

Determination of MCPA through Electrocatalysis by Manganese Species

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MnO₂-modified carbon paste (CP) electrodes and Mn-modified glassy carbon (GC) electrodes show the electrochemistry of Mn species which strongly depends on the solution pH. Both types of modified electrodes are capable of catalytically reducing monochlorophenoxy acetic acid (MCPA), a herbicide. However, the catalytic wave appears at a lower potential at the MnO₂-modified CP electrode than that at the Mn-modified GC electrode, thus enabling the modified CP electrode for the determination of MCPA. Amperometric determination of MCPA at the MnO₂-modified CP electrode results in a very low detection limit of 0.20 ppm. The application of the proposed method for quantitative analysis of an MCPA formulation provides reliable results. Interaction of MCPA with MnO₂ is observed even in the absence of applied potentials mimicking the real situation in the environment where MCPA, when introduced to farmland, would interact with MnO₂ if present in soil.

Keywords: MCPA; Electrocatalysis; Modified electrodes; MnO₂; Carbon paste

1. INTRODUCTION

Electrocatalysis of organic substances by transition metal ions has been an attractive area of electrochemical research for many years (1-4). Transition metal ions having multiple oxidation states in solution has been of special attraction (5, 6). In this context, the stable form of the metal ion is usually oxidized/reduced *in situ* to form the more active form, upon the application of an appropriate potential, which subsequently reacts with the species of interest chemically/electrochemically. The species, when combined with the catalyst, would undergo electron transfer reactions at lower potentials due to the decrease in the overpotential toward electroactivity. In the absence of a suitable catalyst, many organic functionalities would not be active within the working potential range of solid electrodes, especially in aqueous medium, proving the necessity of searching for efficient electrocatalytic schemes.

This approach has recently been extended for electrocatalysis of many environmental pollutants, including pesticides, using solid electrodes on which the electrocatalyst consisting of a suitable metal, such as Mn, Fe and Co, is deposited as a thin film (7-9). However, the use of a solid electrocatalyst as an integral part of the electrode (e.g., carbon paste) to initiate the electro-action of pesticides (10) and other substances (11, 12) has begun recently, although some investigation has been focused on carbon paste electrodes modified with biological materials for the detection of environmentally and clinically significant substances (13-15).

Possibility of using MnO₂-modified carbon paste electrodes for catalytic electroreduction of metachlorophenoxyacetic acid (MCPA) is investigated in this research. Direct electroanalysis of MCPA is impossible due to its high overpotentials for oxidation/reduction. Consequently, detection of MCPA via electrocatalytic reduction with MnO₂ is accomplished with sensitive amperometric detection at a predetermined potential. Additionally, detailed investigation on interaction of MCPA with Mn species deposited on glassy carbon electrodes and MnO₂ incorporated into carbon paste under applied potentials conditions, and with MnO₂ packed in a column under dynamic conditions is also reported.

2. EXPERIMENTAL PART

Materials: A technical grade (brown colored) sample of MCPA was recrystallized from ethanol/water for all experiments. The purity of the product was confirmed by melting point determination (Melting point = 119.0 °C to 120.5 °C). A commercial formulation of MCPA [Lankem M 50 (40 % w/w)] was purchased from the local market, which was used in this research without any purification.

Analytical grade electrolytes and chemicals (NaCl, KCl, Na₂SO₄, LiCl, KH₂PO₄, KHP, NaOH, MnO₂ and MnSO₄), constituents of carbon paste: graphite powder and mineral oil, and HPLC grade organic solvents (CH₃CN and C₂H₅OH) were purchased from Aldrich, USA. All the electrolyte solutions were prepared in distilled deionised water, and the standard solutions were prepared daily.

Instrumentation: A cyclic voltammograph and an X-Y recorder, both from Bioanalytical Systems (BAS), USA, were used for all cyclic voltammetric and amperometric experiments. The three-electrode cell consisted of a carbon paste (CP) or glassy carbon (GC) working electrode, a platinum wire counter electrode and a saturated calomel reference electrode (SCE). All potentials were reported with respect to SCE, and all experiments were conducted under N₂ saturated conditions.

Preparation of Modified Working Electrodes: The packing material of the carbon paste electrode was prepared by thorough mixing of graphite powder (60% w/w) with mineral oil (40% w/w). This was incorporated into the cavity of the electrode body, and the surface was smoothed on an oil paper. Appropriate amounts of finely ground black MnO₂ powder were mixed with carbon paste to construct catalytic electrodes. Mn-modified GC electrodes were prepared by cycling the potential between +1.00 V and -1.00 V in 0.1 mol dm⁻³ KCl.

Cyclic Voltammetric and Amperometric Experiments: Cyclic voltammetric experiments of bare and MnO₂-modified CP electrodes were carried out in simple electrolytes such as NaCl, KCl and

Na_2SO_4 , and in buffered systems of *pH* 1, 3 and 5. Cyclic voltammetric studies of these electrodes were initially conducted in each medium in the absence of MCPA to observe the electrochemistry of MnO_2 alone. The study was then repeated with $2 \times 10^{-4} \text{ mol dm}^{-3}$ MCPA (prepared in 1:3 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$). Voltammetric responses of CP electrodes containing varying amounts of MnO_2 (0%, 2%, 4%, 6%, 8%) were investigated in order to optimize the catalytic loading. Cyclic voltammetric experiments of bare and Mn-modified GC electrodes in 0.1 mol dm^{-3} KCl in the absence and presence of MCPA were carried out in a similar manner

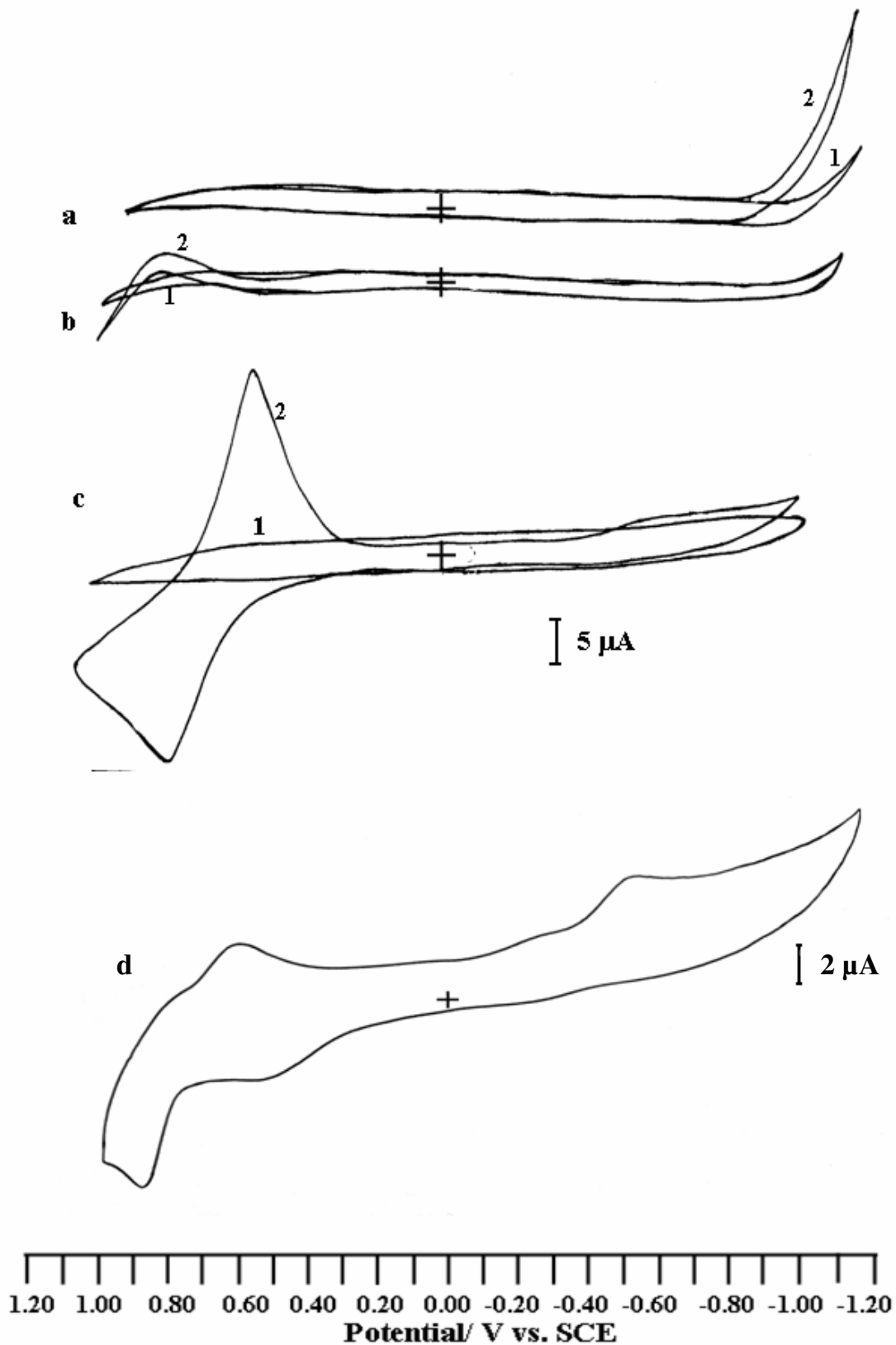
Amperometric experiments were conducted in 0.1 mol dm^{-3} KCl at MnO_2 -modified CP electrodes using standard solutions of MCPA ($1.0 \times 10^{-4} \text{ mol dm}^{-3}$ and $2.5 \times 10^{-5} \text{ mol dm}^{-3}$), and calibration curves were constructed using the resulting amperograms. The amperometric method developed was used to quantify MCPA present in a commercial formulation. Interaction of MnO_2 with MCPA in the absence of applied potentials was investigated by passing a standard solution of MCPA through a column packed with MnO_2 powder. Soluble Mn species eluted was determined using atomic absorption spectroscopy.

3. RESULTS AND DISCUSSION

Solution Chemistry of Mn Species: Cyclic voltammetric experiments conducted in MnSO_4 solutions at unmodified CP electrodes reveal that manganese ions in solution show electroactivity that strongly depends on the *pH* of the medium (Figure 1). At low acidic *pH*s, electroactivity of manganese species is not visible within the solvent breakdown potentials. Appearance of electroactivity starts at *pH* = 3, which is enhanced and shifted toward less positive potentials as the medium *pH* is increased. At *pH* = 5, one redox process is observed while further increase in *pH* such as the KCl medium, two main redox processes are apparent. Based on thermodynamic arguments and the effect of MnO_2 on carbon-air electrodes (16), it is reasonable to assign the first redox process for the Mn(IV)/Mn(II) couple, while the second process for the Mn(III)/Mn(II) couple. Change in the electrode material (from CP to GC) does not significantly change the electroactivity of Mn species. Further increase in *pH* beyond *pH* = 7 prevents the appearance of any activity at either electrode, probably due to the formation of insoluble Mn species at such *pH*s.

It has already been reported that transition metal ions with multiple oxidation states are able to catalyze the reduction of organohalides such as propanil and 2,4-D (7, 8). In such situations, lower oxidation states, which are generated *in situ* are responsible for the reduction. Nevertheless, cyclic voltammetric features of MnSO_4 solution observed in 0.1 mol dm^{-3} KCl at GC electrodes are diminished and no new features appear when MCPA is introduced, indicating that soluble Mn(II) species (of MnSO_4) do not show any catalytic effect toward the reduction of MCPA. This could be due to strong adsorption of MCPA, owing to the carboxylic acid group, on the glassy carbon surface preventing the approach of Mn(II) species at the electrode surface. This situation is not improved even when CP electrodes are used. The intimate contact between Mn(II), MCPA and the carbon particles in the carbon paste matrix is a crucial issue for the reduction of MCPA by Mn species. Although Mn(II)

species are present in solution, they are probably not diffused on to the reactive sites of the electrode, *i.e.*, carbon paste, fast enough for any charge transfer reaction to occur.



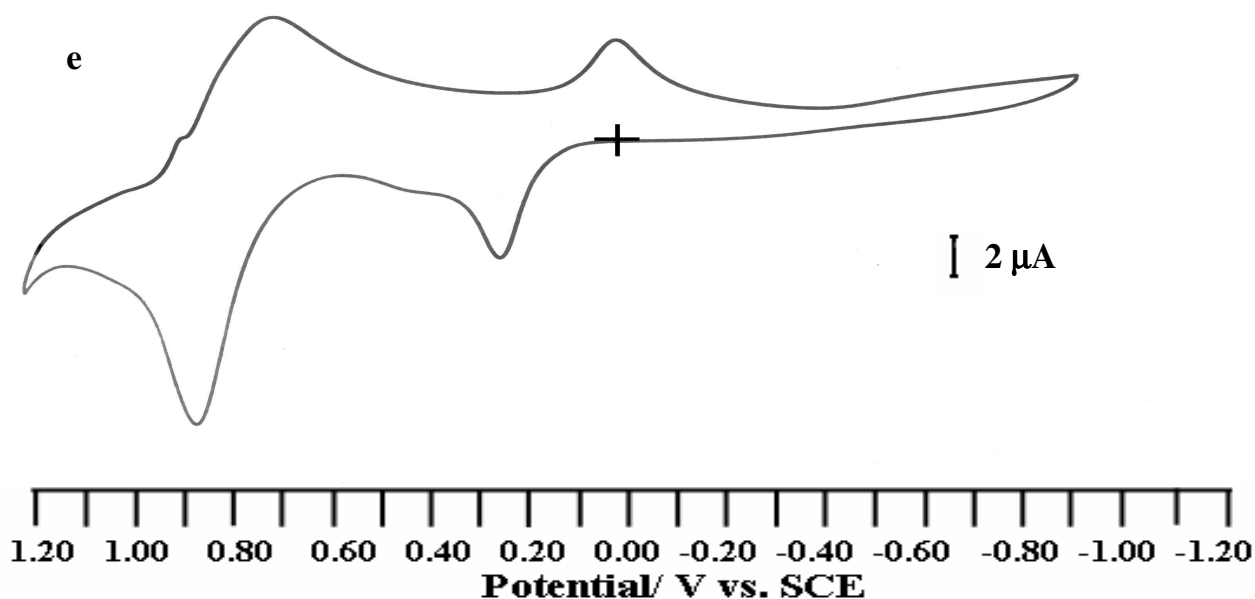


Figure 1. Cyclic voltammograms of $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ MnSO}_4$ at a scan rate of 25 mV s^{-1} under N_2 saturated in 0.1 mol dm^{-3} supporting electrolyte (a) pH = 1 buffer at CP electrode (b) pH = 3 buffer at CP electrode (c) pH = 5 buffer at CP electrode (d) KCl at CP electrode (e) KCl at GC electrode. In figures (a), (b) and (c), 1 = electrolyte only and 2 = MnSO_4 , and the current (Y) scale is different from that of (d) and (e); In figures (d) and (e), electrolyte response is not shown.

This problem was successfully addressed by modifying the electrode surface/electrode packing material with a suitable catalyst consisting of Mn species.

Modification of GC and CP Electrodes: Continuous cyclic voltammetric scans of a GC electrode in $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ MnSO}_4$ solution recorded for 2 hr indicate that electrochemical features continuously increase with potential cycling between +1.0 V and -1.0 V. Additionally, two pre-adsorption peaks associated with the first reduction and a post-adsorption peak associated with the second reduction are developed with more potential cycles indicating strong adsorption of manganese species on the GC surface (Figure 2). Thorough rinsing of the GC electrode after continuous scanning in the MnSO_4 solution reproduces the same electrochemistry in a fresh electrolyte solution, supporting the suggestion of adsorption.

A different approach was used to modify CP electrodes where MnO_2 acted as an integral part forming a single composite. However, MnO_2 -modified CP electrodes do not show sharp electrochemical features within the cyclic voltammetric time scale in all electrolytes investigated, suggesting restricted mobility of neutral MnO_2 molecules toward the electrode surface. Such

observations are not surprising because electrodes modified with neutral catalytic molecules such as metalloporphyrins have not shown sharp electrochemical features under certain conditions, although they are able to catalyze a vast number of reactions (8).

Interestingly, Mn-modified GC electrodes and MnO₂-modified CP electrodes constructed using the methods described above introduce some activity on MCPA which is otherwise completely inactive at unmodified electrodes within the solvent breakdown potentials of the electrodes. This clearly indicates the catalytic activity of Mn species toward the reduction of MCPA.

A broad reduction peak between +0.60 V and -0.20 V, centered at +0.05 V, is developed at MnO₂-modified CP electrode in the presence of 2.0×10^{-4} mol dm⁻³ MCPA in 0.1 mol dm⁻³ KCl (Figure 3 top). In other electrolyte media, such as buffer systems of pH 1, 3, 5, 7 and 9, almost zero response resulted. NaCl and LiCl produce results similar to that in 0.1 mol dm⁻³ KCl, while slightly lower signal is observed in Na₂SO₄ solution. Similar broad catalytic reduction peak appears for MCPA at Mn-modified GCE, but at more positive potentials (Figure 3 bottom). The change in the potential may be attributed to change in surface properties of the two types of electrodes and change in the catalytic material: Mn on GC electrode vs. MnO₂ with CP. Although both the Mn-modified GC electrode and the MnO₂-modified CP electrode have the potential for detection of MCPA, it is recommended that the latter electrode be more suitable due to lower potential for catalytic activity. Another advantage of MnO₂ modified-CP electrodes is that the catalytic loading can be optimized for better response, which would subsequently increase the sensitivity of detection.

Cyclic voltammetric studies of CP Electrodes with different MnO₂ loadings indicate that increment of the amount of MnO₂ in CP electrodes enhances the catalytic peak associated with MCPA (Figure 4). The amount of the catalyst used in the preparation of the working electrode is thus an important factor for the sensitivity of the response of MCPA. However, more than 10% MnO₂ generates a response with high noise probably due to reduced conductivity. Therefore, loading of 10% MnO₂ be recommended for electrochemical investigation of MCPA.

Amperometric Determination of MCPA: As can be noticed in Figure 5, all potentials attempted in the vicinity of the broad catalytic peak of MCPA, + 0.60 V to -0.20 V, produce amperograms at MnO₂-modified CP electrode of similar sensitivity. Thus, the potential of +0.1 V was selected as the optimum value for the determination of MCPA. At more positive potentials, easily oxidizable interferents, if present, would be active altering the response of MCPA when real samples are analyzed.

The linear dynamic range, sensitivity and the minimum detection limit, based on the signal-to-noise ratio (S/N) of 3, of the MnO₂-modified CP electrodes for the detection of MCPA are 3.8×10^{-6} mol dm⁻³ to 1.07×10^{-5} mol dm⁻³, $0.0327 \mu\text{A mol}^{-1} \text{dm}^3$ and 9.7×10^{-7} mol dm⁻³, respectively. This is a great achievement in electroanalysis because such a low minimum detection limit of about 0.2 ppm is not usually achievable with many electrochemical detection schemes, demonstrating the effectiveness of the catalytic features of Mn species toward the reduction of MCPA. It should be noted that the amperometry was not conducted at modified GC electrodes due to the higher potential of the catalytic reaction as shown in Figure 3 (bottom).

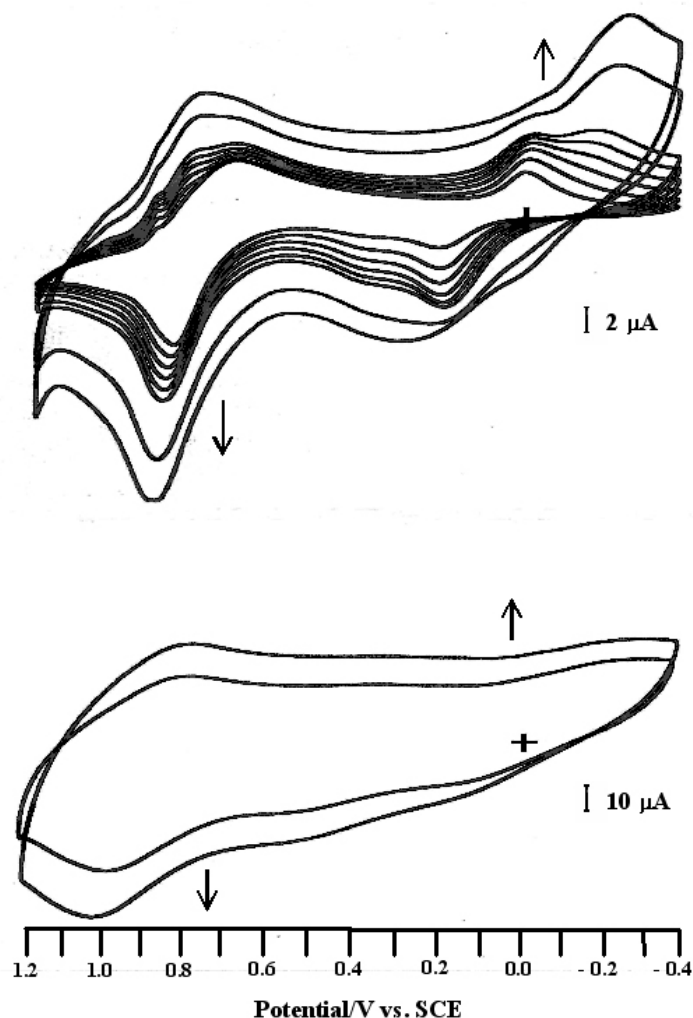


Figure 2. Continuous cyclic voltammetric responses of GC electrode in $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ MnSO}_4$ ($0.1 \text{ mol dm}^{-3} \text{ KCl}$) at a scan rate of 25 mV s^{-1} under N_2 saturated. Arrows indicate the direction of change when more scans are applied. Recorded voltammograms are scan 1, scan 2, scan 3, scan 4, scan 5, scan 6, scan 12 and scan 18. The lower voltammograms are recorded at scans 50 and 100, respectively.

Interferences: As MCPA is active at a potential as low as $+0.10 \text{ V}$ at the MnO_2 modified CP electrode, interference problems can be greatly minimized. Propanil and chloroacetic acid, produce no detectable responses when tested amperometrically using similar conditions employed for the detection MCPA. These substances were especially selected as possible interferent species because they both are herbicides used in similar applications.

Life-time of the Sensor: According to amperometric experiments conducted on regular basis for a representative sample of MCPA, the activity of the MnO_2 modified CP electrode was determined to be stable up to a period of 10 weeks at room temperature. The response of the sensor started decaying slowly after this period.

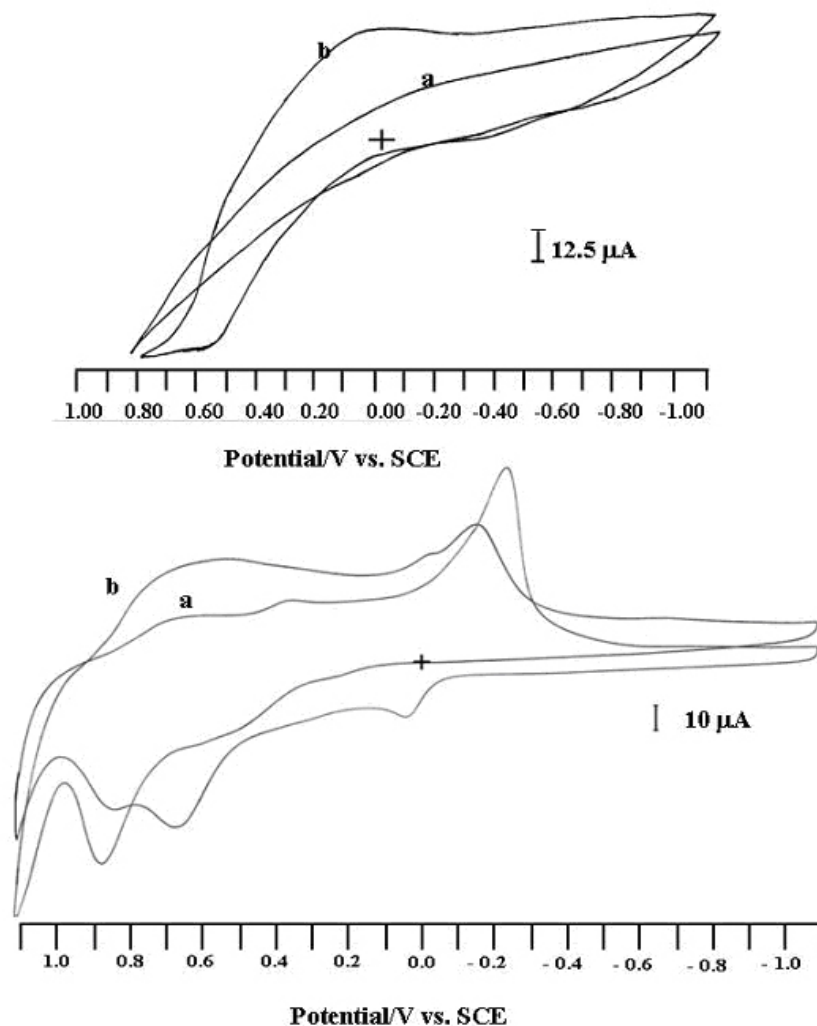


Figure 3. Cyclic voltammograms of MnO₂ (10 %)-modified CP electrode (top) and Mn-modified GC electrode (bottom) in 0.1 mol dm⁻³ KCl at a scan rate of 25 mV s⁻¹ under N₂ saturated (a) electrolyte only (b) 2.0 × 10⁻³ mol dm⁻³ MCPA.

Application of the Method: The method developed was successfully applied for the detection of MCPA in a commercial formulation that was reported to have 40% (w/w) MCPA. An amperometric experiment conducted for a diluted solution of this sample resulted in reproducible responses. According to the calibration curve obtained for the amperogram recorded at -0.2 V (Figure 5i), the concentration of MCPA in the formulation was determined to be (35.6 ± 0.07) % w/w.

The error of this result, although is at acceptable level, may be accounted for many factors such as possible degradation of the active ingredient in the formulation, quality of the pesticide formulation, experimental errors and unknown matrix effects. Slow degradation of the active ingredient is possible even during the shelf-life. Degraded product(s) of MCPA may also be electroactive within the working potential limits.

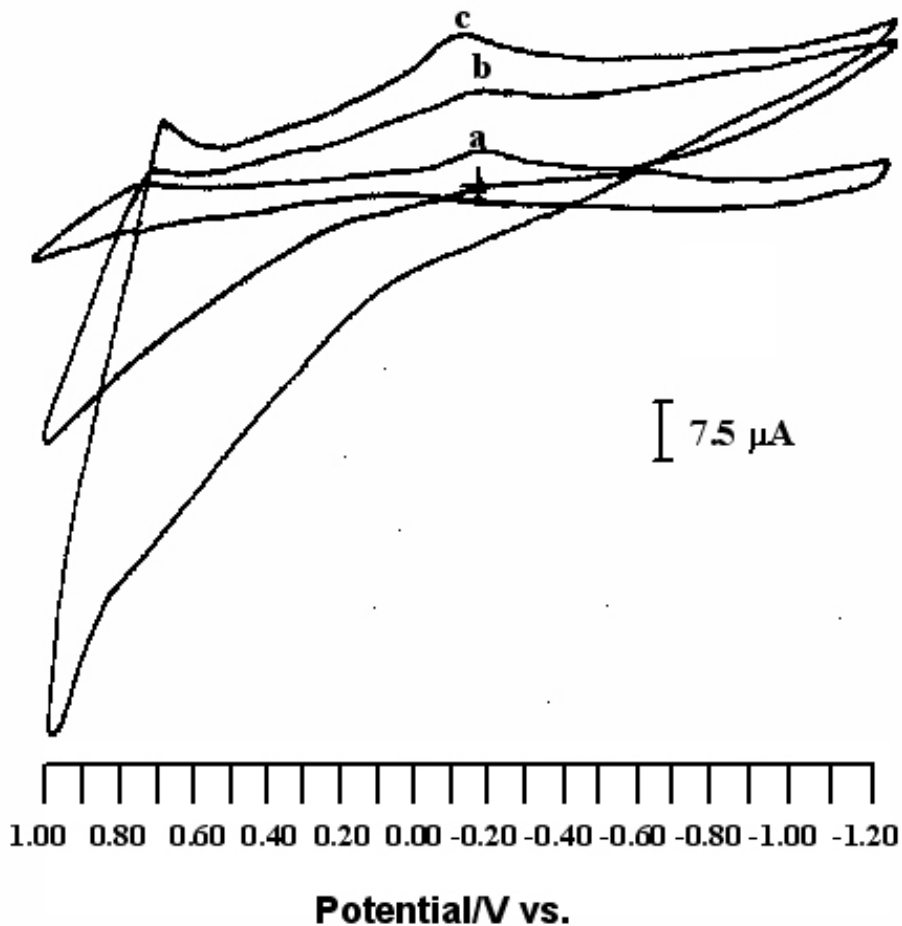


Figure 4. Cyclic voltammograms of 1.0×10^{-3} mol dm⁻³ MCPA at MnO₂ modified CP electrode with different catalytic (MnO₂) loadings, (a) 3% w/w (b) 6% w/w (c) 9% w/w. Supporting electrolyte 0.1 mol dm⁻³ KCl; Scan rate of 25 mV s⁻¹; N₂ saturated.

Atomic Absorption Spectrophotometric Studies: Passing a solution of MCPA (5.0×10^{-3} mol dm⁻³ prepared in CH₃CN/H₂O of 1:3) through a column packed with 25.0 g MnO₂ at a rate of 1.0 cm³ min⁻¹ resulted in the release of soluble Mn(II) according to atomic absorption spectroscopic analysis of fractions collected at different time intervals (Figure 6). The amount of Mn(II) released from the column is increased when more time is given for the interaction of MCPA with MnO₂. This experiment provides further information on interaction between Mn(IV) (in MnO₂) with MCPA, possibly a redox chemical step, resulting in degraded products of the herbicide. It is believed that MCPA is degraded through a chemical reaction with Mn species at a slower rate in the absence of applied potentials. This further provides the possibility of interaction of MCPA, when introduced to farmland, with MnO₂, a common constituent of soil.

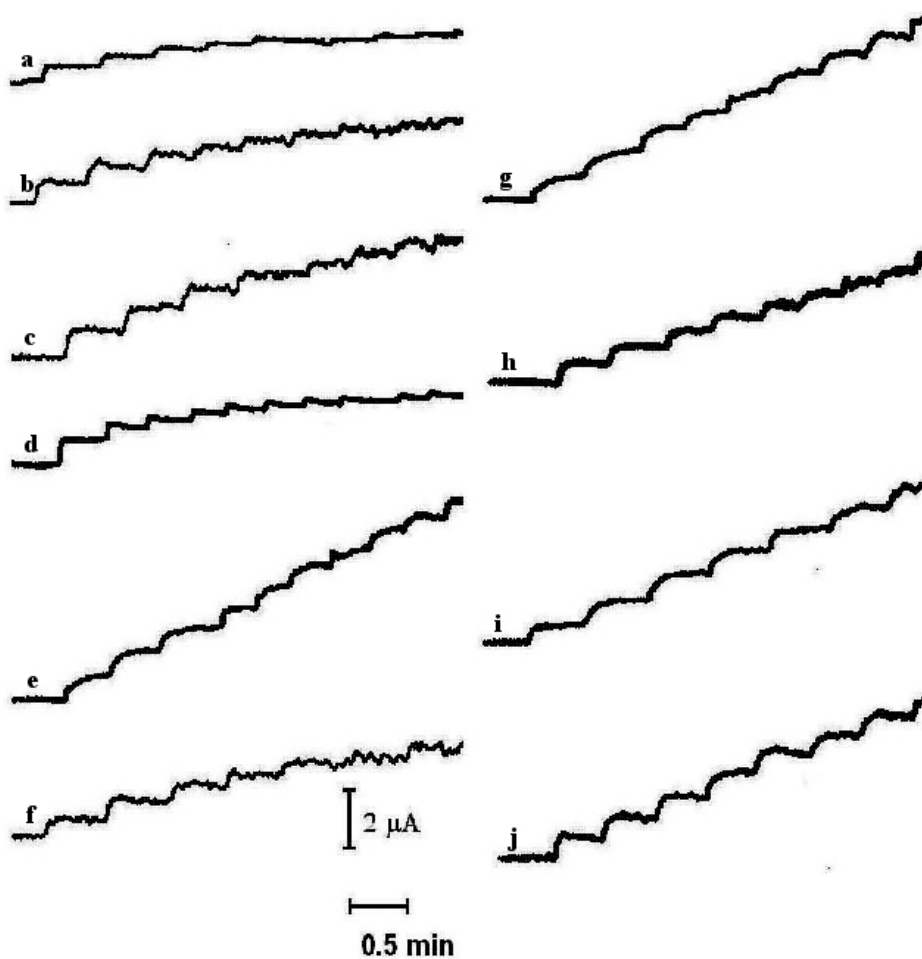


Figure 5. Steady state amperometric responses with MCPA additions of $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ increments at MnO_2 (10%)-modified CP electrode in 0.1 mol dm^{-3} KCl at a scan rate of 25 mV s^{-1} under N_2 saturated. Applied potentials (a) +0.6 0 V, (b) +0.5 V, (c) +0.4 V, (d) +0.3 V, (e) +0.2 V, (f) +0.1 V, (g) 0.0 V, (h) -0.1 V, (i) -0.2 V, (j) -0.3 V.

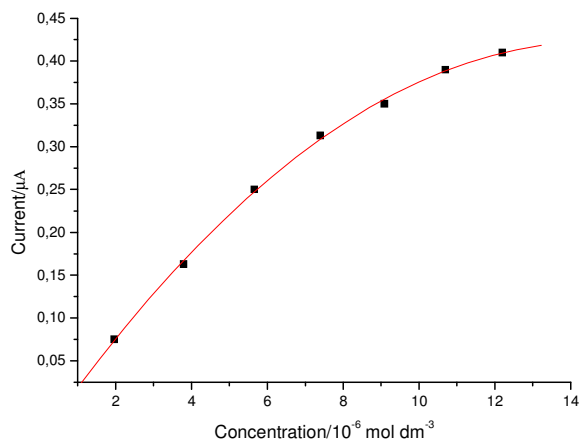


Figure 6: Amount of soluble Mn released from MnO_2 packed column as a function of time of interaction.

4. CONCLUSIONS

The catalytic activity of transition metal oxides, where the metal atom has multiple oxidation states, was demonstrated using MnO₂-modified CP electrodes and Mn-modified GC electrodes for the reduction of monochlorophenoxy acetic acid (MCPA). However, amperometric detection of MCPA is recommended at modified CP electrodes as the catalytic wave appears at lower potentials compared to that at modified GC electrodes. This electrocatalysis does not occur in the solution phase, probably due to adsorption effects of MCPA on GC electrodes, and restricted diffusion of Mn(II) toward CP electrodes.

The linear dynamic range, sensitivity and the minimum detection limit, based on the signal-to-noise ratio (S/N) of 3, of the MnO₂-modified CP electrodes for the detection of MCPA are 3.8×10^{-6} mol dm⁻³ - 1.07×10^{-5} mol dm⁻³, $0.0327 \mu\text{A mol}^{-1} \text{dm}^{-3}$ and 9.7×10^{-7} mol dm⁻³, respectively. The minimum detection limit achieved with the electroanalytical method developed is very attractive as it is comparable with sophisticated methods. Expansion of such low-cost and simple analytical methods in real analysis is thus justified. The relatively low potential of operation of +0.1 V is another advantage of this method.

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