MnFe$_2$O$_4$/1-Butyl-3-methylimidazolium hexafluorophosphate modified carbon paste electrode: an amplified food sensor for determination of gallic acid in the presence of ferulic acid as two phenolic antioxidants

Tahereh Zabihpour$^a$, Seyed-Ahmad Shahidi$^a$*, Hassan Karimi-Maleh$^{b,c,*}$, Azade Ghorbani-Hasan Saraei$^a$

$^a$Department of Food Science and Technology, Ayatollah Amoli Branch, Islamic Azad University, Amol 46311-39631, Mazandaran, Iran

$^b$Laboratory of Nanotechnology, Department of Chemical Engineering, Quchan University of Technology, Quchan 94771-67335, Iran

$^c$Department of Chemistry, University of Johannesburg, Johannesburg 17011, South Africa

Received: 25 September 2019, Accepted: 14 November 2019, Published: 02 December 2019

Abstract

A MnFe$_2$O$_4$ nanoparticle/1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF$_6$) was incorporated into carbon paste electrode (MnFe$_2$O$_4$/BMIM-PF$_6$/CPE) and used as food electrochemical sensor for the study of the electrochemical determination of gallic acid in the presence of ferulic acid for the first time. The structure and morphology of MnFe$_2$O$_4$ nanoparticle was investigated by TEM methods. Meanwhile, the electrochemical performance of the MnFe$_2$O$_4$/BMIM-PF$_6$/CPE towards gallic acid and ferulic acid determination was demonstrated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The MnFe$_2$O$_4$/BMIM-PF$_6$/CPE exhibited a wide linearity of 0.005–220.0 µM for gallic acid and 0.3–250 µM for ferulic acid with detection limits of 1.0 nM and 0.1 µM, respectively. Furthermore, the ability of MnFe$_2$O$_4$/BMIM-PF$_6$/CPE was tested for the determination of gallic acid and ferulic acid in food products.

Keywords: Gallic acid; ferulic acid; MnFe$_2$O$_4$ nanoparticle; 1-Butyl-3-methylimidazolium hexafluorophosphate; antioxidant.

Introduction

Antioxidants are one of the ingredients in foods that are neutralize free radicals [1]. The presence of antioxidants in body is very important for the human health [2]. There are different types of antioxidants that are useful for human health such as minerals, proteins (amino acid), enzymes and coenzymes and phytonutrients/phytochemicals [3]. The gallic acid and ferulic acid are two important phytonutrients/phytochemicals (phenolic type) antioxidant with more application in different types of food products [4,5]. The gallic acid as
powerful antioxidants is present in a variety of foods and herbs such as walnuts, blueberries, flax seed, apples and tea [6]. Gallic acid is not prescribed for patients who are being treated with high blood pressure. The determination of food additives and especially food antioxidants such as gallic acid and ferulic acid is very important for study food quality [7-12]. Accordingly, there are many scientific reports for fabrication of food antioxidant analytical sensors in recent years [13,14].

In between reported analytical sensors for food compound analysis, the electrochemical modified sensors showed more advantages compared to other analytical strategy due to portable ability, fast response and low cost [15-19]. Due to diversity of modification process in fabrication of electrochemical sensors [20-29], the electrochemical sensors could be useful for nanomolar and simultaneous analysis of food additives [30-35].

The nanomaterials and especially metal oxide nanoparticles were suggested as conductive mediators for fabrication of different electrochemical sensors [36-41]. Due to high conductivity, metal oxide nanoparticles and especially iron oxide nanoparticles could be useful for improvement limit of detection electrochemical sensors [42-45]. On the other hand, the coupling of metal based nanoparticles with other mediators such as ionic liquids are an interesting attraction for designing highly sensitive electrochemical sensors [46-48].

In this regards and in continuous efforts of our research team for fabrication electrochemical sensors, we design MnFe$_2$O$_4$/BMIM-PF$_6$/CPE as new electrochemical tool for determination of gallic acid in the presence of ferulic acid as food antioxidants in the real samples such as mango dried powder, white rice and blueberry samples.

**Experimental**

**Chemicals and solutions**

Graphite powder, gallic acid, phosphoric acid, and ferulic acid, were purchased from Merck Co. Ethanol, manganese sulfate monohydrate, nujol oil and iron(III) chloride were purchased from Sigma-Aldrich Co. A standard stock solution of 0.01 M gallic acid and ferulic acid were prepared by dissolving analytes in distilled water and was preserved at 4 °C. The phosphate buffer solution (PBS) (0.1 M) was prepared by phosphoric acid solution and addition of 2.0 M sodium hydroxide.

**Apparatus**

Electrochemical investigation was performed on a Metrohm 910 PSTAT Mini Electrochemical Machine controlled with a PSTAT software. An electrochemical voltammetric cell was adopted. The new sensor as working electrode was a MnFe$_2$O$_4$/BMIM-PF$_6$/CPE, the reference and auxiliary electrodes were an Ag/AgCl/KCl sat (Azar Electrode Co.) and platinum wire, respectively. The TEM machine model Zeiss EM900 was used for surface and shape investigation of MnFe$_2$O$_4$ nanoparticle. The XRD machine model ARL PERFORM'X was used for structure investigation.

**Synthesis of MnFe$_2$O$_4$ nanoparticle**

Chemical co-precipitation strategy was used for synthesis of MnFe$_2$O$_4$ nanoparticle using manganese sulfate monohydrate and iron(III) chloride as a precursor with molar ratio of Mn to Fe as 1:2 in 100 mL distilled water. The solution containing Mn to Fe solution stirred (2000 rpm) and the precipitating agent (2.0 M sodium hydroxide) was added dropwise. The colloidal results was ultrasonicated at 200 W at a
temperature of 85 °C for 1.5 h. After cooling colloidal solution to room temperature, the result sample was filtered and washed with distilled water until precipitate pH reaches 7.0. In the final step, MnFe₂O₄ nanoparticle was dried at temperature of 80 °C for 13 h.

**Preparation of MnFe₂O₄/BMIM-PF₆/CPE**

The MnFe₂O₄/BMIM-PF₆/CPE was prepared by thoroughly mixing 0.97 g graphite powder with 0.03 g MnFe₂O₄ nanoparticle in a mortar in the presence of diethyl ether as solvent. After evaporation of solvent, the resultant paste was obtained using addition of nujol oil+ BMIM-PF₆ (ration of 9:1 V: V). The resultant paste immediately was inputed in end of glass tube with copper wire as a conductive system.

**The real sample analysis**

The mango dried powder, white rice and blueberry samples were used for investigation ability of MnFe₂O₄/BMIM-PF₆/CPE for real sample analysis. The 2.0 g real sample powders was treated with 50% ethanol solution and the resulted solution was sonicated for 1 h. The obtained solution was filtered using Whatman paper (No. 1), and then the lipophilic impurities were removed from the resulted solution. The samples were used for determination of gallic acid and ferulic acid by MnFe₂O₄/BMIM-PF₆/CPE sensor using standard addition method.

**Results and discussion**

**Characterization of MnFe₂O₄ nanoparticle**

The XRD pattern of MnFe₂O₄ nanoparticle is present in Figure 1A and the presence of planes with miler indexes [220], [311], [222], [400], [331], [422], [333], [440], [531] and [442] confirm the synthesis of MnFe₂O₄ nanoparticle with JCPDS card no. 01-074-2403. The particle size of MnFe₂O₄ nanoparticle was determined using Scherrer equation and found d ~ 25 nm. The TEM image of MnFe₂O₄ nanoparticle is present in Figure 1B and the results show spherical shape for the synthesized MnFe₂O₄ nanoparticle with diameter ~10 nm.

**Electrochemical oxidation of gallic acid at surface of MnFe₂O₄/BMIM-PF₆/CPE**

The CVs of gallic acid was recorded at surface of MnFe₂O₄/BMIM-PF₆/CPE at different pH values (5.0<pH<9.0) (Figure 2 insert).
The negative shift of gallic acid oxidation signal with increasing pH and linear relation between $E_{\text{pa}}$ vs. pH with slope 64.4 mV/pH confirm the presence of equal value of $H^+$ and electron in oxidation mechanism of gallic acid (Figure 2). The maximum oxidation signal of gallic acid at surface of MnFe$_2$O$_4$/BMIM-PF$_6$/CPE was detected at pH=7.0 and this pH was used as optimum condition for electrochemical determination of gallic acid.

**Figure 2.** The EP vs. pH curve for electro-oxidation of 500.0 µM gallic acid at surface of MnFe$_2$O$_4$/BMIM-PF$_6$/CPE. The CVs of 500.0 µM gallic acid at surface of MnFe$_2$O$_4$/BMIM-PF$_6$/CPE in the pH range 5.0-9.0

CV method was used to examine the catalytic activity of MnFe$_2$O$_4$/BMIM-PF$_6$/CPE (curve d) toward gallic acid determination (Figure 3). Herein, the redox signals of gallic acid was compared with other modified BMIM-PF$_6$/CPE (curve c), MnFe$_2$O$_4$/CPE (curve b) and unmodified CPE (curve a) at pH=7.0. As expected, MnFe$_2$O$_4$/BMIM-PF$_6$/CPE displayed the maximum $I_{\text{pa}}$ about 64.47 µA at a low $E_{\text{pa}}$ of 0.32 V compared with CPE ($I_{\text{pa}}$=18.34 µA; $E_{\text{pa}}$=0.39 V). The increase in oxidation current of gallic acid after addition of MnFe$_2$O$_4$ and BMIM-PF$_6$ into carbon paste matrix is relative to high surface area and good electrical conductivity of mediators. The results confirm that the synthesis of MnFe$_2$O$_4$ nanoparticle and BMIM-PF$_6$ in carbon paste matrix showed unique sensing behavior toward gallic acid electro-oxidation.
Hence, the variation in scan rate on the MnFe$_2$O$_4$/BMIM-PF$_6$/CPE surface in the presence of gallic acid provided effective information about the type of analyte transfer from solution to electrode surface in redox system. Figure 4 inset displays the CV curves of MnFe$_2$O$_4$/BMIM-PF$_6$/CPE in the presence of gallic acid at various scan rates (10 to 100 mV s$^{-1}$). The results displayed increased $I_{pa}$ with increased $v^{1/2}$ with $R^2=0.9936$ that confirm diffusion control process for electro-oxidation of gallic acid at surface of MnFe$_2$O$_4$/BMIM-PF$_6$/CPE.
Figure 4. The Plot of $I_{pa}$ vs. $v^{1/2}$ in the solution containing 500.0 µM gallic acid at surface of MnFe$_2$O$_4$/BMIM-PF$_6$/CPE. Inset) The CVs of 500.0 µM gallic acid at surface of MnFe$_2$O$_4$/BMIM-PF$_6$/CPE at a scan rates a) 10.0, b) 15.0, c) 20.0, d) 40.0, e) 70.0 and f) 100 mV/s.

The value of diffusion coefficient (D) of gallic acid was determined using chronoamperometric investigation. The chronoamperograms of 200 µM, 400 µM, 600 µM and 800 µM gallic acid were recorded using applied potential 500 mV (Figure 5A). The value of D was determined ~2.8×10$^{-5}$ cm$^2$/s using slopes of cottrell plots showed in Figure 5B.

**Simultaneous determination of gallic acid and ferulic acid**

The differential pulse voltammetric signal of gallic acid and ferulic acid were recorded separately at surface of MnFe$_2$O$_4$/BMIM-PF$_6$/CPE. The results showed linear dynamic ranges 0.005–220.0 µM with equation ($I_{pa} = 0.6377 C + 8.6330$; $R^2=0.9942$) and 0.3–250 µM with equation ($I_{pa} = 0.7459 C + 6.1739$; $R^2=0.9967$) for gallic acid and ferulic acid, respectively. The detection limit 1.0 nM and 0.1 µM were detected for determination of gallic acid and ferulic acid at surface of MnFe$_2$O$_4$/BMIM-PF$_6$/CPE. These values of LDR or LOD for determination of gallic acid are significantly better than the values reported by previous groups (Table 1).
The differential pulse voltammogram of MnFe₂O₄/BMIM-PF₆/CPE in the presence of different concentration of gallic acid and ferulic acid was recorded and the results were shown in Figure 6A. The results showed two separated oxidation signals for gallic acid and ferulic acid at potential 0.31 V and 0.68 V with ΔE=0.37 V, respectively. In addition, the obtained sensitivity for gallic acid and ferulic acid in simultaneous investigation were obtained 0.6233 µA/µM and 0.7380 µA/µM that are very near to obtained sensitivity in dynamic range investigation (Figure 6B and 6C). These results confirm high performance ability of MnFe₂O₄/BMIM-PF₆/CPE for simultaneous determination of gallic acid and ferulic acid.

Table 1. Comparison of the efficiency of published electrochemical sensors in the determination of gallic acid

<table>
<thead>
<tr>
<th>Electrode</th>
<th>pH</th>
<th>LDR (µM)</th>
<th>LOD (µM)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>glassy carbon electrode</td>
<td>1.88</td>
<td>1.0-20.0</td>
<td>0.663</td>
<td>[49]</td>
</tr>
<tr>
<td>carbon paste electrode</td>
<td>1.7</td>
<td>0.8-100</td>
<td>0.25</td>
<td>[50]</td>
</tr>
<tr>
<td>carbon paste electrode</td>
<td>2.0</td>
<td>1.0-33.75</td>
<td>0.27</td>
<td>[51]</td>
</tr>
<tr>
<td>carbon paste electrode</td>
<td>7.0</td>
<td>0.005-220.0</td>
<td>0.001</td>
<td>This work</td>
</tr>
</tbody>
</table>

Figure 5. A) Chronoamperograms obtained at the surface of MnFe₂O₄/BMIM-PF₆/CPE in the solution containing (a) 200, (b) 400, (c) 600 and d) 800 µM gallic acid. B) Cottrell plots obtained from Chronoamperograms signals.
Figure 6. A) The DPVs of MnFe$_2$O$_4$/BMIM-PF$_6$/CPE in the solution containing a) 40.0+25.0; b) 75.0 + 50.0; c) 90.0 + 55.0; d) 100.0 + 55.0; e) 110.0 + 70.0 and f) 120.0 + 80.0 µM gallic acid + ferulic acid. B) The plots of the $I_{pa}$ as a function of gallic acid concentration. C) The plots of the $I_{pa}$ as a function of ferulic acid concentration.

**Stability investigation of MnFe$_2$O$_4$/BMIM-PF$_6$/CPE**

The storage stability of MnFe$_2$O$_4$/BMIM-PF$_6$/CPE was measured by storing MnFe$_2$O$_4$/BMIM-PF$_6$/CPE for one month. MnFe$_2$O$_4$/BMIM-PF$_6$/CPE showed 91.8% of its initial response in the presence of 500 µM gallic acid after 30 days, which showed the MnFe$_2$O$_4$/BMIM-PF$_6$/CPE had the ability for efficient voltammetric determination of gallic acid (Figure 7).

**Interference study**

The selectivity of MnFe$_2$O$_4$/BMIM-PF$_6$/CPE as a new analytical tool for determination of gallic acid and ferulic acid was tested with acceptable error 5% in current and the results are present in Table 2. According to the reported results in this table, the MnFe$_2$O$_4$/BMIM-PF$_6$/CPE showed good selectivity toward determination of gallic acid and ferulic acid in food samples.
Figure 7. The diagram relative to oxidation 500 μM gallic acid at the surface MnFe₂O₄/BMIM-PF₆/CPE in different period time

Table 2. The selectivity investigation results in the presence of 50.0 μM gallic acid and ferulic acid

<table>
<thead>
<tr>
<th>Species</th>
<th>Tolerant limits (W_{interference}/W_{gallic acid})</th>
<th>Tolerant limits (W_{interference}/W_{ferulic acid})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻, K⁺, Mg²⁺, Na⁺, Br⁻, Cu²⁺</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Glucose, lactose, sucrose</td>
<td>500</td>
<td>400</td>
</tr>
<tr>
<td>Lecine, alanine, glycine</td>
<td>300</td>
<td>200</td>
</tr>
</tbody>
</table>

Real sample analysis
Real-sample determination was further conducted using standard addition method for the practicability of MnFe₂O₄/BMIM-PF₆/CPE toward gallic acid and ferulic acid in food samples. The prepared real-sample solutions in section 3.4 was used for investigation of MnFe₂O₄/BMIM-PF₆/CPE ability in real sample analysis and obtained data are present in Table 3. Results showed that MnFe₂O₄/BMIM-PF₆/CPE was identified as a suitable tool for determination of gallic acid and ferulic acid in food samples.
Table 3. The obtained results for determination of gallic acid and ferulic acid in real samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added gallic acid (µM)</th>
<th>Added ferulic acid (µM)</th>
<th>Founded gallic acid (µM)</th>
<th>Founded ferulic acid (µM)</th>
<th>Recovery for gallic acid %</th>
<th>Recovery for ferulic acid %</th>
</tr>
</thead>
<tbody>
<tr>
<td>blueberry</td>
<td>---</td>
<td>---</td>
<td>&lt;LOD</td>
<td>&lt;LOD</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>5.00</td>
<td>4.96±0.33</td>
<td>5.19±0.27</td>
<td>99.2</td>
<td>103.8</td>
</tr>
<tr>
<td>white rice</td>
<td>---</td>
<td>---</td>
<td>&lt;LOD</td>
<td>&lt;LOD</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>10.00</td>
<td>10.00</td>
<td>10.34±0.58</td>
<td>10.43±0.72</td>
<td>103.4</td>
<td>104.3</td>
</tr>
<tr>
<td>mango dried powder</td>
<td>---</td>
<td>---</td>
<td>3.21±0.29</td>
<td>&lt;LOD</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>10.00</td>
<td>10.00</td>
<td>12.98±0.78</td>
<td>9.82±0.88</td>
<td>98.25</td>
<td>98.2</td>
</tr>
</tbody>
</table>

Conclusion
We developed MnFe$_2$O$_4$ nanoparticles coupled with BMIM-PF$_6$ for modification of CPE and the resulted sensor was suggested as the selective electrochemical sensor for determination of gallic. The MnFe$_2$O$_4$/BMIM-PF$_6$/CPE showed good ability for determination of gallic acid in the presence of ferulic acid as two important phenolic antioxidants with ΔE=0.37 V. The MnFe$_2$O$_4$/BMIM-PF$_6$/CPE exhibited a wide linearity of 0.005–220.0 µM for gallic acid and 0.3–250 µM for ferulic acid with detection limits of 1.0 nM and 0.1 µM, respectively. The MnFe$_2$O$_4$/BMIM-PF$_6$/CPE was used as highly sensitive food analytical sensor for determination of gallic acid and ferulic acid in food samples.

Acknowledgements
The authors wish to thank Quchan University of Technology for their support.

References

How to cite this manuscript: Tahereh Zabihpour, Seyed-Ahmad Shahidi, Hassan Karimi-Maleh, Azade Ghorbani-Hasan Saraei. MnFe₂O₄/1-Butyl-3-methylimidazolium hexafluorophosphate modified carbon paste electrode: an amplified food sensor for determination of gallic acid in the presence of ferulic acid as two phenolic antioxidants. *Eurasian Chemical Communications*, 2020, 2(3), 362-373.