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PAPER

Electrochemical and spectroelectrochemical investigations of quercetin on unmodified and DNA-modified carbon paste electrode and its determination using voltammetry†

A. K. Satpati,*[a] S. Sahoo,[a] M. K. Dey,[a] A. V. R. Reddy[a] and T. Mukherjee[b]

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The electrochemistry of quercetin on a carbon paste electrode in non aqueous and aqueous media has been investigated. Cyclic voltammetric experiments were carried out and the basic electrochemical parameters such as diffusion coefficient, exchange current density and the anodic Tafel slopes were determined. A differential pulse voltammetric procedure was proposed for the determination of quercetin in aqueous solution using a carbon paste electrode, and the detection limit was obtained as 38.5 nM L^{-1}. The electrochemical properties of quercetin were studied using a DNA-modified carbon paste electrode using electrochemical impedance measurements. From spectroelectrochemical measurements it was evident that the hydroxyl groups at the 3′ and 4′ positions were oxidized in the presence of Cu(II) and are responsible for DNA damage. Impedance measurements supported the intercalation of quercetin into the DNA strands.

1. Introduction

Quercetin is a member of the flavonoids family and is an antioxidant (Chart 1). It has many biological activities such as cardiovascular protection, anticancer activity and antiallergy activity.[1,2] A wide range of fruits and vegetables contain quercetin as an important constituent.[3–5] The importance of quercetin in biological and nutritional sciences has attracted attention towards the development of analytical methodologies to determine quercetin in biological matrices and food materials. Although chromatographic and spectroscopic methods for the determination of quercetin are well known,[6–9] electrochemical methods provide a better understanding of the molecular phenomena during the analysis besides being more informative.[10–15] In the present study, the electrochemical behavior of quercetin has been investigated using a carbon paste electrode in non aqueous and aqueous media. In previous electrochemical studies, either carbon nanotube-based or graphitic carbon powder-based electrodes have been used in the determination of quercetin.[15–17] In the present study a graphite powder-based carbon paste electrode has been used to evaluate parameters such as transfer coefficient, average exchange current density and the diffusion coefficient of quercetin and the findings have been reported. A method of determination of quercetin based on differential pulse voltammetry has been proposed.

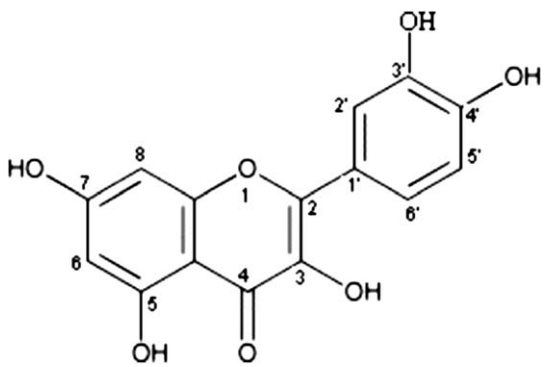

Chart 1 Chemical structure of quercetin molecule.

Apart from analytical methods for the determination of quercetin, electrochemical techniques provide information about the interaction of quercetin with DNA. There has been enormous attention on flavonoids due to their antiproliferative effect[18,19] on various cancer cells and their antioxidative potential.[20–26] It has been evident from numerous studies that flavonoids have chemopreventive properties. Some contradicting results are reported from excessive use, as flavonoids themselves are mutagenic and were shown to have DNA damaging activity.[27,28] The quercetin molecule in the presence of transition metal ions shows enhanced mutagenic activity,[27,28] and it has been shown that the flavonoids

[a]*Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, 40085, India. E-mail: asatpati@barc.gov.in; Fax: +91-22-25505151; Tel: +91-22-25590326*
[b]*Chemistry Group, Bhabha Atomic Research Centre, Trombay, Mumbai, 40085, India*

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reduce the transition metal ions and, in turn, a highly oxidizing OH radical is formed, which is the probable cause of DNA damage and mutagenic activity. The possibility of chelate complex formation with the transition metal ions is reported in the literature.[29–31] Some studies have reported the intercalation of quercetin bound with transition metal ions into the DNA helix.[32,33] Brett and coworkers have reported electrochemical evidence of DNA damage by quercetin in the presence of Cu(II) and the release of adenosine and guanine residues.[34] Basic aspects of the interaction between DNA or monophasic nucleotides and the biomimetic oxidation of quercetin has been reported from electrochemical and spectral measurements.[35–37] In the present study, we have also attempted to investigate the interaction of quercetin and double stranded DNA in the presence of Cu(II) in aqueous solution, using a DNA-modified carbon paste electrode employing electrochemical impedance spectroscopy. A spectroelectrochemical study was carried out to determine the binding site of Cu(II) and quercetin, responsible for quercetin–DNA interactions. Such a study on the electrochemistry of quercetin in aqueous and non aqueous media, and electrochemical impedance spectroscopy on a DNA-modified carbon paste electrode together with the spectroelectrochemical measurements will be interesting to the literature and useful for the determination of quercetin in aqueous solution.

2. Experimental procedure

2.1. Instrumentation

All the experiments were carried out under potentiostatic control using Eco Chemie Potentiostat, AUTOLAB-100 with the VA663 stand. Electrochemical impedance measurements were carried out using the frequency response analyzer (FRA) module attached with Autolab-100 potentiostat. Impedance scan was measured at the frequency range of 10 kHz to 0.1 Hz with an amplitude of 10 mV. After obtaining the optimum frequency for maximum capacitive behavior at 100 Hz, impedance measurements were carried at a single frequency of 100 Hz at different applied potentials. All the potentials applied and measured were with respect to the saturated calomel electrode, SCE. The electrolyte solution was purged for 300 s using high purity nitrogen gas before every electrochemical scan. In the case of non aqueous samples, tetraethyl ammonium perchlorate was used as the supporting electrolyte. Experiments were carried out at room temperature (25 ± 1 °C). The glassy carbon electrode was successively polished with 5, 1, 0.3 and 0.05 μm alumina polish and then rinsed with 8 M nitric acid, distilled water and then ultrapure water before its use. In the case of the carbon paste electrode and the mercury electrode, a fresh electrode surface was generated before every scan.

2.2. Reagents

Spectroscopic grade carbon powder obtained from E-Merck Ltd., India was used as received for the preparation of the paste. Silicon oil was obtained from SD Fine Chemicals, Mumbai, India and quercetin was obtained from Aldrich, and used without further purification. Calf thymus double stranded DNA solution was prepared in 0.1 M acetate buffer solution of pH 4.5.

2.3. Preparation of the carbon paste electrode

The spectroscopic grade carbon powder was heated at 400 °C for 4 h in an inert atmosphere, taking 0.5 g of the powder in a quartz boat. After heating, the powder was transferred to a beaker containing high purity paraffin dissolved in *n*-hexane. The mixture was kept in a fume hood maintained at negative pressure and the *n*-hexane was allowed to evaporate. After that the mixture was kept under a hot air blower for complete removal of *n*-hexane. Heating removed the adsorbed gases from the surface of the carbon paste and upon paraffin impregnation the re adsorption of gases is minimized. In this study ~1.5% (weight %) of paraffin wax was added to the carbon powder. After paraffin impregnation, the required quantity of silicone oil was added as the binder (25% of the mass of the modifier and carbon powder) and ground well to get a homogeneous paste. The carbon paste was filled into a glass tube with 1.5 mm diameter from the bottom end. A platinum wire was used to connect the carbon paste electrode to the instrument.

3. Results and discussion

3.1. Electrochemical behavior in non aqueous media

Voltammetric experiments were carried out in acetonitrile (ACN) and in methanol (ME) solutions of quercetin using a carbon paste and also a glassy carbon (GC) electrode to study the oxidation behavior of quercetin. A static mercury drop electrode (SMDE) was used to study the electroreduction process. The cyclic voltammetric response of quercetin with varying scan rates in ACN and ME media using the carbon paste electrode (CPE) was shown in Fig. 1 and 2 respectively. Two well-resolved oxidation peaks of quercetin were observed in the cyclic voltammetric scan in ACN and ME solutions. With increasing scan rates the peak current values were found to increase with respect to the square root of scan rates (see insets of Fig. 1 and 2). The correlation between the peak current and the square root of the scan rates was found to be linear with an intercept. The presence of an intercept indicated contribution due to the adsorption of quercetin molecules on the electrode surface. Jin *et al.* and Xiao *et al.* have reported the non-linear correlation of the

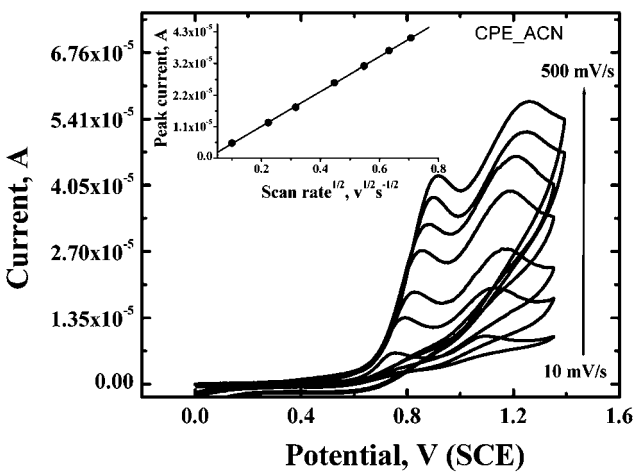

Fig. 1 Cyclic voltammetry of 0.1 mM quercetin in ACN solution using CPE with different scan rates of 10, 50, 100, 200, 300, 400, 500 mV s^{-1}. Inset: variation of peak current of the first oxidation peak with the square root of the scan rates.

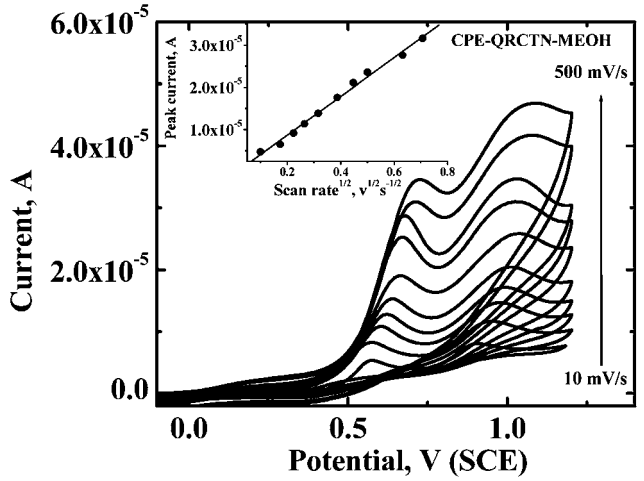

Fig. 2 Cyclic voltammetry of 0.1 mM quercetin in ME solution using CPE with different scan rates of 10, 30, 50, 70, 100, 150, 250, 400, 500 mV s^{-1}. Inset: variation of peak current of the first oxidation peak with the square root of the scan rates.

peak current with the square root of scan rates.[15,16] Zare *et al.*[35] have reported a linear variation of the peak current with respect to the square root of scan rates similar to the present observation. In our concentration dependent study (discussed later) we have seen that the peak current values increased linearly with the quercetin concentration in differential pulse mode. The observation from the scan rate dependence in the cyclic voltammetric measurements along with the concentration dependent study indicated that the electrooxidation process was diffusion controlled. However the contribution of adsorption to the overall electrochemical process could not be ruled out.

The electrooxidation behavior of quercetin using the GC electrode was also investigated and the corresponding plots in ACN and ME solution are shown in Fig. S1 and S2, ESI† respectively. Two clear oxidation peaks of quercetin were observed using the GC electrode. The peak current *vs.* square root of scan rates were plotted and shown in the insets of Fig. S1 and S2, ESI† respectively. The correlation between the peak current and the square root of the scan rate was found to be linear with an intercept, similar to that obtained in the case of the CPE. The diffusion coefficients of quercetin in ACN and ME media were obtained as 5.57×10^{-6} and 1.93×10^{-7} cm^2 s^{-1} respectively. The lower diffusion coefficient in ME solution compared to that in ACN solution could be due to the strong H-bonding interaction between quercetin and ME, which was absent in ACN solution.

The reduction behavior of quercetin was investigated using a hanging mercury drop electrode (HMDE) as the working electrode. A reduction peak was obtained at −0.82 V, the corresponding figure was shown as Fig. S3, ESI.† The electroreduction behavior of quercetin was found to be reversible in nature. With increasing scan rates the peak current increased, but the peak shape and the peak position did not change significantly. Similar to the oxidation peak, the correlation between the peak current and the square root of the scan rate was found to be linear (inset of Fig. S3, ESI†) with an intercept referring to the adsorption of quercetin on the mercury electrode surface.

3.2. Tafel analysis result

A Tafel plot was constructed at the rising position of the first oxidation peak of quercetin in ACN medium using CPE and GC electrodes (see Fig. 1 of main text and Fig. S2, ESI†). This part of the cyclic voltammogram is called the Tafel region and the electrochemical reaction is governed by electron transfer rates of the quercetin molecule at the electrode–electrolyte interface. The data points fitted well to a straight line with the correlation coefficient varying from 0.996 to 0.999 at different scan rates. In the case of the CPE, the Tafel slope of the quercetin oxidation varies in the range of 0.0055 to 0.0063 mV^{-1} (shown in Fig. 3, the Tafel slope values are equivalent to 181 mV dec^{-1} to 158 mV dec^{-1}). The Tafel slope values were found to be low. Considering $\alpha = 0.65$,[38] the electrooxidation process should be a two electron transfer process, as the Tafel slope $\alpha nF/2.303RT$ (at 298 K) was found to be similar to the present observation. In the case of the GC electrode (Fig. S4, ESI†), at lower scan rates up to 30 mV s^{-1} the Tafel slope remained in the 0.0051 and 0.0056 mV^{-1} (the Tafel slopes are equivalent to 196 mV dec^{-1} to 178 mV dec^{-1}) range, however, at higher scan rates the Tafel slope decreased to ~0.0042 mV^{-1}. This decrease in the Tafel slopes indicated the decrease in the electron transfer kinetics on the GC electrode surface at higher scan rates, whereas in the case of the CPE, the electron transfer rates remained high at higher scan rates. This observation indicated that the CPE facilitated the electron transfer process of the quercetin molecule compared to the GC electrode. In the report from Zare *et al.*[35] on the quercetin oxidation in aqueous solution on the GC electrode a transfer coefficient of 0.65 was used. With this value of the transfer coefficient (0.65) the prediction of one electron transfer electrooxidation behavior did not correlate with the expression for the Tafel slopes ($\alpha nF/2.303RT$). It is most likely that two electron transfer was involved in the oxidation process. The exchange current densities of the quercetin oxidation with both CPE and GC electrodes were obtained in the range of 1×10^{-7} to 3×10^{-7} A cm^{-2} respectively.

3.3. Electrochemical behavior in aqueous media

Quercetin has a lower solubility in aqueous solutions compared to that in non aqueous solution, therefore differential pulse

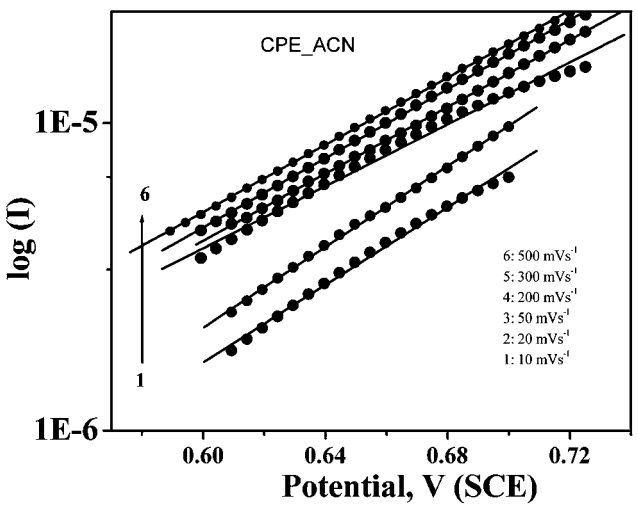

Fig. 3 Tafel plot of quercetin oxidation in ACN media on the CPE electrode.

voltammetry was performed to obtain the electrochemical response of quercetin in aqueous media. One clear oxidation peak was obtained for a solution of quercetin in water, with a peak potential at 0.28 V.

The effect of pH on the electrooxidation behavior of quercetin was investigated by differential pulse voltammetric measurements with varying pH in Britton–Robinson (BR) buffer solution, the corresponding responses in the voltammogram were shown in Fig. 4. The sharp peak at 0.28 V for the oxidation of quercetin at a concentration of 10^{-6} M was monitored. The peak position was found to shift towards a less positive direction with increasing pH of the solution. The change in voltammetric peak position with change in pH was shown in the inset of Fig. 4. The peak position was found to follow a straight line correlation as a function of pH with a negative slope of 66.4 mV/pH, which indicated the involvement of equal numbers of electrons and protons in the electron transfer step.[39] As the electrooxidation step of quercetin was characterized as a two electron process,[10] the overall process of the electrooxidation step of quercetin can be summarized as a two electron and two proton transfer process. From the Tafel analyses we have also observed the two electron transfer step as the rate determining step in non aqueous solution. The peak current value was found to increase with increasing pH, reaching a maxima at a pH value of ~5 and then reducing upon further increase in pH. It was expected that with increase in alkalinity the expulsion of a proton became easier, and eventually the peak current increased. Even at higher pH values there was a definite possibility of deprotonation of the quercetin molecule in alkaline media. This partially deprotonated quercetin molecule would gain higher solvation stabilization in the supporting electrolyte media, thereby the diffusion current was expected to decrease. At pH values higher than 6, the peak current value decreased with increasing pH.

3.4. Determination of quercetin in aqueous media

Analytical determination of quercetin in aqueous solution using CPE has been proposed by differential pulse voltammetric techniques. Differential pulse experiments were carried out using a pulse amplitude of 25 mV with a pulse duration of 0.02 s and a step potential of 3 mV. The calibration was obtained with varying quercetin concentration from 1 μM to 5 μM and the differential pulse experiments were carried out without any preconcentration process. The corresponding plots were shown in Fig. 5. The peak current was found to increase with increasing concentration, and the peak position remained unchanged. The corresponding calibration plot of current *vs.* concentration of quercetin was shown in the inset of Fig. 5. The correlation was found to be linear and the regression line followed the equation; $i_p = 65.55 + 2.032\ C$ ($r = 0.998$), where i_p is the peak current in nA and C is the concentration in M L^{-1}. The standard deviation of the current measurements was 4.22×10^{-9} A. The 3 sigma detection limit of this procedure for the determination of quercetin was obtained to be 38.5 nM L^{-1}. Sensitivity can be improved by adsorbing the quercetin molecule at the active site of carbon particles or nanotubes.[40] The electroactive sites of the carbon nanotubes were responsible for the preconcentration of quercetin at open circuit conditions. In the present case also, the graphitic particles are found to preconcentrate the quercetin molecules on dipping at the test solution at open circuit potential. However, to avoid the memory effect of quercetin, the present analysis procedure was proposed without any preconcentration step. The RSD value was obtained as 1.5% ($n = 10$).

3.5. Interaction of quercetin with DNA-modified carbon paste electrode

DNA-modified CPE was prepared by physically modifying the electrode surface with DNA solution in acetate buffer of pH 4.5. Modification was carried out by a controlled drop drying method. After modification with DNA solution, the electrode was washed with ultra pure water and made ready for use in electrochemical scans. In some reports, electrochemical investigations of quercetin on DNA-modified electrodes and related studies were previously described.[34,41–45] In those studies, breaking of DNA strands and the release of amino acids were

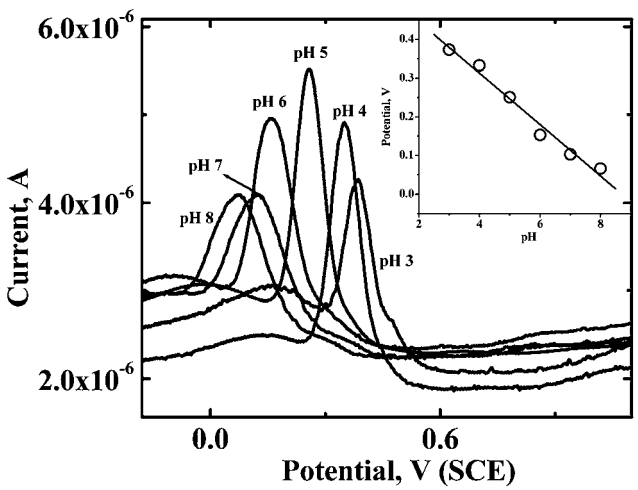

Fig. 4 Differential pulse voltammetric plot of quercetin at different pH values. Inset: variation of the peak potential with the experimental pH value in BR buffer solution.

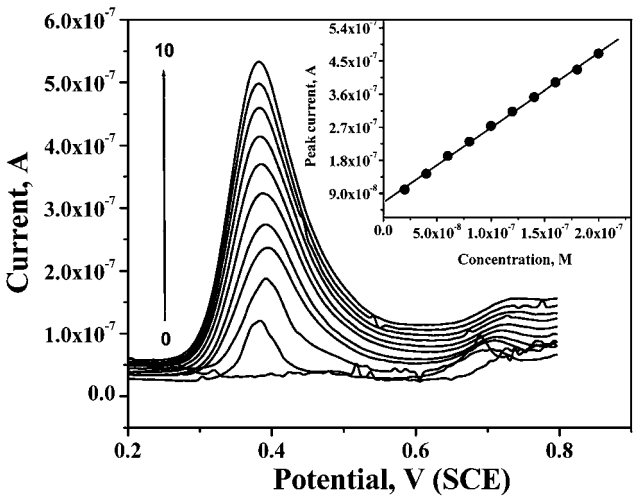

Fig. 5 Differential pulse voltammograms of quercetin in aqueous solution with varying concentrations. (0) blank; corresponding concentrations can be read from the calibration plot in the Inset of the figure.

reported in the presence of transition metal ions, Cu(II). Such studies were based on pulsed voltammetric measurements. Electrochemical impedance measurements, especially the potential dependent capacitance measurements, might be similarly informative and the interaction phenomena could be explored. Potential dependent capacitance measurements were carried out at a fixed frequency of 100 Hz and the potential was scanned from −1.0 V to 1.6 V. Corresponding plots were shown in Fig. 6. The capacitance of the bare CPE remained constant with the change in potential in the potential range studied. The DNA-modified electrode was found to show a wide adsorption hump at the potential region of −0.03 V due to the adsorbed DNA at the electrode surface. When quercetin was added in the electrochemical solution, oxidation behavior due to quercetin was observed with a clear peak at +0.32 V. In the same test solution 50 μg ml^{-1} of Cu(II) was added and after 15 min of incubation impedance measurements were carried out (see plot 4 of Fig. 6). The quercetin peak at +0.32 V was reduced considerably and a new peak due to Cu(II) reduction was observed at −0.04 V. Interestingly, three small peaks were also observed at +0.95 V, +1.11 V and +1.28 V. Oliveira-Brett *et al.* have reported the release of amino acid residues from the DNA strand using DNA-modified electrodes by differential pulse voltammetric measurements.[34] The baseline of the capacitance plot was found to be increased from that of the DNA-modified electrode upon the addition of quercetin in the test solution, and further increased upon addition of Cu(II) in the test solution. This was due to the change in double layer structure in the DNA-modified electrode, which again underwent a change on addition of quercetin and Cu(II). This observation indicated the incorporation of the fully or partially charged species at the electrochemical double layer. The increase in the baseline upon addition of quercetin indicated the preferential adsorption/incorporation of the quercetin molecule into the DNA-modified electrode. The driving force for such preferential adsorption/incorporation was indicative of the intercalation property of quercetin into the DNA double helix. In order to validate the results, blank experiments were carried out with a bare carbon paste electrode without DNA modification. The corresponding plot due to quercetin is shown in Fig. 6 (blue line). In the test solution Cu(II) was added, and after a similar type of incubation to that of the DNA-modified electrode, the capacitive nature was obtained and shown as a red line in Fig. 6. The peak due to quercetin was found to remain unchanged with addition of Cu(II) in the solution. This was indicative of the intercalation behavior of quercetin into the DNA strands, and under that environment only was Cu(II) able to oxidize quercetin. Due to such oxidation the capacitive peak due to quercetin was reduced in the DNA-modified electrode in the presence of Cu(II). Support of such an observation was also obtained from the spectroelectrochemical study discussed in the following section. Electrochemiluminescence is another important technique used to study the intercalation behavior of DNA.[46–49] Some biologically important organometallic complexes were reported to intercalate into the DNA,[46–49] and electrochemiluminescence properties were reported to be enhanced on intercalation.[49]

3.6. Spectroelectrochemical measurements

The change in spectral properties of quercetin was studied in the presence of Cu(II) and DNA solution. Continuous spectral measurements were also carried out using a dip probe assembly during the electrooxidation process of quercetin on application of 1.0 V at a platinum gauss electrode. In Fig. 7, plot (a) shows the absorption spectra of DNA, plot (b) shows quercetin with DNA and plot (c) to plot (g) show the change in the absorption spectra with time after addition of Cu(II). The spectrum of quercetin showed four absorption bands at 362, 300, 253 and 228 nm. With the addition of DNA, the 253 and 300 nm bands of quercetin were merged and combined with the 260 nm band of DNA, resulting in a broad band with a peak at 256 nm. The spectral characteristics of quercetin with DNA and also quercetin with Cu(II) remain unchanged with time. However, when Cu(II) was added into the quercetin–DNA solution [plot (c) to (g) of Fig. 7], the 362 nm band

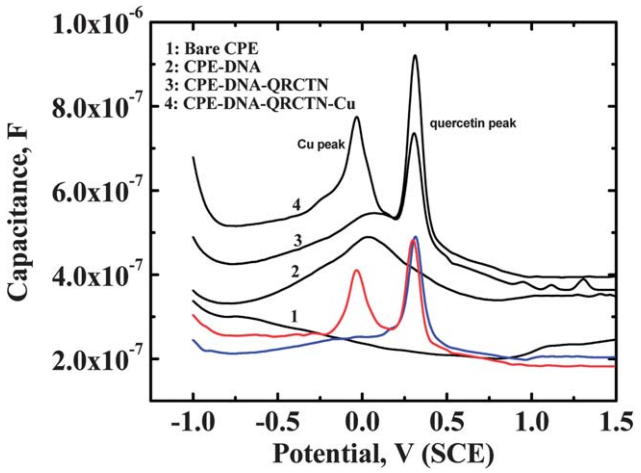

Fig. 6 Impedance response of the DNA-modified carbon paste electrode with varying potential. (1) Bare CPE (2) DNA-modified CPE (3) DNA-modified CPE with 0.1 mM quercetin (4) DNA-modified CPE with quercetin and 100 μM $CuSO_4$. The results with the unmodified CPE for quercetin (blue line) and quercetin with Cu(II) (red line) were also shown.

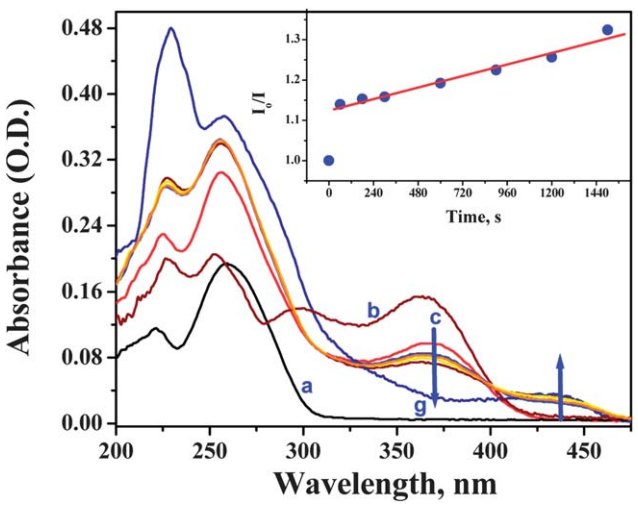

Fig. 7 Absorption spectra of (a) DNA in aqueous solution (b) Quercetin with 50 mM Cu(II) (c) to (g) Quercetin + DNA + 50 mM Cu at varying times of 0, 5, 10, 30 min and 24 h.

of quercetin began to disappear over time and a new band at 440 nm appeared. At the first measurement point (after 1 min) the OD corresponding to 362 nm has decreased significantly, and then the rate of decrease in OD became slower and linear with respect to time. The rate of change of the OD was presented in the inset of Fig. 7, where I_0 is the initial OD at 0 time and I is the OD at different measured times. Except at the initial time (of 60 s) all the other data points showed a linear correlation with time. The initial abrupt change in the OD might be due to the static interaction in the DNA–quercetin–Cu(II) system. After 10 h of measurement the 362 nm band had disappeared (plots not shown). These observations indicated that the quercetin molecule intercalated with double stranded DNA, resulted in the broadening and mixing of the adsorption spectra. However it could not damage the DNA strands on its own. The immediate change in the absorption spectra on addition of Cu(II) indicated the formation of a charge transfer complex of quercetin with Cu(II).[50,51–53] It was also observed that the quercetin spectra did not change with time in the presence of Cu(II) without DNA. These observations indicated that the quercetin molecule intercalated into the DNA double helix and facilitated the charge transfer complex formation with Cu(II), resulting in the decrease in the 362 nm band. As a result, a new charge transfer band at 440 nm was formed. The Cu(II) ion oxidized the intercalated quercetin molecule in the intercalated state, and the Cu(I) formed in this process reduced O_2 to the superoxide radical anion $O_2^{\cdot-}$. The reactive $O_2^{\cdot-}$ radical formed at a highly localized site of the quercetin–DNA–Cu(I) complex. The $O_2^{\cdot-}$ radical was then transformed to the hydroxyl radical OH through radical propagation and damaged the DNA at specific sites; the explanation of the mechanism of such a process was attempted by Yamashita *et al.*[54] The localized type of damage in the DNA double helix was evident from the static nature of the correlation of OD *vs.* time.

At this juncture we will try to answer the question of why the 362 nm band of quercetin decreased upon addition of Cu(II). Was it due to the formation of the charge transfer complex of quercetin with Cu(II), or due to the oxidation of the quercetin moiety at the intercalated DNA–quercetin–Cu(II)? In order to understand the process in detail, spectroelectrochemical experiments of quercetin were carried out at an applied potential of 1.0 V to the working electrode and the absorption spectrum was measured simultaneously and stored with a time interval. The change in the spectral characteristics with time was shown in Fig. 8. It was observed that the 362 nm and 253 nm bands decreased, the 300 nm band increased and the 228 nm band remain unaffected on electrolysis at 1.0 V. The disappearance of the 362 nm band upon oxidation at 1.0 V was similar in behavior to that observed due to the addition of Cu(II) in the DNA–quercetin solution. Thus, the diminishing of the 362 nm band due to the addition of Cu(II) into the DNA–quercetin solution, and also the observation of a similar effect due to the oxidation of quercetin under potentiostatic conditions, suggested that Cu(II) oxidized the OH groups present at the 3′ and 4′ positions of the quercetin moiety which interacted with the DNA double helix. The present observation from the spectroelectrochemical measurements supported the scheme of the interaction between quercetin–DNA with Cu(II) ion as described in the earlier report.[54] The change in I_0/I with respect to time of the 362 nm band was shown in the inset of Fig. 8. The correlation was found to be linear, indicating

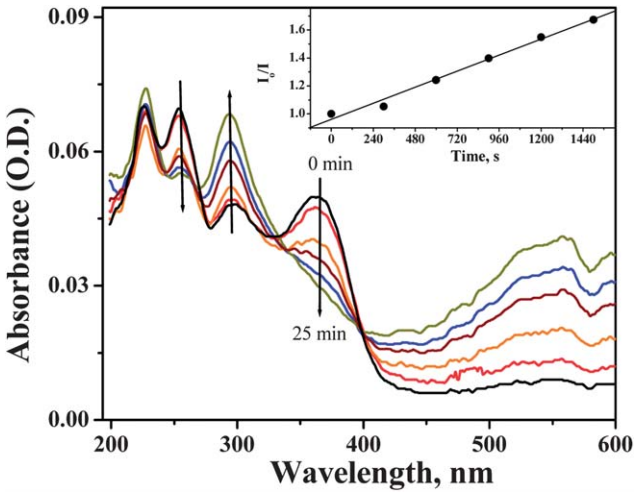

Fig. 8 Online absorption spectral measurements of quercetin during electrooxidation at 1.0 V (SCE). Different spectra correspond to different times of electrolysis of 0, 5, 10, 15, 20 and 25 min.

a linear and dynamic interaction without any short time (static) interaction. In this type of measurement, a linear dynamic type of interaction was expected as the electrolysis was carried out with a Pt gauge working electrode with a large surface area under constant stirring conditions.

4. Conclusion

The electrochemistry of quercetin was investigated on a carbon paste electrode in non aqueous and aqueous media. Detailed cyclic voltammetric investigations were carried out and the basic electrochemical parameters, diffusion coefficient, exchange current density and the anodic Tafel slopes were determined. The exchange current density of the quercetin oxidation with both CPE and GC electrodes was obtained in the range of 1×10^{-7} to 3×10^{-7} A cm^{-2}. A differential pulse voltammetric procedure was proposed for the determination of quercetin in aqueous solution using a carbon paste electrode and the detection limit was obtained to be 38.5 nM L^{-1}. Electrochemical properties of quercetin were studied using a DNA-modified carbon paste electrode using impedance measurements. From spectroelectrochemical measurements it was evident that the hydroxyl groups at the 3′ and 4′ positions were oxidized in the presence of Cu(II) and eventually responsible for DNA damage.

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