DEVELOPMENT OF ELECTROANALYTICAL DETECTION SCHEMES FOR SOME SELECTED PESTICIDES

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Pesticides are considered as priority environmental pollutants and health hazards. Detection of pesticides by reliable means would therefore be an important early step in control of environmental pollution, biosphere conservation, and avoiding most poisoning and other health problems. Development of alternative, simple methodologies has drawn much attention due to drawbacks of currently used chromatographic and spectrometric methods. In this study, development of alternative methods for the detection of pesticides, based on electrochemical techniques, in particular cyclic voltammetry and amperometry, was attempted. Different types of electrodes were used with emphasis on the electroactivity of pesticides under the influence of applied potentials.

The dithiocarbamate fungicide, thiram was found to be electroactive at unmodified glassy carbon electrodes in aqueous medium. The electrochemical behavior of this compound was extensively studied using cyclic voltammetric experiments. The amperometric method, which was developed under optimized conditions; applied potential of +0.50 V and in the supporting electrolyte of pH 10 borate buffer, produced reproducible responses with a minimum detection limit of 1.0×10^{-8} mol dm^{-3}, based on the signal to noise ratio (S/N) of 3. This method was applied to quantify thiram in water leaches of a model soil bed, and in an agricultural bean seeds sample.

Some electrode processes are kinetically disfavored towards oxidation and/ or reduction due to high over-potentials associated. This kinetic barrier could successfully overcome by the selection of a suitable electrocatalytic scheme. Electrocatalysts are capable of catalyzing electrochemical processes, as they decrease the overpotential for oxidation/reduction. Use of both chemical and biological catalysts for the detection of pesticides is reported here.

A voltammetric biosensor containing apple tissue (10% w/w) as the biological component was able to detect thiram at levels as low as 1.0×10^{-6} mol dm^{-3}. During this process, the inhibition of the enzyme polyphenol oxidase present in apple tissue by thiram was observed. The response of the biosensor was optimum for a period of 2-3 weeks.

Transition metal oxides with variable oxidation states were found to be excellent electrocatalysts for many pesticides, if conditions such as electrolyte, working potential/potential range and the catalytic loading were optimized. The phenoxy acid herbicide, MCPA (4-chloro-2-methylphenoxyacetic acid), was detected at a catalytic carbon paste electrode, containing MnO_2 black powder (10% w/w). The amperometric sensor produced a minimum detection limit of 9.7×10^{-7} mol dm^{-3}, based on S/N = 3. This method was successfully applied to quantify the active ingredient in an old commercial formulation. The sensor showed a satisfactory lifetime of about 8-10 weeks. Cyclic voltammetric investigation revealed the possible interaction between Mn^{2+} and MCPA, according to the variations of solution electrochemistry of Mn^{2+} ions.

Another organochlorine herbicide, propanil, was determined at a carbon paste electrode, constructed using 10% (w/w) CuO, with a minimum detection limit of 6.0×10^{-8} mol dm^{-3} (S/N = 3) amperometrically. The sensor response was optimum over a period of 6-7 weeks.

Metalloporphyrins are another group of electrocatalysts, used in the electrochemical reduction of organohalogens. The metallic electrodes; Pt and Au, together with glassy carbon electrodes, modified with 5,10,15,20-tetraphenylporphyrinatoiron(III) chloride [Fe(III)TPPCl] catalyzed the reduction of some organochlorine pesticides. In this case it was found that the detection was more sensitive with metallic electrodes.

Glassy carbon electrodes modified with Fe(III)TPPCl were used for the detection of propanil in water, leached out from a model rice bed. Simple gravity column preconcentration could enhance the sensitivity of electrochemical detection. Such studies indicate the practical applicability of electroanalytical techniques in real sample analysis.