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The Use of a PANI/*Caraia*-Gum Composite in Electrochemical Sensor for Herbicide Quantifications

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Abstract – The electrochemical behavior of the herbicide paraquat was studied for an electrode modified with a PANI/*Caraia*-Gum composite by means of square wave voltammetry. It was obtained an analytical curve in the range of $1x10^{-7}$ to $3x10^{-4}$ $molL^{-1}$ using the following parameters: frequency of 20 Hz, wave amplitude of 80 mV, scan increment of 5 mV, an acetate buffer (pH=10) as electrolyte solution and paraquat pre-concentration of 4 minutes at the open circuit potential. The detection limit obtained was $2x10^{-6}$ $molL^{-1}$. The results showed that the modifiers act synergistically with each other, forming a composite with properties not observed when both modifiers are separated in the respective electrodes.

The paraquat or 1,1 '-dimethyl-4, 4'-bipiridina-dichloride is a contact herbicide, non-selective and is an important target molecule due to its the large volume of commercialization and due to its specific toxicity (highly toxic). It acts in the body causing oxidative stress by the formation of free radicals [1].

The application of electrochemical techniques for detection and quantification of paraquat is recent, but it has been widely disseminated. Usually, when using electrochemical techniques the preparation of samples is not required, the cost of analysis and tools is small and rapid and sensitive analysis could be performed. Besides the technical advantages of electrochemical techniques the use of square wave voltammetry (SWV), minimizes the capacitive current increasing the sensitivity of the analysis. For these reasons the electrochemical quantification of paraquat has been described in the literature using several surface electrodes, among them it could be mentioned the chemically modified electrodes (QMEs) [2]. The use of polyaniline (PANI), as modifier of electrodes is interesting because it exhibits chemical stability in environmental conditions, it has a simple processability, polymerization and doping, low cost and improves the selectivity of the electrode. In this context, this work aims at the application of an electrode modified with a composite formed by polyaniline and a natural polysaccharide, *Caria*-Gum, in the determination of paraquat.

The modified electrodes of the composite polyaniline and *Caria*-Gum (E-PANIG) were prepared by mixing by maceration of graphite (Fluka ®), PANI and the Gum at a ratio of 38:1:1, respectively. Binder was used as the mineral oil Nujol ®. The mixture obtained by this maceration was compressed into a cylindrical electrode of area 0.07 cm^2 and volume of 0.014 cm^3. The electrochemical measurements of cyclic voltammetry and square wave voltammetry (SWV) were performed with an electrode of the $Ag/AgCl_{sat}$ as a reference, a Pt electrode as the counter-electrode, and the E-PANIG as working electrode. The used electrolyte solution was an acetic acid/sodium acetate (AcOH/Ac-) buffer. The measurements were performed at a Potentiostat/Galvanostat from PalmSens. The optimization of the parameters followed a systematic study of the electrochemical response as a function of peak current. The potential range of work varied with the redox potential of paraquat.

The optimization of analytical parameters for the SWV in a solution with $1x10^{-4}$ mol L^{-1} of paraquat indicated a higher current peak for the frequency of 20 Hz, wave amplitude of 80 mV, scan increment of 5 mV and electrolyte solution with pH = 10.0. It was also observed a better response for a pre-concentration of paraquat for 4 minutes in open circuit potential. The modification of the electrode with the composite PANI/*Caria*-Gum resulted in the development of an electrode that provide a good stability, it is not expensive, it is versatile (it could renewed the electrodic surface) and giving high current relating to redox process of paraquat. The detection limit obtained ($2x10^{-6}$ mol L^{-1} or 0.48 mg L^{-1}), permit the analysis on samples of food and watercourses. It should be noted that the proposed electrode was more sensitive than other electrodic materials found in the literature[3]

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