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Voltammetric Determination of Sumatriptan by an Overoxidized Poly(*p*-aminophenol) Modified Glassy Carbon Electrode

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This study aims to develop a promising electrochemical sensor based on polymer film overoxidation following the electrochemical polymerization of *p*-aminophenol on a bare glassy carbon electrode (GCE) surface for the voltammetric determination of sumatriptan succinate (SUM). Cyclic voltammetry (CV), Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and square wave voltammetry (SWV) were employed to characterize the electroanalytical performance and morphology of the modified electrode. The results indicated a significant improvement in electrode sensitivity to SUM after electrochemical polymerization and overoxidation of poly(*p*-aminophenol). We also investigated the effect of all effective instrumental and experimental parameters on sensor response. Under the optimum conditions (accumulation for 60 s at 0.055 V and pH = 2.0), the electrode SWV response to SUM within the range of 1.0-100.0 µM with a limit of detection (LOD) of 0.294 µM was linear under optimized conditions. We also evaluated the selectivity of the designed sensor to different interfering species, suggesting no significant interference. The designed sensor was also used to determine SUM in pharmaceutical preparations and human serum samples with minimal matrix effects, admissible recoveries (99-106), and satisfactory repeatability (1.2-5.1 %RSD). The proposed sensor exhibited admissible repeatability, reproducibility, and stability.

Keywords: Sumatriptan, Square wave voltammetry, Poly(4-aminophenol), Glassy carbon electrode

INTRODUCTION

Sumatriptan succinate (SUM) is one of the tryptamine-based medicines that is prescribed for treatment of cluster and migraine headaches (Fig. 1) [1]. SUM induces its therapeutic effects by binding selectively to serotonin type-1D receptors in the basilar vein and aiding levels of serotonin in the brain. The function of the trigeminal nerve is also seen to decline, which presumably reflects the potency of SUM in the treatment of cluster headaches [2-4]. However, high doses of SUM (200 mg day^{-1}) cause serious adverse effects such as ataxia, convulsion, tremor, cyanosis, sulfhemoglobinemia, and paralysis. Therefore, its determination is very important [5-7].

Different analytical techniques have been reported for the determination of SUM including high-performance liquid chromatography (HPLC) [8], capillary electrophoresis [9], UV-Vis spectrophotometry [10], liquid chromatography-mass spectrometry (LC-MS) [11], high-performance thin-layer chromatography (HPTLC) [12] and liquid chromatography-tandem mass spectrometry (LC-MS/MS) [13]. However, all of the referred techniques have several disadvantages such as intricate and expensive instrumentation, being time-consuming, requiring experienced operators to implement sample preparation steps, consuming high amounts of toxic organic solvents, and, in some cases, low selectivity and sensitivity [14-16]. Therefore, developing a simple, economical, environmentally friendly, and rapid analytical method for SUM measurement is really demanded. Fortunately, electrochemical sensors meet all of the desired features. This type of sensor offers different privileges such as

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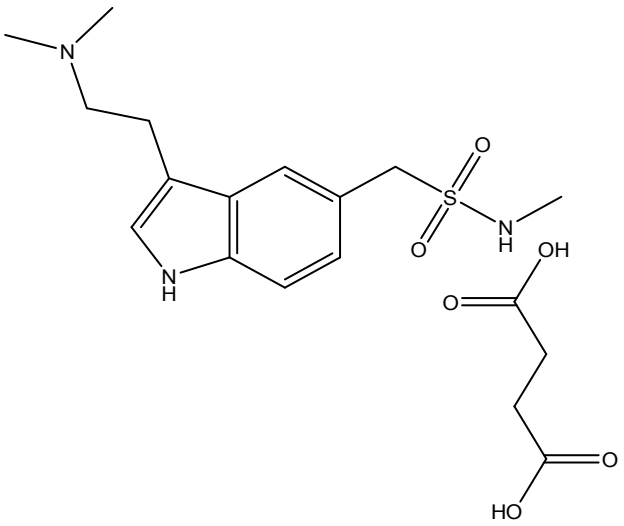


butanedioic acid;1-[3-[2-(dimethylamino)ethyl]-1H-indol-5-yl]-N-methylmethanesulfonamide

Fig. 1. The chemical structure and IUPAC name of SUM.

straightforward and low-cost instrumentation, high selectivity, admissible sensitivity, short analysis time, wide linear range and applicability in colored or opaque specimens. Besides, electrochemical sensors can be designed in portable forms [17-20]. Amongst the different electroanalytical methods, SWV is one of the most promising techniques for quantitation of the analytes at trace amounts because of its great resolution, superb sensitivity, and outstanding ability to differentiate between the Faradaic and charging current [21-23].

The use of the electropolymerization method for modification of electrodes with conductive polymers to promote the electrocatalytic features of analytes, ameliorating the electron transfer, and lowering the overpotential has grown dramatically in the field of electrochemical sensors [24-26]. While in the drop-casting technique, the reproducibility of the modified electrodes is really poor, in electropolymerization, the characteristics of the created films are completely under the control of the operator, and the thickness of the polymer can be changed easily by altering the electrosynthesis conditions [27-29]. As a result, the prepared electrodes by electropolymerization procedure are more reproducible [30, 31]. Among the conductive polymers, the distinguished properties of poly(4-aminophenol) (PAP) make it more preferable for sensing purposes. Poly(4-aminophenol) has two oxidizable functional groups in its chemical structure, OH and NH_2. Consequently, more reactive sites for interacting with analytes are created on the surface of the polymerized film compared to other polymers like polyaniline [32-34]. Moreover, poly(4-aminophenol) has high stability, superb electrocatalytic activity, and great antifouling features. Moreover, poly(4-aminophenol) can be overoxidized by applying a constant positive potential. In the overoxidation process, the porosity, conductivity, and permselectivity of the polymerized film improved substantially [34]. In addition, by overoxidization, other reactive oxygen-containing functional groups, including carbonyl and carboxyl, can be generated on the surface of the poly(4-aminophenol) film, which can augment the interaction of analyte species with the electrode surface through hydrogen bonding. For the aforementioned excellent features of the overoxidized poly(4-aminophenol) (Ox-PAP), this conductive film was used as a modifier for sensitive determination of various analytes, including epinephrine, uric acid, ascorbic acid, dopamine, tryptophan,

and glucose [35-37].

In this regard, the applicability of Ox-PAP glassy carbon electrode as a simple and economic electrochemical sensor for the determination of SUM in pharmaceutical preparations and human serum plasma was investigated for the first time, in this research.

EXPERIMENTAL

Chemicals and Reagents

All employed reagents and components were obtained from Merck Company (Darmstadt, Germany) or Sigma-Aldrich and utilized without further purification. SUM was purchased from Hakim Pharmaceutical Company (Tehran, Iran). The stock solution of SUM (1.0×10^{-3} M) was prepared by double distilled water (DDW). It was attempted to prepare a supporting electrolyte by mixing potassium nitrate (KNO_3) (1.0×10^{-1} M) and hydrochloric acid (HCl) (1.0×10^{-2} M) in all electrochemical measurements. SUM tablets were bought from a nearby pharmacy for recovery tests. Besides, fresh human serum samples were obtained from the Hamadan province blood transfusion organization (Hamedan, Iran). DDW was used to prepare all solutions.

Apparatus

The Metrohm 797 VA Computrace Polarograph was used as a base to perform all the electrochemical experiments, including CV and SWV. The pH was measured using a Metrohm 827 pH meter (Herisau, Switzerland) with a combined glass electrode. Saturated calomel electrode (SCE), GCE, and Pt electrode were all purchased from Azar Electrode Company (Urmia, Iran). A three-electrode GCE-containing system (2 mm in diameter), a modified GCE used as working electrode, a platinum electrode used as the counter electrode, and a saturated calomel electrode (SCE) used as a reference electrode were employed. SEM-EDS (MIRA3 TESCAN) was used to evaluate the surface morphology of the developed electrode. Infrared spectra of samples were collected by a Perkin-Elmer model spectrum GX, FT-IR spectrometer with the spectral range of 4000-500 cm^{-1}.

Fabrication of the Modified Electrode

Before each measurement, the GCE surface was polished on a polishing cloth with 0.3 μm alumina slurry for 60 s and underwent ultrasonic cleaning, each for 10 min, with ethanol and redistilled water. CV was utilized to conduct poly(*p*-aminophenol) (PAP) electrochemical deposition on GCE in a 5 M SDS + 5 M *p*-aminophenol + 1 M HCl solution [37]. Polymerization voltammograms were achieved through ten repetitive potential cycles from -0.645 to 1.955 V *vs*. SCE at a scan rate of 100 mV s^{-1}. The PAP/GCE was overoxidized for 30 s at +1.2 V in 0.1 M NaOH solution for a stronger conductive and porous surface. Ultra-pure water was used to wash the modified electrode, referred to as Ox-PAP/GCE.

Pharmaceutical Sample Solution Preparation

Thirty SUM tablets (50 mg) were powdered and then homogenized. The measured volumes of homogenized powder were then carefully weighed and imported into a 50 ml volumetric flask. The powder was then dissolved for 15 min with sonication and centrifuged at 4000 rpm for 20 min. Afterward, we filtered the resulting mixture and transferred a proportionate amount into a 25 ml volumetric flask and diluted up to 0.1 M KNO_3 (pH 2.0). We finally determined the electrochemical signal [38].

Serum Sample Preparation

Different quantities of SUM were spiked to a 1 ml serum sample. Then, 0.8 ml acetonitrile was applied for serum protein removal. To extract the serum protein residues, we centrifuged the mixture for 20 min at 4000 rpm. The supernatant was then carefully taken and moved to a 25 ml flask and diluted with the supporting electrolyte. Finally, it was possible to determine the electrochemical signal and obtain a percent recovery using the SWV technique [39].

Experimental Procedure

We sought to the cycle of the modified electrode several times in the range 0.055-1.655 V with a scan rate of 100 mV s^{-1} in a 1.0×10^{-1} mol KNO_3 and 1.0×10^{-2} M HCl prior to any voltammetric measurement until reaching a reproducible response. The modified electrode was then moved to an electrochemical cell containing a proportionate volume of SUM and 0.1 mol^{-1} KNO_3 (pH = 2.0). The electrochemical experiments, such as SWV and CV, were

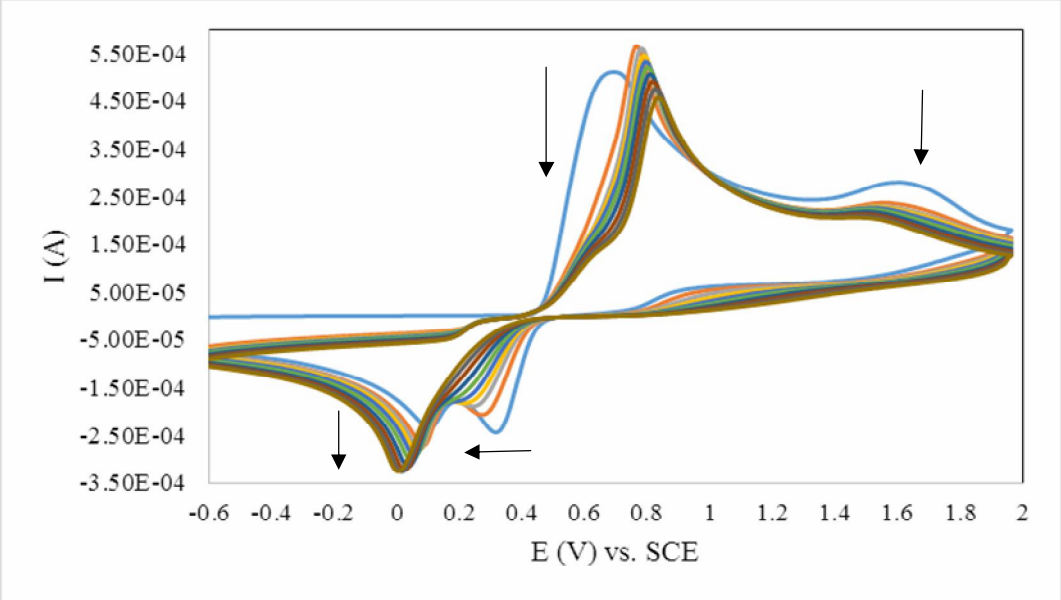


Fig. 2. Cyclic voltammogram of p-aminophenol electropolymerization in a 5 mM *p*-aminophenol monomer + 1 M HCl solution on a GCE in the presence of 5 mM SDS at a scan rate of 100 mV s^{-1}. The arrows indicate the trends of current during CVs.

carried out as is common upon accumulation for 60 s at 0.055 V. Experimental parameters for SWV were: 50 mV pulse amplitude, 75Hz frequency, and 10 mV phase voltage.

RESULTS AND DISCUSSION

Electrosynthesis and Characterization of the Polymer Film

Figure 2 demonstrates the cyclic voltammograms of *p*-aminophenol electropolymerization. The modified electrode was donated as PAP/GCE. An irreversible oxidation peak was detected during a CV scan at 1.56 V for *p*-aminophenol without corresponding cathodic processes during the reverse scan. Furthermore, reduction peaks and quasi-reversible oxidation were identified at ≈ +0.67 and +0.31 V, respectively. During the p-aminophenol oxidation process, the peaks may be produced by the intermediate species [37]. The gradual decline of the peak currents of the two anodic peaks and the increase of the cathodic peak current with its potential shift to more negative values with repetitive CV cycles demonstrated a high polymer content on the electrode surface [36]. The PAP/GCE overoxidized with + 1.2 V for 300 s in 0.1 M NaOH solution to ensure a more porous surface and higher conductivity. The overoxidization process was implemented in an intense basic aqueous media because in the electro-oxidation procedure of PAP some electrons and protons are produced (Red - ne - $nH^+ \rightarrow$ Ox), and according to Le-Chatelier's principle, this reaction is more favorable in alkaline solutions.

To obtain the highest sensitivity of the modified electrode for voltammetric determination of SUM, the effect of the main parameters of the electrosynthesis conditions, including the number of CV cycle and overoxidation time, was investigated. For this purpose, the polymer film was electrosynthesized on GCE's surface at different conditions. Then, the square wave voltammogram of a 10 µM of SUM in 0.1 M KNO_3 (pH 2.0) was recorded. Afterward, the peak current was drawn as a function of the CV cycle number and overoxidation time. The obtained results are presented in Fig. 3. As seen, the best sensitivity of the modified electrodes towards SUM was observed at 10 CV cycle numbers and overoxidation time of 300 s at 1.2 V in 0.1 M NaOH solution.

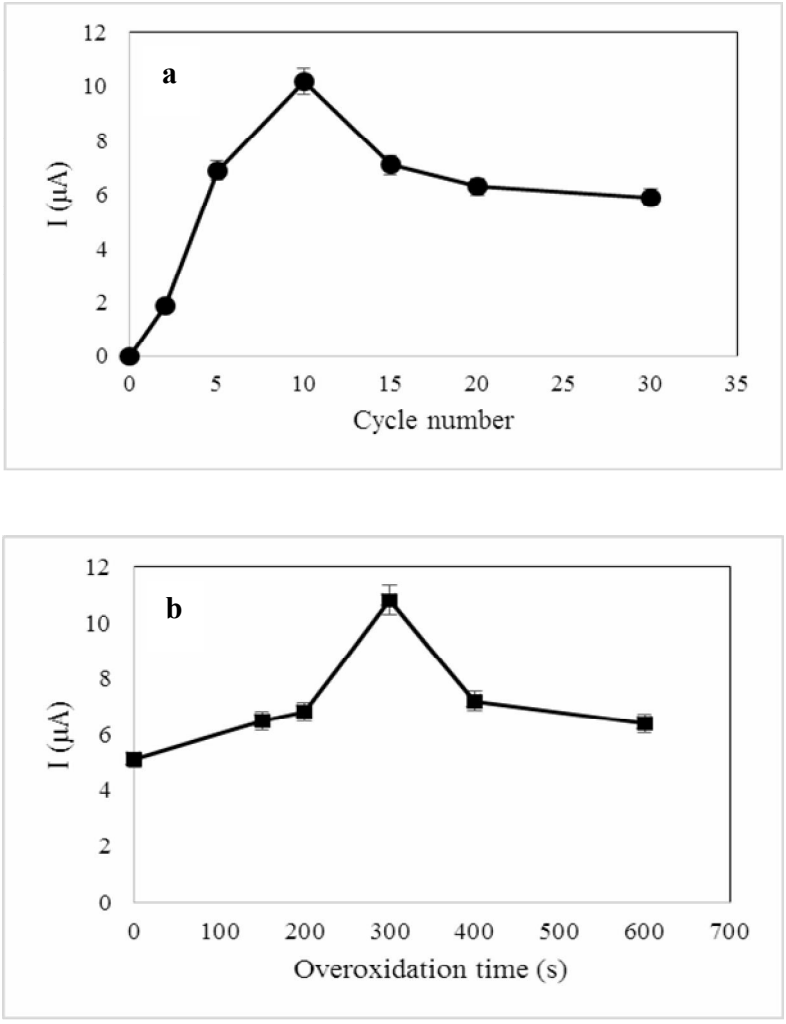


Fig. 3. The effect of CV cycle number (a) and the effect of the overoxidation time (b) on the peak current for a 10 µM solution of SUM in 0.1 M KNO_3 (pH 2.0).

Under the optimized conditions of the electrosynthesis of the polymer film, the electrochemical behavior of SUM was examined by CV (at a scan rate of 100 mV s^{-1} in the 0.2-1.25 V potential range) and SWV methods. For this purpose, the cyclic and square wave voltammograms of a 50 µM solution of SUM in 0.1 M KNO_3 (pH 2.0) was recorded on the surface of bare GCE, PAP/GCE and Ox-PAP/GCE electrodes, whose results are illustrated in Fig. 4. As shown, there was no peak for SUM on the surface of bare GCE in both voltammetric techniques. After the electropolymerization of PAP, a well-defined anodic peak emerged in both cyclic and square wave voltammograms at 0.99 V *vs*. SCE. The amount of the peak current enhanced significantly after the overoxidation of the polymer film in the basic medium [38]. Therefore, it can be deduced that overoxidation of the polymer film enhances the modified electrode sensitivity to SUM substantially, and Ox-PAP/GCE was selected for the rest of the experiments.

Electrochemical sensor response is a function of its physical morphology. In this respect, the morphology of the electrode surface during the modification process was evaluated by SEM, and the obtained SEM images are

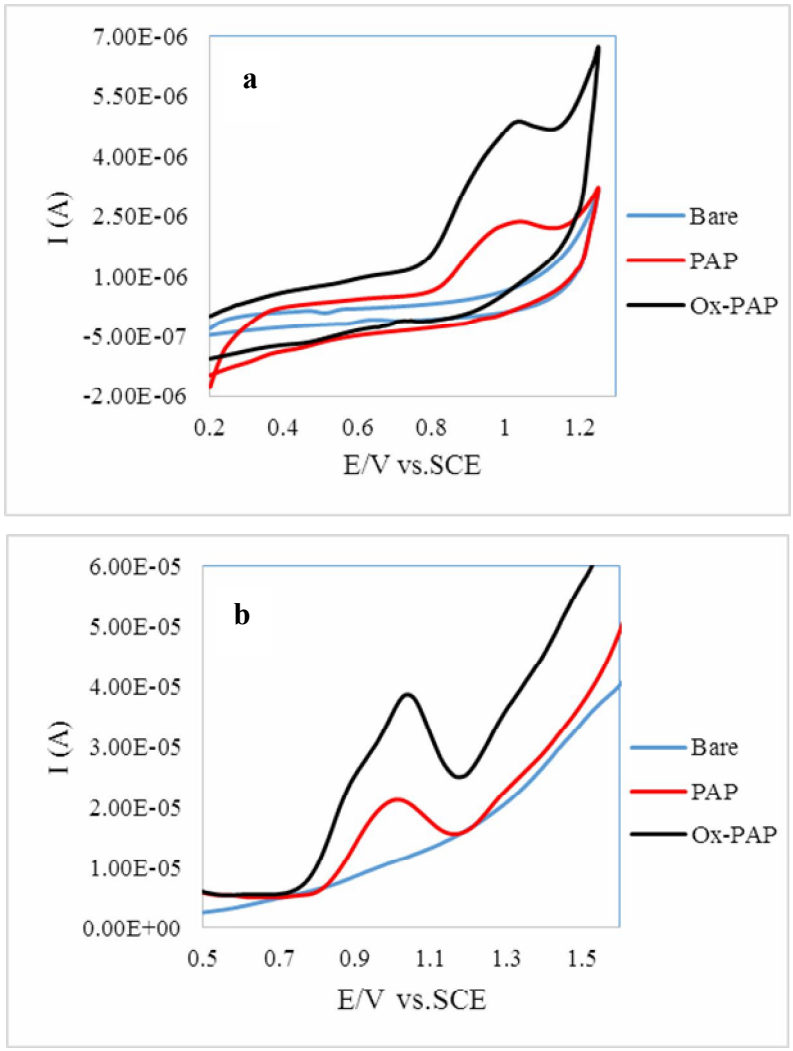


Fig. 4. The CVs (a) and SWVs (b) for a 50 µM solution of SUM in 0.1 M KNO_3 (pH 2.0) on the surface of bare GCE, PAP/GCE and Ox-PAP/GCE.

presented in Fig. 5. As can be seen, after electropolymerization, a thin layer film with a globular structure covered the surface of GCE homogeneously [37]. Then, by overoxidizing the PAP film at high potentials, the coated polymeric substrate changed significantly. As it is obvious from Fig. 5B, the surface of the Ox-PAP/GCE electrode is covered by a swollen like a heterogeneous film with randomly distributed large spherical particles and the layer porosity enhanced remarkably in comparison to the PAP/GCE [36].

In order to obtain a further insight about how overoxidation of PAP enhances the electrochemical response of the sensor towards SUM, the FT-IR spectrums of the electrosynthesized polymer film before and after overoxidation process (PAP and Ox-PAP films) were recorded, the results are given in Fig. 6. As it is obvious, after overoxidization of PAP, various nitrogen and oxygen containing functional groups are created on the surface of the modified electrode (such as carbonyl and amine groups)

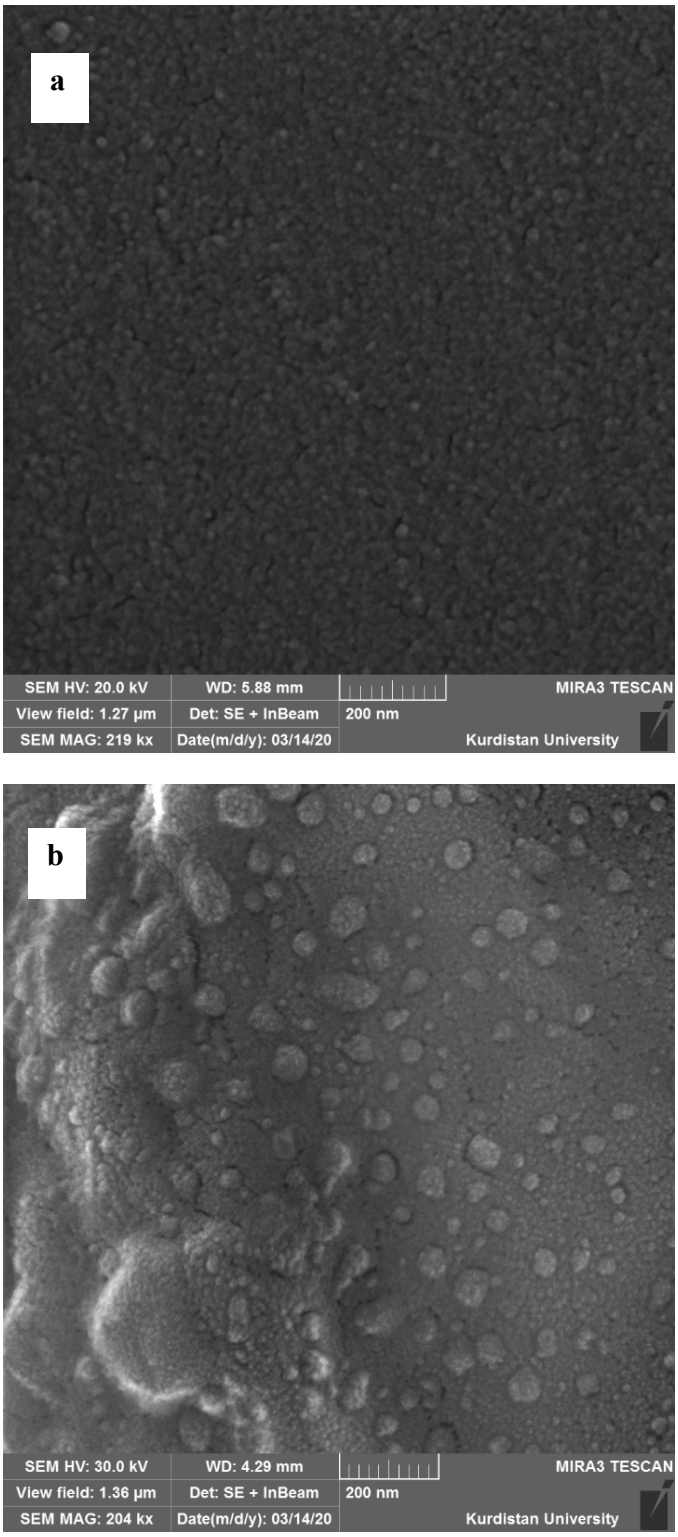


Fig. 5. The SEM images of PAP/GCE (a) and Ox-PAP/GCE (b).

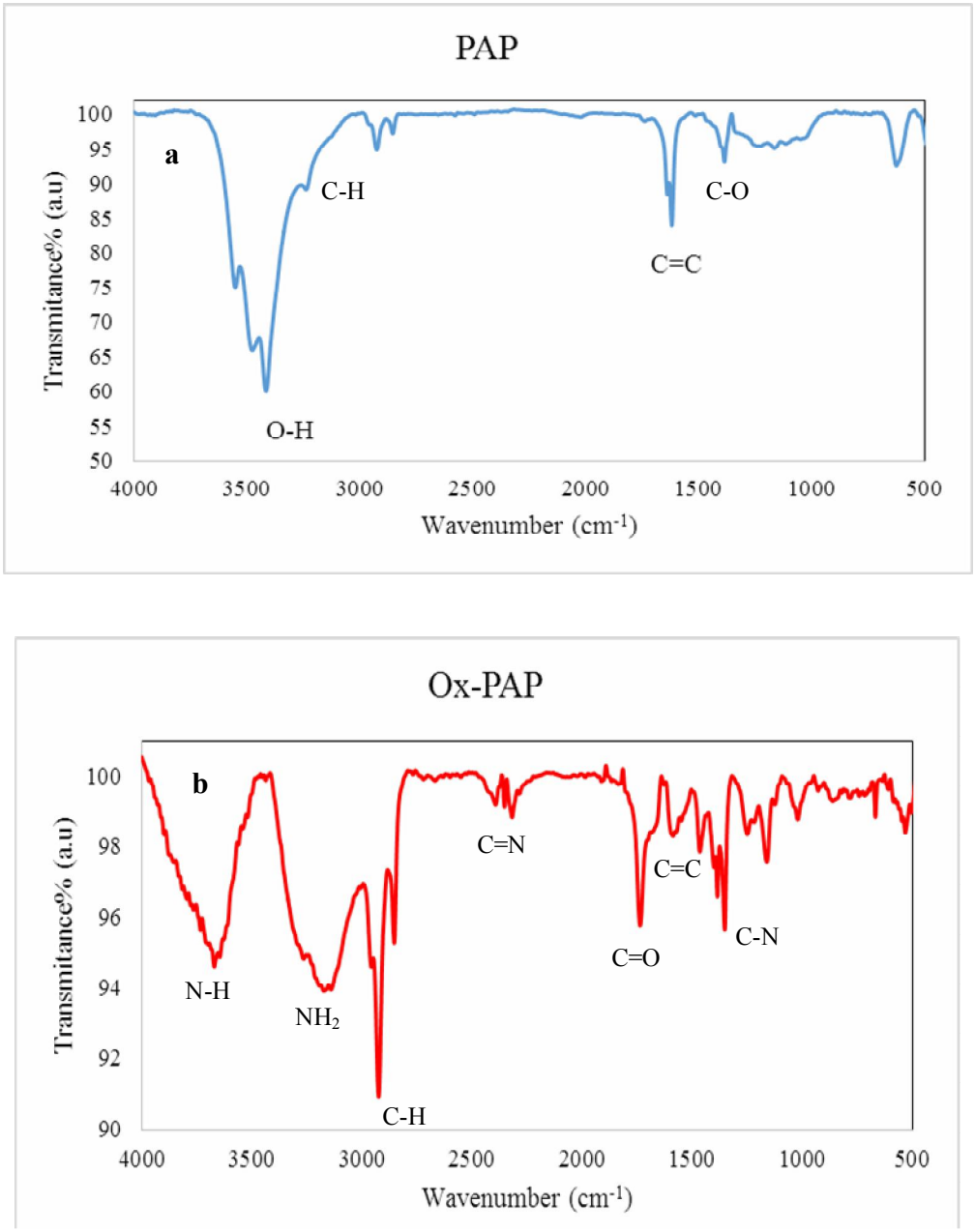
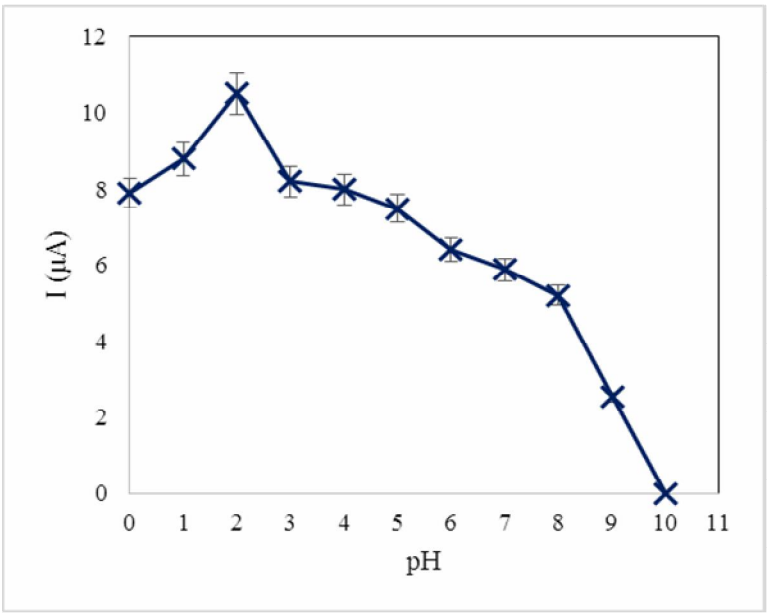


Fig. 6. The FTIR spectrums of PAP (a) and Ox-PAP (b) films.

which can augment the interaction of the analyte with the electrode surface through hydrogen bonding [34].

Effect of pH

In the pH range between 0.0 and 10, the pH effects on the SUM peak current were analyzed, the findings are shown in Fig. 7. As clearly demonstrated by the results, the peak current increases gradually by decreasing the solution pH from 10.0 to 2.0 and then declines remarkably. Hence, the maximum peak current was seen at a pH of 2.0. This pH



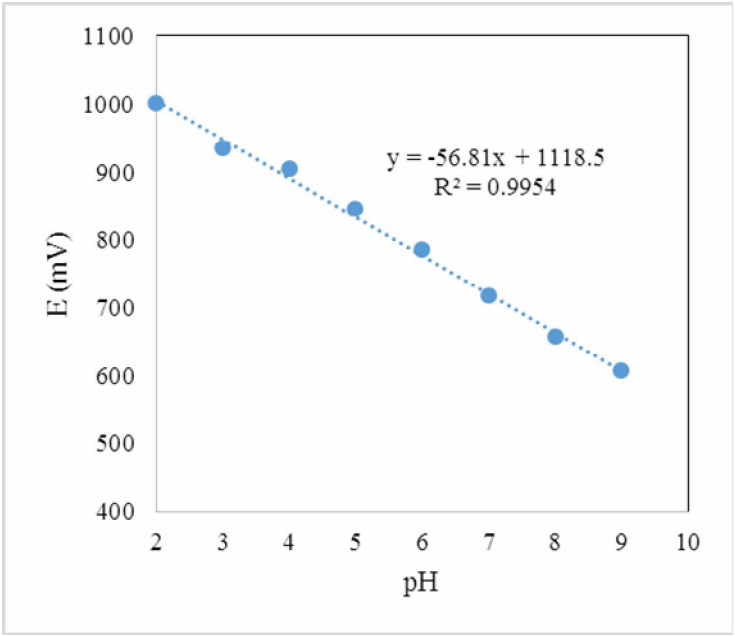
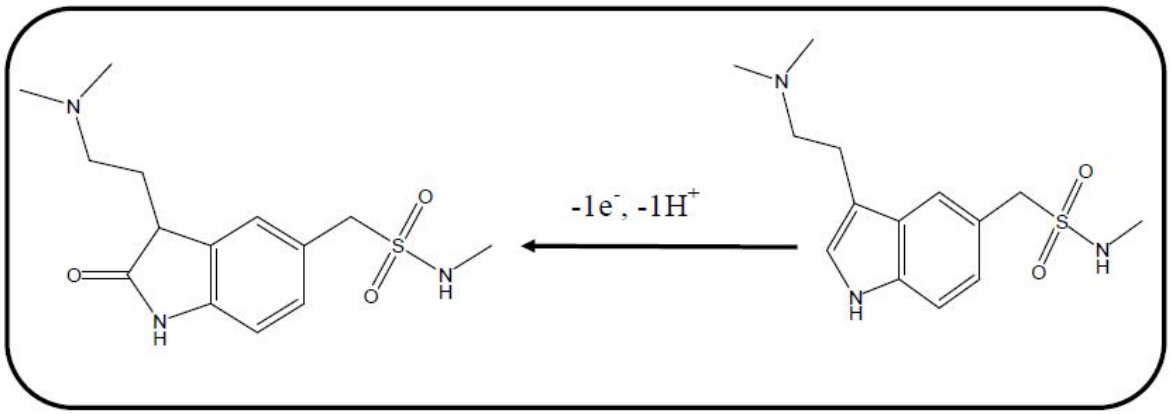


Fig. 7. The influence of solution pH on the SUM current response at the Ox-PAP/GCE (a), the SUM potential peak (E_{pa}) as a function of solution pH.

was selected as the optimum pH for further experiments [38]. The effect of pH on the peak potential was also checked out. The provided data in Fig. 7 indicate that by increasing the solution pH from 2.0-9.0, the peak potential shifts gradually to smaller positive values, implying that proton is involved in oxidation. A linear relation to the pH



Scheme 1. Probable oxidation mechanism for SUM [5]

Table 1. The Optimum Values of the Studied Instrumental Parameters

Parameter	Range studied	Optimum value
Accumulation potential (V)	-0.5 to +0.2	+0.055
Accumulation time (S)	0-300	60
Pulse amplitude (mV)	10-100	50
Voltage step (mV)	1-15	10
Frequency (Hz)	25-140	75

of the supporting electrolyte was discovered by the E_{pa} for SUM oxidation at Ox-PAP/GCE. The equation obtained is shown as follows:

$$E_{pa}\ (mV) = -56.81\ pH + 118.5\ (R^2 = 0.9954)$$

The obtained equation has a slope similar to the Nernstian theoretical value -59 mV, suggesting that the same number of electrons and protons are involved in the electrochemical process [39]. This finding is consistent with the SUM electrochemical reaction, as demonstrated in Scheme 1 [5].

Effect of Instrumental Parameters

Measurement of the current dependency was examined to assess the effect of all instrumental parameters, such as accumulation time and potential, pulse amplitude, voltage step, and frequency, on the SWV response [40]. These parameters were optimized to achieve a peak signal-to-noise ratio (PSNR), the results obtained are shown in Table 1. The impact of the accumulation potential on anodic stripping peak current was investigated within the potential range 0.500-0.200 V *vs*. SCE under the optimal conditions above. As illustrated in Table 1, the maximum peak current was reached at an accumulation potential of 0.055 V *vs*. SCE. Thus, 0.055 V *vs*. SCE was chosen as an accumulation potential in the process. Also, tested in the range of 0-300 s was the dependency of the maximum stripping peak current on accumulation time. The stripping peak current rose in proportion from 0 to 60 s under the other optimal conditions. Thus, the peak current was constant, and 60 s

was chosen for accumulation time. Other beneficial parameters such as pulse amplitude, phase voltage, and frequency on SWV response were also tested. The optimal values of 50 mV, 10 mV and 75 Hz were selected for the parameters above, respectively.

Effect of Scan Rate

The effect of scan rate (ν) on the oxidation reaction of SUM on the surface of Ox-PAP/GCE was investigated by cyclic voltammetry. Cyclic voltammograms for 100 µM of SUM in 0.1 M KNO_3 (pH 2.0) by the modified glassy carbon electrode at different scan rates ranging from 10-500 mV s^{-1} were recorded, and then the peak current (I) and the logarithm of peak current (logI) were depicted as functions of the square root of the scan rate ($\nu^{0.5}$) and the logarithm of the scan rate (logν), respectively. As shown in Fig. 8, an appropriate linear relationship was observed between I and $\nu^{0.5}$ ($R^2 = 0.9977$), suggesting that the process is diffusion-controlled [38]. In addition, a linear relationship was obtained between logI and logν ($R^2 = 0.989$) and due to the fact that the slope of the resulting line (0.4154) is lower than 0.5, it seems that the SUM electro-oxidation process is diffusion-controlled [39].

Analytical Parameters of the Sensor

Under the optimal conditions alluded to above, the SWV procedure was used for sensitive measurement of SUM. A calibration curve was achieved from at least three replicate measurements on average (Fig. 9). As indicated, the peak current linearly rose with a rise in concentration from 1 to 100.0 µM. The SUM concentration (C_{SUM}) and peak current are linearly correlated with two linear equations of I (µA) = 1.677 C_{SUM} (µM) + 1.2135 (R^2 = 0.9918) and I (µA) = 0.1475 C_{SUM} (µM) + 10.241 (R^2 = 0.9973) within the range 1.00-6.00 µM and 6.00-100.00 µM, respectively.

It seems that in the lower concentration range (1-6 µM), the analyte reaches the surface of the electrode by adsorption mechanism, and the achieved higher slope (1.677) in this range justifies this conclusion, but in the second dynamic range (6-100 µM) the diffusion mechanism is predominant and consequently the slope declines tangibly to 0.1475. The LOD was estimated as 0.294 µM according to IUPAC ($3S_b/m$).

The Selectivity of the Proposed Sensor

The selectivity of an analytical technique has an important effect on the accuracy of the obtained results. In this respect, the effects of various species on the analytical response of the designed sensor were examined. Thus, a 50 µM solution of SUM in the supporting electrolyte was prepared. Different amounts of the interfering species were added to the solution. The voltammogram of the sample was measured in the presence of other interfering species. The tolerance limit, defined as the maximum volume of the interfering species causing an error not higher than ±5% in the peak current of SUM, was calculated for the studied interfering species. The obtained results are presented in Table 2. The results indicated that the designed electrode show an acceptable selectivity towards SUM over a wide range of compounds coexisting with SUM in pharmaceutical samples, biological specimens, and some medicines prescribed simultaneously with SUM.

Repeatability, Reproducibility, and Stability of the Modified Electrode

The SWV measurements of the 50.0 µM SUM solution were performed to test the repeatability, reproducibility, and stability of Ox-PAP/GCE. For investigating the repeatability of the proposed sensor, five different solutions of SUM with the same concentration were prepared, and their peak current was measured. Then, the relative standard deviation (RSD%) was calculated, which was 3.52%. While the modified electrode reproducibility was explored by measuring the peak current of one SUM solution with five different electrodes, the RSD% was 4.87% for five measurement assays. To test the electrode stability, the electrode was stored for 21 days at room temperature in the lab. The SWVs were recorded and compared to SWVs achieved before storage [38]. The findings revealed only minor changes in the peak current and the excellent repeatability, reproducibility, and stability of the modified electrode.

Applicability of the Proposed Sensor for Determination of SUM in Human Serum Samples and Pharmaceutical Preparation

SUM was determined in serum and tablet samples to show the capabilities of the modified electrode to assess

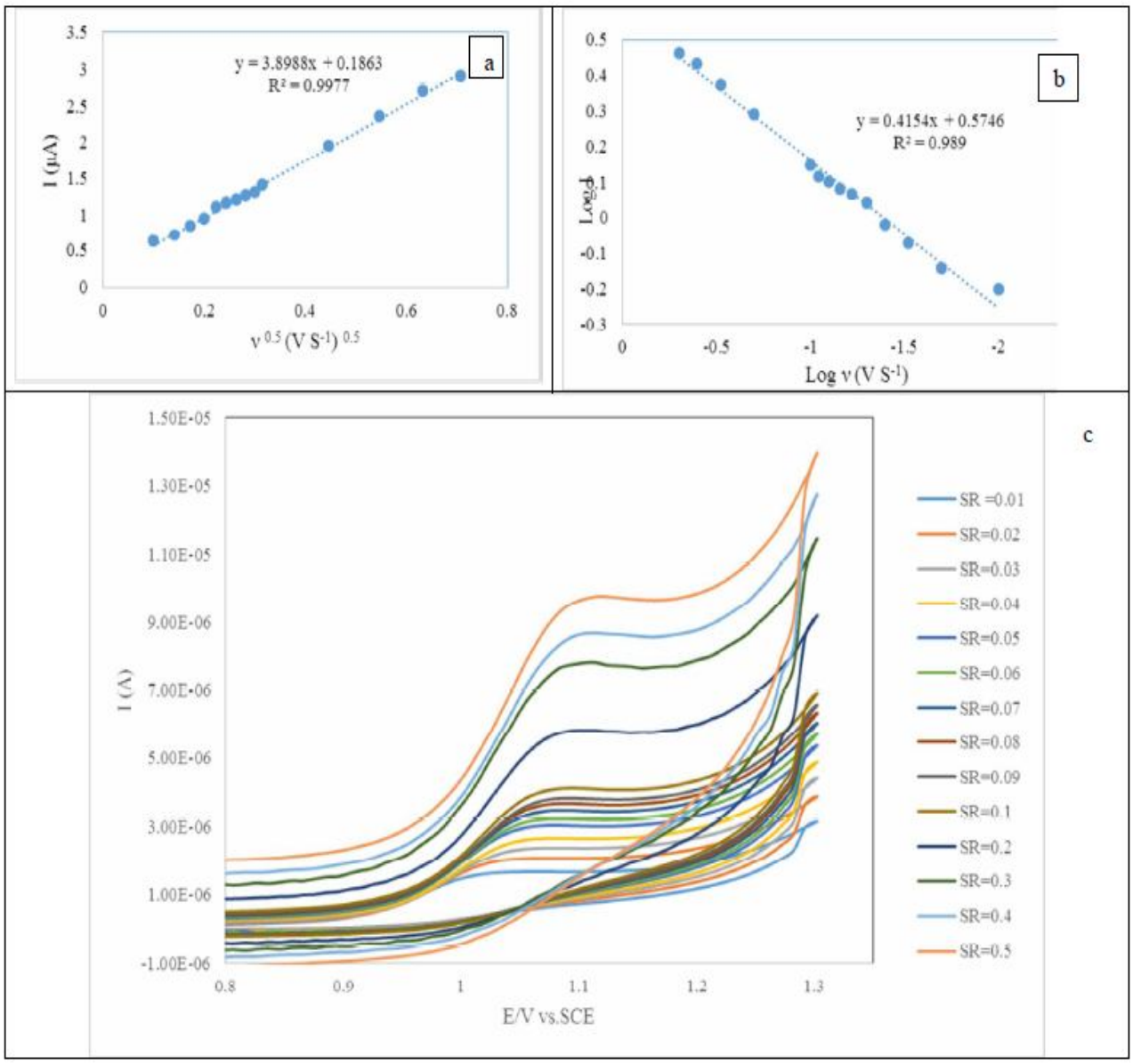


Fig. 8. The plot of peak current *vs.* square root of scan rate (a), the logarithm of peak current as a function of the logarithm of scan rate (b), CVs of 100.0 μM SUM on the Ox-PAP/GCE at different scan rates (10 to 500 mV s^{-1}) in 0.1 M KNO_3 of pH 2.0 (c).

SUM in real samples. As previously mentioned, the SWV techniques were utilized upon sample preparation and the necessary dilution measures for determining SUM in human serum samples and pharmaceutical preparations. Table 3 and Table 4 display the results. The average outcomes of the three determinations for SUM pharmaceutical preparation were close to the values on the labels. A recovery test was carried out to verify the accuracy and applicability of the technique examined in pharmaceutical preparations for SUM determination in the human serum

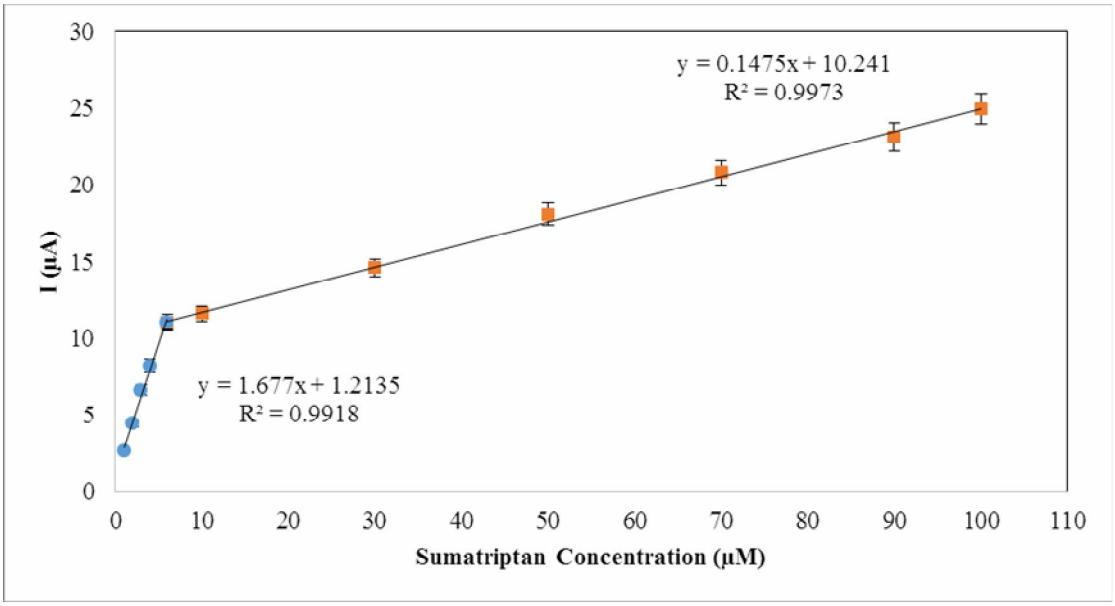


Fig. 9. Plot of SWV oxidation peak current as a function of SUM concentration.

Table 2. The Influence of some Interfering Species on the Measurement of SUM (50 µM) by the Proposed Method

Interfering species	Tolerance limit
Cl^-	1400
Na^+, Ca^{2+}	700
Glucose, Lactose, Fructose, Maltose, Sucrose	400
Ibuprofen, Urea	300
L-Cysteine	200
Ascorbic acid	70
Levodopa	50
Uric acid, Caffeine	20
Oxycodone	10

sample. The findings of a recovery test in Tables 3 and 4 show that SUM can be determined in both human serum samples and prescription formulations using the modified electrode.

CONCLUSIONS

In this study, a novel, rapid, and simple voltammetric sensor was developed for determining SUM in human

Table 3. Determination Results of SUM in the Pharmaceutical Sample (n = 3)

Tablet	Labelled (mg)	Found (mg)	Recovery (%)	RSD (%)
Sumatriptan	50	49.66 ± 2.56	99.33	5.16

Table 4. Determination Results of SUM in Serum Specimen (n = 3)

Sample	Added (μM)	Found (μM)	Recovery (%)	RSD (%)
	-	-	-	-
Serum	3	3.17 ± 0.15	105.74	4.73
	50	53.28 ± 0.67	106.56	1.27
	90	89.43 ± 2.07	99.37	2.31

serum samples and pharmaceutical preparations. For this purpose, *p*-aminophenol was electropolymerized on a GCE surface and then overoxidized by applying a constant potential in a basic solution to increase the porosity and conductivity of the polymer film. Several techniques, including scanning electron microscopy (SEM), cyclic voltammetry (CV), and square wave voltammetry (SWV) were employed for investigating the electroanalytical performance and morphology of the modified electrode. The influence of various parameters such as pH, overoxidation time, electrosynthesis CV cycle numbers, accumulation potential, accumulation time, frequency, voltage step, and pulse amplitude was optimized to obtain the highest sensitivity towards SUM. Under optimum conditions, the electrode response was linear to SUM concentration within the range of 1.00-100 μM with a LOD of 0.294 μM. The proposed electrode showed an eminent selectivity towards SUM. It was successfully applied for specimens with acceptable recovery values.

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