

# Electrochemical Determination of 2,4-Dichlorophenoxyacetic Acid using Bismuth Film Modified Screen-printed Carbon Electrode

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## ABSTRACT

In this work, the development of an electrochemical method for the determination of 2,4-dichlorophenoxy acetic acid (2,4-D) (indirectly by converting to its electroactive nitrated form) using a modified screen-printed carbon electrode with bismuth film is reported. The electrode modification has been done by a single potential step electrodeposition of bismuth film on screen-printed carbon electrodes. Under the optimized conditions, the nitrated 2,4-D showed a dynamic linear concentration range in pH 11 buffer from 11.1 to 74.3  $\mu\text{M}$  with regression coefficient ( $R$ ) of 0.9988. The limits of detection and quantification were 3.15  $\mu\text{M}$  and 10.5  $\mu\text{M}$ , respectively. The proposed method offered higher sensitivity compared to bare screen-printed carbon electrodes. The modified electrode showed good reproducibility, repeatability, stability and recovery for the analysis of 2,4-D. The developed method was used for electroanalysis of 2,4-D in soil and water samples collected from Sito Kebele, Dedo district Jimma zone.

## KEYWORDS

Electroanalysis, herbicide, screen-printed carbon electrodes, bismuth film, 2,4-dichlorophenoxyacetic acid.

## 1. Introduction

Electroanalysis can be used as one of the potential analytical methods for the analysis of heavy metal ions in different environments,<sup>1</sup> organic pollutants consisting of hydrazine, phenol,<sup>2</sup> in biomedical packages for the detection of glucose,<sup>3</sup> hormones,<sup>4</sup> cells,<sup>5</sup> and tumors markers.<sup>6</sup> It is used in the detection of extraordinarily low levels of macromolecules like proteins<sup>7</sup> and nucleic acids.<sup>8</sup> In pharmaceuticals industries, it is used for the determination of the level of the components of drugs.<sup>9,10</sup> Furthermore, it is a tool for the detection and determination of electroactive organic compounds used for pest and herb control.<sup>11</sup>

Even though numerous techniques had been reported for the determination of 2,4-D (consisting of high performance liquid chromatography,<sup>12</sup> and gas chromatography coupled with mass spectrometry and spectrophotometry<sup>13</sup>), there are few electroanalytical techniques reported for the determination of herbicide 2,4-D using traditional carbon electrodes and mercury electrodes.<sup>14,15,16</sup> The 2,4-D and its by-product reveal slow electron transfer, suggesting that the redox method is electrochemically irreversible. The electroinactivity of 2,4-D has been reported and the determination of this compound through electrochemical strategies is not straightforward at present.<sup>17</sup> So, to determine 2,4-D and its residue with the aid of electrochemical methods, the conversion of electroinactive 2,4-D to its electroactive species is required, and this has been accomplished by labelling it with a nitro group.

Electroanalytical methods have received a great deal of interest because of their simplicity, portability, lower detection limit, and inexpensiveness because of its good sensitivity, reduction in solvent and sample consumption, high-speed analysis, portability as well as simplicity.<sup>18</sup> With the advancement in electroanalytical science, traditional carbon electrodes and mercury electrodes are cumbersome to use.<sup>19</sup> Traditional carbon elec-

trodes require polishing and electrode treatments whereas mercury electrodes are inconvenient due to their well-known toxicity. Furthermore, in electroanalytical techniques, working electrodes might be insensitive to use in the detection of a few chemical substances. So electrode surface modification is needed to enhance the sensitivity, selectivity and stability of the electrodes to acquire enhanced response for analytical need.<sup>20</sup> For this reason, disposable screen-printed carbon electrodes (SPCEs) have proven to replace the above-mentioned electrodes with the surface modification by immobilization of a modifying agent on the electrode surface. Because SPCE avoids contamination and also eliminates problems which include the lack of responses due to surface fouling of the electrodes as it is used once and then discarded.<sup>21</sup>

Therefore, in this work, we report the development of an electroanalytical technique using a disposable screen-printed carbon electrode modified with a bismuth film for electroanalysis of 2,4-D.

## 2. Materials and Methods

### 2.1. Chemicals

Bismuth nitrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , 98 %, M & B laboratory reagent); boric acid ( $\text{H}_3\text{BO}_3$ , 99.5 %, Techno Pharmachem), 2,4-Dichlorophenoxyacetic acid ( $\text{C}_8\text{H}_6\text{O}_3\text{Cl}_2$ , 97 %, Aldrich), sodium perchlorate ( $\text{NaClO}_4$ , 98 %, Sigma), potassium nitrate ( $\text{KNO}_3$ , 99–100.5 %, Riedel de Haen), dichloromethane ( $\text{CH}_2\text{Cl}_2$ , BDH), hydrochloric acid ( $\text{HCl}$ , 37 %, Riedel de Haen), potassium hexacyanoferrate ( $\text{K}_3\text{Fe}(\text{CN})_6$ , 97 %, Labmark Chemicals), sodium hydroxide ( $\text{NaOH}$ , 96 %, LeSOL laboratory reagent), potassium chloride ( $\text{KCl}$ , 99 %, Finkem), phosphoric acid ( $\text{H}_3\text{PO}_4$ , 85 %, Riedel de Haen), glacial acetic acid ( $\text{CH}_3\text{COOH}$ , 100 %, BDH), Britton Robinson (BR) buffer were used as received without any treatment. For aqueous solution preparations double-distilled water was used.

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## 2.2. Instruments

Screen-printed carbon electrodes (Dropsens 110) connected to Epsilon (BASi) electroanalyzer using Dropsens connector (DRP-DSC70506) were used for electrochemical measurements. The BASi Epsilon was operated using Basic Epsilon EC-Version 1.40.70 software. An ATC pH meter (353) was used to measure pH.

## 2.3. Methods

### 2.3.1. Procedure for Nitration of 2,4-D

Nitrated 2,4-D was synthesized using the procedure reported by Maleki *et al.*<sup>17</sup> Briefly, 2 g of 2,4-D was dissolved in 2 mL dichloromethane, and this solution was transferred to 5 mL concentrated sulfuric acid kept in ice bath at 0–5 °C. While the temperature of the solution was maintained at 0–5 °C, 1.5 mL concentrated nitric acid was added dropwise over 30 min to the above solution. A yellow paste was formed in the vessel. The reaction mixture was then transferred into 30 mL 10 % aqueous Na<sub>2</sub>SO<sub>4</sub> and the separated organic phase was washed with 20 mL 10 % aqueous Na<sub>2</sub>SO<sub>4</sub>, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> in a desiccator, and the solvent was evaporated. The dried yellow solid was weighed, the yield of nitrated 2,4-D was calculated and it was found to be more than 97 %. The melting point of the solid compound was measured and it ranged from 141 to 143 °C.

### 2.3.2. Procedure for Preparation of Solution

Stock solution of nitrated 2,4-D (3.72 mM) was prepared in 25 mL volumetric flask, by dissolving 25 mg of the nitrated 2,4-D in a Britton Robinson (BR) buffer of pH 11. The pH of BR buffer was adjusted to the desired level using 1 M NaOH solution. The working solution was prepared by taking an appropriate volume from the stock solution and diluting it with a buffer of pH 11.

### 2.3.3. Electrochemical Measurements

The cyclic voltammetry and amperometric experiments were carried out using a BASi Epsilon voltammetric analyzer (Bio-analytical Systems, USA), controlled with basic Epsilon software EC-Version 1.40.70. The screen-printed carbon electrode (SPCE) (Dropsens 110) was used with carbon as the working electrode and carbon counter electrode and silver as pseudo reference electrode. The potentials reported in all electrochemical measurements were against this reference electrode. A magnetic stirrer (BASi C3 Cell stand) was used for stirring the solutions during amperometric measurements.

### 2.3.4. Electrode Cleaning and Conditioning

SPCEs were first thoroughly flushed with distilled water. The electrochemical conditioning of the electrode was followed by potential scanning from 0 to 1100 mV in 1 M KCl for at least five complete scans at 100 mV s<sup>-1</sup>, during which the high background current due to carbon oxidation was minimized. Then, the CV of bare screen-printed electrodes in the presence of potassium hexacyanoferrate was measured from –200 mV to 400 mV to determine the area of the electrodes. The electrodes were dried and immediately used following the cleaning and conditioning steps.

### 2.3.5. Preparation of Bismuth Film Modified SPCE (BiFE)

Bismuth film modified screen-printed carbon electrodes (BiFE) were prepared by potentiostatic deposition of bismuth on screen-printed carbon electrodes (SPCE) in a Bi(III) bath. Briefly, a constant deposition potential of –1050 mV for 180 s was applied

to the SPCEs in a bismuth deposition bath (2 mM Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O in 1 M HCl). The modified SPCEs were rinsed with distilled water and immediately used for electrochemical studies of nitrated 2,4-D.

### 2.3.6. Modifying Strategies of the Electrodes using Bismuth Films

Parameters for the plating of the screen-printed carbon electrode with bismuth were studied using cyclic voltammetry and chronoamperometry methods based on electrochemical response for the analyte at the electrodes. Plating solution containing Bi (III) in acidic media was used to avoid hydrolysis of the metal cation.<sup>22</sup> Parameters such as initial concentration of the deposition bath, the deposition potential and deposition time were optimized for the electrodeposition of bismuth films. The optimum conditions were selected based on response to the analyte electrochemical signal.

#### i. Optimization of deposition time

As reported by Tufa *et al.*,<sup>23</sup> a bismuth film was deposited on the SPCE from a 2 mM Bi (III) deposition bath at a step potential of –1200 mV. The effect of deposition time was studied by varying the duration of the applied potential for 60, 120, 180, 240, 300 and 360 s. Using the as prepared Bi-film electrodes, the current response for 0.372 mM nitrated 2,4-D was recorded (n = 3). The appropriate deposition time was selected based the response for the nitrated 2,4-D.

#### ii. Optimization of deposition potential

The Bi film deposition potential was optimized within the potential range from –950 mV to –1250 mV as dictated by the CV of 2 mM Bi(NO<sub>3</sub>)<sub>3</sub> at the SPCE. After deposition of the Bi film at selected potentials within this range for 180 s, the modified SPCE was used to measure the reduction peak for 0.372 mM of the nitrated 2,4-D (n = 3). The deposition potential that gave the highest analytical signal was selected.

#### iii. Optimization of bath concentration

Bismuth deposition bath concentrations that range from 0.5 mM to 3 mM was tested to optimized bath concentration at –1050 mV deposition potential for 180 s. For each concentration tested, triplicate measurement was made for the reduction of the nitrated 2,4-D at the Bi film modified electrodes and the average current obtained from different deposition baths was compared to selected the appropriate deposition bath concentration.

#### iv. Optimization of pH

For pH optimization, the amperometry of 0.372 mM nitrated 2,4-D was run at Bi film modified SPCE (obtained from deposition bath of 2 mM, at –1050 mV for 180 s), using the optimized deposition potential, deposition time and concentration. The resulting current signal (average of triplicate measurement) of the nitrated 2,4-D were plotted against the pH of the buffer solution. The pH which gave the highest analytical signal was selected.

#### v. Procedure for collecting data for the calibration curve

Three SPCEs were modified with bismuth film using the selected optimized condition. The amperometry at an applied potential –550 mV of nitrated 2,4-D for concentrations ranging from 11.1 to 74.3 μM was run on the same day under similar conditions using these modified electrodes. The average current signal of the analyte from the modified electrodes was plotted against the concentration of nitrated 2,4-D and the calibration curve was plotted.

Three bare SPCE were taken and the chronoamperometry of nitrated 2,4-D at an applied potential of –550 mV for concentra-

tions ranging from 22.3 to 59.5  $\mu\text{M}$  were run. The average current signal of the analyte from the three different electrodes was plotted against the concentration of nitrated 2,4-D.

#### vi. Procedure for testing reproducibility and repeatability

The reproducibility of the bismuth film modified SPCEs was examined by measuring the same concentration (37.2  $\mu\text{M}$ ) of nitrated 2,4-D on three modified electrodes on three consecutive days with triplicate measurement on each day. The relative standard deviation (RSD) of the measured current signal was calculated to determine reproducibility of the modification strategy among the electrodes.

For the repeatability study, the bismuth film modified electrode was prepared under the optimum conditions. Nine successive voltammetric measurements of 37.2  $\mu\text{M}$  nitrated 2,4-D were made on the same day for a modified electrode. The RSD of the measurements was used to estimate the repeatability of the measurement.

#### vii. Procedure for stability study

Three SPCE were modified with bismuth film under the optimized conditions on the same day. The amperometry of 37.2  $\mu\text{M}$  nitrated 2,4-D was measured on the first day, seventh day and fourteenth day. On each day, six measurements were made at an electrode. The average current signals of the six measurements in the first day were compared to those of the fourteenth day to determine the stability of the modification procedure developed.

#### 2.3.7. Procedure for Sample Collection

Soil and water samples were collected from Dedo district, Sito Kebele around Jimma zone, Ethiopia (UTM 799083N–846083N and 244535E–302787E). Six soil samples from one farmland were randomly collected following standard sampling procedure. The soil samples were mixed and finally one composite soil sample was obtained. In addition, a water sample was collected from Dase River in Sito Kebele about 200 m from the farmland.

#### 2.3.8. Procedure for the Extraction of 2,4-D from Water and Soil Samples

##### i. Extraction of 2,4-D from soil samples

1 g of air dried soil sample was dissolved in 100 mL of water and the pH of the solution was adjusted to  $\sim 9$  with 1 M NaOH solution. Organic materials that could be present in the sample was separated using the procedure reported by Maleki *et al.*<sup>17</sup> Briefly, 10 mL of the soil solution was transferred to a separating funnel. Then the pH of the aqueous solution was adjusted approximately to 1 with 1 M HCl. Using 5 mL dichloromethane separation of the analyte was made. The dichloromethane phase (expected to contain 2,4-D) was back-extracted with 10 mL alkaline aqueous solution (pH  $\sim 9$ ). The aqueous solution obtained was nitrated applying procedures reported by Maleki *et al.*<sup>17</sup> and then analyzed by the proposed electrochemical method.

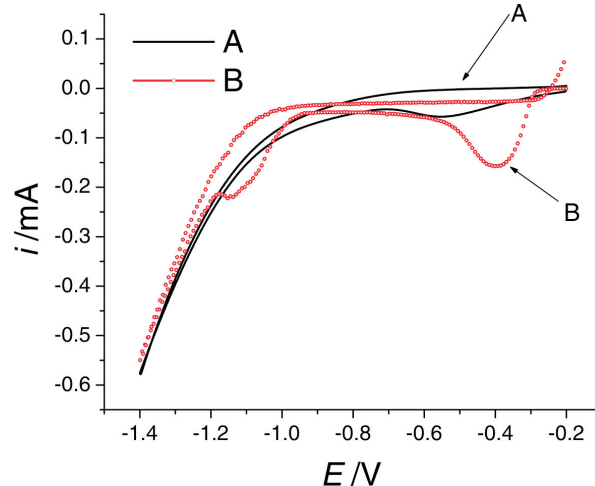
##### ii. Extraction of 2,4-D from water samples

For the analysis of 2,4-D from water samples, 10 mL of water sample was transferred to a separating funnel. The pH of solution was adjusted to approximately 1 with HCl (1 M) and the separation was performed with 5 mL of dichloromethane. The organic phase was back-extracted with 10 mL alkaline solution (pH  $\sim 9$  adjusted with 1 M NaOH). The aqueous solution obtained was nitrated applying procedures reported by Maleki *et al.*<sup>17</sup> Finally it was analyzed by the proposed electrochemical method.

### 3. Results and Discussion

#### 3.1. Cyclic Voltammetry of Bismuth (III) Ion

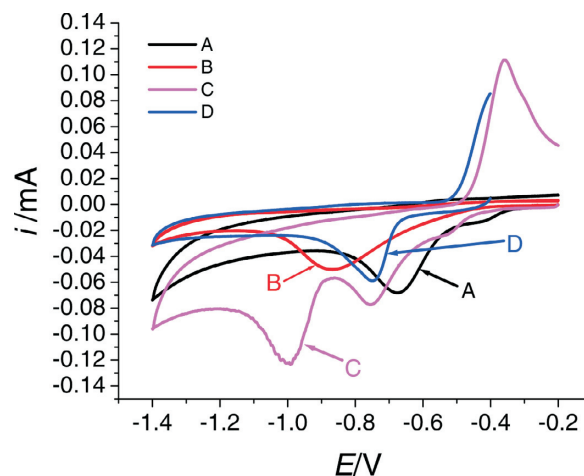
The cyclic voltammogram of Bare SPCE in supporting electrolyte (1 M HCl) and in 2 mM Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O in 1 M HCl is shown in Fig. 1. From the cyclic voltammograms, the potential at which Bi<sup>3+</sup> ion can be reduced to its metallic form was selected (potential lower than  $-950$  mV). The peak at  $-1100$  mV corresponds to the reduction of Bi (III) ion whereas the peak around  $-400$  mV corresponds to reduction of hydrogen ion from HCl.



**Figure 1** Cyclic voltammogram of (A) 1 M HCl and (B) 2 mM Bi (III) ion in 1 M HCl. In both cases bare SPCE was used at a scan rate of 100 mV s<sup>-1</sup>

#### 3.2. Electrochemical Characterization of Nitrated 2,4-D

The cyclic voltammograms of nitrated 2,4-D at the bare, and bismuth film-modified SPCEs (BiFE) are shown in Fig. 2. The major reduction peaks observed for all the electrodes (curves A, B, C and D) are associated with the reduction of hydrogen ions. For bismuth modified electrode cases, the reduction potential of hydrogen has shifted to more negative potentials since they have high overpotential for the reduction of H<sub>3</sub>O<sup>+</sup> to H<sub>2</sub> similar to mercury electrodes.<sup>24</sup> The minor peaks observed at around  $-300$  to  $-500$  mV (curves A and C) are associated with the reduction of the nitrated 2,4-D<sup>16</sup> at bare and Bi film modified SPE, respectively. It is evident that the voltammogram of BIFEs showed an increment in signal for the analyte than that of the bare SPCE within the studied potential window.



**Figure 2** Cyclic voltammogram of (A) nitrated 2,4-D on bare SPCE (B) bare SPCE in buffer of pH 11, (C) nitrated 2,4-D on the bismuth modified SPCE, (D) bismuth modified SPCE in buffer of pH 11.



### 3.3. Optimization of Parameters for the Determination 2,4-D

#### 3.3.1. Effect of Deposition Potential

The optimum potential for bismuth film deposition on the SPCE from the plating solution containing 2 mM Bi (III) in 1 M HCl was studied within the potential range of –950 to –1250 mV. The best deposition potential was selected by comparing the modified electrode response towards 0.372 mM nitrated 2,4-D (Fig. 3). The deposition potential of –1050 mV has given the best analytical signal and the BiFE obtained under these conditions was selected for the electroanalysis of nitrated 2,4-D. This result is in line with the effect of the choice of deposition potential to have best quality of bismuth film which was investigated by Kokkinos *et al.*<sup>25</sup> The selected deposition potential has also an additional advantage as it can eliminate the background hydrogen evolution that occurs at a more negative potential.

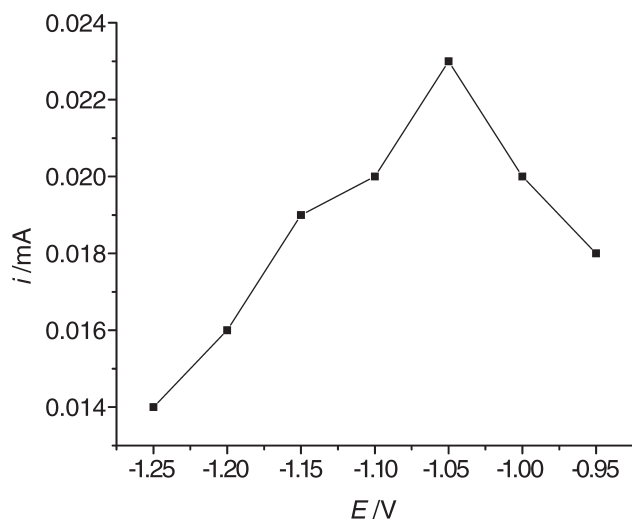
#### 3.3.2. Effect of Deposition Time

The bismuth film deposition time is one of the decisive parameters which may control the thickness of the bismuth film.<sup>26</sup> The effect of the bismuth plating time was studied in the range 60–360 s as shown in Fig. 4. The peak current of the nitrated 2,4-D goes on increasing with increasing bismuth deposition time up to 180 s and remains constant beyond this deposition time which suggest that the deposited layer of bismuth may have covered the surface of the electrode and substantial increment in film thickness prevented as a result of depletion of Bi<sup>3+</sup> at electrode–electrolyte interface.<sup>23,26</sup>

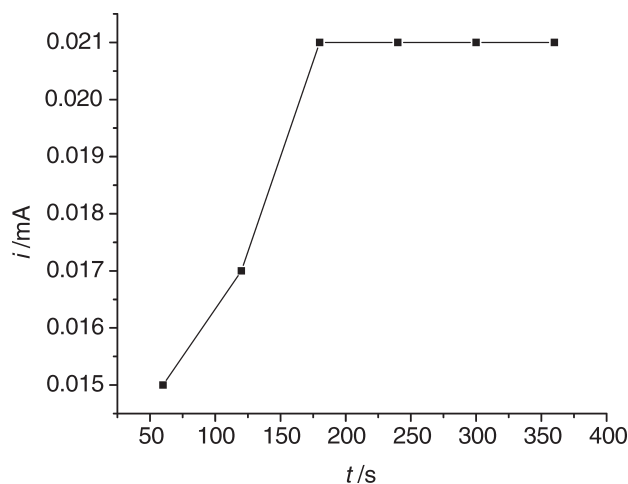
#### 3.3.3. Effect of Bath Concentration

The other important parameter which influences the thickness of bismuth film is the bismuth ion concentration on the peak current of the nitrated 2,4-D. The effect of concentration of bismuth ion was examined in the range of 0.5 to 3 mM as shown in Fig. 5 for 0.372 mM nitrated 2,4-D solution in buffer at pH 11.

The result in Fig. 5 shows that the peak current of the nitrated 2,4-D started increasing up to 2 mM Bi (III) ion and started decreasing for concentration beyond 2 mM Bi (III) ion. The increase in peak current for the increase in Bi (III) ion concentration up to 2 mM is attributed to the increase in the bismuth film thickness.<sup>27</sup> However, when the concentration of Bi (III) ion becomes higher, peaks decreased with increasing bismuth film



**Figure 3** Effect of deposition potential upon voltammetric response for 0.372 mM nitrated 2,4-D. Experimental conditions: 2 mM Bi (III) and deposition time 180 s, each data point represents an average of  $n = 3$ .



**Figure 4** Effect of deposition time upon voltammetric response for 0.372 mM nitrated 2,4-D. Experimental conditions: 2 mM Bi (III) and deposition potential at –1050 mV. Each data point represents an average of  $n = 3$  measurements.

thickness due to cracking of the film at higher concentration. Hence, this result is in agreement with result reported for the optimization of bath concentration.<sup>23,26</sup>

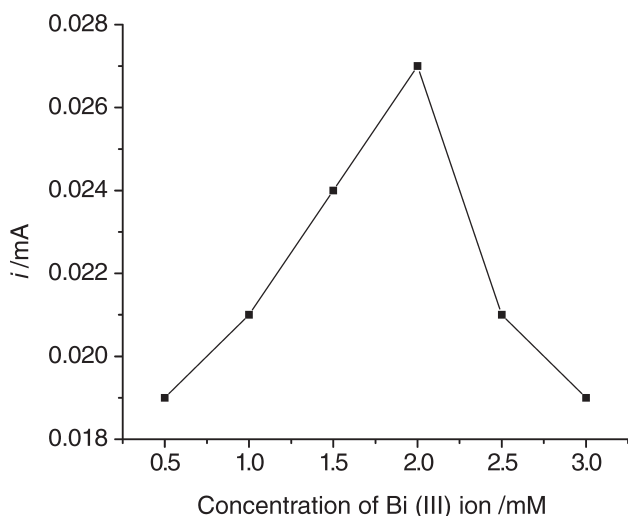
#### 3.3.4. Effect of pH of the Supporting Electrolyte

pH of the electrolyte is an important parameter that could have significant influence on the response of the electrode in electroanalysis. It was studied in the pH range of 1–13 in BR buffer. The results obtained is summarized in Fig. 6 in which the maximum response was observed at pH 11.

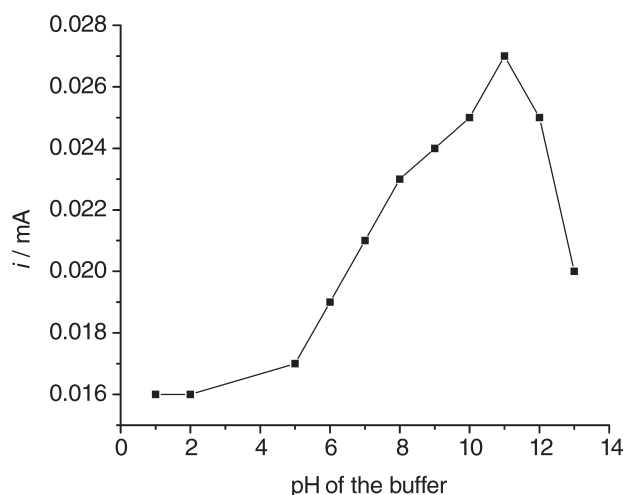
This may be due to the anionic form of the analyte being the redox active component. In addition, it is not advisable to work in pH < 6 solutions as the reduction of the analyte interferes with the hydrogen evolution reaction. Therefore, a pH 11 buffer was taken for the determination of 2,4-D throughout the experiments, in agreement with reports.<sup>17</sup>

### 3.4. Repeatability and Reproducibility

The repeatability and reproducibility BiFEs were determined by successive voltammetric measurements using 37.2  $\mu$ M nitrated 2,4-D in BR buffer solution at pH 11. In the repeatability study, nine successive voltammetric measurements on the same



**Figure 5** Effect of bath concentration upon voltammetric response for 0.372 mM nitrated 2,4-D. Experimental condition: deposition potential –1050 mV and deposition time 180 s. Each data point represents an average of  $n = 3$  measurements.



**Figure 6** Effect of pH of the supporting electrolyte upon voltammetric response for a solution containing 0.372 mM nitrated 2,4-D. Electrode Modification conditions: 2 mM Bi (III) bath, deposition time of 180 s and deposition potential at  $-1050$  mV. Each data point represents an average of  $n = 3$  measurements.

day were made under the same experimental condition, and the RSD was 5.84 %. This suggested that the proposed BiFEs have good repeatability.

The reproducibility of the BiFE was also examined by measuring  $37.2 \mu\text{M}$  of nitrated 2,4-D on three different days with triplicate measurement. The RSD obtained were 4.66 % for three independently prepared modified electrodes. This confirmed that the experimental results for the proposed BiFEs were reproducible.

### 3.5. Stability of the BiFE

The stability of the bismuth film modified SPCE after keeping it for two weeks was studied by amperometric measurements of  $37.2 \mu\text{M}$  nitrated 2,4-D. The mean peak current for 12 days measurement in two weeks for the nitrated 2,4-D was  $0.01125$  mA with RSD of 5.23. When we compare the initial current response (first day signal) to the mean, 93.75 % of the original signal was maintained. This result indicated that there was small peak current change showing that the BiFE had good stability.

### 3.6. Recoveries of 2,4-D from Soil and Water Samples

For the recovery studies, 10 mL of each of the nitrated water and soil samples were transferred into the electrochemical cell. The recovery was performed by spiking three different concentrations of nitrated 2,4-D ( $22.3$ ,  $29.7$ , and  $37.2 \mu\text{M}$ ) to each sample, and the resultant current peak of chronoamperometry was obtained using the proposed BiFEs.

The recovery obtained for 2,4-D in the real samples using the bismuth film modified SPCE ranges from 93.8 to 107.1 % as illustrated in (Table 1) for water and soil samples. These results may suggest that the matrices of the real samples do not have

**Table 1** Recoveries of 2,4-D from real samples ( $n = 3$ ).

Sample	Added/ $\mu\text{M}$	Recovered/ $\mu\text{M}$	Recovery %	RSD %
Water	22.3	22.4	100.4	8.66
	29.7	31.8	107.1	5.97
	37.2	34.9	93.8	5.09
Soil	22.3	23.1	103.6	7.53
	29.7	31.8	107.1	5.41
	37.2	37.7	101.3	4.56

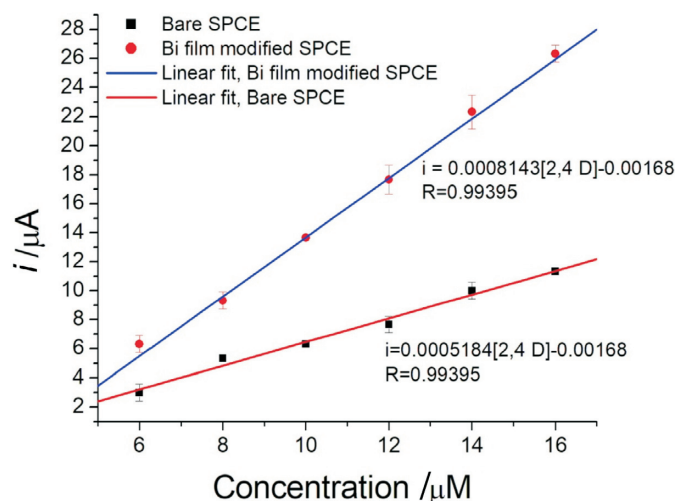
significant effects on the determination of the 2,4-D from real water and soil samples.

### 3.7. Determination of Detection Limit and Limit of Quantification

The calibration curve was constructed under optimum experimental parameters for the determinations of low levels of nitrated 2,4-D with triplicate measurements (Fig. 7). The limit of detection (LOD) which is three times the standard deviation of the blank divided by the slope of the curve and limit of quantification (LOQ), which refers to ten times the standard deviation of the blank divided by the slope of the curve, were calculated to be  $3.15$  and  $10.5 \mu\text{M}$ , respectively. As it is shown in the Fig. 7, the sensitivity of the bismuth modified SPCE is higher than that of the bare SPCE.

### 3.8. Comparison of the Method Developed in this Work with the Literature

The developed electroanalytical method for the determination of 2,4-D herbicide is compared with the values reported in the literature as shown in (Table 2). The proposed method has shown moderate performance.



**Figure 7** Comparison of the calibration curves for nitrated 2,4-D at the bismuth film modified SPCE and bare SPCE in a selected concentration range. For both modified and bare SPCE, the data points are an average

**Table 2** Comparison of the developed method in the present work and other methods described in the literature for the determination of 2,4-D.

Electrodes	Techniques	LOD	Reference
Protoporphyrin IX cobalt(III) chloride modified GCE	CA	$0.98 \mu\text{M}$	28
Silica-gel modified carbon paste electrode	CA	$0.400 \mu\text{M}$	29
Mercury electrode	ADS	$0.226 \mu\text{M}$	30
Static mercury electrode	DPV	$0.0226 \mu\text{M}$	17
Bismuth film modified SPCE	CA	$3.15 \mu\text{M}$	This work

#### 4. Conclusion and Recommendation

In this study, an analytical method for the electroanalysis of 2,4-D using bismuth film modified SPCEs was developed. The method has shown a dynamic linear concentration range from 11.1 to 74.3  $\mu\text{M}$  of the nitrated 2,4-D with regression coefficient of (R)0.9988. The limits of detection and quantification were 3.15 and 10.5  $\mu\text{M}$ , respectively. The method has exhibited very good electroanalytical properties such as high sensitivity, lower limit of detection (LOD) and wide linear dynamic range for the determination of 2,4-D. The method has advantages due to its inexpensiveness, simplicity, fast time analysis and lesser toxicity.

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