulfuric acid from the supporting electrolyte sodium sulfate. To confirm this theory, the ion chromatogram of this peak and its mass spectra of m/z 96.9595 were extracted. The mass spectra showed a characteristic isotopic pattern of sulfur which was the confirmation of the proposed sulfuric acid structure (A abundance 100%, A+2 abundance 4.4%).

3.4 Electrochemical degradation in real water (Danube water)

In order to investigate the influence of the water matrix on electrochemical degradation, the mesotrione degradation was performed in real water (Danube water). The mesotrione concentration in a real water sample was the same as in other experiments (100 ppm). The degradation efficiency of mesotrione in distilled water and river water was compared under optimal electrochemical conditions (Ti/Pt, pH 3, 55.33 mA·cm^{-2}) for the same treatment time

1

(Table 5). River water is very complex and it may contain different organic and inorganic substances which may affect the degradation of pollutants. The degradation efficiency was better with distilled water. The biggest difference in the degradation efficiency could be seen for the first 40 min (86% mesotrione removal in distilled water, 58% in Danube water). At 60 min of treatment, the degradation efficiencies were similar and after 80 min, degradation was complete in both cases. These results could be explained by the presence of organic matter and inorganic ions in Danube water which compete with the reactive species formed during the degradation of mesotrione.

4. Concluding remarks

Electrochemical treatment could be used as a promising technique for the removal of triketone herbicides, mesotrione and sulcotrione. Of all examined electrode systems Zr/Pt, Pd/Pt, C/Pt, Ti/Pt and Nb/Pt, pH values (3, 7 and 9) and current densities (27.66, 55.33, and 110.66 mA·cm^{-2}), the optimal conditions were: electrode material Ti/Pt, pH 3 and 55.33 mA·cm^{-2}. The electrode material highly influences the electrochemical degradation process. The Ti electrode in combination with Pt resulted in the highest degradation efficiency. This electrochemical system achieved a complete mesotrione removal after 60 min of electrolysis, with an energy consumption of 1.5 kWh/m^3. Due to their similar structure there was a good correlation between pesticide and COD removal of mesotrione and sulcotrione under optimal conditions. However, it was necessary to increase the treatment time in order to achieve higher COD removal. After 100 min of electrolysis, the COD removal increased which indicated that after complete pesticide removal their degradation products were further degraded. The MS study revealed five aliphatic and aromatic degradation products for both pesticides. The identified products indicated the opening of the cyclohexane dione structure, while the aromatic structure remained undestroyed. There was a cleavage of the 4-methylsulfonyl group from the aromatic structure (M_5, S_5) and in addition, $-NO_2$ and $-Cl$ groups were replaced with $-OH$ groups (M_4, S_3). It could be expected that other triketone herbicides will behave in a similar way in electrochemical systems and will give analogue degradation products. In the experiment with the Danube water sample, present organic matter lowered the degradation efficiency for the first 40 min of treatment. However, after 80 min the degradation was completed.

References

[1] D. W. Kolpin, J. E. Barbash, R. J. Gilliom, Occurrence of pesticides in shallow groundwater of the United States: initial results from the National Water-Quality Assessment Program, *Environ. Sci. Technol.* **1998**, *32*, 558–

566.

[2] M. Arias-Estevez, E. Lopez-Periago, E. Martinez-Carballo, J. Simal-Gandara, J. C. Mejuto, L. Garcia-Rio, The mobility and degradation of pesticides in soils and the pollution of groundwater resources, *Agric. Ecosyst. Environ.* **2008**, *123*, 247–260.

[3] N. Bensalah, A. Khodary, A. Abdel-Wahab, Kinetic and mechanistic investigations of mesotrione degradation in aqueous medium by Fenton process, *J. Hazard. Mater.* **2011**, *189*, 479–485.

[4] G. Mitchell, D. W. Bartlett, T. E. M. Fraser, T. R. Hawkes, D. C. Holt, J. K. Townson, R. A. Wichert, Mesotrione: a new selective herbicide for use in maize, *Pestic. Manage. Sci.* **2001**, *57*, 120–128.

[5] P. Alferness, L. Wiebe, Determination of mesotrione residues and metabolites in crops, soil, and water by liquid chromatography with fluorescence detection, *J. Agric. Food Chem.* **2002**, *50*, 3926–3934.

[6] R. A. Wichert, J. K. Townson, D. V. Bartler, G. A. Foxon, Technical review of mesotrione, a new maize herbicide, in *Proceedings of the Brighton Crop Protection Conference: Weeds*, BCPC, Farnham, Surrey, UK **1999**.

[7] M. Jović, D. Manojlović, D. Stanković, B. Dojčinović, B. Obradović, U. Gašić, G. Roglić, Degradation of triketone herbicides, mesotrione and sulcotrione, using advanced oxidation processes, *J. Hazard. Mater.* **2013**, *260*, 1092–1099.

[8] K. Y. Foo, B. H. Hameed, Detoxification of pesticide waste via activated carbon adsorption process, *J. Hazard. Mater.* **2010**, *175*, 1–11.

[9] Y. L. Pang, A. Z. Abdullah, Current Status of Textile Industry Wastewater Management and Research Progress in Malaysia: A Review, *CLEAN – Soil Air Water* **2013**, *41*, 751--764.

[10] A. Dalvand, M. Gholami, A. Joneidi, N. M. Mahmoodi, Dye Removal, Energy Consumption and Operating Cost of Electrocoagulation of Textile Wastewater as a Clean Process, *CLEAN – Soil Air Water* **2011**, *39*, 665--672.

[11] K. Brown, A. J. Ghoshdastidar, J. Hanmore, J. Frazee, A. Z. Tong, Membrane bioreactor technology: A novel approach to the treatment of compost leachate, *Waste Manage.* **2013**, *33*, 2188–2194.

[12] A. K. Golder, N. Hridaya, A. N. Samanta, S. Ray, Electrocoagulation of methylene blue and eosin yellowish using mild steel electrodes, *J. Hazard. Mater.* **2005**, *127*, 134-140.

[13] G. S. Cordeiro, R. S. Rocha, R. B. Valim, F. L. Migliorini, M. R. Baldan, M. R. V. Lanza, N. G. Ferreira, Degradation of profenofos in an electrochemical flow reactor using boron-doped diamond anodes, *Diamond Relat. Mater.* **2013**, *32*, 54–60.

[14] D. Arapoglou, A. Vlyssides, C. Israilides, A. Zorpas, P. Karlis, Detoxification of methyl-parathion pesticide in aqueous solutions by electrochemical oxidation, *J. Hazard. Mater.* **2003**, *B98*, 191–199.

[15] L. Bandzuchová, L. Svorc, J. Sochr, J. Svítková, J. Chylková, Voltammetric method for sensitive determination of herbicide picloram in environmental and biological samples using boron-doped diamond film electrode, *Electrochim. Acta* **2013**, *111*, 242–249.

[16] R. Rial Otero, C. Yague Ruiz, B. Cancho Grande, J. Simal Gándara, Solid-phase microextraction–gas chromatographic–mass spectrometric method for the determination of the fungicides cyprodinil and fludioxonil in white wines, *J. Chromatogr. A* **2002**, *942*, 41–52.

[17] C. López-Blanco, S. Gómez-Álvarez, M. Rey-Garrote, B. Cancho-Grande, J. Simal-Gándara, Determination

of carbamates and organophosphorus pesticides by SDME–GC in natural water, *Anal. Bioanal. Chem.* **2005**, *383*, 557–561.

[18] M. Pateiro-Mourea, E. Martinez-Carballo, M. Arias-Esteveza, J. Simal-Gándara, Determination of quaternary ammonium herbicides in soils: Comparison of digestion, shaking and microwave-assisted extractions, *J. Chromatogr. A* **2008**, *1196–1197*, 110–116.

[19] A. Bermudez-Couso, D. Fernandez-Calvino, M. Pateiro-Mourea, J. Carlos Novoa-Munoza, J. Simal-Gandarab, M. Arias-Estevez, Adsorption and desorption kinetics of carbofuran in acid soils, *J. Hazard. Mater.* **2011**, *190*, 159–167.

[20] R. Rial-Otero, B. Cancho-Grande, C. Perez-Lamela, J. Simal-Gándara, M. Arias-Estévez Simultaneous, Determination of the Herbicides Diquat and Paraquat in Water, *J. Chromatogr. Sci.* **2006**, *44*, 539--542.

[21] S. Durand, B. Legeret, A. S. Martin, M. Sancelme, A. M. Delort, P. Besse-Hoggan, B. Combourieu, Biotransformation of the triketone herbicide mesotrione by a Bacillus strain. Metabolite profiling using liquid chromatography/electrospray ionization quadrupole-time of flight mass spectrometry, *Rapid Commun. Mass Spectrom.* **2006**, *20*, 2603–2613.

[22] S. Durand, M. Sancelme, P. Besse-Hoggan, B. Combourieu, Biodegradation pathway of mesotrione: complementarities of NMR, LC–NMR and LC–MS for qualitative and quantitative metabolic profiling, *Chemosphere* **2010**, *81*, 372–380.

[23] I. Batisson, O. Crouzet, P. Besse-Hoggan, M. Sancelme, J. F. Mangot, C. Mallet, J. Bohatier, Isolation and characterization of mesotrione-degrading Bacillus sp. from soil, *Environ. Pollut.* **2009**, *157*, 1195–1201.

[24] M. Murati, N. Oturan, J. J. Aaron, A. Dirany, B. Tassin, Z. Zdravkovski, M. A. Oturan, Degradation and mineralization of sulcotrione and mesotrione in aqueous medium by electro-Fenton process: a kinetic study, *Environ. Sci. Pollut. Res.* **2012**, *19*, 1563–1573.

[25] J. Wiszniowski, A. Ter Halle, C. Richard, A. Hitmi, G. Ledoigt, Photodegradation product of sulcotrione and the physiological response of maize (*Zea mays*) and white mustard (*Sinapis alba*), *Chemosphere* **2009**, *74*, 1224–1230.

[26] G. Erdogdu, S. Titretir, Voltammetric determination of mesotrione at hanging mercury drop electrode, *J. Anal. Chem.* **2007**, *62*, 777–780.

[27] J. K. Wagheu, C. Forano, P. Besse-Hoggan, I. K. Tonle, E. Ngameni, C. Mousty, Electrochemical determination of mesotrione at organoclay modified glassy carbon electrodes, *Talanta* **2013**, *103*, 337–343.

[28] M. S. Jović, D. Manojlovic, D. M. Stanković, A. Milić, M. Sentić, G. Roglić, Voltametric Behavior of Mesotrione Using Silver/Amalgam Electrode, *Int. J. Environ. Res.* **2013**, *7*, 165--172.

[29] C. Comninellis, G. Chen, *Electrochemistry for the Environment*, Springer, New York, USA **2010**.

[30] ISO 6060:1989, *Water quality -- Determination of the chemical oxygen demand*, International Organization for Standardization, Geneva, Switzerland **2012**.

[31] C. Comninellis, Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for waste water treatment, *Electrochim. Acta* **1994**, *39*, 1857--1862.

Figure 1: Mesotrione and sulcotrione

Figure 2: Mesotrione removal at 55.33 mA·cm^{-2} in different electrode systems at pH 3, 7 and 9

Figure 3: Mesotrione removal in the electrode system Ti/Pt at pH 3 with various current values

Figure 4: Base peak chromatograms of pesticide solutions after 40 min of electrolysis under optimal conditions; molecular structures, masses and retention time of identified degradation products detected by LC-MS: (A) mesotrione, (B) sulcotrione

Table 1: Electrical energy consumption for degradation of 100 ppm mesotrione in 1×10^{-4} m^3 with Ti/Pt, pH 3

Current (mA)	Current density (mA·cm^{-2})	Electrolysis time (h)	Cell voltage (V)	Electrical energy consumption (kWh·m^{-3})
50	27.66	3.20	2.40	1.60
100	55.33	1.00	3.20	1.50
200	110.66	0.83	4.60	3.32

Table 2: Pesticide removal and COD removal values of mesotrione and sulcotrione solutions before and during the electrochemical degradation under optimal conditions

	Pesticide removal (%)	σ	COD (mg/L O$_2$)	σ	COD removal (%)
100 ppm mesotrione	0	0	112	2	0
50 min electrolysis	97	6	75	0	33
100 min electrolysis	100	0	55	3	51
100 ppm sulcotrione	0	0	148	3	0
50 min electrolysis	96	4	94	1	37
100 min electrolysis	100	0	74	2	50

Table 3: Mesotrione and identified degradation products under the optimal conditions

Compound	t_R	Molecular formula	DBE[1]	Theoretical m/z, [M-H]$^-$	Experimental m/z, [M-H]$^-$	ppm[2]
M1	2.19	$C_6H_{10}O_5$	2	161.04500	161.04483	1.06
M2	2.87	$C_5H_8O_4$	2	131.03443	131.03453	0.76
M3	3.90	$C_8H_7NO_6S$	6	243.99158	243.99129	1.19
M4	5.42	$C_8H_8O_5S$	5	215.00142	215.00122	0.93
M5	6.46	$C_7H_5NO_4$	6	166.01403	166.01407	0.24
Mesotrione	10.62	$C_{14}H_{13}NO_7S$	9	338.03345	338.03284	1.80

t_R, retention time

[1] double bond equivalent

[2] ppm mass accuracy

Table 4: Sulcotrione and identified degradation products under the optimal conditions

Compound	t_R	Molecular formula	DBE[1]	Theoretical m/z, [M-H]$^-$	Experimental m/z, [M-H]$^-$	ppm[2]
S1	2.36	$C_6H_{10}O_5$	2	161.04500	161.04475	1.55
S2	3.06	$C_5H_8O_4$	2	131.03443	131.03436	0.53
S3	5.60	$C_8H_8O_5S$	5	215.00142	215.00078	2.98
S4	5.65	$C_8H_7O_4ClS$	5	232.96753	232.96684	2.96
S5	8.95	$C_7H_5O_2Cl$	5	154.98998	154.99008	0.65
Sulcotrione	11.27	$C_{14}H_{13}O_5ClS$	8	327.00940	327.00882	1.77

t_R, retention time

[1] double bond equivalent

[2] ppm mass accuracy

Table 5: Comparison of mesotrione degradation efficiency in distilled water and Danube water sample under the optimal conditions

Mesotrione 100 ppm	Removal percentage (%)			
	Distilled water	σ	Danube water	σ
0 min	0	0	0	0
20 min	56	10	32	6
40 min	86	8	58	4
60 min	100	2	94	3
80 min	100	0	100	0
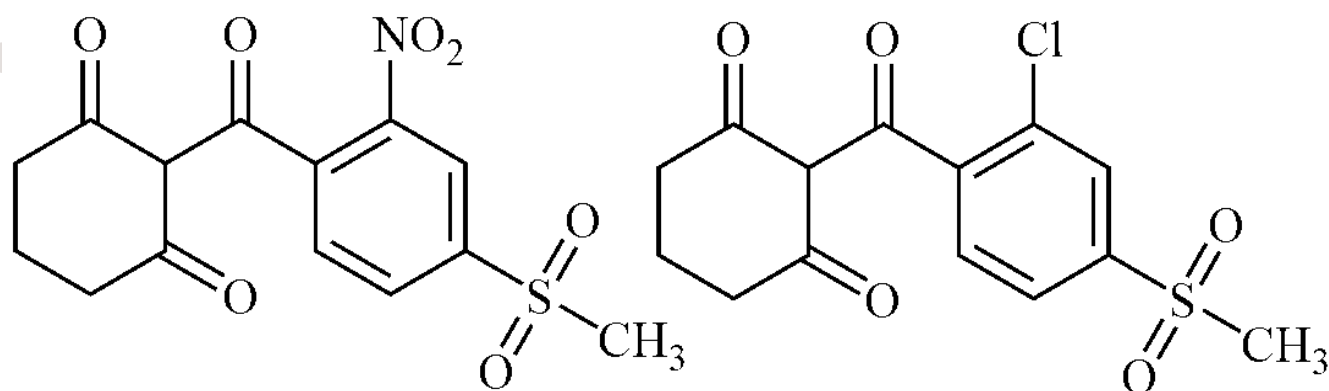
Figure 1
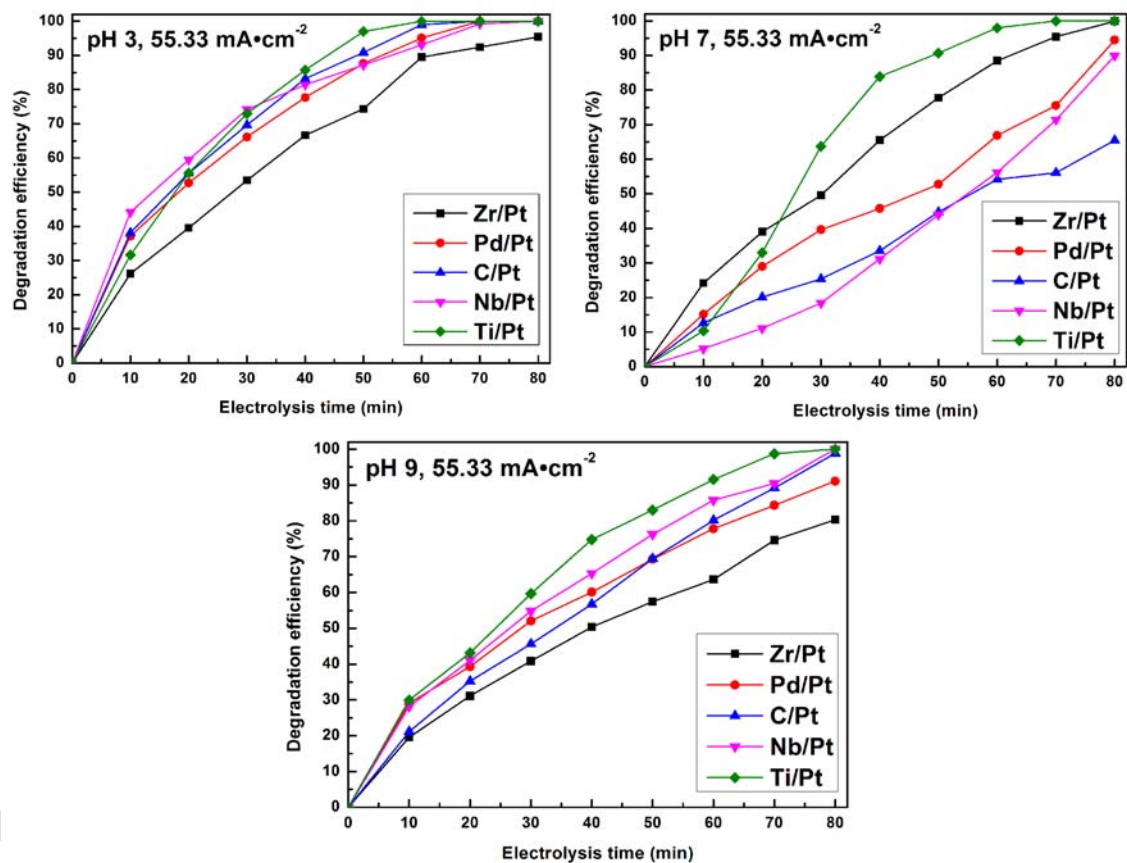
Figure 2

Figure 3

Figure 4