

A Novel fast Fourier Transform Square Wave Voltammetry for Determination of Sulfabenzamide at Er₂(WO₄)₃/CP Electrode

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Received: 29 July 2018 / Accepted: 7 September 2018 / Published: 1 October 2018

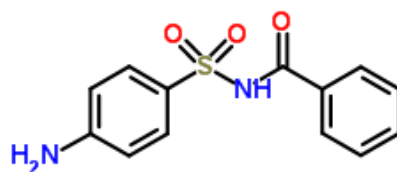
In this study, a novel sensitive sulfabenzamide voltammetric sensor has been developed for use through fast Fourier transform square wave voltammetry (FFTSWV). This is achieved through the modification of a carbon paste electrode with Erbium(III) tungstate nanoparticles (Er₂(WO₄)₃ NPs). The cyclic voltammogram of the analyte contained an irreversible oxidation peak at around 0.92 V vs. Ag/AgCl, which was used for the measurements. To achieve higher sensitivity, the effects of parameters such as, pH, quantity of the nanoparticles used, amplitude and frequency were also optimized. As a result, an optimal linear concentration range of 1.0×10^{-6} – 250.0×10^{-6} M with a limit of detection 0.45×10^{-7} M was reached. Characterization techniques such as transmission electron microscopy (TEM), and X-ray powder diffraction (XRD) were also used to study the size and morphology of the Er₂(WO₄)₃ NPs. The sensor responses proved to have a good reproducibility and repeatability with acceptable RSD levels of (5.6%, 1.79% respectively), in addition to the long-term stability of almost one month.

Keywords: Sulfonamide, Carbon paste electrode, Er₂(WO₄)₃ nanoparticles, Fast Fourier transform Square wave voltammetry

1. INTRODUCTION

Sulfonamides (sulphonamides) constitute a family of medications. The original antibacterial sulfonamides are synthetic antimicrobial agents containing the sulfonamide group [1]. Sulfabenzamide is an antibacterial/antimicrobial agent often used for together with sulfathiazole and sulfacetamide (trade name - Sultrin) as a topical, intravaginal antibacterial preparation. The structure of sulfabenzamide is shown in Scheme 1. Statistically speaking, the overall incidences of adverse

medication reactions for sulfa antibiotics reach around 3%, which is close to that of penicillin. Therefore, precise, simple and practical methods, both in terms of time and cost, monitoring the residual concentrations, and controlling processes, are of great interest. The -NH_2 and $\text{-SO}_2\text{NH-}$ group of sulfonamide compounds can be electrochemically oxidized and reduced respectively [2].



Scheme 1. Structure of sulfabenzamide

This is, to the best of our knowledge, the first report on the electrochemical analysis of sulfabenzamide. Given that electroanalytical methods can help overcome many problems of the pharmaceutical and medical applications due to their high degree of accuracy, precision, sensitivity and selectivity, they are commonly used in these areas. From among the diverse working electrodes, which can be used as the basis for constructing sensors, carbon paste electrodes have received extensive attention due to their advantages like ease of preparation, biocompatibility, low-costs, renewable surfaces, high stability and wide operation potential windows. Besides, incorporation of modifiers, especially nanomaterials, into carbon electrodes has been found to enhance their performance and make them suitable for various electroanalytical applications [3-15]. Furthermore, the efficiency of chemically-modified carbon paste electrodes (CPEs) is a function of the properties of the modifier, which in turn influences the selectivity of the electrodes toward the analytes.

Lanthanides are 15 f-block metallic elements with atomic numbers in the range of 57 to 71, which possess unique photogenic, magnetic, mechanical, and nuclear properties and have therefore, found widespread applications in glass and ceramic manufacturing, metallurgy, electronics, and agricultural industries. Their good optical properties of lanthanides nanoparticles, including large effective Stokes shifts, sharp emission peaks with narrow band width, low photo-bleaching, stability to photochemical degradation and low toxicity, make them further promising candidates for optical applications [16-18]. Yet there have been no reports on the application of lanthanides nanoparticles as modifiers in electrochemical sensor.

Square wave voltammetry (SWV), on the other hand is a sensitive electrochemical detection technique, with detection limits that can be greatly enhanced. Hyphenating fast Fourier transformation with SWV methods, for trace detection of different compounds, has been reported to be a very sensitive system for improving detection limits [19-25]. The fast Fourier transformation (FFT) approach separates the voltammetric signal from those of the background in the frequency domain. Accordingly, the detection limit is improved by digitally filtering some of the environmental noises.

Here attempts have been made to fabricate modified CPEs for a pharmaceutical electroanalysis, using $\text{Er}_2(\text{WO}_4)_3$ nanostructures. The electrode was used in the determination of sulfabenzamide in pharmaceutical formulations by using an FFTSWV approach under optimized conditions of pH, amount of the modifier, and FFTSWV parameters. The influence of the scan rate was also studied. It

has been proved that the application of an FFT approach leads to a highly sensitive techniques, which with broad applications [26, 27].

2. EXPERIMENTAL

2.1. Materials and reagents

Paraffin oil with high purity and the graphite powder, sulfabenzamide and other solvents and chemicals were supplied by Merck. A 1.0 mM standard stock solution of sulfadiazine was prepared using a 0.01M phosphate buffer solution (PBS) as the supporting electrolyte. The PBS solutions were prepared by mixing stock standard solutions of NaH_2PO_4 and Na_2HPO_4 and adjusting the required pH using 0.01M NaOH. Doubly distilled water was used in all experiments. Erbium(III) tungstate nanoparticle ($\text{Er}_2(\text{WO}_4)_3$ NP) was prepared through the previously reported procedure [28].

2.2. Tools

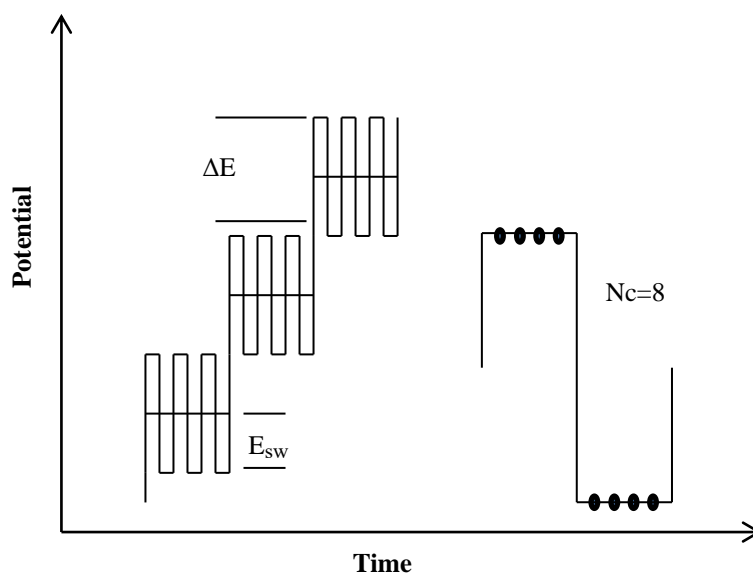


Figure 1. Schematic of potential wave in the SWV experiments

Voltammetric measurements such as cyclic voltammetry (CV) and FFTSWV were performed on a homemade potentiostat, connected to a PC equipped with an analogue to digital (A/D) data acquisition board (PCL-818H, Advantech Co.) for generating the potential waveform and acquiring data current. The data of the potential waveform applied to the working electrode were acquired, and stored using Lab Wiremen Software.

Figure 1 displays the waveform containing multiple SW pulses with respective amplitude and frequency of E_{sw} and f_o , which were overlaid on a staircase potential which changed by a small potential step of ΔE . The potential pulse values of SW (E_{sw}) and ΔE were in a small range (10–50

mV). For each SW polarization cycle, the current was sampled four times in each potential ramp. A three electrode cell configuration was used. In this setup a bare or modified CPE (3 mm diameter) was used as the working electrode, a graphite bar was the auxiliary electrode and a saturated Ag/AgCl electrode acted as the reference electrode.

2.3. Preparation of the bare and unmodified electrodes

Typically 0.1g of the paste forming the working electrode, and paraffin oil as a binder, were thoroughly mixed with graphite at a 70/30 (w/w) ratio. A portion of the resulting carbon paste was tightly pressed into the end cavity (3-mm i.d.) of the working electrode body equipped with a copper wire through the paste. The electrode surface was smoothed using a piece of clean paper. The modified CPES were prepared by mixing 66.5/28.5/5 (w/w/w) graphite powder/paraffin oil/ $\text{Er}_2(\text{WO}_4)_3$. The surface of the working electrode was renewed by scratching out an excess of paste and displacing the carbon paste after each measurement.

3. RESULTS AND DISCUSSION

3.1. Characterizing the $\text{Er}_2(\text{WO}_4)_3$ particles

Erbium(III) tungstate nanoparticles (NPs) were synthesized through the chemical precipitation approach using the Taguchi robust design (TRD) to study the effects of the synthesis conditions on the product [28]. The XRD pattern of $\text{Er}_2(\text{WO}_4)_3$ NPs, shown in Fig. (2), contains XRD features at $2\theta = 28, 29, 33, 34, 37, 47, 49$ and 50° reflecting the monoclinic structure of $\text{Er}_2(\text{WO}_4)_3$ with the crystal structure data of $a=b= 7.3$ and $c= 9.3$.

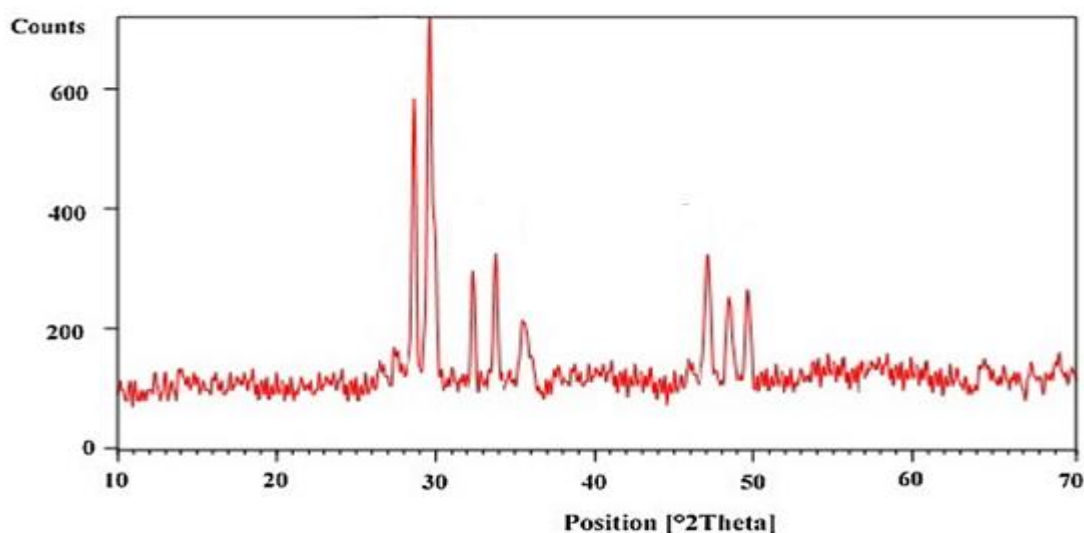


Figure 2. XRD pattern for synthesized $\text{Er}_2(\text{WO}_4)_3$ NPs

Also, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) analyses helped study the size and structure of the $\text{Er}_2(\text{WO}_4)_3$ and the results (Fig. 3) indicated the diameter of the synthesized $\text{Er}_2(\text{WO}_4)_3$ particles to be about 33 nm.

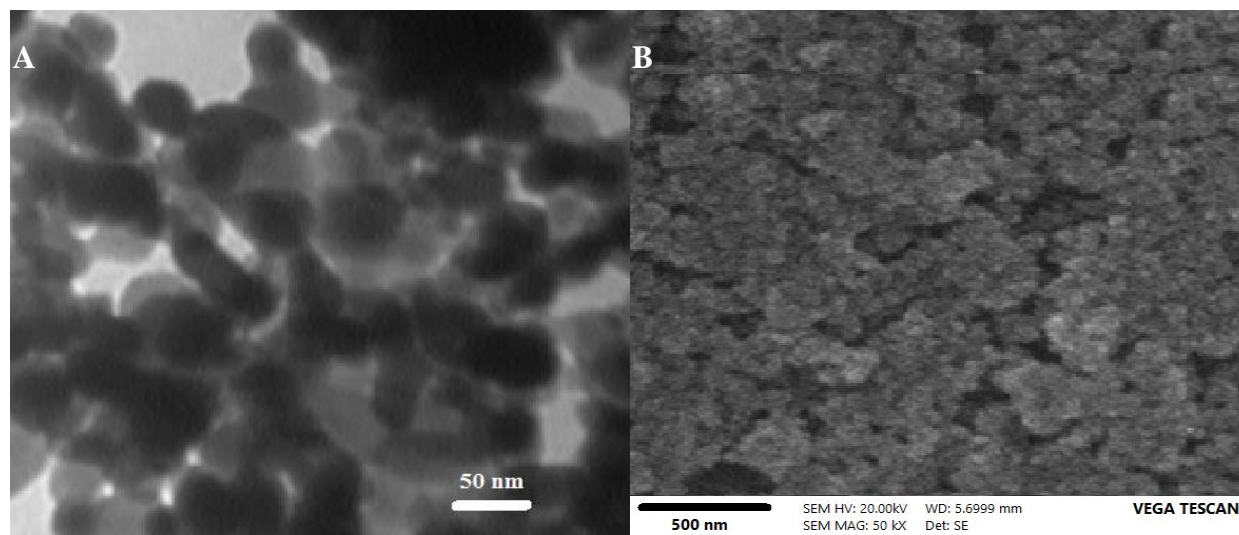


Figure 3. (A) TEM and (B) SEM images of $\text{Er}_2(\text{WO}_4)_3$ nanoparticles

3.2. FFT cyclic voltammetry

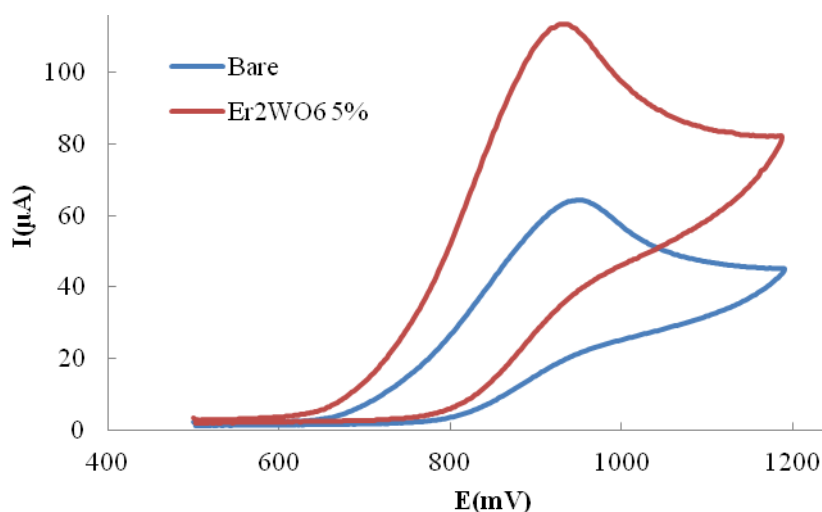


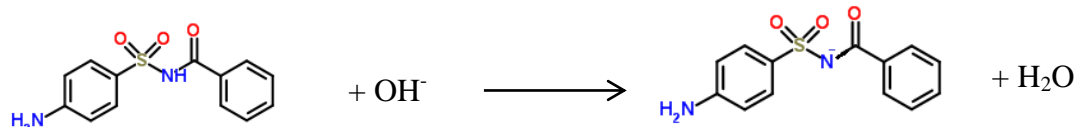
Figure 4. Cyclic voltammograms of electro-chemical oxidation of a 1.0mM solution of sulfabenzamide in PBS (pH=8.0), using unmodified (blue line) and modified CPE (7% $\text{Er}_2(\text{WO}_4)_3$ /CPE (red line)) at 0.1 V/s.

To obtain a proper overview of the effects of the $\text{Er}_2(\text{WO}_4)_3$ particles present in the modified electrode on the sulfabenzamide determination, CV responses acquired using the electrodes were studied [10-14]. Fig. (4) shows the cyclic voltammograms of a solution of 1.0 mM sulfabenzamide in 0.01M PBS (pH=8.0) using a bare and 7% $\text{Er}_2(\text{WO}_4)_3$ NPs modified CPE at a scan rate of 100mV/s.

The CVs Fig. (4) reflect an irreversible oxidation peak at around +0.92 V. In the case of the modified electrode however the existence of $\text{Er}_2(\text{WO}_4)_3$ NPS in the CPE matrix led to an almost 89% increase in the peak current, which could be attributed to the electrocatalyst properties of the $\text{Er}_2(\text{WO}_4)_3$ NPs.

3.2. Effect of pH

The relationship between the electrode response and the pH of solution was studied in 1.0 mM sulfabenzamide and 0.01 M PBS (Fig. 5). Do to the scheme 2, alkaline rezones were required for solving the active ingredient of sulfabenzamide. To study the impact of pH, 0.1 M NaOH was used to adjust the pH of PBS at 8, 9, 10 and 11. Increasing the pH shifter the oxidation peak potential toward more negative values and increased the current density from pH=8.0 to 10.0 and then decreased this value. As seen in Scheme 3, the negative shift of potential is due to the involvement of protons in the electrode reaction process. Since the maximum peak current occurred at pH=10.0, this pH was chosen and applied as the optimal pH in further studies.



Scheme 2. The proposed reaction for solvation of sulfabenzamide in alkaline media

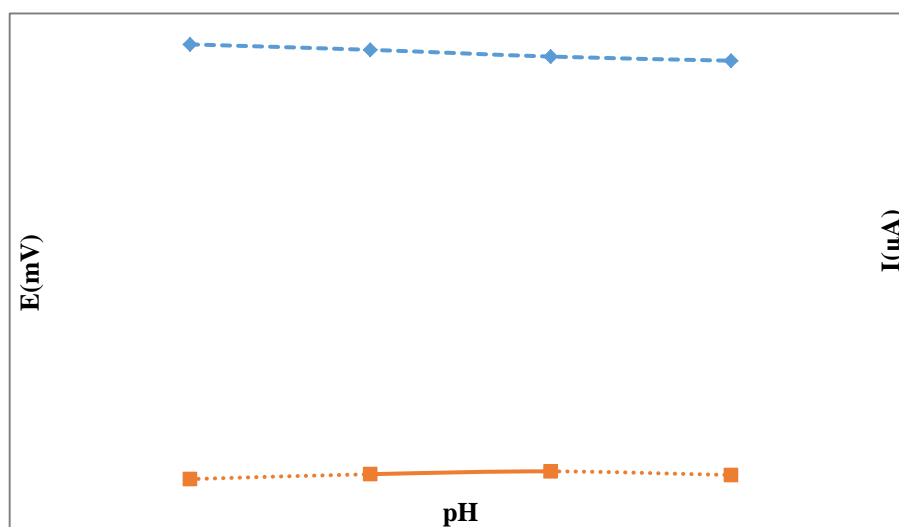
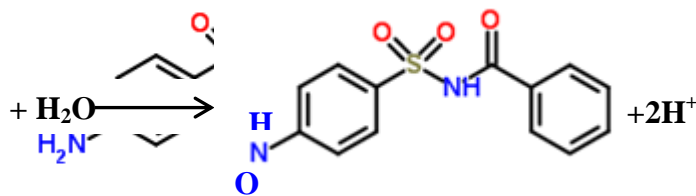


Figure 5. Plot of pH vs. peak current for $\text{Er}_2(\text{WO}_4)_3/\text{CPE}$ at different pH values, scan rate 100 mVs^{-1}



Scheme 3. The proposed reaction for electro-oxidation of sulfadiazine

3.3. Effect of the amount of $\text{Er}_2(\text{WO}_4)_3$ nanoparticles

The $\text{Er}_2(\text{WO}_4)_3$ content of the CPEs were also optimized to reach the best response [10,12]. To this end four electrodes with different quantities of $\text{Er}_2(\text{WO}_4)_3$ were tested and based on the results (Fig. (6)) the oxidation peak current of sulfabenzamide was enhanced by increasing the amount of $\text{Er}_2(\text{WO}_4)_3$ up to 7% (w/w), but decreased beyond this value. The decrease in signal may correspond to the decline in the conductivity of the electrode composition. Based on the results 7% (w/w) of $\text{Er}_2(\text{WO}_4)_3$ was chosen as the optimal amount of the modifier to be used in the paste.

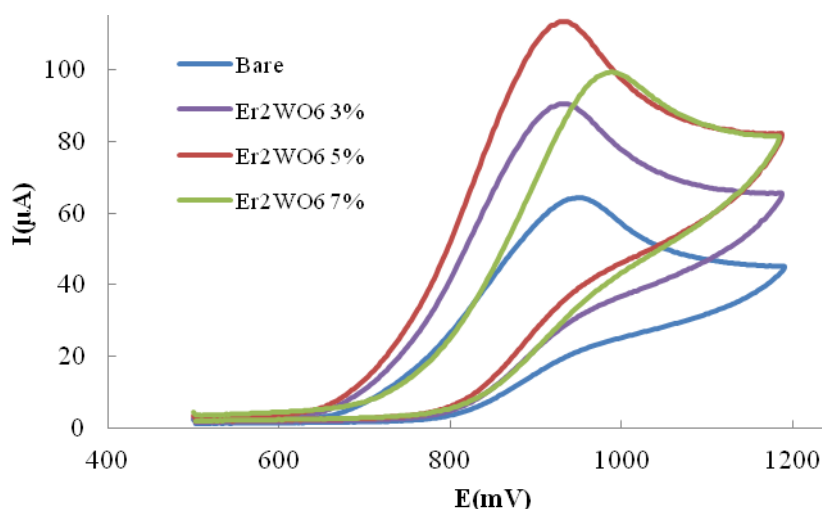


Figure 6. CVs obtained bare CPE (blue line), 3% $\text{Er}_2(\text{WO}_4)_3/\text{CPE}$ (violet line), 5% $\text{Er}_2(\text{WO}_4)_3/\text{CPE}$ (red line) and 7% $\text{Er}_2(\text{WO}_4)_3/\text{CPE}$ (green line) working electrodes in a 1.0 mM solution of sulfabenzamide in 0.01 M PBS solutions ($\text{pH}=10.0$), at 100 mVs^{-1} .

3.4. Effect of scan rate

Figure 7 illustrates the changes in the cyclic voltammograms with the potential scan rate window of $10\text{-}1000 \text{ mV s}^{-1}$ for the modified CPE in a 1.0 mM solution of sulfbenzamide in 0.01 M PBS at $\text{pH}=10.0$ [6,7,11]. Also, Fig. (5B) illustrates that the anodic peak currents (I_p) change linearly with the square root of scan rate ($v^{1/2}$) in this window, which indicates that the electrochemical process is diffusion-controlled.

According to the Laviron equation [29], using the changes in the anodic peak potentials with the logarithm of scan rate, one can determine the charge transfer coefficient (α) of a reaction. The slope obtained from Fig. (7C) (i.e. changes of peak potentials (E_p) as a function of the logarithm of the potential scan rate) can be used to determine the kinetic parameter α_a . The slope of the linear segment is equal to $2.303RT/(1 - \alpha)nF$ for the anodic peaks. Given that the oxidation of sulfonamide has been reported as a two-electron process [30], anodic transfer coefficient (α_a) was calculated to be 0.99.

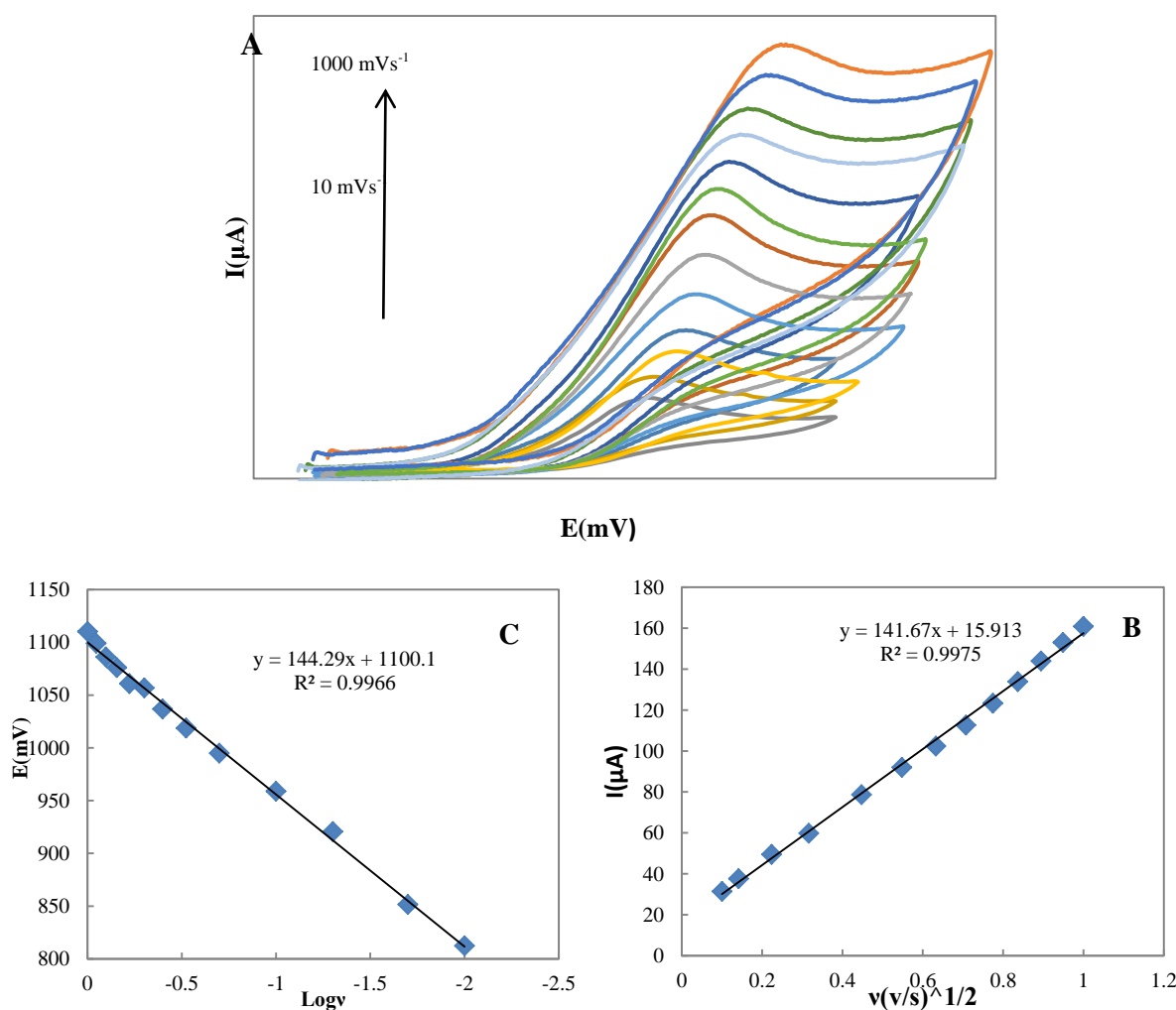


Figure 5. (A) CVs obtained using $\text{Er}_2(\text{WO}_4)_3/\text{CPE}$ in a 0.1mM solution of sulfabenzamide in 0.01M PBS ($\text{pH}=10.0$), at various scan rates, from inside the plots correspond to scan rates of 10, 20, 50, 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 mVs^{-1} , respectively. (B) Variations of the peak current versus square root of scan rates (C) Variation of E_p versus the logarithm of the scan rate.

3.5. Optimization of the FFTSWV parameters

FFTSWV, which is a well-established pulse voltammetric approach [31-33], was used as the electroanalytical technique for determination of sulfabenzamide. According to the Fig. (1), the

response depends on parameters like the frequency (f) and amplitude (E_{sw}). Hence, to determine the optimal conditions for the measurement, the effects of the instrumental factors on the peak current response of a 0.1mM solution of sulfabenzamide in 0.01 M PBS (pH=10.0) were monitored. As it can be seen in Fig. (8) the respective optimal values for the frequency and amplitude were 88 and 15.

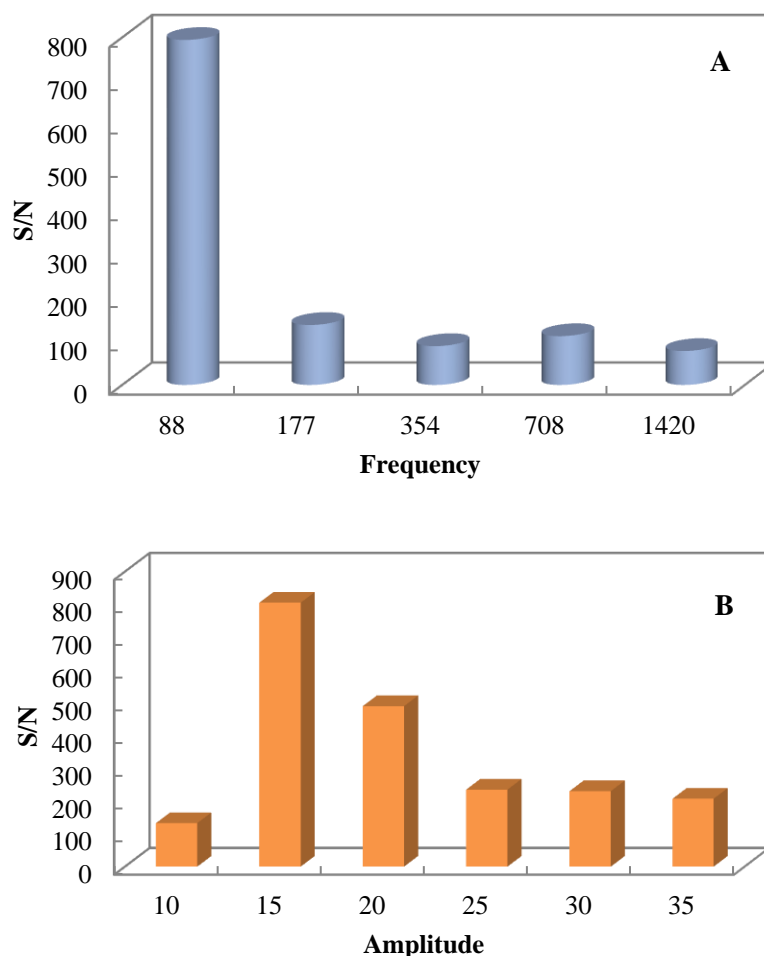


Figure 8. Effects of frequency (A) and amplitude (B) observed for a 0.1 mM solution of sulfadiazine in 0.01 M phosphate buffer pH=10.0 using $Er_2(WO_4)_3/CPE$ as the working electrode

3.6. Reproducibility and Repeatability of the results

To determine the reproducibility of the measurements performed using the modified CPE, 5 electrodes were prepared and used to analyze a 0.1 mM sulfabenzamide solution on 5 different days. The relative standard deviation (RSD) calculated for the results of these experiments was 5.6% which reflects reproducibility of the electrodes. Under the same conditions, the repeatability of the results obtained using $Er_2(WO_4)_3/CPE$ was tested 5 times on a single day, and the calculated RSD was determined to be 1.79%. Under ambient conditions, the electrodes showed long-term stability (almost one month).

3.7. Calibration curve analysis

To achieve better limit of detection, FFTSWV which produces sharper and better-defined peaks was used in the analysis of sulfabenzamide in PBS (0.01 M, pH 10.0) under optimal conditions and the results are given in Fig. 9 [19-25]. The linear section of the curve in Fig. 9 (B) extends from 1.0×10^{-6} to 250.0×10^{-6} M. The limit of detection of the analysis was 0.46×10^{-7} M.

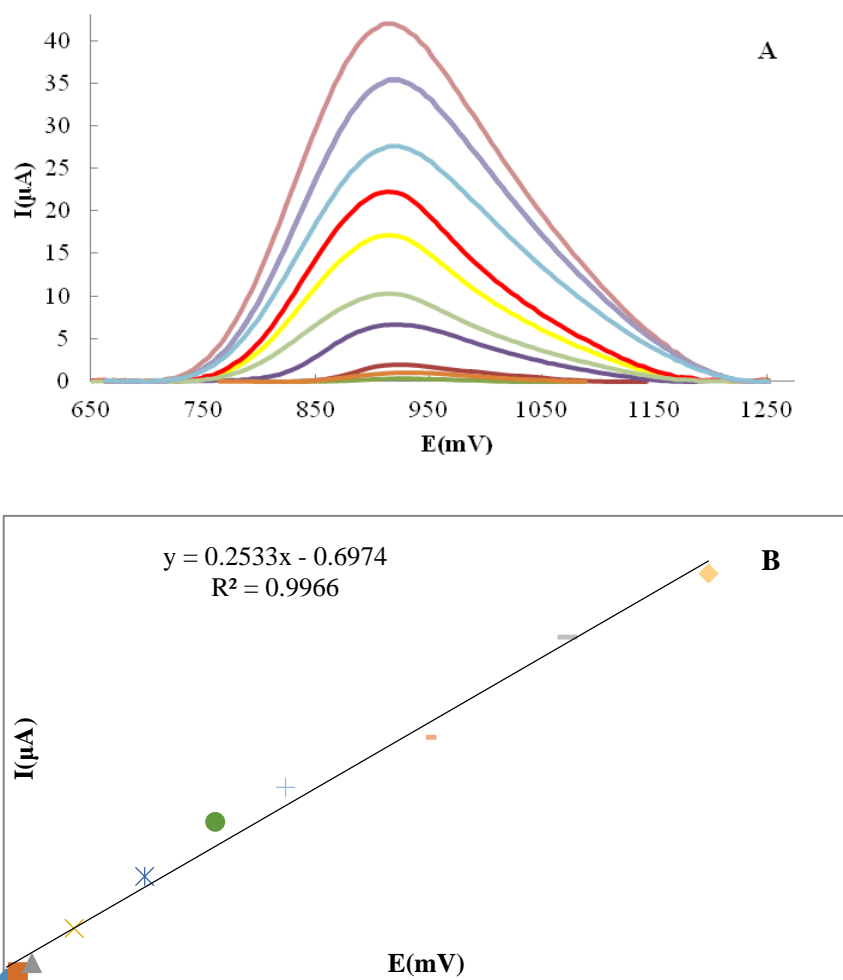


Figure 9. (A) FFT Square wave voltammograms; (B) Calibration plot for different 1.0-250.0 μM (from inside to outside) solutions of sulfabenzamide in 0.01M PBS (pH=10.0) at $\text{Er}_2(\text{WO}_4)_3/\text{CPEs}$

3.8. Effect of potential interfering species on the determination of sulfabenzamide

The influence of possible interfering species was also investigated. 1000-fold excess of Mg^{2+} , Na^+ , K^+ , Ca^{2+} , CO_3^{2-} , H_2PO_4^- , NO_3^- , I^- , Cl^- ; 100-fold excess of glucose and maltose; 40-fold excess of uric acid; and 20-fold excess of ascorbic acid were used in the experiments and relative errors less than 5% in the oxidation current of sulfabenzamide in the presence of interfering species was

considered as the tolerance limit. The results are listed in Table 2, indicating that the performance of the sensor was not significantly influenced by the presence of the various species studied.

Table 2. Results of interference studies using a 0.01mM sulfabenzamide in PBS pH=10.0 at $\text{Er}_2(\text{WO}_4)_3/\text{CPE}$

Species	Tolerance limits ($C_{\text{species}}/C_{\text{naproxen}}$)
Mg^{2+} , Na^+ , K^+ , Ca^{2+} , CO_3^{2-} , H_2PO_4^- , NO_3^- , I^- , Cl^-	1000
Glucose, Maltose	100
Uric acid, Ascorbic acid	50

4. CONCLUSION

The low detection limits obtained for the analysis of sulfabenzamide (0.46×10^{-7} M) demonstrate that the developed electroanalytical tool is very attractive and appropriate for trace analyses of the analyte. To the best of our knowledge, there has been no electrochemical no such reports on the electrochemical determination of sulfabenzamide in the literature. Beside the low detection limit and good sensitivity of the developed sensor leads to good reproducibility with advantages of fast response time, simplicity of preparation and renewable electrode surface that change the developed electrode to a good electrochemical sensor for use in different systems. $\text{Er}_2(\text{WO}_4)_3$ nanoparticles exhibited a good electrocatalytic activity to oxidize sulfadiazine and the presence of $\text{Er}_2(\text{WO}_4)_3$ in the modified carbon paste electrode and FFTSWV technique led to the development of a promising route for the determination of sulfabenzamide.

ACKNOWLEDGEMENTS

The financial support of this work by University of Tehran and Iran National Science Foundation (INSF; Grant Number: 950019) is gratefully acknowledgments.

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