

Electroanalytical chemistry of Bispiribac Sodium

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Bispiribac sodium (sodium 2,6-bis[(4,6dimethoxypyrimidin-2-yl)oxy]Benzoate) is a post emergence pyrimidinyl oxybenzoic acid herbicide used to control grasses, sedge and broad-leaved weeds, especially *Echinochloa* spp in directly seeded rice. In this research preliminary electrochemical characterization was done using cyclic voltammetry and steady state amperometry.

Cyclic voltammetric experiments of 0.1 mol dm⁻³ Bispiribac sodium in water of 0.1 mol dm⁻³ NaCl showed a reduction peak at potential -0.506 V vs. the saturated calomel. Scan rate dependency studies at constant concentration of Bispiribac sodium yielded a straight line when log of the peak current (log *i*_p) was plotted against the log of the scan rate (log ν) with the slope of 0.56. The above cyclic voltammetric characteristics indicate the irreversible electrochemistry of Bispiribac sodium and the slope of 0.56 for the plot of log *i*_p vs. log ν supports the fact that electrochemistry of the bispiribac sodium is diffusion controlled. pH dependency of Bispiribac sodium reduction was showed that at acidic medium (pH 3, 4) it forms a white precipitate and at higher pH's (greater than pH 7) it undergoes electrochemical reduction.

The optimum operational potential for the amperometric experiments was found to be -0.506 V with respect to saturated calomel reference electrode and amperometric measurements at the above potential showed there is a rapid reduction with the sequential addition of Bispiribac sodium at bare glassy carbon electrode.

ATR-FTIR (Attenuated Total Reflection Fourier Transformation Infrared Spectroscopy) analysis before and after the electrochemical reduction showed that the peak around 3300 cm⁻¹ is shifted to 3500cm⁻¹ after the electrochemical reduction and there are no significant changes in other functional groups. Therefore it can be suggested that the peak lies at 3500 cm⁻¹ is characteristic to the carboxylic group and it has reduced electrochemically.

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Investigation of interactions between heavy metal ions (Cd^{2+} , Pb^{2+}) and Thiram

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Abstract

Thiram (tetramethyl thiuramdisulfide) is a well-known dithiocarbamate fungicide widely used against a variety of plant pathogenic fungi. There have been enormous increases in usage of thiram over the past several decades. Usually in soil, the degraded metabolites of thiram are carbonyl sulfide (COS), carbon disulfide (CS_2), dithiocarbamate and metal-dimethyl dithiocarbamate. Thiram and metabolites of it remaining in the environment may interact with heavy metals and potential of heavy metals entering to the food chain may increase. This study provides UV-Visible, Fourier Transform Infrared (FTIR) spectroscopy, atomic absorption spectroscopy (AAS) and cyclic voltammetric evidences to support interactions between thiram and heavy metal ions (Cd^{2+} , Pb^{2+}). A water insoluble white complex forms between thiram and Pb^{2+} or Cd^{2+} . The UV- Visible spectra of pure thiram and metal complexes are very different to each other which indicate the change of electronic distribution of thiram due to complexation. When the pH of the media is 8 to 9, it favours the complexation between thiram and metal ions where 99.5% removal of lead and 20.5% removal of cadmium are obtained within 48 hours. The disappearance of thiram and lead peaks in cyclic voltammetric analysis of supernatant liquid of lead complexes shows that the thiram reacts with lead in a mole ratio of 1:1. FTIR studies confirm the bidentate nature of the chelation of the dithiocarbamate ligands with cadmium and lead. The efficient reaction in basic pHs and bidentate nature of the dithiocarbamate indicates that thiram undergoes base hydrolysis to form dithiocarbamate ions first and reacts with metal ions. High percent removal of lead when compared to cadmium from aqueous solution within a given period of time indicates that the rate of formation of metal complex is higher for lead than cadmium. Thiram dissolved in NaOH gives turbidity very quickly. This indicates that the reaction between metal ions and dithiocarbamate ion is very fast. But the formation of turbidity (metal complexes) within some hours indicates that the rate of degradation of thiram into dithiocarbamates depends on the heavy metal ions present in the environment. Furthermore, this study may provide some insight to thiram binding to heavy metal ions (Cd^{2+} , Pb^{2+}) in biological systems.

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