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Electrochemical Oxidation of Herbicides

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1. Introduction

Remediation of water polluted by toxic organic compounds such as herbicides, dyes, pesticides, pharmaceuticals, detergents, among many other highly toxic compounds, even at very low concentration, has been the subject of many investigations (Brillas et al., 2007; Weiss et al., 2007). These organic pollutants are responsible for a lot of environmental damage, especially when they accumulate in the environment, both in landfields and water (Relyea, 2005). Since water contamination affects not only aquatic species, but also humans and animals consuming it, one of the major concerns of environmentalists is the contamination of groundwater, which receives much of the slurry containing organic compounds. This serious situation has engaged environmental councils worldwide in the supervision of both water consumption and infection. In Brazil, the Environmental Sanitation Technology Company (CETESB) began to register the contaminated areas in the state of São Paulo in 2002. The number of contaminated areas has increased continuously over the last 8 years, reaching a total of 2500 contaminated areas in 2009. A considerable portion of the contamination process can be attributed to the activity of oil refineries, as well as chemical, textile and pharmaceutical industries, not to mention the large contribution from agriculture. The worldwide growth of agricultural production has led to increased demand for agrochemicals. The ever-growing need for food and fibers requires an agricultural system with high productivity per cultivated area, consequently giving rise to a situation in which the consumption of agrochemicals is escalating. In recent years, the intensive use of herbicides has significantly increased environmental concern, mainly because of the adverse effects of these pollutants on soil and aquatic microorganisms.
Generally, water contamination by herbicides can occur through:

- transport from aerial or ground spraying;
- leaching through the soil and water erosion;
- disposal of commercial packaging;
- cleaning of spray-contaminated tanks.

A problem of major concern is the resistance of these organic compounds to the available wastewater treatment techniques, which culminates in lower efficiency of pollutant removal from water streams. In the current scenery in which water resources are continuously diminishing while both population and consumption are increasing, many research teams worldwide have focused on alternatives and new technologies for the treatment of

persistent toxic organic compounds in the environment (Brillas et al., 2007; Comninellis, 1994). Some approaches for the treatment of these substances are available, and the main goal is to obtain a viable process that will allow for complete removal of contaminants or at least lead to the formation of biodegradable compounds. Several processes aim at the degradation of organic pollutants in the environment or at least at their oxidation to less toxic compounds. The choice of methodology involves factors related mainly to cost and efficiency, so each method offers advantages as well as limitations. The methods currently available for the treatment of effluent can be basically separated into two broad classes. The first involves the classic physical-chemical treatments such as sedimentation, filtration, centrifugation, flotation, and adsorption onto activated carbon. Although these methods display highly efficient rates for the removal of contaminants, they consist of phase-transfer process, i. e., further disposal is required after treatment, which is a major drawback In the second class are the oxidative methods, i. e., methods in which there is not only pollutant phase-transfer, but also its oxidation to inert compounds. Nowadays, the majority of industries generating large amounts of effluent opt for remediation using biological treatment, since it is relatively inexpensive. However, its degradation kinetics is very slow; limiting its action to compounds with low toxicity and effluents with low concentration of contaminants (Freire et al., 2000). Because conventional chemical and biological methods are no longer efficient due to the resistance gained by many compounds to wastewater treatment, some approaches for the treatment of toxic organic materials that will remove or convert these pollutants to biodegradable compounds have been developed. Electrochemical (Comninellis, 1994), electro-Fenton (Sires et al., 2007), ozonation (Canizares et al., 2007), Fenton, and photo-Fenton (Brillas et al., 2007) processes have been frequently proposed for the treatment of organic pollutants. Regardless of the selected methodology, the generation of high oxidative species such as hydroxyl radical (E^o = 2.80 V vs. SCE) must take place, in order to ensure elimination of the toxic organic compound. Table 1 shows the generation of hydroxyl radical in the most common advanced oxidation technologies investigated to date (Martínez-Huillé & Brillas, 2009).

Tecnique	•OH production
Electrochemical	$MO_x + H_2O \rightarrow MO_x(\bullet OH) + H^+ + e^-$
Fenton reaction, electro-fenton, and photoelectro-fenton	$H_2O_2 + Fe(II) \rightarrow \bullet OH + Fe(III)$
Photocatalysis	$TiO_2 + h\upsilon \rightarrow TiO_2(h + e)$ $TiO_2(h) + OH^- \rightarrow \bullet OH$
UV-peroxide	$H_2O_2 + h\upsilon \rightarrow 2\bullet OH$
Sonolysis	$H_2O +))) \rightarrow \bullet OH + \bullet H$
Radiolysis	$H_2O + \gamma \rightarrow e_{aq}, \bullet OH, \bullet H$

Table 1. Mechanism of generation of hydroxyl radical in the most common advanced oxidation technologies
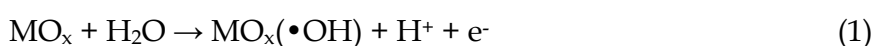
2. Electrochemical treatment of organic pollutants

2.1 Electrochemical process for organic mineralization

The concern about the increasing environmental contamination, which consequently affects water quality, forces the development of many alternatives for the treatment of organic pollutants. In this context, electrochemical processes have always been claimed to be an attractive approach due to their versatility, easier operation, effectiveness, and lower cost (Gandini et al., 2000). The efficiency of the electrochemical process depends on many factors; however, the main focus is placed on electrode activity and lifetime and, consequently, on the electrode material. Besides catalytic activity, the choice of electrode material will also consider characteristics such as mechanical strength, physical and chemical stability under drastic operational conditions (high current density and high potential), and cost. Metallic oxide electrodes containing RuO_2 have been widely employed in environmental electrochemistry because of their mechanical resistance, inexpensiveness, and successful scale-up in the electrochemical industry. Apart from leading to chloro-alkali production, dimensionally stable anode (DSA®) electrodes are also a good alternative to the oxidation of various organic compounds (Trasatti, 2000). Another material good candidate material for the electrochemical oxidation of organic compounds is the boron-doped diamond (BDD), because of its generally large potential window and feasibility of the produced hydroxyl radicals (Panizza et al., 2008b). Although the BDD electrode is an extremely efficient material for organic mineralization, its use in large-scale operational conditions is still limited due to the high cost of BDD production.
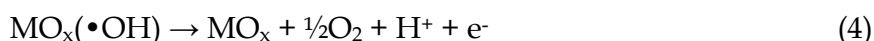
2.2 DSA® electrodes

The metallic oxide electrodes introduced by Beer in 1966 consist of an inert metal support coated with noble metal oxides such as RuO_2 and IrO_2. In addition to the noble metal oxides, oxide electrodes also contain the so-called modulators, which are oxides such as SnO_2, TiO_2, Ta_2O_5, and PbO_2, whose function is to enhance the electrochemical characteristics related to electrode lifetime, mechanical stability, and catalytic activity, not to mention cost reduction. Electrode preparation is usually performed by thermal decomposition of the precursor's salts, which are then deposited onto an inert support material (titanium is the most commonly employed material for this purpose, due to its relatively low cost). There are several studies focusing on the use of oxide electrodes in the electrochemical degradation of toxic organic compounds. These materials have been shown to display excellent catalytic activity, resistance to corrosion, dimensional stability, high electrochemically active area, low maintenance cost, and low power consumption (Trasatti, 2000). Moreover, the use of DSA® with photoactive surface enables accomplishment of heterogeneous photocatalysis (Pelegrini et al., 1999). The mechanism of organic compound oxidation by electrochemical processes, as described by Comninellis (1994), can occur directly at anodes through generation of physically adsorbed hydroxyl radicals (Eq. 1). These processes may ultimately result in fully oxidized reaction products such as CO_2 (Kapałka et al., 2008). The •OH radical undergoes a fast reaction to form higher oxide (Eq. 3) on DSA-type anodes. Although this mechanism has been proposed long ago, only recently has experimental evidence from Electrochemical Differential Mass Spectroscopy been able to confirm participation of the higher oxide species (Fierro et al., 2007)

$$MO_x + H_2O \rightarrow MO_x(\bullet OH) + H^+ + e^- \qquad (1)$$

$$R + MO_x(\bullet OH) \rightarrow CO_2 + \text{inorganic ions} + MO_x + H^+ + e^- \tag{2}$$

$$MO_x(\bullet OH) \rightarrow MO_{x+1} + H^+ e^- \tag{3}$$

It is well known that the higher oxide species (MO_{X+1}) are much milder oxidants than the weakly bound radical formed in reaction 1. However, many modifications to material design, such as preparation methodology and changes in the modulator oxide have been introduced, in order to enhance the catalytic activity of the electrode material. The oxygen evolution reaction (OER) is an undesirable side reaction responsible for the lower current efficiency of organic compound oxidation during the electrochemical process. The mechanism proposed for this reaction involves the discharge of water molecules at the metal oxide surface (Eq. 1). Depending on the characteristic of the anode material, oxygen evolution proceeds via two different pathways: oxidation of weakly adsorbed hydroxyl radicals (Eq. 4) or formation of the higher oxide followed by oxygen evolution (Eq. 5 and 6).

$$MO_x(\bullet OH) \rightarrow MO_x + \tfrac{1}{2}O_2 + H^+ + e^- \tag{4}$$

$$MO_x(\bullet OH) \rightarrow MO_x{}^{+1} + H^+ + e^- \tag{5}$$

$$MO_{x+1} \rightarrow \tfrac{1}{2}O_2 + MO_x \tag{6}$$

In order to increase the oxidation rate of DSA-kind materials, electrochemical remediation frequently calls for more powerful oxidizing conditions as well as electrogeneration of large amounts of hydroxyl radical or other oxidizing species such as Cl_2, ClO^-, or O_3. These requirements can be met by changing the electrode material (SnO_2, PbO_2, BDD) or the supporting electrolyte (SE).

2.3 Electrolysis in chloride media and formation of organochlorinated compounds

Knowing that electrochemical remediation seeks more powerful oxidizing conditions, the electrolysis in chloride medium is a good alternative when more efficienty organic compound oxidation is desirable. NaCl is one of the most attractive media in the field of indirect oxidation owing to its straightforward impact on electrochemical technology. Oxide electrodes such as DSA® anodes are very active for Cl_2 evolution, so many studies have reported on quite advantageous features concerning the use of this medium in the oxidation of organic pollutants. Considering the standpoint of thermodynamics, electrolysis in chloride medium should favor OER in detriment of chlorine evolution reaction (ClER), since the reversible thermodynamic potential for oxygen evolution (1.23 V) is below the potential for ClER (1.36 V). However, the kinectics of ClER is favoured for DSA-type materials and, in practice, it occurs at lower overpotential. As described in the literature, the mechanism of ClER on metal oxide electrodes proceeds as follows (Trasatti, 1987):

$$2Cl^- \leftrightarrows Cl_{2(el)} + 2e^- \tag{7}$$

$$Cl_{2(el)} \leftrightarrows Cl_{2(sol)} \tag{8}$$

Adsorbed chlorine, $Cl_{2(el)}$, will form free species in solution, $Cl_{2(sol)}$, which will further react to form reactive species such as hypochlorous acid (HClO) and hypochlorite (ClO^-), which are responsible for faster organic compound degradation:

$$Cl_{2(sol)} + H_2O \rightarrow HClO + Cl^- + H^+ \tag{9}$$

$$HClO \leftrightarrows H^+ + ClO^- \tag{10}$$
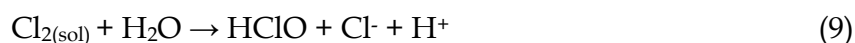
Nevertheless, despite its several advantages, besides promoting faster oxidation of the organic compound (Eq. 11), electrolysis in chloride medium also enables formation of organochlorine compounds (RCl), as seen in Eq. 12:

$$ClO^-_{(sol)} + R \rightarrow CO_2 + \text{inorganic ions} + H^+ + e^- \tag{11}$$

$$ClO^-_{(sol)} + RCl \rightarrow R \tag{12}$$

The main concern of different groups is that the presence of a C─Cl bond affects the chemical properties of the organic compound and therefore its toxicological behavior. In general, the introduction of chlorine in the organic molecule increases the chemical and biological reactivity of the chlorinated compound, thereby significantly enhancing the toxicity of these substances. Due to their high reactivity, these compounds usually have large lipophilicity, favoring interactions with enzymes and promoting biotransformations, for example. Furthermore, organochlorine compounds display several genotoxic effects depending on the chemical structure of the generated compound. Some literature studies have also shown that these compounds are responsible for different mutagenic and carcinogenic effects (Henschler, 1994). Nevertheless, the formation of organochloride species in solution during electrolysis in chloride medium has not received much attention; in fact, only a few studies have investigated the influence of experimental parameters on the formation of RCl compounds (Comninellis & Nerini, 1995). In this context, the possible formation of RCl during electrolysis makes the determination and evaluation of these compounds extremely important, mainly when electrolysis in chlorine medium is proposed as an alternative route for wastewater treatment. On the basis of the large number of literature papers focusing on the electrochemical degradation of herbicides, we are going to present the results on the degradation profile of different herbicides. Based on the results obtained by our research group, we will also focus on data regarding the electrochemical degradation of the glyphosate herbicide (GH) (Aquino Neto & De Andrade, 2009a; Aquino Neto & De Andrade, 2009b). Regarding the electrochemical oxidation behavior of GH, we are willing to discuss the performance of the RuO_2-based anode. Moreover, the effect of different parameters such as SE, pH, and current density on electrode activity will be presented. It is known that metallic oxide electrodes display good performance for the anodic mineralization of organic pollutants in chloride medium; however, the formation of organochloride compounds during electrolysis in the latter medium has not received much attention, since just a few reports have investigated the influence of this parameter. For this reason, a full discussion regarding the formation of these toxic species will be presented here. Besides the standard sample degradation behavior, the oxidation of commercial GH formulation will also be discussed. Finally, the very recent literature focusing on the degradation of different herbicides will be presented.

3. Glyphosate contamination

In recent years, the intensive use of herbicides has increased environmental concern, partly because of the adverse effects of these chemicals on soil and aquatic microorganisms (Farah et al., 2004). One of the most commonly employed agrochemicals is glyphosate (Fig. 1). N-(phosphonomethyl) glycine is a highly effective broad-spectrum, post-emergence, non-

selective herbicide widely used in agriculture worldwide (De Amarante et al., 2002). GH is highly soluble in water (12 g L^{-1} at 25 °C), and it is currently utilized in more than 30 types of crops, to control a wide variety of annual weeds, mainly in the case of sugarcane and soybean plantations.
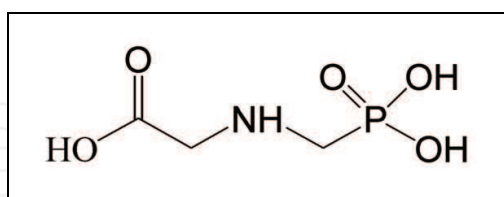

Fig. 1. Chemical structure of GH.

GH is commercialized as an isopropylamine salt. Formulations found in the market generally contain surfactants, to prevent formation of drops and to reach larger sprayed areas. Some of these components are serious irritants and toxic to fish; moreover, the commercial formulations display more toxicity and are more persistent than the active ingredient. The most common commercial formulations contain surfactants based on ethylamine alone, which is significantly more dangerous than GH itself and very toxic for invertebrates and fish (De Amarante et al., 2002). The half-life of the commercial formulations is relatively long, about 7-70 days (Giesy et al., 2000). According to resolution 375 of the National Brazilian Environmental Council (CONAMA), the maximum value allowed for GH in sweet water is 0.280 mg L^{-1}. The US Environmental Protection Agency also classifies GH as "extremely persistent". The main reason for the widespread use of this chemical worldwide is its relatively low toxicity to humans and animals. However, despite low toxicity, its quick biodegradation to the main metabolite aminomethylphosphonic acid (AMPA) is a matter of concern because this compound is considered more toxic and persistent than the original herbicide (Williams et al., 2000). Increased use of GH is expected due to the development of transgenic plants tolerant to this compound (Owen & Zelaya, 2005). Even though commercial GH formulations are considered to have low toxicity, there are evidences of noxious effects on the environment after its prolonged use, mainly because of the resistance gained by the annual weeds. In this context, the exposure of non-target aquatic organisms to this herbicide is the concern of many ecotoxicologists. Several in vivo and in vitro studies on animals have revealed the mutagenic and carcinogenic effect of GH (Lin & Garry, 2000) as well as its impact on the environment and aquatic life (Tsui & Chu, 2003). Some studies conducted with GH commercial formulations have demonstrated the potential toxicity of these formulations to the environment. Electron microscopy studies on fish of the Cyprinus carpio species have shown that this herbicide causes disruption of the inner mitochondrial membrane (Tsui & Chu, 2003). Another investigation has pointed out that some formulations are largely responsible for the toxicity in the energy levels of mitochondrial oxidative phosphorylation in rat livers (Peixoto, 2005). Due to the great concern about GH contamination, many studies have focused on degradation of this compound. Shifu and Yunzhang (2007) have reported the photocatalytic degradation of GH using TiO$_2$ as photocatalyst and a mercury lamp of 375 W, with the concentration of herbicide being maintained at 42 mg L^{-1}. The results showed that 92% GH were mineralized after 3.5 h of illumination. Chen et al. (2007) have investigated the photodegradation of GH in a system using ferrioxalate as Fe^{2+} source, a metal halide lamp of 250 W, and a constant concentration of GH of 5 mg L^{-1}. The efficiency of GH mineralization reached values around

60%. Barret & Mcbride (2005) have evaluated the oxidative degradation of GH on manganese oxide. There was no significant herbicide degradation (10 mg L^{-1}), and much of the herbicide simply adsorbed onto the manganese oxide. Huston & Pignatello (1999) have investigated the degradation of several active ingredients of pesticides as well as several commercial herbicides formulations via photo-Fenton reaction. The experiments were carried out in a solution containing 10^{-5} mol L^{-1} Fe (III) and 10^{-2} mol L^{-1} H$_2$O$_2$, and the initial GH concentration was 33 mg L^{-1}. A reactor with 16 black light lamps of 14 W was employed, and the results showed that 35% GH were mineralized after 2h of irradiation. Castro et al. (2007) have examined the biodegradation of GH (500 mg L^{-1}) using the Fusari fungus. Efficiency of removal of the active principle reached values around 40%. Speth (1993) investigated different processes for GH removal from drinking water, such as adsorption onto activated carbon at various pH values, as well as the efficiency of different oxidants for GH degradation. The initial amount of treated herbicide was 1.75 mg L^{-1}. Adsorption of the herbicide on activated carbon proved to be quite high. Results from treatment by coagulation, sedimentation, and sand filtration revealed a removal efficiency of 7% only. Degradation with chlorine led to higher efficiency, with almost complete removal of the contaminant. Munner and Boxall (2008) have investigated the photocatalytic degradation of GH in TiO$_2$ suspension with 12 black lamps of 15 W, using initial concentration of GH equal to 170 mg L^{-1}. Good degradation rates were achieved, and 90% GH removal was observed. Bazot and Lebeau (2008) have evaluated the efficiency of GH oxidation using the bacterium Pseudomonas 4ASW. The initial concentration of GH was 80 mg L^{-1}, and 80% of active ingredient removal was obtained after 80 h of treatment. In this chapter, results from the electrochemical degradation of GH using oxide electrodes obtained by our research group will be presented.

4. Experimental procedures

4.1 Preparation of DSA® electrodes

The choice of a methodology for the preparation of DSA® electrodes is very important, since the final properties and characteristics of the electrode are highly dependent on the method of preparation. The preparation techniques aim at films with adequate mechanical stability as well as oxide mixtures with high catalytic activity. The methodology usually employed in the preparation of oxide electrodes with greater stability is the thermal decomposition of suitable precursors. This procedure consists of successive steps in which thin layers of the precursor solutions are applied onto the inert support, followed by calcination at elevated temperatures (T > 400 °C) and appropriate O$_2$ flow (Trasatti & Lodi, 1981). Several methods for the production of oxide electrodes are found in the literature: the thermal decomposition of chlorides (traditional methodology; Beer, 1966), spray-pyrolysis method (De Battisti et al., 1997), the sol-gel method (Diaz-Flores et al., 2003), and the thermal decomposition of polymeric precursors (also known as Pechini method, Pechini, 1967). The traditional method is still the most frequently employed. It consists of the thermal decomposition of inorganic precursors, usually employed in the form of chlorides. The traditional method has been adopted since the 60 s, and has been used in the preparation of several films in various areas. In this methodology, the deposition of thin layers of the precursor salt solutions (usually chlorides of the desired metals in a solution of HCl and water 1:1) occurs via brushing or dipping into the precursor solution (dip-coating method). After this step, the supports are calcined at high temperatures (usually above 400 °C), to obtain the respective metal oxides. The great advantage of this method is the easy preparation, prompt

availability, and relatively lower cost of the employed salts. The main feature of the films obtained by this kind of preparation is the "mud-cracked" morphology (Trasatti & Lodi, 1981). Recent work employing the traditional method using isopropanol as solvent instead of an acid solution has also furnished very promising results, since the films displayed excellent mechanical stability and catalytic activity (Coteiro & De Andrade, 2007). Another more recent method of preparation is the thermal decomposition of polymeric precursors. In this method, the formed polymeric resin "captures" the metal atoms, which provides better control of both stoichiometry and particle size (Pechini, 1967). Because the polymer is formed before the calcination process, metallic atoms such as tin are trapped in this matrix, thereby avoiding evaporation and consequent losses, and enabling production of films with better handled composition. Film deposition on the inert support material occurs in the same way as in the case of the traditional methodology, with the difference that a polyester is initially formed. Preparation of oxide electrodes by this methodology has been shown to provide uniform films with more homogeneous surfaces. Moreover, the decomposition of polymeric precursors culminates in largely reduced particle size, thus furnishing materials with high surface area. These features make this a promising method for the preparation of oxide films, with potential application in different scientific areas (Santos et al., 2005).

4.2 Electrolytic system and electrodes

The results from GH degradation presented in this chapter were obtained using the experimental conditions described below. The electrochemical measurements were conducted in an open system, using a three-compartment electrolytic cell consisting of a main body (50 mL solution) and two smaller compartments containing the counterelectrodes, which were isolated from the main body by coarse glass frits. The electrolyses experiments were accomplished in the galvanostatic mode, under magnetic stirring. Electrochemical experiments (cyclic voltammetry and galvanostatic electrolyses) were performed using a potentiostat/galvanostat Autolab, mode SPGSTAT30. All experiments were carried out at 25 ± 1 °C. The working anodes were 2 cm² large and were prepared by thermal decomposition. The precursor mixtures were applied on both sides of the pre-treated Ti support by brushing, as described in previous works (Coteiro & De Andrade, 2007; Aquino Neto & De Andrade, 2009a). For the electrochemical oxidation of GH, the composition $Ti/Ru_{0.30}Ti_{0.70}O_2$ was employed. Details about the preparation, methodologies, and the physical and electrochemical characterization of the anode are given elsewhere (Aquino Neto & De Andrade, 2009a). Two spiraled platinized platinum wires (15 cm), placed parallel to each other, were used as counterelectrodes. All potentials are referred to the saturated calomel electrode (SCE). H_2SO_4 and NaOH were employed to adjust the pH values of the solutions. In all experiments, the ionic strength was kept constant ($\mu = 1.5$) by adjusting the Na_2SO_4 and NaCl concentrations. Solutions were prepared with high-purity water from a Millipore Milli-Q system, and pH measurements were carried out with a pH electrode coupled to a Qualxtron model 8010 pH meter.

4.3 Quantification of glyphosate

The chemical structure of GH does not display a chromophore group, so spectroscopic determinations have to be performed only after its derivatization reaction. Hereafter, two different derivatization reactions for GH determination were used. The first derivatization consisted of the reaction of ninhydrin in the presence of the Na_2MoO_4 catalyst at 100 °C

(Bhaskara & Nagaraja, 2006), which produces the Ruhemann´s purple product with a maximum absorption at 570 nm (Fig. 2A). GH degradation was also followed by nitrosation reaction in acidic media (Food and agriculture organization of the United Nations, 2001), which produces a UV spectrophotometrically active compound at 243 nm (Fig. 2B).
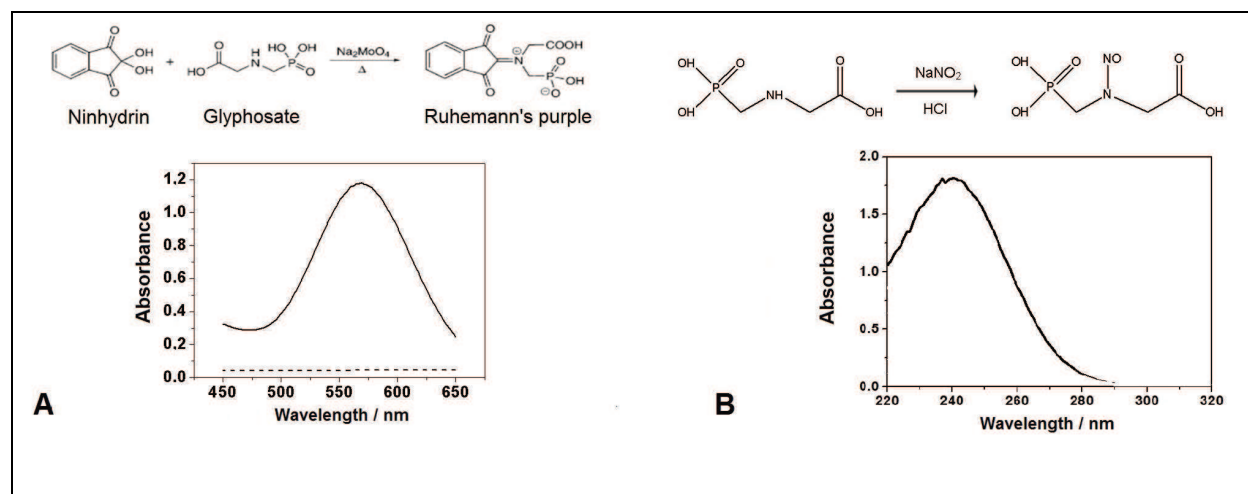

Fig. 2. Derivatization reaction of GH with ninhydrin produces the Ruhemann´s purple product with a maximum absorption at 570 nm (A). Nitrosation reaction of GH in acidic media produces a UV spectrophotometrically active compound at 243 nm (B)

As depicted in Fig. 3, both spectrophotometric methods (ninhydrin and nitrosation) give exactly the same degradation rate, indicating the good accuracy of the proposed methods. Therefore, from now on all the results presented here will be related to the determination using the nitrosation reaction, which is simple and employs readily available materials.
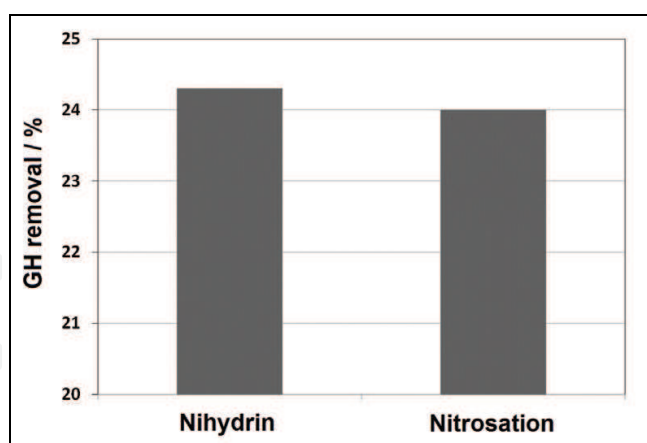

Fig. 3. GH removal as a function of both derivatizations reactions employed after 4 electrolysis at 50 mA cm^{-2}, $\mu = 1.5$ (Na$_2$SO$_4$ + NaCl, pH = 3)

As shown in Eq. 13, GH total oxidation produces PO$_4^{-3}$ ions as one of the final degradation products. For this reason, the PO$_4^{-3}$ release rate is a good indication of complete GH degradation. Its determination can be easily performed colorimetrically by the molybdenum blue method, according to the standard method (American Public Health Association, 1998).

$$C_3H_8O_5NP + 8H_2O \rightarrow 3CO_2 + PO_4^{-3} + NO^{-3} + 24H^+ + 20e^- \qquad (13)$$
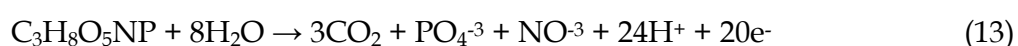
For analysis of GH total combustion, both chemical oxygen demand (COD) and total organic carbon (TOC) were also performed after electrolysis.

4.4 Organochlorine analysis

The amount of adsorbable organic halide (AOX) encountered in water samples is generally very low; for this reason, the analytical procedures involve a pre-analytical step for sample concentration. To this end, the constituents are loaded onto activated charcoal before the assay or, in the case of organic material extraction from mud, organic solvents are employed. To convert the AOX compounds into an analyzable form, the dissolved organic material is initially concentrated via adsorption onto activated charcoal. Then, nitrate ions are added to the mixture, to eliminate the inorganic chloride also adsorbed onto the activated charcoal by competition. Next, the "loaded" activated charcoal containing the sample is burned in a furnace at ~ 950 ° C; in this step, hydrogen halides, carbon dioxide, and water are formed. After drying of the generated gases, the halides are determined by microcoulometry, which involves a process that occurs in acetic acid medium according to the following equation:

$$Ag^+ + X^- \rightarrow AgX \tag{14}$$

The silver ions used for the precipitation of the halides are electrolytically generated at the silver anode. After quantitative conversion of the halide, concentration of the silver ions in the electrolyte increases indicating the the end point of the titration, as determined by a pair of polarized indicators electrodes. The amount of halide present in the sample is then measured using Faraday's law. AOX analysis during the electrochemical oxidation of GH was performed by means of the multi X 2000 analyzer (Analytik Jena, Germany) and the shaking method. This equipment allows for the direct determination of organochlorinated compounds adsorbed previously onto activated carbon from an aqueous solution containing AOX over 10 μg L^{-1}. However, the sample should meet the following criteria prior to the analysis:

*   TOC should be less than 10 mg L^{-1};
*   The amount of inorganic chloride should be less than 1 g L^{-1};
*   Oxidant species wastes (ClO$_3^-$, Cl$_2$ etc.) must be removed by addition of the proper amount of sodium sulfite.

All experiments were performed at 25 ± 1 ° C, and the results are presented as the average of triplicate measurements.

5. Results of herbicides degradation

5.1 Electrochemical oxidation of the GH herbicide

We began our investigation by carrying out the electrochemical oxidation of an standard GH sample. Once the most efficienty electrolysis conditions had been established, the electrooxidation of a commercial formulation (Roundup®) was also investigated. Cyclic voltammograms in both the absence and presence of GH were conducted. Electrochemical characterization showed that GH is not electroactive in the potential window 0.2 -1.2 V vs. SCE, so its oxidation hindered by OER. This is a very common characteristic of DSA-type anodes once they are very active for OER and this reaction occurs simultaneously with the oxidation of organic compounds in aqueous medium. The competition between the

oxidation of the organic compound and OER is responsible for a significant reduction in the efficiency of the electrochemical process (Aquino Neto & De Andrade, 2009a).

Establishment of the best degradation conditions

Aiming at finding the best conditions for the electrolysis, the preliminary stage of the investigation consisted of selecting the most suitable experimental setup, so that the highest rate possible of electrochemical degradation would occur. In this step, the evaluation of pH, current density, and supporting electrolyte should be performed. There are many ways to measure the real efficiency of a treatment technology. In general, both energy consumption and organic combustion are evaluated. An easy way for judging the performance of DSA® anodes in electrochemical degradation studies is to determinate the current that is effectively used for oxidation of the organic compound. The instantaneous current efficiency (ICE) is obtained considering that during electrochemical incineration two parallel reactions (organic compound oxidation and OER) takes place. So, ICE is defined as the current fraction used for the organic oxidation (Comninellis & Pulgarin, 1991; Pacheco et al., 2007) and was calculated considering the values of chemical oxygen demand (COD) of the wastewater before and after the electrolysis, using the relation

$$ECI = \frac{FV}{8I} \frac{\left[(DQO)_t - (DQO)_{t+\Delta t}\right]}{\Delta t}, \qquad (15)$$

where F is the Faraday constant (C mol^{-1}), V is the volume of the electrolyte (m^3), I is the applied current (A), and (COD)$_t$ and (COD)$_{t+\Delta t}$ are the chemical oxygen demand (g O$_2$ m^{-3}) at times t and t + Δt (s), respectively.

After 4h of electrolysis at a constant current density of 50 mA cm^{-2} in Na$_2$SO$_4$ medium, 24% of the starting material (1000 mg L^{-1}) was oxidized, and the mineralization rate reached c.a. 16%. When one compares this value with the rate reported for the degradation of phenol (Comninellis & Pulgarin, 1991), which is a compound generally referred as a model for organic degradation, we can confirm the recalcitrant behavior of herbicides in aqueous solution. Due to the low degradation rate of GH, the ICE in these conditions was very low, less than 5 %, indicating that OER is an important side reaction in the electrochemical process. The difference between the data obtained from spectrophotometric methods (24%) and TOC removal (16 %) has been explained by us previously (Aquino Neto & De Andrade, 2009a) and is related to the formation of recalcitrant intermediate products such as AMPA (metabolite aminomethylphosphonic acid) and sarcosine (n-methylglycine).

To understande the degrability of GH as a function of time, long-term electrolyses (12 h in Na$_2$SO$_4$ medium, pH 3, at 50 mA cm^{-2}) were performed. The results of GH degradation as a function o time showed that after 12 h of electrolysis only 43 % GH had been oxidized. In order to improve the degradation rate, pH and concentration effects must be investigated. The best results for the electrochemical oxidation of GH were found in acidic medium (Aquino Neto & De Andrade, 2009a). The low oxidation rates obtained in Na$_2$SO$_4$ medium can be explained by the general mechanism of organic compound oxidation (Comninellis, 1994). Briefly, the oxidation power of the anode is directly related to the overpotential for oxygen evolution. For DSA-like anodes, the •OH radicals strongly bind to the surface, eventually leading to the indirect oxidation of organics via formation/decomposition of an oxide of higher valence (De Oliveira et al., 2008). In order to increase the oxidation rate of DSA-kind materials, different approaches have been proposed in the literature, such as the

use of PbO_2 (Cestarolli & De Andrade, 2003; Aquino et al., 2010; Panizza et al., 2008a) and BDD (Panizza et al., 2008b), and changes in the supporting electrolyte (Aquino Neto & De Andrade, 2009b).

Electrolysis in chloride medium

The electrolyses in chloride medium were performed as a function of chloride concentration. The assays were carried by varying the amount of chloride from 200 to 3500 mg L^{-1}. An increase in the initial concentration of chloride ion leads to a significant enhancement in the rate of the oxidation reaction. In the case of GH oxidation, there is an increase of 42% PO_4^{-3} release and 53% GH removal even at a very low NaCl concentration (220 mg L^{-1}). When a high concentration of chloride ions is employed (1000 mg L^{-1}), over 80% PO_4^{-3} release is obtained (Aquino Neto & De Andrade, 2009b). It is noteworthy that as the medium becomes more active toward organic compound oxidation, as in the case of chloride medium, there is no significant influence of the anode composition or current density on the oxidation rate. Therefore, one can improve the electrolysis by changing the supporting electrolyte, which culminates in less drastic conditions. This procedure offers two main advantages, namely a decrease in total energy consumption and maximized oxidation rate and larger electrode lifetime, which both contribute to diminishing the cost of the electrolytic system. Figure 4 shows the electrochemical oxidation profile of standard GH and of a commercial formulation of this herbicide as a function of time.
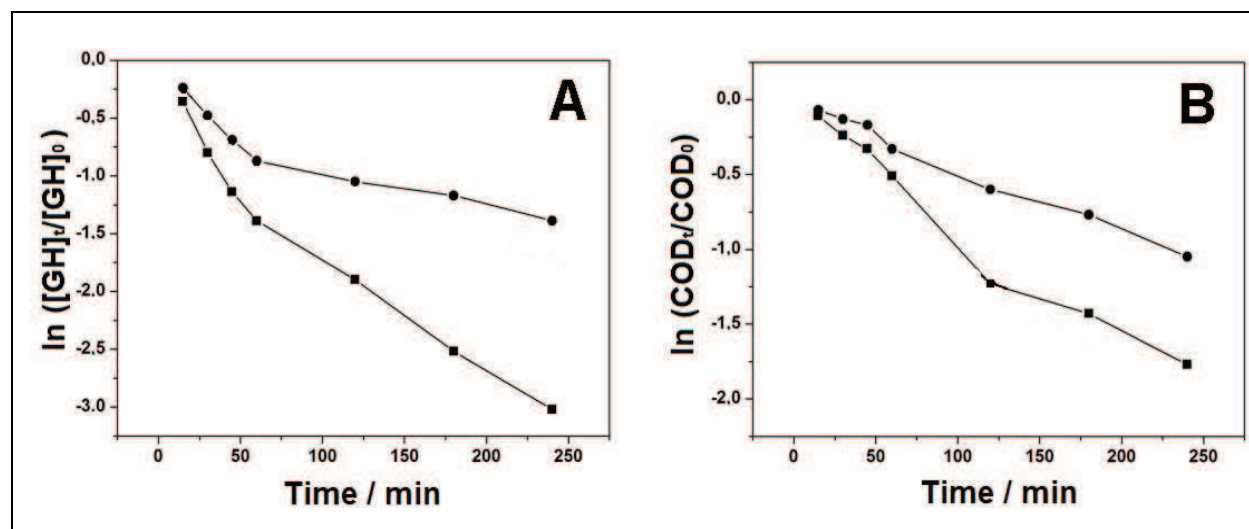

Fig. 4. Linearized removal (A) and COD removal (B) as a function of electrolysis time. Electrode composition Ti/Ru$_{0.30}$Ti$_{0.70}$O$_2$, i = 30 mA cm^{-2}, [Cl$^-$] = 2662 mg L^{-1}, μ = 1.5 (Na$_2$SO$_4$ + NaCl, pH 3). ■ = standard GH sample; ● = commercial GH formulation

The kinetic data reveal a complex oxidation profile. This behavior can be explained considering the competition between the oxidation of the starting material and of the byproducts formed within the first minutes of electrolysis. However, a linear decay is obtained within the first 60 min of electrolysis, as depicted in Fig. 4A and Fig. 4B. A pseudo first-order kinetic behavior is achieved, so assuming that this is the case in the first 60 min (Pelegrino et al., 2002), the oxidation rate can be written as:

$$dC_{(t)}/dt = -kC_{(t)} \tag{16}$$

$$C_{(t)} = C_{(0)} \, e^{-kt} , \qquad (17)$$

where $C_{(0)}$ corresponds to the initial GH concentration and k is the constant of velocity of GH oxidation. The k value is obtained by the following equation:

$$k_{HG} = k \, V/A, \qquad (18)$$

where V is the solution volume (m^3) and A is the electrode area (m^2). In the same way, the kinetic constant for COD removal was obtained. Table 2 summarizes the kinetic constants for standard GH and its commercial formulation:

Herbicide	k_{GH} / 10^{-3} m s^{-1}	k_{COD} / 10^{-3} m s^{-1}
GH commercial formulation	3.48 ± 0.10	2.40 ± 0.12
GH standard sample	5.75 ± 0.11	1.37 ± 0.15

Table 2. Kinetic constants of standard GH and its commercial formulation for the first 60 min of electrolysis. Composition Ti/Ir$_{0,30}$Sn$_{0.70}$O$_2$, i = 30 mA cm^{-2}, [Cl$^-$] = 2662 mg L^{-1}, μ = 1.5 (Na$_2$SO$_4$ + NaCl, pH 3)

Data from Table 2 demonstrate the higher oxidation rate of the active ingredient in relation to its commercial formulation (the kinetic constant is 1.6 times larger). Considering the COD decay, the commercial formulation displays the largest kinetic constant, because of the higher organic load of commercial formulations, which, apart from the active ingredient, present "inert compounds" such as carriers, wetting agents, antifreezes, and other compounds employed to facilitate handling and application. Most of the components of commercial formulations are surfactants that increase the spreading and the penetration power. Taking into account the kinetic data it can be inferred that these compounds are much less recalcitrant than the active principle. Also, these data provide some interesting information concerning GH oxidation compared to the electrochemical oxidation of other organic compounds. The k_{COD} values of GH presented here are far superior to the ones found for the electrochemical oxidation of phenols (Coteiro & De Andrade, 2007) particularly, 4-chlorophenol (Alves et al., 2004). It is clear that some experimental conditions must also be considered, in order to evaluate the real efficiency of the electrode material. However, the data presented here demonstrate that the electrochemical process is really satisfactory for the treatment of organic pollutants in chloride medium. Finally, the anodic mineralization of organic pollutants in chloride medium perhaps may open the possibility of using DSA-type materials under mild oxidation conditions for the treatment of organic waste in water.

5.2 Study of AOX formation

As reported before in an early investigation (Aquino Neto & De Andrade, 2009b), the electrode material has a great effect on the amount of organic chloride species formed along of the electrolysis. The choice of material depends on the structure and complexity of the sample to be electrolyzed. For this reason, we cannot make a straightforward generalization for the best electrode material. However, our investigation has pointed Ti/(RuO$_2$)$_{0.70}$(Ta$_2$O$_5$)$_{0.30}$ or Ti/Ru$_{0.30}$Sn$_{0.70}$O$_2$ as compositions displaying longer lifetime and environmental friendly electrode composition (Aquino Neto & De Andrade, 2009b). The results also showed that an increase in the applied current leads to an increase in the amount of ClO$^-$ (Eq. 10), so the yields of AOX species are enhanced. The AOX formation

behavior is exponential in the case of commercial formulations. For the standard sample, the formation of organochloride compounds during electrolysis increases almost linearly with the applied current, and the AOX concentration remains below the allowed values almost in the entire investigated current window. Although some papers have shown that once the R─Cl compound is formed, it is quickly consumed before the end of the electrolysis, giving a volcano type curve (Comninellis & Nerini, 1995; Rajkumar et al., 2005), the results of AOX formation as a function of time reported by our research group reveal a different behavior for AOX formation. Even in the case of long-term electrolysis (14 h), there still is a mild increase in the production of organochloride compounds. These results may be attributed to the lower quantity of AOX compounds formed along the electrolysis, compared with results found elsewhere (Comninellis & Nerini, 1995). These data may be understood by considering the competition between the degradation of the generated AOX species and the organic compounds present in the solution. Although the formation of AOX is faster in the beginning of the electrolysis, the quantity formed within the first hours of treatment is very low compared with the remaining organic load. For this reason, an ascending behavior of AOX formation is observed for the entire investigated time window (Aquino Neto & De Andrade, 2009b). Finally, the results of AOX formation as a function of many experimental parameters show that the formation of organochloride compounds is straightly related with factors like chloride concentration, anode material, and current density, among others. For this reason, it is very important that these parameters are carefully evaluated when an alternative treatment that allows the formation of this species in solution is proposed.

6. Electrochemical oxidation of different formulations

A reduced number of papers deal with the oxidation of herbicides using electrochemical methods; indeed, the majority of the works focuses on photochemical processes. However, a literature search reveals that there is increased interest in the former subject. Table 3 lists the latest papers dealing with the electrochemical degradation/treatment of herbicides. Studies of Diuron photocatalytic degradation show that the herbicide mineralization rate reaches almost 97% after 8 hours of irradiation with light of 280nm. Studies combining photo-Fenton treatment afford 82.5% COD removal from wastewater generated by the sugarcane industry (Katsumata et al., 2009). Recently, Oturan et al. (2010) have used the electro-Fenton process to oxidize a group of phenylurea herbicides. The results showed that the degradation rate increases with the number of chlorine groups, being Diuron the most reactive herbicide. The authors observed that even with pronounced COD reduction, the treatment in mild conditions also produces several aromatic byproducts (Oturan et al., 2010). An interesting approach involving combination of biological and electrochemical oxidation processes has been proposed by Liu et al. (2010). They showed that the open ring byproducts formed during the electrochemical process can maintain the activity of microorganisms on a biofilter, consequently enhancing the activity of the process. A comparison between different electrochemical methods has been reported by Yatmaz & Uzman (2009), who used organophosphorus pesticides as a model compound. The authors claimed that the degradation of the pesticides proceeds with the following decreasing selectivity: indirect electrooxidation processes using Ti electrodes > electrocoagulation using Fe electrodes > electro-Fenton process using Fe electrodes. The herbicide Alachlor is also frequently investigated as a model of chloroacetamide compounds. A variety of effective techniques for the treatment of effluents containing alachlor are available. Herbicides such as 2,4-D have

been efficiently degraded by several advanced oxidation processes in which the oxidizing hydroxyl radical (•OH) is produced by chemical, photochemical, and photocatalytic systems, such as H_2O_2/Fe^{+2}. Alternative procedures such as anodic oxidation and electrochemical methods with indirect electro-oxidation by generation of H_2O_2 are also employed for 2,4-DP removal from water (Brillas et al., 2007). Badellino et al. (2007) have studied the degradation of 2,4-DP in an electrochemical flow reactor with generation of H_2O_2 and Fenton's reagent, and obtained open ring acids as the main final products.

Herbicide	Methodology	Reference
Desethyl atrazine and desethyl terbutylazine	Electrochemical reduction	Colombini et al., 1998
Ethylene thiourea	Electrochemical and Fenton treatment	Saltmiras & Lemley, 2000
2,4-D (2,4-dichlorophenoxyacetic acid)	Electro-Fenton	Wang & Lemley, 2001
S-Triazine	Electrochemical reduction	Galvin et al., 2001
Bendiocarb, pirimiphos-methyl, coumatetralyl and chlorophacinon	Photoelectro-Fenton	Aaron & Oturan, 2001
Phenoxyacetic acid (4-chlorophenoxyacetic acid (4-CPA), 4-chloro-2-methylphenoxyacetic acid (MCPA)	Electron-Fenton e BDD	Brillas et al., 2004
Thiocarbamate herbicides	Electroflotation, Electrochemical and photocatalytic	Mogyorody, 2006
2,4-DP (2-(2,4-dichlorophenoxy)-propionic acid)	Electrochemical reactor for H_2O_2 and Fe production	Badellino et al., 2007
2,4-DP (2-(2,4-dichlorophenoxy)-propionic acid)	Electro-Fenton	Brillas et al., 2007
Atrazine	Electrochemical oxidation Ti/β-PbO$_2$	Vera et al., 2009
Organophosphorus pesticides	Electrochemical, electron-Fenton and electrocoagulation	Yatmaz & Uzman, 2009
Diuron and fenuron	Electro-Fenton	Oturan et al., 2010

Table 3. Latest papers dealing with the electrochemical degradation/treatment of herbicides

7. Conclusion and perspectives on the electrooxidation of toxic organic compounds

The electrochemical technology is potentially useful for the treatment of organic pollutants. Some important features such as easy automation, rare need for addition of reagents, robustness, versatility, and operation at mild temperatures make this technique quite

promising for wastewater decontamination. Although several studies have focused on the use of phenolic intermediates, it can also be noted that the number of papers proposing electrochemical treatment of herbicide is still modest. In this scenery, electrochemical treatment using Fenton's reaction stands out. This is a straightforward result of the great interest shown by the use of Fenton's reagent in the photochemical investigation of herbicides degradation. As stated recently by Anglada et al. (2009), an efficient treatment of contaminated effluents is rarely performed by a single process; indeed, usually two or three associated processes must be involved, so that a reduction in the energy consumption and low level of organic material can be achieved. The main conclusion is that the oxidation of herbicides through electrochemical technology represents a viable technique for reducing the toxicity of wastewater. The use of this type of treatment may provide a breakthrough in the handling of toxic waste in the coming years. This is the reason why great efforts have been made in order to couple electrochemical treatments with established methodologies such as the biological ones.

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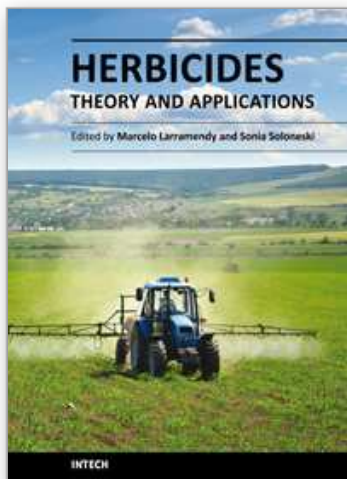
Herbicides, Theory and Applications

Edited by Prof. Marcelo Larramendy

The content selected in Herbicides, Theory and Applications is intended to provide researchers, producers and consumers of herbicides an overview of the latest scientific achievements. Although we are dealing with many diverse and different topics, we have tried to compile this "raw material" into three major sections in search of clarity and order - Weed Control and Crop Management, Analytical Techniques of Herbicide Detection and Herbicide Toxicity and Further Applications. The editors hope that this book will continue to meet the expectations and needs of all interested in the methodology of use of herbicides, weed control as well as problems related to its use, abuse and misuse.

How to reference

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