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Electrochemical Determination of Mangiferin Using Modified Screen Printed Electrode

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In this research, the utilization of $ZnFe_2O_4$ nanoparticles modified screen printed electrode ($ZnFe_2O_4$ /SPE) was focused on as a sensor to determine mangiferin. The modified electrode performance was examined via the differential pulse and cyclic voltammetric methods. Mangiferin electrochemical behavior in phosphate solution of pH 7.0 was assessed by utilizing unmodified SPE and $ZnFe_2O_4$/SPE. Results indicated that $ZnFe_2O_4$/SPE electrochemical response to mangiferin was considerably advanced. Linear responses were exhibited by $ZnFe_2O_4$/SPE in mangiferin electrochemical oxidation within concentration range 0.1-600.0 μM. The $ZnFe_2O_4$/SPE sensor exhibited suitable response for mangiferin with 0.03 μM (S/N=3) detection limit. $ZnFe_2O_4$/SPE analytical application was tested with favorable results in determining mangiferin in real samples.

Keywords: Mangiferin, Voltammetry, Modified electrode, antioxidants, $ZnFe_2O_4$ nanoparticles

1. INTRODUCTION

Progression in the ethno-pharmacology field has caused surges in the drug industry. Identifying, portraying and pragmatic examinations of indigenous drug ingredients is becoming prominent making it necessary to understand relevant therapeutic and toxic impacts. One of these ingredients under recent close investigation is mangiferin, which is of the xanthone family and is a yellow oxygenated heterocyclic. It has been secluded from an array of plants and Mangiferaindica L [1,2]. Such plants consist of roots, heartwood, stem bark, fruits, and leaves. Various notes on its extraction from, Davalliasolida rhizome, Coffeapseudozanguebariae leaves, Hibiscus miastrum leaves, Cratoxylumcochinchinense leaves, Bersamaengleriana stem bark and Iris nigricans rhizome are also mentioned in the paper. The pharmacological potential of mangiferin has recently attracted significant

and growing attention. Such potentials include possessing effective antidepressant, antiviral, antifungal, antibacterial, anti-diabetic, antitumor, anti-inflammatory, anti-allergic, radio-protective and antioxidant properties. Vast data is available on the pharmacological competencies of mangiferin [3-6].

Today, vast data focusing on purification, isolation and extraction techniques are available that lead to mangiferin from heartwood, roots, fruits and leaves of Mangiferaindica L. Such methods mostly consist of mass spectrometry [7], nuclear magnetic resonance [8], micro-extraction [9] and chromatographic methods [10]. Electrochemical processes are being examined further and may progressively serve as substitutes to spectral and chromatographic methods due to the low costs, speedy analysis time and small size. Furthermore, they provide exceptional sensitivity within a vast useful concentration range for organic and inorganic species [11-20].

Lately, magnetic nanoparticles with custom surface chemistry have been used extensively in numerous application fields including drug extraction [21], magnetic resonance imaging and sensing [22], along with therapeutic uses [23] such as hyperthermia and AC magnetic field based cancer treatment [24]. Such medical and technological uses require super-paramagnetic nanoparticles that are miniature in size and exhibit narrow distribution leading to uniform physical and chemical attributes [25]. $ZnFe_2O_4$ magnetic nanoparticles are spinel ferrite compounds and show higher stability when exposed to air. These particles can be separated by using a magnet [26-28]. Many other applications are also being considered such as photochemical hydrogen production from water and solar energy conversion because of its low costs, suitable stability and light response [29, 30]. Nanostructured materials exhibit particular catalytic, magnetic, electrical and optical properties because of their size, shape and structure which are distinctive compared to that of the bulk counterpart. Thus, nanometer sized materials controlled synthesis is vital for examining the structure property connections of the nano-materials. Moreover, it maintains intrinsic peroxidase like catalytic activity and is implemented in colorimetric biosensors to detect urine glucose [31-37]. Electroanalytical methods have attracted more attention in recent years for environmental and biological compound determination due to their sensitivity, accuracy, lower cost, and simplicity [38-44].

In this paper, the formation of a new screen printed electrode modified with $ZnFe_2O_4$ nanoparticles is explained and its performance to determine mangiferin in aqueous solutions is examined as an original experiment.

2. EXPERIMENTAL

2.1 Apparatus and chemicals

An Autolabpotentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands) was utilized to conduct electrochemical measurements. The General Purpose Electrochemical System (GPES) software was used to control the defined experimental settings. A graphite working electrode, a silver pseudo reference electrode and a graphite counter electrode are the parts that form the screen printed electrode (Drop Sens, DRP-C110, Spain). In order to take PH measurements, a 710 pH meter metrohm was used.

Analytical grade mangiferin was used along with all other analytical grade reagents which were obtained from Merck, Darmstadt, Germany. Orthophosphoric acid was used to prepare buffer solution. The relevant salts were above 2.0-9.0 pH range.

2.2 Preparation of the electrode

$ZnFe_2O_4$ nanoparticles were used to coat the bare screen electrode as presented below. Upon the dispersion of 1 mg of $ZnFe_2O_4$ nanoparticles with ultrasonication for an hour, a stock $ZnFe_2O_4$ nanoparticles solution in 1 ml aqueous solution was arranged while while 2 µl of aliquots of the $ZnFe_2O_4/H_2O$ suspension solution was applied on the carbon working electrodes. The solvent was then left to evaporate at room temperature.

2.3 Preparation of real samples

Upon collecting urine samples, they were promptly kept in a refrigerator. 15 minute at 2000 rpm centrifugation was implemented for 10 ml of the samples. A 0.45 µm filter was used to filter the supernatant. Then, various solution volumes were put into a 25 ml volumetric flask prior to being diluted with PBS of pH 7.0 to the mark. Various volumes of mangiferin were used to spike the diluted urine samples. The proposed method was used to analyse the mangiferin contents via the standard addition method.

3. RESULT AND DISCUSSION

3.1 Electrochemical behaviour of mangiferinat the surface of various electrodes

Mangiferin electrochemical activities are dependent on the aqueous solution's pH value. Thus, the solution pH optimization is vital to acquire favorable results for mangiferin electro-oxidation. Moreover, mangiferin electrochemical behavior was examined via a 0.1 M phosphate buffer solution (PBS) in various pH values in the 2.0-9.0 range by voltammetry at $ZnFe_2O_4$/SPE surface. Results indicated that mangiferin electro-oxidation at $ZnFe_2O_4$/SPE surface is more favourable under neutral circumstances compared to acidic or basic medium state. The optimal pH for mangiferinat was selected at pH 7.0 at $ZnFe_2O_4$/SPE surface. 100.0 µM mangiferin oxidation at the $ZnFe_2O_4$/SPE (Curve a) and unmodified SPE (Curve b) are illustrated in Fig.1 Because of mangiferin oxidation, that is approximately 130 mV more negative compared to the unmodified SPE, the peak potential happens at 300 mV. Furthermore, regarding mangiferin oxidation, $ZnFe_2O_4$/SPE exhibits more anodic peak current in comparison to unmodified SPE which is a sign that unmodified SPE modification with $ZnFe_2O_4$ nanoparticles has considerably enhanced electrode performance towards mangiferin oxidation.

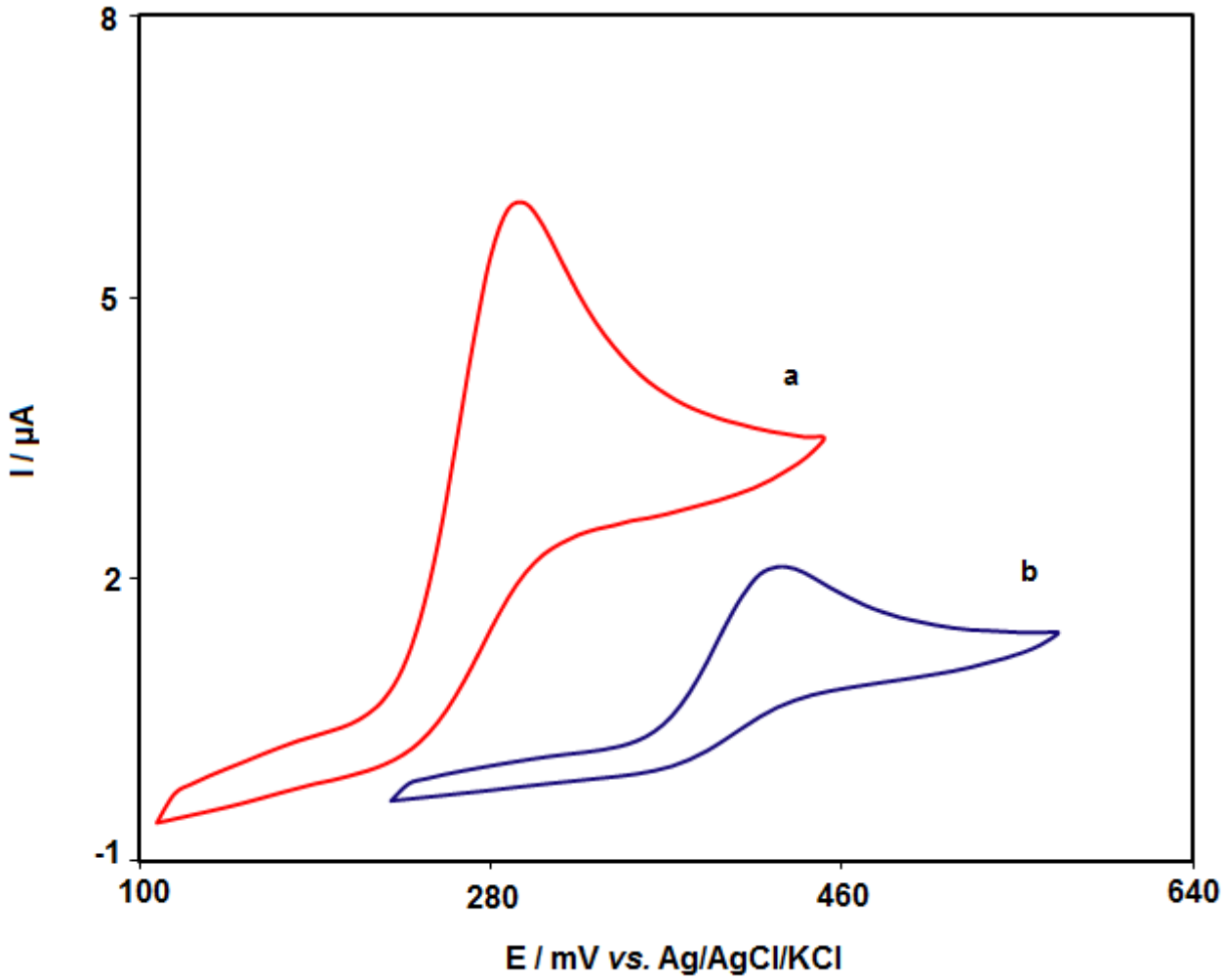

Figure 1. CVs of a) $ZnFe_2O_4$ /SPE and b) unmodified SPE in the presence of 100.0 µM mangiferinat pH 7.0. In all cases, the scan rate was 50 mVs^{-1}.

3.2 Effect of scan rate

Fig. 2 illustrates the impact of potential scan rates on mangiferin oxidation current. Results indicated that the peak current can be increased by increasing the potential scan rate. Additionally, diffusion control is applied to the oxidation processes, as derived from anodic peak current (Ip) linear dependence on potential scan rate ($v^{1/2}$) square root for analyte (Fig. 2A).

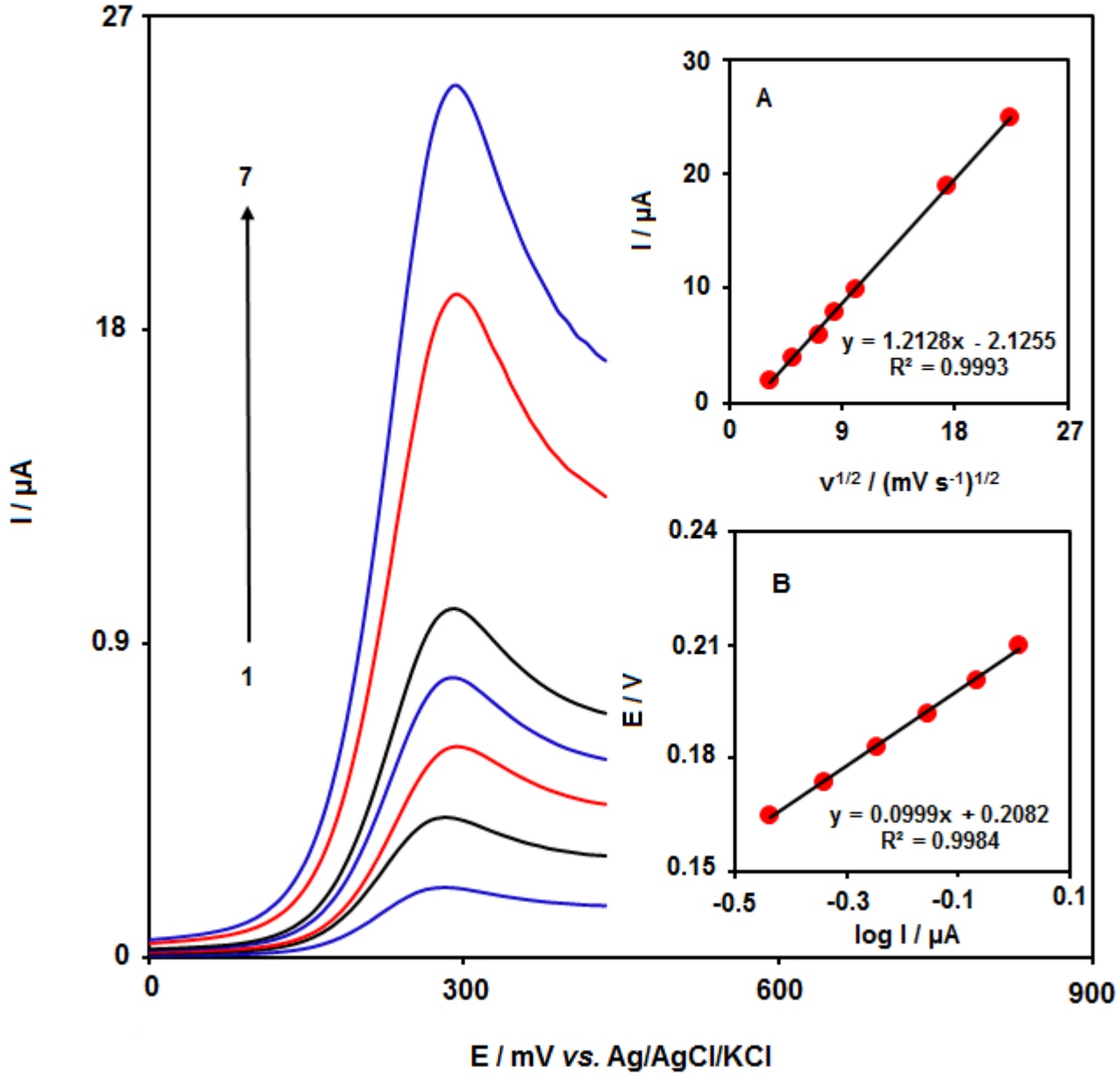

Figure 2. LSVs of $ZnFe_2O_4$ /SPE in 0.1 M PBS (pH 7.0) containing 100.0 µM of mangiferinat various scan rates; numbers 1-7 correspond to 10, 25, 50, 70, 100, 300 and 500 mV s^{-1}, respectively. Insets: (A) variation of anodic peak current vs. square root of scan rate and (B) Tafel plot derived from the LSV at the scan rate of 10 mV s^{-1}.

Tafel plot was drawn from the data of the rising part of the current-voltage curves recorded at a scan rate of 10 mVs^{-1} for mangiferin(Fig. 2B).

Tafel slopes of 0.999 V was obtained, which agree well with the involvement of one electron at the rate determining step of the electrode process [45], assuming charge transfer coefficients $\alpha = 0.41$ for mangiferin.

3.3 Chronoamperometric measurements

Mangiferin at $ZnFe_2O_4$/SPE chronoamperometric measurements was conducted by modifying the working electrode potential at 350 mV vs. Ag/AgCl/KCl (3.0 M) for different mangiferin concentrations as depicted in Fig.3 at PBS (pH 7.0).

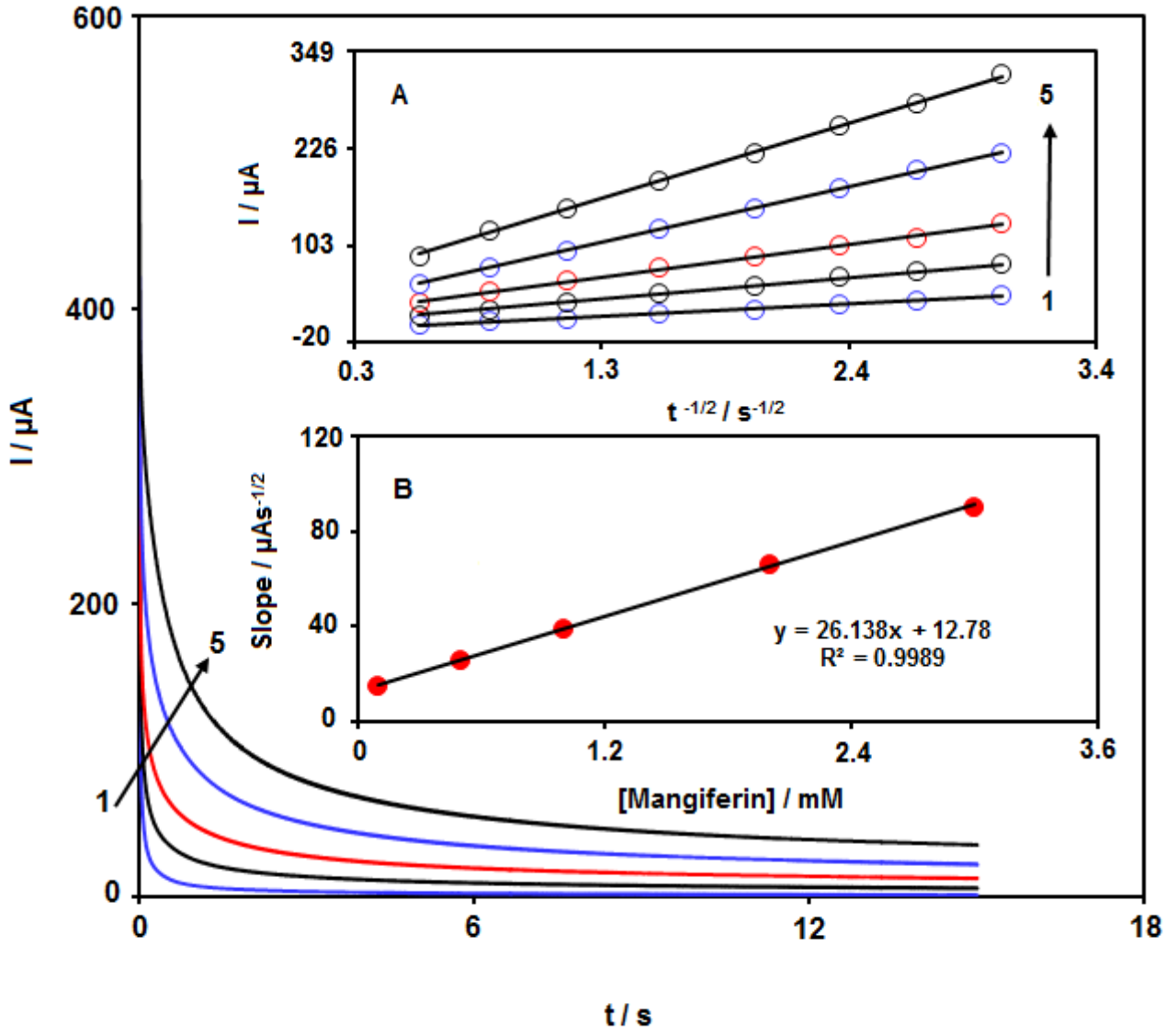

Figure 3. Chronoamperograms obtained at $ZnFe_2O_4$/SPE in 0.1 M PBS (pH 7.0) for different concentrations of mangiferin. The numbers 1-5 correspond to 0.1, 0.5, 1.0, 2.0 and 3.0 mM of mangiferin. Insets: (a) Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms 1-5. (b) Plot of the slope of the straight lines against mangiferin concentrations.

Regarding electro-active materials, in this case mangiferin, with D as the diffusion coefficient, thus electrochemical reaction current at mass transport limited status is presented by the Cottrell equation [1]:

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2}$$

Here, D and C_b are the diffusion coefficient in terms of (cm^2 s^{-1}) and the bulk concentration in terms of (mol cm^{-3}), respectively. I vs. $t^{-1/2}$ test plots were used to determine the most suitable fits for various mangiferin concentrations. The resultant straight line slopes were then plotted versus mangiferin concentrations. The Cottrell equation and resultant slope were used to derive D mean values which was 5.8×10^{-5} cm^2/s for mangiferin.

3.4 Calibration plot and limit of detection

Mangiferin electro-oxidation peak currents at $ZnFe_2O_4$/SPE surface can be utilized for mangiferin determination within the solution. The benefit of differential pulse voltammetry (DPV) is possessing enhanced sensitivity and features for analytical uses [12]. By the use of $ZnFe_2O_4$/SPE in 0.1 M PBS possessing different mangiferin concentrations, DPV experimentation was conducted as presented in Fig.4.

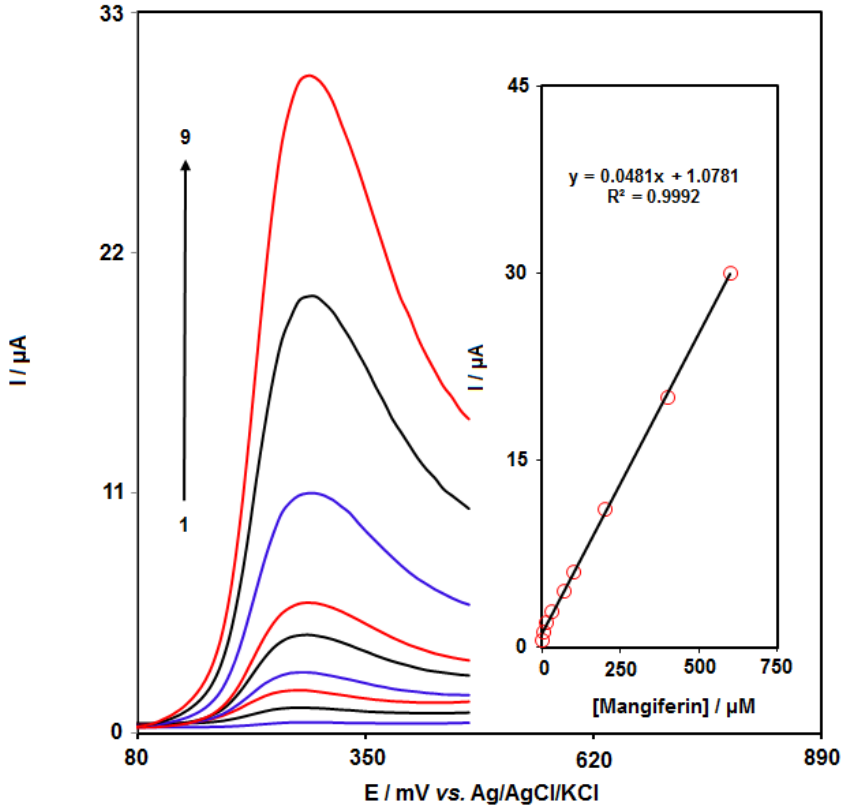

Figure 4. DPVs of $ZnFe_2O_4$/SPE in 0.1 M PBS (pH 7.0) containing different concentrations of mangiferin. Numbers 1-9 correspond to 0.1, 5.0, 15.0, 30.0, 70.0, 100.0, 200.0, 400.0, and 600.0 µM of mangiferin. The inset shows the plot of the peak current as a function of the mangiferin concentration in the range of 0.1-600.0 µM.

Results indicate that for mangiferin peak currents at $ZnFe_2O_4$/SPE surface, there is linear dependency on mangiferin concentrations within range of 0.1-600 μM, with 0.9992 correlation coefficient. The acquired detection limit (3σ) was 0.03 μM. The obtained values correspond to values recorded by other researchers regarding mangiferin oxidation at chemically adjusted electrode surfaces. These results are presented in Table 1.

Table 1. Comparison of the efficiency of some electrodes used in detection of mangiferin.

Electrode	Modifier	LOD	LDR	Ref.
Carbon paste	Graphene nanosheets and an ionic liquid (n-hexyl-3-methylimidazoliumhexafluoro phosphate)	20.0 nM	5.0×10^{-8} - 2.0×10^{-4} M	4
Glassy carbon	Au-Ag nanoparticles (NPs) on multi-walled carbon nanotubes/sulfonated graphene sheets	0.017 μM	0.05-500.0 μM	5
Carbon paste	Chitosan	1.84 μM	2.06×10^{-6} M - 6.74×10^{-5} M	6
Screen printed	$ZnFe_2O_4$ nanoparticles	0.03 μM	0.1-600.0 μM	This work

3.5 The repeatability and stability of $ZnFe_2O_4$/SPE

$ZnFe_2O_4$/SPE long term stability was assessed for a period of three weeks. There were reduction of less than 2.3% in comparison to first response in current and mangiferin oxidation peak potential had no changes. Also, antifouling characteristics of modified electrode for oxidation of mangiferin were examined using CVs. Results showed that after 20 cycles, there were reduction of less than 2.5% in comparison to first response in current and mangiferin oxidation peak potential had no changes.

3.6 Real sample analysis

The proposed method was applied to determine mangiferin in urine sample via the standard addition method for the purpose of assessing the method's analytical applicability.

Table 2. Determination of mangiferin in urine sample. All the concentrations are in μM (n=5).

Spiked	Found	Recovery (%)	R.S.D. (%)
0	-	-	-
5.0	4.9	98	3.1
10.0	10.3	103	2.1
15.0	14.9	99.3	1.9
20.0	20.3	101.5	2.8

Table 2 presents the results for the determination of mangiferin in urine samples. Acceptable recoveries regarding experimental results were obtained for mangiferin and method reproducibility was demonstrated by mean standard deviation (R.S.D).

4. CONCLUSIONS

Mangiferin electrochemical behavioral activities were examined for the first time at $ZnFe_2O_4$ nanoparticles screen printed electrode surface. The recommended modified electrode exhibited minimal detection limit and adequate linear range as well as suitable reproducibility enabling it to be a sufficient mangiferin sensor for practical uses.

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