

INTERACTION OF MONOCHLOROPHOENOXYACETIC ACID (MCPA) WITH MANGANESE SPEICES

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Electrochemical detection of pesticides has drawn much attention during recent times owing to its advantages compared to other detection methodologies. However, MCPA (4-chloro-2-methylphenoxyacetic acid or monochlorophenoxyacetic acid), a commonly used organochloro-herbicide, is not electroactive within the working potential range of unmodified carbon paste electrodes in 0.1 mol dm⁻³ KCl, indicating the need for a catalyst to promote its electroactivity. As transition metals such as Mn species show different oxidation states in aqueous solution at different applied potentials, an appropriate oxidation state can be selected to catalyze MCPA through an electrocatalytic mechanism.

Cyclic voltammetry of MnSO₄ solutions (1.0 × 10⁻³ mol dm⁻³) in 0.1 mol dm⁻³ KCl shows many oxidation and reduction peaks due to various oxidation states of Mn species. More interestingly, a mixture of MCPA and MnSO₄, each at 1.0 × 10⁻³ mol dm⁻³ level, shows electrochemistry different from that of a MnSO₄ solution alone. The reversibility of the couple centered at +0.1 V is completely lost with the disappearance of the oxidation branch suggesting an interaction of MCPA with Mn species. Further, a shift in the reduction branch toward negative potentials together with an increase in the peak height is observed, suggesting that MCPA undergoes reductive dehalogenation. Phenoxyacetic acid does not show such reactivity indicating the necessity of an organo-chloro moiety. The current associated with the reductive dehalogenation peak is directly proportional to the bulk concentration of MCPA at a constant concentration of the Mn salt, indicating the direct involvement of MCPA in the electrochemical process. A peak at a similar potential is observed during cyclic voltammetric investigation of MCPA at carbon paste electrodes modified with MnO₂ confirming the electroactivity of MCPA catalyzed by Mn species.

The solution eluted from a column packed with MnO₂ through which a standard solution of MCPA was passed showed the presence of soluble Mn(II), a reduction product of MnO₂, as determined by atomic absorption measurements. This supports the fact that interaction between MCPA and MnO₂ introduces a chemical reaction between the two substances even in the absence of an applied potential. It is therefore suggested that MCPA be degraded in soil through interaction with MnO₂, if available, and the degradation would be facilitated under applied potentials conditions.

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