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ELECTROCHEMISTRY

Determination of Metribuzin with a Cobalt Phthalocyanine-Modified Carbon Paste Electrode

Eduardo Carneiro Figueira[a], Mayara Regina dos Santos Ruy[a,b], Ademar Wong[a], Luís Moreira Gonçalves[c,d], and Maria del Pilar Taboada Sotomayor[a,b]

[a]Department of Analytical Chemistry, Institute of Chemistry, UNESP – Univ Estadual Paulista, Araraquara, SP, Brazil; [b]National Institute for Alternative Technologies of Detection, Toxicological Evaluation and Removal of Micropollutants and Radioactives (INCT-DATREM), Araraquara, SP, Brazil; [c]REQUIMTE/LAQV, Faculdade de Ciências, Universidade do Porto, Porto, Portugal; [d]Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo (USP), SP, Brazil

ABSTRACT
Metribuzin is a widely used pesticide with a half-life of up to 2 months and high affinity to organic matter that should be carefully monitored. Here is reported the development of a modified carbon paste electrode using cobalt phthalocyanine as a biomimetic catalyst for the determination of metribuzin. The diffusion coefficient of metribuzin at room temperature was $(59 \pm 16) \times 10^{-6}$ cm^2 s^{-1} and the apparent Michaelis–Menten constant (K_M^{ap}) was $(7.4 \pm 0.6) \times 10^{-6}$ mol L^{-1}. Electroanalytical measurements were performed by amperometry and the following figures of merit were obtained: limit of detection of 5.3×10^{-6} mol L^{-1} (1.14 mg L^{-1}), linear range up to 2.0×10^{-4} mol L^{-1}, recoveries above 93% (performed on spiked water samples), interday repeatability of 4.5% and intraday repeatability of 3.5%, and suitable selectivity.

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Biomimetic sensor; cyclic voltammetry; electroanalysis; electrocatalysis; metallophthalocyanine complexes

Introduction

Pesticides have been widely used as a strategy to improve agricultural productivity, however their use poses environmental and toxicological risks, making groundwater contamination a major concern. Metribuzin (4-amino-6-*tert*-butyl-3-methylsulfanyl-1,2,4-triazin-5-one) belongs to a class of triazines developed for selective, pre and postemergence control of weeds in many agricultural productions like tomatoes, soybeans, and potatoes, acting by inhibiting photosynthesis (Trebst and Wietoska 1975). In the environment, metribuzin shows half-life of up to 2 months depending on soil texture and climatic conditions, being moderately adsorbed in most soils and having moderate to high affinity with organic matter (Stenrød et al. 2008). The effects of exposure of this pesticide are still being studied, nevertheless it seems metribuzin may have both acute and chronic effects on human health (Zagal et al. 1999).

Various analytical methods have been used to detect metribuzin in water and/or soil. The most common methods are chromatographic with several detection instruments and several sample preparation techniques (Wells, Riemer, and Wells-Knecht 1994; Papadakis and

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CONTACT Maria del Pilar Taboada Sotomayor ✉ mpilar@iq.unesp.br Instituto de Química (IQ) Unesp, Av. Prof. Francisco Degni, 55, Jardim Quitandinha, Araraquara, SP 14800-900, Brazil.
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Papadopoulou-Mourkidou 2002; Huertas-Pérez et al. 2006; Zhang et al. 2009; Kai et al. 2011; Swarna, Babu Naidu, and Naidu 2012). To avoid the drawbacks of these methods, like cost, time, and lack of portability, electrochemical alternatives can be a suitable option (Vyskočil and Barek 2009). Recently, Stojanovic et al. (2016) briefly reviewed the published electroanalytical methodologies; not surprisingly, initial methods included the use of pure mercury electrodes (de Erenchun et al. 1997; Ludvík et al. 1998; Ludvík and Zuman 2000; Skopalová et al. 2001; Skopalová and Navrátil 2007); more recently, carbon (Lima et al. 2009), bismuth (Moreno et al. 2009; Tutunaru et al. 2015), amalgam (Janíková et al. 2016), polymer (norvaline) film (Jia et al. 2016), and thin-film mercury-based (Stojanovic et al. 2016) electrodes have been applied. The use of chemically modified electrodes based on carbon paste is attractive, mainly due to the simplicity and low cost of paste preparation. Additional advantages of these electrodes include easy surface renewal, good stability, low residual current, portability, and potential for miniaturization.

Biomimetic sensors based on the use of artificial redox enzymes have been used to develop more stable and durable amperometric detectors. Compared to conventional biosensors, advantages of these devices include better availability and stability as well as lower cost. They offer improved electron transfer between the electrode/active site (biomimetic catalyst/substrate) while maintaining some of the selectivity shown by enzymatic systems. An additional advantage is that the signal obtained using biomimetic sensors is direct, rather than derived from a relation of inhibition. All P450 enzymes contain a common active site, iron protoporphyrin IX, which catalyzes numerous chemical reactions in organisms, usually producing metabolites that are physiologically essential or beneficial (Danielson 2002). Materials derived from the phthalocyanines and porphyrins of iron and other metals (such as manganese or cobalt) have been successfully used in the construction of biomimetic chemical sensors for analytical use (Dobson and Saini 1997; Griveau et al. 2003; Arguello et al. 2008; Savéant 2008; Moraes et al. 2009; Santos et al. 2009; Boni et al. 2011; Wong et al. 2013; Guo et al. 2015; Xu et al. 2015; dos Santos et al. 2017) and even in fuel cells (Lu and Reddy 2008), since these compounds mimic the chemical structure of P450 active site (of iron protoporphyrin IX).

Herein, a sensor consisting on a carbon paste electrode modified with cobalt phthalocyanine was developed for the selective and sensitive amperometric determination of metribuzin. It is a simple, low-cost, and environmentally friendly sensor.

Materials and methods

Chemicals and samples

All chemicals used were of analytical or HPLC grade and were used as received without further purification. Metribuzin, cobalt phthalocyanine, mineral oil, and graphite powder were acquired from Sigma-Aldrich; sodium hydroxide, monopotassium phosphate, sodium acetate, and nitric acid were obtained from Synth-Brazil; and phosphoric acid was obtained from Mallinckrodt. Ultrapure water (resistivity not lower than 18.2 $\mathrm{M\Omega \cdot cm}$ at 298 K) from a Direct-Q 3UV water purification system (Millipore) was used in all experiments.

A metribuzin stock solution (1.0×10^{-3} mol $\mathrm{L^{-1}}$) was prepared by dissolving 0.011 g in 500 µL of acetonitrile and then the volume was completed up to 50.0 mL with ultrapure water. The 0.08 mol $\mathrm{L^{-1}}$ Britton–Robinson buffer solution was prepared mixing acetic acid, boric acid, and phosphoric acid. The pH was adjusted by addition of sodium hydroxide of 1.0 mol L^{-1}.

Water samples were collected from rivers near the city of Araraquara (SP, Brazil), namely: Chibarro, Jacaré-Pepira, and Jacaré-Guaçu.

Electrochemical measurements

The electrochemical measurements were performed using a PalmSense potentiostat (Palm Instruments). The potentiostat was connected with a conventional electrochemical cell containing three electrodes: an Ag|AgCl (KCl_{sat}) as the reference electrode (potentials throughout the manuscript are all versus Ag|AgCl), a platinum coil as the counter electrode, and the modified carbon paste electrode as the working electrode. Between measurements, the working electrode surface was renewed by simple polishing on a clean sheet of paper. Measurements were performed without any oxygen degasification with nitrogen.

Preparation of modified carbon paste electrode

The working electrode was composed of a glass tube containing an embedded platinum wire in contact with a 5-mm-diameter platinum disk placed at a depth of 1 mm from one end of the tube, providing a cavity suitable for the incorporation of carbon paste, the working electrode's area was 0.196 cm^2.

The carbon paste was prepared by mixing 85 mg graphite and 15 mg of cobalt phthalocyanine with 0.1 mol L^{-1} phosphate buffer (pH 7.0). The material was carefully homogenized with a stainless steel spatula and then left to dry at room temperature. Mineral oil (Nujol) was added to the dried material to obtain the carbon paste. The prepared paste was then packed into the cavity of working electrode and polished in clear paper for electrochemical measurements.

Results and discussion

Initially, the electrochemical behavior of metribuzin (in 0.08 mol L^{-1} Britton–Robinson buffer, pH 2.0) was studied with the developed sensor by cyclic voltammetry in the potential range from −0.8 to +0.8 V with a scan rate of 50 mV s^{-1}. As is seen in Figure 1a, in the presence of metribuzin (4.8×10^{-5} mol L^{-1}), there was an increase in the cathodic current starting at −250 mV due to the reduction of metribuzin on the sensor surface. The effect of cobalt phthalocyanine can be better visualized when compared with a sensor not using the catalyst (Figure 1b). There is a subtle yet noticeable difference. The absence of an anodic current attributes irreversibility to the electrochemical reaction.

The electrochemical mechanism of metribuzin reduction using the developed sensor was studied by varying the scan rate of cyclic voltammetry from 30 to 200 mV s^{-1} (Figure 2). In this range, the linear dependence of the cathodic current as a function of square root of the scan rate (inlay of Figure 2) indicates that the mass transport of metribuzin on the sensor surface is controlled by diffusion. If it was mostly controlled by adsorption, the peak current would be proportional to scan rate and not to the square of the scan rate (Batchelor-McAuley et al. 2010; Gonçalves et al. 2010; Tavares et al. 2013). It was also possible to calculate the diffusion coefficient (D_0) using the Randle–Ševčík equation (Randles 1948; Ševčík 1948) [Eq. (1)] adapted for irreversible

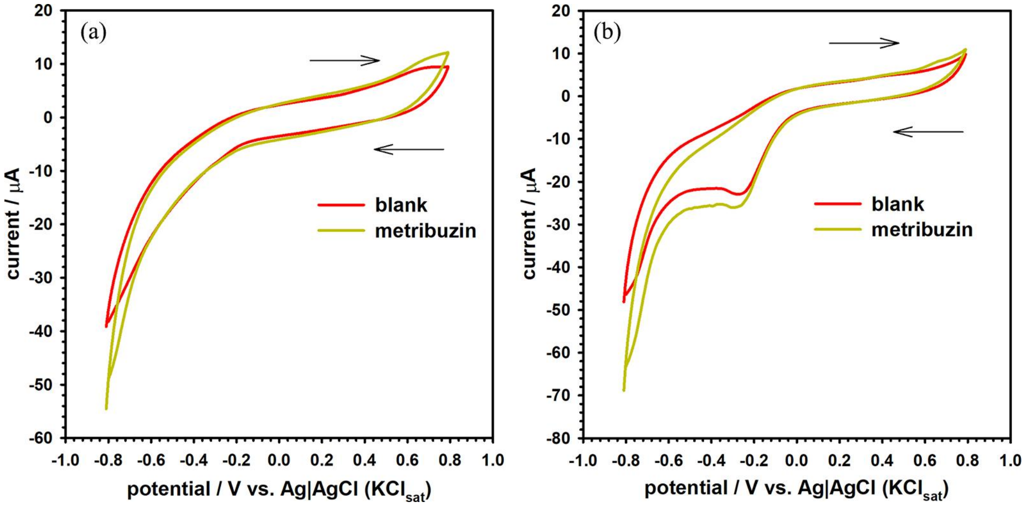

Figure 1. Cyclic voltammograms obtained in the absence and presence of metribuzin, 4.8×10^{-5} mol L^{-1} in Britton–Robinson buffer (0.1 mol L^{-1}, pH 2.0), with a carbon paste electrode in the (a) absence and (b) presence of cobalt phthalocyanine at a scan rate of 50 mV s^{-1}.

processes (Zahn et al. 2012):

$$i_p = 0.4961nFAC\sqrt{\frac{\alpha nFD_0}{RT}}\nu^{0.5} \tag{1}$$

In this equation, there is a linear relationship between the peak current (i_p) in A and the square root of the scan rate (ν) in V$^{0.5}$ s$^{-0.5}$, C is the concentration of metribuzin in mol cm^{-3} (48.0×10^{-9} mol cm^{-3}), n is the number of electrons, F is the Faraday constant (96,485 s A mol^{-1}), R is the ideal gas constant (8.314 A V s K^{-1} mol^{-1}), α is the transfer

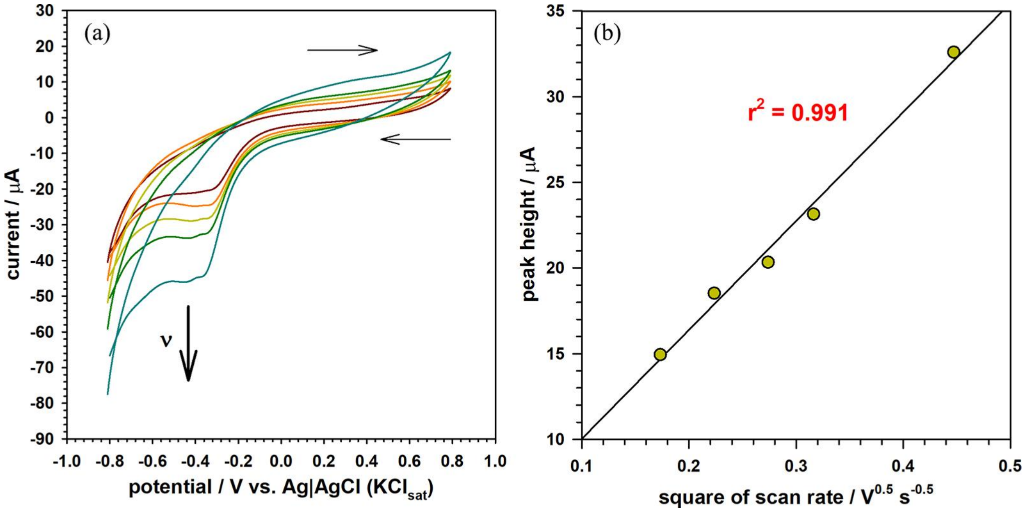

Figure 2. (a) Cyclic voltammograms of metribuzin, 4.8×10^{-5} mol L^{-1}, with scan rates of 30, 50, 75, 100, and 200 mV s^{-1} and (b) peak current as a function of the square root of the scan rate.

coefficient (calculated as 0.20), and A is the electrode area in cm^2 (ca. $0.196\,\mathrm{cm}^2$). The obtained D_0 was $(59.1 \pm 16.4) \times 10^{-6}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$, this calculation was performed with two electrons based on the work of Skopalová et al. (2001) who studied the metribuzin reduction in mercury electrodes.

A theoretical value for the D_0 (in $\mathrm{cm}^2\,\mathrm{s}^{-1}$) was calculated using the Wilke and Chang (1955) equation (2):

$$D_0 = \frac{7.4 \times 10^{-8} T \sqrt{\varphi M_{\mathrm{solvent}}}}{\mu V_{\mathrm{m}}^{0.6}} \tag{2}$$

where T is the temperature in K (room temperature of 298 K), φ is the association factor for the solvent [in the case of water it is 2.6 (Wilke and Chang 1955)], M_{solvent} is the molecular mass of the solvent in $\mathrm{g\,mol}^{-1}$ (water: $18.015\,\mathrm{g\,mol}^{-1}$), μ is the viscosity of the solvent in $\mathrm{mPa \cdot s}$ (the same as $\mathrm{g\,m}^{-1}\,\mathrm{s}^{-1}$, $0.891\,\mathrm{mPa \cdot s}$), and V_{m} is the molar volume of the solute at its boiling point in $\mathrm{cm}^3\,\mathrm{mol}^{-1}$ (water: $163.58\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$). The obtained theoretical D_0 was $(8.0 \pm 0.8) \times 10^{-6}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$. The few studies found by authors in the literature publish values from 0.1 to $4.5 \times 10^{-6}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ in water with various contents of soil (Scott and Paetzold 1978), which means the determined value in this work is within the reasonably expected limit.

The catalytic properties of the sensor were evaluated using high metribuzin concentrations which produced a hyperbolic profile (current as a function of the metribuzin concentration, data not shown) characteristic of biomimetic sensors, where it occurs saturation of the active sites. Although this sensor does not make use of any enzyme, one can apply the Michaelis–Menten model since mimicking systems are being studied (Gayathri and Kumar 2013; Wong and Sotomayor 2013). To estimate the apparent Michaelis–Menten constant ($K_{\mathrm{M}}^{\mathrm{ap}}$), a double-reciprocal graph was plotted (Wong and Sotomayor 2013; Gonçalves et al. 2014; Prado et al. 2015) (Figure 3):

$$\frac{1}{\Delta i} = \frac{K_{\mathrm{M}}^{\mathrm{ap}}}{\Delta i_{\mathrm{max}}[MTZ]} + \frac{1}{\Delta i_{\mathrm{max}}} \tag{3}$$

The obtained value for $K_{\mathrm{M}}^{\mathrm{ap}}$ was $(7.4 \pm 0.6) \times 10^{-6}\,\mathrm{mol\,L}^{-1}$, this value is within expected ranges for biomimetic sensors using electron mediators (Nassef, Radi, and O'Sullivan 2006; Apetrei et al. 2012; Wong and Sotomayor 2013; Wong et al. 2015).

The proposed mechanism for the biomimetic sensor is based on the metribuzin reduction in acidic medium promoting the oxidation of two molecules of cobalt phthalocyanine; then, at the electrode surface, each cobalt phthalocyanine molecule is reduced by one electron arising from the electrode creating a measurable current (Figure 4) (Zagal et al. 1999; Griveau et al. 2003; Milczarek and Ciszewski 2005).

The optimization of the sensor response was performed by amperometry. The pH was studied between 2.0 and 8.5 (using a $0.08\,\mathrm{mol\,L}^{-1}$ Britton–Robinson buffer solution) and the cobalt phthalocyanine composition between 7 and 20% (m/m). The best response was obtained with pH 2.0, which is compatible with the literature values (Lima et al. 2009; Janíková et al. 2016) and applying a potential of −690 mV and cobalt phthalocyanine composition of 15% (m/m) (data not shown). The response of the sensor under optimized conditions is shown in Figure 5, and the corresponding analytical curve (inlay of Figure 5) showed a linear response to metribuzin with concentrations up to $2.0 \times 10^{-4}\,\mathrm{mol\,L}^{-1}$, a sensitivity of $(15 \pm 4) \times 10^4\,\mu\mathrm{A\,L\,mol}^{-1}$, r^2 greater than 0.999, and limits of detection

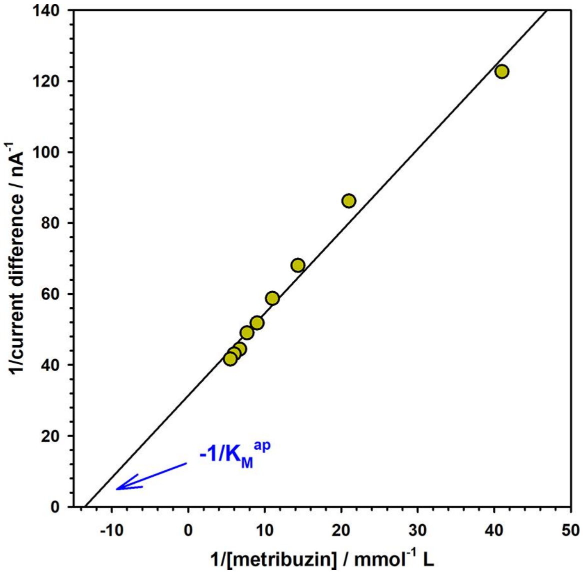

Figure 3. Michaelis–Menten double-reciprocal plot in the optimized conditions to obtain the apparent Michaelis–Menten constant (K_M^{ap}), current differences were obtained at −690 mV in Britton–Robinson buffer (0.1 mol L^{-1}, pH 2.0).

and quantification of 5.30×10^{-6} (1.14 mg L^{-1}) and 17.7×10^{-6} mol L^{-1} (3.79 mg L^{-1}), respectively. The limit of detection and quantification were calculated as 3 and 10 times the standard deviation of the intercept/slope, respectively.

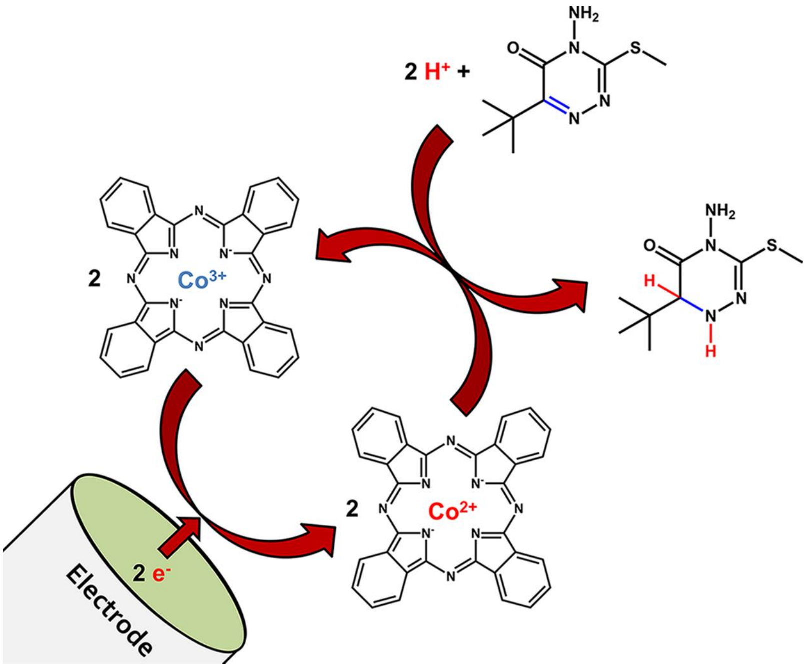

Figure 4. Scheme for the proposed electrochemical mechanism.

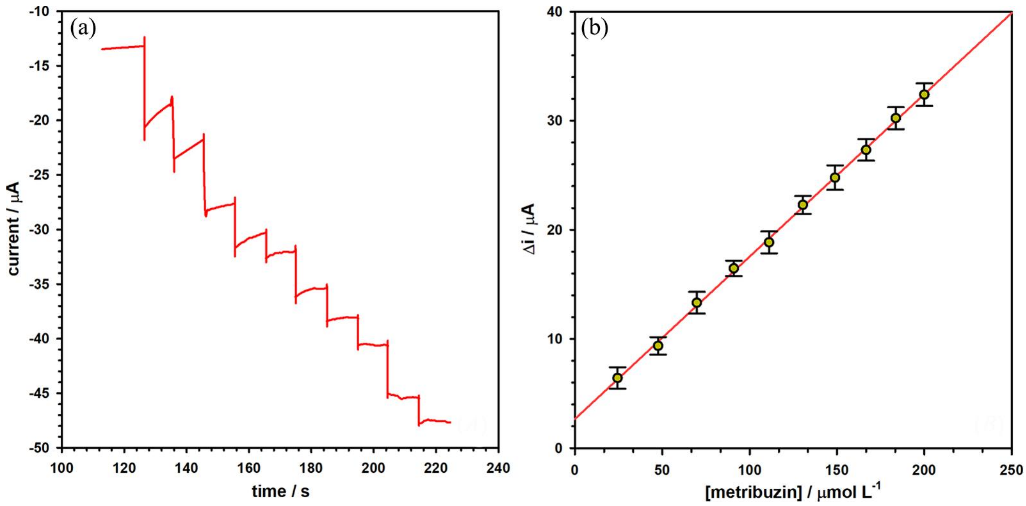

Figure 5. (a) Typical amperogram measurements were performed at −690 mV in Britton–Robinson buffer (0.1 mol L^{-1}, pH 2.0) and (b) analytical curve at concentrations of 2.44, 4.76, 6.98, 9.09, 11.1, 13.0, 14.9, 16.7, 18.4, and 20.0 × 10^{-5} mol L^{-1} metribuzin.

The repeatability of biomimetic sensor was verified by the values obtained by the average of relative standard deviation for the sensitivity of five analytical curves obtained in five different days (interday) and on the same day (intraday), respectively. The interday repeatability was 4.5% and the intraday repeatability was 3.5%. This also showed that the sensor signal was maintained above 95% during 5 days, showing a suitable sensor's period of life. Studies concerning the selectivity of the sensor were performed by comparing the metribuzin amperometric response to six other pesticides (carbendazim, carbofuran, chlorpyrifos, 3-(3,4-dichlorophenyl)-1,1-dimethylurea, hexazinone, 2,4-dichlorophenoxyacetic acid, all in at concentrations of 1.0×10^{-3} mol L^{-1} in 1% acetonitrile in water) with an applied potential of −690 mV. The selectivity of the proposed sensor was confirmed since only metribuzin showed an electrochemical response different from blank (data not shown).

Recovery studies were performed with water samples from local river water spiked with 2.40×10^{-5} mol L^{-1} of metribuzin by amperometry at −690 mV. The samples were filtered to remove any solid residues and mixed with buffer in a 1:1 (v/v) ratio. As is seen in Table 1, results indicate recoveries close to 100%. In comparison with other sensors in the literature, the developed sensor has the advantage of being mercury-free (Ludvík et al. 1998; Skopalová et al. 2001; Janíková et al. 2016) and holds similar sensitivity to other carbon-based electrodes (Lima et al. 2009; Moreno et al. 2009; Stojanovic et al. 2016).

Table 1. Recovery studies for metribuzin performed in samples from three rivers. Measurements were performed in triplicate.

River	Added metribuzin (10^{-5} mol L^{-1})	Determined metribuzin (10^{-5} mol L^{-1})	Recovery (%)
Jacaré Pepira	2.40	2.38 ± 0.07	99 ± 3
Jacaré Guaçu	2.40	2.35 ± 0.08	98 ± 4
Chibarro	2.40	2.23 ± 0.07	93 ± 3

Conclusion

This work described the development of a sensitive and selective amperometric methodology for the determination of metribuzin using a modified carbon paste electrode with a cobalt phthalocyanine. The obtained results suggest that the cobalt phthalocyanine complex acts as convenient substitute for natural proteins being a biomimetic catalyst in the two-electron electrochemical reduction of metribuzin. The sensor showed suitable analytical parameters and was satisfactorily applied in river water samples.

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ORCID

Luís Moreira Gonçalves http://orcid.org/0000-0002-4290-656X

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