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Stripping voltammetric determination of Epinephrine applying sulfacetamide modified glassy carbon electrode

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In the present work, sulfacetamide (SFA)-modified glassy carbon electrode(MGCE) was successfully constructed by electrochemical modification applying simply cyclic voltammetry (CV) scans. It is well observed that the excellent electrocatalytic ability of SFA film led to much higher oxidation peak current responses compared with bare GCE for epinephrine (EP) oxidation. The EP oxidation takes place at a potential about 120 mV less positive compared with that of an unmodified GCE at the optimum pH 5.5 of phosphate buffer solution (PBS). Applying the anodic stripping differential pulse voltammetry (ASDPV) method and under the optimum conditions, the linear dependence of oxidation peak current on analyte concentrations was found to be ($1.0x10^{-7}$ -$1.5x10^{-6}$) mol L^{-1}, giving detection limit of $2.1x10^{-8}$ mol L^{-1} and quantification limit of $6.9x10^{-8}$ mol L^{-1} for EP. The proposed modified electrode exhibited excellent selectivity in the presence of ascorbic acid (AA), glucose (Glu) and uric acid (UA) species whereas dopamine (DA) interfere seriously at higher concentrations. The proposed method showed simplicity, reproducibility, high sensitivity and adequate selectivity. The modified electrode was successfully devoted to EP determination in pharmaceutical formulations and biological fluids; human plasma and urine with acceptable results.

Keywords: Epinephrine; Sulfacetamide; Electrochemical modification; Anodic stripping differential pulse voltammetry

1. INTRODUCTION

Epinephrine (EP), has the IUPAC name [1-(3,4-dihydroxyphenyl)-2-methyloaminoethanol], plays a vital role as an important catecholamine neurotransmitter and hormone in mammalian central nervous system with specific physiological functions and pharmacological actions [1,2] as shown in (Figure 1). EP represents an aryl-β-ethanolamine derivative synthesized naturally in human body from L-tyrosine [3,4]. Secretion of this fight or flight hormone [5] occurs by adrenal glands into the blood stream as a result of stimulation of sympathetic nervous system [6,7]. Boosting the supply of oxygen

and glucose to the brain and muscles help the body for preparing an action by EP to overcome emergency situations. World Anti Doping Agency forbidden using EP in competitive games as a doping agent to improve the performance of athletes in sports [8]. It is well known that low levels of EP cause parkinsonism diseases [9]. In addition, EP is widely used as a common medicine; in the treatment of cardiac arrest, sepsis, severe allergic reactions, asthma and anaphylaxis [10-13]. Therefore, development of simple, fast and accurate analytical method for EP is required.

Several methods have employed in EP determination such as high performance liquid chromatography coupled with mass spectroscopy (HPLC-MS) or chemiluminescence (HPLC-CL) [14,15], capillary electrophoresis direct chemiluminescence [16], flow injection analysis coupled with chemiluminescence [17], spectrophotometry [18,19], fluorimetry [20] and amperometry [21,22]. Careful investigation of literature revealed that the majority of these techniques are high cost [15,17-19], time consuming [14,15,17-20], need severe sample pre-treatment [14-17,20] and have low sensitivity [15-19, 22] and selectivity [14-22].

Applying electroanalytical methods for EP determination, as an electroactive compound in body fluids and pharmaceuticals is required. Consequently, these methods have unique advantages such as quick response, cost effectiveness, amenability for miniaturization, low power requirement and wide concentration range with high sensitivity and adequate selectivity [23-25]. In spite of all these advantages, a large anodic over potential and accumulation of oxidized products on the electrode surface hinder EP determination [26, 27].

It is worthy to mention that ascorbic acid (AA) and uric acid (UA) biomolecules coexist as organic cations with EP in physiological samples and having the same oxidizing potentials on the traditional working electrodes [28]. Therefore, modification of electrodes should be used to overcome these difficulties. Construction of modified electrodes, involving the direct electron transfer between the analytes and the electrodes was considered [29-31].

Modified sensors have many merits such as simple construction, inexpensive, remarkable wide potential window, ease modification, excellent electrical conductivity and large surface area. Consequently, the modifier adsorption takes place on sensor surface [32-34].

Recently, many modified sensors for EP detection have been published including: poly (eriochrome black T) [35], DNA immobilized on carbon fiber [36], nano composite film [37], gold nanoclusters electrodeposited on overoxidized polypyrrole [38], poly(caffeic acid) [39], graphene/poly(brilliant cresyl blue) [40], multi-walled carbon nanotube modified [41] and over-oxidized polypyrrole/multi-walled carbon nanotube composite [42].

In the present work, SFA is used for the first time as a modifier for the glassy carbon electrode to determine EP. Sulfacetamide (SFA), IUPAC name *N*-[(4-aminophenyl) sulfonyl] acetamide ,represents an important class of sulfonamide group and acts as synthetic antibacterial agent used for treatment of various dermatological aberrations [43]. In addition, analytical applications of the proposed sensor had been used in the determination of L –dopa [44]. SFA film had electrocatalytic activity for oxidation reaction of EP (Scheme 1). SFA is selected as a modifier since there is a primary amine which can be oxidized to give a cation radical as an intermediate step [45]. The cation radical forms carbon –nitrogen linkages at the surface of glassy carbon electrode [46].

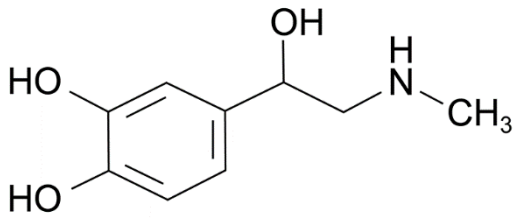
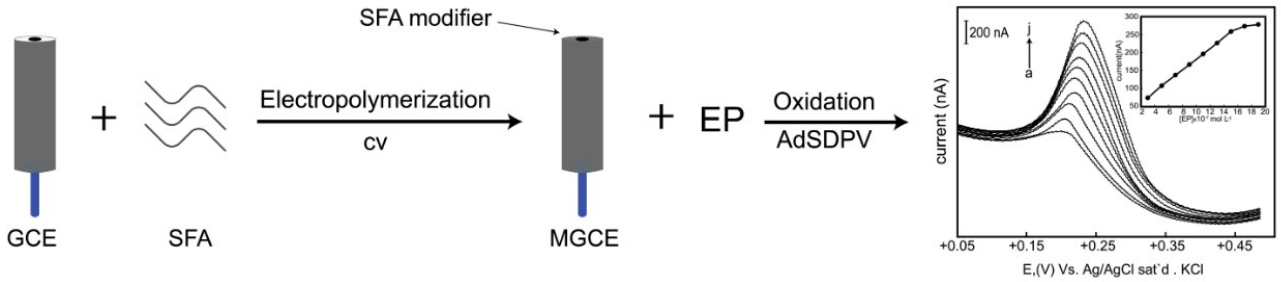


Figure 1. Chemical structure of Epinephrine.



Scheme 1 Schematic representation of SFA /GCE for EP determination.

2. EXPERIMENTAL

2.1. Reagents and solutions

Epinephrine (EP), ascorbic acid (AA), uric acid (UA), glucose (Glu), dopamine (DA), sulfacetamide (SFA), sulfuric acid, phosphoric acid, sodium hydroxide, potassium ferrocyanide were purchased from Sigma Aldrich and hydrogen chloride was obtained from Merck. The selectivity of the method has been tested. All the chemicals mentioned were all of analytical grade used as received without any further purification. Injectable adrenaline ampoule (epinephrine injection) was obtained from chemical industries development company (CID), Egypt.

The stock solution 1.0x 10^{-3} mol L^{-1} EP was prepared by dissolving required amount of epinephrine in double distilled water containing 200 µL HCl (37% w/w) in 100 ml measuring flask and it was maintained in a refrigerator at 4 C° before use.

The phosphate buffer solutions (PBS) with different pH levels were prepared by mixing solutions of Na_2HPO_4 and NaH_2PO_4 solutions at different ratios. The pH levels were adjusted by adding 1.0 x10 $^{-1}$ mol L^{-1} CH_3COOH and/or 1.0x10^{-1} mol L^{-1} NaOH solution and PBS was used as a supporting electrolyte. All the experiments were obtained at room temperature 25 C° and N_2 gas was purged through the experimental solutions for 15 min prior to electrochemical measurements.

2.2. Apparatus

All electrochemical experiments including cyclic voltammetry(CV) at scan rate 100 mVs^{-1} and anodic stripping differential pulse voltammetry (ASDPV) at scan rate 10 mVs^{-1}, pulse amplitude 15mV, equilibrium time 5 sec and pulse time 2 sec were performed using an EG& G Princeton Applied Research Corporation model 264A stripping analyzer, coupled with a PAR Model 303A cell.

A conventional three electrode system was used in a single compartment electrochemical cell with Ag / AgCl as a reference electrode, platinum wire as a counter electrode and bare glassy carbon electrode (GCE) or SFA modified GCE as working electrode. pH values were recorded using Hanna microprocessor pH model 211.

2.3. Preparation of the working electrode

Prior to modification, BGCE was polished successively with 0.05 μm alumina slurry on a microcloth pad and rinsed with 1:1 HNO_3 solution then ethanol was used to remove residual alumina particles that were trapped on the surface and double distilled water after each polishing step. Cyclic voltammetric method was applied to carry out electrochemical modification of SFA on the BGCE. The modification process was performed in aqueous solution containing $1.0x10^{-3}$ mol L^{-1} SFA in $1.0x10^{-1}$ mol L^{-1} H_2SO_4. Formation of SFA film was achieved by applying a potential between +0.4 and + 1.4 V at the scan rate of 100 mVs^{-1} for 20 cycles, then GCE washed with double distilled water.

2.4. Preparation of real samples

The content of adrenaline ampoule (1mg / ml) was diluted by using double distilled water in 50 ml measuring flask, then 20 μl was introduced in the voltammetric cell and completed to 10 ml with $1.0 x10^{-2}$ mol L^{-1} PBS (pH = 5.5).

Urine sample from healthy person was diluted (1:1000) using PBS without pretreatment, then 10 ml from diluted urine sample was added to the voltammetric cell. The diluted sample was spiked with standard concentrations of EP. The serum sample was centrifuged for 10 min at a speed of 1500 rpm using EDTA as anticoagulant and then diluted with PBS (pH = 5.5). Ten mL of solution was transferred into the voltammetric cell to be analysed without any further pre-treatment and various standard EP solutions was added.

3. RESULTS AND DISCUSSION

3.1. Effect of SFA concentration

Figure 2 demonstrates the effect of change SFA concentrations on GCE in a solution containing $5.0x10^{-7}$ mol L^{-1} EP in presence of $1.0 x 10^{-2}$ mol L^{-1} PBS (pH 5.5). The peak current response increases with increasing SFA concentration and achieves a maximum value at $1.0 x10^{-3}$ mol L^{-1}, then the current decreases gradually with increasing SFA concentrations. Consequently, the subsequent experiments were performed using a $1.0x10^{-3}$ mol L^{-1} SFA.

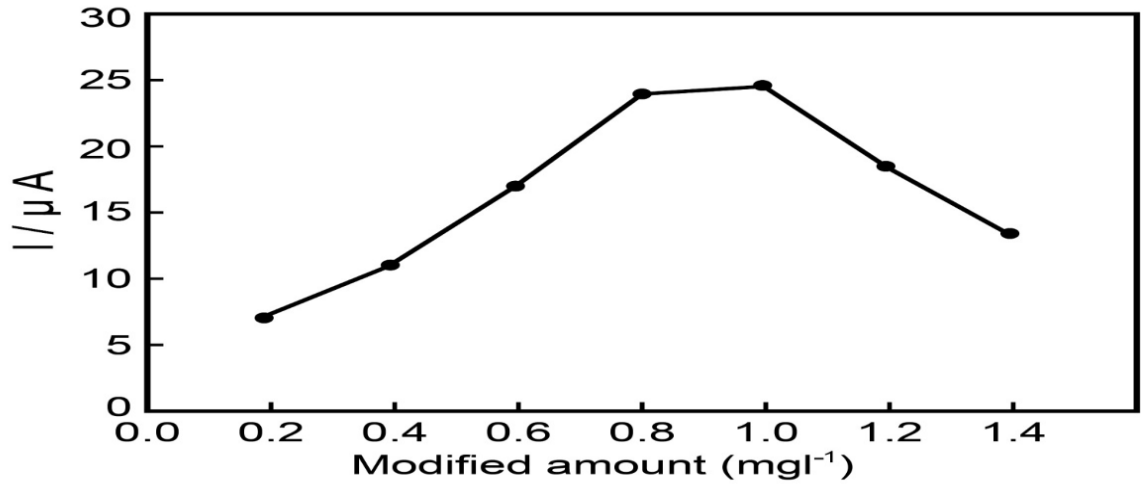


Figure 2. Plot of anodic peak current of $5.0x10^{-7}$ mol L^{-1}EP in $1.0x10^{-2}$ mol L^{-1} PBS pH 5.5 recorded at GCE according to amounts of modifier (SFA), scan rate 100 mVs^{-1}.

3.2. Electrochemical modification of SFA on BGCE

The voltammgram shown in Figure 3 revealed that the anodic peak currents decreased gradually. This behaviour indicated the formation of an electroactive layer on the sensor surface. The current during the cycling become constant and more stable. This means that electrochemical modification achieved the maximum saturation level [47]. Scheme 2 described the electrochemical modification mechanism of SFA on GCE as the oxidation process of SFA occurs based on amino group to form cation radical which forms carbon – nitrogen linkages at the surface of glassy carbon electrode. The electrochemical reaction between GCE and compounds containing amino group is based on steric effects as well as diffusion rates[46]. Thus, modification of GCE with SFA leads to kinetics effect; consequently, increase in the rate of electron transfer from EP is observed.

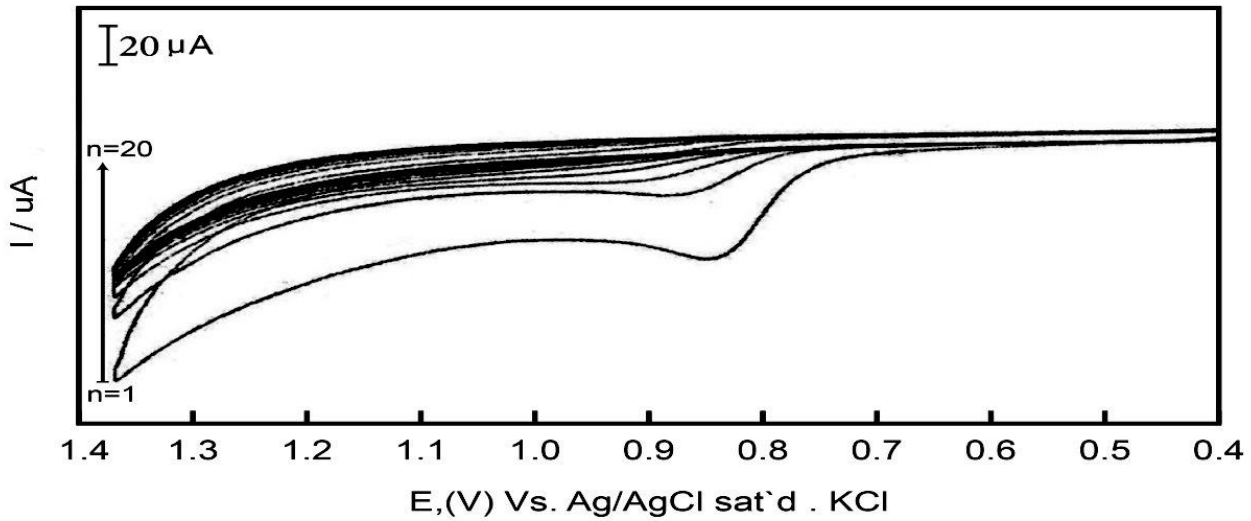
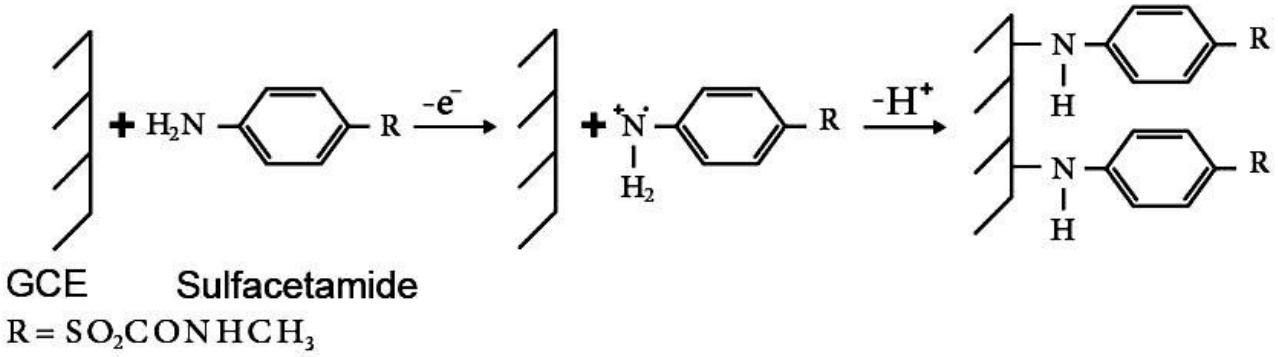


Figure 3. Cyclic voltammograms of electrochemical modification of SFA over the range of +0.4 to +1.4 V at scan rate of 100 mVs^{-1} for 20 cycles in a solution containing $1.0x10^{-1}$ mol L^{-1} H_2SO_4 and $1.0x10^{-3}$ mol L^{-1} SFA.



Scheme 2. Electrochemical modification mechanism of SFA on the surface of BGCE.

3.3. Characterization of the modified sensor

Figure 4 showed the recorded cyclic voltammograms and illustrated that curve a for BGCE and curve b for the modified sensor at the scan rate 100 mVs^{-1} to investigate the performance of sulfacetamide film. It is apparent to note that the modified sensor exhibited improvement of redox peak current, electron transfer kinetics and electrocatalytic activity of the modified sensor toward potassium ferrocyanide and decrease in ΔEp compared with BGCE.

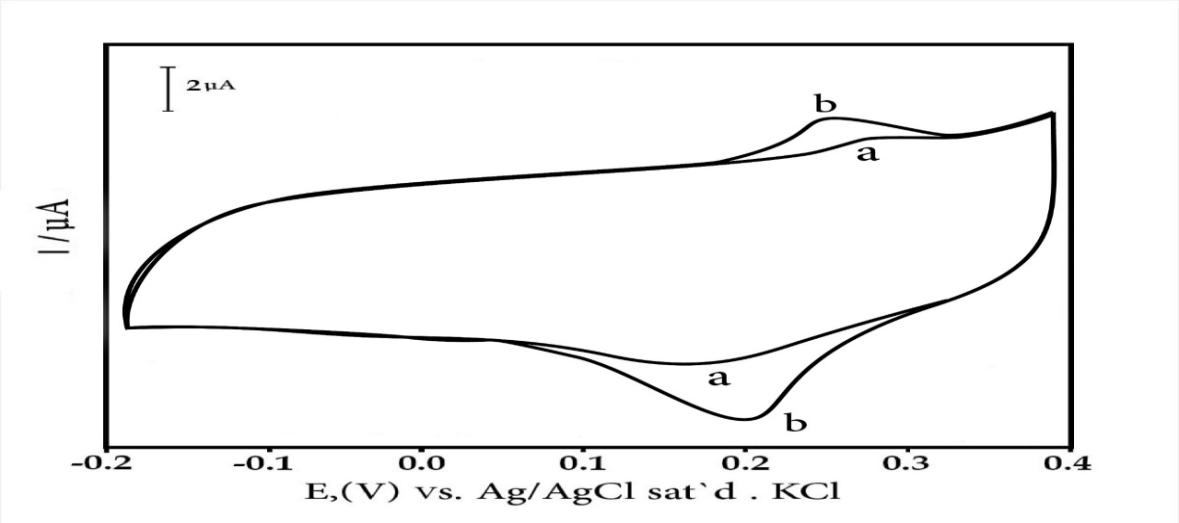


Figure 4. Cyclic voltammograms of 5.0 x 10^{-3} mol L^{-1} Potassium ferrocyanide at BGCE (curve a) and SFA -modified GCE (curve b) in 1.0x10^{-1} mol L^{-1} Potassium chloride as supporting electrolyte at scan rate 100 mVs^{-1}.

3.4. Effect of buffer

The behaviour of different buffers (phosphate, acetate and universal buffers) was tested to improve EP determination. The highest peak current response is observed using Phosphate buffer at pH value 5.5. Anodic stripping differential pulse voltammograms were recorded for 5.0x10^{-7}mol L^{-1} EP at the modified sensor. It is observed that the current response decreased slightly in the solution with increasing the pH (Figure 5a). This may be ascribed to the formation of unprotonated EP. Also,

the effect of oxidation peak potential with respect to the change in pH is investigated. The data revealed that with increasing the pH, the oxidation peak potential shifted to less anodic potential indicating that Epa is affected linearly with the pH values in the range 3.8 – 6.9 with a slope 0.053 V/pH ($r^2 = 0.977$) as shown in (Figure 5b), showing that the number of protons equals that for electrons in the oxidation mechanism (Scheme 3) as reported previously [48].

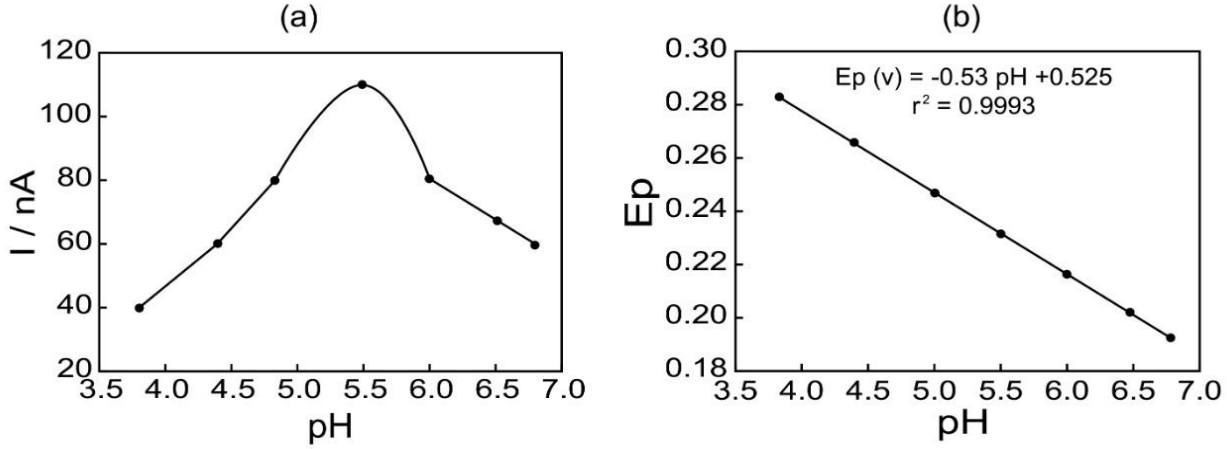
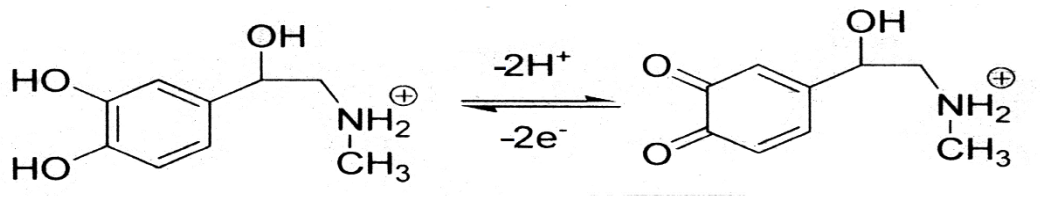


Figure 5. Effect of PH on (a) the peak current and (b) the peak potential for the oxidation of 5.0 x 10^{-7} mol L^{-1} EP in 1.0x10^{-2} mol L^{-1}PBS (scan rate = 10 mVs^{-1}).



Scheme 3. Mechanism of EP oxidation at SFA –modified GCE.

3.5. Electrocatalytic oxidation of EP

The anodic peaks of EP were shifted to 230 mV at the MGCE compared with that of unmodified electrode at 350 mV. The decrease in the anodic potential of about 120 mV for EP indicates the electrocatalytic activity of SFA / GCE toward EP. The cathodic peak currents remained constant with the scan rate as the rate of reverse scan is not sufficient to give appropriate signal toward EP reduction of the oxidized form of EP. It is of great interest to show that a quasireversible behaviour for EP oxidation at SFA- modified GCE is observed [49]. It was found that the anodic peak currents (I_p) values were linearly dependent on the different scan rates (ν) over the range 10-200 mVs^{-1} (Figure 6a) with a slope of 0.78. This phenomenon confirmed that the oxidation process is controlled by diffusion process with adsorption component.

The anodic peaks (E_{pa}) were proportional to logarithm of scan rate (log ν) and shifted to more positive direction at higher scan rates as shown in (Figure 6b). This behaviour agree well with the theoretical approach by Laviron [50]. As expected, Ep plots versus log ν yielded a straight line with slope 2.3RT/ (1 - α) nF where α denotes the transfer coefficient and equals 0.77.

Evaluation of the apparent charge transfer rate constant (ks) at the interface between the unmodified sensor and adsorbed layer of SFA should be considered. In this way, the ks value of the investigated sensor was calculated to be 3.6 s^{-1} depending upon the known ΔEp at each ν. The ks was significantly higher than reported previously [51,52].

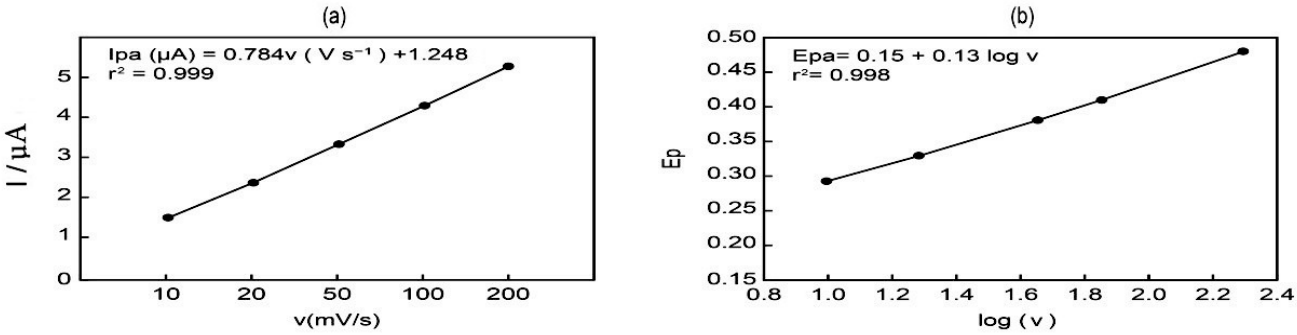


Figure 6. (a) Variations of Ip vs. scan rate. (b) Variation of Ep vs. logarithm of scan rates.

3.6. Effect of accumulation potential

Since the electrode reaction at the MGCE is an adsorption process, the influence of accumulation potential on the peak current response of EP on the MGCE applying ASDPV was investigated in the range of – 0.05 to 0.2 V using 5.0 x10^{-7} mol L^{-1} EP at pH 5.5 over an accumulation time of 60 sec. It was observed that the peak current response reaches the highest at the accumulation potential +0.05 V. Consequently, accumulation potential of +0.05 V was chosen as the optimum accumulation potential.

3.7. Effect of accumulation time

Enhancement of the peak current as well as increasing the accumulation time was observed by increasing the EP amount on sensor surface. Applying ASDPV as a recent and sensitive technique, plots of Ipa versus accumulation time for different EP concentration (1.0, 3.0, 5.0, 7.0, 9.0x10^{-7} mol L^{-1}) were shown in Figure 7. Improvement the accumulation time led to increase of accumulated EP at the modified electrode surface due to the adsorption ability of SFA and at the same time remarkable increase in the peak height of EP was observed. After a certain accumulation time, the peak height did not increase which can be attributed to the surface adsorption equilibrium [53]. It was recorded that the suitable accumulation time is 60 sec.

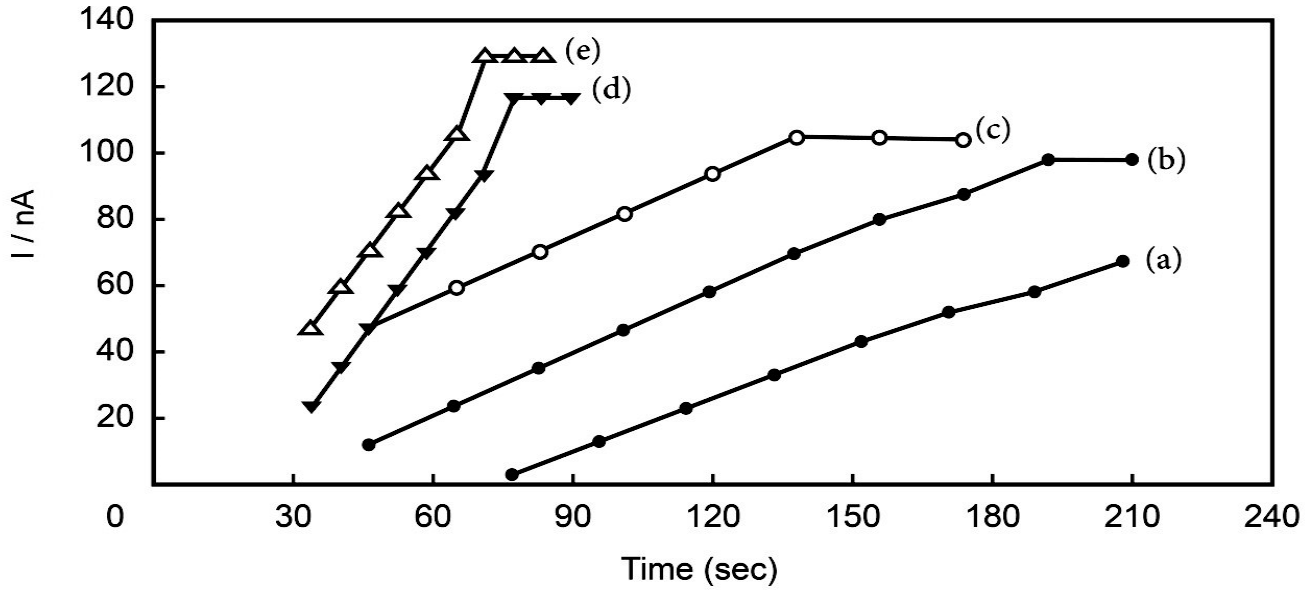


Figure 7. Effect of accumulation time on the ASDP voltammograms of EP in $1.0x10^{-2}$ mol L^{-1}PBS pH 5.5, scan rate 10 mVs^{-1} and different concentrations (a) $1.0 x10^{-7}$, (b) $3.0x10^{-7}$, (c) $5.0 x10^{-7}$, (d) $7.0 x 10^{-7}$ and (e) $9.0 x 10^{-7}$ mol L^{-1} EP.

3.8. Effect of EP concentration

The electrocatalytic oxidation of EP was performed applying different concentrations of the drug at the examined sensor (Figure 8a). Different concentrations of EP were applied ($1.0 x10^{-7}$ to $1.9x10^{-6}$ mol L^{-1}), at the same time the I_{pa} increased towards more positive direction. Plotting the current values (I_{pa}) against EP concentration gave a straight line with high linearity (Figure 8b). The linear regression equation

Ipa (nA) = 13.85 C (EP)(mol L^{-1}) +42.87, (N = 9, r^2 = 0.9817) was obtained.

The detection limit was evaluated to be $2.1x10^{-8}$ and the calculated quantification limit was $6.9 x10^{-8}$ [54,55]. The data revealed that the investigated sensor exhibited a relatively lower detection limit compared with those reported previously [28,35,39,56-64] (Table 1).

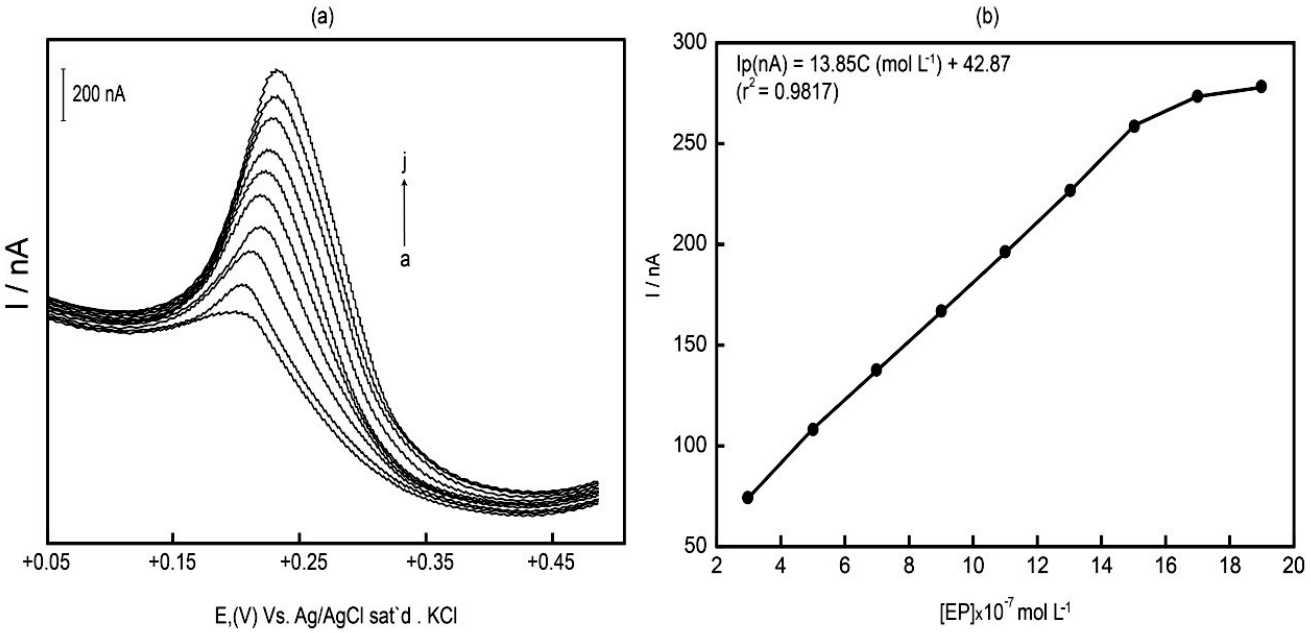


Figure 8. (a)ASDP voltammogramms of EP in $1.0x10^{-2}$ mol L^{-1} PBS solution of pH 5.5 at SFA – modified GCE at scan rate of 10 mV/s with different concentration (a- j: 1.0×10^{-7}, $3.0x10^{-7}$, $5.0x10^{-7}$, $7.0x10^{-7}$, 9.0×10^{-7}, $1.1x10^{-7}$, $1.3x10^{-7}$, $1.5x10^{-6}$, $1.7x10^{-6}$, $1.9x10^{-6}$ mol L^{-1}). (b) Graph of anodic peak current versus concentration of EP.

Table 1. Comparison between the proposed method and previously published methods

Voltammetric method	Modifier	pH	D.L (mol L^{-1})	Ref.
DPV	PBCB/Fe_2O_3	7.0	$3.1x10^{-7}$	[56]
DPV	GAIN/Cu	6.0	$2.7x10^{-7}$	[57]
SWV	SnO_2/graphene	7.0	$1.7x10^{-8}$	[58]
SWV	P(L-Asp)/ERGO	4.0	2.5×10^{-8}	[28]
DPV	PBCACPM	4.0	3.0×10^{-8}	[59]
SWV	PMel	4.5	5.0×10^{-8}	[60]
DPV	Poly(taurine)	7.0	3.0×10^{-7}	[61]
DPV	EBT	3.5	3.0×10^{-7}	[35]
CV	CA	7.7	2.0×10^{-7}	[39]
CV	TX-100	7.0	$1.0x10^{-6}$	[62]
DPV	$Dy_2(WO_4)_3$ nanoparticles	7.0	$5.0x10^{-7}$	[63]
DPV	CoPc	4.0	1.0×10^{-6}	[64]
ASDPV	SFA	5.5	2.1×10^{-8}	P. W

Abbreviations: D.L: Detection limit; PBCB/Fe_2O_3NP:Polymers-poly(brilliant cresyl blue)/ iron (III) oxide nanoparticles; GAIN/Cu: Graphene augmented inorganic nanofibers / Cu nanoparticles; P(L-Asp)/ERGO: Poly (L-aspartic acid)/electrochemically reduced graphene oxide; PBCACPM: Poly (3,3′-bis[N, N-bis(carboxymethyl)amino methyl]-o-cresolsulfonephthalein); PMel: Poly-melamine; EBT: Poly (eriochrome Black T); CA: Caffeic acid; $Dy_2(WO_4)_3$ **:** Dysprosium tungstate; CoPc: Co^{II}phthalocyanine; P.W: Present work.

3.9. Selectivity

The examined modified sensor has been investigated voltammetrically in the presence of the principal coexisting substances applied to detect EP in biological fluids. In this respect, careful examination was applied for different concentrations showing the effect of uric acid (UA), ascorbic acid (AA), glucose(Glu) and dopamine(DA). In fact, ASDPV is considered an excellent voltammetric technique to detect EP in mixtures [65], a good peak resolution and current sensitivity could be obtained. Different concentrations of UA ($1.0 – 8.0x10^{-6}$ mol L^{-1}) were examined in the presence of $5.0x10^{-7}$ mol L^{-1} EP applying ASDPV (Figure 9). It is observed that two well – defined oxidation peaks for UA-EP mixture were obtained, the difference was 120 mV.

In case of AA and Glu applying $1.0x10^{-5}$ and $2.5\ x10^{-5}$ mol L^{-1}, respectively, no peaks were detected, which can be attributed to the low electrochemical activity. This means that presence of SFA film on GCE eliminated the signals of both AA and Glu completely. Unfortunately, it was observed that DA showed serious interference with respect to EP determination applying $1.0x10^{-6}$ mol L^{-1} DA in the mixture containing the same concentration mentioned previously of EP.

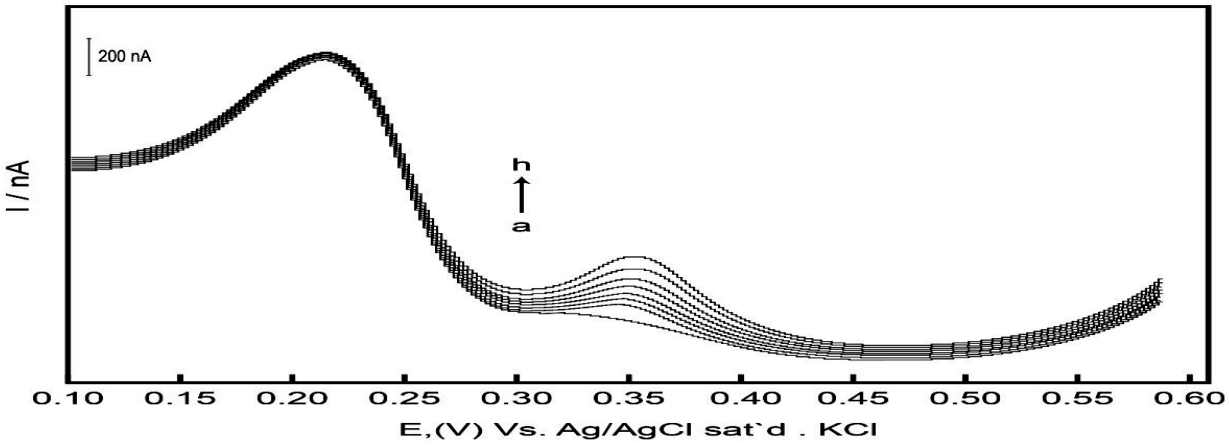


Figure 9. ASDPV at SFA-modified GCE in PBS pH 5.5 (containing $5.0x10^{-7}$ mol L^{-1} EP) in the presence of different concentrations of UA (mol L^{-1}) :(a) $1.0x10^{-6}$, (b) $2.0x10^{-6}$, (c) $3.0x10^{-6}$, (d) $4.0x10^{-6}$, (e) $5.0x10^{-6}$, (f) $6.0x10^{-6}$, (g) $7.0x10^{-6}$ and (h) $8.0x10^{-6}$.

3.10. The reproducibility, repeatability and stability

The reproducibility was performed applying six independently constructed sensors using ASDPV technique for detection of $5.0x10^{-7}$ mol L^{-1} EP. The calculated relative standard deviation (RSD) was 4.6% confirming excellent reproducibility for the proposed sensor.

Six successively independent measurements of EP were investigated using the same sensor were applied and RSD value did not exceed 3.4% confirming adequate repeatability of the modified sensor.

The modified sensor was examined for 15 days concerning its stability. The sensor was stored at room temperature. In this respect, EP oxidation was examined applying ASDPV technique at room

temperature and the reaction reached about 95.4% of its initial peak current. It is of great interest to note that the proposed sensor recorded a higher value compared with SnO_2/graphene sensor [58] and a lower value for Fe_3O_4@SiO_2/GR nanocomposite modified graphite sensor [66]. This can be attributed to the high electroconductivity of Fe_3O_4@SiO_2 [67] compared with sulfacetamide on glassy carbon sensor, indicating an excellent stability of the proposed sensor. It is worthy to mention that the peak potential value is considered to check the stability of the sensor [68].

3.11. Analytical applications

Evaluation of the validity and reliability of the proposed method have been performed successfully applying the standard addition method aiming to determine EP in pharmaceutical sample preparation, human serum and urine samples applying ASDPV technique under optimum conditions. The amount of EP in the ampoule was found to be 0.99 mg which agree well with claimed value of the ampoule label (1.0 mg / ml). Table 2 includes the values of recoveries range (94.2 to 100.0 %) with accepted RSD values (2.7 to 3.0), confirming the successful EP determination in real samples applying SFA as a modifier.

Table 2. Determination of EP in biological fluids samples using SFA/ GCE

	Urine			Serum		
EP spiked (mol L^{-1})	EP detected (x10^{-7} mol L^{-1})	Recovery (%)	R. S. D (%)	EP detected (x10^{-7} mol L^{-1})	Recovery (%)	R. S. D (%)
5.0 x10^{-7}	4.71	94.2	2.90	4.85	97.0	2.70
6.0 x10^{-7}	5.95	99.1	3.00	6.00	100.0	2.85

4. CONCLUSION

A simple glassy carbon electrode modified with SFA was constructed for EP determination. MGCE showed electrocatalytic ability towards oxidation of EP and higher peak current response as well as good peak potential separation compared with BGCE were observed. The investigated sensor exhibited high precision, high stability and adequate selectivity. The proposed method was successfully applied for EP determination in pharmaceutical formulations and biological fluids. In future, this study will be confirmed applying computational and chemometric investigation.

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