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A Voltammetric Sensor for Determination of Methyldopa in the Presence of Hydrochlorothiazide Using Fe:Co Nanoalloy Modified Carbon Paste Electrode

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In this research the electrochemistry of methyldopa (MDOP) was studied by electrochemical methods at a carbon paste electrode modified by Fe:Co nano-alloy (Fe:Co/NL/CPE). For this goal we describe synthesis of Fe:Co/NL using ball mill method and then characterize with different methods such as scanning electron microscopy (SEM) and X-ray diffraction (XRD) in the first step. The oxidation peak potential of the MDOP at a surface of Fe:Co/NL/CPE appeared at 480 mV that was about 100 mV lower than the oxidation peak potential at the surface of the unmodified carbon paste electrode (CPE) under similar condition. Result shows for the mixture containing MDOP and hydrochlorothiazide (HCTZ), the peaks potential well separated from each other. Under the optimized conditions, the oxidation peak current of MDOP showed linear dynamic range (in 0.06–600 μM) with a detection limit of 0.03 μM, using square wave voltammetry (SWV) method. The proposed sensor was successfully applied for the determination of MDOP in real samples such as tablet, serum and urine.

Keywords: Methyldopa, Hydrochlorothiazide, Fe:Co nano-alloy, Carbon paste electrode

1. INTRODUCTION

Methyldopa is an alpha-adrenergic agonist psychoactive drug used as a sympatholytic or antihypertensive. Its use is now mostly deprecated following the introduction of alternative safer classes of agents. However, it continues to have a role in otherwise difficult to treat hypertension and gestational hypertension [1]. Hydrochlorothiazide has gained attention because it is a benzothiazide diuretic that acts directly on the kidney by increasing the excretion of sodium chloride and water and, to a lesser extent, that of potassium ions. HCTZ is an antihypertensive substance and improves the action of other hypotensive substances, allowing a decrease in the dose of those below the level where these substances present secondary effects [2]. The above compounds are important drugs in treatment of hypotensive. So, simultaneous determination of them is very important.

The nanoscience and nanotechnology has created large excitement and expectation in the recent years at the nano-scale fundamental properties changes [3-10]. Metal based nanomaterials and especially nanoalloy were used as suitable mediator in the preparation of electrochemical sensor in environmental, pharmaceutical and biological compounds analysis [11–20] and starting materials for preparing advanced structural ceramics. Also, nano based materials with variety of shapes, sizes and compositions are changing nowadays the analytical measurement [20-30].

Electrochemical sensors modified with nanomaterials have received much attention due to their specific characteristics such as wide electrochemical windows and good conductivity in the last decade [30-40]. Based on the above mentioned points, application of metal based nanomaterials in electrode modification show some novel properties in the preparation of voltammetric sensors in environmental, pharmaceutical and biological compounds analysis [41-50].

Therefore, in continuation of our studies concerning the preparation of chemically modified electrodes for electroactive compounds analysis [51–70], in the present work, we describe preparation of a new Fe:Co/NL/CPE and investigate its performance for the electro-oxidation determination of MDOP in the presence of HCTZ in aqueous solutions. We also evaluate the analytical performance of the modified electrode for determination of above compounds in real samples.

2. EXPERIMENTAL

2.1. Chemicals

All chemicals used were of analytical reagent grade purchased from Merck (Darmstadt, Germany) unless otherwise stated. Doubly distilled water was used throughout.

A 1.0×10^{-2} M MDOP solution was preparing daily by dissolving 0.211 g MDOP in water and the solution was diluted to 100 mL with water in a 100-mL volumetric flask. The solution was kept in refrigerator at 4 °C in dark. More dilute solutions were prepared by serial dilution with water.

A 1.0×10^{-3} M HCTZ solution was preparing daily by dissolving 0.029 g HCTZ in ethanol-water (1:1) solution and the solution was diluted to 100 mL with water in a 100-mL volumetric flask.

The solution was kept in refrigerator at 4 °C in dark. More dilute solutions were prepared by serial dilution with water.

Phosphate buffer (sodium dihydrogen phosphate and disodium monohydrogen phosphate plus sodium hydroxide, 0.1 mol L^{-1}) solutions (PBS) with different pH values were used.

High viscosity paraffin (d = 0.88 kg L^{-1}) from Merck was used as the pasting liquid for the preparation of the carbon paste electrodes.

2.2. Apparatus

Cyclic voltammetry, chronoamperometry, and square wave voltammetry were performed in an analytical system, Autolab with PGSTAT (Eco Chemie, the Netherlands). The system was run on a PC using GPES software. A conventional three-electrode cell assembly consisting of a platinum wire as an auxiliary electrode and an $Ag/AgCl/KCl_{sat}$ electrode as a reference electrode was used. The working electrode was a CPE and Fe:Co/NL/CPE. X-ray powder diffraction studies were carried out using a STOE diffractometer with Cu-Ka radiation (k = 1.54 Å).

2.3. Synthesis of Fe:Co alloys

Fe:Co alloys were prepared by mechanical alloying. The starting materials used in this study included high purity powders of Fe (99.9% purity and particle size <10 μm) and Co (99.99% purity and particle size <1 μm) were loaded into a 250 ml steel container (vial) under argon atmosphere (99.9% purity) with a blend of ball bearing steel balls (m_1 = 4.11 g and m_2 = 33.09 g). The total weight of the powder was about 10 g and the ball to powder weight ratio was kept at 10:1. Milling was carried out for 32 h in a planetary ball mill at the container rotation speed of 420 rpm.

2.4. Preparation of the sensor

Fe:Co/NL/CPE was prepared by mixing of 0.1 g of Fe:Co/NL, 0.5 g of the liquid paraffin, and 0.8 g of graphite powder. Then the mixture was mixed well for 55 min until a uniformly wetted paste was obtained. A portion of the paste was filled firmly into one glass tube as described above to prepare Fe:Co/NL/CPE. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it on a weighing paper.

2.5. Preparation of real samples

The tablet solution was prepared by dissolving a tablet of MDOP labeled 250 mg in 100 mL water by ultrasonication. Then, 0.1 mL of the solution was diluted with the buffer solution (pH 7.0) in a 10-mL volumetric flask. The MDOP content was analyzed by the proposed method using the standard addition method.

Urine samples were stored in the refrigerator immediately after collection. Ten milliliters of the sample was centrifuged for 20 min at 1,500 rpm. The supernatant was filtered out using a 0.45 μm filter and then diluted four times with universal buffer solution (pH 7.0). The solution was transferred into the voltammetric cell to be analyzed without any further pretreatment. The standard addition method was used for the determination of MDOP in real samples.

3. RESULTS AND DISCUSSION

3.1. X-Ray diffraction of Fe:Co nanopowder

The XRD patterns of the Fe:Co showed diffraction peaks absorbed at 2θ values (Fig. 1).

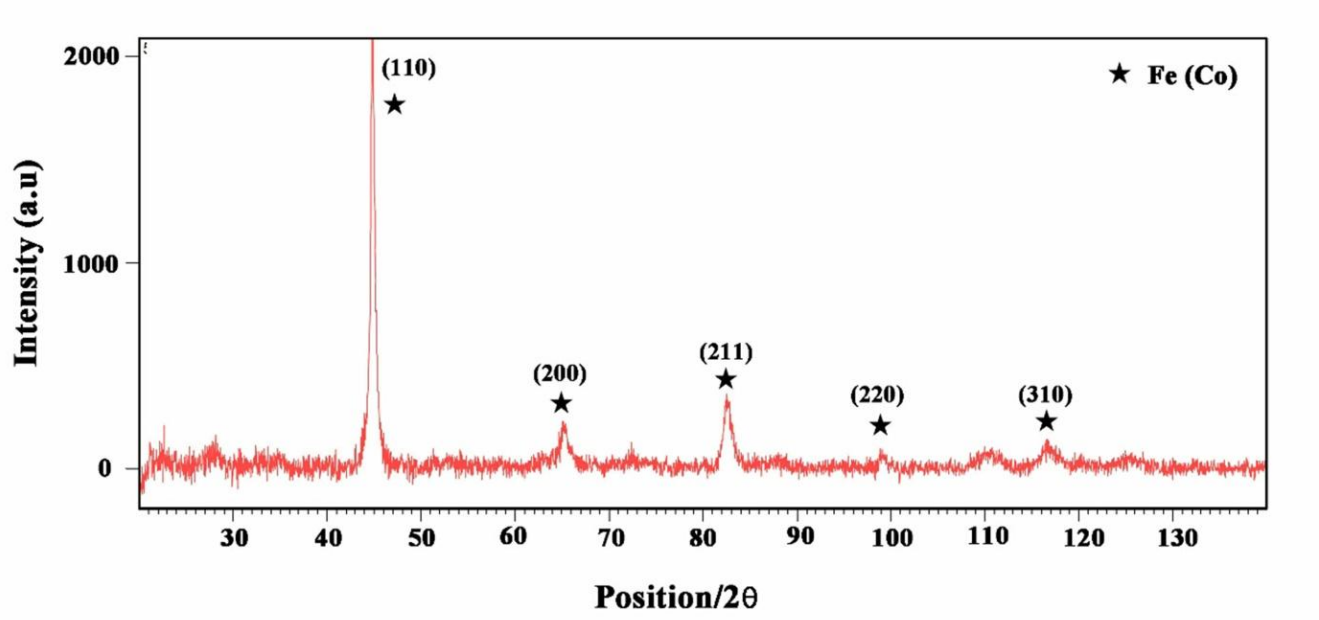

Figure 1. XRD patterns of Fe:Co nanopowder.

The prominent peaks were used to calculate the grain size via the Scherrer equation, expressed as follows:

$$D=K\lambda/(\beta \cos\theta) \quad (1)$$

Where λ is the wavelength (λ = 1.542 Å) (CuKα), β is the full width at half maximum (FWHM) of the line, and θ is the diffraction angle. The grain size of the Fe:Co nanostructure was 34 nm. The morphology of the as-grown nanostructures was characterized by SEM and technique. Figure 2 shows the SEM images of the product synthesized. It is clear that in this case, Fe:Co nanoparticle was successfully prepared.

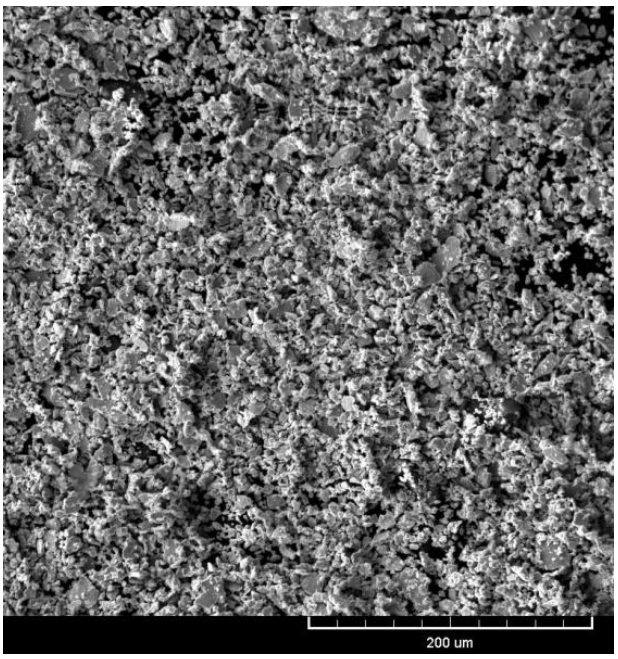

Figure 2. SEM image of Fe:Co nanopowder synthesis by ball mill method

3.2. Voltammetric investigation

The active surface area of the modified electrode was estimated according to the slope of the I_P versus $\nu^{1/2}$ plot for a known concentration of $K_4Fe(CN)_6$, based on the Randles–Sevcik equation:

$$I_p = 2.69\times10^5 n^{3/2} A D^{1/2} \nu^{1/2} C_O \quad (2)$$

where I_{pa} refers to the anodic peak current, n the electron transfer number, A the surface area of the electrode, D_R the diffusion coefficient, C_0 the concentration of $K_4Fe(CN)_6$ and ν is the scan rate. For 1.0 mmol L^{-1} $K_4Fe(CN)_6$ in 0.10 mol L^{-1} KCl electrolyte with n = 1 and $D_R = 7.6 \times 10^{-6}$ cm s^{-1} and from the slope of the I_{pa}–$\nu^{1/2}$ relation, the microscopic areas were calculated. They were 0.14 and 0.09 cm^2 for Fe:Co/NL/CPE and CPE, respectively. The results show that presence of Fe:Co cause increasing the active surface of the electrode.

MDOP as a catechol derivative can be oxidized at positive potential depends on the electrode type and solution pH. The effect of solution pH on the response of MDOP was investigated by cyclic voltammetry over the pH range of 4.0–8.0. The peak currents also change with pH with the largest anodic current appearing at pH 7.0, so this value was selected throughout the experiments (Fig. 3).

Fig. 4 (curves a & b) showed the electrochemical responses of Fe:Co/NL/CPE, and CPE in 450 μM MDOP in PBS solution (pH 7.0), respectively. At Fe:Co/NL/CPE, and CPE, MDOP showed an irreversible oxidation peak, with oxidation peak potential (E_{pa}) of 0.48 V, and 0.58 V, respectively. However, the peak current of MDOP at Fe:Co/NL/CPE was much larger than that at the CPE; it was about 2.77 times larger than CPE by cyclic voltammetry. Thus, the modified electrode exhibited a catalytic activity toward the oxidation of MDOP. This further testified the superiority of Fe:Co/NL/CPE to CPE and indicated that the use of Fe:Co as modifier facilitated the electron transfer between MDOP and electrode.

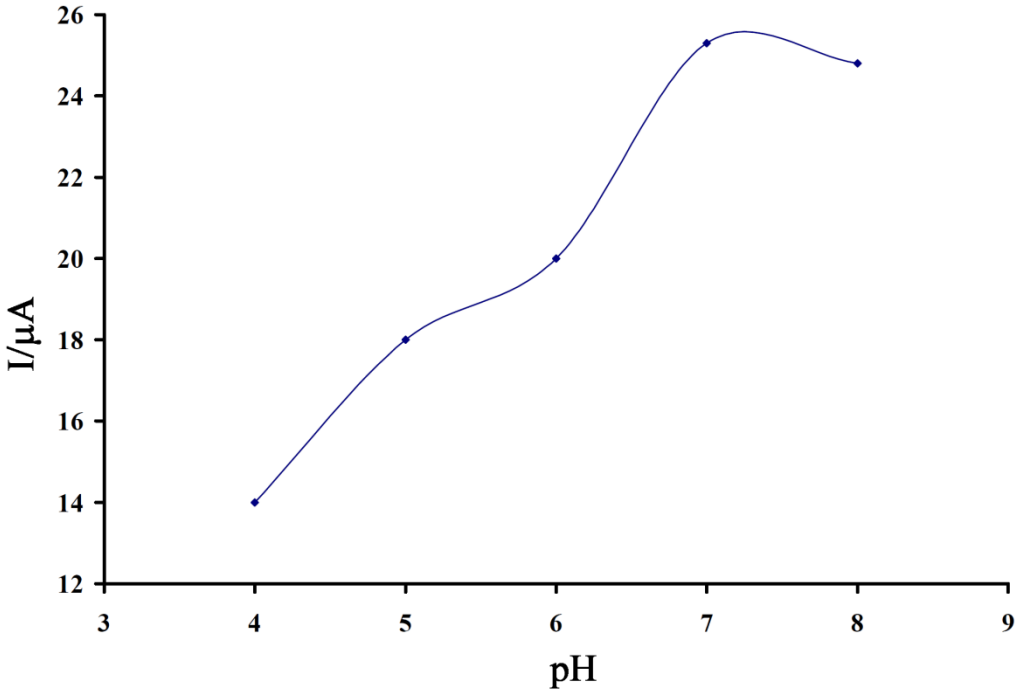

Figure 3. Current–pH curve for electrooxidation of 450 µM MDOP at Fe:Co/NL/CPE with a scan rate of 50 mV s^{-1}.

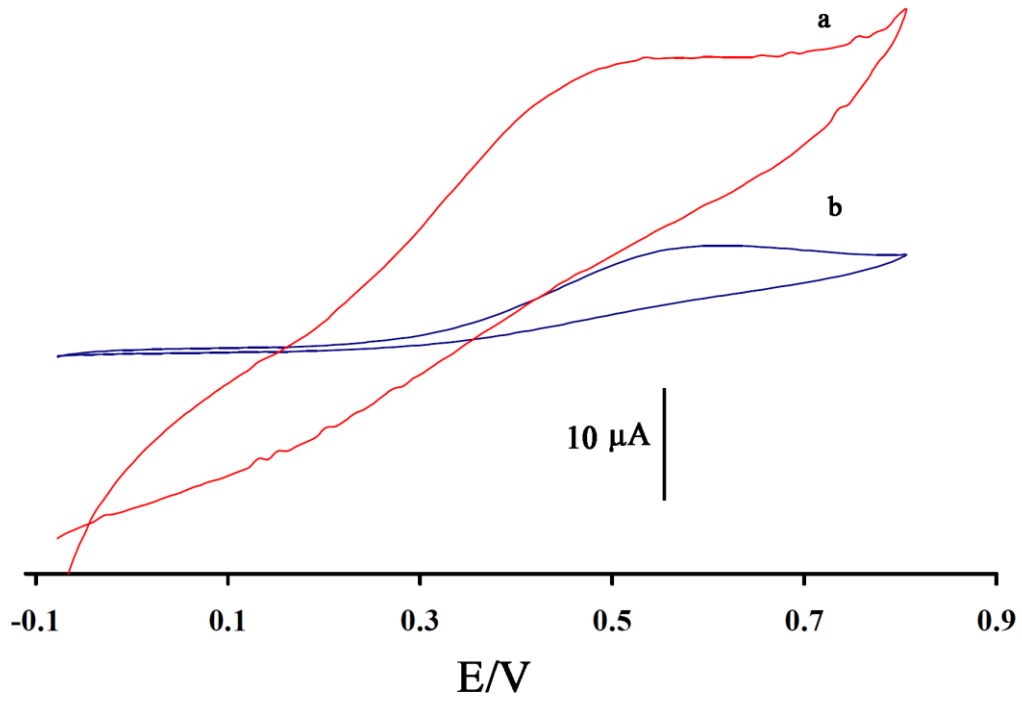

Figure 4. Cyclic voltammograms of a) Fe:Co/NL/CPE and b) CPE in the presence of 450 µM MDOP at pH 7.0, respectively

The influence of potential scan rate (ν) on I_p of 500 µM MDOP at the Fe:Co/NL/CPE was studied by linear sweep voltammetry at various sweep rates (Fig. 5 inset). As shown in Fig. 5, the peak

currents of MDOP grow with the increasing of scan rates and there are good linear relationships between the peak currents and $\nu^{1/2}$. The regression equation is I_{pa} = 3.505 - 6.762 $\nu^{1/2}$ (I_{pa}: µA, ν: mVs^{-1}, R^2= 0.995), indicating the redox process of MDOP at the Fe:Co/NL/CPE was diffusion-controlled [71-80].

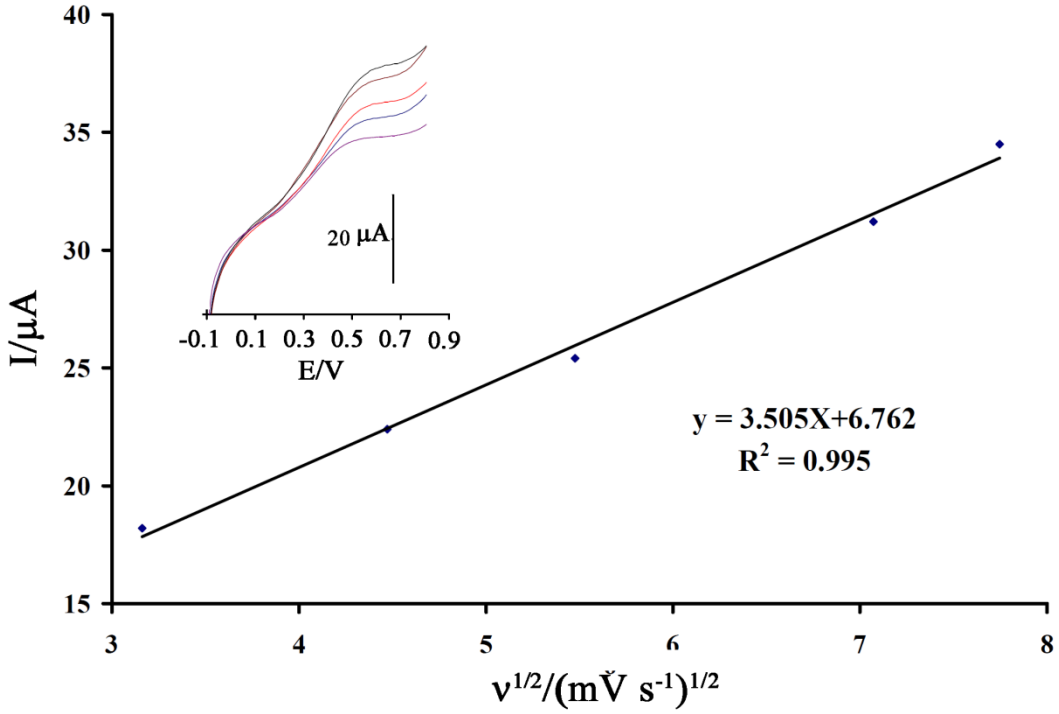

Figure 5. Plot of I_{pa} versus $\nu^{1/2}$ for the oxidation of MDOP at Fe:Co/NL/CPE. Inset shows cyclic voltammograms of MDOP (500 µM) at Fe:Co/NL/CPE at different scan rates of 10, 20, 30, 50 and 60 mVs^{-1} in 0.1 M phosphate buffer, pH 7.0

To obtain further information on the rate determining step, a Tafel plot was developed for the MDOP at a surface of Fe:Co/NL/CPE using the data derived from the raising part of the current–voltage curve (Fig. 6). The slope of the Tafel plot is equal to $n(1-\alpha)F/2.3RT$ which comes up to 0.1792 V $decade^{-1}$. We obtained α as 0.83

Chronoamperometric measurements of MDOP at Fe:Co/NL/CPE were carried out by setting the working electrode potential at 550 mV vs. $Ag/AgCl/KCl_{sat}$ for the various concentration of MDOP in buffered aqueous solutions (pH 7.0) (Fig. 7A). For an electroactive material (MDOP in this case) with a diffusion coefficient of D, the current observed for the electrochemical reaction at the mass transport limited condition is described by the Cottrell equation. Experimental plots of I vs. $t^{-1/2}$ were employed, with the best fits for different concentrations of MDOP (Fig. 7B). The slopes of the resulting straight lines were then plotted vs. MDOP concentration. From the resulting slope and Cottrell equation the mean value of the D was found to be 6.2×10^{-5} cm^2/s.

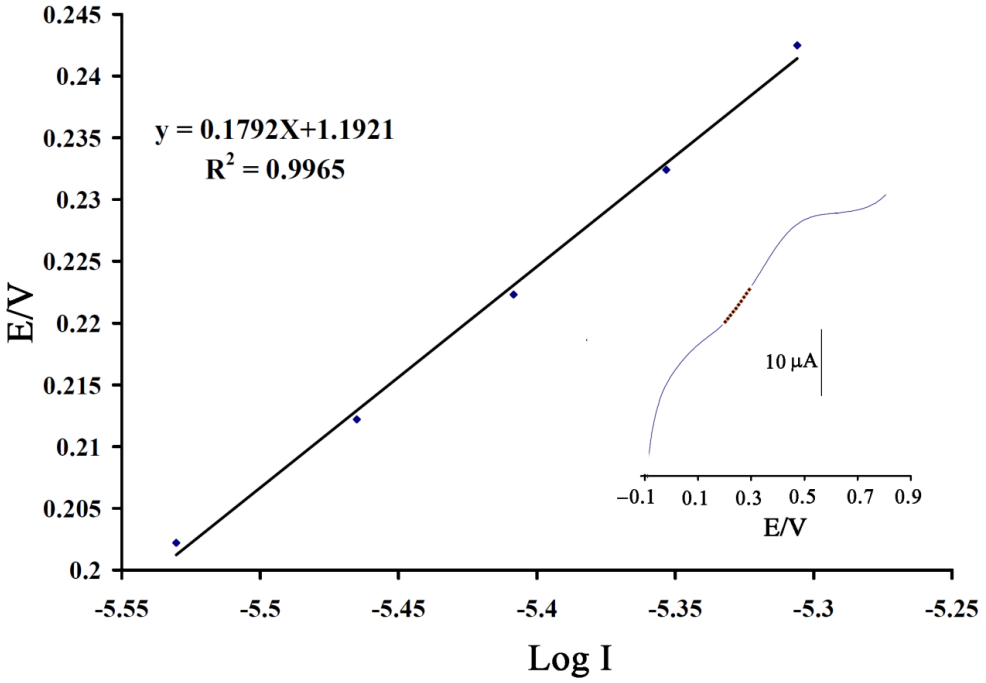

Figure 6. Tafel plot for Fe:Co/NL/CPE in 0.1 M PBS (pH 7.0) with a scan rate of 20 mVs^{-1} in the presence of 500 µM MDOP.

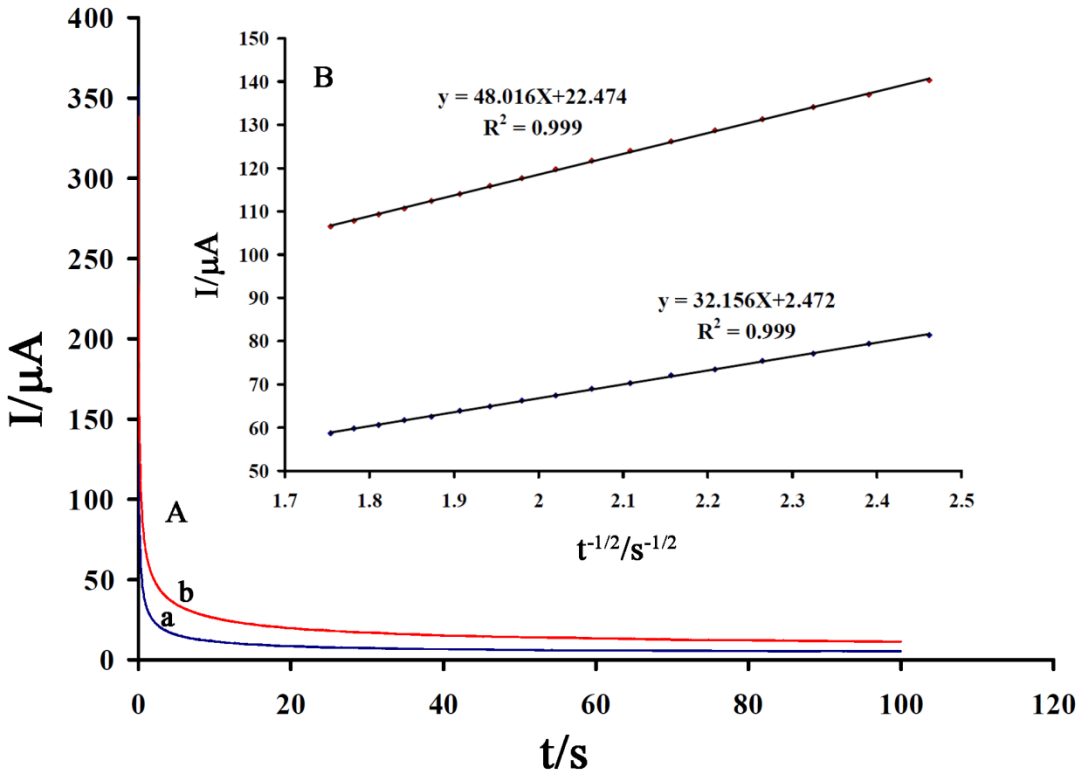

Figure 7. (A) Chronoamperograms obtained at Fe:Co/NL/CPE in the presence of (a) 400 and (b) 500 µM MDOP in the buffer solution (pH 7.0). (B) Cottrell'splot for the data from the chronoamperograms.

3.3. Stability and reproducibility

The repeatability and stability of Fe:Co/NL/CPE was investigated by SWV measurements of 15.0 μM MDOP. The relative standard deviation (RSD%) for ten successive assays was 1.2%. When using five different electrodes, the RSD% for seven measurements was 1.8%. When the electrode stored in the laboratory, the modified electrode retains 97% of its initial response after a week and 95% after 10 days. These results indicate that Fe:Co/NL/CPE has good stability and reproducibility, and could be used for MDOP.

3.4. Analytical features

Since SWV has a much higher current sensitivity and better resolution than cyclic voltammetry, it was used for the determination of MDOP in this work. The SW voltammograms clearly show that the plot of peak current vs. MDOP concentration is linear for 0.06–600 μM of MDOP, the regression equation being $I_p(\mu A) = (0.1501 \pm 0.0142)C_{MDOP} + (2.5318 \pm 0.6252)$ (r^2 =0.9939, n =11), where C is μM concentration of MDOP and I_p is the peak current. The detection limit was 0.03 μM MDOP according to the definition of $Y_{LOD} = Y_B + 3\sigma$.

The main object of this study was to detect MDOP and HCTZ simultaneously using Fe:Co/NL/CPE. This was performed by simultaneously changing the concentrations of MDOP and HCTZ, and recording the SWVs. The voltammetric results showed well defined anodic peaks at potentials of 480 and 800 mV, corresponding to the oxidation of MDOP and HCTZ, respectively. This is indicating that simultaneous determination of these compounds is feasible at Fe:Co/NL/CPE as shown in Fig. 8 inset. The sensitivity of the modified electrode towards the oxidation of MDOP in the presence of HCTZ was found to be 0.1501 μA/μM (Fig.8). This is very close to the value obtained in the absence of HCTZ (0.1494 μA/μM) indicating that the oxidation processes of these compounds at the Fe:Co/NL/CPE are independent and therefore, simultaneous determination of their mixtures is possible without significant interferences.

3.5. Interference studies

The influence of various substances as potentially interfering compounds with the determination of MDOP was studied under the optimum conditions with 20.0 μM MDOP at pH 7.0. The potential interfering substances were chosen from the group of substances commonly found with MDOP in pharmaceuticals and/or in biological fluids. The tolerance limit was defined as the maximum concentration of the interfering substance that caused an error of less than ±3% for the determination of MDOP.

After the experiments, we found that neither 900–fold of glucose, sucrose, lactose, fructose, nor 800–fold of methanol, ethanol Li^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Al^{3+}, NH_4^+, F^-, Na^+ and ClO_4^-, nor 650–fold methionine, alanine, phenylalanine, valine, tryptophan and lysine affected the selectivity. Nor did saturation of starch solution and 300–fold of urea and thiourea were interfered with the determination of MDOP.

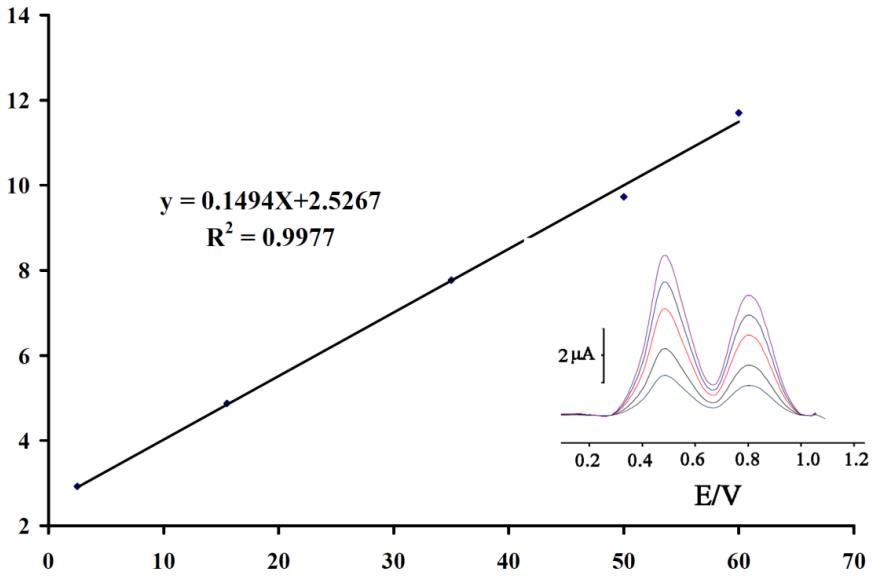

Figure 8. The plots of the electrooxidation peak current as a function of MDOP concentration. Inset; SWVs of Fe:Co/NL/CPE in 0.1 M PBS (pH 7.0) containing different concentrations of MDOP–HCTZ in µM. (from inner to outer): 2.5 + 50.0; 15.5 + 75.0; 35.0 + 125.0; 50.0 + 160.0 and 60.0 + 200.0, respectively.

3.6. Determination of MDOP in real samples

Electrochemical methods are high performance techniques for determination of electroactive compounds in real samples [78-89]. Therefore, to evaluate the applicability of the proposed modified electrode for the voltammetric determination of MDOP in real samples, its utility was tested by determining MDOP in tablet, pharmaceutical serum and in human urine samples. Standard addition method was used for measuring the MDOP concentrations in the real samples. The proposed sensor was also compared with a published method [90] in real sample analysis, the results of which are given in Table 1. The results indicate that the determination of MDOP using the electrode is effective and can be applied for their detection of MDOP in real samples.

Table 1. Determination of MDOP in drug and urine samples (n=3).

Sample	Added (µM)	Expected (µM)	Founded (µM)	Published method (µM) [90]	F_{exp}	F_{tab}	t_{exp}	$t_{tab(95\%)}$
Tablet [a]	—	5.0	4.85±0.33	5.20±0.42	8.0	19.0	1.9	3.8
	15.0	20.0	20.45±0.67	20.85±0.95	—	—	—	—
Urine	—	—	<LOD	<LOD				
	15.0	15.0	15.76±0.79	15.97±1.1	12.5	19.0	2.9	3.8
Pharmaceutical Serum	—	—	<LOD	<LOD				
	50.0	50.0	50.86±1.05	49.75±1.10	13..5	19.0	3.2	3.8

±Shows the standard deviation.

[a]250 mg tablet produced by Zahravi Drug Company

4. CONCLUSION

In this study, the Fe:Co nano-powder modified carbon paste electrode was used to investigate the electrochemical behaviors of MDOP. The novel sensor showed great improvement to the electrode process of MDOP compared to the unmodifed carbon paste electrode. The propose sensor successfully resolves the overlapped voltammetric peaks of MDOP and HCTZ by ≈ 320 mV, so that the modified electrode displays high selectivity in the SWV measurement of MDOP and HCTZ in their mixture solutions. In addition, the modified electrode exhibited a distinct advantage of simple preparation, surface renewal, good reproducibility and good stability.

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