

Sensitive determination of herbicide trifluralin on the surface of copper nanowire electrochemical sensor

Ali Mirabi-semnakolaii · Parandis Daneshgar ·
Ali Akbar Moosavi-Movahedi · Mehdi Rezayat ·
Parviz Norouzi · Ali Nemati · Mohammad Farhadi

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Abstract A novel voltammetric method for the determination of trifluralin is proposed based on a composite of carbon paste and copper nanowire as a sensitive sensor. The presence of copper nanowire in the composite film enhance the conductivity and as a result increased the electron transfer rate constant and so the current will increase. The composite exhibits a promising higher electrocatalytic activity towards

the oxidation of trifluralin in pH 4.0 aqueous solution. The reduction peak currents of trifluralin increased remarkably and the reduction peak potential shifted positively at the nanostructuring electrode, compared with that at a bare CPE which show the enhanced effect of nanowire. The support electrolyte to provide a more defined and intense peak current for trifluraline determination was 0.05 mol L⁻¹ phosphate buffer at pH 4.0. The fast Fourier transform square wave voltammetry was used as a new electrochemical technique in flow injection system to obtain more sensitivity by application of discrete fast Fourier transform method by background subtraction and two-dimensional integration of the electrode response over a selected potential range and time window, the signal-to-noise ratio has significantly increased and made the sensitivity to be higher than other methods. The effective parameters such as frequency, amplitude, and pH were optimized to get the best sensitivity. As a result, the sensor showed a valuable response in linear concentration range of 100–0.02 nmol L⁻¹ with a (limit of detection) LOD of 0.008 nmol L⁻¹ and (limit of quantification) LOQ of 0.15 nmol L⁻¹ for trifluralin. A good recovery was obtained for assay spiked urine samples and a good quantification of trifluralin was achieved in soil samples.

A. Mirabi-semnakolaii
Islamic Azad University, Faculty of Science,
Department of Chemistry, Ghaemshahr Branch,
Mazandaran, Iran

P. Daneshgar (✉) · A. A. Moosavi-Movahedi
Institute of Biochemistry and Biophysics, University of Tehran,
Tehran, Iran
e-mail: Daneshgar@ibb.ut.ac.ir

M. Rezayat
School of Medicine, Department of Pharmacology,
Tehran University of Medical Science,
Tehran, Iran

P. Daneshgar · P. Norouzi
Center of Excellence in Electrochemistry,
Department of Chemistry, University of Tehran,
Tehran, Iran

A. Nemati
Department of Inorganic Chemistry, Department of Chemistry,
University of Tehran,
Tehran, Iran

A. A. Moosavi-Movahedi
Center of Excellence in Biothermodynamics, IBB,
University of Tehran,
Tehran, Iran

M. Farhadi
ENT-HNS Research Center of Iran,
University of Medical Sciences,
Tehran, Iran

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Introduction

Trifluralin is a selective, pre-emergence dinitroaniline herbicide used to control many annual grasses and broadleaf weeds in a large variety of tree fruit, nut, vegetable, and grain crops and it is included in the US Environmental Protectionency list of endocrine disrupter

reference compounds (EPA). Pre-emergence herbicides are applied before weed seedlings sprout. Trifluralin should be incorporated into the soil by mechanical means within 24 h of application. Granular formulations may be incorporated by overhead irrigation. As a microtubule inhibitor, trifluralin has been widely used in agricultural applications as a selective, pre-emergence herbicide in various plant cultures from 1970 [1]. The amount of seasonal release of trifluralin (TFL) is about 25% of that applied and also there are some contaminations from the residues of TFL. Trifluralin, a persistent compound in the atmosphere [2], was found in air, rainwater, and micro-layer [2, 3]. The particle phase of trifluralin accounted for 3% of total trifluralin in the atmosphere [4]. For its widespread use and physical–chemical properties, trifluralin are an important pollutant for ground and surface water resources. Developing highly sensitive methods for trifluralin assay is very important because of its presence at trace levels in the environment.

Nanotechnology offers new materials for the design of sensitive nanostructured transducer surfaces and, thus, new methods for the preparation of electrochemical biosensors [5]. Besides nanoparticles [6], nanowires [7] and nanotubes [8], membranes comprised of randomly oriented fibers ranging from microns to nanometers in diameter (nanofibers) can be a promising support for the build-up of bio-sensing devices [9]. Recently, several nanomaterials have been applied in electrochemistry. One-dimensional (1D) nanostructures have attracted considerable attention owing to their novel physical and chemical properties, and the potential applications in a new generation of nano-devices [10–12].

To our knowledge, no paper has appeared for the determination of trifluralin using chemically modified electrode in flow solution [13, 14]. Here, a novel sensitive voltammetric method based on a nanostructure-modified electrode (copper nanowire/carbon paste) was developed for the determination of trifluralin. Carbon paste electrodes (CPEs), due to their ease of construction, renewability, and compatibility with various types of modifiers, have been widely used as a suitable matrix for preparation of modified electrodes. Further, they show rather low background current compared to the solid graphite or noble metal electrodes [15]. In recent years, application of carbon nanotube-modified paste electrodes (CNT/CPE) showed considerable improvements in electrochemical behavior of biologically important compounds [16, 17]. Metal nanowires such as copper showed behavior like carbon nanotubes. A CPE containing 15% (w/w) of CuNW, in comparison with CPE without nanowire, showed a very effective catalytic activity in the electrochemical oxidation of trifluralin. Using fast Fourier transform method, we prepared a very sensitive system in combination with electrochemical method for trace detection of compounds [18–34]. This paper describes a fundamentally different approach to square wave voltamme-

try (SWV) measurement, in which the detection limits are improved, while preserving the information content of the SW voltammogram. The approach is designed to separate the voltammetric signal and background signal in frequency domain by using discrete fast Fourier transformation (FFT) method. SWV measures the current response while rapid alternating potentials are applied during a staircase scan, whereas cyclic voltammetry, which uses only a forward and reverse linear dc scan, is not sensitive to the potential dependence of changes that occur in the double layer.

However, most of the above methods require several time-consuming manipulation steps, sophisticated instruments, and special training. For these reasons, the rapid, simple, and accurate method with high sensitivity is expected to be established. This newly proposed method possesses advantages such as high sensitivity, rapid response, low cost, and simplicity.

Experimental

Materials and reagents

All chemicals and reagents were of analytical grade quality. Trifluraline pure powder was purchased from Sigma-Aldrich. A stock solution of 1.0×10^{-3} mol L⁻¹ TFL was prepared in by dissolving the compounds in ethanol and kept in the dark at 4 °C. The phosphate buffer (pH 2–9), Britton-Robinson (0.05 mol L⁻¹ of phosphoric acid, acetic acid, and boric acid), and acetate buffer were prepared using analytical grade reagents and were used as supporting electrolytes. Unless otherwise stated, a phosphate buffer (0.05 mol L⁻¹, pH 4.0) was used as the supporting electrolyte for trifluralin determination. Certain volume of standard solution of trifluralin was added into the 10 mL cell containing phosphate buffer. All the solution was made by double-distilled water. The copper nitrate was purchased from Merck (Germany), CAT no. 1.12151.0010.

Instrumentation

Synthesis of CuNW

Polycrystalline Cu(OH)₂ nanowires with an average diameter of ca. 8 nm and lengths of up to hundreds of micrometers were synthesized by using a simple chemical route at ambient temperature. The synthesis of Cu(OH)₂ nanowires has been done based on the reported procedure [35]. Briefly, the synthesis of Cu(OH)₂ nanowires includes the following steps: 0.998 g CuSO₄·5H₂O was dissolved in 100 ml distilled water, which was stirred with a magnetic stirrer. This solution was stirred for 15 min to ensure that the CuSO₄ dissolved completely. Then 30 mL of

0.15 mol L⁻¹ NH₄OH was fast added into CuSO₄ solution, under constant stirring. After stirring for 15 min, 6 mL of 1.2 mol L⁻¹ NaOH was added dropwise into the above solution, under constant stirring. A blue precipitate of Cu(OH)₂ was produced. After stirring for 15 min, the blue Cu(OH)₂ precipitate was washed with distilled water several times, filtered, and dried in an oven at 35 °C for 24 h. In Fig. 1, the TEM image of synthesis nanowire shows the average diameter of nanowire is about 8 nm.

Carbon paste electrode

The CuNW/CPE was prepared by hand-mixing 0.96 g graphite powder, 0.13 g CuNW, and 0.34 ml paraffin oil adequately in agate mortar. A portion of the resulting paste was then packed firmly into the electrode cavity (1.0 mm diameter) of a polytetrafluorethylene sleeve. The unmodified CPE was prepared in a similar way using 1.25 g graphite powder and 0.45 ml paraffin oil. Electrical contact was established via a copper wire. The surfaces of all the modified and unmodified CPEs were carefully smoothed on weighing paper and rinsed with twice distilled water prior to each measurement.

The electrochemical instrument

A homemade potentiostat were used for the present voltammetric measurements. The working electrode was the CuNW/CPE with 2 mm diameter. An Ag/AgCl was used as a reference electrode and a Pt electrode as a counter electrode and the electrochemical cell was the same as our previously reported paper [22–25]. All the electrochemical experiments were done using a setup comprised of a PC PIV equipped with a data acquisition board (PCL-818 H, Advantech Co.) which used to output an analog waveform

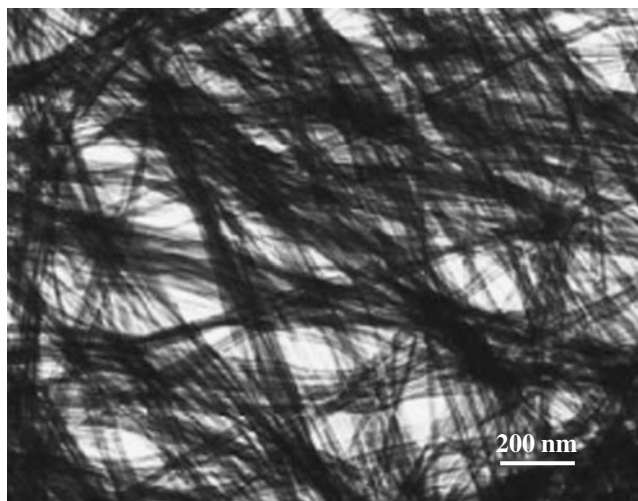


Fig. 1 The TEM image of Cu nanowire

to the working electrode and acquire current readings from the working electrode that connected to a custom-made potentiostat. The more detail about the electronic characteristic of CPU and algorithm used to interpret the current could be found at our previous papers [22–34]. Most of the waveform parameters could be modified within the software; including the pre- and post-scan potential/time, square wave frequency/amplitude, dc ramp initial/final potential, and ramp time.

Stripping voltammetry

In this new method to improve the detector sensitivity, the FFT-SWV technique was modified in the potential excitation waveform, current sampling, and data processing (Fig. 2). The potential waveform consisted of three sections; (a) electrode cleaning (conditioning) E_{c1} to E_{c2} ; (b) accumulation part, E_{acc} (for accumulation of TFL on the surface of electrode); and (c) measurement the potential waveform, E_{sw} . The measurement part of the waveform contains multiple SW pulses (which the current sampling has been done eight times per every pulse, $N_c=8$) with amplitude of E_{sw} and frequency of f , were superimposed on a staircase potential function, which was changed by a small potential step of ΔE . The values of potential pulse of SW (E_{sw}) and ΔE were in a range of few millivolts (10 to 50 mV). In potential ramp, the currents sampled four times per each SW polarization cycle. After preparing the solution, the measurements were carried out in the continuous fast Fourier transform stripping square wave voltammetric mode (FFT-SW). A typical experiment consisted of three consecutive steps with the following experimental conditions: the pre-concentration at -100 mV versus Ag/AgCl for 100 ms, and a polarization (stripping step) run from -300 to $1,000$ mV by applying a $f=300$ Hz, and the pulse height, $E_{sw}=40$ mV.

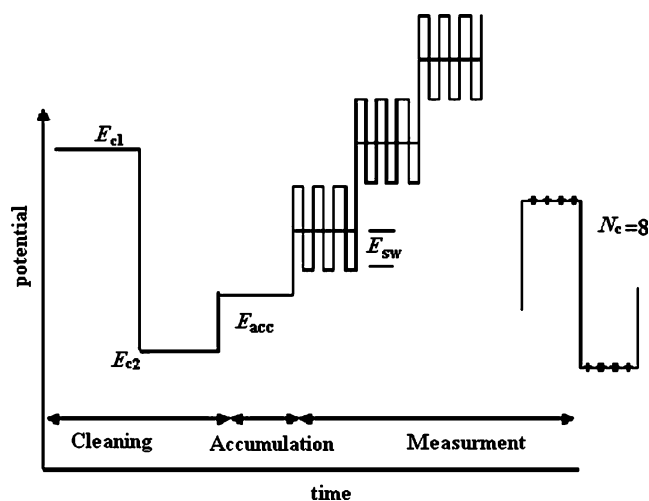


Fig. 2 The diagram of potential waveform used in measurements

Preparation of sample solutions

The soil samples were dried on filter paper at room temperature and then sieved through a metal sieve (20 meshes). Dried soil (50 g) was transferred into a 50-mL flask containing 20.0 mL acetone. After shaking about 7 h at room temperature, all samples were filtered using paper filter for quantitative analysis. The sample was diluted by phosphate buffer and used for injection into the system.

Result and discussion

Electrochemical behavior of trifluralin by using modified CuNW/CPE

Figure 3 shows the electro-reduction of TFL on the surface of the modified (a) and unmodified (b) carbon paste electrode. One irreversible cathodic peak due to reduction of nitro group of aromatic molecule at both bare and CuNW/CPE was exhibited. Using CuNW-modified electrode, a well-defined and very sharp anodic peak with a higher current and peak potential of -250 mV is obtained for TFL at pH 4.0 in phosphate buffer which is about 30 mV less than unmodified electrode (the second peak appeared at -280 mV as shown in Fig. 3 for unmodified carbon paste electrode). On the basis of these observations, it can be postulated that the addition of CuNW to the matrix of CPE exhibits an effective catalytic fashion in the electrochemical oxidation of TFL, leading to the remarkable enhancement of the cathodic peak current. In the potential range of -500 – 0 mV (versus Ag/AgCl) by increase of potential scan rates (from 20 to 200 mV s⁻¹), peak current increase. The peak current of TFL at the

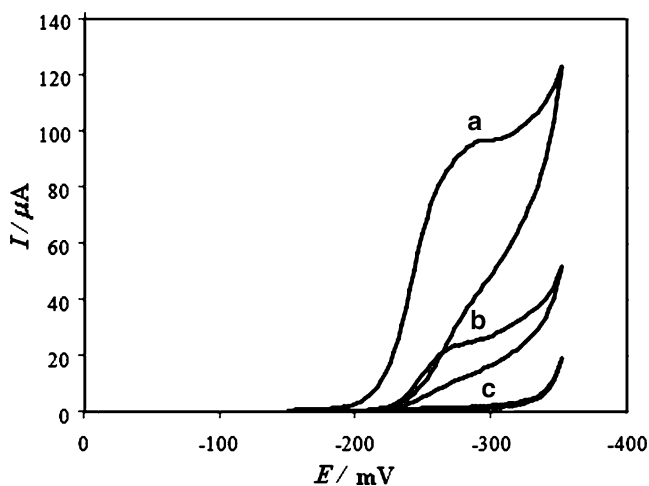


Fig. 3 The cyclic voltammograms of 1.0×10^{-7} mol L⁻¹ TFL on the modified (a), unmodified (b), and bare carbon paste electrode in 0.05 mol L⁻¹ phosphate buffer pH 4.0

CuNW/CPE is enhanced greatly by approximately 150% and is accompanied by a slight negative shift of 25 mV in the oxidation potential. This indicates that the CuNW/CPE improves electrochemical reactivity toward the oxidation of TFL compared with bare CPE. Furthermore, based on some experiments (data not shown) after repetitive cycles the current of herbicide oxidation peak decreases which means the component can be adsorbed on the surface of electrode. So to get better sensitivity for determination of TFL, the adsorptive behavior of compound on the surface of electrode was used and the accumulation time and potential were optimized.

Effect of carbon paste composition

It is well known that the electrochemical characteristics of the CPE electrodes depend significantly on the paste composition. Thus, the influence of the amounts of modifier (Cu(OH)₂ nanowire), oil, and graphite powder on the response of the electrode to concentration of TFL was investigated by cyclic voltammetry. Electrodes with different percents of modifier (0%, 5%, 10%, 15%, and 20%), graphite powder (69%, 66%, 63%, 60%, and 57%), and paraffin oil (31%, 29%, 27%, 25%, and 23%) were prepared and examined for their voltammetric signals under identical conditions. The results showed that, in the absence of modifier (Cu(OH)₂ nanowire), the electrode had lower response towards herbicide. However, the maximum peak current was obtained for 15% of Cu(OH)₂ nanowire in the paste. According to these results, a carbon paste composition of 15% modifier Cu(OH)₂ nanowire, 60% graphite, and 25% paraffin oil was the optimum composition with higher peak currents and used in further studies.

Effect of pH

The influence of the supporting electrolyte such as Britton-Robinson buffer (pH 2.0–10.0), phosphate buffer (pH 3.0–9.0), and acetate buffer (pH 3.0–8.0) was also analyzed in the response of the drug oxidation peak current after pre-concentration of 100 ms at -100 mV. The peak current was pH dependent and much more developed in phosphate buffer solution. The dependence of peak potential (E_p) and peak current (I_p) of TFL at concentration of 1.0×10^{-6} mol L⁻¹ on pH for phosphate buffer solution was shown in Fig. 4a and b, respectively. From the dependence of I_p on pH, it can be seen that different ionic species present different diffusion coefficients in the solution. An increase was observed for pH values between 2.0 and 4.0, but for pH values higher than 5.0, I_p decreased to pH 10.0. Clearly, large currents could only be obtained at pH 4.0. The best results with respect to enhancement of the peak current, shape, and reproducibility were obtained in

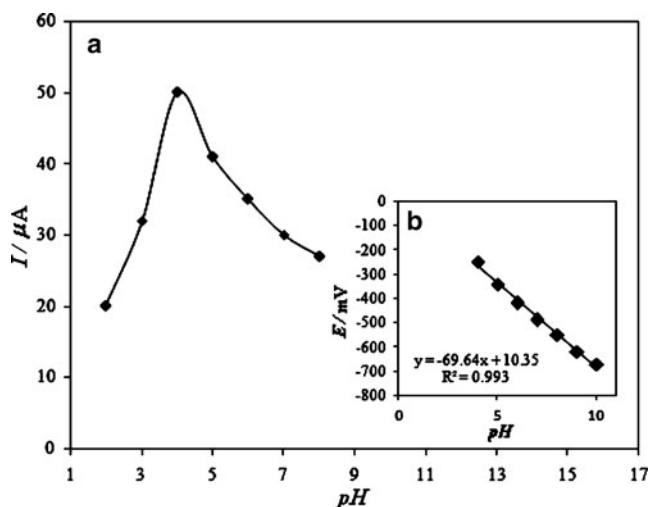


Fig. 4 Diagram of influence of pH on the redox potential and current. The inset is the effect of pH on the potential for 2.0×10^{-7} mol L⁻¹ TFL in acetate buffer (pH=4.0) after 100 ms accumulation time; E_{acc} -100 mV, $f=300$ s⁻¹, and $E_{sw}=40$ mV

0.05 mol L⁻¹ phosphate buffer solution at pH 4.0. It was found that the peak potential is shifted to more negative values with increasing pH of 2.0–10.0, which could indicate the presence of chemical reaction (proton-transfer reaction) precedes the electrode process. The equation of dependence of E_p vs. pH is $E(\text{mV}) = -69.64 \cdot \text{pH} + 10.35$. The electro-reduction of nitro group in organic compounds is a complex process in which a nitro group can receive up to six electrons until complete reduction to corresponding amine [36]. Trifluralin contains two nitro groups located symmetrically to the alkylated amino group. Figure 3 shows that only one peak is observed for the reduction of trifluralin in acidic medium, and this is a result of the strongly reduced electron density at the nitro groups owing to the protonation of the amino nitrogen as well as to the presence of the electrophilic trifluoromethyl group. It can be proposed that both nitro groups are almost simultaneously reduced and the total electrode process is an eight-electron and eight-proton reduction [37, 38].

The multi-cyclic voltammograms of trifluralin at a modified electrode illustrated the reduction peak of trifluralin almost disappeared from the forth cyclic potential sweep and keeps constant during the successive cyclic potential sweeps. This phenomenon may be caused by the fact that the adsorbed trifluralin at the electrode reduced completely during the first potential sweep and its corresponding reductive product is inactive. The experimental results also showed that the regeneration of the electrode can be easily achieved by successive cyclic potential scans from 0.1 to -0.8 V in blank phosphate buffer solution, which indicated that reductive product is weakly adsorptive.

Effect of accumulation potential and time

The dependence of the peak current on the accumulation potential was evaluated over the range of -500 to 500 mV for 1.0×10^{-7} mol L⁻¹ of TFL at 0.05 mol L⁻¹ phosphate buffer at pH 4.0 and in the open circuit condition, Fig. 5a. The obtained results show that the I_p values are in maximum value for an accumulation potential -50 mV and the current change was very negligible, so the potential -50 mV was selected as a best accumulation potential.

As expected, the extent pre-concentration is a function of the accumulation time (t_{acc}). The dependence of peak current on accumulation time was studied at concentration level of TFL 1.0×10^{-7} mol L⁻¹ that showed in Fig. 5b. The peak current increased with increasing of accumulation time till 50 ms and after that it decreased. For a period longer than 100 ms indicating the saturation of the herbicide, where the surface of the electrode of CuNW/CPE shows most current were chosen to evaluate the best work conditions to the proposed method.

Rapid adsorption of trifluralin on the surface of the CuNW/CPE is responsible for this phenomenon. However, for a longer accumulation time, the plot levels off, indicating, presumably, that a limiting amount of trifluralin on the electrode surface has been adsorbed. Further increase of the accumulation time leads to only slight increase in the amount of TFL adsorbed on the electrode owing to surface saturation.

Optimization of FFT-SW frequency and amplitude

To study the effect of these factors, the SW frequency and amplitude between 50 and 500 Hz and amplitude of 5 to 50 mV were examined. In Fig. 6, the importance of

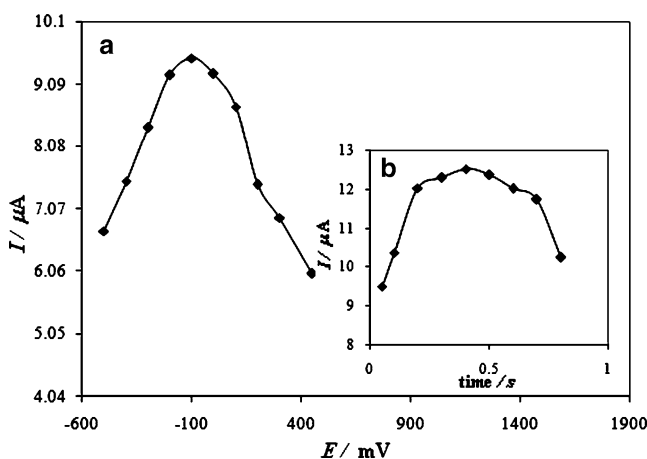


Fig. 5 a Effect of the accumulation potential on the peak current in the presence for TFL solution (a) 1.0×10^{-7} mol L⁻¹ and b effect of the accumulation time of 1.0×10^{-7} mol L⁻¹ on current in phosphate buffer at pH=4.0. E_{acc} -100 mV, $f=300$ Hz, and amplitude=40 mV

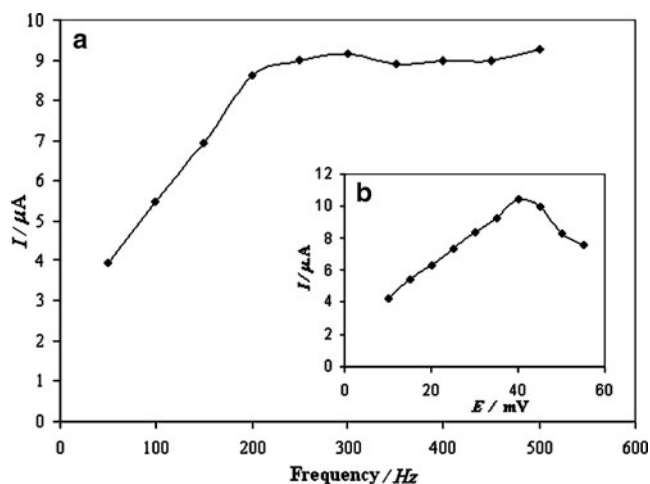


Fig. 6 The effect of accumulation time and potential on the adsorption of trifluralin in for 1.0×10^{-7} mol L^{-1} TFL in phosphate buffer 0.05 mol L^{-1} , pH 4.0

frequency and amplitude is demonstrated for TFL determination. In fast voltammetric analysis, the SW frequency and amplitude are important factors since analyte signal, background noise, and peak shape rely on speed of excitation signal. It should be noted that the solution resistance, electrode diameter, and stray capacitance of the system will limit the sensitivity gains obtained by raising the SW frequency. However, increasing the SW frequency will increase the SW peak current, or the sensitivity, but this will be tempered by a higher charging/faradic current ratio. Due to this fact that the SW frequency act similar to sweep rate in cyclic voltammetry therefore, using very high SW frequencies causes a shorter potential scan times. Consequently, the response peak for the analysis becomes smaller and skewed, due to insufficient time for oxidation of the electrode surface but for the redox reaction it should be optimized in accordance with electron transfer rate. While application of lower SW frequencies results to a longer potential scan times, result to lower number of potential scan for each injected sample zone. A series of SW frequencies were examined to determine the optimal frequency for the detection of TFL. A plot of SW frequency versus ΔQ showed that a frequency of 300 Hz was the best frequency for this system. Thus, further studies of SWV detection used 400 Hz with a dc ramp time of 100 ms to provide an overall sample rate of 20 Hz.

Theoretically, the optimal square wave amplitude for a reversible system is $50/n$ mV. To determine influence of SW amplitude on ΔQ , various amplitudes were investigated. The inset of Fig. 6 shows the effect of SW amplitude on increasing of ΔQ . It is clear that ΔQ increase by increasing amplitude until 40 mV and after that it decreased when amplitudes greater than 40 mV were used. Low-frequency noise (baseline drifting) was more pronounced when SW

amplitudes above 10 mV were used. SW amplitude of 40 mV and frequency of 300 Hz was found to be optimal.

Figure 7 shows the three-dimensional figure of injection of TFL for oxidation on the CuNW/CPE, caused by the addition of a solution of $50 \mu\text{L}$ of 1.0×10^{-7} mol L^{-1} TFL and it was recorded using FFT-SW method. The FFT-SW modulation had amplitude of 40 mV and a frequency of 300 Hz. Before each scan, the electrode was held at E_{c1} potential (1,400 mV) for 60 ms; the E_{c2} potential at -100 mV for 60 ms; and accumulation potential, E_s , at -100 mV for 100 ms. Because of the adsorption behavior of the compound, the fouling of the electrode surface was expected and the experiments shows that after four experiment run the surface of electrode should be renewed mechanically by cutting the paste and smoothing the surface of electrode on the paper. So the lifetime of electrode is not more than four to five runs. To characterize the reproducibility of the modified electrode, replicate measurements were performed for a solution of 1.0×10^{-7} mol L^{-1} TFL. A coefficient of variation of 1.8% was obtained for results from 11 successive measurements.

Calibration curve

Figure 8 illustrates the obtained calibration curves and SWV for measurements of TFL in 0.05 mol L^{-1} phosphate buffer at pH 4.0. The experimental conditions were set up at optimized condition in order to obtain the best detection limits.

As mentioned above, the electrode response could be expressed in various ways like peak heights or peak areas. For this reason, the magnitude of injection peaks depends on the choice of the data processing methods. Like

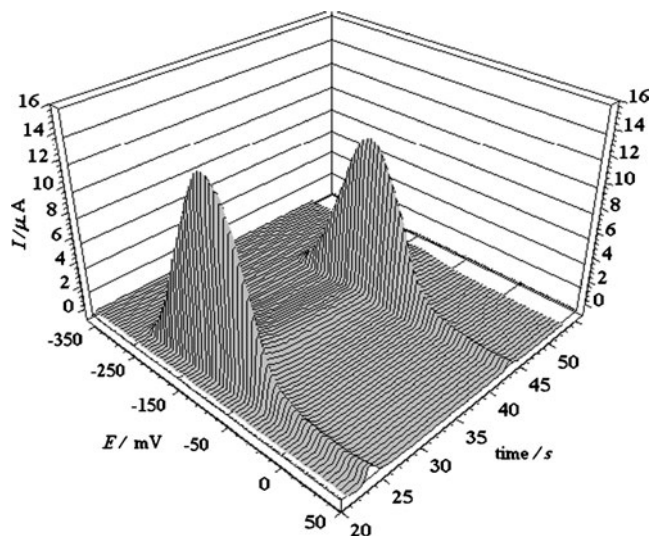


Fig. 7 The effect of frequency and amplitude on the response of CuNW/CPE for 1.0×10^{-7} mol L^{-1} TFL in 0.05 mol L^{-1} phosphate buffer at pH 4.0

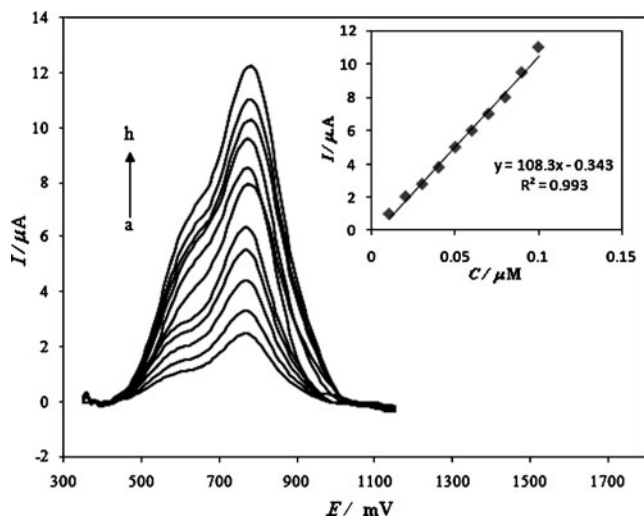


Fig. 8 Three-dimensional FFT square wave voltammograms at a CuNW/CPE recorded during some injection experiment. The bulk solution was 0.05 mol L⁻¹ of phosphate buffer and the frequency was 300 Hz. The injected amount of solution contained 1.0 × 10⁻⁶ mol L⁻¹ TFL in the buffer at pH 4.0. Adsorptive square wave voltammograms obtained for the increasing concentration of TFL in phosphate buffer at pH=4.0, (a–h) TFL concentration (0.00002–0.1 μmol L⁻¹) respectively. *Inset* Dependence of peak current on the TFL concentration. All condition is the same as optimized condition which mentioned before

stripping voltammetry methods, here, the electrode response is proportional to the electrode coverage. Measurements carried out for small analyte concentrations allow the estimation of the detection limit C_{DL}:

$$C_{DL} = \frac{3S_b}{\text{slope}}$$

Where S_b is the standard deviation (or noise) of the baseline around the peak.

The linearity was evaluated by linear regression analysis, which was calculated by the least square regression method [39]. The calibration curves constructed for TFL were linear over the concentration range of 1.0 × 10⁻⁷–2.0 × 10⁻¹¹ mol L⁻¹. Peak areas of TFL were plotted versus its concentration and linear regression analysis performed on the resultant curve. A correlation coefficient of R=0.9998 with %RSD values in the range of 0.22–2.4% across the studied concentration range were obtained following linear regression analysis. Typically, the regression equation for the calibration curve was found to be Y=108.31X–0.343 with RSDs 0.1 and 0.15 for slope and intercept, respectively. Figure 8 shows the calibration graph that obtained for the monitoring of TFL in a 0.05 mol L⁻¹ phosphate buffer. The LOD was measured as the lowest amount of the analyte that may be detected to produce a response which is significantly different from the blank solution. Limit of detection was approved by calculations based on the

standard deviation of the response (δ) and the slope (S) of the calibration curve at the levels approaching the limits according to equation LOD=3.3 (δ/S) [40]. The LOD for TFL was 8.0 × 10⁻¹² mol L⁻¹. The LOQ was measured as the lowest amount of analyte that can be reproducibly quantified above the baseline noise, for which triplicated injections resulted in a RSD ≤ 1.5%. A practical LOQ showed a good precision and additionally acceptable accuracy was to be 1.5 × 10⁻¹⁰ mol L⁻¹.

Precision

Precision was investigated by injecting nine replicate samples of each of the 0.04, 0.008, and 0.0008 μmol L⁻¹ standards. The final mean concentrations were found to be 0.035, 0.0083, and 0.00085 μmol L⁻¹ with associated % RSDs of 0.3, 0.9, and 1.0, respectively. The inter-day precision was assessed by injecting the same three concentrations for three consecutive days, resulting in mean TFL concentrations of 0.035, 0.0084, and 0.0008 μmol L⁻¹ with associated %RSD values of 0.5%, 0.8%, and 0.9%, respectively.

Accuracy

Interpolating of replicate (n=6) peak areas of three accuracy standards (0.04, 0.008, and 0.0008 μmol L⁻¹), the accuracy of the method was assessed by a calibration curve prepared as previously described. In each case, the percent relevant error and accuracy was calculated. The resultant concentrations were 0.04 ± 0.001, 0.008 ± 0.002, and 0.0007 ± 0.0004 μmol L⁻¹ with relevant error percentage of 0.67%, 0.88%, and 0.91%, respectively.

Table 1 Influence of changes in experimental conditions on the performance of FIA system

Parameter	Modification	TFL (% recovery)
pH	4.8	100.2
	5.0	99.8
	5.8	101.4
Flow rate (mL/min)	2.8	101.0
	3.0	101.0
	3.2	100.5
Buffer composition (M)	0.04	100.4
	0.05	99.99
	0.06	101.2
Lab. temperature (°C)	20	101.3
	25	102.0
	30	100.4

Table 2 Results of trifluralin analysis in soil samples ($n=5$)

Soil samples	Spiked ($\mu\text{g g}^{-1}$)	Found ($\mu\text{g g}^{-1}$)	RSD (%)	Recoveries (%)
1	7.0	7.11	2.16	101.5
2	10.11	10.05	1.98	99.3
3	12.01	12.18	2.08	101.4

Ruggedness/robustness

The ruggedness of the method was assessed. Comparing of the intra- and inter-day assay results for TFL some concentrations was used to check the ruggedness of the method. The %RSD values for intra- and inter-day assays of TFL in the cited formulations performed in the same laboratory by the two analysts did not exceed 3.5%, this way the ruggedness of the method is illustrated.

In addition, the robustness was examined under a variety of conditions such as small changes in the pH of eluent, in the flow rate, in the buffer composition, and in the laboratory temperature [39]. Table 1 demonstrates that the TFL recovery percentages were good under most conditions, not showing any significant change when the critical parameters were modified.

Recovery

In order to perform the recovery test, TFL standard powder was used to make concentration of $1.0 \times 10^{-8} \text{ mol L}^{-1}$ and it was added to samples of known amounts in 0.4, 0.08, and $0.008 \mu\text{mol L}^{-1}$ and then the voltammograms were recorded. The assay was repeated ($n=9$) over three consecutive days to obtain intermediate precision data. The resultant %RSD for this study was found to be 0.9% with a corresponding percentage recovery value of 99.95%.

Analytical application

After the application of the method to the Iranian market injection, the resulting data showed a recovery percentage value of 99.88% and a respective RSD value about 1.92%. The proposed method was also applied to the determination of TFL in spiked urine and plasma samples. The results of analysis of spiked human plasma ($n=5$) and urine ($n=5$) is shown in Table 2. The results are satisfactory, accurate, and precise. No interference was noticed from the urine content

just after dilution with the supporting electrolyte. The major advantage of the method which applied to plasma and urine samples is that no prior extraction step is required.

Comparison of the detection limit of the proposed method with the other reported methods was presented in Table 3. It is clearly obvious that the sensitivity of the method is superior to all previously reported methods. The data reveals that the detection limit of the method is about 2.5 times lower than the most sensitive reported method [41–43].

Conclusions

This report described a novel, sensitive, and widely applicable FFT-SWV detection method using of modified CPE. FFT-SWV was demonstrated to provide sensitive detection of a wide range of analytes based on reduction of TFL on the carbon paste electrode surface.

The square wave adsorptive voltammetry on a carbon paste electrode can be used to determine TFL at trace levels because of its high sensitivity and making high oxidation current value. TFL can be effectively accumulated from aqueous solutions or soil samples onto the surface of a CuNW/CPE increasing sensitivity of the method. The electrochemical methods for soil samples analysis have been proven to be fast, precise, and simple which the interference from sample determination, and consequently, extraction procedures are not needed. The above methods can be suggested as a good alternative for the routine quality control of this antibiotic drug in pharmaceutical formulation.

Finally, the principal advantage of the electroanalytical method is simplicity, fast, and more sensitive than the reported method [41–43] with precision and accuracy equivalent. It is hoped that this will make FFT-SWV easier to use as well as provide enhanced sensitivity. Also, application of FFT-SWV to high-performance liquid chromatography is being considered.

Table 3 Comparison of the detection limit of the proposed method and other reported methods

No.	Method	LOD ($\mu\text{g mL}^{-1}$)	Reference
1	GC-mass	0.01	41
2	Gas chromatography	0.005	42
3	Capillary gas chromatography	0.02	43
4	FFT-SWV flow injection analysis	0.002	This work

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