

Full Paper

Magnetite Nanoparticles Impregnated Carbon Paste Electrode as a New Sensing Platform for Voltammetric Determination of Citric Acid in Fruit Juice Samples

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Abstract- In this work, a new method was introduced for citric acid determination in real samples. The method is based on a carbon paste electrode, impregnated with magnetite nanoparticles (Fe₂O₃). The electrocatalytic activity of magnetite nanoparticles-modified carbon paste electrode (Fe₂O₃-CPE) was substantiated utilizing cyclic voltammetry (CV). Performing of CV in different pH values as well as various scan rates resulted in some evidences on the citric acid electrooxidation mechanism. Electrochemical impedance spectroscopy gave obvious indication for the enhancement of charge transfer rate by the magnetite nanoparticles. Various parameters, affecting the electrode performance were studied and optimized. Square wave voltammetry (SWV) method was found to be an appropriate analytical technique to obtain enhanced electrooxidation signal and thus it was adopted as the signal recording method. Using SWV and Fe₂O₃-CPE, a linear dynamic range of 2.5×10^{-5} - 1×10^{-3} mol L⁻¹ as well as detection limit of 1 μmolL⁻¹ was obtained for citric acid determination. Relative standard deviation percent of three repeated determinations was found to be about 4.1%. The developed method was utilized for citric acid amount estimation in different commercial fruit juices samples which led to satisfactory results.

Keywords- Magnetite nanoparticles, Square wave voltammetry, Carbon paste, Fruit juice

1. INTRODUCTION

Magnetite, (iron (II, III) oxide), has an inverse spinel structure in which Fe^{3+} species occupy octahedral and tetrahedral sites, while the rest octahedral locations are filled by Fe^{2+} species [1]. This material shows unique magnetic and electrical characteristics, based on the electron exchange between Fe^{2+} and Fe^{3+} in the octahedral sites. Magnetite (Fe_2O_3) is considered as both n- and p-type semiconductor with a relatively small band gap (0.1 eV) which is quite smaller, compared to other iron oxides. Furthermore, Fe_2O_3 exhibits almost metallic conductivity ranged from of 10^2 to $10^3 \Omega^{-1} \text{cm}^{-1}$. This is assigned to the exchange of electrons between ferric and ferrous cations in the inverse spinel structure described above [1, 2].

As an important nanomaterial, Fe_3O_4 nanoparticles have been widely used in MR contrast agents, protein separation, biosensors, cancer therapy and removal of metal ions [3-5]. Magnetite nanoparticles have also been applied for the design and fabrication of electrochemical sensors [5-9].

On the other hand, some important properties such as stability, reproducibility, wide potential window, low residual current, renewability of the electrode surface and ease of modification with various modifying agents, have made the modified carbon paste electrode (CPE) as an attractive electrochemical transducer [10-14].

Citric acid is a key tribasic acid involved in both plant and animal aerobic respiration and thus it can be found in different natural products [15]. It is naturally exists in several fruits and vegetables such as orange and lemon [16]. Citric acid is mainly used as a preservative and an acidulant agent in industry. Both flavor and aroma of food products is conventionally improved and protected by addition of citric acid in the products. Deterioration of color and flavor of food products, caused by the trace metal ions, existing in the sample, is usually forbidden by adding citric acid in the products. In this case, it functions as the chelating compound to inactivate trace metals ions [16].

Several methods including ion [17], liquid [18] and gas [19] chromatography have been applied for citric acid measurement in different samples. However, these methods are time consuming and in most cases the sample pretreatment and clean-up is required, before the chromatographic analysis. Some other conventional procedures including conductometric [20] and spectrophotometric [21] methods cannot exhibit satisfactory selectivity; because, they are based on the non-specific reaction of carboxylic acid functional groups of the molecule.

As an electrochemical technique, potentiometric method has been utilized for analyses of many species [22-26] also for determination of citrate ion [27,28]. However, voltammetric method is more advantageous, compared to potentiometry, due to its high sensitivity and versatility [29-31]. In this regard, polarographic methods have been reported for citric acid assay [32]; however, the use of polarography technique is now restricted because of potential

toxicity of mercury. Modified platinum electrode [33] as well as boron-doped diamond electrode [34] has been also reported as the electrochemical transducers for voltammetric measurement of citric acid.

In spite of many useful electrochemical properties of conventional carbon based electrodes, they cannot be utilized for citric acid determination; because, CA is not an electroactive compound at these electrodes [35]. Modifying of carbon-based electrodes with an electrocatalyst material such as cobalt phthalocyanine (CoPC) has been proposed as the effective approach for overcome the problem and electrooxidation of citric acid at the carbon-based electrode [36,37].

To the best of our knowledge, this is the first report on the utilization of Fe₂O₃ nanoparticles-modified carbon paste electrode as the effective electrochemical sensor for citric acid determination. Carbon paste electrode, impregnated with magnetite nanoparticles, showed excellent electrocatalytic activity for electrooxidation of citric acid. The electrode showed also acceptable selectivity for target compound of citric acid, making it as a new and efficient sensing device for CA determination in real samples.

2. EXPERIMENTAL

2.1. Instrument and reagents

A potentiostat/galvanostat instrument (Drop Sens (Palm Instruments BV, The Netherlands), interfaced with a laptop, was employed for the voltammetric measurements. The analytical procedures performed by the described electrochemical set were controlled by the Drop Sens PC software (Dropview). A conventional three-electrode system was employed for the cyclic voltammetry (CV) and square wave voltammetry (SWV) measurements. Carbon paste electrode, modified with magnetite nanoparticles, was employed as the working electrode. A platinum rod and a calomel electrode were used as the counter and reference electrodes, respectively. Electrochemical impedance spectroscopy (EIS) was performed using a potentiostat/galvanostat (Netherlands, Ivium VERTEX) that was controlled by IviumSoft (Version 2.422). The above described electrodes were also used in the EIS experiment. The EIS analysis were carried out in the solution of CA (0.5 mmol L⁻¹) and acetate buffer (50.0 mmol L⁻¹, pH=5.5) at frequency range of 100 KHz–0.010 Hz, ΔE_{ac} =200 mV and dc potential of 1.3 V. Stock solutions of CA were prepared by dissolving CA in deionized water and diluting with acetate buffer solution (PH=5.5).

Iron (II, III) oxide (Fe₃O₄) nanopowder (50-100 nm particle size) was purchased from Sigma-aldrich (china). All other chemicals were of analytical grade and were purchased from Merck (Germany). These chemicals employed without further purifications. Deionized water was used throughout this study.

2.2. Preparation of the magnetite nanoparticles-modified electrode

For the fabrication of the magnetite nanoparticles-modified carbon paste electrode ($\text{Fe}_2\text{O}_3\text{-CPE}$), 70 mg of graphite powder was homogenized in a mortar with 5 mg of Fe_3O_4 nanopowder for 10 min. Subsequently, n-eicosane (25 mg) was melted in a dish (at 50 °C) and mixed with the graphite/ Fe_2O_3 blend by a stainless steel spatula. The paste obtained was used to fill a hole (4.0 mm in diameter), located at the end of an electrode. After cooling the paste, the excess of solidified paste was smoothed by a paper sheet. This modified electrode could be reused, after each experiment, only by moving the electrode surface on a paper sheet to eliminate a thin layer of the electrode surface.

2.3. Sample preparation and determination method

Samples of commercial fruit nectars were acquired from local grocery stores. The samples were then centrifuged at 3000 rpm for 10 min. The supernatants obtained were diluted 50-fold with the working buffer (acetate buffer, 0.1 mol L⁻¹, pH=5.5) and then subjected to the measurements. To assay the citric acid level in the prepared samples, the developed electrode ($\text{Fe}_2\text{O}_3\text{-CPE}$) was immersed in the samples and then the solution was stirred at 200 rpm for 100 second. Then, square wave voltammetry method was applied to obtain the analytical signal. The working conditions of SWV method was set as: $E_{\text{step}}=0.01$ V, $E_{\text{amplitude}}=0.09$ V, Frequency=25 Hz, potential scanning range=0.0-1.5 V. The recorded oxidative current peak was used to estimate the citric acid content of the sample with respect to the calibration curve, established before.

3. RESULTS AND DISCUSSION

3.1. cyclic voltammetry study of electrocatalytic oxidation of citric acid at $\text{Fe}_2\text{O}_3\text{-CPE}$

Fig. 1(I) shows the cyclic voltammetry responses of citric acid, recorded using unmodified CPE and the Fe_2O_3 nanoparticles-modified CPE. It can be seen that citric acid exhibits no oxidative peak at unmodified carbon paste electrode between the potential range applied to the electrode (curve "a"). However, at the same condition, application of the $\text{Fe}_2\text{O}_3\text{-CPE}$ to electrooxidation of citric acid gives rise to a well-defined peak at potential of about 1.45 V (*vs.* calomel electrode, curve "b"). Because of absence of any oxidation peak in the absence of citric acid, when applying $\text{Fe}_2\text{O}_3\text{-CPE}$ (curve "c"), it can be deduced that the magnetic nanoparticles are responsible for the facilitated electrooxidation of citric acid on the modified-carbon paste electrode.

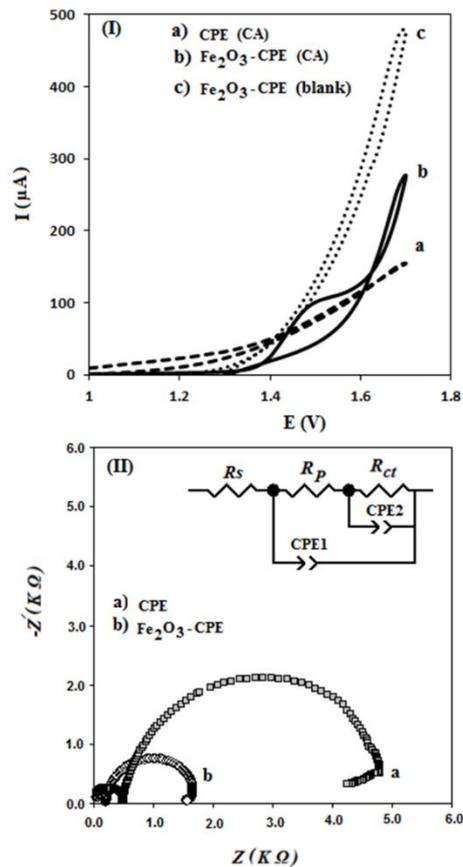


Fig. 1. cyclic voltammetry responses of CPE (a) and Fe_2O_3 -CPE (b, c) to citric acid (a,b) and blank(c); [citric acid] $=1\times 10^{-4}$ mol L^{-1} , concentration of acetate buffer solution $=0.1$ mol L^{-1} (pH=5.5), CV scan rate $=150$ mVs^{-1} (I); Nyquist plots of electrochemical impedance spectroscopy experiment, obtained by unmodified (a) and modified carbon paste electrode in the presence of 0.1 mM of citric acid and 0.1 mM of acetate buffer solution (pH=5.5); equivalent electrical circuit assigned for the electrode surface/solution interface; EIS conditions: applied potential frequency range $=100$ KHz–0.010 Hz, $\Delta E_{ac}=200$ mV, dc potential $=1.3$ V (II)

3.2. Electrochemical impedance spectroscopy study of citric acid electrooxidation

Electrochemical impedance spectroscopy was also used to investigate the electron transfer event on the Fe_2O_3 -CPE. The experiment described was performed in the presence of citric acid. The obtained results are presented as the so called Nyquist plots in Fig. 1(II). It can be seen that the Nyquist plots, obtained using two electrodes of CPE and Fe_2O_3 -CPE, are different significantly; meaning that, the charge transfer behavior is altered as a result of presence of Fe_2O_3 nanoparticles in the electrode composition. The Nyquist plots of both CPE and Fe_2O_3 -CPE exhibit a small and a big semicircles which are appeared, respectively, in high and low frequency regions. The first semicircle is attributed to the bulk resistance (R_b) in

parallel with constant phase element (CPE_1) which normally accounts for conductive pathways across the carbon wax/polymeric particles. The second semicircle is also attributed to the charge transfer resistance (R_{ct}) in parallel with second constant phase element (CPE_2), being as the electrochemical characteristic of the double layer structure, formed at the electrode/solution interface. The impedance data of this combination is obtained at relatively lower frequency region in Nyquist plot, compared to the first combination.

Comparing of the diameters of the second semicircles in the Nyquist plots of two electrodes, which are indications of charge transfer resistance magnitude, shows that the charge transfer resistance of the citric acid is noticeably decreased as a result of the modification of carbon paste electrode with the magnetite nanoparticles.

The results obtained herein are in good accordance with the cyclic voltammetry results, described previously. This means clearly that Fe_2O_3 nanoparticles can act as the electrocatalyst material for electrooxidation of citric acid, when existing in the electrode composition as the modifying agent.

3.3. investigation of the citric acid oxidation mechanism by the cyclic voltammetry

The effect of the scan rate variation (from 10 to 250 $mV s^{-1}$) on the voltammetric properties of Fe_2O_3 -CPE in a solution of 0.5 $mmol L^{-1}$ of citric acid was studied. The results obtained are illustrated in Fig. 2(I), (II) and (III). As can be seen in the Fig. 3(I), the anodic currents of the cyclic voltammograms increase and the related peak potentials shift to positive values, as the scan rate of the potential increases. This observation, suggests a kinetic limitation in the electrochemical reaction of citric acid at the Fe_2O_3 -CPE.

When the peak current values were plotted versus $\nu^{1/2}$ (Fig. 2(II)), a linear relationship with $R^2 = 0.9993$ was obtained in the scan rate range of 50-250 mVs^{-1} . This behavior hints that the oxidation process is ruled by diffusion in the cited scan rate region. To investigate further the electrochemical reaction of citric acid at Fe_2O_3 -CPE, the scan rate normalized current ($I/\nu^{1/2}$) was plotted vs. the scan rate between 10 to 250 mVs^{-1} . The results obtained are illustrated in Fig. 2(III). As can be seen, the scan rate normalized current decreases as the scan rate increases up to 100 mVs^{-1} and after, it keeps relatively constant. This is the typical shape of an *electrocatalytic* (regenerative) EC' mechanism [38].

In order to check the effect of pH on the electrode performance for citric acid electrooxidation, the cyclic voltammetry curves were recorded in different pH values in the presence of fixed concentration of citric acid. Fig. 3(I) represents oxidative current peaks variation as a function of solution pH. It is clear that the signal of CA is affected significantly by the solution pH, leading to appearance of maxima at pH of about 5.5 which is close to pK_{a2} of CA (4.7). We think that the deprotonated form of CA is preferred to be accumulated on the electrode surface, containing magnetic nanoparticles as modifier agent.

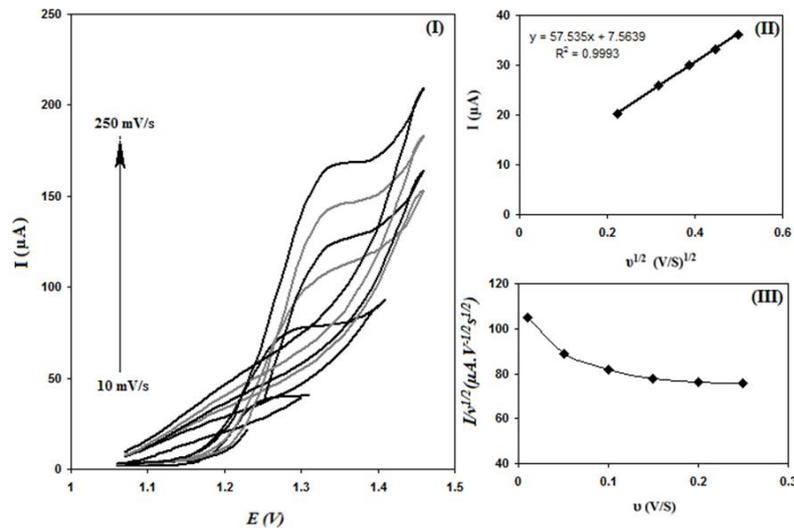


Fig. 2. Cyclic voltammetry responses of 5×10^{-4} mol L $^{-1}$ of citric acid solution, fixed to pH of 5.5, at Fe $_2$ O $_3$ -CPE recorded in various scan rates (I); the plot of peak current versus $v^{1/2}$ (II) and scan rate normalized current ($I/v^{1/2}$) vs. the scan rate (III)

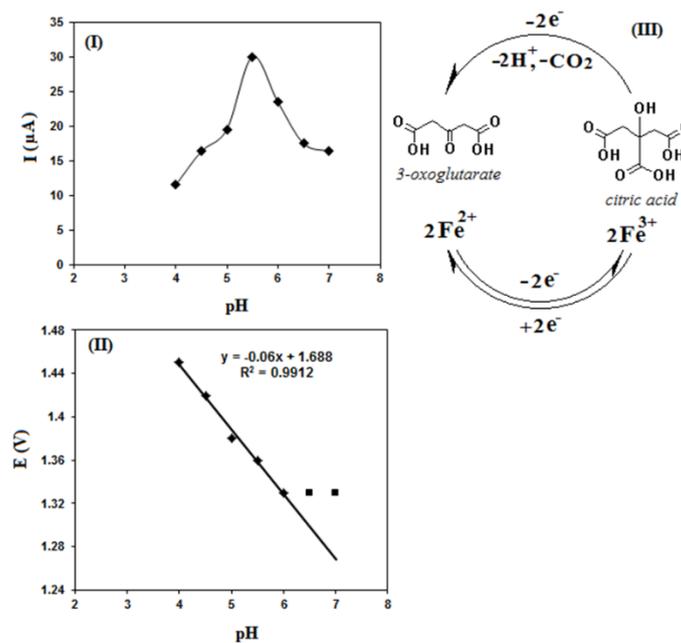


Fig. 3. Dependence of CA oxidative peak current magnitude as well as its related peak potential value for pH of the solution; citric acid concentration = 0.1 mmol L $^{-1}$, potential scanning rate 150 mVs $^{-1}$; schematic representation of citric acid electrooxidation on the Fe $_2$ O $_3$ -CPE

The pH dependence of anodic peak potentials of CV curves, obtained at the Fe $_2$ O $_3$ -CPE, is also represented in Fig. 3(II). As can be seen, the peak potential values decreases linearly with increasing of pH value from pH 4 to pH 6 and then it keeps constant. The linear portion exhibits a slope of 60 mV/pH which is clear indication for the involvement of an equal

number of protons and electrons in the overall oxidation process of CA. Based on the previous reports about the electrochemical behavior of CA [37] and the electrocatalytic activity principal of Fe_2O_3 [39,40] as well as with respect to the results, described above, an electrooxidation mechanism, represented schematically in Fig. 2(III), is proposed for CA electrooxidation on the Fe_2O_3 -CPE. According to the scheme, during the electrochemical reaction at the electrode surface, an electron transfer process happens between Fe^{3+} and Fe^{2+} within the Fe_3O_4 catalysts which is followed by a chemical oxidation of citric acid via the newly created Fe^{3+} (EC' mechanism).

3.4. The effect of the Fe_2O_3 -CPE composition on its performance

During our study it was found that square wave voltammetry led to significantly enhancement in the analytical signal of citric acid at the developed electrode. Therefore, SWV was chosen as the final electrochemical signal harvesting approach in this work. The effect of Fe_2O_3 content of the paste electrode on its SWV response for CA electrooxidation, was evaluated to increase the analytical signal, as far as possible. This was performed by the preparation of several carbon paste electrodes, modified with various amount of Fe_2O_3 , followed by their utilization for electrocatalytic determination of CA via square wave voltammetry technique.

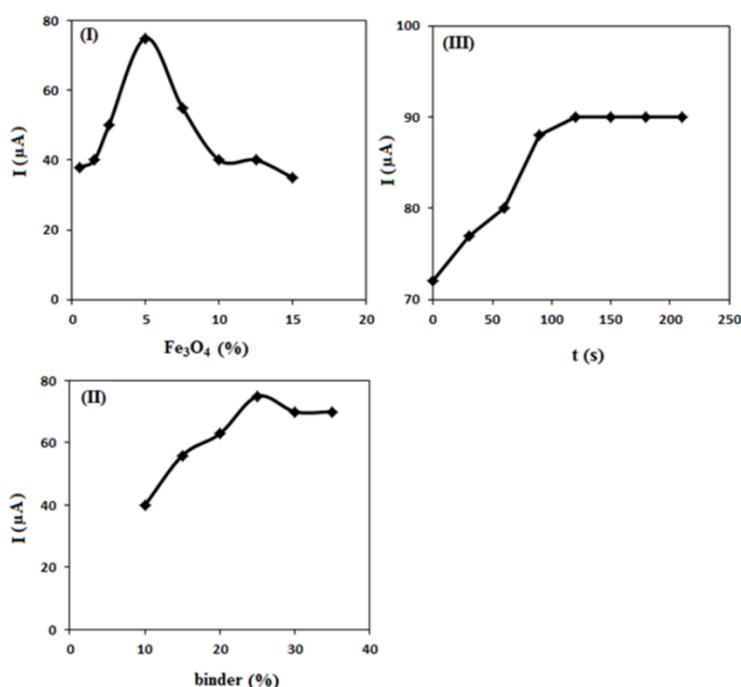


Fig. 4. the effect of Fe_2O_3 (I) and binder (II) contents of the electrode on its SWV response to a fixed amount of citric acid (1 mmol L^{-1}); the effect of the citric acid accumulation time on the SWV signal of the electrode (III)

As shown in Fig. 4(I), increasing of the magnetite content of the electrode, results in an increase in the electrode signal to citric acid. This is because of increasing of the electrocatalytic sites on the electrode surface. However, after a maximum point (5%, magnetite mass /total mass percent), the electrode signal starts to drop with increasing of the magnetite amount of the electrode. The descending part of the curve may also be assigned to the enhancement of the electrical resistance of the electrode as a result of magnetite amount increasing.

Fig. 4(II) shows the effect of binder content of the paste electrode on its electrocatalytic activity for CA. As can be seen, increasing of binder content from 10 to 25 percent (binder mass per total mass percent) leads to a sharply increase in the electrode signal and afterwards, the signal decreases slightly with an increase in the binder content. Based on this finding, the electrode, composed of 25% binder, was chosen as the best electrode for CA electrooxidation.

3.5. The effect of accumulation time on the electrode response

It was found that applying an open circuit accumulation, before electrocatalytic determination of citric acid by the developed electrode, led to significantly enhancement in the electrode response to CA. Fig. 4(III) represent the effect of the accumulation time on the electrode response. As a result of increasing of electrode incubation time, a distinct augmentation can be observed in the electrode response to CA up to about 100 s and then the signal reaches to a steady state. Therefore, an accumulation time of 100 s was adopted for CA analysis by the Fe₂O₃-CPE.

3.6. Analytical Characterization

Fig. 5(I) illustrates the square wave voltammetry signal of various concentrations of citric acid at the optimized Fe₂O₃-CPE. A calibration curve was also plotted based on the represented voltammograms for the aim of determination of CA which is shown in Fig. 5(II). Each point in the calibration curve is the average of three repeated determination signals. As can be seen, there is a good linear relationship ($R^2=0.998$) between the oxidative current responses and CA concentrations in the range of 2.5×10^{-5} - 1×10^{-3} mol L⁻¹. The relative standard deviation percent (RSD%) was also calculated to be 4.1% (n=3). Based on the $3S_b/m$ formula (at which S_b and m stand for standard deviation of the blank and slope of the calibration curve, respectively), the detection limit of the method was calculated to be 6.1×10^{-6} mol L⁻¹. Furthermore, it was found that the signal of Fe₂O₃-CPE to a fixed concentration of CA and at the optimized conditions did not change significantly (confidence level of 95%) after 7 months. It was also observed that the electrode response to a determined concentration of citric acid could be regenerated only by simple polishing of the electrode surface on a paper sheet.

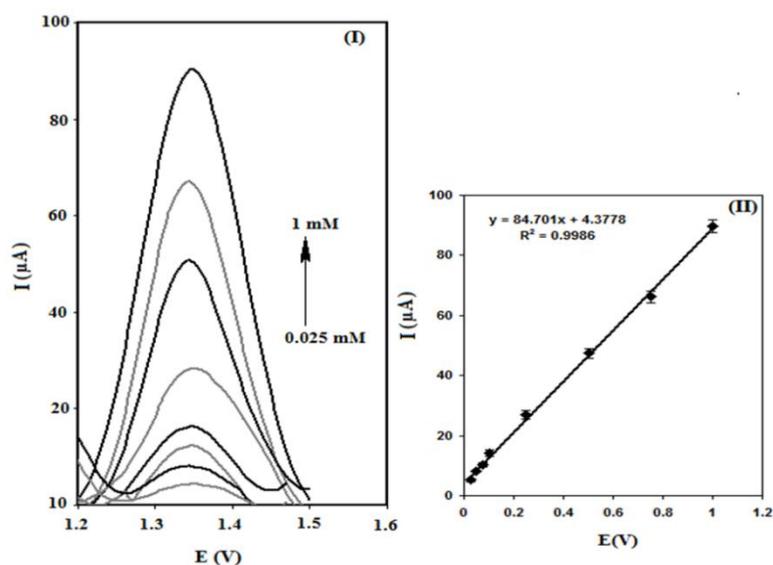


Fig. 5. square wave voltammetry curves obtained for various concentrations of citric acid at the Fe₂O₃-CPE; the calibration curve established for citric acid determination based on the oxidative current peaks of the square wave voltammetry responses

3.7. Interferences study

The interference effect of several compound on the analytical signal of the Fe₂O₃-CPE to CA were examined. It was found that up to 500-fold molar excess of urea, glucose and fructose as well as 12-fold molar excess of lactic acid and ascorbic acid had no significant effect on the electrode response to SA. Both maleic acid and benzoic acid influenced the electrode signal when they were added 10-fold excess to citric acid solution. Tartaric acid and oxalic acid showed their interference effect at 5-fold molar excess. The CA signal at the electrode was not affected by Cd²⁺ up to 15-molar excess. In the case of Ca²⁺ the interference effect was observed when the foreign ion concentration was 10 times higher than citric acid. However, Mg²⁺ and Zn²⁺ were found to be most important interfering agents since they influenced the electrode signal when being higher than 3-fold molar excess. It must be noted that the interference levels of the described species were accepted as the interfering agent/CA concentration ratio (molar ratio) that led to about 5% variation in the electrode response to CA.

3.8. Real sample analysis by the Fe₂O₃-CPE

The optimized electrode, considered as a selective sensor for CA, was employed for citric acid determination in some fruit juices as the real samples. The amount of citric acid in the described fruit juice samples were determined by the method and in order to check the significance of the analysis results, the samples were also spiked with determined amount of

CA and then analyzed again with the electrode. The obtained results were included in table 1. Regarding the recovery results as well as the confidence intervals shown, it is concluded that the method has acceptable merit to be used for CA analysis in the real sample.

Table 1. Determination of CA in Fruits Nectars by the modified electrode (n=3, confidence level=95%)

Sample	Initial value of CA (mM)	CA spiked (mM)	CA found (mM)	Recovery (%)
Mango Nectar	0.050	0.010	0.058±0.003	96.66
		0.050	0.098±0.004	98.00
		0.100	0.148±0.006	98.66
		0.250	0.297±0.011	99.00
		0.500	0.535±0.015	97.27
orange nectar	0.250	0.010	0.251±0.008	96.54
		0.050	0.295±0.009	98.33
		0.100	0.341±0.008	97.42
		0.250	0.493±0.025	98.60
		0.500	0.723±0.031	96.40
Peach Nectar	0.080	0.010	0.086±0.003	95.55
		0.050	0.127±0.005	97.69
		0.100	0.175±0.007	97.22
		0.250	0.320±0.008	96.97
		0.500	0.566±0.013	97.58

4. CONCLUSION

A new citric acid selective electrode was developed based on a modified electrode. The electrode was a carbon paste electrode modified with an appropriate amount of commercially obtained Fe₂O₃ nanoparticles. The capability of magnetite to electrocatalytic oxidation of citric acid was demonstrated using cyclic voltammetry experiments. The effect of Fe₂O₃ on the charge transfer rate enhancement on the modified electrode was also substantiated by electrochemical impedance spectroscopy. Square wave voltammetry was found to be an effective electrochemical technique for citric acid signal recording. The developed electrode was used a new citric acid determination approach in some commercially sold fruit juice samples.

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