DEVELOPMENT OF AMPEROMETRIC SENSORS FOR DETECTION OF CYHALOTHRIN AND PROPANIL

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ABSTRACT

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An electrochemical oxidation of cyhalothrin, 3-(2-chloro-3,3,3-trifluro-1 propenyl)-2,2-dimethylcyclopropane carboxilyic acid cyano(3-phenoxyphenyl) methyl ester which is an active ingredient of Grenade 5 EC insecticide was carried out at a bare glassy carbon electrode in an aqueous solution of 0.1 mol dm^{-3} NaCl using cyclic voltammetry and amperometry techniques.

Cyhalothrin is a synthetic pyrethroid and the acute oral LD_{50} value for male rats is 243 mg/kg. The solubility of cyhalothrin in water at 25° C is 0.004 mg/l. It is used to control *haematobia* irritants on cattle and lice.

Preliminary electrochemical characterizations were conducted by cyclic voltammetry and which indicated that the oxidation of cyhalothrin occurred at + 0.72 V vs. SCE, and it is a completely irreversible system. The amperometric detection of cyhalothrin

at bare glassy carbon electrode was interfered with noise signals at the optimum potential + 0.80 V vs. SCE. The noisy signals could be successfully eliminated by using a thin coating by dipping with electro-inactive coating of stearic acid on top of the glassy carbon electrode surface at optimized potential + 0.80 V vs. SCE, and it results in the reduction of the instrumental responses. Sensitivity of the sensor was estimated to be 0.0592 A mol^{-1} dm^3 using calibration plot and, the linear dynamic range was found from 1.75 x 10^{-6} to 1.40 x 10^{-5} mol dm^{-3}. The life time of the sensor was found for at least ten days. The response time (t_{90}) was measured as 5.4 s. The sensor responded for very low concentration with the minimum detection limit of 1.75 x 10^{-7} mol dm^{-3} when signal to noise ratio is 3 .The coefficient of variation (CV) was 1.72%.

Propanil (3,4-DPA), N- (3,4-dichlorophanyl) propanamide is a contact herbicide used in post emergence control of grasses (Echinochloa) and broad leaf weeds in rice and potato fields. It is toxic to most leaf plants (inhibit photosynthesis) to most leaf plants and non- toxic to tolerance plants as such plant contain the enzyme aryl acylamidase which can metabolize propanil into 3,4-dichloroaniline (3,4-DCA) and propionic acid. 3,4-DCA is the primary residue of the propanil which could exist in the environment through subsequent pathways and more toxic than propanil. As a result of the application of propanil, its residues can get into the environment, which remain in the agricultural commodities and the food stuffs. Furthermore, propanil is stable only in

the pH range of 7-10 and it degrades under extreme pH conditions. In this study we specifically aimed at the residue analysis of propanil both in the commercial samples and as a residue in the rise grains through cost effective electroanalytical methods. The cyclic voltammetry is a basic electroanalytical technique and is used to study the electrochemical behavior of the propanil residues. Subsequently it was possible to develop the amperometric sensor to detect 3,4-DCA as the popanil residue.

The steady-state amperometric measurements were obtained at stearic acid modified glassy carbon electrode in 0.1 mol dm^{-3} phosphate buffer (pH = 7) at the optimized potential at + 0.70 V vs. SCE and, the amperometric calibration curves were obtained for 3,4-DCA. The linear dynamic range for the sensor was from 1.0×10^{-4} to 5.3×10^{-3} mol dm^{-3} and the sensitivity was obtained to be 0.005 A dm^3 mol^{-1}. The minimum detection limit of the sensor was 2.0×10^{-5} mol dm^{-3} at signal to noise ratio is 3.