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# Electrocatalytic Measurement of Trace Amount of Captopril Using Multiwall Carbon Nanotubes as a Sensor and Ferrocene as a Mediator

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A new sensitive and selective electrochemical sensor was developed for determination of captopril (CAP) in tablet and human patient urine. Captopril is an inhibitor of the angiotensin-converting enzyme and is widely used for the treatment of hypertension and congestive heart failure. A voltammetric study of captopril has been carried out at the surface of carbon paste electrode modified with multi-wall carbon nanotubes as a sensor and ferrocene as a mediator. The electrochemical oxidation of captopril was investigated by chronoamperometry, cyclic and differential pulse voltammetric techniques. The dependence of peak currents on pH, concentration and the potential scan rate was investigated. Two linear dynamic ranges of 0.5–12 μM and 12–300 μM with a detection limit of 0.15 μM was obtained in phosphate buffer of pH = 9. Differential pulse voltammetry as a simple, rapid, sensitive and selective method was developed for the determination of captopril in tablet and human urine without any treatments.

**Keywords:** Captopril, ferrocene, carbon nanotubes paste elecrode, electrocatalysis

## 1. INTRODUCTION

Captopril is used in the treatment of severe essential and renovascular, where other therapy has failed, and congestive heart failure. Its antihypertensive effect results from a decrease in peripheral vascular resistance. Captopril is initially administered in doses of 25 mg, two or three times each day. Captopril is metabolized chiefly to disulphide conjugates with other sulfhydryl-containing molecules. The half-life of captopril is less than 3 h. Blood levels correlate poorly with clinical response. Maximal blood pressure response is seen 2–4 h after the doses. At 1–2 weeks intervals, doses can be increased until blood pressure is controlled. Toxicity from captopril is uncommon, but when it occurs, it may

include bone marrow suppression and proteinuria [1]. Therefore, determination of this compound is very important.

Several methods have been proposed for the determination of captopril including high-performance liquid chromatography with pre- or post-column derivatization [2–7], colorimetry [8], fluorimetry [9–11], chemiluminescence [12–14], capillary electrophoresis [13–18], spectrophotometry [19–23] and electrochemical methods [24-31].

Carbon nanotubes have been proved to be a novel type of nanostructure with unique structural, electronic and mechanical properties and have drawn extensive attention since their discovery [32-34]. Research over the past decade has revealed that the carbon nanotubes constitute a new form of carbon materials that are finding striking applications in many filed, such as energy conversion and storage [35,36] electrochemical sensing [37-42] and so forth.

In this work, we describe the use of ferrocene as a mediator in the multi walled carbon nanotubes paste electrode for the electrooxidation of CAP in aqueous media at pH 9.0. This electrode was used for the determination of CAP in pharmaceutical and urine samples. Results showed that, this electrochemical sensor were selective and sensitive for determination of CAP in real samples.

## 2. EXPERIMENTAL

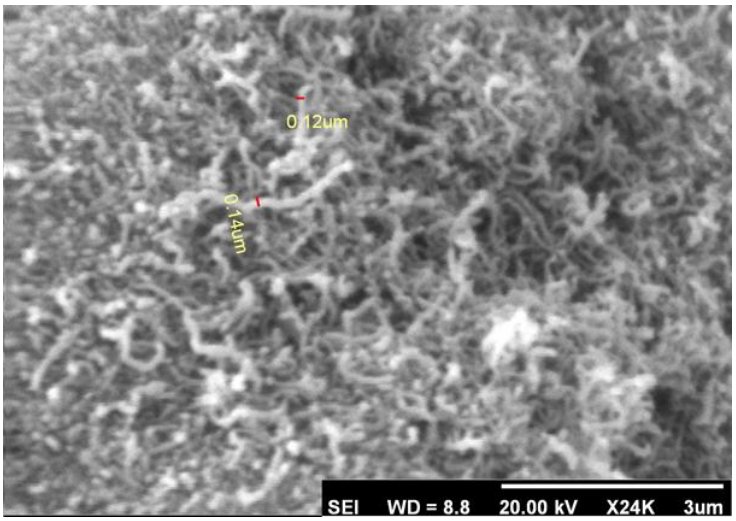
### *2.1. Materials and apparatus*

All of the solutions were freshly prepared using double-distilled water. Captopril and ferrocene were analytical grade (Fluka). Graphite fine powder (Merck, Darmstadt, Germany) and paraffin oil (DC 350, Merck, density=0.88 g $cm^{-3}$) were used as binding agents for the graphite pastes. All flasks and containers before use were soaked in 6 M $HNO_3$ at least for 24 hours and then rinsed with deionized water. The buffer solutions were prepared from ortho-phosphoric acid and its salts with pH range of 7.0-10.0. Voltammetric measurements were carried out using a computerized potentiostat/galvanostat (SAMA500 Electrochemical Analysis System, SAMA research center, Isfahan, Iran). A Pentium IV computer controlled all settings and data processing of the system. All the electrochemical studies were performed at 25 ± 1 °C. A three electrode assembly was employed for the experiments in a 50 mL glass cell containing an Ag/AgCl electrode as reference electrode, a platinum wire counter electrode and ferrocene modified multi wall carbon nanotube paste electrode (FCMWCNTs) as working electrode. All of the potentials were measured and reported *vs.* Ag/AgCl reference electrode. The pH of the solutions was controlled with a Genway pH meter (model 3030).

### *2.2. Synthesis of multi-walled carbon nanotubes*

The nanotubes were grown by chemical vapor deposition. Several transition metal catalysts have been shown to be active for generation of carbon nanotubes [43]. In this work MWCNTs were synthesized from acetylene on a Fe:Co: $CaCO_3$ catalyst at 720 $^oC$. For the production of carbon nanotubes, approximately 100 mg of catalyst containing 5 wt % Fe- Co with a mole ratio of 1:1 was

weighed and spread into a thin layer onto a quartz boat positioned horizontally inside of a resistive tube furnace under nitrogen flow. The furnace temperature was then set at the reaction temperature, while accurately controlled. When temperature reached to 720 $^{o}$C, acetylene was introduced at 3.0 ml/min, while the flow of nitrogen maintained at 200 ml/min. After rinsing the system with nitrogen, reaction product was collected from the quartz boat. For purification, raw MWCNT samples were sonicated (40 kHz) in diluted nitric acid (30% $HNO_3$) for 30 min, filtered, washed with distilled water to remove acid and finally dried at 120 $^{0}$C overnight. The residue of as-prepared MWCNTs was placed inside a Pyrex tube and oxidized in a furnace at 350 $^{o}$C in air for different time periods to remove carbon impurities (scheme 1). The diameter, length, purity and other specifications of synthesized MWCNTs are summarized in Table 1.




**Scheme 1.** SEM for multi-wall carbon nanotubes.

**Table 1.** Specification of synthesised multi-walled carbon nanotubes by chemical vapor deposition method

| Catalyst | Co: Fe |
|---|---|
| Color | Black |
| Purity | > 95% |
| Outside Diameter (OD) | 120 – 140 nm |
| Inside Diameter (ID) | 100 – 120 nm |
| Length | 10 – 50 μm |
| Special Surface Area (SSA) | 235 $m^2/g$ |
| Bulk density | 0.07 $g/cm^3$ |
| True density | ~2.1 $g/cm^3$ |

*2.3. Preparation of the electrodes*

A 0.01 g of ferrocene was dissolved in diethyl ether and mixed with 89-times its weight of graphite powder and 10-times its weight of multi wall carbon nanotubes with a mortar and pestle. The solvent was evaporated and 5ml paraffin were added to this mixture and mixed for 20 min until a uniformly-wetted paste was obtained. The paste was then packed into the end of a glass tube. Electrical contact was made by pushing a copper wire down the glass tube into the back of the mixture. When necessary, a new surface was obtained by pushing an excess of paste out of the tube and polishing it on a weighing paper. Unmodified carbon nantubes paste was prepared in the same way without adding ferrocene to the mixture and was used for comparison purposes.

*2.4. Preparation of real samples*

Ten tablets of captopril labeled with amount of 25 and 50 mg per tablet were completely ground and homogenized. Ten milligrams of the powders was accurately weighted and dissolved in 100 ml of water with sonication. After mixing completely, the mixture was filtered with an ordinary filter paper. Then, 1.0 ml of the solution plus 9.0 ml of the buffer (pH 9.0) were used for the analysis with standard addition method.

The urine samples were analyzed after 2.5 h of their sampling, except stated. The urine samples were taken from humans and were used for measurements after its centrifuged and diluted five times with water without any further pretreatment. The standard addition method was used for the determination of the captopril contents after dilution of the sample.

## 3. RESULTS AND DISCUSSION

*3.1. Electrochemical behavior of FCMWCNTs*

Recently the properties of ferrocene carbon nanotubes paste electrode were studied in buffered aqueous solution by cyclic voltammetry [44]. Figure 1 (insert) shows the cyclic voltammograms of this electrode at various scan rates, ($\upsilon = 10 - 350$ mV $s^{-1}$).

The experimental results show well-defined and reproducible anodic and cathodic peaks related to $Fc/Fc^+$ redox couple with quasi-reversible behavior, with peak separation potential of $\Delta Ep$ ($E_{pa} - E_{pc}$ = 110 mV). These cyclic voltammograms were used to examine the variation of the peak currents versus scan rates of potential. The plot of the peak current was linearly dependent on $\upsilon^{1/2}$ with a correlation coefficient of 0.9943 at the all scan rates (Fig. 1). This behavior indicates that the nature of redox process is diffusion controlled.

*3.2. pH Effect on the electrochemical behavior of CAP*

It is well known that the electrochemical behavior of CAP is dependent on the pH value of the aqueous solution, whereas the electrochemical properties of the $Fc/Fc^+$ redox couple are independent

of pH. Therefore, we studied the electrochemical behavior of CAP in buffered solution (0.1 M phosphate) with various pHs (7.0<pH<10.0) at the surface of FCMWCNTs by cyclic voltammetry. Figure 2 shows the variation of $I_{pa}$ versus pH for CAP oxidation at the surface of this modified electrode. As can be seen, the maximum electrocatalytic current was obtained at pH 9.0. Therefore, pH 9.0 was chosen as the optimum pH for electrocatalytic oxidation of CAP at FCMWCNTs and all electrochemical experiments were done at this pH.

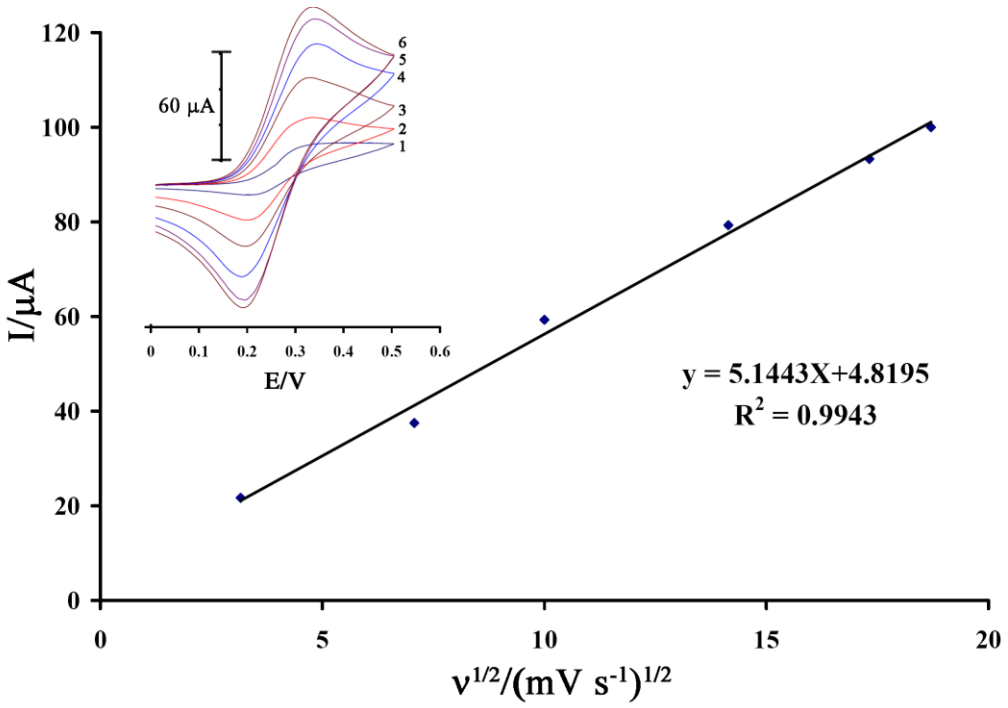



**Figure 1.** Plots of anodic peak current of FCMWCNTs vs. $\nu^{1/2}$ from cyclic voltammograms of (Insert). Insert shows cyclic voltammograms of FCMWCNTs in 0.1 mol $L^{-1}$ PBS at pH 9.0, and at various scan rates of 1) 10; 2) 50; 3) 100; 4) 200; 5) 300 and 6)350 mV $s^{-1}$

*3.3. Catalytic effect*

CAP is an oxidisable compound and can be detected by electrochemical methods based on anodic oxidation. Result shows, at the surface of a bare electrode, CAP could not oxidize until the potential reached +1.0 V (Fig. 3 curve a). Also, anodic peak current that is observed for FCMWCNTs in absence of CAP (Fig. 3.curve d) increases greatly in 1.0 mM CAP solution, while the corresponding cathodic peak disappeared on the reverse scan (curves b).

Therefore, the $Fc^+$ electrogenerated at the FCMWCNTs surface undergoes a catalytic reduction by CAP back to Fc, which can then be electrochemically reoxidized to produce an enhancement in the anodic current. The process could be expressed as follows:

$$Fc \longrightarrow Fc^+ + e^- \qquad (1)$$

$$2Fc^{+} + CAP_{(Red)} \longrightarrow Fc + CAP_{(Ox)} \quad (2)$$

Therefore, oxidation of CAP at the surface of FCMWCNTs is performed at about 0.280 V versus Ag|AgCl|$KCl_{sat}$. In same condition, when we compared the oxidation of CAP at the surface of FCMWCNTs (curve b) and ferrocene modified carbon paste electrode (FCMCPE) (curve c), it was observed that a dramatic enhancement of the anodic peak current occurred at FCMWCNTs *vs.* the value obtained with FCMCPE. In other words, the data obtained clearly show that the combination of multi wall carbon nanotubes and the mediator definitely improve the characteristics of the electrode for the oxidation of CAP.

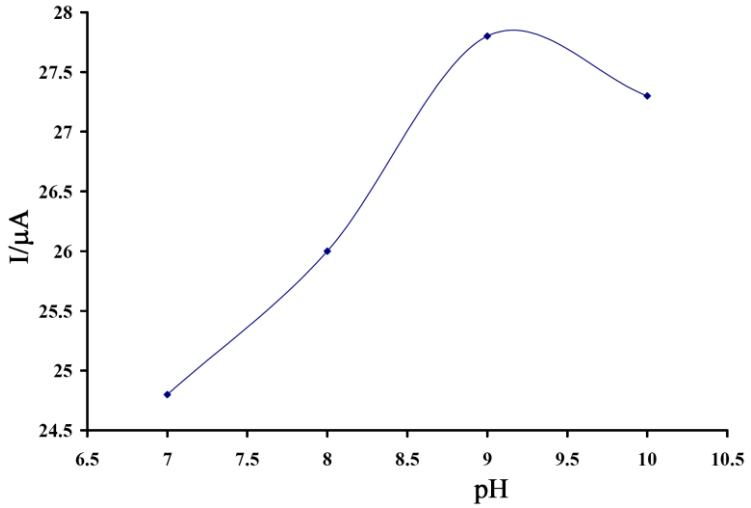



**Figure 2.** Current-pH curve for electro-oxidation of CAP in 0.1 M phosphate buffer solution with various pH values at the surface of FCMWCNTs with scan rate of 10 mV $s^{-1}$.

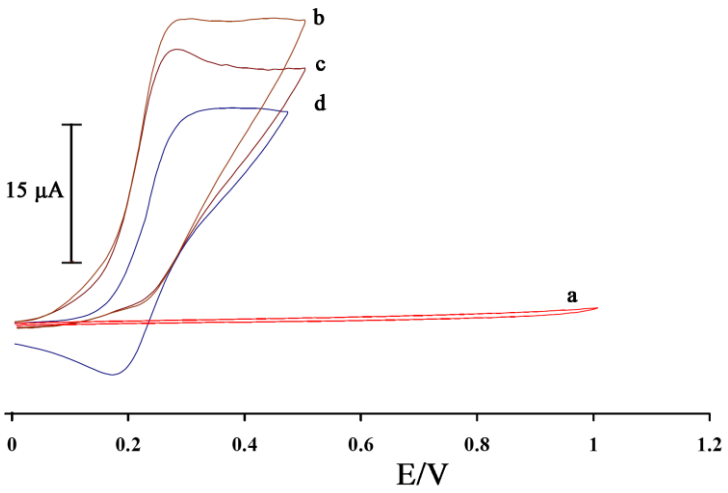



**Figure 3.** Cyclic voltammograms of FCMWCNTs with scan rate of 10 mV $s^{-1}$ in the buffer solution (pH 9.0). (d) In the absence and (b) in the presence of 1.0 mM CAP; (c) as (b) at a surface of FCMCPE. (a) as a (b) for an unmodified carbon nanotubes paste electrode.

In order to get the information about the rate determining step, a Tafel plot was developed for FCMWCNTs using the data derived from the raising part of the current–voltage curve (Fig. 4 insert). The slope of the Tafel plot is equal to $n(1-\alpha)F/2.3RT$ or to 5.9650 V decade$^{-1}$. Using this data gives $n\alpha$ = 0.64. If assuming $n$ = 1, then $\alpha$ = 0.64.

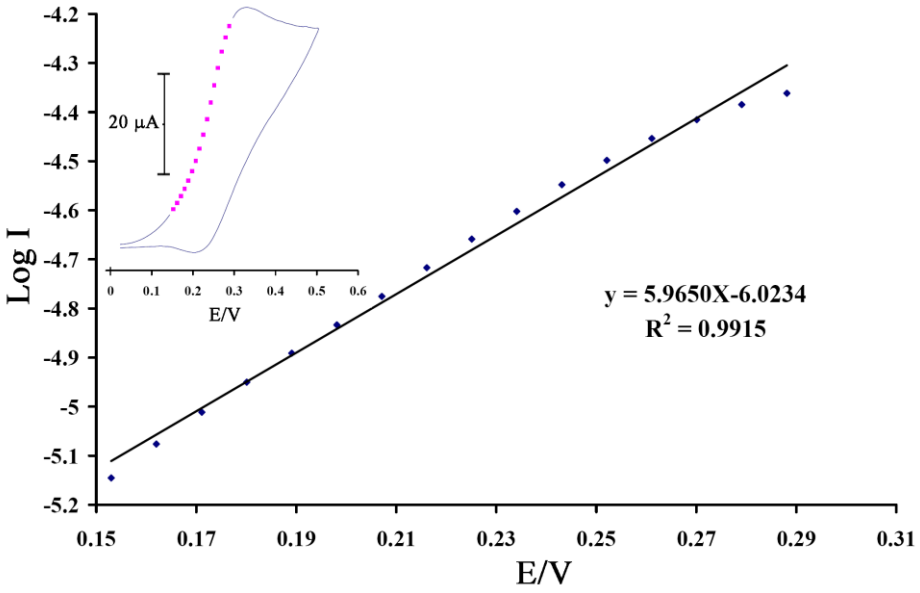



**Figure 4.** Tafel plot for FCMWCNTs in the presence of 1.0 mM CAP in 0.1M phosphate buffer solution (pH =9.0) at scan rate 20 mVs$^{-1}$

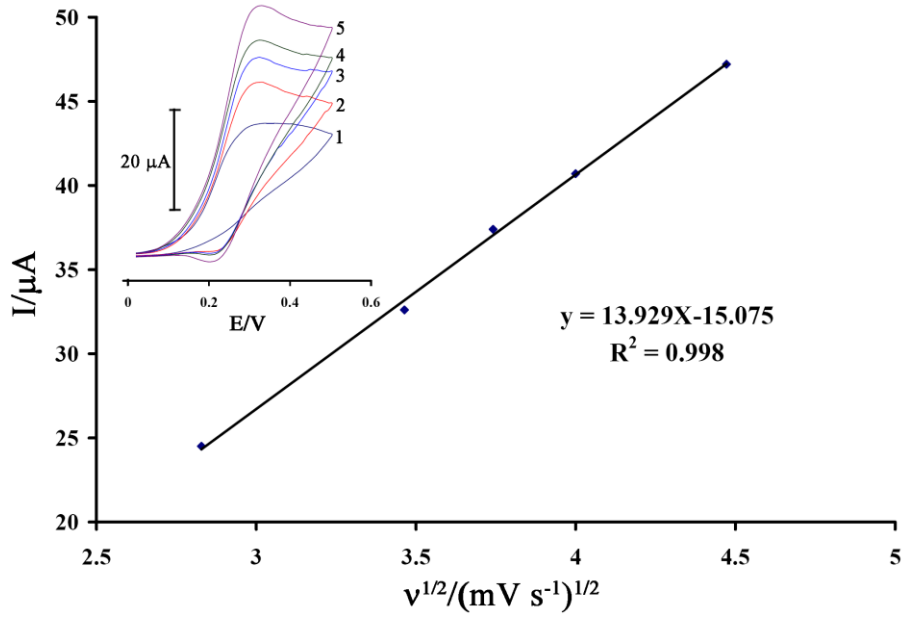



**Figure 5.** Plot of $I_{pa}$ versus $\nu^{1/2}$ for the oxidation of CAP at FCMWCNTs. Insert; Cyclic voltammograms of 1.0 mM CAP at various scan rates; 1) 8.0; 2) 12.0; 3) 14.0; 4) 16.0 and 5) 20 mV s$^{-1}$ in 0.1 mol L$^{-1}$ PBS (pH 9.0).

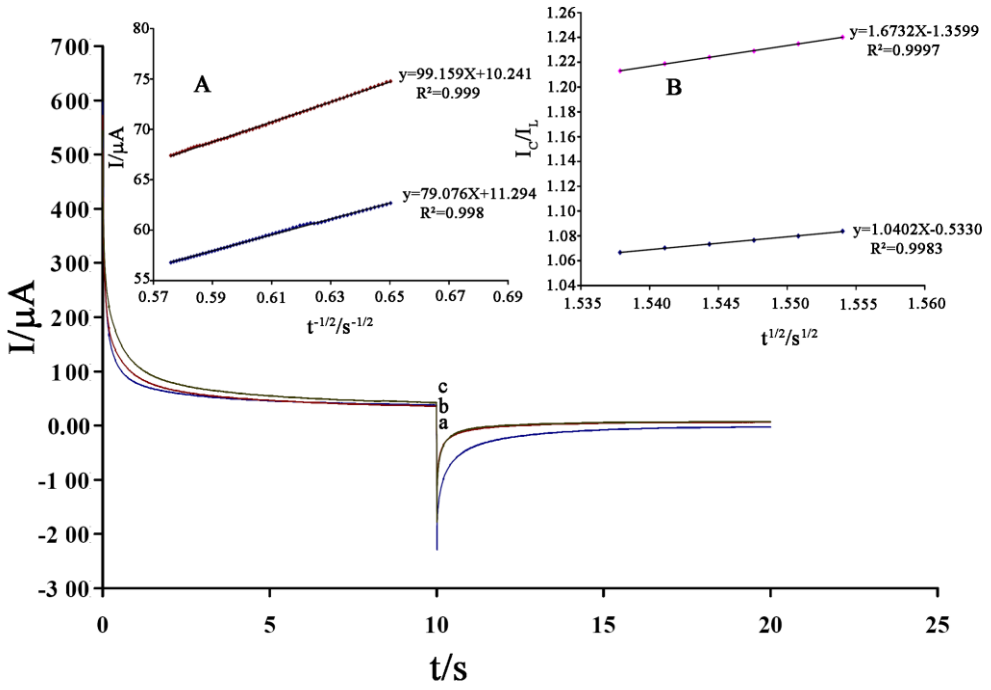



**Figure 6.** Chronoamperograms obtained at the FCMWCNTs in the absence a) and presence of b) 1.0 and c) 3.0 mM of CAP in the buffer solution (pH =9.0). Insert A) Cottrell's plot for the data from the chronoamperograms and insert B) Dependence of $I_c/I_L$ on the $t^{1/2}$ derived from the chronoamperogram data.

The effects of the scan rate on the peak current at the FCMWCNTs in a 0.1 mol $L^{-1}$ PBS was investigated in the range of 8.0–20.0 $mVs^{-1}$ by cyclic voltammetry in the presence of 1.0 mM CAP at pH=9.0 (Fig. 5 insert). The results are shown in Fig. 5. As shown, the peak current increased linearly with the square root of the scan rate, which indicates a diffusion controlled oxidation process occurring at the FCMWCNTs. In addition, with increasing the potential scan rate, the catalytic oxidation peak potential gradually shifts towards more positive potentials, suggesting a kinetic limitation in the reaction between the redox site of the ferrocene and CAP.

### *3.4. Chronoamperometric study*

The catalytic oxidation of CAP by FCMWCNTs was also studied by chronoamperometry. Chronoamperometric measurements using different concentrations of CAP at FCMWCNTs were performed by setting the working electrode potential to 200 mV (step 1) and 500 mV (step 2) (Fig. 6). In chronoamperometric studies, we have determined the diffusion coefficient (D) of CAP. Experimental plots of I versus $t^{-1/2}$, with the best fits for different CAP concentrations, were employed. The slopes of the resulting straight lines were then plotted versus CAP concentrations (Fig. 6, inset A). Using the Cottrell equation and these slope values, we calculated a diffusion coefficient of $4.53 \times 10^{-5}$ $cm^2$ $s^{-1}$ for CAP.

The rate constant for the chemical reaction between CAP and redox sites in FCMWCNTs, $k_h$ can be evaluated by chronoamperometry according to the method described in [45]:

$$I_C / I_L = \pi^{1/2} \gamma^{1/2} = \pi^{1/2} (K_h C_b t)^{1/2} \quad (3)$$

Where $I_C$ is the catalytic current of FCMWCNTs in the presence of CAP and $I_L$ is the limited current in the absence of CAP, $C_b$ is the bulk concentration of CAP (mol $L^{-1}$), $k_h$ and t are the catalytic rate constant ($M^{-1}$ $s^{-1}$) and time elapsed (s) respectively. The above equation can be used to calculate the rate constant of catalytic process ($k_h$). The value of $k_h$ can be simply calculated for a given concentration of substrate from the slope of $I_C/I_L$ versus $t^{1/2}$ plot. The calculated value of $K_h$ is $3.11\times10^2$ $M^{-1}$ $s^{-1}$ using the slope of $I_C/I_L$-$t^{1/2}$ plot (Fig. 6B). This value of $k_h$ explains as well as the sharp feature of the catalytic peak observed for catalytic oxidation of CAP at the surface of FCMWCNTs.

## 4. ELECTROCATALYTIC DETERMINATION OF CAP

Differential pulse voltammetry was used to determine the CAP concentration. Result shows that the plot of peak current versus CAP concentration is comprised of two linear segments with different slopes (slope: 0.2392 μA $\mu M^{-1}$ for the first linear segment and 0.0278 μA $\mu M^{-1}$ for the second linear segment). These correspond to two different ranges of substrate concentration, including 0.5 to 12.0 μM for the first linear segment and 12.0 to 300.0 μM for the second linear segment. The decrease in sensitivity (slope) for the second linear range was likely due to kinetic limitation. The detection limit (3σ) for CAP in the lower range region was found to be 0.15 μM. This value is comparable to those reported by other research groups.

## 5. INTERFERENCE STUDY

The influence of various substances as potential interference compounds on the determination of CAP under the optimum conditions with 5.0 μM CAP at pH = 9.0 was studied.

**Table 2.** Interference study for the determination of 5.0 μM CAP under the optimized conditions.

| Species | Tolerante limits($W_{substance}/W_{CAP}$) |
|---|---|
| $K^+$, $I^-$, SCN. $CO_3^{2-}$. $Br^-$, $NH_4^+$, $Ca^{2+}$, $ClO_4^-$, $SO_4^{2-}$, $SCN^-$, $F^-$, $Cl^-$ | 800 |
| Glucose, fructose, lactose, sucrose, urea, glycine, valine, methionine, lucine, alanine | 500 |
| Starch | Saturation |
| Ascorbic acid, cysteine | 2 |

* Although ascorbic acid is interference, but interference from ascorbic acid can be minimized by using ascorbic oxidase enzyme.

The tolerance limit was defined as the maximum concentration of the interfering substance that caused an error less than 5% for determination of CAP. The results are given in Table 2.

## 6. DETERMINATION OF CAP IN REAL SAMPLES

In order to demonstrate the electrocatalytic oxidation of CAP in real samples, we examined this ability in the voltammetric determination of CAP in tablet and urine samples and these results were compared with spectrophotometric method [46] which is usually used for CAP determination. The results are listed in Table 3.

**Table 3.** Determination of captopril in tablet and urine sample.

| Sample | Added (µM) | Expected (µM) | Founded (µM) | Standard Method (µM) |
|---|---|---|---|---|
| Tablet [a] | --- | 5.0 | 5.11±0.15 | 5.2±0.20 |
| | 10.0 | 15.0 | 14.9±0.11 | 15.3±0.35 |
| Tablet [b] | --- | 50.0 | 50.7±0.85 | 51.1±1.21 |
| | 10.0 | 60.0 | 60.5±0.62 | 60.9±1.15 |
| Urine | --- | <LOD | <LOD | --- |
| | 20.0 | 20.0 | 19.4±0.82 | 19.9±0.79 |

[a] 50 mg tablet, Darou Pakhsh Company, Iran
[b] 25 mg tablet, Darou Pakhsh Company, Iran

For more investigation, we analyzed CAP in patient human urine that has used CAP. However, repelling of CAP was happening from 1─4 h after consumption of the tablet and from 2.5 h this repelling is maximum (see table 4) [30].

**Table 4.** Determination of captopril in human patient urine.

| Sample | Founded (µM) | Standard Method (µM) |
|---|---|---|
| Urine<br>After 1 h | 0.60±0.01 | 0.62±0.22 |
| After 2 h | 1.10±0.05 | 1.30±0.08 |
| After 2.5 h | 2.10±0.10 | 2.30±0.40 |
| After 3.0 h | 1.71±0.12 | 1.95±0.22 |
| After 4.0 h | 1.25±0.11 | 1.29±0.13 |

Those results demonstrated the ability of FCMWCNTs for voltammetric determination of CAP in real samples with the good recoveries of the spiked CAP and good reproducibility.

## 7. CONCLUSION

A carbon paste electrode modified with ferrocene and multi-wall carbon nanotubes has been fabricated and used for electrocatalytic determination of CAP. The electrochemical behavior of FCMWCNTs as a new electrochemical sensor for captopril determination has been studied using cyclic voltammetry, chronoamperometry. The kinetic parameter of the electrocatalytic process and the diffusion coefficients of captopril in an aqueous solution were determined. Finally, this modified electrode was also examined as a selective, simple and precise new electrochemical sensor for the determination of captopril in real samples such as drug and urine.

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