Int. J. Electrochem. Sci., 14 **(2019)** 3418 – 3433, doi: 10.20964/2019.04.60

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Voltammetric Techniques for Pesticides and Herbicides Detection- an Overview

Priscila Fernanda Pereira Barbosa[1], *Eduardo Guimarães Vieira*[2], *Loanda Raquel Cumba*[3], *Leonardo Lataro Paim*[4], *Ana Paula Rizzato Nakamura*[5], *Rômulo Davi Albuquerque Andrade*[6], *Devaney Ribeiro do Carmo*[1,*]

[1] São Paulo State University (Unesp), Department of Physics and Chemistry, Ilha Solteira, Brazil.
[2] Department of Fundamental Chemistry, Institute of Chemistry, University of São Paulo, São Paulo, Brazil.
[3] School of Chemical Sciences, Dublin City University, Dublin 9, Ireland.
[4] São Paulo State University (Unesp), Energy Engineering, Campus of Rosana, Brazil.
[5] São Paulo State University (Unesp), Department of Chemistry, Rio Preto, Brazil.
[6] Institute of Education, Science and Technology of Goiás, Luziânia, Brazil.
[*]E-mail: devaneydocarmo@hotmail.com

Received: 12 September 2018 / *Accepted:* 13 February 2019 / *Published:* 10 March 2019

Pesticides and herbicides contamination in soil, groundwater, rivers, lakes, rainwater and air is considered a matter of concern. Some techniques are used to detect the presence of those compounds, here in this review is considered some recent voltammetric techniques such as cyclic voltammetry, square wave voltammetry, differential pulse, electrochemical impedance spectra and bifferential pulse polarography. Besides, the most used materials in their electrodes such as carbon, polymers, clay materials, biomolecules, metal oxides and micro and nanostructured materials are briefly considered. For all those techniques and materials are shown some current studies, researches and new approaches, considering their high sensitivity and specificity for pesticides and herbicides detection.

Keywords: Pesticides; Herbicides; Detection; Voltammetric techniques

1. INTRODUCTION

Population growth is one of the current concerns because there was an increase of 2.5 billion in 1950 to 7 billion in 2014 and according to United Nations it is estimated that the population will reach 9 billion in 2050 [1]. This population growth intensifies the demand for food, especially food coming from agriculture activities. In addition, Food and Agriculture Organization explains that will be necessary an increase of 70% in global food production to suppress the demand [2].

The food production *per capita* can be increased using different types of alternatives, that include: increasing and enhancing agricultural area, raising the area of crops by using agrochemical compounds, organic fertilizers, biological controls and/or water and soil management can be improved [3]. Experts have pointed out that an association of agrochemicals with biological solutions is the more appropriate alternative for modern and extensive agriculture, providing a proper direction and low environmental impact, combining biology and sustainability in the best possible way [4].

Some of these alternatives have already been developed and used worldwide. The results found may be encouraging, but some of them are controversial. It is known that the scarcity of water is a big problem, in addition both drinking water is scarce as water used for irrigation. Furthermore, increase of agriculture land is difficult due to the actual trend: decrease of agriculture land [5]. This fact is a result of soil erosion and desertification, population growth, reduction of soil fertility and salinization. All these aspects point out to an intensive and exhausting use of agrochemicals [6].

Pesticides are widely used in agriculture around the word and represent an important tool to control weed, insects and pathogens. They are considered compounds or mixtures of chemical substances used to repel, destroy, prevent or inhibit the occurrence or effect of living organisms capable of damaging agricultural crops [7]. Since 1960 the increased pesticide use has helped farmers greatly expand production without suffering crop excessive losses to pests [8].

Herbicides are a kind of pesticide used to eliminate or impede growth of weeds. They are classified according to their activity (contact or systemic), use (applied in soil, pre-emergents or post-emergencies) and the mode of action on the plant biochemistry mechanism [9]. Besides, their classification is according to the target: non-selective (destroy all plants around) and selective (attack just the weed and preserve the crop) [10]. Among the most used herbicides are glyphosate (N-(phosphonomethyl) glycine), followed by Atrazine (2-chloro-4-ethylamino-6-isopropylamine 1,3,5-triazine) and 2,4D-dichlorophenoxyacetic acid), among others [11].

However, herbicides also have negative impacts and excessive use of them (more than necessary) to achieve productivity gains affect wild fauna and flora. They can cause contamination in soil, groundwater, rivers, lakes, rainwater and air [12]. Ribeiro *et al* [13] report that, even in low concentrations, herbicides residues are found in groundwater samples in countries such as Britain, Germany, United States, Greece, Bulgaria, Spain, Portugal and Brazil [13]. Some studies suggest that herbicides induce oxidative stress, thus increasing the possibility of cancer development [14, 15], women infertility [16], kidney damage [17], miscarriages, dermatological and respiratory illnesses [18] and contribute to initiate mental problems like autism, Alzheimer's and Parkinson's disease [19, 20].

A test with some residues that was conducted by UK- Food Standart Agency registered a worrisome situation. The test was performed in October 2012 and it registered glyphosate residues of aproximataly 0.2 mg/kg in 27 out of 10 bread samples (Monitoring program, 2012). US Department of Agriculture realized another test in 2011 and it showed a high glyphosate residues level, 90.3% of 300 soybean samples was contaminated, and it was found AMPA (Aminomethylphosphonic acid) in 95.7% of samples at concentrations of 1.9 ppm and 2.3 ppm, respectively [21]. The residue left in plant products, soil, water, sediment among others in the environment has become quite worrisome. In this way, there is the necessity to develop new strategies or techniques to quantify or detect such compounds in various sample matrices. Determining in a carefully way the impact of pesticides and herbicides in the environment and on human health is a big deal issue, so monitoring and exposure data are so crucial.

In recent years much progress is been made in this area, but still there is the necessity to develop new analytical methods with better sensitivity, precision, accuracy and selectivity. However, these new advanced methods must not be high cost and should be possible to adapt for field measurement. The most used analytical methods nowadays are: Gas-liquid chromatography (GLC or GC), X-ray and electron diffraction, High performance liquid chromatography (HPLC), Spectral laser, Mass spectrometry, Activation analysis, Fluorimetry, Spectrophotometry and Capillary electrophoresis [22]. These techniques work quite well but most of them require a proper professional to operate the equipment and they are also considered quite expensive. Methods like those cited above are limited in some aspects, for example, GLC or GC is limited to volatile compounds and commercially detectors for HPLC are restricted in sensitivity and/or selectivity. In addition, most of them are difficult for *in situ* or online monitoring.

Some approaches have been made concerning herbicides and pesticides determination and/or quantification, among them, multi syringe flow injection (MSFIA), bioanalytical methods and electrochemical methods [22-24] are the most used. Between the cited techniques, electrochemical methods are more attractive due their several advantages such high sensitivity, ease of use, fast measurement, cost effectiveness, and efficient on application in field conditions among others [25].

Science is changing every day to help the society to deal with new challenges, in this context the development of a suitable (modified or not) chemical sensor in order to detect low traces of pesticides or herbicides improves the studies of processes, impacts and agrochemicals modeling in environment [26]. The necessity of development these new devices is seen in current papers that describe how the actual detection methods are restricted.

The first documented electrochemical sensor was dated in 1950s and was used for oxygen monitoring [27]. An electrochemical sensor can be defined as device or instrument that determine the detectable presence, concentration, or quantify of a given analyte. It operates by interacting with the analyte and consequently making available an electrical signal proportional to the analyte concentration. A common electrochemical sensor contains: a working electrode where occurs an electrochemical reaction of electron transference, a reference electrode that measures and controls the potential of working electrode and the auxiliary electrode in which passes all the current necessary to balance the current observed at the working electrode [28]. For a better understanding, an electroactive sample is oxidized or reduced when a potential is applied in the working electrode in contact with that sample. Thus the electrode surface suffers a change in its concentration and it results in mass transference in the electrode where a current flows. In addition, the potential is swept with the time and the current is recorded resulting in a curve that is called voltammogram. Recording the current as function of the applied potential is homologous to the curve obtained. Electrochemical sensors nowadays are based upon potentiometric, amperometry, or conductivity measurements [29]. Figure 1 summarizes all the process behind the herbicides application and the necessity to detect them. In addition, there are several types of electrodes developed with different materials, for example, a matrix can be modified with metals, metal oxides, polymers, clay materials or micro or nanoparticles to achieve specific properties and improve the detection limit.

In this review, it will be discussed about reported techniques for herbicides detection and the materials used in the electrode modification. Development in devices for real sample analysis will also be discussed. This review covers publications related to electrochemical sensors for herbicides detection that showed up in print between 1990 and 2018.

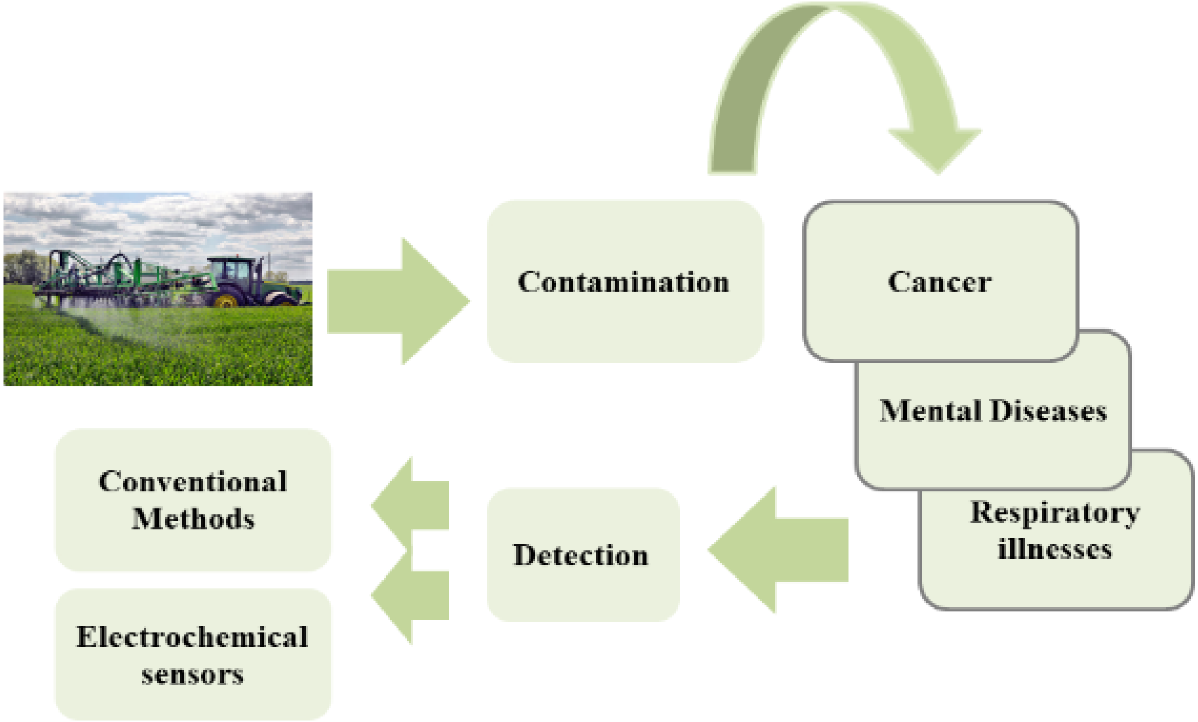

Figure 1. Herbicides application and its risks to population.

2. ELECTROANALYTICAL TECHNIQUES FOR THE HERBICIDE ANALYSES

2.1 Electrochemical analysis

2.1.1 Cyclic voltammetry (CV)

This technique is widely used for detection of metals via electroanalysis [30]. It located the redox potentials in the system and evaluates the effect of components in the media in the redox process. The process involves the application of a linear sweep potential E_i to the working electrode until it reaches a switching potential E_f . When the maximum value of the potential is reached, the sweep is inverted, returning to the initial values, forming the voltammogram [31]. An instrumental parameter called scan rate controls timescale in the experiment and a current derivative from the potential applied is recorded. Briefly, a voltammogram consists of characteristics defined by cathode and anode potential, cathodic and anode currents [32] (Figure 2).

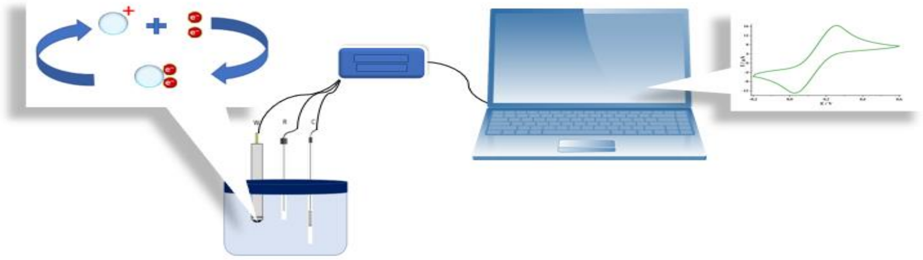

Figure 2. A schematic representation of cyclic voltammetry technique.

The herbicide 1- (5-tert-butyl-1,3,4-thiadiazol-2-yl) -1,3-dimethylurea is a compound widely used in soybean, sugarcane and corn crops, this compound is called tebuthiuron or TBH. In a detection study, Assis *et al* [33] detected points of concentration of tebuthiuron in brown sugar crystals. Assuming that compound detection can be performed via cyclic voltammetry, researchers are constantly developing new devices to supply market demand using this technique. For the detection, it was used an electrode containing open glassy carbon and an electrolytic solution of KOH 0.10 mol L^{-1}. The oxidation peak potential was found in the range of + 1.03V. In the same work, the results showed that with the electrode using real samples of brown sugar crystals it was possible to detect concentrations of TBH at 0.090 mg. L^{-1} (0.396 µmol L^{-1})

Another herbicide, Fenclorim, was studied by Babu *et al* [34] using some electrochemical techniques, including cyclic voltammetry at Carbon Nano Tubes Paste Electrodes. They studied the pH effect on the voltammograms by recording the current voltage curves of fenclorim 0.5 mM in universal buffer systems between 2.0 to 6.0 pH range. According to the obtained results, the technique showed effective where fenclorim could exhibit a single well-defined wave / peak. In addition, this behavior could be explained by the irreversible reduction azomethine group involving two electron process. It was made a scheme for a process better understanding (Figure 3).

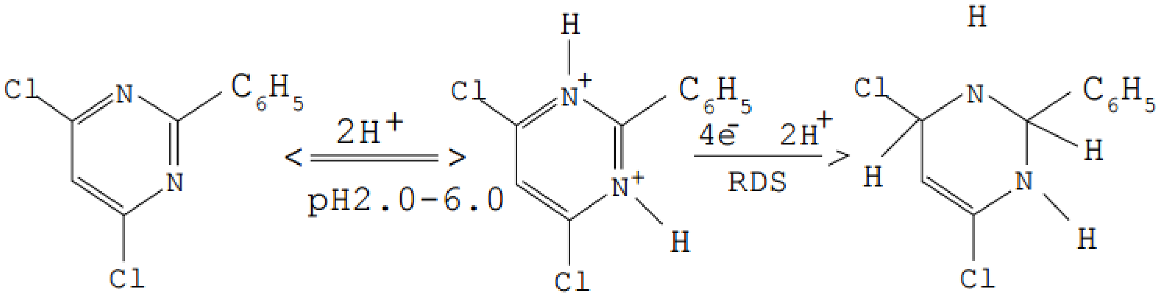

Figure 3. Electrode mechanism of Fenclorim.

Songa *et al* [35] used a biosensor based on an enzyme called horseadish peroxidase (HRP) to detect glyphosate in solutions. This biosensor was generated by the electrochemically deposition of poly(2,5-dimethoxyaniline (PDMA) doped with poly(4-styrenesulfonic acid) (PSS) onto the gold electrode surface, in addition, it has been promoted the binding of the HPR enzyme via electrostatic onto the PDMA-PPS composite film. The experiment was based on the exhibition of HPR activity by glyphosate, using H_2O_2 as substrate, studying the HPR response to the substrate before and after its interaction to glyphosate. The herbicide inhibited the HPR activity causing a decrease in the biosensor reponse to H_2O_2 . The prepared electrode had a detection limit of 170 µgL-1 (0.01 µM) for glyphosate, using cyclic voltammetry.

2.1.2 Square wave voltammetry

Square wave voltammetry (SWV) is the most pulse voltammetric technique fast and sensible. The wave form of the currrent-potential curve is derivative by overlaying on potential ramp in form of steps in which direct pulse of the square wave coincides with the beginning of the ramp step. The reverse pulse of the square wave in turn coincides with half stage of ramp steps [36]. The current measurement in SWV is done by sampling the same twice during each cycle of the square wave, once at the end of the direct pulse and the other at the end of the reverse pulse. The current difference between the two samplings is registered as a function of the potential of the ramp step [37, 28, 38].

Aclonifen (2-chloro-6-nitro-3-phenoxyaniline) is a diphenylether herbicide used as a pre-emergence control of broad-leaves and grass weeds in several countries [39]. Inam *et al* [40] studied the SWM method for the aclonifen herbicide detection. The herbicide showed electroactivity on the glassy carbon working electrode in which allowed the development of an analysis methodology using SWV. The optimization of the experimental parameters showed that the best electrochemical response was obtained in pH 4 (E_{acc}= +400 mV, t_{acc}= 90s, ΔE_s= 7 mV, f=100 Hz, ΔE= −30 mV). In this condition, it was possible to observe the oxidation peak at +1175 mV. After experimental condition optimization, a work curve was constructed and the methodology was then used for analysis in spiked soil and river water samples.

Sarıgül and Inam studied cyclosulfamuron herbicide determination by square wave voltammetry associated with square wave stripping voltammetry (SWSV). The authors used the SWV technique to verify the influence of pH on the voltammetric behavior. Better results were found at pH 6.0. After analyzing all parameters in the experiment, the optimum conditions selected were: E_{acc} = −400 mV, t_{acc} = 60 s, ΔE_s = 5 mV, f = 100 Hz, ΔE= −50 mV. The detection limit and the sensitivity (quantification limit) values were 3.5 and 10 µg L^{-1}, respectively. The proposed method was used in the analysis of this pesticide spiked in tap water and soil samples and a linear calibration plot was constructed for the two samples. The voltammograms obtained from tap water resulted in a linear relationship between current peak and concentrations in the range of 25–200 µg L^{-1}. They confirmed that the use of SWV associated with SWSV for the cyclosulfamuron determination seemed to be a suitable analytical methodology that makes possible an easy application, high levels of reproducibility, low detection limits, accuracy and selectivity [41].

2.1.3 Differential pulse voltammetry

In differential pulse voltammetry, pulses of fixed amplitudes superimposed on a ramp of increasing potential are applied to the working electrode. [42]. The current is measured twice, one before the application of the pulse (S_1) and another end of the pulse (S_2). The first current is instrumentally subtracted from the second, and the currents difference is plotted against of the potential applied. The obtained voltammogram is the resulted of current peaks of Gaussian form, whose area of this peak is directly proportional to the concentration of analyte [43].

Paraquat is a herbicide used to combat weeds in many agricultural areas worldwide. Due to its high toxicity levels some countries banned it and made it restrict [44]. Farahi *et al* [45] built a sensitive and fast method to determine this compound using a silver rotating electrode (SRE) in 0.1 mol L^{-1} Na_2SO_4 solution. Paraquat presented two negative peaks around 0,7 and 1.0 V. Some parameters were studied such as deposition time, frequency, amplitude and step amplitude and they chose the better ones for DPV study. A calibration curve was plot with the results from paraquat concentration added, the range was 1.0×10^{-8} and $1.0\times l0^{-3}$ mol L^{-1}. A calibration curve was made to obtain the values of detection and quantification limits, and the values found were 7.1×10^{-9}mol $L^{-1}$and 23.9×10^{-9} mol $L^{-1}$for peak 1, respectively and for peak 2 were 2.8×10^{-9} mol L^{-1} and 9.2×10^{-9}mol L^{-1}, respectively. The author concluded that the technique is efficient to determine low concentration of Pq.

Diuron, 2,4-D, Tebuthiuron [46], Triasulfuron [47], Bromacil [48], Hexazinone [49], Picloran [50] were all detected by unmodified and/or modified sensors using DPV method.

2.1.4 Electrochemical impedance spectra (EIS)

The principle of this technique is to apply an alternating signal of small amplitude (5 to 20 mV) to an electrode inserted in an electrolyte. The initial perturbation (applied) is then compared to the electrode response, by the measurement of the phase change of the current and voltage components and by the measurement of their amplitudes. This can be done in time domains or frequency domains, using either a spectrum analyzer or a frequency response analyzer, respectively. The initial perturbation is a sinusoidal potential perturbation (ΔE), which must be imposed at the stationary state of the system, and the electrode response is a sinusoidal current (ΔI), but with a phase difference Φ in relation to the applied signal. Therefore, the impedance, which is represented by Z, measures the relationship between ΔE and ΔI [51]. The basic concept involved in EIS is that an interface can be viewed as a combination of passive circuit elements, i.e., resistance, capacitance and inductance. The system response contains information about the interface, its structure and occurring reaction. Akinbulu *et al* [52] fabricated a fast and newly manganese acetate octakis-(2-diethyaminoethanethiol) phthalocyanine (AcMnODEAETPc) modified electrode for bentazon herbicide determination using EIS tecnique. Chen *et al* [53] prepared 3D Au nanocluster for modifying a glassy carbon electrode (GCE) for picloram herbicide detection in peach fruit and excess sludge supernatant. Due to the Nyquist plot performed, the authors concluded that the correspondingly increasing resistance indicated that the development of the immunosensor was feasible to the work.

2.1.5 Differential pulse polarography (DPP)

DPP is a voltammetry technique in whose operational principal is the same of DPV. The study takes place around two electrodes, one polarizable and one unpolarizable, using dropping mercury electrode or a static mercury drop electrode as indicator electrode [27]. Sarigül *et al* [54] studied and developed a differential pulse polarography method to detect triasulfuron in spiked soil, natural water and in a commercial formulation. Their method allowed to determine low quantities of triasulfuron and it was considered simple, fast and inexpensive. Mercan *et al* [55] used the method for thiazopyr detection in fruit juice and soil samples. The pH effect on the peak current and potential was analyzed, and it was observed a presence of double well-defined differential pulse peaks. These and other studies take together this present technique with others, such as, SW and CV measurements, in this case, the approach offers improvement in selectivity and sensitivity.

3. ELECTRODE MATERIALS

3.1 Carbon electrode materials

An electrode based on carbon materials such as carbon nanotube, films, fullerene and graphene oxide are largely used in many different fields such as, electrochemical sensors, biosensors, energy storage device and herbicide sensor applications. These materials have been intensively investigated due to their non-toxicity,accessibility, reasonable cost, processability, chemical stability and wide range temperature. Recently, a study was conducted with a carbon electrode that was modified with multi-walled carbon nanotubes (GCE/MWCNTs) demonstrated efficient in determining low concentrations of propham herbicide. It was the first report on the topic [56].

A glassy carbon electrode chemically modified with carbon black (CB/GCE) in the presence of cetyltrimethylammonium bromide (CTAB), a cationic surfactant, was developed for the mesotrione detection by square-wave voltammetry (SWV). The (CB/GCE) showed good linearity calibration curve with detection limit value of 0.026 μmol L^{-1} [57]. Đorđević *et al* [58] have reported the fabrication of a carbon paste electrode with tricresyl phosphate (TCP-CPE) as liquid binder for the sensitive determination of the herbicide 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea commercially known as Linuron. They reported that the developed analytical procedure offered good linearity in the concentration range of 1.25–44.20 μg mL^{-1}.

A carbon paste electrode modified with the same modifier as cited above, tricresyl phosphate, was used to quantify Aclonifen. The use of this modifier is explained by its properties and for what can it offers, for example, extreme polarisation limits and could be polarised from –2 to +2 V in an ammonia buffer [59]. In the same scientific area, an efficient sensor obtained by covering a multiwalled carbon nanotubes (MWCNT) glassy carbon electrode modified with β-cyclodextrin (β -CD) included in a polyaniline film was used to detect bentazone herbicide [60]. More recently, a novel modified glassy carbon electrode was built using nanocomposite containing acid-activated multi-walled carbon nanotube (A-MWCNT) and fumed silica (FS). It has been shown that A-MWCNT-FS nanocomposite greatly changed the electrochemical behavior of GC electrode and the GC/A-MWCNT-FS showed high sensitivity towards clopyralid (CLp) by detecting low concentrations of CLP (0.8 nM) [61].

Modifications in electrodes come to enhance the sensor properties, predefined them and may form the basis of new applications of electrochemistry and novel devices. As demonstrated by these examples, carbon electrode materials and their modifications are a useful tool for electroanalytical detection of herbicides.

3.2 Metal oxide electrode material

Metal oxides (SnO_2, TiO_2, WO_3, ZnO, Fe_2O_3, In_2O_3, Al_2O_3, CuO, RuO_2, MnO_2, V_2O_5 and MgO) have been investigated in sensing applications for more than five decades. Their addition on electrode matrix improves the selectivity and stability [62] and metal oxides have uniform size, identical shape and well-defined crystallinity nature. They can be disposed in form of tubes, fibers, wires, needles or rods and nanoparticles, depends on the methods of preparation and the metal oxides morphological shapes. The modifiers immobilized on the electrode surface have usually been used for two purposes: preconcentration or electrocatalysis. The modified electrodes properties depend on the formation and characteristics of the film formed on the electrode surface. [63]. Figure 4 illustrates the electrode modification with metal or metal oxides, in this case the modification is made in the carbon graphite paste.

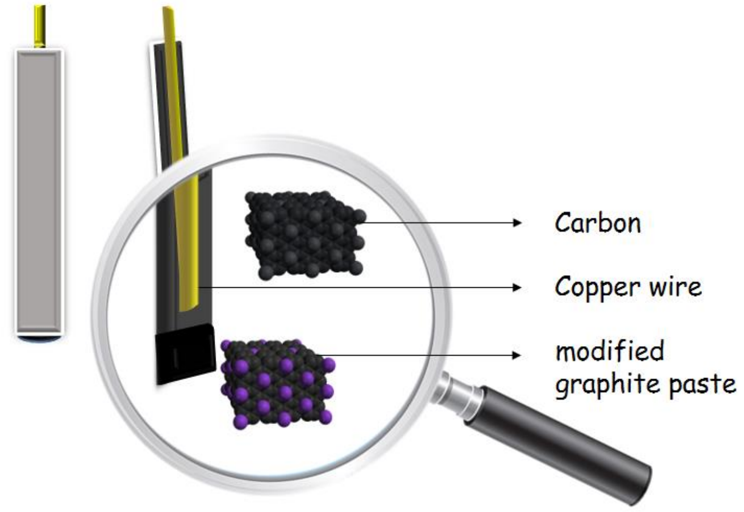

Figure 4. Illustration of an electrode modified with a metal or metal oxide.

A very recent work developed an electrochemical sensor for chlorophenols (CPs) based on the enhancement effect of Al-doped mesoporous cellular foam (Al-MCF) [64]. Other modified electrode with TiO_2 was prepared for Cps detection [65], both of them achieved great results with detection limit around 0.080 mgL^{-1}. A Reduced graphene oxide-cobalt nanocube-gold (rGO-Co_3O_4@Au) was prepared for hydrazine detection using amperometry technique and the limit of detection was found to be 0.443µM. The authors confirmed that the conducting support material used enhance the heterogeneous catalysis, catalyst dispersion, electrocatalysis and the stability for sensitive detection of hydrazine [66].

Gajdár *et al* [67] performed a study with same substrates electrodes like namely Cu, Au, Ag, polished silver solid amalgam, glassy carbon electrode and antimony film electrodes (SbFEs). The last one (SbFEs) provided the best result and it was also confirmed that trifluralin herbicide provided voltammetric response on the SbFAuE electrode, but the bare AuE electrode could not be used for the trifluralin detection. All these examples show how the use of a metal oxide improves the electrode sensitivity and accuracy.

3.3 Polymer electrode materials

Modified electrodes with polymers have been recently used to analyze metals, dyes, pesticides and herbicides *in situ* or in real samples [68]. Polymers present differentiated characteristics such as increase of electrode stability and several analytical possibilities due to the versatility of the electrochemical polymerization [69]. In addition, they present tolerance to organic solvents making them interesting for the analysis of some herbicides of commercial formulation and they are relatively low-cost materials. The most common polymers used for electrodes are chitosan, polyaniline, polyacetylene, polypyrrole, polythiophene and its derivatives. In many cases, modification of the working electrode with the conjugated polymer increases the signals by several orders of magnitude when compared to the unmodified electrode [70].

Wong *et al* [71] developed an electrochemical sensor modified with a molecularly imprinted polymer (MIP) and carboxylfunctionalized multi-walled carbon nanotubes (MWCNT-COOH). The sensor was built for the sensitive and selective diuron detection in river water samples. The detection limit obtained was 9.0 x10^{-9} mol L^{-1}. The authors added that the new electrode showed an enhanced electrochemical response, greater than carbon paste electrode (CPE). Trifularim (TRF) herbicide was quantify by modified electrode based on chitosan, several techniques were employed to determine the herbicide in real samples like food, soil and water. Using differential pulse voltammetry, it was possible to observe the proportional relationship between reduction current and TRF concentration, with detection limit of 7.45×10^{-8} mol L^{-1} [72].

Paraquat residues in environmental samples were investigated by a chitosan-modified glassy carbon electrode. The proposed methodology was compared with chromatographic methods (HPLC-UV) and the obtained results pointed to a greater sensitivity, precision and efficiency for the new technique tested. The detection limit achieved by cyclic voltammetry was 9,6 x 10^{-7} mol L^{-1} [73]. The best response for 2,4 D detection was for CP3, the effect of herbicide presence on polyaniline cyclic voltammograms were observed and it increased both anodic and cathodic currents [74].

3.4 Clay modified electrode

Clays are compounds that can be classified in two classes: cationic clays that have negatively charged alumino silicate layers; and anionic clays with positively charged hydroxide layer. They are classified according to their crystalline arrangement. Cationic ones are the most common mineral on earth’s surface and they are used to produce ceramics, cosmetics and have other important applications like catalysts, adsorbents, and ion exchangers [75]. Clays demonstrate attractive properties when electrode surfaces are synthetized for analytical applications, whereas their stability and low cost. Their well-defined layered structures, flexible adsorptive properties and potential as catalysts or catalytic supports make clays interesting materials compared to other modifications. Ion exchange and adsorption property are characteristics not only applied on electrochemistry determination of herbicides, pesticides, drugs or heavy metals, but also to a biosensor development [76].

Since 1990's clay-modified electrodes (CLME) have been extensively studied, principally its electron transfers phenomenon. Common clays used are moroccan montmorillonite, kaolinite, and goethite [77]. Kasmi *et al* [78] tried to achieve the validation of Moroccan clay as the modifier of graphite electrode to determine paraquat in food samples (potato, lemon, orange). The authors explained the methodology success by the interaction between clay and carbon paste electrode, they said that the modifier exhibited a good binding ability and high retention for paraquat ions. An organoclay was prepared by exchanging cationic surfactants from natural Cameroonian smectite-type clay to cetyltrimethylammonium (CTA) and didodecyldimethyl ammonium (DDA). This process was realized with the purpose of developing a new glassy carbon electrode based on organoclay (as a modifier) to quantify mesotrione herbicide by square wave voltammetry. The detection limit was of 0.26 mM and this electrode was also applied for the commercial formulation CALLISTO, used in European maize market [79]. Isoproturon is a selective herbicide and it is considered a toxic class III herbicide which means that it is medically toxic. It was determined by a hetero polyacid montmorillonite clay (HPMM) modified glassy carbon electrode with presence and absence of surfactant, cetyl trimethylammonium bromide (CTAB). The procedure achieved to limits of determination down to ng mL^{-1} levels. Advantages such as high sensitivity, good reproducibility and simple instrumentation were observed and the authors said that the methodology can be used to analyze spiked soil and water samples [80].

3.5 Micro and nanostructured materials in electrochemical sensors

Incorporation of Micro (MPs) or Nanoparticles (NPs) into different matrices to make nanocomposite films is attracting much attention in the last years, principally due to their advantages such as low cost and unique size-dependent properties [81]. M/NPs are also unique due to their optical mechanical, electrical, catalytic and magnetic properties as well as their extremely high surface area per mass. Electrochemical, electroanalytical and bioelectrochemical are areas that these materials have been intensively used for different applications. This new technology combined with modern electrochemical techniques makes possible the introduction of powerful, reliable electrical devices for successful process and pollution control [82]. There are several different M/NPs materials, but they are divided into six classes according to their chemical nature: (1) metals; (2) metal oxides; (3) carbonaceous; (4) polymeric; (5) dendrimeric; and, (6) composites [82]. The most relevant works in designing an electrochemical sensor were based in metals and metal oxides. For example, zirconia (ZrO_2)- NPs were used to detect some herbicides and zirconia use was explained due to its strong affinity towards phosphorous groups. The ZrO_2-NP also provides a large surface area and it increases the interaction between compounds that contain phosphorous groups [83].

A similar work involving Au nanoparticles was proposed to detect hydrazine. The sensor was developed by Au nanoparticles (AuNPs) coated on carbon nanotubes electrochemically reduced on graphene oxide composite film (CNTs-ErGO) on glassy carbon electrode (GCE). The results were obtained by cyclic voltammetry and potential amperometry, the enhancement of the sensor performance was attributed to the synergistic effect between AuNPs and CNTs-ErGO film and the outstanding catalytic effect of the Au nanoparticles. In addition, the method was successfully used in tap water [84]. The M/NPs system has proved to be a great tool to monitor environmental contaminants but most of the researches in this area give more attention in developing new methodologies for construction of new sensors in place of optimizing their performance (sensitivity or selectivity). Moreover, sensors are rarely tested with real or industrial samples (e.g., wastewater), which show considerable analytical complexity where M/NPs sensors may offer further advantages. There is the necessity to improve the actual sensors existed and test them in real samples to understand better the M/NPs reactivity, chemistry and possible mechanisms involved in their interaction with the analyte. But the existing materials and the possible sensor built enable more studies around the advanced electrochemical sensor systems to be devised in the near future.

3.6 Biosensors based on biological element

Since last years the biosensors development for the herbicide detection has received considerable attention as a satisfactory alternative. A biosensor is a self-contained device that incorporates an immobilized biological element (e.g. enzyme, DNA probe, antibody) that recognizes the analyte (e.g. enzyme substrate, complementary DNA, antigen) and a transduction element that is used to convert the (bio) chemical signal resulting from the interaction of the analyte with the bioreceptor into an electronic one [85]. They are divided into classes: electrochemical, optical, piezoelectric and mechanical according to the signal transduction technique. Advantages as specificity, fast response times, low cost, portability, ease of use, a continuous real time signal and their biological base make biosensors ideal for toxicological measurement of agrochemicals, while conventional techniques can only measure concentration. The biosensors for herbicides are based on the signal reduction (physicochemical signal proportional to target analyte concentration) by inhibition of the biocomponent activity [86]. Figure 5 introduces a schematic representation of a biosensor.

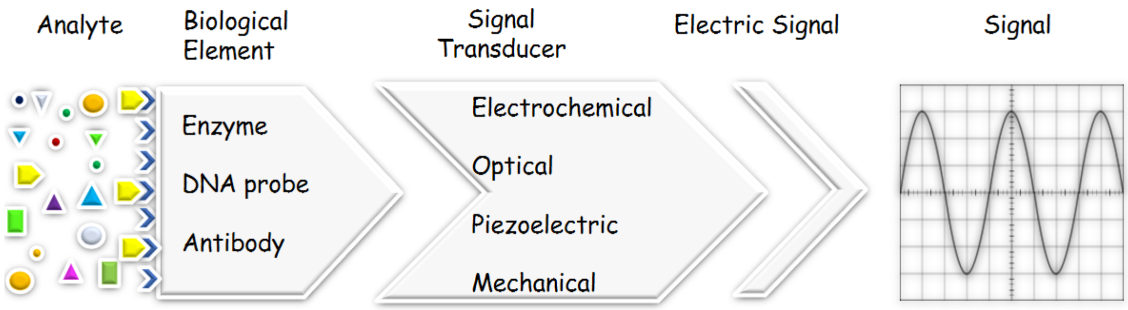

Figure 5. A schematic representation of a biosensor.

Rhodobacter sphaeroides is a purple bacterium that can obtain energy from photosynthesis. Purple bacterial reaction centers from species such as *Rba. sphaeroides* offer many advantages, principally as an experimental system for the biosensors development. One research provides an overview about the direct manner in which the photocurrent generates by *Rba. sphaeroides* reaction centers adhered to an unfunctionalized gold electrode showed how it could provide the basis of a biosensor for atrazine and its relatives detection [87]. Besides, table 1 presents some examples of herbicides detected by biosensors using different biosensing elements.

Table 1. Important biosensors developed for the detection of some herbicides.

Analytes	Biosensing elements	Transducers	Samples	References
2,4- D	Acetyl cholinesterase	Amperometric	Soil	[88]
Diuron, paraquat	Cyanobacterial	Bioluminescence	Soil	[89]
Simazine	Peroxidase (Biocatalytic)	Potentiometric	Soil and waste water	[90]
Atrazine	Antibody	Amperiometric	Orange Juice	[91]
2,4-D	Antibody	Impedance	Soil	[92]
Isoproturon	Antibody	Potentiometric	Drinking water	[93]
Hydrazide	Acetyl cholinesterase	Potentiometric	Soil	[94]

4. CONCLUSIONS

Electrochemical sensors are good candidates for monitoring the environment and have been successfully produced by different types of electrode materials. The applicability of voltammetry techniques and its advantages towards classical methods of herbicides analysis were also demonstrated. The electrode modification increases its properties allowing detect or quantify low concentrations of a specific analyte, for metals or metal oxides based electrode become possible to detect herbicides that are not electroactive. It has also been noticed that nanostructures provide many advantages and it is promising research area. There is a considerate number of articles related to biosensors, offering exciting new opportunities to improve their performance for the detection of herbicides. Most of the discussed works used real samples like tap and lake water, spiked soil and food (fruits and vegetables) to determine toxic compounds, but it remains the necessity to integrate those new devices to commercial analysis or industries.

ACKNOWLEDGEMENTS
The authors are grateful to the Coordenação de Aperfeiçoamento de Nível Superior (CAPES) and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for the financial support.

References

1. United Nations, World population projected to reach 9.6 billion by 2050, New York, United States of America, 2014, 2.
2. FAO, The future of food and agriculture – Trends and challenges, FAO (2017) Rome, Italy.
3. F.P. Carvalho, *Environ. Sci. Policy*, 9 (2006) 685.
4. G. da. S. Souza, T. B. S., Moreira, E. G. Gomes, *Pesp. Oper., 31* (2011) 79.
5. C. E. P. Cerri, G. Sparovek, M. Bernoux, W.E. Easterling, J.M. Melillo, C.C Cerri, *Scient. Agric*, 64 (2007) 83.
6. P.L. Pingali*, Proceed. Nati. Acad. Scie.*, 109 (2012)12302.
7. M.F.O. Silva, L.M. Costa, *Pestic. indus.*, 35 (2012) 233.
8. N. Ghimire, R.T. Woodward, *Ecology Economics., 89* (2013) 73.
9. P.C. Gupta (2012). Veterinary Toxicology, Academic Press (2012) Hopkinsville, USA.
10. R. Annett, A. Hontela, H.R. Habibi, *J. Apll. Toxicol., 34* (2014) 458.
11. F.P Lamego, R.A. Vidal, *Planta Daninha.*,26 (2008) 467.
12. F. Islam, J. Wang, M.A. Farooq, M.S.S. Khana, L. Xuc, J. Zhua, W. Zhoua, *Environm. Intern.*, 111 (2017) 332.
13. M.L. Ribeiro, C. Lourencetti, S.Y. Pereira, M.R.R. Marchi, M.R.R. *Quím. Nova*, 30 (2007) 688.
14. C.C. Lerro, F.L.E. Beane, L. Portengen, D. Kang, K. Lee, A. Blair, R.C. Vermeulen, *Environm. Molec. Mutagen.*, 58 (2017) 30.
15. N. Sathiakumar, P.A. MacLennan, J. Mandel, E. Delzell, *Crit. Rev.Toxic.*, 41 (2011) 1.
16. M. Krüger, P. Schledorn, W. Schrödl, H.W Hoppe, W. Lutz, A.A. Shehata, *J. Environm. Anal. Toxicol.*, 4 (2014) 210.
17. C. Jayasumana, S. Gunatilake, P. Senanayake*, Inter. J. Environm. Res. Pub. Heal.*, 11 (2014) 2125.
18. A. Camacho, D. Mejía, *J. Heal. Econ.*, 54 (2017) 147.
19. K. Fluegge, K. Fluegge, *Pol. J. Environm. Studies*, 25 (2016) 1489.
20. N.L. Swanson, A. Leu, J. Abrahamson, B. Wallet, *J. Organ. Syst*., 9 (2014) 6.
21. Agricultural Marketing Service, Pesticide data program annual summary, Department of Agriculture (2013) Washington, D.C, USA.
22. G. Javad and A. R. Amir, *J. Electroanal. Chem.*, 85 (2017) 1.
23. W. Boonjo, M. Miró, V. Cerdà, *Anal. Chem*., 80 (2008) 7319.
24. W. Tian, H.Q. Xie, H. Fu, X. Pei, B. Zhao, B. *Sensors*, 12 (2012) 16710.
25. J. Ghodsi, A.A. Rafati, *J. Electroanal. Chem.*, 807 (2017) 1.
26. *J.* Álvarez, J. Souto, M.L. Rodríguez-Méndez, J.A. Saja, *Sens. Actuators B Chem*., 48 (1998) 339.
27. S.K. Islam, M.R. Haider. Sensors and Low Power Signal Processing, Springer, (2009) New York, USA.
28. T. K. Ignas, E. Ngameni, Voltammetric Analysis of Pesticides, Pesticides in the Modern World - Trends in Pesticides, Intechopen, (2011) Baja California, Mexico.
29. N.R. Stradiotto, H. Yamanaka, M.V.B. Zanoni, *J. Braz. Chem. Soc.*, *14* (2003) 159.
30. E. S. Gil, Eric, C.H. Andrade, N.L. Barbosa, R.C. Braga, S.H.P. Serrano, Sílvia, *J. Braz. Chem. Soc.,* 23 (2012) 565.

31. M.A. Kulandainathan, K. Kulangiappar, T. Raju, A. Muthukumaran, *Port. Electrochim Acta,* 23 (2005) 335.
32. R. Gulaboski, C.M. Pereira, Electroanalytical techniques and instrumentation in food analysis. In: Handbook of food analysis instruments, Taylor & Francis, (2008) Boca Rotan, USA.
33. A.P. Assis, L.L Okumura, A.A. Saczk, M.F. Oliveira, *J. Braz. Chem. Soc.*, 25 (2014) 27.
34. R.T Babu, R.S.S Reddy, P. Sujana, *J. Adv. Chem. Eng.,*4 (2014) 109.
35. E.A. Songa, O.A. Arotiba, J.H.O. Owino, N.J. Jahed, P. G.L. Baker, E.I. Iwuoha, *Bioelectrochemistry*, 75 (2009) 117.
36. D. Souza, L. Codognoto, A.R. Malagutti, R.A. Toledo, R. A., V.A. Pedrosa, R.T.S. Oliveira, S.A.S Machado, *Quím. Nova,*27 (2004) 790.
37. Wang, J. Controlled-potential techniques, In: Analytical electrochemistry (3rd Edition), John Wiley & Sons. (2006), New Jersey, USA.
38. D. Souza, S.A.S. Machado, L.A. Avaca, *Quím. Nova*, 26 (2003) 81.
39. O. Kilinc, R. Grasset, S. Reynaud, *Pest. Biochem. Phys.*, 100 (2011) 193.
40. R. Inam, Z. Çakmak, *Anal. Methods,* (2013) DOI: 10.1039/c3ay40333e.
41. T. Sarıgül, R. Inam, *Electrochim. Acta,* 54 (2009) 5376.
42. M.N. Catrinck, L.L. Okumura, A.A. Silva, A.A Saczk, M.F. Oliveira, *J. Braz. Chem. Soc., 26* (2015) 1751.
43. *S. P* Kounaves, *J. Ame. Chem. Soc.,* 120 *(1998)* 709.
44. R. H. Poppenga, FW. Oehme, Hayes' Handbook of Pesticide Toxicology (Third Edition), Elsevier, (2010) Riverside, USA.
45. A. Farahi, S. Lahrich, M. Achak, L. El Gaini, M. Bakasse, M.A. El Mhammedi, *Anat. Chem,* 1 (2014) 16.
46. E.H. Duarte, J. Casarin, E.R. Sartori, C.R.T. Tarley, *Sen. Actuators B Chem.*, 255 (2018) 166.
47. L. Bandzuchová, R. Selesovská, T. Navrátil, J. Chylková, *Electrochim. Acta*, 113 (2013) 1.
48. M Brycht, T. Özmen, B. Burnat, K. Kaczmarska, A. Leniart, M. Taştekin, S. Skrzypek, *J. Electroanal. Chem.*, 770 (2016) 6.
49. M J.U Toro, L.D. Marestoni, M.D.P.T. Sotomayor, *Sens. Actuators B Chem.* 208 (2015) 299.
50. L. Bandzuchová, R. Selesovská, T. Navrátil, J. Chylková, *Electrochim. Acta*, 111 (2013) 242.
51. D.V. Ribeiro, C.A.C. Souza, J.C.C. Abrantes, *Rev. IBRACON Estrut. Mater.*, *8* (2015) 529.
52. I.A. Akinbulu, T. Nyokong, *Electrochim. Acta*, 55 (2009) 37.
53. L. Chen, G. Zeng, Y. Zhang, L.Tang, D. Huang, C. Liu, Y. Pang, J.Luo, *Anal. Biochem*., 407 (2010) 172.
54. T. Sarıgül, R. Inam, *Bioelectrochemistry*., 75 (2009) 55.
55. H. Mercan, R. Inam, *Int. J. Environm. Anal. Chem.*, 88 (2008) 879.
56. A. Leniart, M. Brycht, B. Burnat, S. Skrzypek, *Sens. Actuators B Chem.*, 231 (2016) 54.
57. P.B. Deroco, B.C. Lourencao, O. Fatibello-Filho, *Microchem. J.*, 133 (2017) 188.
58. J. Đorđević, Z. Papp, V. Guzsvány, I. Švancara, T. Trtić-Petrović, M. Purenović, K. Vytřas, *Sensors,12* (2012) 148.
59. V. Novotný, J. Barek, *Ecol. Chem. Eng., 22* (2015) 451.
60. V, Rahemi, J.M.P.J. Garrido, F. Borges, C.M.A. Brett, E.M.P.J. Garrido, *Electroanal*., 25 (2013) 2360.
61. A. Özcan, M. Gürbüz, *Sens Actuators B Chem.*, 255 (2018) 262.
62. E. Comini, G. Sberveglieri, *Mat. Today*, 13 (2010) 36.
63. D. R. Do Carmo, R.M. Da Silva, N.R. Stradiotto, *Eclet. Quím.,* 27 (2002) 197.
64. Y. Ya, C. Jiang, F. Yan, L. Xie, T. Lia, Y. Wang, L. Wei., *J. Electroanal. Chem.*, 808 (2018) 107.
65. Y. Wu, *Sens Actuators B Chem.*, 137 (2009) 180.
66. M.M. Shahid, P. Rameshkumar, W.J. Basirunc, U. Wijayantha, W.S. Chiu, P.S. Khiew, N. M. Huang, *Electrochim. Acta,* 259 (2018) 606.
67. J. Gajdár, J. Barek, J. Fischer, *J. Electroanal. Chem.*, 778 (2016) 1.

68. G. March, D. Nguyen, B. Piro, *Biosensors*, 5 (2015) 241.
69. E. Medeiros, J. Oliveira, N. Consolin-Filho, L.G.Paterno, L.H.C. Mattoso, *Ver. Elet. Mat. Proc (REMAP)*, 7 (2012) 144.
70. C.M.F. Calixto, R.K. Mendes, A.C. Oliveira, L.A. Ramos, P. Cervini, E.T.G. Cavalheiro, *Mater. Res.*, 10 (2007) 109.
71. A. Wong, M.V. Foguel, S. Khan, F.M. De Oliveira, C R.T. Tarley, M.D.P..T Sotomayor, *Electrochim. Acta*, 182 (2015) 122.
72. A.M.S Melo, Valentim, I.A. Barros, M.O.F Goulart, F.C. De Abreu, *J. Braz. Chem. Soc.*, 19 (2008) 704.
73. G.T. Corrêa, Electroanalytical determination of herbicide paraquat in aqueous solutions on electrode modified with chitosan system, Master's thesis (2013) Federal University of Maranhão, São Luís, Brazil.
74. F.R Simões, L.H.C Mattoso, C.M.P Vaz. *Sensor Lett*, 2 (2004) 221.
75. C. Mousty, Appl.Clay Sci., 27 (2004) 159.
76. Y. Xiang, G. Villemure, *J. Electroanal. Chem.* 381 (1995) 21.
77. A.M. F Guimarães, V.S.T. Ciminelli, W.L.Vasconcelos, *Mater. Res*, 10 (2007) 37.
78. S. El Kasmi, S. Lahrich, A. Farahi, M. Zriouil, M. Ahmamou, M. Bakasse, M.A. El Mhammedi, J Taiwan Inst Chem Eng, 58 (2016) 165.
79. J.K. Wagheu, C. Forano, P. Besse-Hoggan, I.K. Tonle, E. Ngameni, C. Mousty, *Talanta*, 103 (2013) 337.
80. P. Manisankar, G. Selvanathan, C. Vedhi, *Talanta*, 68 (2006) 686.
81. L. Rassaei, M. Amiri, C.M. Cirtiu, M. Sillanpaa, F. Marken, M. Sillanpaa, *Trends Anal. Chem.*, 30 (2011) 1704.
82. R.L.S Mello, F.I Mattos-Costa, H.M Villullas, L.O.S Bulhões, *Eclé. Quím., 28* (2003) 69.
83. G. Liu, Y. Lin, *Anal.Chem.*, 77 (2005) 5894.
84. Z. Zhao, Y. Sun, P. Li, W. Zhang, K. Lian, J. Hu, Y. Chen, *Talanta*, 158 (2016) 283.
85. A. Sassolas, B. Prieto-Simón, J-L.Marty, *Amer. J. Anal. Chem.*, 3 (2012) 210.
86. N. Verma, S.S. Dhillon, *Intern. J. Environ. Studies*, 60 (2003) 29.
87. D.J K. Swainsbury, V.M. Friebe, R.N. Frese, M.R. Jones, *Biosen. Bioelectron.*,58 (2014) 172.
88. H. Akhtar, J.L. Marty, *Frontiers in Chemistry*, 2 (2014) 1.
89. S. Rodriguez-Mozaz, J. Maria, L. De Alda, D. Barcelo, *Anal. Bioanal. Chem*., 386 (2006) 1025.
90. A.M. Salgado, L.M Silva, A.F. Melo, Biosensor for environmental applications, Intechopen, (2001) Rio de Janeiro, Brazil.
91. E. Zacco, R. Galve, M.P. Marco, S. Alegre, M.I. Pividori, *Biosen. Bioelectron*, 22 (2007) 1707.
92. I. Navrátilová, P. Skládal, *Bioelectrochem.* 62 (2004) 11.
93. M.F. Gouzy, M.Kess, P.M Kramer, *Biosen. Bioelectron.* 24 (2009) 1563.
94. C. Tran-Minh, P.C. Pandey, S. Kumaran, *Biosens. Bioelectron*. 5, (1990) 461.