



Development and characterization of iron (III) phthalocyanine modified carbon nanotube paste electrodes and application for determination of fluometuron herbicide as an electrochemical sensor



Ersin Demir ^{a,*}, Özge Göktug ^b, Recai İnam ^c, Doğukan Doyduk ^c

^a Department of Analytical Chemistry, Faculty of Pharmacy, Afyonkarahisar Health Sciences University, 03030 Afyonkarahisar, Turkey

^b Department of Chemistry, Faculty of Science, Yıldız Technical University, 34100 Istanbul, Turkey

^c Department of Chemistry, Faculty of Science Gazi University, 06500 Ankara, Turkey

ARTICLE INFO

Keywords:

Fluometuron
Modified Electrode
Phthalocyanine
Electrochemistry
Determination

ABSTRACT

This study is the first electroanalytical study conducted for the determination of fluometuron herbicide. For this purpose, a new electrode was prepared by combining iron (III) phthalocyanine – 4,4',4'',4'''-tetrasulfonic acid, oxygen monosodium salt hydrated compound (FePc) and multi-walled carbon nanotube powders (MWCNTP). The FePc/MWCNTP composite (hybrid) material prepared in this way was coated on glassy carbon electrode (GCE) and multi-walled carbon nanotube paste electrode (MWCNTPE) using the drop-dry method. Compared to both the bare GCE and MWCNTPE, the modified FePc/MWCNTPE increased the anodic peak current of fluometuron by approximately six fold. Calibration plots of the fluometuron were constructed using the standard addition method with differential puls stripping voltammetry (DPSV) and square wave stripping voltammetry (SWSV) under the optimum conditions. While the working range was determined as 0.4–15.0 mg/L in pH 6.0 Britton Robinson (BR) buffer solution on FePc/MWCNTP electrode with DPSV, this range was found to be 0.4–7.5 mg/L with SWSV. In addition, the limit of detection (LOD) and the limit of quantification (LOQ) values were 69.8 µg/L and 233.0 µg/L, respectively, by DPSV. On the other hand, these two validation values (LOD and LOQ) were 101 µg/L and 337 µg/L by SWSV, respectively. Subsequently, cyclic voltammetric (CV) studies were carried out to elucidate the electrochemical behavior and electrode mechanism of the fluometuron herbicide. In addition, the interference effects of some cations and pesticides in the determination of fluometuron were examined. Finally, studies of recovery of fluometuron herbicide from tap water and determination of fluometuron in Cottonex 500 SC® commercial pesticide formulation using the proposed DPSV method and modified FePc/MWCNTP electrode were performed with very low relative error.

1. Introduction

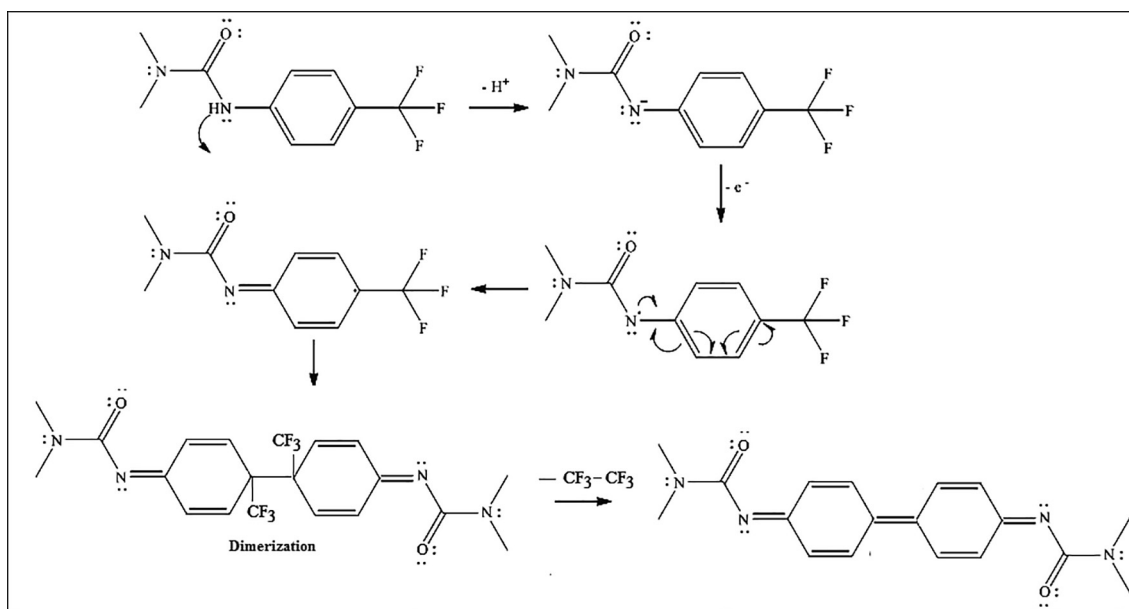
Fluometuron (1,1-dimethyl-3- [3-(trifluoromethyl) phenyl] urea), from the phenyl urea herbicide group, is a pesticide used to control broad-leaved weeds such as dicotyledons and some monocotyledons. Generally, it is preferred for production of cotton and sugar cane [1]. The fluometuron herbicide is applied before planting crops or as soon as broad-leaved weeds appear [1]. Moreover, fluometuron is also known as an herbicide that selectively inhibits photosynthesis [2]. This herbicide is also in Class 3 toxicological grouping as moderately toxic compound, reported lethal dose (LD₅₀) value of 6416–8900 mg/kg in rat [3,4] and causes negativity in human reproductive and respiratory systems [5]. In addition, when exposed for a

long time, it causes “conjunctivitis” [5]. Other symptoms seen in fluometuron poisoning are collapse muscle weakness, extreme fatigue, and tearing or watering [1]. Furthermore, according to the European Union pesticide data-base, the maximum residual limit (MRL) value of fluometuron herbicide in sugar cane, drinking water and citrus fruits was determined as 0.01 mg/kg [6]. Since its solubility in water is moderate, it has a half-life of 12 to 171 days in soil environment, while this life is very long, approximately 25 to 36 months in water [1]. For this reason, it is crucial to carry out the residue analysis of fluometuron pesticides in environmental and food samples with sensitive and reliable methods (see Scheme 1).

It is a shortcoming that there are few studies of determinations in natural samples and commercial formulations of fluometuron pesti-

* Corresponding author.

E-mail address: dr.ersindemir@yahoo.com (E. Demir).



Scheme 1. Possible electrode-oxidation mechanism for fluometuron herbicide.

cide, which is crucial for the environment and human health. [7–13]. Most of the studies have been done by chromatographic methods [10–13], and a few spectrometric techniques have been available [1,2,8]. However, gas chromatography (GC) is not used directly for the analysis of phenyl urea herbicides due to their polar and thermolabile nature [14–16]. For this reason, conventional analytical methods either by high performance liquid chromatography (HPLC) or other analyzer systems such as HPLC's hyphenated techniques like fluorescence detector [11] mass spectrometer [7; 10], diode array detector (DAD) [12,13] have been used for the determination of fluometuron. These analytical methods have some drawbacks such as long analysis time, use of a large number of solvents, the need for long pre-treatment, and using expensive equipment [17–19]. Nevertheless, they successfully performed the determination of fluometuron in natural samples [7–13]. However, a novel, cheaper, faster, more sensitive and selective analytical method is needed to determine the fluometuron analyte even in complex matrix environments or biological samples. Electrochemical methods have attracted great interest recently due to their fast analysis time, no need for pre-treatment and their cheapness [20–22]. Furthermore, electrochemical methods, with numerous modified electrodes developed with the discovery of incredible new materials such as polymers, nanoparticles, clays and phthalocyanines have been used successfully to evaluate ultra-trace analytes [23–29].

In electrochemical methods, using working electrodes produced by many different hybrid materials, it is possible to investigate the electrode reaction of many molecules and to elucidate their electrochemical behavior [22,30–33]. The electroanalytical methods are of great interest in green chemistry, since very little organic solvent is used compared to traditional analytical methods [22,32–35]. Electrochemical identification is the best substitute for detecting large numbers of compounds, even in very complex matrices such as pharmaceutical and biological samples [22,29–35]. In addition, it is possible to obtain indicator electrodes with superior properties by using different catalytic materials in order to increase the sensitivity, selectivity and stability of the electrode in the analysis of electroactive compounds. [29,35]. In the last decade, due to their superior catalytic properties, Pc's are preferred as sensors not only in qualitative analysis but also in quantitative analysis of countless substances [29,36,37]. Due to its incredible physical and chemical properties, it has applications in

many different fields such as photovoltaic solar cells, reduction photo catalysis reactions, semiconductor materials, electrochemical and gas sensors [26]. When looking at sensor applications of PCs, it is seen that they have a wide potential range, superior selectivity, trace level substance determination and wonderful kinetics [29,36,37]. Carbon nanotube modified paste electrodes have advantages such as easy and fast preparation, low cost, easy and quick surface construction and renewal. In addition, its use has increased significantly in recent years, thanks to its ability to contain many biosensor materials at the same time, its wide operating potential range and very low ground currents.

Until now, no electrochemical study has been found in the literature for the determination of fluometuron, despite to carry out by other analytical methods [11–14]. In the light of these issues, the aim of this study is to illuminate the electrochemical behavior of the fluometuron herbicide for the first time, as well as to perform its quantitative analysis in natural samples. Moreover, a new composite (hybrid) materials such as iron (III) phthalocyanine/multi walled carbon nanotube electrode (FePc/MWCNTPE) and iron (III) phthalocyanine/glassy carbon electrode (FePc/GCE) which are rapid, sensitive, selective and portable sensors were used in the determination of herbicide. Surface characterization of the electrode, which affects repeatability, accuracy and applicability, was carried out by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) methods. Also, among the electrochemical methods, square wave stripping voltammetry (SWSV) and differential pulse stripping voltammetry (DPSV) were preferred for quantification and cyclic voltammetry (CV) technique was carried out to elucidate the electrochemical behavior of fluometuron. Furthermore, the determination of fluometuron was successfully carried in natural samples such as tap water and its herbicide formulation by DPSV on modified FePc/MWCNTPE.

2. Experimental

2.1. Apparatus

IVIUM Vartex.one model potentiostat/galvanostat electrochemical analyzer was used for electrochemical measurements. In the voltammetric cell, there is a three-electrode cell configuration, which is car-

bon-based modified FePc/MWCNTPE (in BASi MF-2010, a diameter $\phi = 3$ mm) as the working electrode, Ag/AgCl (3 M NaCl, BASi, MF-2052) as the reference electrode and platinum wire (BASi, MW-1032) as the counter electrode. For pH measurements, a portable ISO-LAB trademark pH meter was used. Sartorius trademark balance (± 0.0001 g precision) was used for weighing of all chemical reagents. Ultrasonic bath was used for homogeneous sample preparation.

2.2. Reagents

The solvents required for the accurate and precise preparation of stock solutions were used in analytical purity. Analytical reagent grade fluometuron ($C_{10}H_{11}F_3N_2O$; Mwt 232.20) was obtained from Merck and its stock solution was prepared daily as 500 mg/L by dissolving 0.0050 g of fluometuron in 5.0 mL acetone and diluting up to 10 mL volume with distilled water. For the modifying iron (III) phthalocyanine (FePc), iron (III) phthalocyanine-4,4',4'',4'''-tetrasulfonic acid, oxygen monosodium hydrated salt ($C_{32}H_{15}FeN_8O_{14}S_4Na \cdot xH_2O$; 942.60, anhydrous basis) purchased from Sigma-Aldrich was used. The mineral oil used as a binder, multi walled carbon nanotube powder, dimethyl formamide (DMF) and acetone were purchased from Sigma-Aldrich for analytical purity. A 0.1 M hydrochloric acid solution was prepared to have a pH 1.0. Britton Robinson (B-R) stock buffer solution contains 0.04 mol/L boric acid 0.04 mol/L acetic acid (Glacial, ReagentPlus®) and 0.04 mol/L phosphoric acid. 2.0 M NaOH or 2.0 M HCl solutions were added to this stock buffer solution with pH-meter control, and buffers were prepared at different pH's between pH 2.0 and pH 12.0. Distilled water was used for the preparation and dilution of all the stock solutions needed during the experimental measurements, and also, when the stock solutions were not used, they were kept in a dark refrigerator. Moreover, before the bare electrodes were modified, the surfaces of both electrodes were thoroughly cleaned, washed sequentially with distilled water, ethanol and acetone, and dried in a 40 °C oven for 2 h.

2.3. Preparation of bare and modified electrodes

The bare multi walled carbon nanotube paste electrode (MWCNTPE) was prepared using a mixture of about 70% multi-walled carbon nanotube powder (MWCNTP) and 30% mineral oil by mass. First, the mineral oil was weighed precisely in a porcelain mortar, and then multi-walled carbon nanotube powder was added until the mass ratio of 70/30 MWCNTP-mineral oil was reached. After that, this solution was mixed for about 2 h to be homogeneous.

In the preparation of modified electrodes, the -OH end groups in Fe (III) phthalocyanine were converted into chloride. For this procedure, Fe (III) phthalocyanine was reacted with phosphorus oxychloride ($POCl_3$) by refluxing in $POCl_3$ for about 16–20 h. Thus, Fe (III) phthalocyanine and MWCNTP interacted easily and a new hybrid material (composite) was obtained. The resulting FePc-Cl was suspended in 1.0 mL of dimethylformamide (DMF) by stirring in an ultrasonic bath for 1.0 h. This FePc-Cl suspension and the NH_2 functionalized multiwalled carbon nanotubes (NH_2 -MWCNTP) were reacted at room temperature for 16 h under reflux. This mixture was then filtered using filter paper (Whatman No. 42). Finally, the precipitate was washed sequentially with dichloromethane, water and acetone and dried under vacuum. Approximately 1 mg of FePc/MWCNT hybrid material obtained was dispersed in 1.0 mL of DMF solvent in an ultrasonic bath at 2 h at room temperature. 10 μ L of this dispersion solution was taken with the help of a micropipette and the electrodes were modified by applying the drop-dry technique onto the bare MWCNTPE and GCE surfaces. Also, the proposed electrodes are ready for the measurement again with the washing process with water. In order to ensure the reversibility on the surface of the bare and modified electrodes, reverse potential was applied with CV to remove the contamination.

3. Results and discussion

The electrochemical behavior of the fluometuron herbicide on modified FePc / MWCNTPE electrodes and the mechanism of electrode reaction were searched, and then the applications on natural samples were performed by square wave stripping voltammetry (SWSV), differential pulse stripping voltammetry (DPSV) and cyclic (CV) voltammetry. Accordingly, first modified electrodes were fabricated and then surface characterization studies were carried out. After selecting the best modified indicator electrode, the optimum supporting electrolyte solution was determined. Then, the voltammetric behavior of fluometuron on these electrodes was examined. For the selection of the most suitable stripping technique for quantitative analysis in natural samples, validation parameters such as working potential range and detection limits were taken into consideration. It was determined that the most suitable method for fluometuron detection was DPSV on modified FePc/MWCNTPE electrode. After all, interference studies and analytical applications were performed with DPSV using modified FePc/MWCNTPE electrode.

3.1. Fabrication of modified electrodes

With a process, -OH end groups in Fe (III) phthalocyanine were converted into chloride (St. 1). Fe (III) phthalocyanine was reacted with phosphorus oxychloride ($POCl_3$) after boiling under reflux for 16–20 h in $POCl_3$. The reaction mixture turned a dark blue color, and then the solvent of the mixture was removed under reduced pressure.

Our aim in carrying out this reaction is to transform Fe (III) phthalocyanine into electrophilic rich functional end groups. Thus, FePc can easily interact with MWCNTPE to obtain a new hybrid material (composite) (Fig. 1). The resulting FePc-Cl was suspended in 1.0 mL of dimethylformamide (DMF) by stirring in an ultrasonic bath for 1.0 h. This FePc-Cl suspension and the NH_2 functional multi-walled carbon nanotube (NH_2 -MWCNTPE) were reacted at room temperature for 16 h under reflux. It was then filtered with strainer paper (Whatman No. 42). Finally, the precipitate was washed sequentially with dichloromethane, water and acetone and dried under vacuum.

Synthesized 10 μ L FePc-NH-MWCNTPE suspension was coated on the bare MWCNTPE surface by the drop-dry method. In addition, in order to compare different indicator electrodes FePc-NH-MWCNTPE/GCE electrodes were prepared by modifying the glassy carbon electrode (GCE). For this procedure, 10 μ L of FePc-NH-MWCNTPE suspension was dropped onto the renewably GCE surface and left at room temperature for 1 day to dry. Thus, the targeted modified FePc-NH-MWCNTPE/MWCNTPE and FePc-NH-MWCNTPE/GCE indicator electrodes for fluometuron determination were obtained. Surface cleaning and activation process of the prepared modified electrodes was carried out by conducting potential scans between +1500 mV and -1000 mV with cyclic voltammetry (CV).

Voltammetric behavior of the 5.0 mg/L fluometuron herbicide was examined by using square wave stripping voltammetry (SWSV) and differential pulse stripping voltammetry (DPSV) in Britton Robinson buffer solution at pH 6.0 on the bare MWCNTPE and GCE (Fig. 2).

While an oxidation peak at approximately 1065 mV was obtained on the bare GCE with the DPSV technique, no anodic peak was observed by using SWSV (Fig. 2). In studies conducted with bare MWCNTPE, anodic peaks of fluometuron herbicide were obtained at 1070 mV and 1090 mV, respectively, with both techniques under the same experimental conditions (Fig. 2).

When bare GCE and MWCNTPE were compared, it was observed that the anodic peak current of fluometuron was greater with that of MWCNTPE, in other words, it can be said that the bare MWCNTPE electrode is more sensitive in determining fluometuron. The main reason for this is that MWCNTPE electrodes have high mechanical strength,

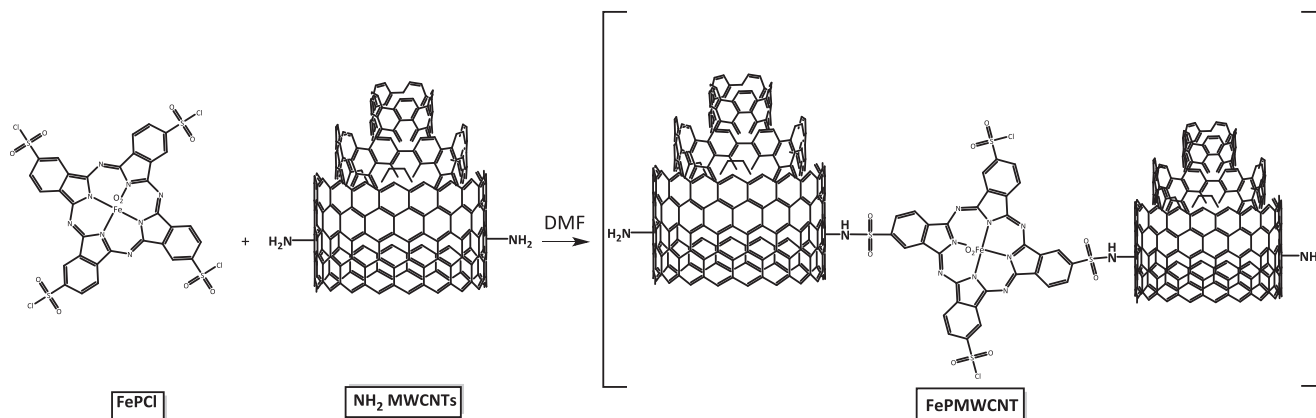


Fig. 1. Fe (III) phthalocyanine-based modified multi-walled carbon nanotube hybrid material.

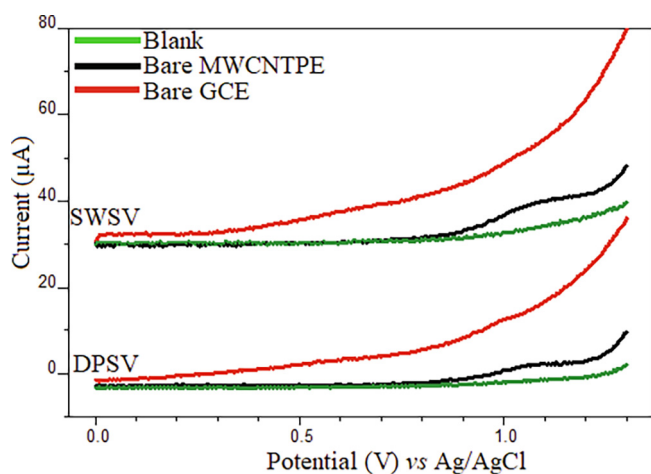


Fig. 2. DPS and SWS voltammograms obtained by using bare GCE and MWCNTPE for the 5.0 mg/L fluometuron in pH 6.0 BR buffer solutions.

good conductivity and fast electron transfer over large surface area [38,39]. In addition, when the literature is reviewed, it is known that MWCNTPE electrodes are more sensitive than GCE [38,39] and our results are consistent with that ones.

3.2. Activation process of modified electrodes

The activation process of both modified electrodes, FePc-NH-MWCNT/GCE and FePc-NH-MWCNT/MWCNTPE, were performed in pH 6.0 BR buffer (blank) solutions by recording voltammograms of 10 cycles between -1000 mV and $+1500$ mV (St 2). After activation, no anodic peak was observed from the voltammograms of blank solutions recorded by SWS and DPS.

3.3. Comparison of the sensitivities

The DPS and SWS voltammograms were recorded for 5.0 mg/L fluometuron in pH 6.0 BR buffer solutions on FePc-NH-MWCNT/GCE electrode. According to the DPSV data, an anodic peak of $0.235 \mu\text{A}$ at 1065 mV was obtained on the bare GCE electrode, while an anodic peak of $1.375 \mu\text{A}$ at approximately 1025 mV was obtained under the same experimental conditions on the modified FePc-NH-MWCNT/MWCNTPE. On the other hand, while no fluometuron peak was obtained on bare GCE, an oxidation peak with a current intensity of $0.727 \mu\text{A}$ at approximately 1095 mV was obtained on the FePc-NH-

MWCNT/GCE by SWSV (Fig. 3). According to these results, we can say that the modified FePc-NH-MWCNT/GCE electrode has both better catalytic properties and conductivities compared to the bare GCE. Furthermore, due to the catalytic property of FePc, the anodic peak of the fluometuron was not only sensitive but also shifted less positive potential. The anodic peak of the fluometuron shifting to less positive potential about 40 mV by DPSV indicates that the electrode reaction for the oxidation of fluometuron occurs more easily on the modified electrodes surface.

DPS and SWS voltammograms were obtained in the presence of 5.0 mg/L fluometuron under the same experimental conditions to compare modified FePc/MWCNTPE with bare MWCNTPE (Fig. 3). According to the data obtained with both techniques, it was observed that the FePc/MWCNTPE was quite sensitive compared to the bare MWCNTPE (Table 1). Accordingly, it was found that fluometuron anodic peak current intensity increased approximately 3.3 times by using the hybrid electrode compared to bare MWCNTPE.

As a result, according to both DPSV and SWSV measurements, the modified FePc/MWCNTPE electrode appears to be quite sensitive for fluometuron determination compared to the other three electrodes (Bare GCE, bare MWCNTPE and modified FePc/MWCNT/GCE). In measurements with FePc/MWCNTPE, the fluometuron peak is approximately 300% higher than bare electrodes and approximately 25% higher than modified FePc/MWCNT/GCE. Therefore, all subsequent work continued by using FePc/MWCNTPE.

3.4. Surface characterization of bare and modified electrodes

In order to clarify whether the modifying FePc hybrid material was coated on the bare electrode or not, the surface morphology of bare and modified electrodes was illuminated with scanning electron microscopy (SEM). Visualization of the surface morphology of the prepared bare MWCNTPE (Fig. 4a) and iron (III) phthalocyanine treated with MWCNTPE (FePc/MWCNTPE) (Fig. 4b) was recorded by SEM with different magnifications such as $\times 500$, $\times 1000$ and $\times 2000$. As shown in Fig. 4, iron (III) phthalocyanine carbon composite material on the surface of the modified carbon electrode formed homogeneity.

The FTIR spectra of the bare MWCNTPE and modified FePc/MWCNTPE carbon electrodes were recorded. It was observed that there was no change in the dominant characteristic peaks of the modified electrode compared to the bare carbon electrode in FTIR spectra. Absorption bands of 1578 cm^{-1} and 1445 cm^{-1} in the spectrum of the bare carbon electrode are the most typical indicators of C–C stretching vibrations. In addition, the observed bands between 2845 cm^{-1} and 2900 cm^{-1} correspond to the characteristic aromatic CH_2 stretching vibrations of symmetry and asymmetry, respectively.

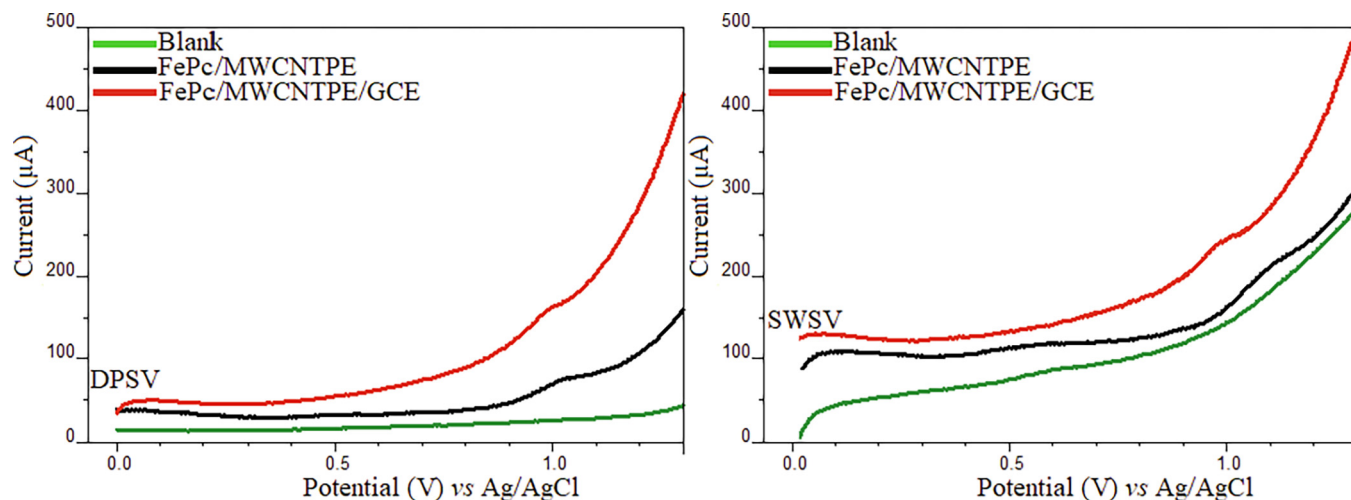


Fig. 3. SWS and DPS voltammograms obtained with modified hybrid GCE and MWCNTPE for the 5.0 mg/L fluometuron in pH 6.0 BR buffer solutions.

Table 1

The peak potentials and currents using the bare and modified electrodes for 5 mg/L fluometuron determination.

Technique	Bare GCE		Modified FePc-MWCNT/GCE		Bare MWCNTPE		Modified FePc-MWCNT/MWCNTPE	
	Peak Current (µA)	Peak potential (mV)	Peak Current (µA)	Peak potential (mV)	Peak Current (µA)	Peak potential (mV)	Peak Current (µA)	Peak potential (mV)
DPSV	0.235	1065	1.375	1025	1.015	1070	3.358	1015
SWSV	–	–	0.727	1095	0.625	1090	2.691	1095

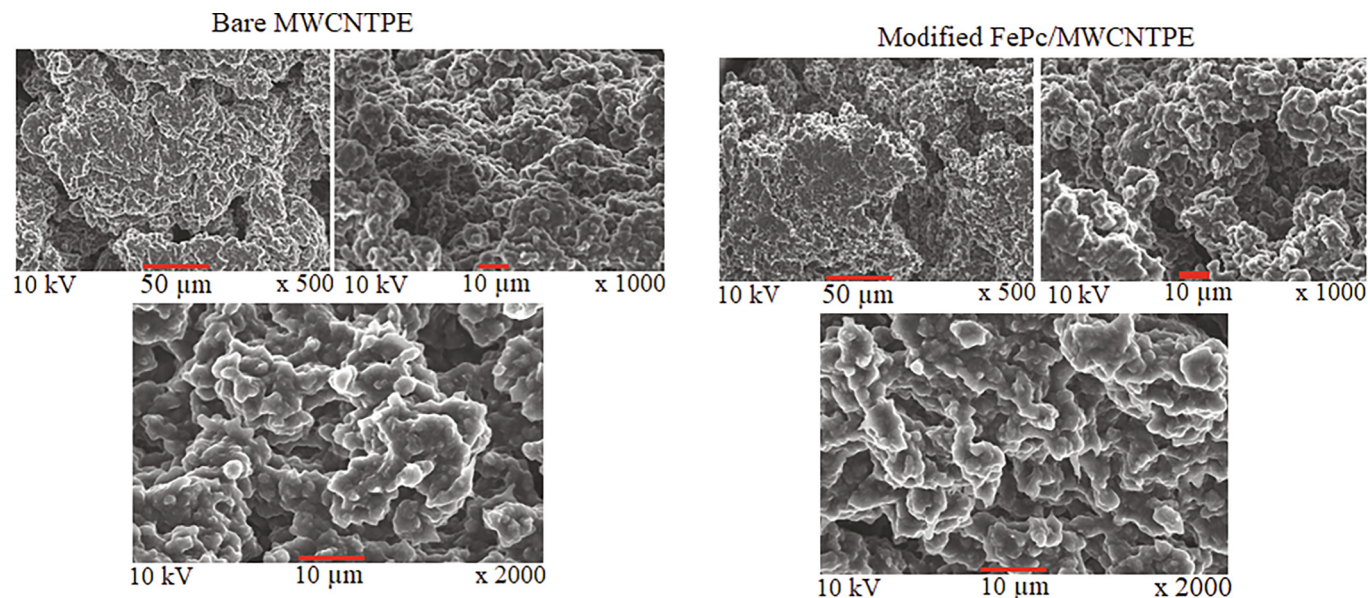


Fig. 4. SEM images of a bare MWCNTPE (a) and FePc/MWCNTPE at different magnifications.

Peaks at 2000–2100 cm^{-1} belong to the C=C stretching vibration of the aromatic ring. The most distinctive peak in the FTIR spectrum of the modified carbon electrode was found at 1620 cm^{-1} indicating –C=N stretching vibration. The characteristic peaks for FePc were obtained between 600 and 1000 cm^{-1} which are important evidence for Pc molecules coated on electrode. Both SEM and FTIR analysis are indicative of the successful production of composite electrodes containing iron (III) phthalocyanine with multi walled carbon nanotubes.

In addition, the bare and modified electrodes were characterized by X-Ray diffraction (XRD) analysis (St 3). According to the XRD measurements, the peak (002) originates from well-aligned carbon nanotubes on the electrode surface. Also, the intensity of the main peak (002) is almost the same in both electrodes. The basic process here is that electron-rich layers originating mainly from π - π bonds between carbon layers take a dominant role in composite material conductivity. As a result, XRD analysis is not useful for distinguishing the

microstructural details of both electrodes, but can help determine sample purity.

3.5. Voltammetric behavior of fluometuron

After determining that the most suitable electrode in the determination of fluometuron was modified FePc/MWCNTPE in line with the obtained data, we started to study the electrochemical behavior of fluometuron. First, the supporting electrolyte was optimized, which significantly affects the peak current and peak potential [40]. In order to examine the electrochemical behavior of fluometuron, the effect of the supporting electrolyte at different pHs was examined with SWSV and DPSV techniques on modified electrode. For the supporting electrolytes, 0.1 M hydrochloric acid (HCl) at pH 1.0 and Britton Robinson buffer solutions (between pH 2.0 – pH 11.0) were used. While the oxidation peak of fluometuron was exhibited in the pH range of 2.0 to 10.0 with DPSV, no peak was observed at pH 1.0 and pH 11.0 (Fig. 5a). After 3 repeated measurements, the peak currents and peak potentials were calculated as mean and standard deviations. The pH 6.0 BR buffer where the most sensitive fluometuron peak obtained was chosen as the optimum supporting electrolyte. In addition, with increasing pH effect, the anodic peak potential of fluometuron shifted to a less positive direction, with two different slopes, 50 mV/pH and 33 mV/pH, in two linear sections in the range of pH 2.0 to pH 8.0 and pH 9.0 to pH 10. This is an indication that the proton (H^+) contributed in the electrode reaction of the fluometuron.

The shift of the peak potential depending on the pH can be represented with the following equations with two different slopes:

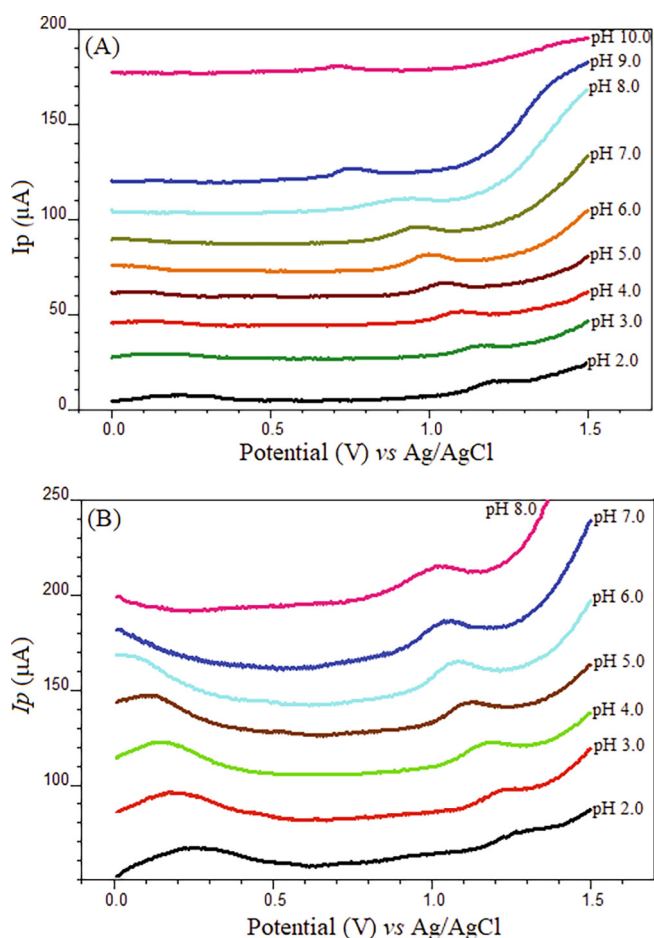


Fig. 5. pH effect in the DPSV (A) and SWSV (B) determination of fluometuron on FePc/MWCNTPE.

$$E_p \text{ (mV)} = -50.179 \text{ pH} + 1317.8 \quad r^2 = 0.9899 \text{ for the pH 2.0 - pH 8.0}$$

$$E_p \text{ (mV)} = -33.333 \text{ pH} + 1053.3 \quad r^2 = 0.9785 \text{ for the pH 8.0 - pH 10.0}$$

The pH effect on determination of fluometuron was also determined by SWSV as performed in DPSV and pH 6.0 BR buffer was selected as the optimum supporting electrolyte because of the highest sensitive current obtained (Fig. 5b). In addition, due to the increasing pH, the fluometuron anodic peak potential shifted to less positive values by 51 mV/pH. This indicates that the proton (H^+) contribution in the fluometuron electrode reaction.

$$E_p \text{ (mV)} = -51.071 \text{ pH} + 1412.5 \quad r^2 = 0.9620 \text{ for the pH 2.0 - pH 8.0}$$

After determining the optimum supporting electrolyte and pH medium, the electrochemical behavior of fluometuron was examined by cyclic voltammetry (CV) on the modified FePc/MWCNTPE (St 4). Cyclic voltammograms were recorded by potential scanning in the anodic and cathodic directions at different scanning rates (10 mV/s–500 mV/s) in the range of 0 mV and +1300 mV. While fluometuron showed an oxidation peak at about +1075 mV in anodic scanning direction, no reduction peak was observed in cathodic pathway. This phenomenon clearly shows that the fluometuron herbicide is an electroactive compound which has an irreversible electrode reaction.

According to studies conducted with CV, it was observed that the peak potential of fluometuron shifted to more positive direction with increasing scanning rates. According to the relationship between E_p and $\log \nu$ the following equation is obtained:

$$E_p \text{ (V)} = 0.118 \log \nu \text{ (V/s)} + 1.146 \quad (r = 0.9769)$$

The effect of scanning rate gives clear insight into whether substance transport is diffusion or adsorption control. The relationship between the logarithm of the scan rate and the logarithm of the peak current according to the CV of the fluometuron obtained from different scanning rates between 10 mV/s and 500 mV/s in pH 6.0 BR buffer using modified FePc/MWCNTPE is as follows:

$$\log I_p \text{ (}\mu\text{A)} = 0.344 \log \nu \text{ (V/s)} + 1.491 \quad (r = 0.9961)$$

Accordingly, a linear equation with a slope of 0.344 $\mu\text{A}/(\text{V/s})$ was obtained. Since the slope is closer to the theoretical value (0.5) which is valid for irreversible electrode reactions and accepted for diffusion-controlled material transport [41], it can easily be said that the fluometuron mass transfer to the electrode surface is diffusion controlled.

A significant parameter of the kinetic model studies with CV is the square root of the scanning rate and the peak current of the analyte. We studied the effect of the square root of different scanning rates in the range of 10 mV/s – 500 mV/s for the anodic peak current of fluometuron. A linear equation was obtained between square root of scan rate and peak current. The linear relationship between peak current and square root of scan rates is given below.

$$I_p \text{ (}\mu\text{A)} = 29.942 \nu^{1/2} + 4.384 \quad (r = 0.9898)$$

3.6. Electro-oxidation mechanism of fluometuron

Measurements of potential scanning rates made by CV are one of the most useful parameters in kinetic studies. In general, the effects of different scanning rates on the peak current and peak potential of the analyte are studied. These data provide meaningful information about whether the electrons and protons are involved in the electrode reaction. Therefore, cyclic voltammograms of 15.0 mg/L fluometuron in pH 6.0 BR buffer solution at different scanning rates from 10 mV/s to 500 mV/s were obtained on the modified FePc/MWCNTPE. From the relation between the logarithm of the different scanning rates between 10 mV/s and 500 mV/s and the peak potentials of the analyte, a linear equation with a slope of 0.118 was obtained. In order to find the number of electrons (n) transferred in the irreversible electrode reaction, the n number was calculated with the Laviron equation [42]:

$$E_p = E^0 + \left(\frac{2.303RT}{nF} \right) \log \left(\frac{RTk^0}{nF} \right) + \left(\frac{2.303RT}{\alpha nF} \right) \log v$$

In this equation, symbols R , T , n , F , k^0 , α , and v are respectively: universal gas constant (8.314 J/K mol), temperature (K), number of electrons transferred (n), Faraday constant (96485C/mol), standard heterogeneous reaction rate constant (k^0), electron transfer coefficient (α), and potential scan rate (v). When all fixed values were put into the Laviron equation " αn " value in fluometuron oxidation process could be calculated as 0.501. For irreversible electrochemical reactions, the " α " value is usually taken as 0.5, from which the " n " is directly calculated as 1.002. In other words, the number of electrons transferred in the fluometuron electrode reaction is 1. On the other hand, due to increasing pH's, the fluometuron peak potentials have shifted towards a more positive direction, and the peak potential shift corresponding to each pH unit change is approximately 51 mV. In the light of these results, the fluometuron electrode reaction is dependent on ambient pH and includes proton (H^+) participation. When all these experimental results are evaluated, the possible oxidation mechanism for the fluometuron electrode reaction is suggested as follows.

3.7. Optimization of instrumental parameters

Analytical performance and validity of SWSV technique were performed in pH 6.0 BR buffer solutions by using FePc/MWCNTPE electrode. The indispensable parameters in square wave stripping technique such as frequency, step potential, pulse amplitude, accumulation potential and accumulation time were optimized. Firstly, the step potential was optimized and for this purpose SWS voltammograms of fluometuron were recorded at different step potentials between 1 mV and 10 mV. While fluometuron peak intensity increased up to 4 mV, a significant decrease was observed at step potentials beyond 4 mV. Accordingly, 4 mV with the smoothest peak shape and highest peak current was chosen as the step potential. SWS voltammograms were also recorded at different accumulation potentials from -200 mV to $+400$ mV for the optimization of the accumulation potential. Accordingly, the peak current of the fluometuron was not affected by varying accumulation potentials. Therefore, optimum accumulation potential was chosen as 0 mV in the fluometuron assay. The effect of pulse amplitude, another parameter in the stripping method, was searched by recording SWS voltammograms on the FePc/MWCNTPE at different pulses between 10 mV and 100 mV. The peak current of fluometuron rose with increasing pulse amplitudes up to 60 mV, and there was a noticeable decrease on the peak current in the pulses applied further. Therefore, 60 mV at which the highest peak current, was chosen as the optimum pulse amplitude. SWS voltammograms of the fluometuron were also recorded at different frequencies from 10 Hz to 150 Hz for the optimization of the frequency, which is one of the most parameters affecting the peak current and potential. The fluometuron peak current increased linearly with a frequency varying up to 100 Hz, and after 125 Hz, a significant decrease in peak current was detected. Therefore, optimum frequency was chosen as 100 Hz. The accumulation time, which is one of the parameters affecting the peak intensity, was optimized in the presence of 5 mg/L fluometuron at pH 6.0 BR buffer solutions. According to the SWS voltammograms recorded on the hybrid electrode at different accumulation times within 10 s and 80 s, it was observed that the peak current increased in a linear pattern up to 60 s and remained almost constant during the subsequent accumulation times, so the optimum accumulation time was chosen as 60 s. All optimum parameters recorded by SWSV technique are listed in St. Table 1.

The instrumental parameters such as accumulation time, accumulation potential, pulse amplitude and scanning rate which influence on the peak current and potential by the proposed DPSV method were optimized. In order to determine the optimum accumulation potential in the DPSV method, different accumulation potentials between

-200 mV and 300 mV were applied in pH 6.0 BR buffer by using modified FePc/MWCNTPE. When the examining the effect of different accumulation potentials on fluometuron peak current, $+100$ mV was selected as the optimum due to obtain the highest peak signal. In order to determine the optimum accumulation time with DPSV, deposition was applied in pH 6.0 BR buffer at a different times between 10 s and 50 s. The peak signal of fluometuron increased significantly up to 40 s and then there was no significant change in the peak current. Therefore, 40 s was chosen as the optimum accumulation time. In the DPSV technique, different pulses between 10 mV and 160 mV were applied in pH 6.0 BR buffer to determine the optimum pulse amplitude, and the fluometuron peak signal increased significantly at the beginning with increasing pulse amplitude until 140 mV. Then there was no significant increase on peak signal of fluometuron, therefore, 140 mV was chosen as the optimum pulse amplitude. To determine the optimum scan rate, different rates between 10 mV/s and 80 mV/s were applied in pH 6.0 BR buffer solutions, causing significant increases in fluometuron peak current up to 60 mV/s and the peak current remained almost constant and therefore 60 mV/s was chosen as the optimum one. All the optimum values obtained by DPSV are summarized in St. Table 2.

3.8. Method validation

Calibration graphs were constructed with standard addition method for determination of fluometuron using both DPSV and SWSV techniques under the optimized parameters and conditions (Fig. 6).

The linear dynamic range obtained by DPSV and SWSV was within 0.4–15.0 mg/L and 0.4–7.5 mg/L, respectively. Limit of detection (LOD) and limit of quantification (LOQ) values were calculated using " $3s/m$ " and " $10 s/m$ " relations, respectively [43–46], where " s " in these equations indicates the standard deviation of the cut-off point in the calibration equation, and " m " shows the slope of the calibration line. Accordingly, the LOD and LOQ values were determined as 69.8 $\mu\text{g/L}$ and 233 $\mu\text{g/L}$, respectively for the DPSV. In the study with SWSV, these two validation parameters were determined as 101 $\mu\text{g/L}$ and 337 $\mu\text{g/L}$, respectively.

As a result, the DPSV technique in determination of fluometuron was found to be superior to SWSV due to its wider working range and lower LOD and LOQ values on modified electrode. Therefore, selectivity and analytical application studies were carried out with DPSV on the modified FePc/MWCNTPE.

Using the fabricated FePc/MWCNTPE hybrid electrode, the intra-day and inter-day reproducibility was carried out in the presence of 0.75 mg/L fluometuron with DPSV in pH 6.0 BR buffer solution. As a result of seven different measurements for intra-day repeatability, the relative standard deviation (% RSD) of peak signal and peak potentials were found to be 3.83% and 0.75%, respectively, while the inter-day relative standard deviation (RSD%) was 5.86% and 1.05%, respectively. In addition, day-to-day repeatability was studied to examine the lifetime of the fabricated modified hybrid electrode. According to DPSV measurements recorded in the presence of 0.75 mg/L fluometuron, a relative decrease of 1.82% on peak signal was observed after seven days. Since these values can be assumed within an acceptable range of error, the developed electrode is suitable in terms of robustness and repeatability. The calibration equations obtained for the determination of fluometuron on the modified FePc/MWCNTPE electrode in pH 6.0 BR buffer with DPSV and SWSV under optimal conditions are as follows:

$$I_p (\mu\text{A}) = (4.596 \pm 0.107) C (\text{mg/L}) - (1.717 \pm 0.768)$$

$$r^2 = 0.9973 \text{ for DPSV}$$

$$I_p (\mu\text{A}) = (4.092 \pm 0.138) C (\text{mg/L}) - (1.783 \pm 0.537)$$

$$r^2 = 0.9950 \text{ for SWSV}$$

It appears that this electrochemical method, which was developed for the first time to determine fluometuron, can be an alternative to existing analytical methods based on validation parameters. Due to

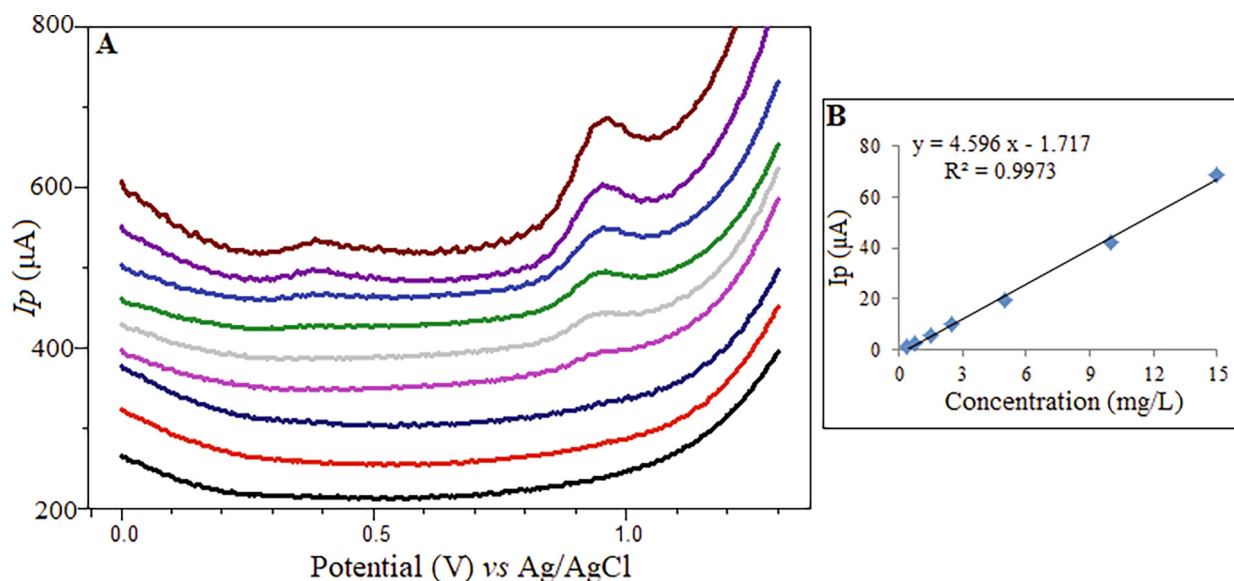


Fig. 6. Calibration graphs on the FePc/MWCNTPE modified electrode for fluometuron determination by DPS voltammograms (A) Calibration graph (B).

its low detection limit and wide working, this hybrid electrode exhibited a great performance when used with DPSV and SWSV techniques. Regression data for fluometuron determination by DPSV and SWSV are summarized in Table 2 and St Table 3, respectively.

With comparing to the current analytical methods in the literature for determination of fluometuron, this study has a wider dynamic range than ES-QIT-LC-MS and chemiluminometry methods (Table 3). In terms of detection limits, it is seen that they are superior to photo-induced fluorimetry and chemiluminometry. Also, in terms of analysis time and pre-treatment application, DPSV is more outstanding than any analytical method available in fluometuron determination.

3.9. Selectivity of the method

One of the most crucial validation parameters of a fabricated electrode to be used in a voltammetric technique is its selectivity. In this respect, the interference effects of some cations and pesticides in the determination of fluometuron with DPSV were examined on the modified FePc/MWCNTPE. The percent recovery studies were performed for 1.0 mg/L fluometuron in the presence of 5.0 mg/L captan (electro-active), halosulfuron methyl (electro-active), monocrotophos (electro-active), pencycuron (electro-active), tolclofos-methyl (electro-inactive) and teflubenzuron (electro-inactive) pesticides (Fig. 7). Recoveries were calculated as percent recovery \pm percent standard deviation obtained with triplicate measurements. Firstly, the peak cur-

rent of 1.0 mg/L fluometuron was measured and then co-existing species were added by 1:5 by mass ratio. The peak signal of fluometuron was measured by DPSV in pH 6.0 BR buffer solutions and the percent change (% recovery) in the presence of interfering species was calculated. As shown in Fig. 7, 1.0 mg/L fluometuron in the presence of interfering species has been successfully determined within 5% tolerance by the proposed DPSV method. In addition, the interference effects (1:5 by mass) of some cations such as Cu (II), Fe (II), Pb (II) and Zn (II) were investigated. Since these cations have an interference effect within 5% tolerance, they cause little error in determining fluometuron. As a result, the determination of fluometuron in the presence of "1:5 pesticide/metal ion" was performed with high recovery and low relative error by using the proposed method and electrode. Accordingly, it can be said that both the fabricated electrode and the proposed voltammetric method are highly selective.

3.10. Analytical application to natural samples

Fluometuron determination was performed by DPSV method using FePc/MWCNTPE electrode in natural samples such as tap water and commercial herbicide formulations (Cottonex 500 SC®). Primarily, 0.1 mL spiked tap water samples were transferred to 10 mL pH 6.0 BR buffer in the voltammetric cell and DPS voltammograms were recorded. While no peak was obtained in non-spiked tap water samples, a peak of fluometuron was observed at around +1000 mV in the prepared spiked tap water samples. Then, 0.75 mg/L standard additions were made on this sample and DPS voltammograms were recorded. As expected, this peak showed a proportional increase with the standard additions, and 0.72 ± 0.02 mg/L fluometuron was detected in tap water with 0.75 mg/L fluometuron spiked. In other words, analytical application in tap water was successfully performed with a high recovery of $96.0 \pm 2.7\%$ and a relative error of -4.0% , respectively. Herewith, it has been shown that trace amounts of fluometuron can be detected by DPSV on the proposed hybrid electrode with high recovery, low relative error, good precision and accuracy.

Precision and accuracy studies were carried out for fluometuron detection in agricultural formulation such as Cottonex 500 SC® pesticide, which is used to control unwanted weeds in cotton farming. Initially, 0.1 mL of Cottonex 500 SC® pesticide was dissolved in 10.0 mL of acetone and the prepared solution was transferred to the pH 6.0 BR buffer in the voltammetric cell. Standard fluometuron additions were

Table 2

Regression data for fluometuron determination by DPSV.

Parameters (Unit)	Values
Peak Potential (mV)	985 mV
Working Range (mg/L)	0.40–15.0 mg/L
Slope ($\mu\text{A L/mg}$)	4.596 ± 0.107
Cutoff Point (μA)	1.717 ± 0.768
Regression coefficient (R^2)	0.9973
Limit of detection (LOD) ($\mu\text{g/L}$)	69.8
Limit of quantification (LOQ) ($\mu\text{g/L}$)	233.0
Repeatability of the intra-day peak current (RSD%) ^a	0.75
Repeatability of the intra-day peak potential (RSD%) ^a	3.83
Repeatability of the inter-day peak currents (RSD%) ^a	1.05
Repeatability of the inter-day peak potential (RSD%) ^a	5.86

^a (n = 7).

Table 3
Comparison of validation parameters of existing analytical methods for the determination of fluometuron.

Method	Linear range	LOD	LOQ	Analytical application	Refs.
Photo-induced fluorimetry	0.01–4.0 mg/L	100 µg/L	–	Human urine, soil, formulation and water	[1]
Chemiluminometry	0.1–5 mg/L	–	–	River and tap waters	[5]
ES-QIT-LC-MS	1–100 mg/L	0.01 µg/L	–	River water	[7]
Fluorodensitometry	50–2500 ng	0.1 µg/L	–	Drinking water	[8]
FTIR	–	6.5 µg/g	–	Commercial pesticide samples	[9]
SPE-LC-ESI-MS	7–11 ng/L	0.05–2 µg/L	–	River water	[10]
HPLC with fluorescence detection combined with UV	0.01–1.0 mg/L	2 µg/kg	7 µg/kg	Rice and corn	[11]
DLLME-LC-DAD	0.2–200 µg/L	0.05 µg/L	–	River and tap waters	[12]
HPLC/UV-DAD	0.01–10.0 mg/L	10 µg/kg	–	Stem of coconut palm	[13]
DPSV	0.40 – 15.0 mg/L	69.8 µg/L	233 µg/L	Commercial formulation and tap water	This work

ES-QIT-LC-MS = Electrospray quadrupole ion trap liquid chromatography-mass spectrometry.

FTIR = Fourier-transform infrared spectrometry.

SPE-LC-ESI-MS = Solid-phase extraction and liquid chromatography electrospray ionisation mass spectrometry.

DLLME-LC-DAD = Dispersive liquid-liquid microextraction liquid chromatography-diode array detector.

HPLC/UV-DAD = High performance liquid chromatography with ultraviolet diode array detection.

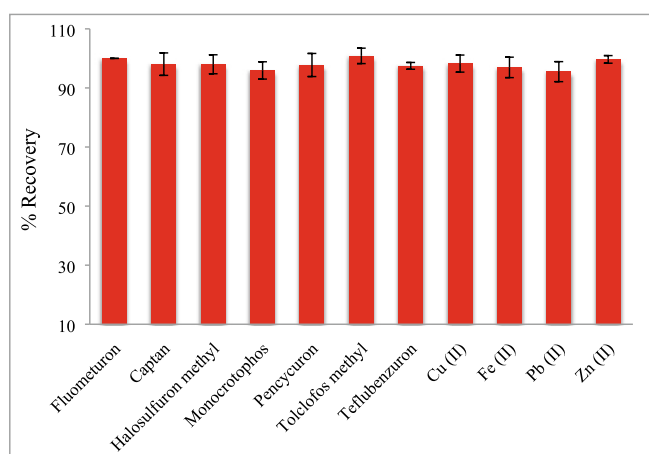


Fig. 7. Percent recovery of 1.0 mg/L fluometuron in the presence of some cations and pesticides (5.0 mg/L) using modified electrode by DPSV in pH 6.0 BR buffer solution.

made on the fluometuron peak around +1000 mV and the amount of fluometuron was determined using the anodic peak increases in these DPS voltammograms (Fig. 8). As a result, the fluometuron herbicide was successfully determined in Cottonex 500 SC® with a relative error

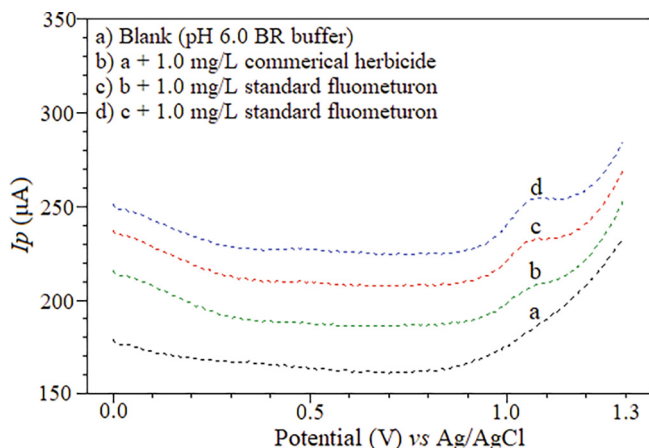


Fig. 8. Determination of fluometuron in Cottonex 500 SC® agricultural formulation by DPSV on modified FePc/MWNTPE.

Table 4

Determination of fluometuron in commercial herbicide formulation and tap water.*

	Cottonex® 500 SC	Spiked tap water
Spiked	500 g/L	0.75 mg/L
Found	497 ± 2.72 g/L	0.72 ± 0.02 mg/L
RSD (%)	0.55	2.67
Relative Error (%)	–0.60	–4.00

*n = 5.

as low as 0.6% and relative standard deviation as low as 0.55% (Table 4).

4. Conclusions

It was concluded that the modified electrode (hybrid material) based on iron (III) phthalocyanate, (FePc)-multi walled carbon nanotube (MWCNTPE), which was fabricated for the first voltammetric determination of fluometuron herbicide, was successful in the determination of fluometuron by DPSV and SWSV. The surface characterization of the modified hybrid electrode, whose repeatability, accuracy and applicability were found to be successful, was elucidated by SEM, XRD and FTIR methods. Finally, the determination of fluometuron using DPSV method and modified FePc/MWNTPE was successfully performed in natural samples such as tap water and its agricultural drug formulation

CRediT authorship contribution statement

Ersin Demir: Conceptualization, Investigation, Methodology, Project administration, Writing - review & editing. **Özge Göktug:** Investigation, Methodology, Validation. **Recai İnam:** Supervision, Writing - review & editing. **Doğukan Doyduk:** Data curation, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This study was supported by the Scientific and Technological Research Council of Turkey (TUBITAK) (Project number:118Z489)

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jelechem.2021.115389>.

References

- [1] I. Cydzik, J.R. Albert-Garcia, J. Martinez Calatayud, J. Fluoresc. 17 (2007) 29–36.
- [2] J. Martinez Calatayud, M. Catalia Icardo, Environmental pollution monitoring, ISBN 973–0–03917–8, Bucarest (2005).
- [3] W.H. Ahrens, M.T. Edwards, Weed Science Society of America, Herbicide Handbook, 7th ed., Champaign, IL, 1994.
- [4] F.C. Fonger U.S. National Library of Medicine, Hazardous Substances Databank 1995 Bethesda, MD
- [5] F. Sá, D.L. Malo, J. Martínez Calatayud, Anal. Lett. 40 (2007) 2872–2885.
- [6] EU pesticides database, <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32020R0785>, 2020.
- [7] W.M. Draper, J. Agric. Food Chem. 49 (2001) 2746–2755.
- [8] M. Hamada, R. Wintersteiger, JPC–Journal of Planar Chromatography-Modern TLC 15 (2002) 11–18.
- [9] G. Quintás, A. Morales-Noé, C. Parrilla, S. Garrigues, M. la Guardia, Vib. Spectrosc. 31 (2003) 63–69.
- [10] R. Carabias-Martinez, E. Rodríguez-Gonzalo, E. Herrero-Hernández, J. Hernández-Méndez, Anal. Chim. Acta 517 (2004) 71–79.
- [11] R.X. Mou, M.X. Chen, J.L. Zhi, J. Chromatogr. B 875 (2008) 437–443.
- [12] M. Saraji, N. Tansazan, J. Sep. Sci. 32 (2009) 4186–4192.
- [13] J.R. de Jesus, S. Navickiene, Wood Sci. Technol. 48 (2014) 1317–1326.
- [14] A. Bautista, J.J. Aaron, M.C. Mahedero, A., Muñoz de la Peña, Anal. Quim. 27 (1999) 857–863.
- [15] E. Crespo-Corral, M.J. Santos-Delgado, L.M. Polo-Diez, A.C. Soria, J. Chromatogr. A 1209 (2008) 22–28.
- [16] R. Carabias-Martinez, C. Garcia-Hermida, E. Rodríguez-Gonzalo, F.E. Soriano-Bravo, J. Hernandez-Mendez, J. Chromatogr. A 1002 (2003) 1–12.
- [17] R. Inam, E.Z. Gülerman, T. Sarigül, Anal. Chim. Acta 579 (2006) 117–123.
- [18] E. Demir, O. Inam, R. Inam, Anal. Sci. 34 (2018) 771–776.
- [19] Y. Altun, B. Dogan-Topal, B. Uslu, S.A. Ozkan, Electrochim. Acta 54 (2009) 1893–1903.
- [20] O. Inam, E. Demir, B. Uslu, Curr. Pharm. Anal. 16 (2020) 367–391.
- [21] E. Demir, O. Inam, H. Silah, H. Karimi-Malehde, Microchem. J. 159 (2020) 105531.
- [22] S.A. Ozkan, B. Uslu, J. Pharm. Biomed. Anal. 130 (2016) 126–140.
- [23] I. Sadriu, S. Bouden, J. Nicolle, F.I. Podvorica, V. Bertagna, C. Berho, L. Amalric, C. Vautrin-UI, Talanta 207 (2020) 120222.
- [24] N.P. Shetti, S.J. Malode, D.S. Nayak, G.B. Bagihalli, S.S. Kalanur, R.S. Malladi, Ch. V. Reddy, T.M. Aminabhavi, K.R. Reddy, Appl. Surf. Sci. 496 (2019) 1436562.
- [25] M. Pekin, D. Eskiköy-Bayraktepe, Z. Yazan, Ionics 23 (2017) 3489–3495.
- [26] E. Demir, H. Silah, B. Uslu, Crit. Rev. Anal. Chem. (2020), <https://doi.org/10.1080/10408347.2020.1806702>.
- [27] N. Baiga, M. Sajidb, T.A. Saleh, TrAC, Trends Anal. Chem. 111 (2019) 47–61.
- [28] E. Demir, B. Bozal-Palabiyik, B. Uslu, R. Inam, Revue Roumaine de Chimie 64 (2019) 45–54.
- [29] B. Köksoy, D. Akyüz, A. Şenocak, M. Durmuş, E. Demirbas, Food Chem. Toxicol. 147 (2021) 111886.
- [30] J.G. Manjunatha, M. Deraman, Anal. Bioanal. Electrochem. 9 (2017) 198–213.
- [31] B. Dogan, B. Uslu, S.A. Ozkan, P. Zuman, Anal. Chem. 80 (2008) 209–216.
- [32] J.G. Manjunathaa, M. Deraman, N.H. Basri, I.A. Talib, Adv. Mat. Res. 895 (2014) 447–451.
- [33] J.G. Manjunatha, J. Surface Sci. Technol. 34 (2018) 74–80.
- [34] A. Taherkhani, T. Jamali, H. Hadadzadeh, H. Karimi-Maleh, H. Beitollahi, M. Taghavi, F. Karimi, Ionics 20 (2014) 421–429.
- [35] R. Inam, T. Sarigül, E.Z. Gülerman, N. Uncu, Int. J. Environ. Anal. Chem. 86 (2006) 1135–1149.
- [36] B. Köksoy, D. Akyüz, A. Şenocak, M. Durmuş, E. Demirbas, Sens. Actuator A Chem. 329 (2021) 129198.
- [37] N.Y. Praveen Kumar, M. Mounesh, T.M. Sharanakumar, K.R.V. Reddy, Chem. Pap. (2021), <https://doi.org/10.1007/s11696-021-01523-z>.
- [38] H. Mercan, R. Inam, H.Y. Aboul-Enein, Anal. Lett. 44 (2011) 1392–1404.
- [39] P. Kumar-Brahman, R.A. Dar, K.S. Pitre, Arab. J. Chem. 9 (2016) 1889–1896.
- [40] B. Bozal-Palabiyik, B. Uslu, Ionics 22 (2016) 115–123.
- [41] E. Laviron, L. Roullier, C.J. Degrand, J. Electroanal. Chem. 112 (1980) 11–23.
- [42] E. Laviron, J. Electroanal. Chem. 100 (1979) 263–270.
- [43] M. Pari, K.R.V. Reddy, K.B. Chandrakala Fasiulla, Sens., Actuator A Phys. 316 (2020) 112377.
- [44] M. Pari, K.R.V. Reddy, Anal. Bioanal. Electrochem. 11 (2019) 1383–1397.
- [45] B.S. Jilani, C.D. Mruthyunjayachari, M.P. Mounesh, T.M. Sharankumar, K.R.V. Reddy, Sens. Actuator A Chem. 301 (2019) 127078.
- [46] M. Nemakal, S. Aralekallu, I. Mohammed, M. Pari, K.R.V. Reddy, L.K. Sannegowda, Electrochim. Acta 318 (2019) 342–353.