Voltammetric study of saffron in blood mediated by modified glassy carbon electrode (GCE) with carbon nanotube (CNT/GCE)

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Érkezett: 2018. 01. 13. ▪ Received: 13. 01. 2018. ▪ https://doi.org/10.14382/epitoanyag-jsbcm.2018.14

Abstract
Modified glassy carbon electrode with carbon nanotubes (CNT/GCE) was used to study extracted saffron in blood medium to find the effect of oxidation-reduction current peaks of saffron compound. It was found two cathodic current peaks at -0.75 and -1.75 V were appeared in the cyclic voltammogram of saffron in blood medium, so saffron considered as anti-oxidative compound in blood medium. Different concentrations, scan rates and effect of ascorbic acid on the cathodic current peak were studied. Diffusion coefficient of two reduction current peaks of saffron in blood medium was determined from Randel equations with values of saffron in blood medium at -0.75 and -1.75 V are 2.2×10^{-6} and 1.1×10^{-5} cm^2/sec respectively cm^2 sec^{-1}.
Keywords:

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1. Introduction

Saffron considered being an anti-oxidative reagent, especially in blood medium, which can be studied by electrochemical method using the cyclic voltammetric analysis. This method has been used recently through different research [1-6].

It was found that saffron effect on the blood pressure when use as nutrition. Saffron reduced the cross-section area, media thickness, and elastic lamellae number of the aorta. Nutritional saffron prevented BP increases and remodeling of the aorta in hypertensive rats [7]. Saffron has biological activities including antihumoral, cytotoxic, hypolipidemic, anti-inflammatory, etc. In comparison, cholesterol-fed, water-drinking rats had serum triglyceride (TG) levels equal to the rats fed a normal diet. The results of this study indicate that consumption of saffron can reduce serum cholesterol and TG levels in cholesterol-fed rats, suggesting that saffron may be useful in treatment of hyperlipidemia [8]. The chronic administration of saffron aqueous extract could reduce the mean systolic blood pressure (MSBP) in desoxycorticosterone acetate (DOCA) salt treated rats in a dose dependent manner. This compound did not decrease the MSBP in normotensive rats. The data also showed that antihypertensive effects of saffron did not persist [9]. The results demonstrate that while detecting the electroactive neurochemical norepinephrine in blood is more challenging than obtaining the same fast scan cyclic voltammetry (FSCV) measurements in a buffer solution due to biofouling of the electrode, it is feasible to utilize a minimally invasive FSCV electrode to obtain neurochemical measurements in blood [10]. Phenolic antioxidants are ranked by reducing strength and characterized for reversibility using cyclic voltammetry at a glassy carbon electrode. Phenolics with an ortho-diphenol group show a first oxidation peak close to 400 mV (vs. Ag/AgCl) in a model wine solution (12% ethanol, 0.033 M tartaric acid, adjusted to pH 3.6), with a linear concentration dependence below 0.01 mM. Dilution of white wines 10×, and red wines 400×, gave first oxidation peak currents in the 1.5 to 2.2 μA range and 1.9 to 3.4 μC of charge passed by 500 mV, producing values for the concentrations of phenolic antioxidants with low oxidation potentials in the wines. Further peaks in the cyclic voltammograms of the diluted wines correspond to classes of phenolics with higher oxidation potentials, providing a qualitative assessment of wine phenolics based on reducing strength [11].

In this work, saffron was studied in blood medium using modified glassy carbon electrode with carbon nanotubes (CNT/GCE) by cyclic voltammetric method.

2. Experimental

2.1. Reagents and chemicals

Saffron was supplied from EDMAN Company (Iran) as solid material which dissolved in deionized water after filtering by filter paper to use in the experiments. Blood samples were used from healthy human in Baghdad hospital center, and other chemicals and solvents were of annular grade and used as received from the manufacturer. Double distilled water was used for the preparation of aqueous solutions. All solutions were deaerated with oxygen free nitrogen gas for 15 min prior to making the measurement. All experiments were done at room temperature 25°C.

2.2. Preparing the modification of GCE with CNT (CNT/GCE)

Mechanical attachment technical method was employed to prepare the CNT/GCE working electrode as a nano-sensor [12,13]. The method of the modification of GCE included abrasive application of multiwall carbon nanotubes (MWCNT) on the clean surface of GCE, forming an array of MWCNT as modified working electrode MWCNT/GCE and replaced in 10 ml of electrolyte in the cyclic voltammetric cell, then connected all electrodes (working electrode, reference electrode and counter electrode) with the potentiostat.

2.3. Apparatus and procedures

Instruments: EZstat series (potentiostat/galvanostat) NuVant Systems Inc. pioneering electrochemical technologies USA Electrochemical workstations of Bioanalytical system with potentiostat driven by electroanalytical measuring software was connected to personal computer to perform Cyclic Voltammetry (CV), an Ag/AgCl (3M NaCl) and Platinum wire (1 mm diameter) was used as a reference and counter electrode respectively. The glassy carbon working electrode (GCE) was used in this study and cleaning the surface by polishing Alumina (BASi compony USA).

3. Results and discussion

3.1. Study different concentration of saffron in blood medium (calibration graph)

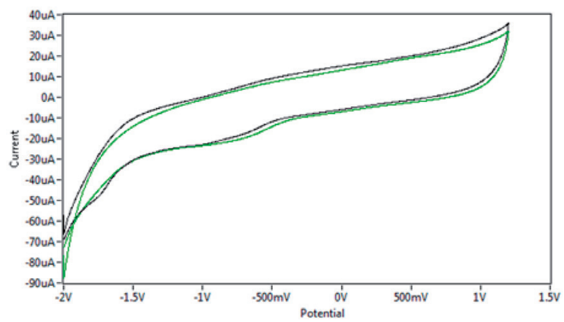

Fig. 1. Cyclic voltammogram of saffron in blood medium at different concentration on CNT/GCE as working electrode versus Ag/AgCl as reference electrode at 100 mV sec^{-1}.
1. ábra Sáfrány ciklikus voltammogramja vér közegben különböző koncentrációkban; mérő elektróda: CNT/GCE, referencia elektróda: Ag/AgCl, adatrögzítési sebesség: 100 mVsec^{-1}

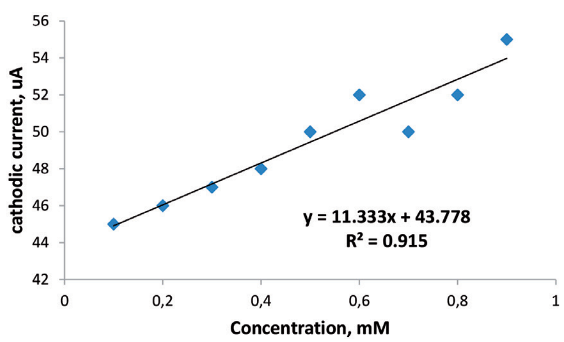

Fig. 2. Plot of cathodic current peak at -1.75 V of saffron in blood medium against to different concentration.
2. ábra Sáfrány különböző koncentrációi vér közegben; katódos áramerősség csúcsértékek -1.75 V feszültségnél

Fig. 1 shows the cyclic voltammogram of extracted saffron solution in blood medium at different concentration (0.1 - 0.5 mM). The two reduction current peaks of saffron in blood medium was appeared at potential -0.75 and -1.75 V and enhance to higher current against to increasing the concentration [14]. It was found the low detection limit of calibration graph as shown in *Fig. 2* with high sensitivity of the graph R^2=0.915, by equation of Y=11.333X+43.778. These results were given a good indicator that the modified electrode CNT/GCE acts as electro-catalyst to detection of low concentration of saffron ions in blood medium [15].

3.2. Scan rate study

Different scan rate (0.01-0.1 V sec^{-1}) was studied for the saffron in blood medium as shown in *Fig. 3*. Also, it can be calculated the diffusion coefficient values of the cathodic current peaks by Randel equation [16]. *Fig. 3* illustrated the effect of different scan rate on the two reduction current peaks which enhance the current with increasing the scan rate and a good relationship between the reduction current peak at -0.75 V versus to the scan rate as shown in *Fig. 4*. A linear relationship was found from the equation of reduction peak is Y=153.28X+6.9013 with high sensitivity R^2=0.9693, it means that the redox process of saffron compound in blood medium was reactant in homogeneous process [17].

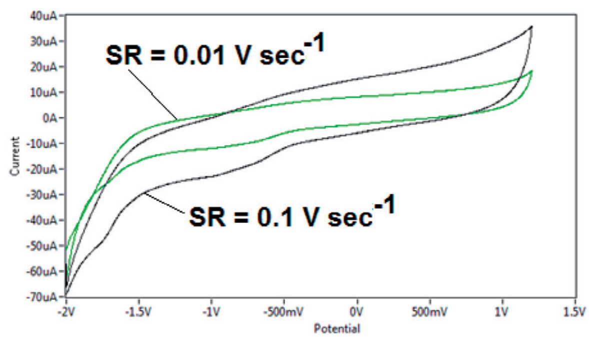

Fig. 3. Cyclic voltammogram of saffron in blood medium at different scan rate (0.01-0.1 mV sec^{-1}) on CNT/GCE versus Ag/AgCl as reference electrode.
3. ábra Sáfrány ciklikus voltammogramja vér közegben különböző adatrögzítési sebesség mellett (0.01-0.1 mV sec^{-1}); mérő elektróda: CNT/GCE, referencia elektróda: Ag/AgCl

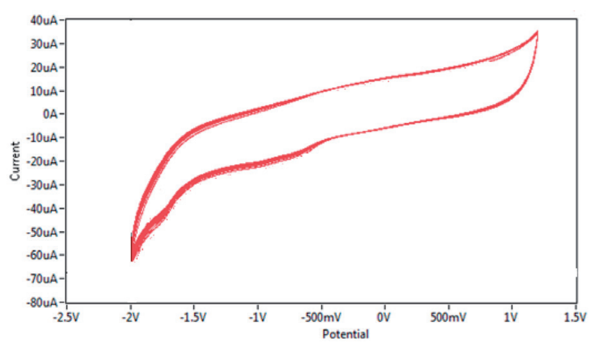

Fig. 4. Plot of cathodic current peak at -1.05 V of saffron in blood medium against to different scan rate (0.01-0.1 V sec^{-1})
4. ábra Sáfrány katódos áramerősség csúcsértékei vér közegben -1.05 V feszültségnél az atrögzítési sebesség függvényében (0.01-0.1 V sec^{-1})

3.3 Diffusion coefficient determination

The usual of mathematical method can be used in finding the diffusion coefficient of the redox process for the saffron compound in the KCl solution from the Randles-Seveik equation described reversible redox couple and the peak current [18,19].

$$I_p = (2.69 \times 10^5)\, n^{3/2}\, A C\, D_f^{1/2}\, v^{1/2} \qquad (1)$$

Where:

I_p is the current peak.

n is the number of moles of electrons transferred in the reaction.

A is the area of the electrode.

D_f is the diffusion coefficient.

V is the scan rate of the applied potential.

It was found the diffusion coefficient of two reduction current peaks at 0.75 and 1.75 V of saffron in blood medium are 2.2×10^{-6} and 1.1×10^{-5} cm^2/sec respectively, the different in values attributed to the size of the ions which moving to the electrode through the blood medium [20].

3.4. Reliability and satiability study

Saffron compound in blood medium was study by modified of glassy carbon electrode with carbon nanotubes (CNT/GCE) in cyclic voltammetry. Ten times of scanning the cyclic voltammetry was studied as shown in *Fig. 5* and determination the relative standard deviation (RSD) for both reduction current peaks at -0.75 and -1.75 V of saffron with values are ± 1.3% and ± 1.5% respectively which has a good reliability and stability of saffron in blood medium with these results [21].

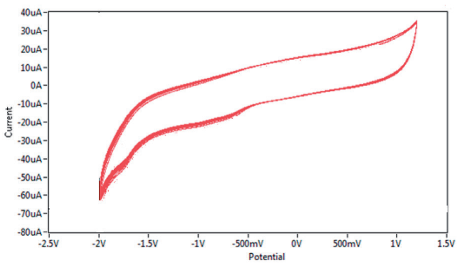

Fig. 5. Cyclic voltammogram of saffron in blood medium on CNT/GCE at ten times against to Ag/AgCl as reference electrode and at scan rate 100 mVsec^{-1}
5. ábra Sáfrány ciklikus voltammogramja vér közegben CNT/GCE mérő elektródán tízszeres szorzóval Ag/AgCl referencia elektródához viszonyítva, 100 mV sec^{-1}adatrögzítési sebesség mellett

3.5. Effect ascorbic acid on the saffron in blood

Ascorbic acid (AA) is good anti-oxidative reagent especially in blood medium, but no effect of AA was appeared on the reduction peaks of saffron as shown in *Fig. 6* [22].

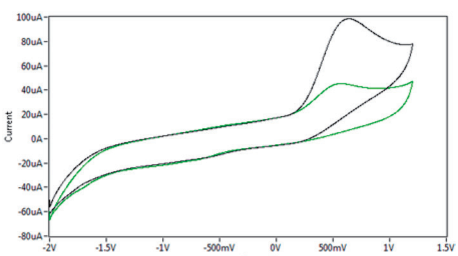

Fig. 6. Cyclic voltammogram of saffron compound with ascorbic acid in blood medium at different concentration on CNT/GCE versus Ag/AgCl as reference electrode and scan rate 100 mV sec^{-1}.
6. ábra Sáfrány ciklikus voltammogramja vér közegben különböző koncentrációkban aszkorbinsav jelenléte mellett; mérő elektróda: CNT/GCE, referencia elektróda: Ag/AgCl, adatrögzítési sebesség: 100 mVsec^{-1}

4. Conclusions

Saffron compound was extracted in aqueous solution was studied by cyclic voltammetric technique using modified glassy carbon electrode with carbon nanotubes to find the electrochemical behavior in blood medium and with ascorbic acid. It was found that saffron compound considered as anti-oxidative reagent in blood medium which appeared two cathodic current peaks in the cyclic voltammogram. Diffusion coefficient values of two reduction current peaks at -0.75 and -1.75 V were determined by Randel equation from different scan rate which has 2.2×10^{-6} and 1.1×10^{-5} cm^2/sec respectively. The study was indicated that saffron compound is good antioxidant reagent in blood medium and there is no affected of ascorbic acid on the reduction current peaks of the saffron compound.

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Radhi, Muhammed Mizher – **Khalaf**, Maysara Samer – **Ali**, Zainab Oun – **Al-Dabbagh**, Thamir Aboud: *Voltammetric study of saffron in blood mediated by modified glassy carbon electrode (GCE) with carbon nanotube (CNT/GCE)*

Építőanyag – Journal of Silicate Based and Composite Materials, Vol. 70, No. 3 (2018), 78–81. p.

https://doi.org/10.14382/epitoanyag-jsbcm.2018.14