SUMMARY

Pesticide pollution has become a threatening problem to the environment. Detection of pesticides by reliable means would therefore be ~~an~~ important step in pollution control. Development of alternative, simple methodologies has taken attraction due to drawbacks of current methods. In this study, development of electroanalytical, and chromatographic was attempted with emphasis on the use of electrochemical methods for mechanistic studies.

Thiram, a dithiocarbamate fungicide, was found to be electroactive on glassy carbon electrodes in aqueous medium. The amperometric method 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 leached through a model soil bed, and in an agricultural beans seed sample (A1, A9, A11, A13).

Use of both chemical and biological catalysts for the detection of pesticides is also investigated. In one application, a voltammetric biosensor containing apple tissue (10%) as the biological component was able to detect thiram at 1.0×10^{-6} mol dm^{-3} level. Transition metal oxides are also found to be excellent electrocatalysts for many pesticides, if conditions are optimized. The phenoxy acid herbicide, MCPA, was detected on a catalytic carbon paste electrode, containing MnO_2 black powder (10%). 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 of MCPA. Cyclic voltammetric investigation revealed the possible interaction between manganese and MCPA (A2, A5, A15).

Another organochlorine herbicide, propanil (a widely used herbicide on rice and potatoes), was amperometrically determined at a carbon paste electrode, constructed using 10% CuO, with a minimum detection limit of 6.0×10^{-8} mol dm^{-3} (S/N = 3) (A8, A14).

Metalloprphyrins are another group of electrocatalysts. The metallic electrodes (Pt and Au), and glassy carbon electrodes, modified with 5,10,15,20-tetraphenylporphyrinato iron(III) chloride [Fe(III)TPPCl] catalyzed the reduction of some pesticides, including propanil and glyphosate (A4, A6). Glassy carbon electrodes modified with Fe(III)TPPCl were used for the detection of propanil in water, leached out from a model rice cultivation. Such studies indicate the practical applicability of electroanalytical techniques in real sample analysis (A10).

Residual analysis of propanil has been successfully conducted using gas chromatography with the electron capture detector. Propanil is fairly stable in aqueous medium between pH 4 and pH 7 for a period of ten weeks. However, in strong acidic medium (pH = 1), it undergoes rapid degradation, while in strong basic medium (pH = 13), its degradation follows first order kinetics with an apparent rate constant of 9.2×10^{-8} s^{-1}. Adsorption characteristics of propanil is also pH dependent, and it is irreversibly adsorbed onto glassy carbon surfaces in basic medium. Fresh solutions of 3,4-dichloroaniline mimic the behavior of propanil after degradation (A3, A12).

The electroactivity of propanil strongly depends on the solution pH and the time of solution preparation. Comparison of the electrochemical behavior of fresh solutions of 3,4-dichloroaniline and that of propanil prepared at different time periods suggest that the principal degradation product of propanil is 3,4-dichloroaniline. Although this degradation process is very rapid at pH = 13, it would probably undergo slow degradation under environmental conditions. Such studies promote the use of economical and simple electroanalytical methods for investigation of the fate of pesticides in the environment, and to design models for pesticide degradation pathways. Gas chromatographic and spectroscopic methods were also used to investigate the degradation patterns of pesticides (glyphosate and propanil) and levels of them in soil (A7, A16, A17).

Cyclic voltammetric studies of the fungicide, Cobox (main constituent is copper oxychloride) at bare glassy carbon electrode indicated two oxidation and two reduction peaks. The scan rate dependence of the peak current of the Cu(II)/Cu(I) couple suggests that the transfer of Cu(II) species toward the electrode surface is mainly due to diffusion. Further, amperometric experiments conducted at the optimum potential of operation (–0.15 V vs. SCE) produced calibration curves with a linear dynamic range from 5×10^{-5} mol dm^{-3} to 1×10^{-4} mol dm^{-3}.

Application of the cyclic voltammetric methodology for tea leaves, on which the recommended dosage of Cobox was sprayed, followed by digestion, produced concentration-dependent electrochemical responses. Nevertheless, broad and ill-defined peaks were resulted in, which would probably be due to interference effects associated with organic substances present in tea leaves. Such observations however suggest the potential utility of glassy carbon electrodes for the detection of Cu species in tea leaves.