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Sensitive Determination of Quercetin in Onion Peel by Voltammetry Using a Poly(4-Aminobenzene Sulfonic Acid) Modified Glassy Carbon Electrode

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Abstract- Poly 4-aminobenzene sulfonic acid modified glassy carbon electrode (poly(4-ABSA/GCE)) was prepared with electrochemical polymerization technique in phosphate buffer solution (PBS) (pH 7.0). The modified glassy carbon electrode (GCE), which has high electrooxidation ability in the pH range of 5-10 with cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques, was successfully developed for the electrochemical determination of quercetin (QR). However, the QR or the products of the oxidation reaction are adsorbed strongly on the modified glassy carbon surface. Therefore, when subsequent sweeps of the CV and DPV voltammograms were recorded, a decrease was observed at the peak current and at peak potential there was a shift to a lower positive potential. The best results for the quantitative determination of QR were obtained by DPV technique in 0.1 M PBS (pH 8.0). A linear calibration curve for DPV analysis was constructed in the QR concentration range of 7×10^{-5} to 9×10^{-4} M. The method was applied for the analysis of QR in onion peel.

Keywords- 4-Aminobenzene sulfonic acid, Modified glassy carbon electrode, Electropolymerization, Quercetin, Voltammetry

1. INTRODUCTION

Quercetin (2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxy-4*H*-chromen-4-one) is one of the most abundant natural flavonoids in the plant kingdom (Fig. 1). It is found in many plants and foods such as onions, green tea, apples, berries and red wine. QR has various beneficial effects on human health. It has anti-oxidant, antibacterial, anti-inflammatory, anti-tumor, anti-ulcer, anti-allergy, and anti-viral effects [1-4] and is used in the treatment of cancer, heart and age-related diseases [5]. Therefore, the determination of QR is important for biochemistry, clinical medicine and natural pharmaceutical chemistry. Simple and sensitive electroanalytical methods are preferred for determination of QR.

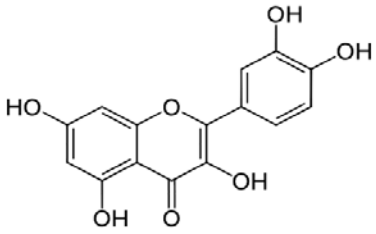


Fig. 1. Chemical structure of quercetin

Several techniques such as novel solid fluorescence method [6], validated HPTLC method [7], isocratic LC method [8], high-performance liquid chromatographic method [9], UV-spectrophotometric analysis [10] and gas chromatography–mass spectrometry [11] have been used for the determination of QR. Electrochemical techniques, which are economic, sensitive and rapid methodologies, have been commonly used to determine QR [12-17]. However, the electrooxidation of QR at carbon electrodes is kinetically slow and requires high overpotentials. Therefore, the use of modified carbon electrodes is preferred for QR oxidation. Chemically modified electrodes were used to enhance the rate of electron transfer and minimize its overpotential. Glassy carbon modified with platinum nanoparticles/poly(hydroxymethylated-3,4-ethylenedioxylthiophene) nanocomposite [18], carbon nanotubes and Nafion [19], a film containing titanium dioxide and a Pt(II)-porphyrin complex [20], and poly(vinylpyrrolidone) [21] are examples of various modified electrodes used in electrocatalytic oxidation of QR.

Poly(4-ABSA/GCE) was used for the determination of phenylephrine and chlorprothixene [22], hydroquinone in the presence of catechol and resorcinol [23], uric acid [24], acyclovir [25], phenazopyridine hydrocloride [26] and Ornidazole [27]. However, the determination of QR at glassy carbon electrode modified with 4-aminobenzene sulfonic acid (4-ABSA) has not been reported to date.

In this study, the direct electrochemical oxidation of QR using glassy carbon electrodes modified by electrochemical polymerization of 4-ABSA was investigated. When the poly(4-

ABSA/GCE) was used as the working electrode, the modified GCE shows high electrooxidation ability for QR in the pH range from 5 to 10. Consequently, QR was successfully determined with a simple, sensitive and rapid method.

2. EXPERIMENTAL SECTION

2.1. Instrumentation

A potentiostat meter (VersaSTAT^3, Princeton Applied Research, USA) was used for the voltammetric measurements. All experiments were carried out in a three electrode system. Glassy carbon electrodes (GCE) (3.0 mm diameter) were purchased from BAS (USA) and used as working electrode. A platinum wire auxiliary electrode and a Ag/AgCl (NaCl 3 M, BAS) reference electrode were also used.

2.2. Reagent and chemicals

QR was supplied by Sigma-Aldrich. A stock solution of 1.0×10^{-2} M of QR was prepared by dissolving an accurate mass in methanol (Sigma-Aldrich) and this was used to prepare the diluted solutions. The working solutions were obtained by dilution with phosphate buffer solution (PBS) (pH 8.0) of the stock solution. 0.2 M PBS (pH 8.) was prepared by mixing appropriate ratios of NaH_2PO_4 H_2O and Na_2HPO_4 (Sigma-Aldrich) of 0.2 M. All solutions were protected from light and were used within 24 h to avoid decomposition. 0.1 M PBS (pH 8.0) was used for the supporting electrolyte solution to investigate the voltammetric behavior of QR. All other chemical substances were commercial Sigma-Aldrich products.

2.3. Polishing and cleaning of GCE

The GCE was polished successively in 1 μm, 0.3 μm, and 0.05 μm alumina slurries made from dry Buehler alumina and ultra pure deionized water on Buehler polishing microcloth. The polished GCE was sonicated in Nanopure water, in a mixture of 1:1 (v/v) nitric acid/water (HNO_3+H_2O) (Fluka) and then in ethanol (Aldrich) for 10 min each. Before the derivatization, the cleaned GCE was rinsed with water and dried under a stream of argon.

2.4. Derivatization of GCE

The surface derivatization of the bare GC electrode was performed using 0.10 M PBS (pH 7.0) containing 2.0×10^{-3} M 4-ABSA. The 4-ABSA solution was deaerated with argon for at least 10 min before the derivatization. Then, the bare GCE was immersed in the 4-ABSA solution. The derivatization of the GC surface was performed using cyclic voltammetry at a scan rate of 100 mVs^{-1} for five cycles between -1.5 and +2.5 V. Finally, the modified electrode was activated by cyclic voltammetry from -1.0 to +1.0 V at a scan rate of 100 mVs^{-}

[1] for ten cycles in 0.10 M PBS (pH 7.0). Consequently, a bare GC electrode and modified GC electrode were used as working electrode.

2.5. Calibration graph for quantitative determination

The stock solution of 10^{-3} M QR was prepared by dissolving an accurate amount of the substance in methanol and diluted with 0.1 M PBS (pH 8.0) to obtain the different QR concentrations. Using the optimum conditions described in the experimental section, a linear calibration curve for DPV analysis was constructed in the QR concentration range from 7×10^{-5} M to 9×10^{-4} M. The repeatability, accuracy and precision were checked. The QR amount in onion peel was determined.

2.6. Extraction of QR from onion peel

Onion peel with mass of 20 g was boiled for 1 h in 1 L pure water. After filtration, the solution was left at room temperature for 24 h. The precipitated pigment was recrystallized with ethanol. A QR sample of 0.13 g was obtained. This sample was used for detection of QR in onion peel.

3. RESULTS AND DISCUSSION

3.1. Electropolymerization of 4-ABSA at the GCE Surface

The cyclic voltammogram of 10 cycles recorded in 0.10 M PBS (pH 7.0) containing 4-ABSA of 2.0×10^{-3} M for electrochemical polymerization of 4-ABSA on the GCE surface is given in Fig. 2. In the first cycle, a weak anodic and cathodic peak were observed with peak potential value at E_{pa}=1.70 V and E_{pc}=-0.60 V, respectively.

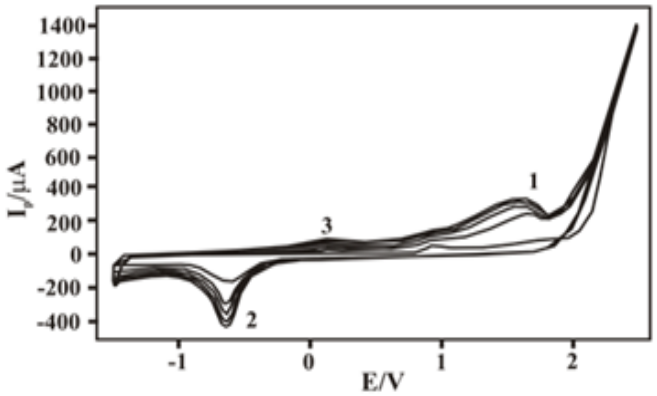
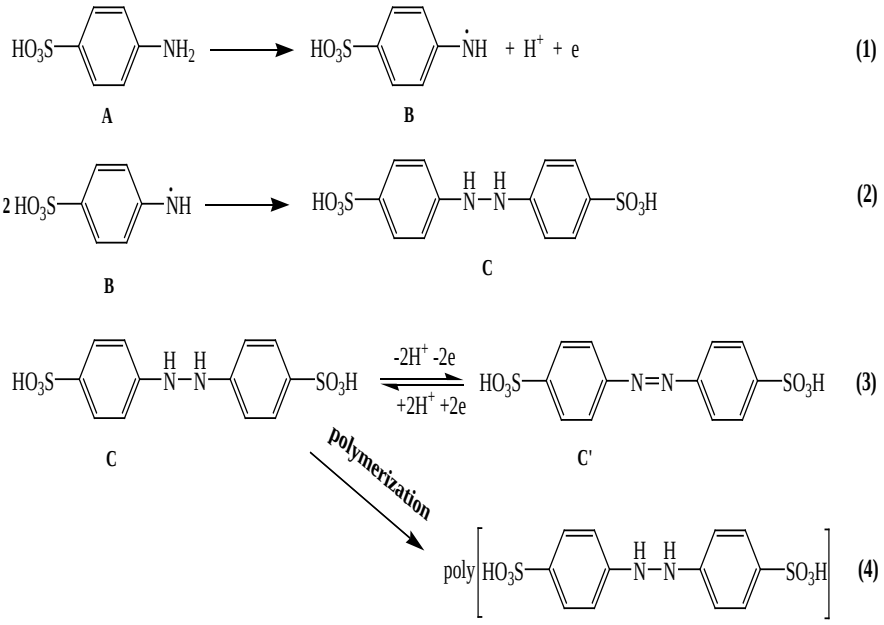


Fig. 2. The cyclic voltammogram of 10 cycles for the solution in 0.10 M PBS (pH 7.0) of 4-ABSA of 2.0×10^{-3} M in the potential range from-1.5 V to +2.4 V (Scan rate 100 mVs^{-1})

The two anodic peaks in the second cycle of the voltammogram appeared at peak potential values of +0.13 V and +1.45 V, respectively. The peak current increases during the subsequent cycles. This behavior reflects the continuous growth of the polymerization film. GCE surface was modified with a blue polymer film [22-27]. The poly(p-ABSA) modified electrode was thoroughly washed with double-distilled water and stored in 0.1 M PBS (pH 7.0) before use.

The mechanism proposed for the electropolymerization behavior of 4-ABSA at GCE is given in Scheme 1 [25].



Scheme 1. Proposed mechanism for electrochemical polymerization of 4-ABSA on GCE surface

p-ABSA (A) was oxidized to free radical (B) (peak 1). (B) was combined rapidly to form hydrazobenzene sulfonic acid (C). (C) was oxidized to azobenzene sulfonic acid (C´) (peak 3). (C´) was reduced to (C) (peak 2). In the end, the electrode surface was covered with the formed polymer film (D).

3.2. Electrochemical oxidation of QR on 4-ABSA modified glassy carbon electrode

The electrochemical responses to QR on the bare GC and 4-ABSA modified GC were studied by using cyclic voltammetry. The cyclic voltammograms of 7×10^{-5} M QR at GCE (a) and the poly(4-ABSA/GCE) (b) at pH 8.0 in PBS at 100 mVs^{-1} are given in Fig. 3.

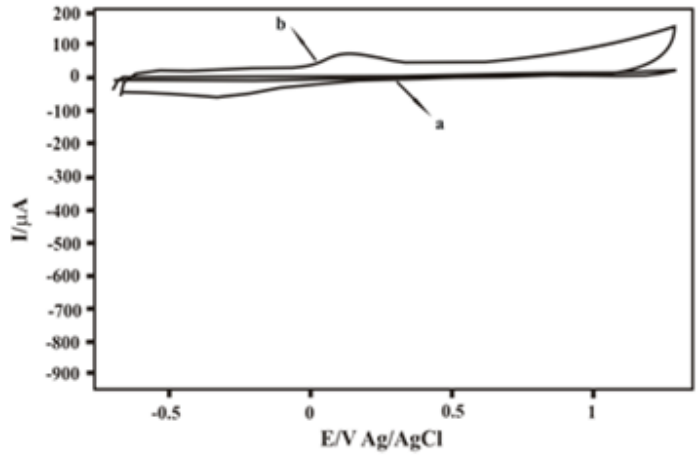


Fig. 3. Cyclic voltammograms of 7×10^{-5} M QR at 4-ABSA modified glassy carbon electrode (a) and bare GC (b) at pH 8.0 in 0.1 M PBS at scan rate 100 mVs^{-1}

At the bare GC electrode, QR creates a featureless voltammogram (Fig. 3a). The smaller CV peak for QR was observed at the GC electrode and the CV oxidation peak was at negative potential, whereas use of the poly(4-ABSA/GC) electrode led to an increase in the CV peak and the oxidation peak potential shifted to more positive values.

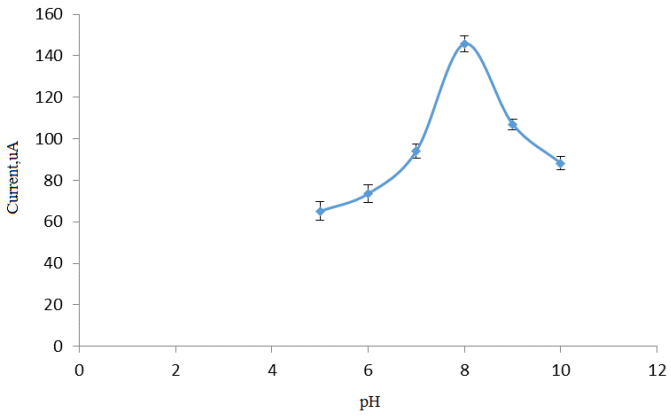


Fig. 4. Dependence of the oxidation peak current of 1×10^{-3} M QR on pH values in 0.1 M PBS buffer, at a scan rate of 100 mVs^{-1}

The peak current and peak potential values recorded at the GC electrode were 6.87 µA and 71.96 mV, respectively. However, at the poly(4-ABSA/GC) electrode these values were observed to be 58.76 µA and 117.97 mV, respectively (Fig. 3b). Consequently, in comparison with the data recorded from the bare GC electrode, an increase in peak current and a decrease in overpotential of QR were obtained at modified GC electrode. Therefore, it was assessed as an electrocatalytic effect for the oxidation of QR on the modified surface.

The pH of the QR solution was changed using buffer solutions ranging from pH 5.0 to 10.0 and its effect on the electrochemical signal was investigated (Fig. 4). The oxidation peak current of QR increased at pH 8.0. Therefore, pH 8.0 was selected for further studies.

When the cyclic voltammogram in the potential range from -0.7 V to 1.3 V in 0.1 M PBS (pH 8.0) at the poly(4-ABSA/GC) electrode was investigated, the oxidation peak is observed at about 0.22 V (Fig. 5). Fig. 5a shows the cyclic voltammogram obtained from the first sweep of QR of 3×10^{-4} M in 0.1 M PBS (pH 8.0) at the poly(4-ABSA/GC) electrode. However, the peak current of the cyclic voltammogram obtained from the second sweep at the modified GC electrode was found to be less than the peak current of the cycle voltammogram obtained from the first sweep and the oxidation peak of QR shifted to more negative values on the modified surface (Fig 5b). The peak current in the subsequent sweeps decreased even more. This behavior was evaluated as the inhibition of oxidation due to the strong adsorption of the reactive or the products of oxidation reactions on the modified GC surface. Therefore, the data recorded from the first experiments of the other voltammetric studies were used for the detection of QR.

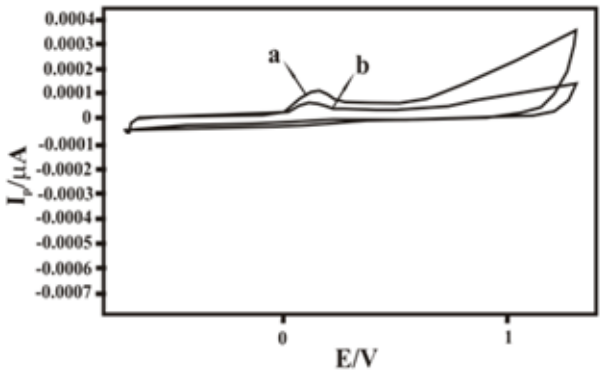


Fig. 5. The cyclic voltammograms were recorded in the potential range from -0.7 V to 1.3 V in 0.1 M PBS (pH 8.0) at the poly(4-ABSA/GC) electrode **(a)** The first sweep **(b)** The second sweep (Scan rate, 100 mVs^{-1})

3.3. Assay of QR

The assay of QR at poly(p-ABSA)-modified GCE was completed with the DPV technique. The following parameters were used for DPV voltammograms recorded in the oxidation potential range from -0.7 V to +1.0 V: pulse amplitude, 50 mV; pulse time, 0.08 s; voltage step, 9 mV and voltage step time, 0.1 s. Under the experimental conditions, the assay of QR with various concentrations was performed (Fig. 6).

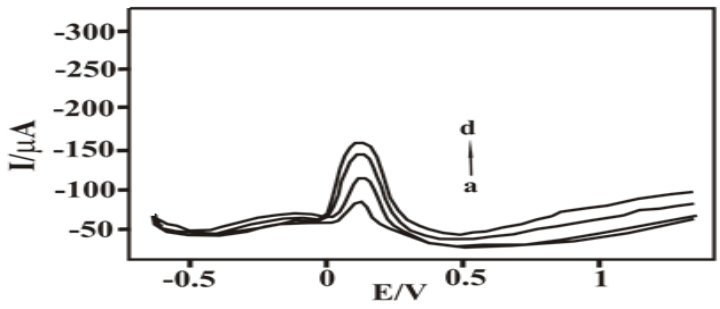


Fig. 6. DPV voltammograms recorded at the poly(4-ABSA/GC) electrode for increasing concentrations of QR in 0.1 M PBS (pH 8.0); a) 7×10^{-7}; b) 9×10^{-7}; c) 3×10^{-4}; d) 7×10^{-4} M

From current and concentration data of these voltammograms, a linear calibration curve was constructed for QR in the range 7×10^{-5} to 9×10^{-4} M in 0.1 M PBS (pH 8.0) supporting electrolyte (Fig. 7).

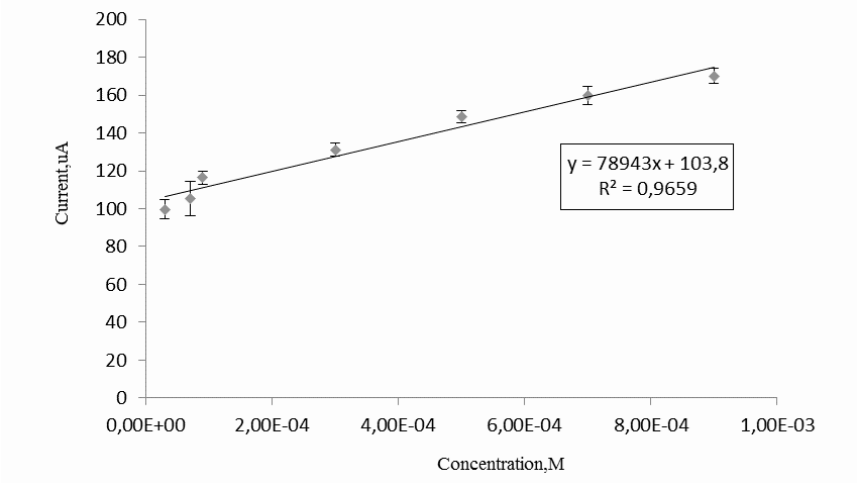


Fig. 7. Plot of concentration versus current obtained from DPV voltammograms of QR in the concentration range from 7×10^{-5} M to 9×10^{-4} M in 0.1 M PBS (pH 8.0) at poly(4-ABSA/GCE)

The plot obtained was linear in the concentration range of 7×10^{-5} to 9×10^{-4} M QR. For the regression plot of the peak current versus QR concentration, the slope was 7.89×10^{4} μA/M, the intercept was 103.8 μA and the correlation coefficient was R^2=0.966.

3.4. Analytical applications

The DPV voltammogram recorded at poly(4-ABSA/GCE) of the QR sample is given in Fig. 8.

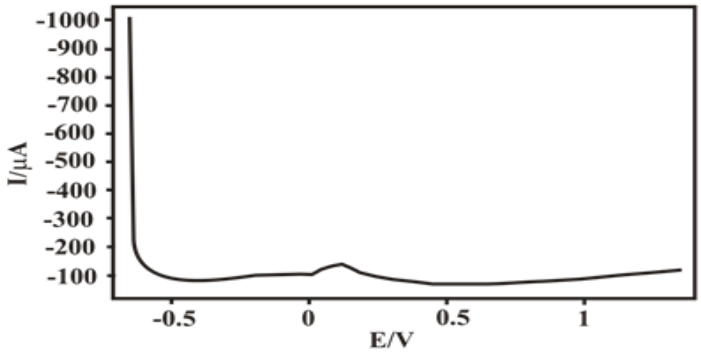


Fig. 8. The DPV voltammogram recorded at poly(4-ABSA/GCE) for QR sample of 0.0082 g dissolved in 10 mL of 0.1 M PBS (pH 8.0)

Onion peel of 20 g was boiled for 1 hour in 1 L pure water. After filtration, the solution was left at room temperature for 24 h. The precipitated pigment was recrystallized with ethanol. A QR sample of 0.13 g was obtained. This sample was used for the detection of QR in onion peel.

Table 1. Calibration data for assay of QR by DPV. SD is standard deviation

Parameters	**Results**
Measurement potential, V	0.220
Linear concentration range, M	7×10^{-5} to 9×10^{-4}
Slope, μAM^{-1}	78943
SD of slope	1861
Intercept, nA	103.80
SD of intercept	0.041
Coefficient of correlation, r	0.9659
Number of measurement, n	4
LOD, M	2.03×10^{-5}
LOQ, M	6.08×10^{-5}

When the DPV voltammogram of the QR sample extracted from the onion peel was recorded, the oxidation peak of QR was observed at about 0.11 V and it was understood that there was no interference. Fig. 8 shows the DPV voltammogram at poly(4-ABSA/GCE) of

the QR sample of 0.0082 g dissolved in 10 mL of 0.1 M PBS (pH 8.0). The values of the peak potential and the peak current are 0.109 V and 137.28 µA, respectively.

Table 2. Assay of QR in onion peel and mean value at poly(p-ABSA)- modified GCE by DPV method. RSD is relative standard deviation

Parameters	**Results**
Onion peel sample, g	0.13
Found QR % (w/w)	13.414
RSD / %	0.13
Bias, %	0.86
Spiked QR, mg	50.00
Found, mg	49.40
Average recovery, %	98.80
RSD / %	0.47
Bias, %	1.20

% Recovery (98.80) value shows that the applied methods could be successfully used for QR assay without any interference**.** The comparison of linear range and limit of detection with different modified electrodes is given in Table 3.

Table 3. Comparison of linear range and detection limits for onion peel to modified electrodes

Working Electrode	**Modifier**	**Linear range (µM)**	**Detection limit (µM)**	**Ref.**
Glassy carbon	MWCNTs	0.8-7.0	0.0890	[28]
Glassy carbon	MWCNTs	0.1-5.0	0.0075	[28]
Glassy carbon	Carbon nanotube and Nafion	0.02-6.3	-	[29]
Glassy carbon	Graphene nanosheets	10-100	0.0039	[30]
Glassy carbon	poly(p-ABSA)	7.0×10^{-5}- 9.0×10^{-4} M (70-900 µM) [a]	2.03×10^{-5} (20.300 µM) [a]	This work

[a] The concentration unit, M, in this study is converted to µM (in parenthesis) for comparison with other modifiers given in the references

The amount of QR in the sample was calculated by using the equation y= 78943x +103.8 obtained from the calibration curve. According to the calculations for the sample of 0.13 g, the sample contains QR in the proportion 13.414% (w/w). Additionally, the onion peel of 20 g was determined to contain QR in the proportion 0.087% (w/w).

3.5. Validation parameters for the QR assay

The analysis parameters such as LOD, LOQ and recovery studies were investigated for validation of the applied method for the assay of QR using the DPV method (Table 1 and Table 2).

The recovery tests were applied by addition of a certain amount of QR to onion peel samples. Good recovery value was obtained (Table 2).

4. CONCLUSION

Glassy carbon electrode coated with poly (4-aminobenzene sulfonic acid) film was used for determination of QR. The modified GE electrode showed good current signal for the oxidation of QR. The modified electrode provides greater sensitivity and selectivity in the determination of QR.

Differential pulse voltammetry technique could be used for the determination of QR in onion peel under the optimum conditions with GCE modified with 4-ABSA as working electrode and 0.1 M PBS (pH=8.0) as supporting electrolyte.

Acknowledgements

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