



ORIGINAL ARTICLE

Electrochemical behaviour of antioxidants: Part 2. Electrochemical oxidation mechanism of quercetin at glassy carbon electrode modified with multi-wall carbon nanotubes



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Abstract Electrochemical oxidation mechanism of quercetin was investigated at glassy carbon electrode modified with multi-wall carbon nanotubes in aqueous 0.2 M phosphate solutions with different pHs. The investigation was carried out using cyclic voltammetry, double potential step chronoamperometric and chronocoulometric techniques. It was found that the oxidation mechanism proceeds in sequential steps, related with the five-hydroxyl groups in the three aromatic rings. The mechanism was proposed to be an ECEC, first-order kinetics. The proposed mechanism was confirmed on comparing the digital simulated cyclic voltammetric responses with the experimental ones. The electrode homogeneous and heterogeneous kinetic parameters of electrode reaction are estimated from the simulated data. Moreover, quercetin molecules adsorb on the electrode surface.

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1. Introduction

Flavonoids represent a large group of polyphenol secondary metabolites that are widely distributed in medicinal plants, fruits, teas and health beverages (Manach et al., 2004). Quercetin, Qu, a derivative of benzo- γ -pyrone, is a bioflavonoid.

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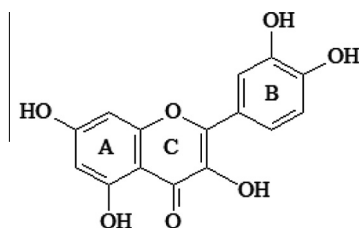


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Bioflavonoids are a large family of naturally occurring organic compounds widely distributed in plants. Bioflavonoids are highly interesting because they may exert a wide range of beneficial effects on human health and have broad pharmacological activities including prevention of cardiovascular diseases and different forms of cancer. Quercetin (3, 3', 4', 5, 7-pentahydroxyflavone) is predominant in vegetables and fruits. It is a penta-hydroxyl antioxidant (Mora et al., 1990 and van Acker et al., 1996). Electrochemical oxidation of quercetin was studied at glassy carbon (Pierozynski and Zielinska, 2011; Zielinska et al., 2010; Medvidović-Kosanović et al., 2010; Zielinska and Pierozynski, 2009; Simić et al. 2007; Timbola et al., 2006; Zare et al., 2005; Nematollahi and Malakzadeh, 2003; Brett and Ghica, 2003), platinum (Mase et al., 2011; Brett and Ghica, 2003), polycrystalline platinum (Pierozynski and Zielinska, 2010),

multi-wall carbon nanotubes (Gutiérrez et al., 2010), paraffin-impregnated graphite disk modified with multi-wall carbon nanotubes (Jin et al., 2006), plastic formed carbon (Yang et al., 2001), procaine and aminophenyl modified (Mulazimoglu and Ozkan 2008) and graphite-wax electrodes (He et al., 2009). The products of quercetin electrochemical oxidation adsorb on glassy carbon electrode surface (Medvidović-Kosanović et al., 2010). The initial step is oxidation of quercetin's two -OH catechol groups in ring B. The following steps are oxidation of the remaining three hydroxyl groups, located in rings C and A. Gutiérrez et al. (Gutiérrez et al., 2010), reported that, in the presence of carbon nanotubes, the oxidation and reduction currents of the less positive wave increase while the peak potential separations almost do not change. The enhancement in the currents is due to the increase of the electroactive area of the modified electrode surface.

Earlier authors reported that, the electrochemical oxidation of quercetin proceeds via two steps. Each step involves transfer of one electron and one proton, to give *semiquinone* and finally the *orthoquinone*. No electrochemical parameters were estimated. Furthermore, little attention has been paid to its electrochemical oxidation mechanism on carbon nanotubes, CNTs. However, in continuation of our work on electrochemical behaviour of antioxidants (Abdel-Hamid and Newair, 2011), in this work, a glassy carbon electrode modified with multi-wall carbon nanotubes was prepared and used to study the electrochemical behaviour of quercetin. The electrochemical oxidation mechanism is investigated, using cyclic voltammetry, double potential step chronoamperometry and chronocoulometry and digital simulation. The electrochemical oxidation mechanism of quercetin is proposed and discussed. The proposed mechanism was confirmed using digital simulation and the electrochemical parameters are estimated. This may play a crucial role in understanding its antioxidant activity. The study is performed in aqueous phosphate solutions on modified electrode.



The chemical structure of quercetin

2. Materials and methods

All the electrochemical experiments were carried out using Model 273A potentiostat from EG & G Princeton Applied Research equipped with EG & G M 270 software. The working electrode was glassy carbon/multi-wall carbon nanotubes modified electrode, GCE/MWCNTs. 1.0 mg/mL suspension of MWCNTs was obtained on dispersing five milligrams of MWCNTs in 5.0 cm³ N,N-dimethylformamide (DMF). The mixed solution was ultrasonically agitated for 6 h. The GCE/MWCNTs, modified electrode was prepared by adding a drop of 1.0 cm³ of MWCNTs suspension (1.0 mg cm⁻³) onto the clean surface of GCE. Then the solvent was evaporated overnight. The glassy carbon electrode was polished with 0.5 μm

alumina powder on a polishing cloth to obtain a mirror-like surface before modification. After rinsing the surface with deionized water, the polished GCE was sonicated for 5 min in water/ethanol to get rid of the trace amount of alumina powder from the surface and rinsed again with deionized water. Then, the surface was fully dried at atmospheric condition with a stream of purified nitrogen. A platinum electrode and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All the potentials were reported with respect to this reference electrode. All experiments were performed at room (25 °C) temperature.

All the chemical reagents used for solutions were of reagent grade from Merck and used as received. The MWCNTs (purity: >90%; carbon basis, D × L 110–170 nm × 5–9 μm) were from Aldrich. All solutions were freshly prepared just before use with deionized water. The uncompensated resistance was corrected by the potentiostat.

3. Results and discussion

3.1. Cyclic voltammetry

The electrochemical behaviour of quercetin, at a glassy carbon electrode modified with multi-wall carbon nanotubes is investigated in 0.2 M phosphate aqueous buffer solutions at different pHs. Fig. 1A shows the cyclic voltammograms, cv, of 2.5 μM quercetin in buffer solution (pH 2.12) at scan rate of 10 mV/s. The overall cyclic voltammogram, cv Fig. 1A, shows four anodic peaks associated with the oxidation centres present in the Qu molecule occurring at potentials of 0.47, 0.56, 0.84 and 1.13 volts. The cv profile is similar to those previously reported (Brett and Ghica, 2003).

The first anodic cv wave, located at ≈0.47 volts, seems to be reversible, its cathodic counter-part is seen, on reversing the potential scan just before the second wave, c.f. Fig. 1B. The peak separation between the anodic peak potential, E_{pa} , and the cathodic peak potential, E_{pc} , $\Delta E_p = E_{pa} - E_{pc}$, is ≈40 mV which agrees with literature data which points to a reversible electrode reaction involving two electrons (Bard and Faulkner, 2001). The somewhat high peak separation value could point to a slow electron-transfer or chemical contribution. On increasing scan rate, E_{pa} is positively shifted and the E_{pc} is negatively shifted. The relationship of anodic peak potential with scan rate indicates that the electron-transfer process couples with a chemical reaction. On plotting peak currents, i_{pa} and i_{pc} as a function of scan rate square root ($v^{1/2}$), a linear relation is obtained with correlation coefficients, r , 0.985. This indicates that the oxidation process of Qu is diffusion-controlled. These findings point out to a diffusion-controlled electrode process involving a follow-up chemical reaction to the electron transfer process (Bard and Faulkner, 2001).

The oxidation products formed in the first peak are electrochemically active, which further oxidize at higher potentials, giving the second cv wave, located at ≈0.56 volt. On reversing the potential scan just before the third wave, a reduction wave appears at about 0.44 V, c.f. Fig. 1C. This wave is the counter-part of first oxidation cv wave. Thus, the second oxidation cv wave is irreversible, its counter-part is not seen. On increasing scan rate, peak potential, E_{pa} , of the second wave is shifted to more posi-

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