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**ELECTROCHEMICAL, GAS CHROMATOGRAPHIC AND
SPECTROSCOPIC METHODS FOR INVESTIGATION OF
THE FATE OF SOME COMMONLY USED
PESTICIDES IN SRI LANKA**

A THESIS PRESENTED BY

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AND SPECTROSCOPIC METHODS FOR INVESTIGATION OF THE
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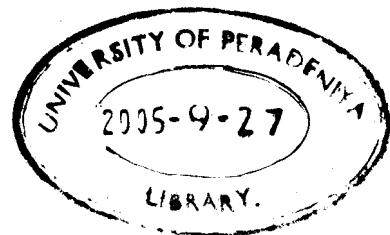
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ABSTRACT

Pollution of our environment due to heavy use of pesticides is of significant concern. Therefore, electrochemical, gas chromatographic and spectroscopic methods were used to investigate the fate of some commonly used pesticides in Sri Lanka. Among these analytical methods, electrochemical methods are generally inexpensive and easy to perform although some skills are necessary. Consequently, electroanalytical methods have been attractive in recent years for quantitative and qualitative analysis, and for mechanistic studies due to their unique advantages over traditional methods.

Propanil is a common and widely applicable herbicide that is extensively used in Sri Lanka on rice and potatoes. Gas chromatography and colorimetry are able to quantitatively determine its presence at 10^{-3} mol dm⁻³ concentration levels in soil, plant and water. Residual analysis of propanil, in the form of its principal degraded product, 3,4-dichloroaniline, has been successfully conducted using gas chromatography with the electron capture detector.

Propanil is fairly stable in mixed water/ethanol medium between pH = 4 and pH = 7 for a period of ten weeks. However, in strong acidic medium (pH = 1), it undergoes slow degradation of pseudo first order with an apparent rate constant of 9.2×10^{-8} s⁻¹, while in strong basic medium (pH = 13), its degradation is very fast. Adsorption of propanil onto glassy carbon surfaces is pH dependent, and is irreversible in basic medium. Fresh solutions of 3,4-dichloroaniline mimic the behavior of propanil after degradation.

Comparison of the electrochemical behavior of propanil and that of fresh solutions of 3,4-dichloroaniline, prepared at different time periods, and the variation of the voltammetric features of these two analytes at different pHs suggest that the principal degraded 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. Appearance of new peaks in gas

chromatographic and spectroscopic analysis confirmed the degradation of propanil in the environmental and laboratory prepared samples.

Copper oxychloride is a commonly used protective fungicide, used to control Anthracnose and Cercospora leaf spot on vegetables, chilies, tobacco and cloves; coffee rust; late blight and early blight on tomato and potatoes; blister blights on tea. It is available with the trade name of Recop, Helmoxy, Cobox, Cuprative and Fernacot. Electroanalytical methods provide an alternative approach for the determination of copper oxychloride in environmental samples, as they are often sensitive and selective with relatively lower cost of instrumentation.

Cyclic voltammetric studies of the cobox fungicide (main constituent is copper oxychloride) showed two oxidation and two reduction peaks at +0.29 V, +0.02 V, -0.12 V and -0.38 V, respectively at bare glassy carbon (GC) electrodes. These 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 surfaces is mainly due to diffusion. Further, amperometric experiments indicate that optimum potential of operation is -0.15 V vs. SCE. Amperometric calibration curves constructed at this potential produced a linear dynamic range from $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ to $1.0 \times 10^{-4} \text{ mol dm}^{-3}$.

Phosphate derivatives constitute an important class of pesticides. Among those, acephate, chlorpyrifos and glyphosate are the most common pesticides in Sri Lanka. Although organophosphates are subjected to a transformation in soil, with a half-life of over two months, persistence of its degraded products could be found even after three months. As a result, such degradation products may be distributed in the natural water and other natural resources. Therefore, the detection and characterization of such compounds are of environmental interest. As these pesticides are not active at bare electrodes, a typical situation for many commonly used pesticides, chemical modification of bare surfaces was conducted. Chemically modified electrodes often find applications where a substance of interest is not active at bare surfaces. Electrochemical techniques gives a characteristic voltammogram for a $5.0 \mu\text{mol dm}^{-3}$ glyphosate solution and an amperogram for a $0.175 \text{ mol dm}^{-3}$ stock solution, indicating that the method serves as a versatile tool for the detection of this compound at low concentrations.

During this research, attempts were also made to identify and characterize organophosphate pesticides in soil by using FT-IR and chromatographic techniques.

FT-IR spectra show significant variations in the bands in the OH-bending region, and in the OH-stretching region along with the Si-OH and Al-OH stretching modes, while the features appear in the chromatograms resemble the spectroscopic evidence except in the case of copper oxychloride.

Thus GC-FTIR techniques can be further developed for the identification and prediction of the degradation patterns of pesticides in soil in combination with other techniques.