Fabrication of a sensitive electrochemical sensor of 2,4-dichlorophenoxyacetic acid herbicide based on synergistic catalysis of silver/manganese oxide nanoparticles and polyalizarin at low potential

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ABSTRACT

A new electrochemical method for determining 2,4-dichlorophenoxyacetic acid (2,4-D) in aqueous solutions was proposed. A glassy carbon electrode was modified with silver, manganese oxide nanoparticles, and alizarin yellow R polymer (Ag-MnOxNPs/PAYR). Scanning electron microscopy, energy dispersive X-ray spectroscopy and electrochemical impedance spectroscopy were used in order to characterize the modified electrode. The electrochemical attributes of 2,4-D at pH 1–13 were studied with the proposed electrode. In order to investigate the electrocatalytical oxidation attributes of this sensor, cyclic voltammetry and differential pulse voltammetry (DPV) were used. The linear range (22–11,752 μM) and detection of limit (7.33 μM) were appraised for oxidation peak at 0.8V by cyclic voltammetry method. In addition, the linear range (6–14,308 μM) and detection of limit (2 μM) were obtained by DPV technique. Results illustrated that the modified electrode has low detection limit, high linear range, and good repeatability at pH 6. Furthermore, this electrode was used for the analysis of 2,4-D in water samples.

Keywords: 2,4-dichlorophenoxyacetic acid herbicide; Silver nanoparticles; Manganese oxide nanoparticles; Alizarin yellow R; Sensor

1. Introduction

In recent years, agricultural pesticides from surface and groundwater sources have become a major community health issue due to irrigation of agricultural land, rainfall and floods. Due to rising population rates and demand for agricultural and food products, the use of agricultural toxins including pesticides has also increased and the over use of these substances has resulted in a serious threat to the environment [1–4]. Pesticides are classified according to their application and function as herbicides, insecticides, fungicides, rodenticide, nematodes and plant growth regulators and insecticides [5]. The use of herbicides is one of the most common agricultural methods for maintaining productivity and growth of plants and it accounts for the largest share of global sales of pesticides (approximately 47.6%) with annual consumption reaching more than 6,000 tons in some countries [6]. Common herbicides include parquet, 2,4-dichlorophenoxyacetic acid (2,4-D), simonize, and diuron [7]. Among the most widely used herbicides, 2,4-D with the chemical formula of $C_8H_6Cl_2O_2$ is a toxic acid and non-volatile and its formulations includes

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numerous esters, acids and salts. 2,4-D is a systemic and selective herbicide which was introduced in the 1940s as the first commercial herbicide. It is also used as a growth regulator in citrus and crops and controls weeds in wheat and barley fields [8–10]. 2,4-D acts as natural auxin causing cell division and cell elongation and increasing shelf life of fruits at low concentrations [11]. In modern agriculture, this type of herbicide is used because of its low cost and high selectivity [12]. Approximately 91.7% of this toxin enters water resources leading to contamination and threatening animal life, vegetation, aquatic life and human health [5]. The US Environmental Protection Agency (US EPA) has placed 2,4-D in Group D of carcinogenicity suspected of endocrine disruption. Moreover, the World Health Organization (WHO) classifies it as a Class 2 toxic herbicide [6,7]. Exposure to oral doses might have adverse effects on the eye, thyroid, kidney and adrenal glands and causes symptoms such as acute oral infection, vomiting, abdominal pain, headaches, dizziness, and abnormal behavior in humans [8]. Due to the low biodegradability of 2,4-D toxin in water, it can be considered as one of the main pollutants in water resources [9].

Therefore, detecting the levels of these herbicides in food and environment is essential [10]. Several techniques have been applied for the detection and determination of 2,4-D including gas chromatography (GC), high-performance liquid chromatography, thin-layer chromatography, and mass spectrophotometry. However, most of these methods are complex, time consuming and require sophisticated and expensive equipment [11,12]. Electrochemical techniques can be considered for the detection and determination of 2,4-D. However, the electrochemical detection of 2,4-D at the surface of unmodified or bare electrodes such as glassy carbon electrode (GCE) is not possible.

Many techniques have been suggested to overcome this problem. One of these is modification of the surface of bare electrodes with various chemical materials such as organic compounds [13], metals [14], biomaterials [15], polymers [16], composites [17] and nanomaterials [18].

Recently, the use of nanoparticle and polymer modified electrodes for the fabrication of electrochemical sensors and biosensors has become of great importance and its advantages include cost-effectiveness, ease of access and ease of sampling. In this work, an electrode modified with a silver, manganese oxide nanoparticles, and alizarin yellow R polymer (Ag-MnOxNPs/PAYR) was fabricated for detecting 2,4-D. This proposed electrochemical sensor was applied for the detection and determination of 2,4-D in real water samples with satisfactory results. In order to detect 2,4-D, most previous research used biosensors and the electrode made was often unstable, complex and costly. This nano-sensor not only did not possess the disadvantages of biosensors but could also analyze 2,4-D in less positive potentials compared to most other sensors, particularly in two areas of potential (0.29 and 0.8 V).

2. Experimental

2.1. Materials

Buffer solutions (0.1 M) were prepared from di-sodium hydrogen phosphate (Na_2HPO_4), sodium dehydrate phosphate (NaH_2PO_4), hydrogen chloride (HCl) and sodium hydroxide (NaOH), silver nitrate ($AgNO_3$), polyvinylpyrrolidone (PVP), potassium nitrate (KNO_3), manganese sulfate ($MnSO_4$), and sodium sulfate (Na_2SO_4) purchased from Merck Company. Alizarin yellow R and 2,4-D solution were purchased from Aldrich company. All electrochemical experiments were carried out at 25°C ± 0.10°C and in order to prepare all solutions, double distilled water was used.

2.2. Apparatus

Scanning electron microscopy (SEM) was carried out (JEOL/EO JSM5900, Tokyo, Japan) at an accelerating voltage of 20 kV. Electrochemical experiments results were obtained from a micro-computer controlled galvanostat/potentiostat (Eco Chemie U/techt, the Netherlands), with GPES software (Eco Chemie). This device consisted of three electrodes: (1) Ag(s)/AgCl(s)/Cl⁻(aq), saturated KCl) reference electrode, (2) a platinum counter electrode (0.2 mm diameter) and (3) glassy carbon working electrode (3 mm diameter). Data was analyzed by a personal computer.

2.3. Electrode preparation and modification

First, the surface of the bare GCE was polished with 0.5 mm alumina and then ultrasonically washed in ethanol for 3 min to remove alumina particles [19]. Then, silver nanoparticles were placed on the glassy carbon electrode
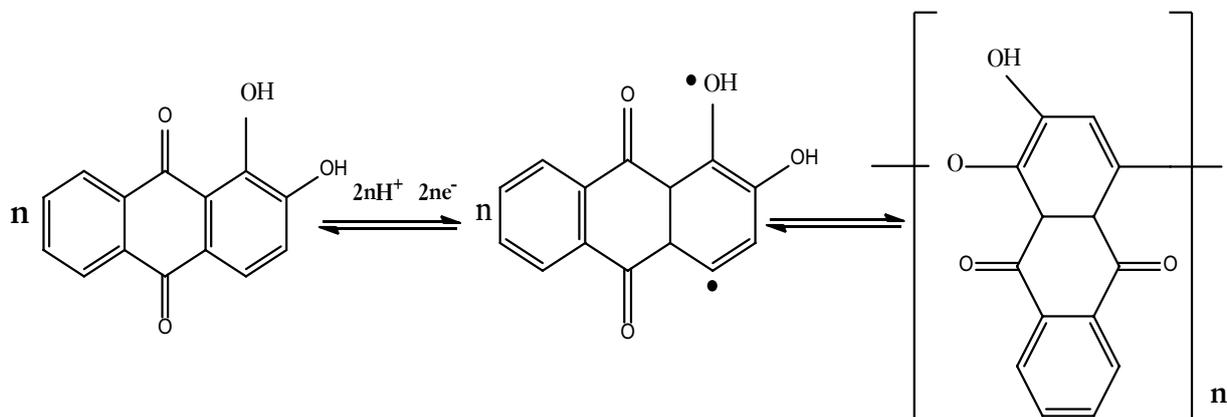
with chronoamperometry technique. For this, the bare electrode was placed in an electrochemical cell containing 0.1 M KNO_3, 15 mM $AgNO_3$ and 2 g/L PVP under potential of −0.4 V for 80 s [20] for fabrication of AgNPs/GC electrode. The next step involved the construction of Ag-MnOxNPs/GCE, AgNPs/GC electrode which was immersed in 1 mM $MnSO_4 \cdot 2H_2O$ solution containing 0.1 M Na_2SO_4 under potential range of −0.8 to 1.8 V and scan rate of 10 mV/s by cyclic voltammetry technique [21]. Finally, for fabrication of Ag-MnOxNPs/PAYR/GCE, with continuous scanning number (15 cycles) and potential range of −1 to 2.2 V at 100 mV/s, redox peak currents were increased showing the successive growth of the PAYR on the Ag-MnOxNPs/GCE by cyclic voltammetry method (Fig. 1) [22]. The mechanism of electropolymerization of alizarin was proposed as follows:

3. Results and discussion

3.1. Morphological and characterization of Ag-MnOxNPs/PAYR /GCE

The SEM images for: (a) AgNPs, (b) Ag-MnOxNPs and Ag-MnOx/PAYR (c) electrodes are illustrated in Fig. 2, respectively. As can be seen, the morphologies of the electrodes are not similar and each modifier are seen to be dispersed uniformly on the surface of glassy carbon electrode.
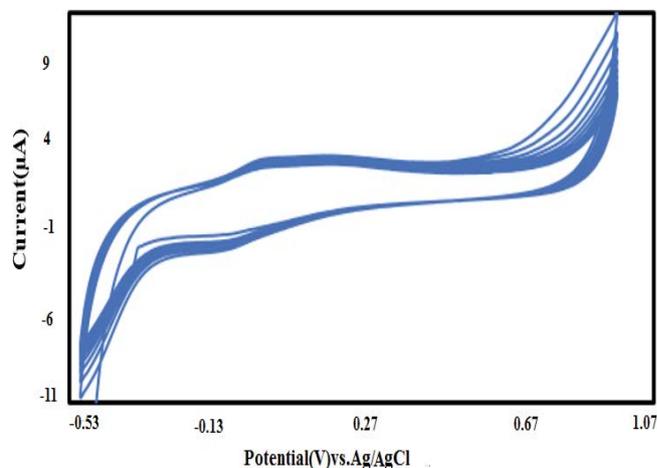
Fig. 1. Successive cyclic voltammograms of the electropolymerization of PAYR on the Ag-MnOxNPs/GCE at potential scan rate of 100 mV s⁻¹.
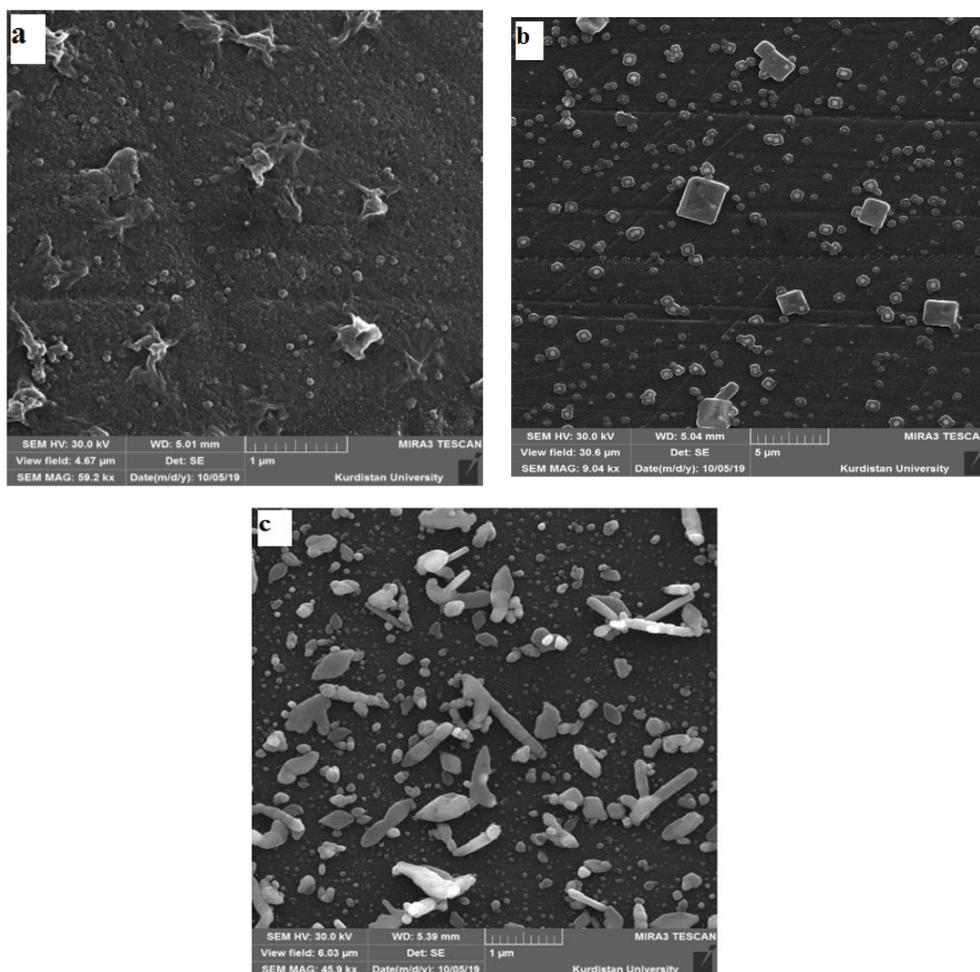
Fig. 2. SEM images for: (a) AgNPs, (b) Ag-MnOxNPs and (c) Ag-MnOx/PAYR GC electrodes.

The energy dispersive X-ray spectroscopy (EDX) analysis was performed for different electrodes. As observed, in Fig. 3a, AgNPs and carbon are deposited on the surface of electrode. Then, the AgNPs, MnNPs and carbon elements were placed as a modifier (Fig. 3b and c). High carbon percentage is attributed to the PVP and polyalizarin components of the modified electrode. These results confirm what we expected.

3.2. Electrochemical impedance spectroscopy study of Ag-MnOx/PAYR GC electrode

For the electrochemical investigation of unmodified and modified electrodes and evaluation of the electrochemical treatment of stepwise modification of electrodes, electrochemical impedance spectroscopy (EIS) is a good method. Fig. 4 shows the impedance spectra as Nyquist curves (Zim vs. Zre) for bare glassy carbon electrode (Fig. 4a), AgNPs/GCE (Fig. 4b), Ag-MnOxNPs/GCE (Fig. 4c), and Ag-MnOx/PAYR GC (Fig. 4d) in 5 mM $Fe(CN)_6^{3/4-}$ at 0.20 V and in the frequency range of 0.01 to 10,000 Hz. The semicircle dramatically decreased for AgNPs/GCE and Ag-MnOx/GCE and became smaller than other electrodes. Thus, in the presence of these nanoparticles not only will the electron transfer be easer but also a new layer can be placed on the surface of bare electrode. For Ag-MnOx/PAYR GC electrode, the semicircle was increased due to the repulsive force between the negative charges of $Fe(CN)_6^{3-/4-}$ and alizarin.

3.3. Electrocatalytic oxidation of 2,4-D on Ag-MnOx/PAYR GC electrode

To investigate the ability of the suggested modified electrode to oxidize 2,4-D and introduce it as a novel electrochemical nanosensor in measuring this toxin, the 2,4-D behavior on (a) bare electrode, (b) AgNPs/GCE, (c) Ag-MnOxNPs/GC and (d) Ag-MnOx/PAYR/GC electrodes in the presence of buffer 6 and 2,4-D were evaluated. Based on the results illustrated in Fig. 5, no anodic peak current was observed with the increase of 2,4-D at the surface of bare electrode. At the surface of modified electrode with AgNPs and Ag-MnOxNPs, low anodic peaks were observed. Furthermore, when the electrode was modified by alizarin, a dramatic increase in anodic peak current of 2,4-D was absorbed. Therefore, the Ag-MnOx/PAYR/GC electrode is a suitable electrochemical sensor for electrooxidation and detection of 2,4-D.

Based on the results obtained from this work and other research [23], a possible electro-oxidation of 2,4-D mechanism can be proposed as per Fig. 6:

In order to investigate the effect of pH on behavior of the proposed electrode for electrooxidation of sample, the cyclic voltammograms of the modified electrode in 10 mL of 0.01 M 2,4-D were recorded at different pH values (1 to13). At pH 6, maximum peak current was observed. At lower pH, the anodic peak currents are very low. At higher pH, the oxidation peaks disappeared. Therefore, pH 6 was suggested as optimum pH for measurement of 2,4-D. In addition, the behavior of Ag-MnOx/PAYR/GC electrode was studied at scan rate ranging from
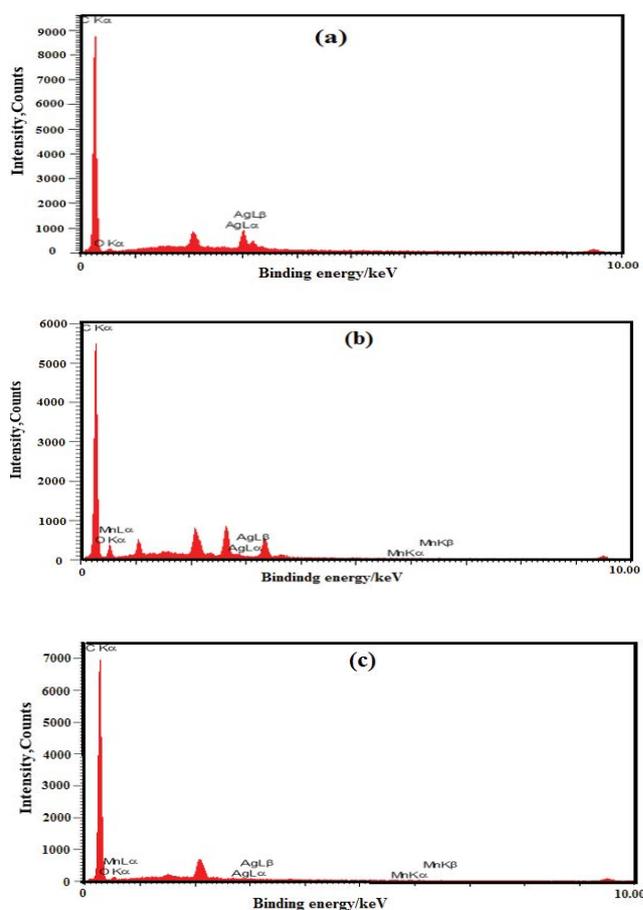
Fig. 3. EDX analysis for different electrodes. (a) AgNPs, (b) Ag-MnOxNPs and (c) Ag-MnOx/PAYR GC modified electrode.
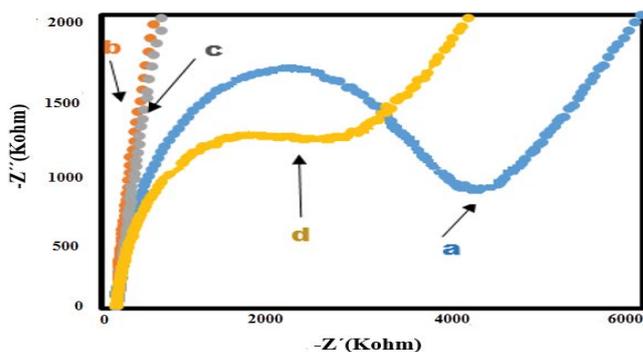
Fig. 4. Electrochemical impedance spectroscopy (EIS) of (a) bare glassy carbon electrode, (b) AgNPs, (c) Ag-MnOx and (d) Ag-MnOx/PAYR GC modified electrode in 5 mM $[Fe(CN)_6]^{3/4}$.

10 to 110 mV/s. The curves of anodic currents vs. square root of scan rate were linear suggesting that the system was controlled by diffusion function (Fig. 7) [24].

Moreover, the cyclic voltammograms of the Ag-MnOx/PAYR/GCE in the presence of different concentrations of 2,4-D were evaluated. As Fig. 8 indicates, the anodic peak current was proportional to the 2,4-D amounts. In addition, Fig. 8 shows the peak current response curve against

the 2,4-D concentration which shows a linear range of 22–11,752 µM using the cyclic voltammetry method [25].

For measuring 2,4-D at lower concentrations, differential pulse voltammetry (DPV) method was considered. Fig. 9 shows the increased of anodic peak current in the potential of about 0.62 V with detection of limit 2 µM and linear range of 6–14,308 µM.
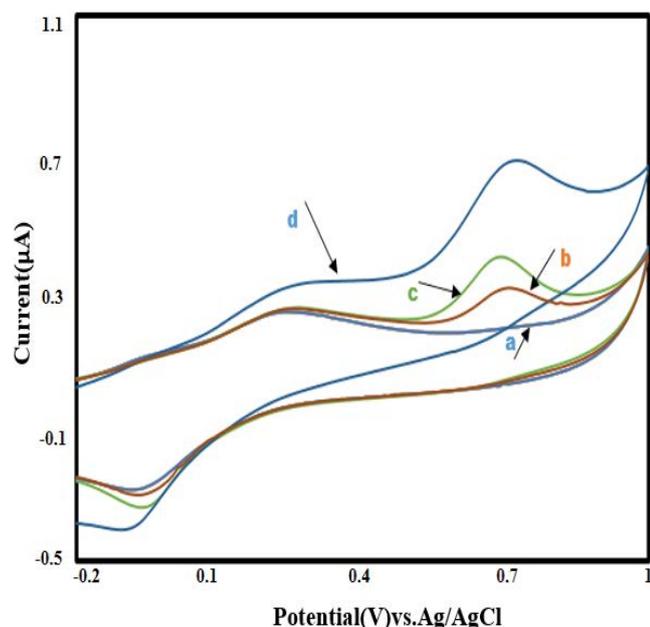
Fig. 5. Cyclic voltammetry response of (a) bare GCE, (b) AgNPs, (c) Ag-MnOxNPs and (d) Ag-MnOx/PAYR GC modified electrodes in the presence of 2,4-D.

3.4. Comparison of the Ag-MnOx/PAYR/GCE with previously reported electrochemical methods

This novel electrode was compared with several other procedures that reported 2,4-D herbicide analysis. The results are shown in Table 1. As can be observed, the linear dynamic range and detection limit of this electrochemical sensor are better or comparable with those of other techniques.

3.5. Interference effect

The modified electrode with Ag-MnOx/PAYR in the presence of some interferences including herbicides, insecticides and phenol were examined at pH 6 containing 2,4-D and 0.5-fold, 1-fold and 2-folds concentrations of emedalkopridi, malathion, and diazinon. These materials did not interfere in the determination of 2,4-D. The anodic peak current of 2,4-D increased with the increase in phenol. Therefore, phenol can be considered as an interference option in detection of 2,4-D.

3.6. Stability and repeatability of modified electrode

The long-time storage stability of the Ag-MnOx/PAYR/ GCE was investigated over a four-week period. When this electrode was stored at laboratory temperature and tested intermittently (every 14 d), after 4 weeks of storage approximately 95% of this electrode was retained. These results demonstrate the good stability of the modified electrode for 2,4-D herbicide analysis. In addition, the repeatability of response current in the Ag-MnOx/PAYR/GCE was investigated at 2,4-D herbicide concentration of 1,100 µM. The variation coefficient was 2.2% for five successive assays.
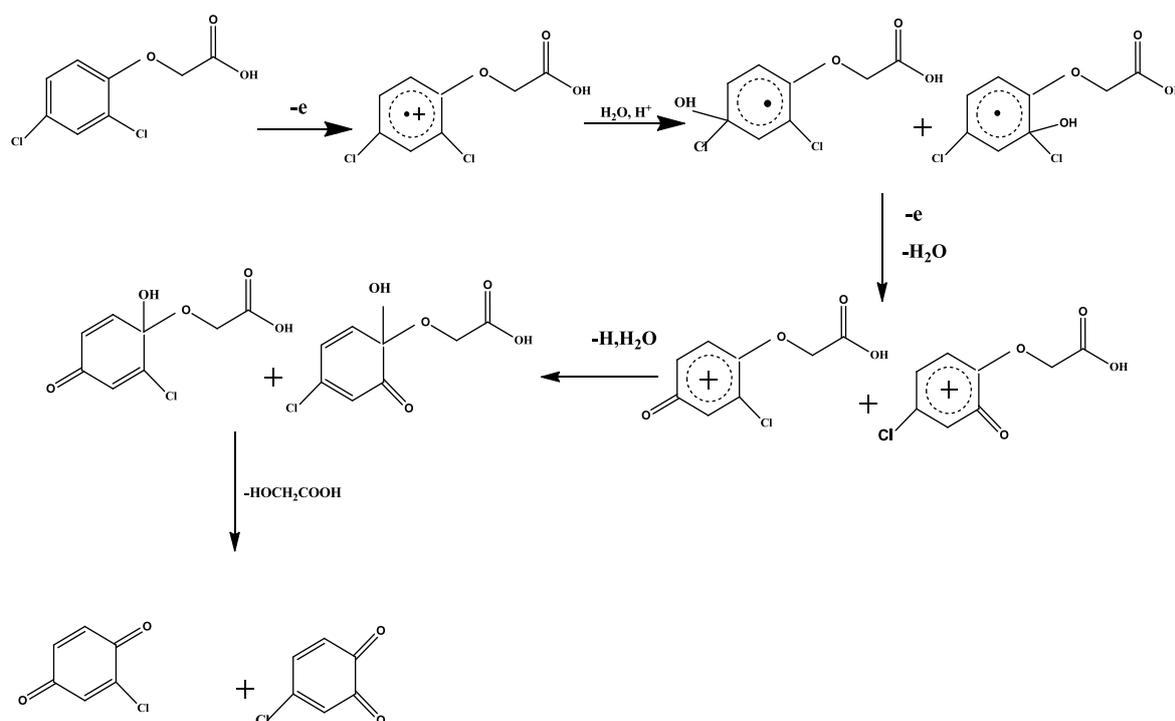
Fig. 6. Electro-oxidation of 2,4-D mechanism.
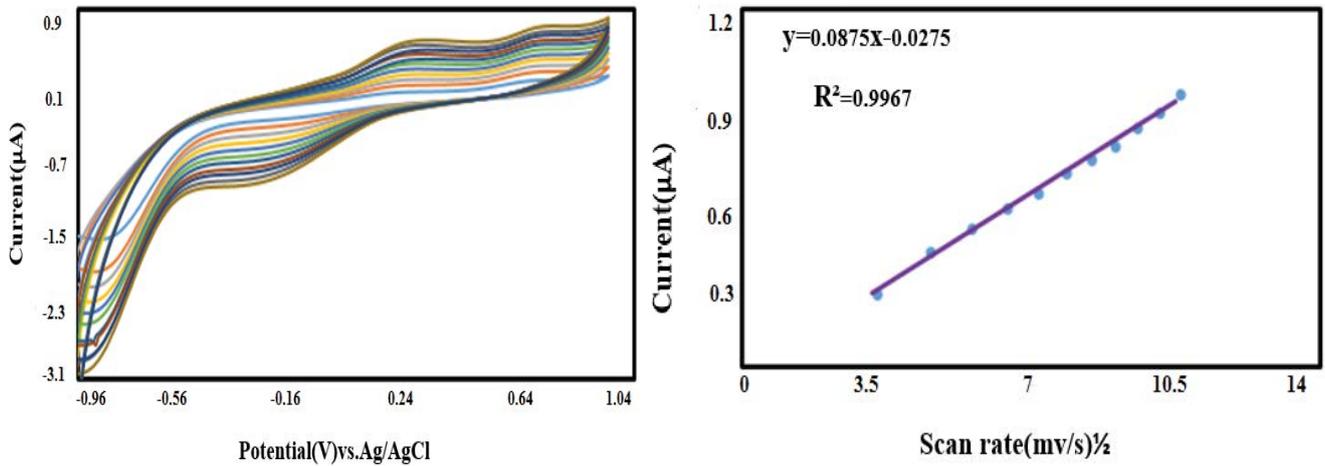
Fig. 7. Cyclic voltammetry response of a GCE modified with Ag-MnOx/PAYR in a 0.10 M phosphate buffer (pH 6) containing of 2,4-D at different scan rates; and the plot of I_p vs. $v^{1/2}$.
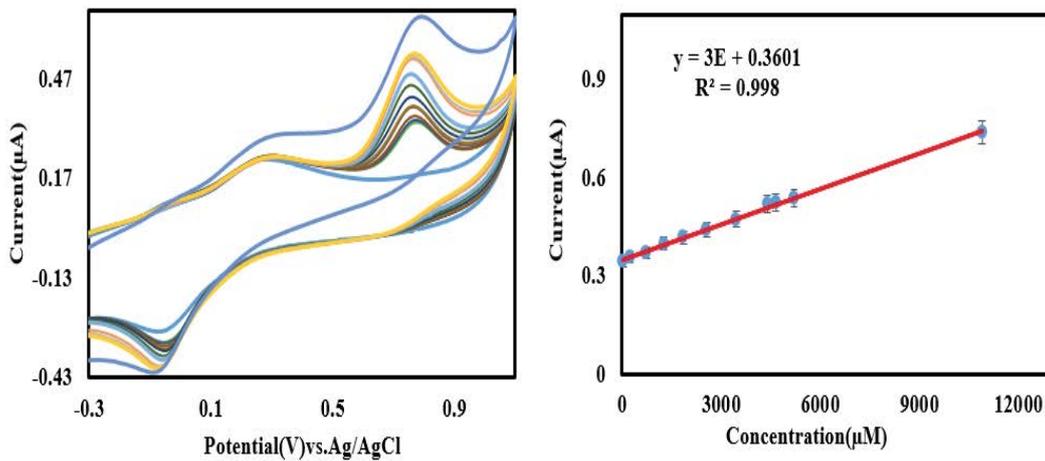
Fig. 8. Cyclic voltammograms of Ag-MnOx/PAYR/GCE in buffer solution pH 6 at scan rate of 30 mV s^{-1} with increasing 2,4-D concentration; and the plots of peak current vs. 2,4-D concentrations.
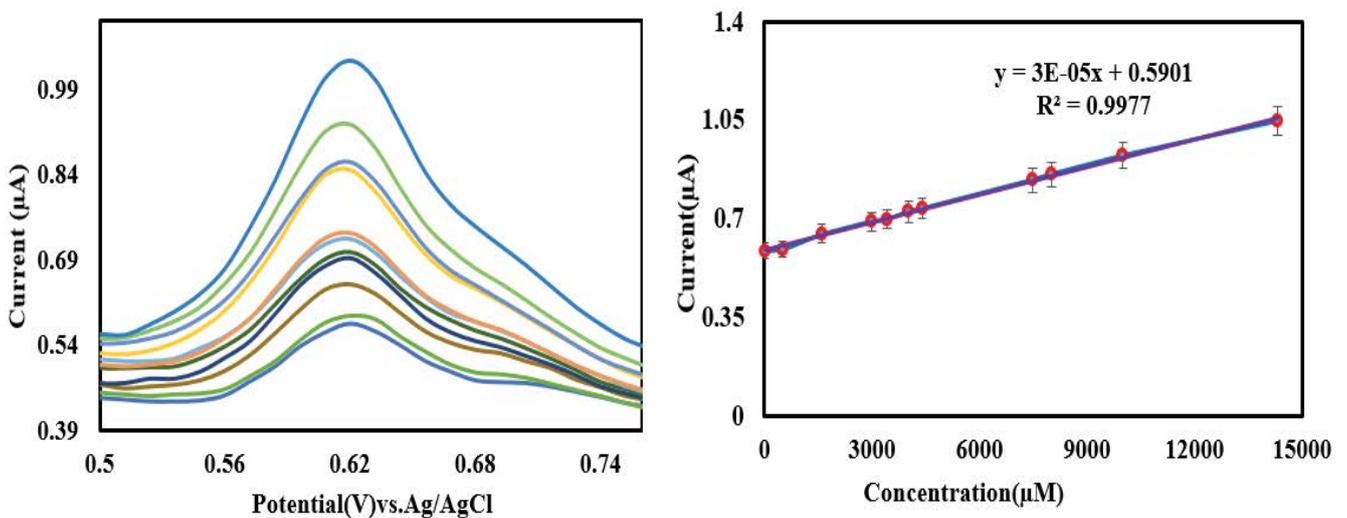
Fig. 9. Differential pulse voltammetry of Ag-MnOx/PAYR/GCE in buffer solution at pH 6 with increasing 2,4-D concentrations; and the plots of peak current vs. 2,4-D concentrations.

Table 1
Some analytical results of several modified electrodes for detection of 2,4-D

Electrode	Modifier	pH	Linear range	Detection of limit	Applied potential (V)	Method	Ref.
GCE	Hp-CaP	7	0.03–3 μM	0.015 μM	−0.25	(CV)	[26]
GCE	Fe$_3$O$_4$	8.5	0.5–30 μg/L	0.167 μg/L	0.6	(CV)	[27]
GCE	PPy@TiO$_2$	7	0.5–13 μM	10 nM	–	(CV)	[28]
SPE	Nafion	9	0.01–100 μg/L	0.01 μg/L	0.425	(CV)	[29]
CPE	Amphiphilic fluoro + hectorite heterostructure clay	7.4	20 μM	6.67 μM	0.8	(DPV)	[30]
GCE	Gold	7	0.3–30 μg/L	0.1 μg/L	–	Amperometric	[31]
GCE	Gold	7	45–450,000 nM	15 nM	–	impedance	[32]
GCE	Ag-MnOxNPs/PAYR	6	22–11,752 μM	7.33 μM	0.8, 0.29	(CV)	This work
			6–14,308 μM	2 μM	0.63	(DPV)	

3.7. Analytical application

The applicability of this electrode was tested for the measurement of 2,4-D herbicide at three different water samples via a recovery study according to the suggested protocol. Satisfactory results with recoveries ranging from 98.5% to 103.7% were obtained.

4. Conclusion

In conclusion, a novel electrochemical sensor was presented based on immobilizing of Ag-MnOx/PAYR on bare glassy carbon electrode. Ag-MnOx/PAYR/GCE can be used for determination of 2,4-D herbicide in water samples. Electro-oxidation of 2,4-D herbicide at the surface of the modified electrode were carried out at pH 6 and appropriate applied potential. The authors believe that this assembly of metal nanoparticles by conductive polymer will obtain novel hybrid nanocomposite with synergetic properties. This method is recommended for construction of electrochemical sensors for detection of various samples.

Acknowledgments

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