ELECTROCHEMICAL BIOSENSOR BASED ON OPTIMIZED BIOCOMPOSITES FOR ORGANOPHOSPHORUS AND CARBAMATES PESTICIDES DETECTION

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Supplementary information

S1. Influence of the enzyme loading on the electrochemical parameters

In order to evaluate the enzyme percentage influence on the biocomposites, it has been performed the characterization by EIS of biocomposites which incorporates 0.24% of AChE (w/w) into the matrix. This study was done for the optimized biocomposite compositions (16% and 17%). On Table S1 are listed the electrochemical impedance parameters of these compositions and they are compared to the same graphite compositions with 0.12% of AChE (w/w). As it can be observed, there are non-

significance differences between R_Ω and R_{ct} values when the amount of AChE increases from 0.12% to 0.24%. Regarding to C_{dl} value, an increase of the enzyme amount produces higher values of this parameter. So, in order to guarantee the optimal signal-to-noise ratio, the lowest enzyme charge is enough from the electrochemical point of view.

Table S1. Comparison of the electrochemical parameters obtained by electrochemical impedance spectroscopy (R_Ω, R_{ct} and C_{dl}) for the biocomposites with 16% and 17% of graphite loading and 0.12% of AChE and 0.24% of AChE.

Electrodes (% graphite)	% AChE (w/w)	R_Ω (Ω)	R_{ct} (Ω)	C_{dl} (F)
16%	0.12%	1131	1381	$2.53 \cdot 10^{-5}$
	0.24%	1146	1259	$2.91 \cdot 10^{-5}$
17%	0.12%	837	874	$2.49 \cdot 10^{-5}$
	0.24%	1106	973	$2.81 \cdot 10^{-5}$

S2. Linear Voltammetry measurements

The linear voltammograms depicted in Fig. S1 show the characteristic shoulder of the oxidation curve of the analyte. The working potential should lie in the range where this shoulder appears. The result obtained in this study shows that the plateau was obtained at 700 mV (*vs.* Ag/AgCl). So, this potential was chosen for the amperometric measurements.

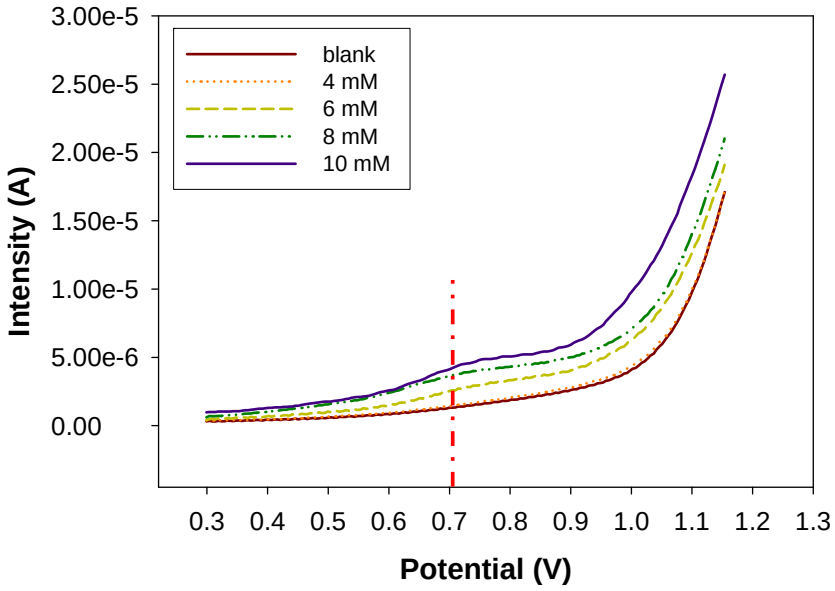


Figure S1. Linear sweep voltammetry response to acetylthiocholine from 0 to 10 mM in phosphate buffer solution (PBS 0.1 M and pH = 7.0). Scan rate 10 mV/s.

S3. Electroanalytical evaluation with acethylthiocholine

In order to evaluate the electroanalytical properties of biosensor response, linear range, detection limit and sensitivity were determined from the calibration plots. These parameters were evaluated by triplicate for the biocomposites with optimal electrochemical behaviour (16% and 17% of graphite loading) and compared to those obtained with 20% of graphite loading or standard composition. The results of the calibration plots are listed in Table S2.

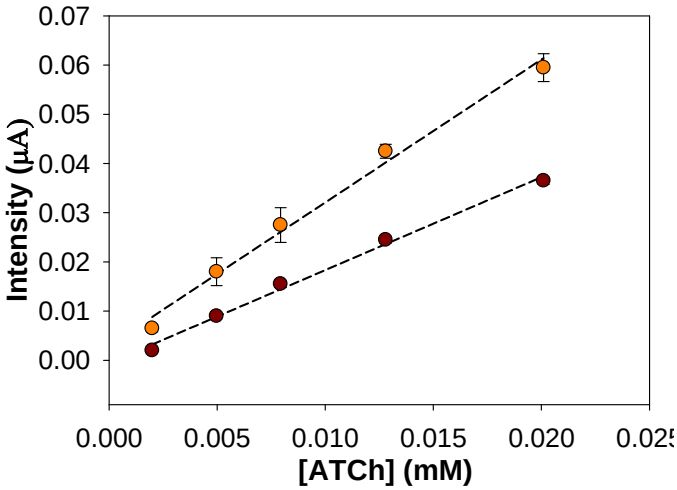
Table S2. The calibration parameters for 20%, 17% and 16% of graphite biocomposite electrode with 0.12% of AChE using amperometric measurements with acetylthiocholine (ATCh) as analyte and PBS 0.1 M at pH = 7.0 as background electrolyte ([a]n = 3, 95% confidence level).

% Graphite	Sensitivity[a] ($\mu A \cdot L \cdot mmol^{-1}$) (RSD 95%)	Limit of detection ($mmol \cdot L^{-1}$)	Linear range ($mmol \cdot L^{-1}$)
16%	1.89±0.04 (2%)	0.006±0.001	0.006-0.020
17%	2.9±0.2 (6%)	0.0013±0.0002	0.0013-0.020
20%	5.6±0.7 (13%)	0.019±0.002	0.019-0.057

As it can be observed, the sensitivity increases when the amount of graphite increases in the biocomposites. However, when it is compared the limit of detection achieved for each biocomposite electrode composition, the detection limit achieved for the biocomposite with 20% of graphite loading is 0.5-1.2 decade of concentration higher, compared with the biocomposites with 16%-17% of graphite loading, respectively. The limit of detection for biocomposites with 16% were 0.006±*0.001* $mmol \cdot L^{-1}$ and with 17% were 0.0013±*0.0002* $mmol \cdot L^{-1}$. For biocomposites with 20% of graphite loading the limit of detection achieved was 0.019±*0.002* $mmol \cdot L^{-1}$. For the 16% of graphite loading electrode (Figure S2(A)), the linear range achieved was from 0.006 mM to 0.020 mM of ATCh and for the 17% of graphite loading electrode was between 0.0013 mM and 0.020 mM. The equation plots for the linear range of both compositions is: $I_{16\%}$ (μA) = 1.89*(±0.08)*[ATCh] – 0.001*(±0.001)*; $r^2 = 0.994$ (n=5) and $I_{17\%}$ (μA) = 2.9*(±0.2)*[ATCh] + 0.003*(±0.002)*; $r^2 = 0.990$ (n=5), respectively. However, for the biocomposite with 20% of graphite loading (Fig. S2(B)), the linear range achieved was from 0.010 mM to 0.057 mM. The equation plot corresponding to the linear range in this case is: $I_{20\%}$ (μA) = 5.6*(±0.3)*[ATCh] + 0.01*(±0.01)*; $r^2 = 0.993$ (n=4). In spite of the loss of sensitivity, the

biocomposites included in the optimum composition range, present better analytical signal stability and signal-noise ratio compared to biosensor with 20% of graphite loading. The results showed that a previous electrochemical characterization and optimization of the biocomposite composition allow improving the final electroanalytical biosensor properties and obtaining more sensitive biosensors from the detection limit point of view.

(A)



(B)

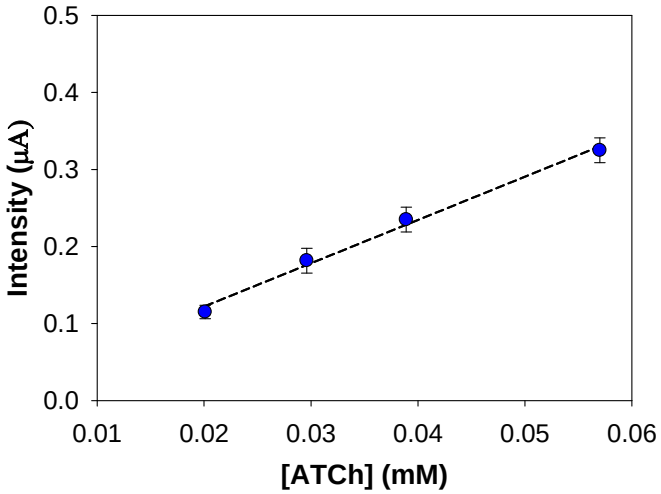


Figure S2. Linear response for biosensors with (A) 16% and 17% of graphite and (B) 20% of graphite loading. Measurements were carried out in 0.1 M phosphate solution at pH = 7.0 and 0.1 M KCl. EAPP = 700 mV.