

Full Paper

A Sensitive determination of Rutin at Fe₃O₄@SiO₂ [FS-MCPE] – A Voltammetric Study

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Received: 26 April 2017 / Received in revised form: 19 May 2017 /

Accepted: 4 June 2017 / Published online: 30 June 2017

Abstract- An electrochemical sensor was developed by decorating a newly synthesized iron oxide magnetite nanoparticle capped silica dioxide (Fe₃O₄@SiO₂ microspheres) on the surface of carbon paste electrode. The developed sensor was further used in the electrochemical determination of Rutin (Vitamin P). Cyclic and differential pulse voltammetric methods were carried out to study the kinetic parameters and the quantitative determination of Rutin respectively. Phosphate buffer solution (0.1 M) with pH 7.5 was used as supporting electrolyte in the present investigation. Various parameters like effect of pH, effect of concentration and effect of scan rate were studied in a systematic manner. A set of cyclic voltammogram redox peaks of Rutin was appeared at 397.2 mV (Epa) and 367.8 mV (Epc). The anodic peak currents were linearly increased with increase in the concentration of Rutin with a dynamic range of 1.6×10⁻⁶-1.6×10⁻⁵ M. The detection limit was calculated and found to be 1.43×10⁻⁶ M. Electrochemical parameters viz., number of electrons transferred (*n*), electrode reaction rate constant (*ks*), and the charge transfer coefficient (*α*), were calculated and found to be 2.0, 0.00149 and 1.09 respectively. Further the developed novel electrochemical sensor was successfully applied for the determination of real samples analysis. The results concluded that the Fe₃O₄@SiO₂ modified carbon paste electrode (FS-MCPE) has showed the long lasting stability, high sensitivity and low detection limits, towards the determination of Rutin.

Keywords- Fe₃O₄@SiO₂, Rutin, Cyclic Voltammetry, Differential pulse Voltammetry

1. INTRODUCTION

Glycosides are bioactive compounds and play an important role in living organisms. Generally they are called as vitamin P and they are clinically well known as antibacterial [1,2], anti-tumor [3], anti-inflammatory [4] and inhibitors in human platelet aggregation [5]. Rutin is one of the most important flavonoid glycosides and it has more anti-oxidant properties [6]. The chemical structure of Rutin (3', 4', 5, 7-tetrahydroxyflavone 3-d-rutinoside) is shown in Fig. 1. Rutin is widely present in plants such as Rutagraveolens, Tartary buck wheat, Flos sophorae and mainly distributed in various parts of plants like buds, leaves, seeds, fruits *etc.* Rutin is used to lower the blood pressure and it can also reduce the capillary permeability of the blood vessel through which some small molecules will flow [7,8]. Thus it is necessary to develop a simple and sensitive technique for Rutin identification and quantification in plants or in pharmaceutical drugs. Many methods were reported for the determination of Rutin such as high performance liquid chromatography (HPLC) [9], chemiluminescence (CL) [10], UV-vis spectrophotometry (UV-Vis) [11], capillary electrophoresis (CE) [12], flow injection analysis (FIA) [13], electrochemical methods [14-16] sequential injection analysis (SIA) [17], derivative technique (DA) [18], Kalman filter approach (KFA) [19] and orthogonal function method (OFM) [20]. The drawbacks associated with some of the above methods are time-consuming, highly expensive, need of well trained technicians to carry out the mechanism and measurements and complications in the extraction of solvents. Since Rutin is an electro active compound, it can be easily subjected to either oxidation or reduction on different kinds of working electrodes such as modified carbon paste electrode (MCPE) [21-24], hanging mercury drop electrode (HMDE) [25,26], modified glassy carbon electrode (MGCE) [27-32], modified carbon ceramic electrode (MCCE) [33], modified gold electrode (MGE) [34] and Fe₃O₄@SiO₂ modified Carbon paste electrode (FS-MCPE). Among all the above electrodes the developed electrode (FS-MCPE) plays better performance towards the detection of Rutin because it possess electrical conductivity, outstanding mechanical strength, high chemical stability and high surface area [35].

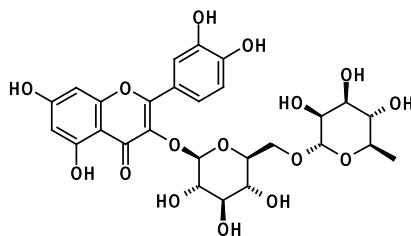


Fig. 1. Molecular structure of Rutin

When compared to other sensors, FS-MCPE is very advantageous due to its chemical stability, biocompatibility, lower limits of detection [36], faster electron transfer kinetics,

more selectivity even with small amount of sample, eco friendly detection, good electro catalytic activity, low price, promptness and versatility in surface qualification. Electrochemical sensors can be developed in small parameters and perfectly suitable for biological samples. FS-MCPE was applied for the determination of Rutin and additionally applied to medicinal samples of Rutin with satisfactory results. Wei Sun et al, [37] investigated the electro oxidation mechanism of Rutin on a pyridinium-based ionic liquid MCPE. Aminate-reduced graphene oxide MCPE was also used as a sensor for sensitive electrochemical determination of Rutin [38]. In the present study, FS-MCPE is used for the determination of electrochemical behavior of Rutin. Although to the best of our knowledge this method was not yet applied for Rutin detection. The advantages of this method are highly sensitive, selective when compared to other analytical techniques, low-cost instrumentation and rapid responses and reduced sample size for the determination of Rutin.

2. EXPERIMENTAL

2.1. Chemicals

All chemicals were of analytical grade reagents and were used without further purification. Rutinhydrate [95% purity], sodium dihydrogen phosphate [NaH_2PO_4], disodium hydrogen phosphate [Na_2HPO_4], silicone oil were supplied from Sigma-Aldrich Laboratories Pvt. Limited, Mumbai, India. Fine graphite powder [particle size is 20 μm] was procured from Hi Media Laboratories Pvt. Limited, Mumbai, India. Iron [III] chloride.hexahydrate [$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$], sodium acetate and ethylene glycol, were purchased from the Fine Laboratories [Pvt. Limited], Mumbai, India. Merk Millipore – Q water system was used to get Millipore water to prepare buffers and other solutions which are used in the experiments. Borosil glassware was used to conduct all the experiments.

2.2. Apparatus

Cyclic and differential pulse voltammetric quantifications were carried with CHI610D (USA) potentiostat with a conventional three electrode cell. Ag/AgCl (saturated) and platinum wire were used as the reference electrode and counter electrode respectively. A bare CPE (3.0 mm diameter) and modified FS-MCPE were used as the working electrodes. Scanning Electron Microscope (Model: EVO ma 15 manufactured by Carl Zeiss) has been used to study the surface morphology. An Elico (LI-120) pH meter was used for pH measurements. All electrochemical measurements were carried out at the room temperature. Sonics Sonicator - XI was used to sonicate the magnetic nanoparticles.

2.3. Synthesis of Fe₃O₄@SiO₂ Microspheres:

The synthesis procedure involves two steps (1) preparation of Fe₃O₄ magnetite nano particles and (2) preparation of Fe₃O₄@SiO₂ microspheres by sol-gel approach.

2.3.1. Preparation of Fe₃O₄ magnetite nano particles

The magnetite nanoparticles (Fe₃O₄) were prepared by using solvo thermal process [39]. Approximately 5.40 g of FeCl₃·6H₂O and 7.20 g of sodium acetate were dissolved in 100 mL of ethylene glycol under vigorous stirring. The resulting homogeneous yellow solution was transferred in to a Teflon-lined stainless steel autoclave, sealed, and heated at 200 °C. After the completion of reaction, the contents were allowed to cool at room temperature. The resulting black magnetite particles were washed several times with ethanol and dried in vacuum at 60 °C for 12 h. The magnetite nanoparticles were 3000 nm diameter in range.

2.3.2. Synthesis of Fe₃O₄@SiO₂ microspheres

The magnetite nanoparticles Fe₃O₄@ SiO₂ microspheres were prepared by following the method in the literature [40]. Fe₃O₄ magnetite nanoparticles (0.10 g) were treated with 0.1 M HCl solution (50 mL) by ultra sonication for 10 min. The magnetite nanoparticles were separated and washed with millipore water. The washed magnetite nanoparticles were homogeneously dispersed in a mixture of ethanol (80 mL), millipore water (20 mL) and aqueous solution of ammonia (1.0 mL, 28 wt %), and it was followed by the addition of tetraethyl ortho silicate (TEOS; 0.03 g, 0.144 mmol). After being stirred for 6 h at room temperature, the Fe₃O₄@SiO₂ microspheres were separated, washed with ethanol and water and dried in vacuum at 60 °C for 6 h.

2.4. Preparation of bare CPE and Fe₃O₄@SiO₂ MCPE

The bare CPE was prepared by hand mixing of graphite powder and silicone oil in the ratio of 70:30 in an agate mortar to acquire a homogenous carbon paste. Then the carbon paste was packed into a hollow of plastic tube with a diameter of 2 mm and smoothed on weighing paper. The modified carbon paste electrode (MCPE) was prepared by the electrochemical deposition of Fe₃O₄@SiO₂ on the surface of CPE. After the electro deposition, the FS-MCPE was placed in dry place to evaporate the solvent. The prepared FS-MCPE was used to perform cyclic voltammetric sweeps in the potential range of 80 mV to 120 mV at the scan rate of 50 mV/s⁻¹ in 0.1 M Phosphate buffer solution (PBS) at pH 7.5.

2.5. Analytical procedure

0.1 M NaH₂PO₄ and Na₂HPO₄ buffer solution (PBS) (pH 7.5) was used as a supporting electrolyte for the determination of Rutin. A stock solution of 0.01 M Rutin was prepared and

diluted to the appropriate concentrations before running the cyclic voltammetric scan. Before each measurement, the three-electrode system was placed in a plain solution and the cyclic voltammetric scan from 50 mVs^{-1} to 500 mVs^{-1} (vs. SCE) was restated individually for six times for the modified electrode. Rutin compound was dissolved in 10 mL of ethanol and then the mixtures were subjected to sonication and filtered.

3. RESULTS AND DISCUSSION

3.1. SEM analysis of the FS-MCPE

SEM analysis gives the surface characteristics and the morphological features of the prepared material. SEM analysis was carried out by using scanning electron microscope (Model: EVO ma 15 manufactured by Carl Zeiss). The surface morphology of bare CPE (A) and FS-MCPE (B) using scanning electron microscopy is showed in Fig. 2. From the figure it was clear that the surface of the bare carbon paste electrode (A) was smooth and randomly shaped with the flakes of graphite. However, $\text{Fe}_3\text{O}_4@\text{SiO}_2$ modified carbon paste electrode (B) has a characteristic regular cluster and spherical arrangement of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ on the surface of the CPE. This confirms that the CPE was deposited by $\text{Fe}_3\text{O}_4@\text{SiO}_2$ particles and leads to the elevation in the surface activity of the FS-MCPE.

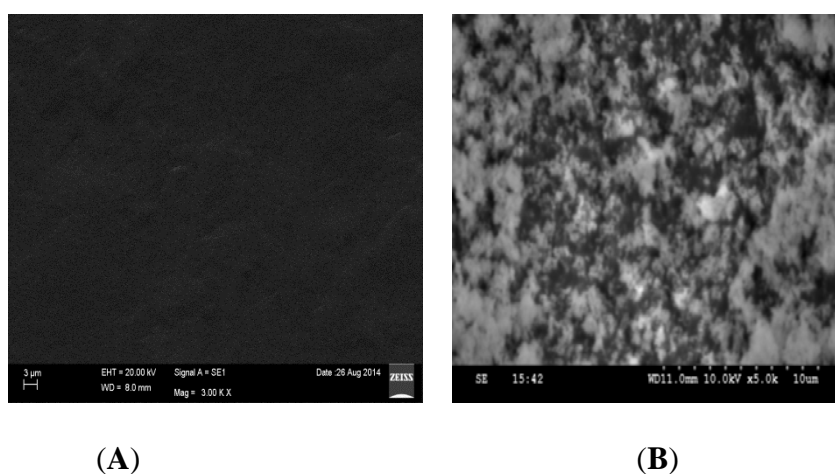


Fig. 2. Scanning electron microscopic images of (A) bare CPE; (B) FS-MCPE

3.2. Electrochemical response of Rutin on FS-MCPE

$\text{Fe}_3\text{O}_4@\text{SiO}_2$ magnetic nanoparticles possess huge surface area and have distinctive magnetic properties. Magnetic nanoparticles are also super paramagnetic, characterized with high magnetic susceptibility and do not show remanence, coercivity and hysteresis. FS-MCPE exhibits excellent electrochemical performance as extensive electrochemical windows, more conductivity, excessive mechanical property and stability [31]. The CV of Rutin with two different working electrodes such as bare CPE and FS-MCPE is shown in Fig.

3. It can be seen that on the bare CPE a couple of redox peak potentials were recorded at 358 mV (E_{pa}) and 322 mV (E_{pc}) (*vs.* SCE). The anodic peak current (I_{pa}) and cathodic peak current (I_{pc}) were recorded at 5.358 μ A and 1.92 μ A respectively, and the redox peak current ratio (I_{pa}/I_{pc}) was calculated. In Fig. 3 Curve b is the cyclic voltammogram of FS-MCPE in 0.1 M PBS. A pair of well-defined redox peak potentials were recorded at 397.2 mV (E_{pa}) and 367.8 mV (E_{pc}) (*vs.* SCE), The anodic peak current (I_{pa}) and the cathodic peak current (I_{pc}) were recorded at 1.906 μ A and 1.29 μ A respectively. The ratio of I_{pa}/I_{pc} was calculated as 1.16 indicating that the electrode process is a reversible process. It is well understood that the increase of the redox peak current and the decrease of the over potential are predictable representations of the electro catalytic reaction.

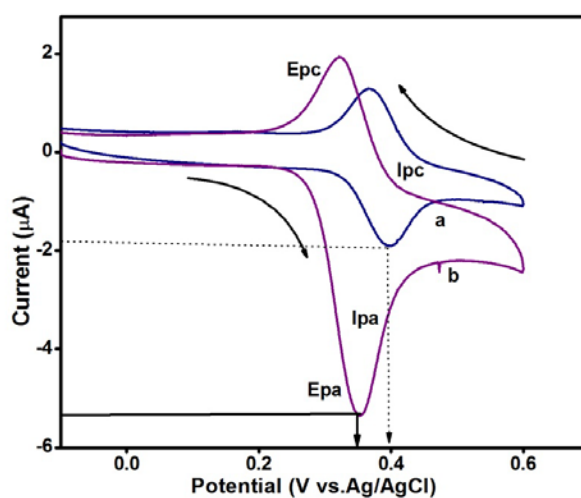


Fig. 3. Cyclic voltammogram of bare CPE (curve a), $\text{Fe}_3\text{O}_4@\text{SiO}_2$ MCPE (curve b) using 0.4 mM Rutin in 0.1 M PBS (pH=7.5) at scan rate of 50 mVs^{-1}

3.3. Effect of scan rate

Fig. 4 shows the CV response for the electro catalytic oxidation of 0.4 mM of Rutin in the presence of FS-MCPE at different scan rates between 50 and 500 mVs^{-1} . The redox peak currents were increased gradually along with the increasing scan rate and it showed a good linear relationship between the anodic peak current and the scan rate (v). The regression equation was $I_{pa}(\text{mM})=5.8733 \text{ Cm}(\text{M/L})+2.214 \text{ mA}(R^1=0.9986)$, $I_{pc}(\text{mM})=5.0719 \text{ CmM/L}+1.477 \text{ mA}(R^2=0.9959)$ between the redox peak currents and the scan rates.

From Fig. 5 it was confirmed that the electrochemical oxidation of Rutin at the FS-MCPE is an adsorption controlled process [41]. In addition to this, E_p values were plotted against logarithmic of the scan rate which is shown in Fig. 6 and it was the kinetic limitation of electrochemical process. According to Laviron theory, the linear slopes of cathodic peak potential (E_{pc}), anodic peak potential (E_{pa}) are $2.3RT/\alpha nF$ and $2.3RT/(1-\alpha) nF$.

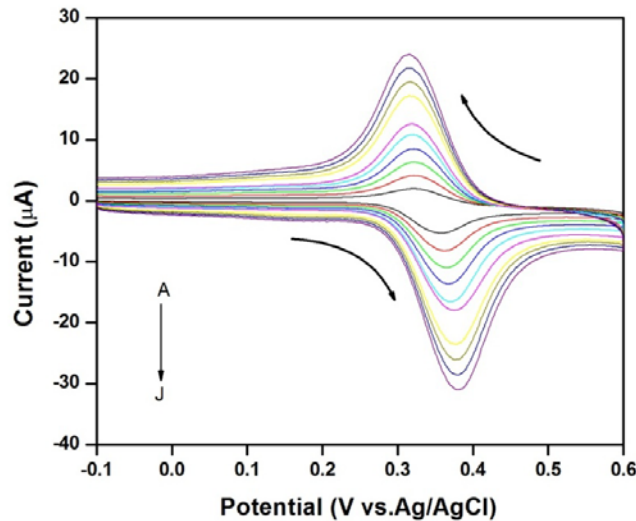


Fig. 4. Cyclic voltammograms obtained for Fe₃O₄@SiO₂ MCPE in the presence of 0.4 mM Rutin in 0.1 M PBS (pH=7.5) with various scan rates (50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mVs⁻¹)

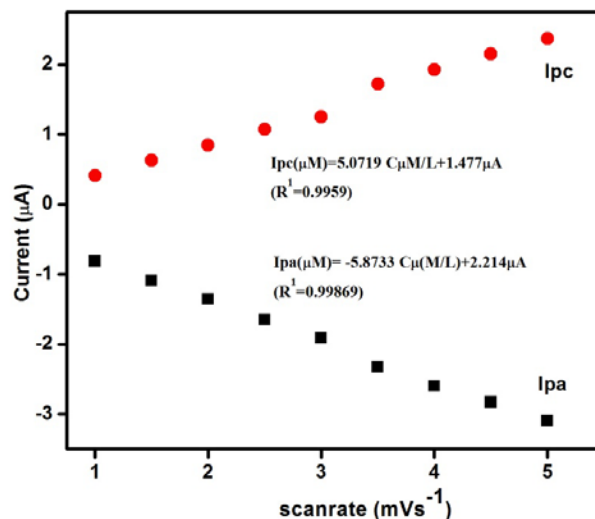


Fig. 5. Calibration plots of cathodic and anodic peak current Vs. various scan rates from 50-500 mVs⁻¹

From Fig. 7 a linear relationship was observed at the scan rate of 350 mV and linear regression equations ($R^1=0.9968$) for cathodic potential (E_{pc}) and ($R^2=0.9994$) anodic potential (E_{pa}) are calculated. The calculated electron transfer coefficient (α) was 1.09. The charge transfer rate constant (k_s) was evaluated using the following Laviron equation [42].

$$\log k_s = \alpha \log(1 - \alpha) + (1 - \alpha) \log \alpha - \log \left(\frac{RT}{nFv} \right) - \alpha(1 - \alpha) \frac{nF\Delta E_p}{2.3 RT}$$

Where, α is electron transfer coefficient, R is the universal gas constant, T is the absolute temperature, n is the number of electrons transferred, k_s is the charge transfer rate constant, F is the Faraday constant and v is the scan rate.

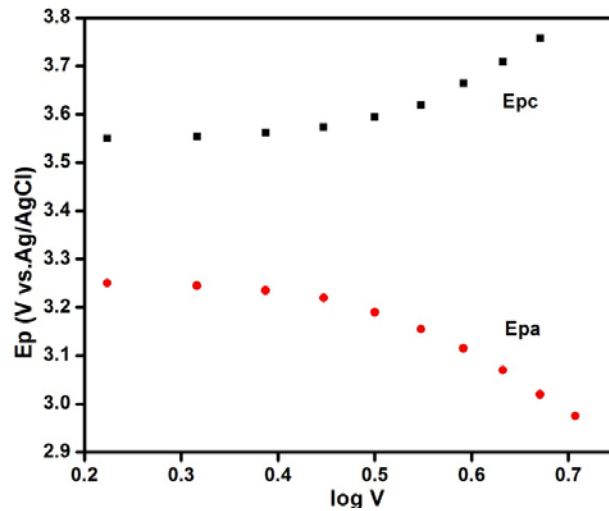


Fig. 6. Plot of variation in the E_p Vs. $\log v$ with scan rates from 50500 mVs^{-1}

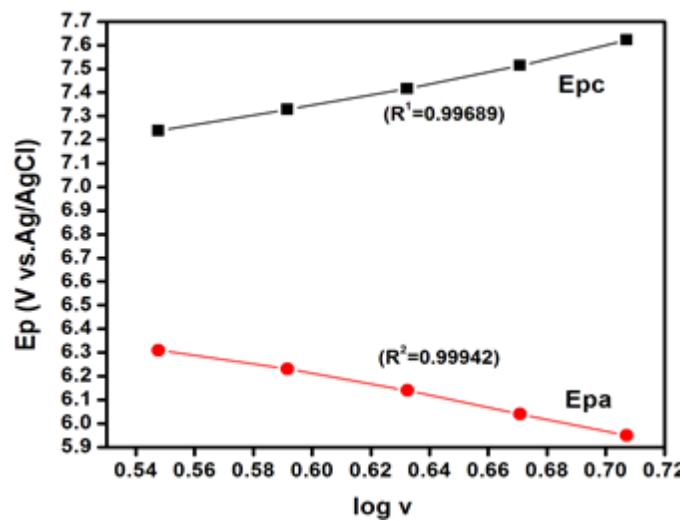


Fig. 7. Linear relationship between E_p values and $\log v$ with scan rates from 350–500 mVs^{-1}

The k_s value was calculated and the value is 0.00149, representing that the electron transfer between the electrode and Rutin was enhanced by the deposition of $\text{Fe}_3\text{O}_4@\text{SiO}_2$. The peak potential difference (E_p) of 29.3 mV was obtained. This is equal to $59/n$ mV, suggesting that the equal number of electrons and protons are involved in the reaction mechanism. From Fig. 8 it was shown that the transfer of two electrons. In Fig. 9 a graph is plotted between E_p and current values and the linear regression recorded is as $R^2=0.9951$.

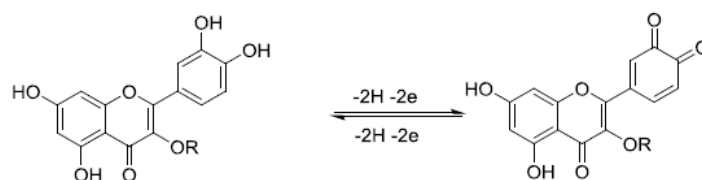


Fig. 8. Electrochemical Redox Mechanism of Rutin

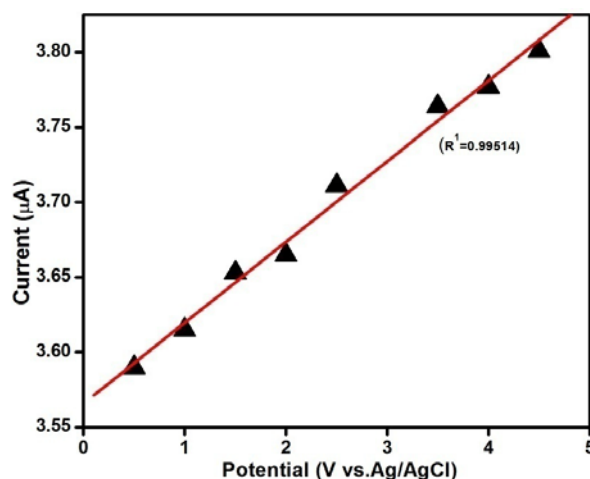


Fig. 9. Calibration plot for oxidation peak current Vs peak potentials of Rutin

3.4. Effect of buffer pH

The effect of buffer pH on the electrochemical responses of Rutin on the FS-MCPE was investigated in the pH range from 5.5 to 8.0 by cyclic voltammetry. From Fig. 10 it was seen that the highest value of reduction peak current was obtained at the pH value of 7.5 and decreased gradually with the increase in pH of PBS. The peak potential was also found to be negatively shifted with the increase of pH value. The results revealed that the proton could involve in the electrochemical reaction. Therefore pH 7.5 PBS was chosen as the favorable supporting electrolyte for Rutin determination in the following experiments. Fig. 11 is a plot of Rutin oxidation peak current Vs. PBS solution pH (6–8) and formal potential Vs. PBS. In the pH range from 6.0 to 8.0, the effect of the buffer pH on the peak potential (E^0) was also investigated. The value E^0 was shifted to the lower direction with the increasing in the buffer pH. A linear regression equation was obtained as E^0 (V) = 0.061pH + 0.8078 ($n=5$, $Y=0.9984$). The slope 0.061 was close to the theoretical value of 0.059 V/pH at 25 °C. According to the equation $0.061x / n = 0.059$, where n is the no. of electrons transfer and x is the number of hydrogen ions participating in the reaction [43]. So the up taking of electron was accompanied by an equal number of hydrogen ions and $x=n=2$.

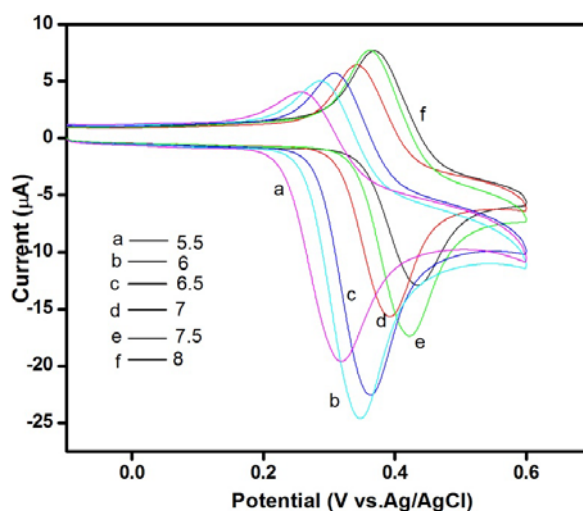


Fig. 10. Cyclic voltammograms obtained at $\text{Fe}_3\text{O}_4@\text{SiO}_2$ MCPE in 0.1 M PBS at pH Value of 5.5 to 8.0

The linearity of formal potential Vs PBS solution pH (6–8) at the scan rate 50 mVs^{-1} is shown in Fig. 12. Based on the results, the possible mechanism for electro-oxidation reaction of Rutin on FS-MCPE was a two electron – two proton processes and the electrode reaction is expressed as follows.

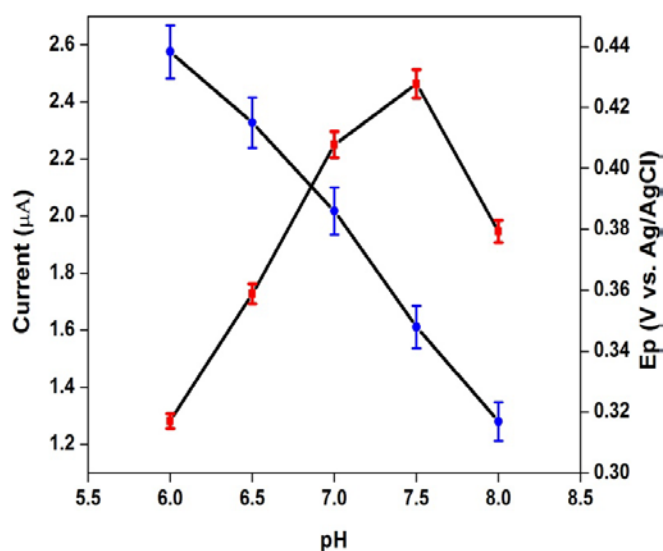


Fig. 11. A plot of Rutin oxidation peak current Vs PBS solution pH (6.0-8.0) and formal potential Vs. PBS solution pH (6.0-8.0) at scan rate 50 mVs^{-1}

In the electro-oxidation mechanism of Rutin first a pre dissociation of a proton takes place to give the monotype anion, which is then oxidized to form a radical anion. The radical

anion undergoes a second reversible one electron ($1e^{-1}$) oxidation to form dehydro-Rutin. The latter species is rapidly dehydrated to yield the final product of 3', 4'-diquinone.

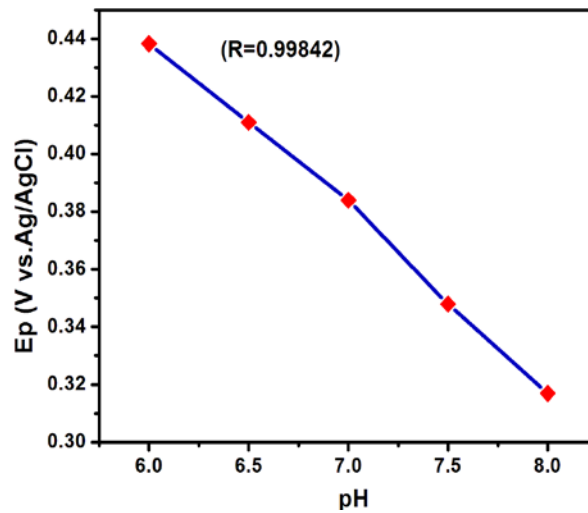


Fig. 12. A linear plot of formal potential Vs PBS solution pH (6.0–8.0) at scan rate 50 mVs^{-1}

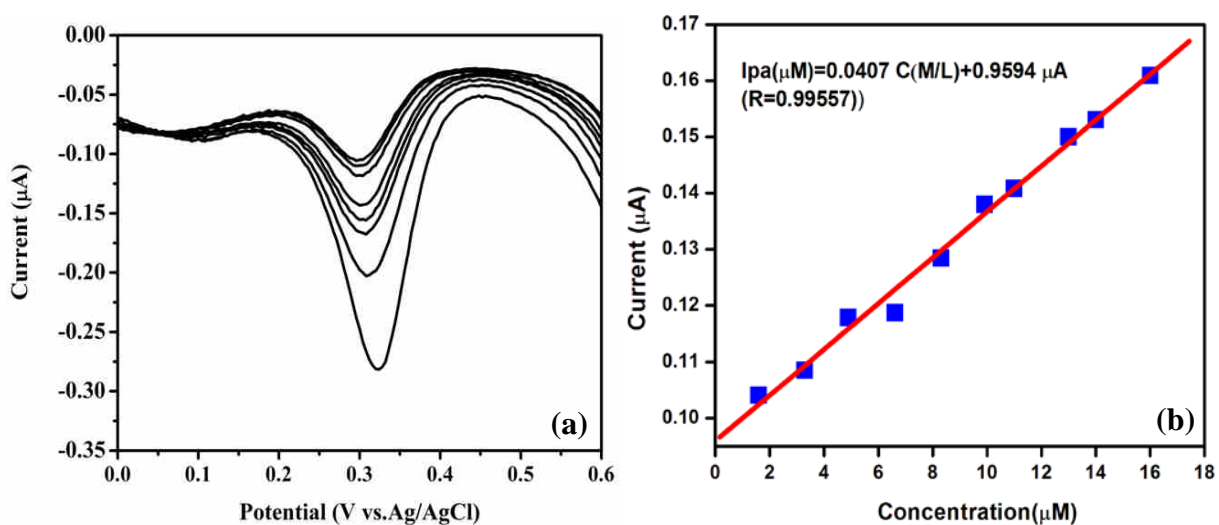


Fig. 13. (a) DPV obtained for $\text{Fe}_3\text{O}_4@\text{SiO}_2$ MCPE due to the addition of 1, 2, 3, 4, 5, 6, 7, 8mM of rutin into 0.1 MPBS (pH=7.0); (b) Calibration plot of oxidation peak current Vs concentration of Rutin (0.4 mM)

3.5. The effect of Rutin concentration

It exhibits the direct determination of Rutin detection limit in the presence of FS-MCPE. The sensitivity of the electrode was determined by using the differential pulse voltammetric technique. Fig. 13b shows the anodic peak current observed at the FS-MCPE at various concentrations of Rutin.

The graph was plotted between I_{pa} against concentration of Rutin which shows the linear dynamic range (LDR) 1.6×10^{-6} - 1.6×10^{-5} M. The linear regression equation for Rutin is expressed as $I_{pa} (\mu A) = 0.95940 C \mu M/L + 1.9 \mu A$ ($R=0.9957$).

The detection limit and quantification limit were calculated by using the formulae [44].

$$LOD = 3 S / M$$

$$LOQ = 10 S / M$$

Where S is the standard deviation, M is the slope obtained from the calibration plots. Then the detection limit of Rutin was found to be 1.43×10^{-6} M.

3.6. Comparison of FS-MCPE with other electrodes

A Comparison was made towards the linear range and detection limit of FS-MCPE with other electrodes for the detection of Rutin and it is shown in the Table 1. By comparing FS-MCPE with other electrodes [45-47] showed that the FS-MCPE is a good electrode due to its high sensitivity and low detection limits towards the determination of Rutin. In addition FS-MCPE was successfully applied for the determination of real samples analysis.

Table 1. Comparison of Linear range and Detection limit of FS-MCPE with other electrodes

Modifier	Linear range	Detection limit, M	Ref.
Chit/ GMGCE	5.0×10^{-5} - 1.04×10^{-5} M	1.0×10^{-6}	[45]
GOMGCE	1.0×10^{-7} - 1.16×10^{-6} M	2.0×10^{-6}	[46]
SWNTMGE	2.0×10^{-8} - 1.0×10^{-8} M.	1.0×10^{-8}	[47]
FS-MCPE	1.6×10^{-6} - 1.6×10^{-5} M.	1.43×10^{-7}	Present work

Table 2. Determination of Rutin in real samples

Sample	Added [mM]	Found [mM]	Recovery [%]	RSD [%]
Apple	0.1	0.098	98.0	3.286
Apple	0.2	0.199	99.5	7.987
Apple	0.3	0.308	102	7.760
Orange	0.1	0.101	101	4.325
Orange	0.2	0.183	91.5	6.358
Orange	0.3	0.295	98.3	9.248
Lemon	0.1	0.093	93.0	8.236

Lemon	0.2	0.197	98.5	9.256
Lemon	0.3	0.285	95.0	5.289

3.7. Real sample analysis

The fabricated sensor was utilized for the analysis of Rutin in real samples like apple, orange and lemon. The method adopted is a standard addition method. The calculated results are summarized in Table 2. As illustrated in the Table 2, the recovery of rutin was between 98.5 and 100.4% using the FS-MCPE. The results demonstrate the capability of the fabricated FS-MCPE sensor for the accurate voltammetric determination of rutin in fruits.

4. CONCLUSION

Rutin manifests a pair of peaks at 397.2 mV (E_{pa}) and 367.8 mV (E_{pc}) at the scan rate of 50 mVs⁻¹ on Fe₃O₄@SiO₂ modified carbon paste electrode in a phosphate buffer of pH 7.5. The electrochemical reaction involves the transfer of two electrons, followed by two protons. The electrode process is adsorption-controlled. FS-MCPE showed both the anodic and cathodic peak current exceptionally. Under the optimized conditions, the anodic peak current was directly proportional to the Rutin concentration in the linear dynamic range of 1.6×10⁻⁶-1.6×10⁻⁵ M with the detection limit of 1.43×10⁻⁷ M. Hence the usage of FS-MCPE is highly selective and sensitive in the determination of Rutin.

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