Chemical Methodologies 4(2020) 743-753

Chemical Methodologies

Journal homepage: http://chemmethod.com

Original Research article

Electrochemical Determination of Folic Acid in Fruit Juices Samples Using Electroanalytical Sensor Amplified with CuO/SWCNTs and 1-Butyl-2,3-dimethylimidazolium Hexafluorophosphate

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ARTICLE INFORMATION

Received: 27 May 2020
Received in revised: 22 August 2020
Accepted: 31 August 2020

DOI: 10.22034/chemm.2020.113657

KEYWORDS

Folic acid analysis
Ionic liquid
Food analysis
Fruit juices
Modified sensor

ABSTRACT

Folic acid is an important food additive found in most food products. This research study focused on making a powerful analytical device to determine the folic acid concentration in food products. An electrochemical amplified sensor based on paste electrode (PE) modified with CuO-CNTs and 1-butyl-2,3-dimethylimidazolium hexafluorophosphate (BDHFP) was fabricated and used to study the electro-oxidation of folic acid. Oxidation current of folic acid was improved about 2.8 times at PE/M/CuO-CNTs/BDHFP compared with that of the PE. In addition, an irreversible and pH dependent oxidation signal was detected for redox reaction of folic acid at surface of PE/M/CuO-CNTs/BDHFP. Active surface area of PE was increased from 0.11 cm^2 to 0.18 cm^2 after modification with CuO-CNTs and BDHFP. Differential pulse voltammetric (DPV) signals displayed a linear dynamic range 3.0 nM–250 µM with detection limit 0.8 nM for measurement of folic acid. To study the ability of the PE/M/CuO-CNTs/BDHFP to determine the folic acid in real samples, apple and orange juices were selected and recovery data between 99.29%-101.6% confirm high performance ability of PE/M/CuO-CNTs/BDHFP for determination of folic acid in real samples.

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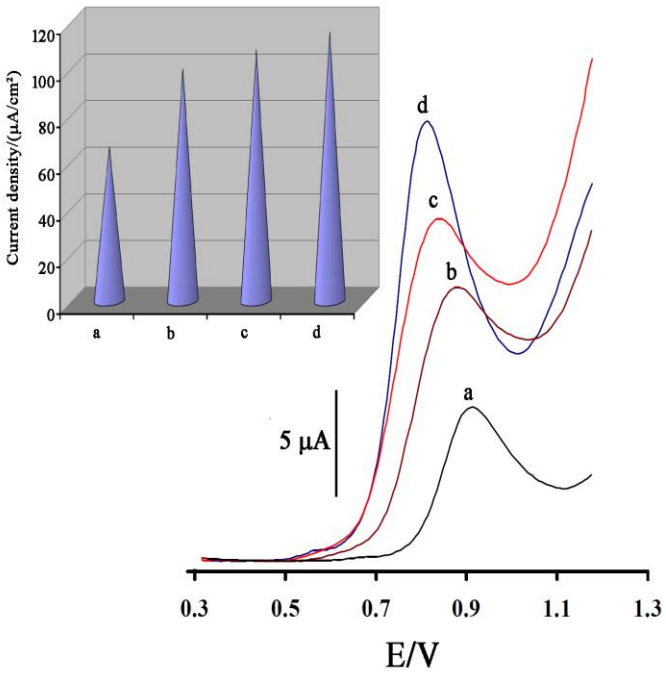
Graphical Abstract



Introduction

Folic acid or vitamin B_9 is one of the synthetic forms of folate with wide range of application in human body for making DNA and different types of genetic material [1]. This compound is prescribed as an essential vitamin for pregnant women [2]. In addition, folic acid has been used in fortified foods [3]. The broccoli, leafy green vegetables, chickpeas, peas and brussels sprouts are the main sources of folic acid in food samples [4]. No toxic effects of folic acid have been reported so far. However, controlling the amount in food samples is very important and necessary to check the enriched products by different companies [5]. For this purpose, various analytical methods for folic acid analysis in food samples have been reported [6-10]. However, simple and fast electrochemical methods have received more attention than the old analytical methods in recent years [11-20].

On the other hand, the possibility of designing different types of electrochemical sensors with high selectivity and suitable sensitivity for rapid growth of the type of analytical tools has increased [21-25]. Also wide ranges of modifiers have been proposed in recent years to increase the selectivity and sensitivity of electrochemical sensors for the analysis of food and drug samples [26-30]. Among these, the most common application is related to the use of nanomaterials with different structures

[31-35]. There have also been recent reports on ionic liquids being used to design high-sensitivity electrochemical sensors [36-40].

By moving from micro to the nano-size, the properties of compounds may change drastically and new unique properties might appear [41-55]. Some of them showed high conductivity and high surface area such as carbon nanotubes and metal nanoparticles (for the metals such as copper) [56-60]. Accordingly, several reports of the use of nanomaterials in the design of analytical sensors for food and pharmaceutical compounds have been presented so far [61-65].

Ionic liquids displays are a new class of electrochemical sensor modifiers that have been used in recent years to increase the sensitivity of pharmaceutical and food sensors [66-70]. High electrochemical conductivity is one of the most important features of ionic liquids and the reason for their use in the design of electrochemical sensors [71-75]. In this study, PE/M/CuO-CNTs/BDHFP was fabricated as new and highly sensitive food electrochemical sensor to determine the folic acid. The PE/M/CuO-CNTs/BDHFP showed an acceptable ability to determine the folic acid in fruit juices samples.

Experimental

Materials and apparatus

Folic acid (>97%), copper(II) acetate, phosphoric acid, acetic acid glacial, sodium hydroxide, graphite powder, 1-butyl-2,3-dimethylimidazolium hexafluorophosphate, paraffin oil were purchased in analytical grade and from Sigma and Merck company. CuO/CNTs were synthesized by reported strategy by published paper by Maleh *et al*. [76].

The μ-autolab machine connected electrochemical cell and in the presence of $Ag/AgCl/KCl_{sat}$ was used for recording to electrochemical signals. Mira-3-XMU machine was used for morphological investigation.

Fabrication of PE/M/CuO-CNTs/BDHFP

After optimizing the mediator percentages in paste matrix, the PE/M/CuO-CNTs/BDHFP was fabricated by mixing 70 mg CuO-CNTs + 930 mg graphite powder in the presence of paraffin oil + BDHFP with ration 80:20 in mortar and pestle. The obtained paste add end of glass tube.

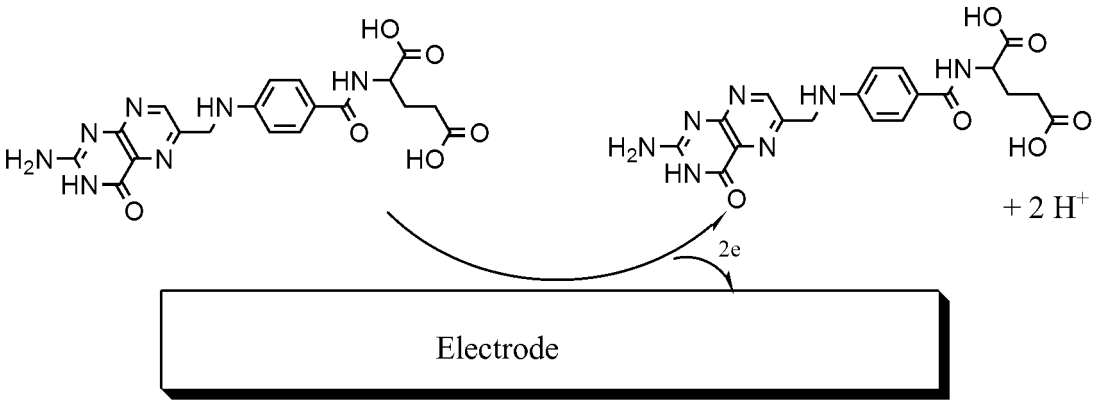
Preparation of real sample

The orange and apple juices purchased from local market and centrifuge with speed 3000 rpm for 15 min. After filtration, the obtained solution was used for determination of folic acid in real samples.

Results and discussion

Electrochemical behavior of folic acid

According to the redox reaction of folic acid displayed in Scheme 1. [9], pH is effective factor in redox signal of folic acid and optimization of this factor is very important. The DP voltammograms of 50 µM folic acid in the 6.0<pH<11.0 was recorded and results are demonstrated in Figure 1. The plot of potential vs. pH showed a linear relation with equation E= -0.0613 pH + 1.3766 (R^2 = 0.9931), that confirmed the presence of electron and H^+ with equal values in redox reaction of folic acid according to Scheme 1. (Figure 1). In addition, maximum oxidation signal of folic acid was observed at pH=9.0 and this condition were selected as optimum condition (Figure 2).



Scheme 1. Suggestion mechanism for electro-oxidation of folic acid

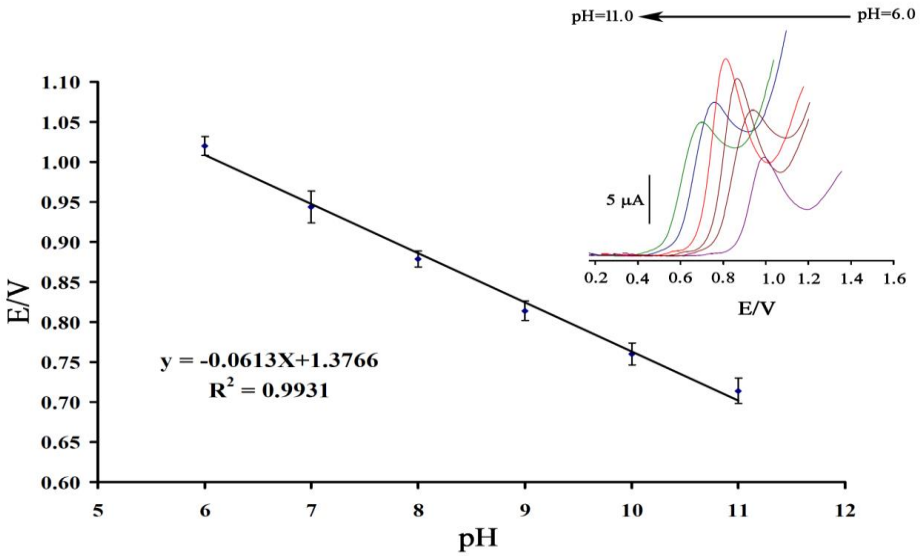


Figure 1. E-pH plot for electro-oxidation of 50 µM folic acid at surface of PE/M/CuO-CNTs/BDHFP (n=4) Inset) relative DP voltammograms for 50 µM folic acid in pH range 6.0-11.0

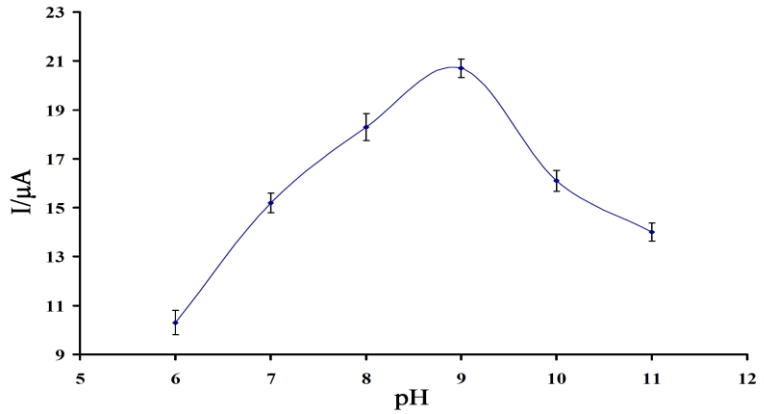


Figure 2. I-pH plot for electro-oxidation of 50 µM folic acid at surface of PE/M/CuO-CNTs/BDHFP (n=4)

The effect of CuO-CNTs nanocomposite and BDHFP in modification process was investigated by recording DP voltammograms 50 µM folic acid at surface of PE (curve a), PE/M/CuO-CNTs (curve c), PE/M/BDHFP (curve c) and PE/M/CuO-CNTs/BDHFP (curve d). The oxidation current and potential for folic acid were detected about 7.32 µA and 914 mV at surface of PE and 20.7 µA and 814 mV at surface of PE/M/CuO-CNTs/BDHFP, respectively. The modification of PE with CuO-CNTs and BDHFP was improved oxidation current of folic acid 2.8 times and was reduced oxidation potential of folic acid about 100 mV.

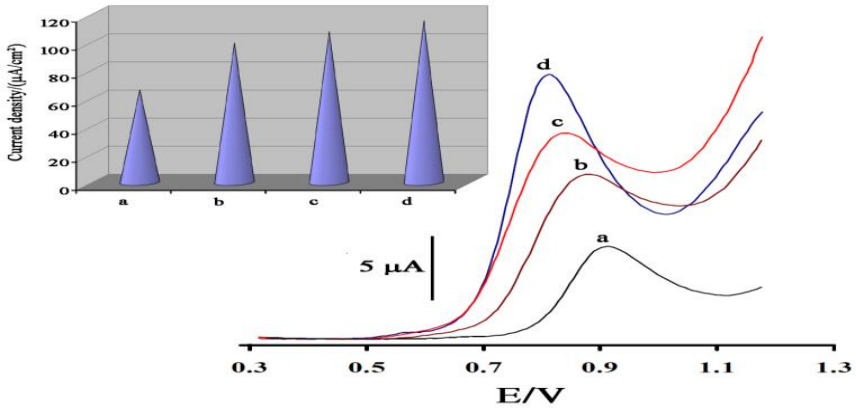


Figure 3. DP voltammograms of 50 µM folic acid at surafce of PE (curve a); PE/M/CuO-CNTs (curve b); PE/M/BDHFP (curve c) and PE/M/CuO-CNTs/BDHFP (curve d)

The linear sweep voltammograms of 600 µM folic acid on the surafce of PE/M/CuO-CNTs/BDHFP in the sacn rate range 30-300 mV/s (Figure 4 inset). Linear relation with eqaution $I = 5.3753\ \nu^{1/2} - 19.4700$ ($R^2=0.9921$) was detected between current and $\nu^{1/2}$ for oxidation of folic acid at surafce of

PE/M/CuO-CNTs/BDHFP that confirm diffusion process [77-87] for the redox reaction of folic acid (Figure 4).

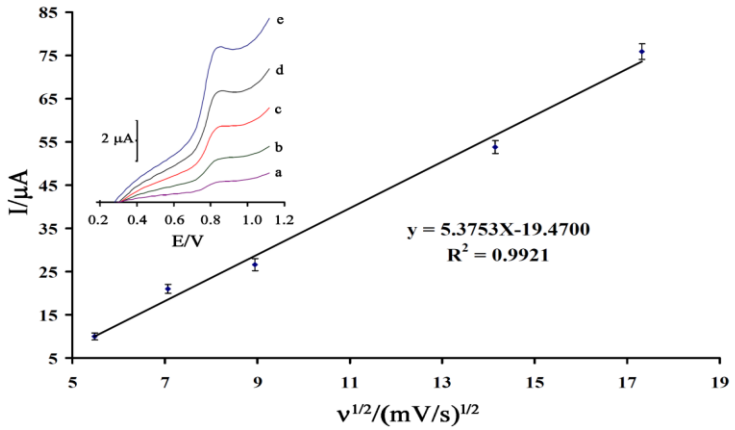


Figure 4. Curent-$\nu^{1/2}$ curve for electro-oxidation of 600 µM folic acid at surafce of PE/M/CuO-CNTs/BDHFP with scan rates a) 30, b) 50, c) 80, d) 200 and e) 300 mV/s (n=4)

The DP voltammograms of different concentration of folic acid was recorded on the surface of PE/M/CuO-CNTs/BDHFP to study the linear dynamic range investigation (Figure 5 inset). As seen in Figure 5, a linear dynamic range between 3.0 nM-250 µM with detection limit 0.8 nM using PE/M/CuO-CNTs/BDHFP as new electrochemical sensor.

On the other hand, ability of PE/M/CuO-CNTs/BDHFP to determine the folic acid in orange and apple juices was tested by standard addition method and data repeated for 3 times. The results are shown in Table 1. and confirm powerful ability of sensor for real sample analysis.

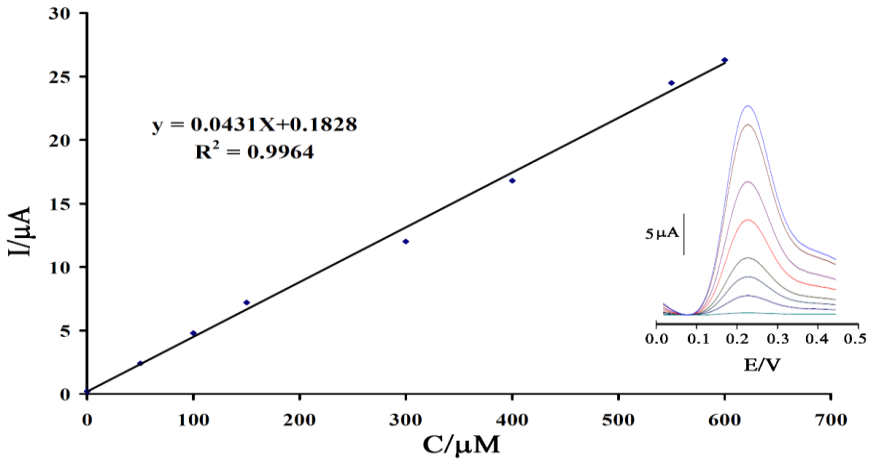


Figure 5. Current-concentration curve for electro-oxidation of folic acid in the range of 3.0 nM-250 µM. Inset) Relative DP volatmmograms of folic acid at surface of PE/M/CuO-CNTs/BDHFP

Table 1. Real sample analysis of folic acid using PE/M/CuO-CNTs/BDHFP (n=4)

Sample	Folic acid added (µM)	Folic acid expected (µM)	Folic acid founded (µM)	Recovery %
Orange juice	---	---	9.89±0.54	---
	10.00	19.89	20.21±0.87	101.6
Apple juice	---	---	8.51±0.34	---
	10.00	18.51	18.38±0.65	99.29

Conclusion

A food electrochemical sensor was design and fabricated to determine the folic acid in juices samples. Differential pulse voltammetric (DPV) signals revealed a linear dynamic range 3.0 nM – 250 µM with the detection limit of 0.8 nM. The PE/M/CuO-CNTs/BDHFP was introduced as working electrode and new electrochemical sensor in an electrochemical investigations. Due to high conductivity, the PE/M/CuO-CNTs/BDHFP showed good catalytic activity on oxidation signal of folic acid and improved its oxidation signal about 2.8 times.

Conflict of Interest

We have no conflicts of interest to disclose.

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How to cite this manuscript: Hossein Sadeghi, Seyed-Ahmad Shahidi, Shahram Naghizadeh Raeisi*, Azade Ghorbani-HasanSaraei, Fatemeh Karimi, Electrochemical Determination of Folic Acid in Fruit Juices Samples Using Electroanalytical Sensor Amplified with CuO/SWCNTs and 1-Butyl-2,3-Dimethylimidazolium Hexafluorophosphate. Chemical Methodologies 4(6), 2020, 743-753. DOI: 10.22034/chemm.2020.113657.