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Electrochemical study for simultaneous detection of procaine hydrochloride and its metabolite in biological samples using a nanostructured strong sensor

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Abstract−Procaine belongs to a type of medicine that excessive dosage creates cardiac arrest and also several allergenic reactions. Thus, continuous monitoring of the drug and its metabolite is necessary for sustainable health management during treatment. The innovative aspect of nanostructure materials has great importance in the advancement of research on modified sensors. In the present study, the electrocatalytic performance of multi-walled carbon nanotubes modified carbon paste electrode was investigated for the simultaneous analysis of procaine hydrochloride and p-aminobenzoic acid with high accuracy and sensitivity. The nanostructured sensor is characterized by microscopic and electrochemical techniques, such as scanning electron microscopy and electrochemical impedance spectroscopy using $[Fe(CN)_6]^{3-/4-}$ as the redox probes. The modified sensor shows an improved voltammetric peak current than the unmodified carbon paste electrode. The electrochemical behavior of the modified sensor was studied by cyclic voltammetry and differential pulse voltammetry. The sensor kinetic parameters containing electron transfer rate constant ($ks=0.47\ s^{-1}$) and charge transfer coefficient ($\alpha=0.23$) were calculated using cyclic voltammetry. The differential pulse voltammetry technique was also investigated in terms of linearity, lower limit of detection, lower limit of quantitation, accuracy and precision, which indicate acceptable results. Under optimized experimental conditions, the concentration linear range for procaine and PABA was obtained in the range of 2.4 to 100.0 μM. The limit of detection values (S/N=3) were calculated to be 62.0 and 49.0 nM for detection of procaine and p-aminobenzoic acid, respectively. Also, the effects of interfering materials, repeatability and stability of the modified sensor were studied. Finally, the proposed sensor was applied for simultaneous and sensitive detection of p-aminobenzoic acid and procaine in real media such as plasma and pharmaceutical products with satisfactory results.

Keywords: Procaine Hydrochloride, P-aminobenzoic Acid, Carbon Nanotubes, Nanostructured Sensor, Electrochemical Techniques

INTRODUCTION

Local anesthetics are substances that are mainly used to relieve the pain sensation from certain areas of the body and widely applied in dentistry. Procaine is usually an organic-based drug that used for the production of regional and local anesthesia, particularly in neural therapy and oral surgery. The drug is applied to reduce bleeding by its advantage of constricting blood vessels [1]. Procaine is a local anesthetic that is used as its hydrochloride form under various trade names, for example, Novocain. In fact, procaine possesses antiarrhythmic and vasodilating effects, therefore helping to decrease bleeding, improve the value of anesthesia, inhibiting the drug from reaching systemic circulation to a large extent, and above all decreases the amount of anesthetic required [2]. Rapid action and minor toxicity than other anesthetics can be described as the reasons for its popularity [3]. Some other therapeutical effects of procaine are perfusion-enhancing, anti-inflammatory, sympatholytic, and mood-enhancing effects [4]. In other local anesthetics the considered molecule has an amide linkage that confers considerable stability against enzymatic splitting. But procaine does not have this stable configuration. Contrarily, it contains an ester bond which is easily broken down in the plasma by enzymatic (cholinesterase) and non-enzymatic hydrolysis. Para-aminobenzoic acid (PABA) and diethylaminoethanol are produced through the hydrolysis of procaine; their chemical structures are illustrated in Scheme 1. PABA as the decomposition product is the principal compound that leads to an allergic reaction in surgery when procaine is administrated as a local anesthetic. It causes anaphylactic shock if its sensitivity is sufficiently strong [5]. Moreover, PABA has been shown toxic in nature. The human body needs a very small amount of PABA, but in excess, it causes liver damage [6]. Also, different studies have proved that DNA is damaged after UV irradiation in the presence of PABA [7]. Therefore, the imperative issue in the quality control of medications containing procaine as active substance is the determination of PABA. On the other hand, procaine-containing drugs show quick actions with some critical side effects, for instance, cardiac

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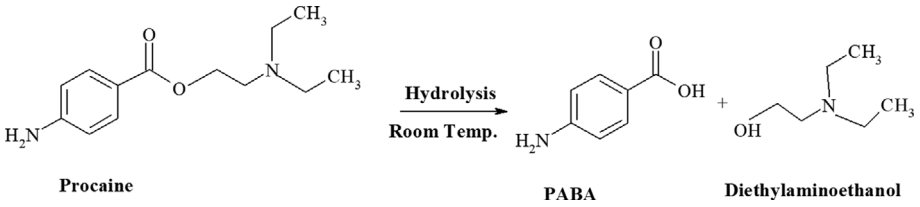

Scheme 1. The hydrolysis reaction of procaine.

and neurological toxicity. In some cases, the drug exhibits allergenic reactions [8]. Therefore, monitoring of patients administered with procaine-containing treatment is necessary in order to analyze any excessive presence of the drugs in the body fluids [9]. Only a few techniques have been reported in the previous literature for the simultaneous analysis of the both chemicals, mostly by HPLC [10], LC-MS/MS [11], UV-visible spectrometry [12] and least-squares coupled to residual tri-linearization (NPLS/RTL) [13]. Among the various methods, electrochemical techniques are more considerable than other methods due to their accuracy, simplicity, sensitivity, good reliability and low cost of instrumentation. On the other hand, electrochemical methods are expected to have good results since both procaine and PABA show electroactive properties and, therefore, can be oxidized at appropriate potentials.

In recent years, MWCNTs have received enormous attention in modern analytical chemistry [14,15] for their excellent properties, for example, extraordinary conductivity and stability as well as high mechanical strength and modulus [16-18]. Furthermore, the subtle electronic performance of MWCNTs discloses that the materials have the capability to support electron-transfer reaction and show a high electrocatalytic property as electrode materials [19]. These effects about nanostructured materials demonstrate advantageous attributes in the developments of chemical sensors [20-22] and biosensors [23] and also their catalytic effects [24-27].

The aim of the present work is development of a simple and strong nanostructured electrochemical sensor for simultaneous determination of procaine hydrochloride and PABA. Therefore, a sensitive and simple MWCNTs modified carbon paste electrode (MWCNTs/CPE) was designed for analysis of the two analytes using differential pulse voltammetry (DPV) technique. The effect of different parameters was investigated to improve the sensitivity of the analysis. Also, electrochemical studies of procaine hydrochloride were investigated using cyclic voltammetry (CV). The advantages of the carbon paste electrodes include the wide range of paste modifications available and the convenience in handling. Furthermore, the study and characterization of the modified sensor were accomplished using different techniques. The proposed voltammetric technique was applied for electrochemical studies and simultaneous detection of PABA and procaine hydrochloride in complicated biological and pharmaceutical samples with acceptable results.

EXPERIMENTAL

1. Apparatus and Chemicals

A three-electrode cell assembly involving a CPE or a nanostructured modified CPE, a Pt wire (Metrohm, Switzerland), and Ag/AgCl/KCl (3.0 M) as the working, counter, and reference electrodes, respectively was applied. Electrochemical impedance spectroscopy (EIS) experiments were carried out by an Autolab potentiostat-galvanostat PGSTAT 35 (Netherlands) that was equipped with GPES software. Other electrochemical experiments were accomplished using a Sama 500 potentiostat (Iran). The scanning electron microscopy (SEM) micrographs were recorded with a KYKY-EM3200 apparatus. A pH meter (Metrohm 691) was employed to prepare different buffers.

MWCNTs were supplied by Chinese Academy of Sciences. Procaine, PABA and other chemicals were obtained from Merck (Darmstadt, Germany) without further purification. Deionized water was used for fresh preparation of all solutions. All electrochemical measurements were conducted in 0.2 M phosphate buffer. Room temperature was used for all experiments.

2. Fabrication of Nanostructured Modified Electrode

CPE was fabricated by mixing graphite powder (0.5 g) with paraffin oil (0.2 mL) as a suitable liquid binder. Also, to fabricate chemically modified electrodes, 5.0 mg of MWCNTs was sonicated in deionized water for 30 min to obtain a homogeneous and stable suspension [28]. Then, the suspension was added to graphite powder. The solvent was volatilized in the mortar and then 1.8 mL of paraffin oil was added and blended with a pestle. The final paste was packed into an electrode cavity containing a Teflon tube with outside diameter of 4 mm, and inside diameter of 2 mm. A copper wire was used to create an electrical conduct. A renewed surface of electrode was prepared prior to each experiment.

RESULTS AND DISCUSSION

1. SEM Analysis

SEM has been a principal tool for investigation of physical and surface properties of the electrodes. Surface properties of the pro-

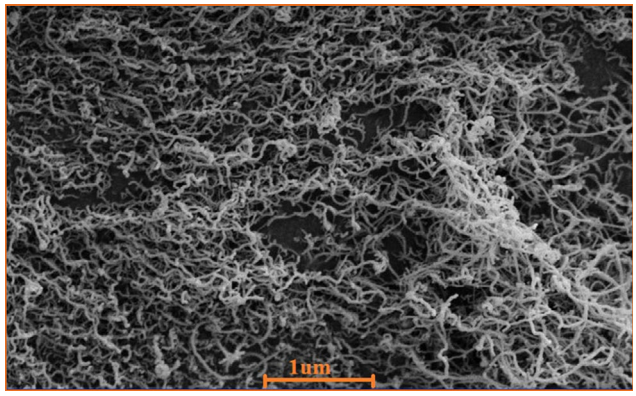

Fig. 1. SEM image of MWCNTs powders.

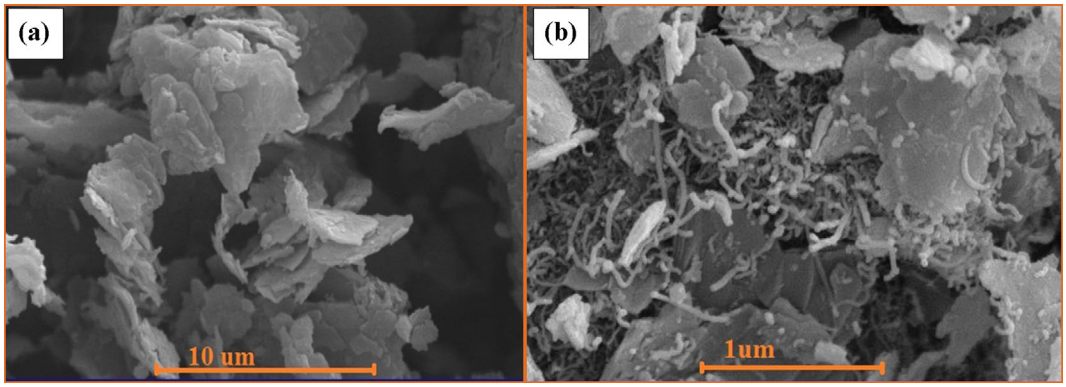

Fig. 2. SEM image of (a) unmodified and (b) modified electrodes.

posed electrodes were studied by a scanning electron microscope. The morphology of MWCNTs is shown using SEM technique in Fig. 1. The micrographs that were obtained by SEM for the CPE (A) and the MWCNTs/CPE (B) are also shown in Fig. 2. It can be observed that the electrode surface without modification is non-uniform. However, Fig. 2(b) shows the presence of MWCNT as modifier at nano size and its immobilization on the surface of the CPE. The inhomogeneity of the unmodified electrode can be attributed to more defects, which are observed on the electrode surface. The defects are formed due to the ineffective binding of the paste components in CPE. The surface of the modified electrode by optimum amount of MWCNTs shows fewer defects, which indicates higher homogeneity of the electrode surface because of the justified mass ratio of compounds.

2. EIS Studies

EIS presents a wide frequency range measurement method that can provide information about impedance changes in the surface of electrodes upon modification. The Nyquist plots of the fabricated electrodes containing bare and nanostructured modified electrodes in the presence of $[Fe(CN)_6]^{3-/4-}$ (5.0×10^{-3} M) in phosphate buffer (0.2 M, pH 7.0) are displayed in Fig. 3. As seen, the impedance spectrum contains semicircle and linear portions. The semicircle portion describes the charge transfer resistance (R_{ct}) at higher frequency, whereas a 45° line defines a region of diffusion limited process.

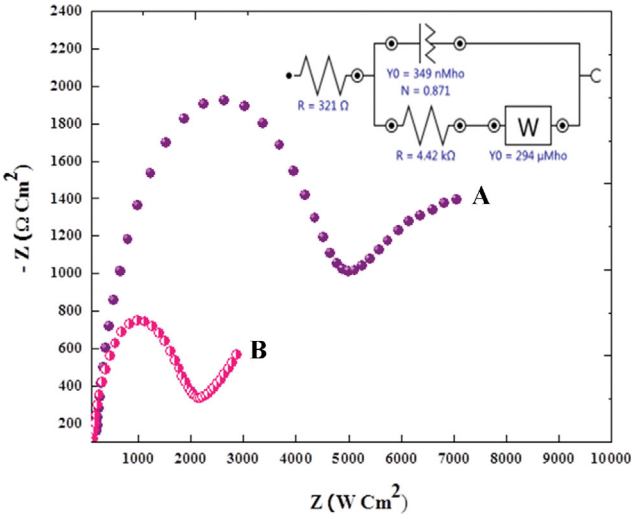

Fig. 3. The Nyquist plot of the (A) CPE and (B) MWCNTs/CPE in phosphate buffer in the presence of 5.0 mM $[Fe(CN)_6]^{3-/4-}$.

The values of the R_{ct} can be approximated by fitting the equivalent circuit. The R_{ct} values that were obtained for the CPE and MWCNTs/CPE are equal to 4.440 KΩ and 1.771 KΩ, respectively. The low R_{ct} value of the modified electrode can be attributed to the high electrical conductivity, improvement of surface area and an enhancement in electrocatalytic properties of the MWCNTs.

3. Voltammetric Studies of MWCNTs/CPE

Potassium ferricyanide ($K_4Fe(CN)_6$) was chosen as a probe to investigate the performance of the fabricated MWCNTs/CPE using CV technique. In Fig. 4, cyclic voltammograms of MWCNTs/CPE in the presence of $[Fe(CN)_6]^{3-/4-}$ redox probe (5.0×10^{-3} M), in 0.2 M phosphate buffer (pH 7.0) at different scan rates (10.0 to 70.0 mV s^{-1}) are shown. The linear relationship in Fig. 4 shows a diffusion process and catalytic behavior of MWCNTs.

Laviron's equation (Eq. (1)) enables us to calculate the apparent charge transfer rate constant (k_s, s^{-1}) and electron transfer coefficient (α) using determining the changing of the peak potentials by variation in scan rates [29].

$$\text{Log } k_s = \alpha\log(1-\alpha)+(1-\alpha)\log\alpha-\log(RT/nFv)-\alpha(1-\alpha)\,n_\alpha F\Delta E_p/2.3RT \quad (1)$$

where, n presents the number of electrons in the redox reaction and is supposed equal to one. Therefore, the amount of α and k_s was achieved equal to 0.23 and 0.47 s^{-1}, respectively.

Furthermore, the electroactive surface areas of CPE and MWCNTs/CPE were calculated by the Randles-Sevcik equation and achieved 0.021 cm^2 and 0.082 cm^2, respectively. These results clearly reveal that MWCNTs/CPE can provide an effective sensing performance as compared to the bare electrode [30,31].

4. Electrochemical Studies of Procaine and PABA at the MWCNTs/CPE

To realize the catalytic activity of the nanostructured electrode, cyclic voltammogram responses of procaine and PABA were examined at the surface of the CPE and MWCNT/CPE. Therefore, cyclic voltammograms of 0.2 M phosphate buffer with pH 7.0 were investigated in the presence and absence of 5.0 µM procaine and PABA. The results are shown in Fig. 5. As can be observed, the voltammetric responses of the modified electrode in phosphate buffer (Fig. 5 curve (a)) and in 50.0 µM procaine and PABA (Fig. 5 curve

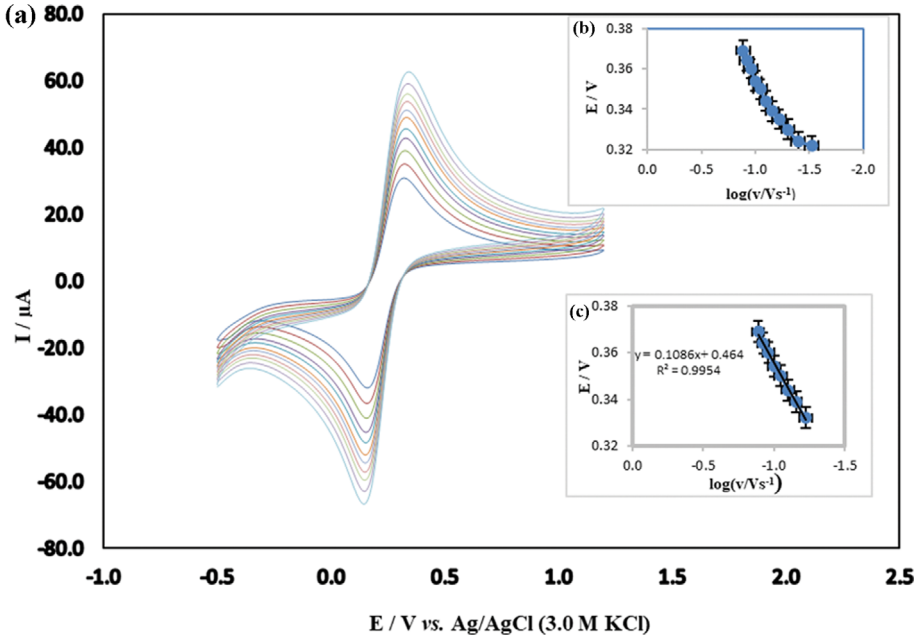

Fig. 4. Cyclic voltammograms of phosphate buffer (in the presence of 5.0 mM $[Fe(CN)_6]^{3-/4-}$ using various scan rates (10.0-100.0 mVs^{-1}); (a), ΔE_p *vs.* log(v/Vs^{-1}); ((b) and (c)).

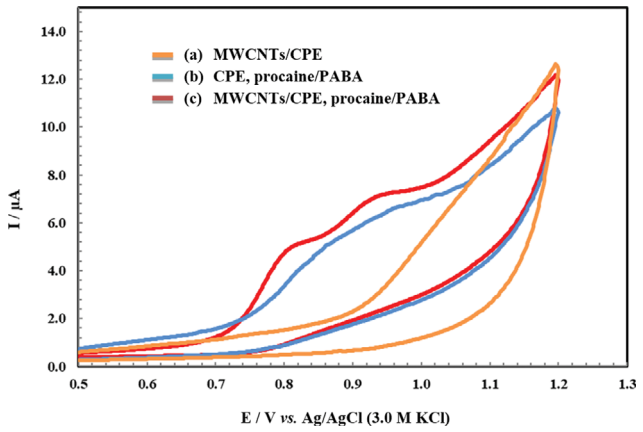

Fig. 5. Cyclic voltammograms of phosphate buffer, (a) at MWCNTs/CPE, (b) and (c) in the presence of 50.0 µM procaine and PABA at CPE and MWCNTs/CPE, respectively.

(c)) compared with bare CPE (Fig. 5 curve (b)) show a clear enhancement in the peak currents. The presence of MWCNTs in the modified electrode creates well-separated voltammetric peaks of the two analytes and acceptable improvement on the peak currents. MWCNTs have been considered important modifiers due to their ability to promote electron transfer in electrochemical reactions, improve sensitivity and chemical inertness. On the basis of the observations, it is clear that addition of MWCNTs exerts a significant catalytic effect on the electrochemical reduction of procaine and PABA leading to decrease of overpotential in the process and an enhancement in the peak current is observed. The reason for the better performance of the MWCNTs/CPE is due to the nanometer dimensions of the MWCNTs, electronic structure and topological effects of MWCNTs surface. Therefore, using a nanostructured electrode an electrocatalytic effect [32-35] is observed and sensitive analysis of the analytes can be performed in complicated samples.

5. Calibration Graph and Limit of Detection

DPV was applied for estimating the detection limit of procaine and PABA at the surface of MWCNTs modified electrode due to having the benefit of higher current sensitivity and better characteristics for analytical studies than CV technique [36-41]. The peak currents for the both analytes enhance linearly with the increase in concentration of respective analytes. The differential pulse voltammograms for a series of procaine and PABA solutions with wide-ranging of concentrations from 2.4 to 100.0 µM under the optimum conditions are illustrated in Fig. 6(a). The linear regression equations of procaine and PABA in different concentrations can be obtained from the plot and expressed as I=0.024 C−0.038 (R^2= 0.9997) and I=0.0367 C−0.0507 (R^2=0.9991), respectively.

Thus, the detection limits (S/N=3) were calculated from the calibration curves, which are 62.0 and 49.0 nM for procaine and PABA, respectively. According to the results, the proposed strategy is more sensitive than the previously reported literatures (Table 1) [10,42-44].

6. Effect of Interfering Compounds and Ions

To study the effect of interference of various compounds in the determination of the two analytes, the peak current of a phosphate buffer (0.2 M) in the presence of 50.0 µM of both compounds was measured. This test was repeated five times and the average standard deviation was obtained. In the next step, the same solution with an interfering compound was prepared and its response was determined. The tolerance limit is a concentration which makes an error £±5.0% for oxidation peak current. Table 2 shows the effect of interference with different combinations. According to the results, some common cations, anions and organic compounds have no influence on the signals of procaine and PABA with deviations below 5%.

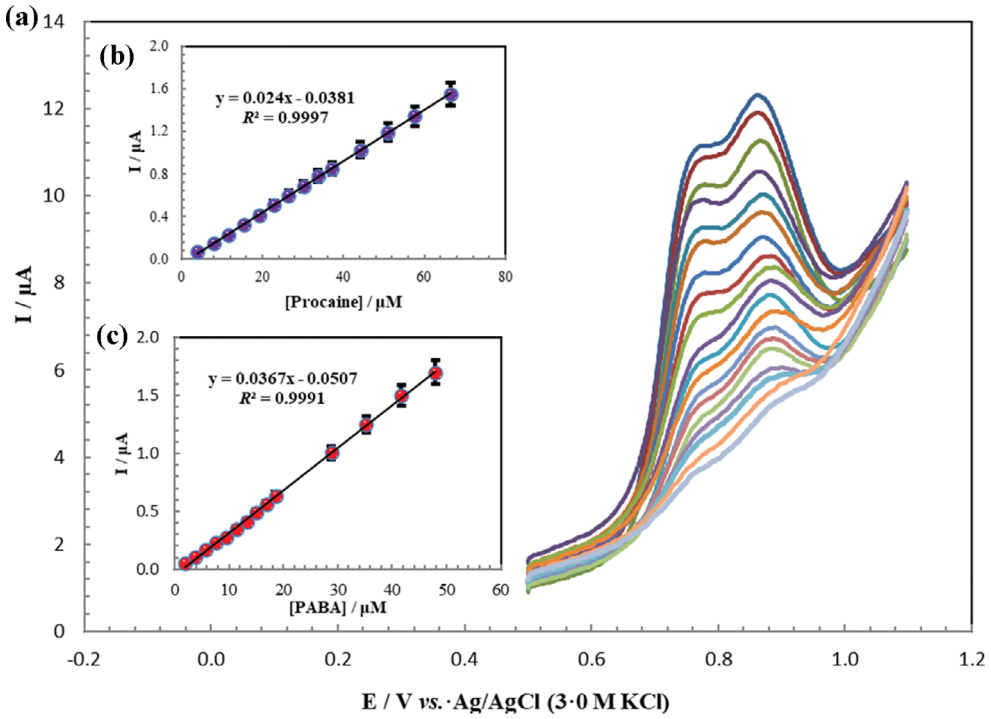

Fig. 6. DPV of MWCNTs/CPE in phosphate buffer (pH=7.0), containing different concentrations of procaine and PABA. a-z correspond to 2.4-100.0 µM of procaine and PABA (a), Plot of the peak current as a function of procaine and PABA concentration (b) and (c), respectively.

Table 1. Comparison of the efficiency of some techniques in the analysis of procaine

Technique	Linear range (µM)	Limit of detection (nM0)	Property	Ref.
SIA-CL[a]	1.8-180.0	1,100.0	High-cost Sample preparation requirement High detection limit	42
CV	5.0-200.0	500.0	High detection limit	43
HPLC-UV	10-5.0 µg/mL	-	Time-consuming Sample preparation requirement	44
HPLC	10.0-750.0	500.0	Time-consuming Sample preparation requirement	10
DPV	0.01-100.0	1.1	Low detection limit No Sample preparation requirement Cost effective Savings in time	This study

[a]Sequential injection analysis (SIA)-Chemiluminescence (CL)

Table 2. Influence of some interference substances in analysis of procaine and PABA

Interference substance	Tolerance limit ($W_{Substance}/W_{procaine}$)	Tolerance limit ($W_{Substance}/W_{PABA}$)
Na^+, K^+, NH_4^+	200.0	200.0
Cl^-, CO_3^{2-}, I^-, NO_3^-	200.0	200.0
Glucose	100.0	100.0
Lactose	100.0	300.0
Phenylalanine	100.0	200.0

7. Repeatability and Stability Studies of the MWCNTs/CPE

For investigation of the repeatability of the modified electrode, five electrodes were replicated. For each electrode, a voltammogram in the presence of phosphate buffer with pH=7.0 containing 50.0 µM of procaine and PABA was separately recorded. Then, the oxidation peak current and the related standard deviation (RSD) of the electrodes response were calculated. The RSDs were 4.2% and 4.7% for procaine and PABA, respectively. The results suggest that the proposed sensor is reasonably repeatable.

Furthermore, stability of the fabricated sensor was checked over

Table 3. Determination of procaine and PABA in plasma sample

Sample of plasma	Analyte	Added amount (μM)	Found amount (μM)	Recovery (%)
1	Procaine	15.68	16.40	104.59
2		23.25	22.70	97.63
3		30.65	29.72	96.25
1	PABA	7.75	8.01	103.35
2		11.49	11.64	101.30
3		15.15	15.07	99.47

Table 4. Determination of procaine and PABA in penicillin G procaine suspension

Pharmaceutical product	Analyte	Added amount (μM)	Found amount (μM)	Recovery (%)
1	Procaine	0	41.30	---
2		4.0	45.22	99.82
3		8.0	49.23	99.85
4		16.0	58.71	102.46
1	PABA	0	0.7	---
2		4.0	5.0	106.39
3		8.0	8.57	98.50
4		12.0	12.45	98.03

two-week period by recording voltammetric responses of procaine and PABA. For this purpose, a phosphate buffer (pH=7.0) in the presence of 50.0 μM of procaine and PABA was prepared. The peak current in MWCNTs/CPE was reduced to only 4.8% of its initial value. Therefore, it seems that the desired electrode has excellent stability.

8. Real Sample Analysis

8-1. Human Blood Plasma Sample

The analytical application of the proposed strategy was investigated using selective studies of the procaine and PABA in human samples containing blood plasma. The standard addition method was applied to test recovery of the nanostructured sensor. At first, the human blood plasma samples were diluted 100 times with phosphate buffer (pH=7.0). Then, a certain amount of the solution was added to the electrochemical cell. The results are demonstrated in Table 3. These results with very good recoveries proved that MWCNTs/CPE can be applied for sensitive detection of procaine and PABA in real complicated samples.

8-2. Procaine G Penicillin Suspension

Procaine G penicillin, is an injectable antibiotic with ®Crysticillin A.S tradename. It is suitable for the treatment of a number of bacterial infections, specifically for mouth infections, pneumonia, diphtheria, cellulitis, and animal bites. To confirm the performance of the modified electrode, electrooxidation of procaine hydrochloride and PABA was investigated in a Penicillin G Procaine suspension as a real sample. For this purpose, 1.0 mL of the suspension was transferred to the cell with 24.0 mL of 0.2 M phosphate buffer with pH=7.0. Then, the concentration of the proposed compounds was measured by the standard addition method. The results for different concentrations of the real sample are shown in Table 4. These satisfactory results in the simultaneous determination of the both compounds prove that the proposed electrode is a sensitive sensor for the quality control of pharmaceutical products containing procaine.

CONCLUSIONS

CPE modified with MWCNT was developed as an efficient and economical electrochemical sensor for the procaine and PABA analysis. PABA is a degradation product of the local anesthetic procaine hydrochloride. Therefore, simultaneous determination of procaine and PABA is essential for the quality control of pharmaceutical products containing procaine. The properties of the nanostructured modified electrode were characterized by SEM, EIS and CV. Under the optimized experimental conditions, the modified electrode indicates an excellent electrocatalytic activity, remarkable enhancement of pick current and separated voltammetry response for procaine and PABA compared with CPE. The MWCNTs/CPE has good operating characteristics like sensitivity, repeatability, low detection limit and wide linearity range. The limit of detection values (S/N=3) was calculated to be 62.0 and 49.0 nM for detecting of procaine and PABA, respectively. The low limit of detection and the slope of the calibration curve proved the sensitivity of the proposed electrode. The MWCNTs/CPE was also used for the analysis of procaine and PABA in spiked human plasma, as well as in pharmaceutical dosage form and indicates satisfactory results in the complicated matrices. Therefore, the study proposes a favorable platform for expansion of the application of carbon paste modified electrodes for simultaneous analysis of electroactive compounds in biomedical and pharmaceutical industries.

Authors Contributions Farzaneh Haghighian: methodology, software, investigation, formal analysis. **Sayed Mehdi Ghoreishi:**

conceptualization, supervision, project administration, data curation, resources, validation. **Abdolmohammad Attaran:** conceptualization, supervision, project administration, data curation, resources, validation. **Fahimeh Zeraatkar Kashani:** formal analysis, software, writing-review and editing. **Asma Khoobi:** methodology, visualization, formal analysis, investigation, conceptualization. All authors analyzed and interpreted the results.

Compliance with Ethical Standards

Conflict of interest. The authors declare that they have no conflict of interest.

Availability of data and materials Not applicable

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