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Original Research Article

Determination of Rutin in Black Tea Samples using a Nanostructure Amplified Electroanalytical Sensor

Bahareh Davarnia[a], Seyed Ahmad Shahidi[a,*], Azade Ghorbani-Hasan Saraei[a], Fatemeh Karimi[b]

[a] *Department of Food Science and Technology, Ayatollah Amoli Branch, Islamic Azad University, Amol 46311-39631, Mazandaran, Iran*
[b] *Department of Chemical Engineering, Laboratory of Nanotechnology, Quchan University of Technology, Quchan, Islamic Republic of Iran*

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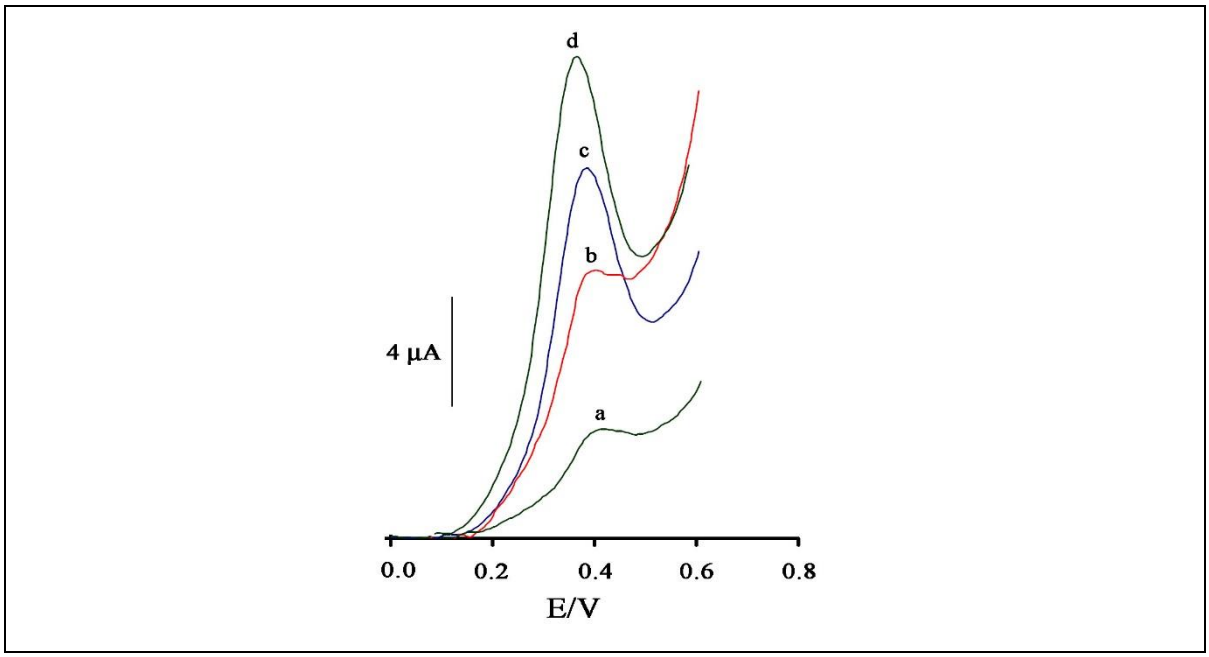
ABSTRACT

Ag nanoparticle and 1-buthyl-3-methyl imidazolium bromide (1B3MIBr) carbon paste electrode (Ag/NP/1B3MIBr/CPE) amplified sensor was fabricated for determination of rutin in this project. The electro-oxidation of rutin occurs at a potential about 0.4 V at the surface of Ag/NP/1B3MIBr/CPE and this value is less positive than the unmodified CPE. pH = 7.0 was selected as an optimize condition for all of electrochemical investigations in this work and for evaluating electrochemical parameters such as diffusion coefficient (5.0×10^{-6} cm^2/s). At the optimized condition for rutin analysis, the differential pulse voltammetry (DPV) peak currents of rutin show a wide linear dynamic range from 0.05-320 µM with a detection limit of 10 nM. Finally, the Ag/NP/1B3MIBr/CPE was used for determination of rutin in soy samples with good selectivity and high sensitivity.

GRAPHICAL ABSTRACT



* Corresponding author's E-mail address: sashahidy@yahoo.com

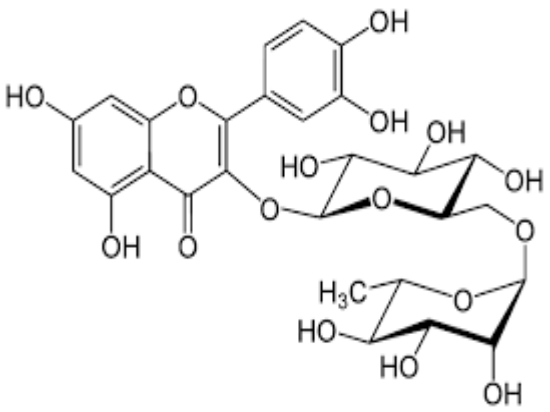
Introduction

Rutin (Scheme 1) is a natural compound and a famous bioflavonoid found in different types of foods samples including most citrus fruits, black tea, apples, soy, figs, and buckwheat samples.

Rutin likes any other flavonoid has strong antioxidant and anti-inflammatory effects in our body [1,2]. It is also used in different medical investigations such as a candidate to improve blood circulation, strengthen blood vessels, collagen production, lower cholesterol, and reduce arthritis symptoms [1]. The name of rutin comes from the plant name Ruta graveolens, which contains these phytonutrients. Chemically, rutin is a glycoside that contains the flavonolic quercetin agilcon with rosin disaccharide. Recent research suggests that rutin flavonoid can help maintain the elasticity of blood vessels, reduce the fragility of blood vessels, reduce the permeability of capillaries, and prevent complications from hypertension [3]. Rutin can act as a therapeutic agent to fight cancer due to its antioxidant and anti-inflammatory effects and it has been shown to induce apoptosis or cancer cell death and display antitumor effects [4]. There is a great deal of research on humans, organisms, and cells that suggests this antioxidant works to reduce tumor size, increase cancer cell death, and increase survival time [5,6]. It has been shown to have anti-cancer effects against a number of cancers, including leukemia, colorectal cancer, colorectal cancer, liver cancer, and lung cancer and rutin helps fight neuroblastoma, a type of cancer often found in the upper glands in children [7]. Research has reported protective effects on brain damage and age-related injuries. It also helps improve brain health because of its anti-inflammatory and antioxidant properties [7]. Researchers at the Harvard Medical Center find that rutin can act as a new strategy to prevent thrombosis in animal models [7]. Deep vein thrombosis is particularly dangerous because it can cause life-threatening complications such as stroke and heart attack [8].

Therefore, the determination of rutin is very necessary for food samples because the overtaking of rutin may cause cancer and hyperactivity in children [9-13]. There are many different methods for the determination of rutin in food samples such as, HPLC method [14-16], LC–MS/MS method [17], microsequential injection analysis [18], cathodic adsorptive stripping voltammetric method [19]. Between these methods, we select the electrochemical method because it is a cheap, fast and rapid, portable and green method [20-33]. In this research, Ag/NP/1B3MIBr/CPE was introduced as a new electroanalytical sensor for the determination of rutin in black team samples. Results showed high quality ability for rutin determination in food samples.

Scheme 1. Structure of Rutin



Experimental

Reagents and apparatus

The entire reagent and chemicals used in this project as rutin hydrate ≥94%, paraffin, sodium hydroxide >97%, phosphoric acid 85% and graphite were purchased from Merck and Sigma-Aldrich. Ag nanoparticles were synthesized according to our previously reported procedure [34]. A μ-Autolab system (Netherland) that connected to the computer with NOVA software included three electrochemical cells such as Ag/NP/1B3MIBr/CPE (as a working electrode) and $Ag/AgCl/KCl_{sat}$ (as references electrode) was used for electrochemical investigation.

Preparation of Ag/NP/1B3MIBr/CPE

The Ag/NP/1B3MIBr/CPE was prepared by mixing of 0.06 g Ag/NPs + 0.94 g graphite powder in the presence of two drops 1B3MIBr and 10 drops of the paraffin oil as binders. The obtaining paste was added into end of glass tube to fabrication of Ag/NP/1B3MIBr/CPE.

Real samples preparation

The extraction and preparation of black tea was done in two steps. In the first step, extraction process was done by 30 mL methanol solvent and in the second step continuous with hot water. For this goal, 3 g of black tea was prepared with 30 mL of methanol solution and results ultrasonicate with hot water for 1 h.

Results and Discussion

Electrochemical behavior of rutin at the surface of Ag/NP/1B3MIBr/CPE

Rutin has a phenolic structure and it is predicted that its redox behavior pH-dependent [35]. Therefore, in the first step we optimized pH value for electro-oxidation of rutin at the surface of Ag/NP/1B3MIBr/CPE. The Figure 1 inset display DP voltammograms of rutin at surface of Ag/NP/1B3MIBr/CPE in the 4.0<pH<8.0.

According to Figure 1, slope of potential-pH curve confirms equal value of electron and H^+ in redox reaction of rutin. In addition, oxidation current of rutin showed that maximum signal could be observed at pH= 7.0 (Figure 2) and this value was selected as optimum condition for next steps.

The role of mediators (Ag/NPs and 1B3MIBr in this case) in improving of the redox reaction of rutin is another important electrochemical parameter that must be an investigation in an electrochemical study. For this goal, the DP voltammograms of 60 µM rutin were recorded at the surface of modified and unmodified electrodes with a scan rate of 100 mV s^{-1} at pH 7.0 (Figure 3).

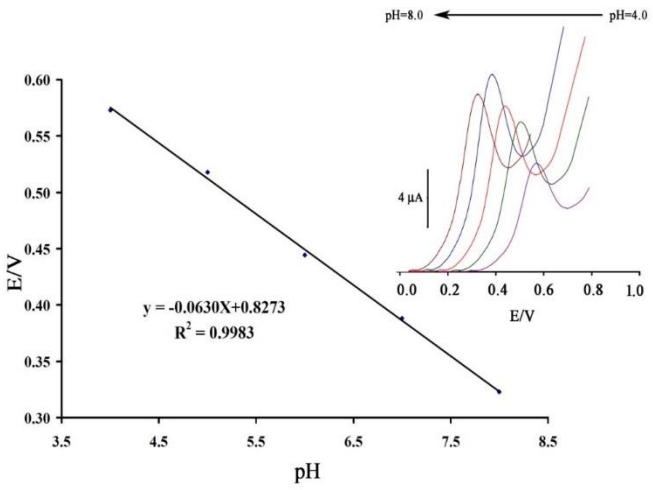


Figure 1. Plot of potential, Ep, vs. pH for the electro-oxidation of 50 µM rutin at surface Ag/NP/1B3MIBr/CPE. Inset: Differential pulse voltammetric response of 50 µM rutin in 4.0<pH<8.0

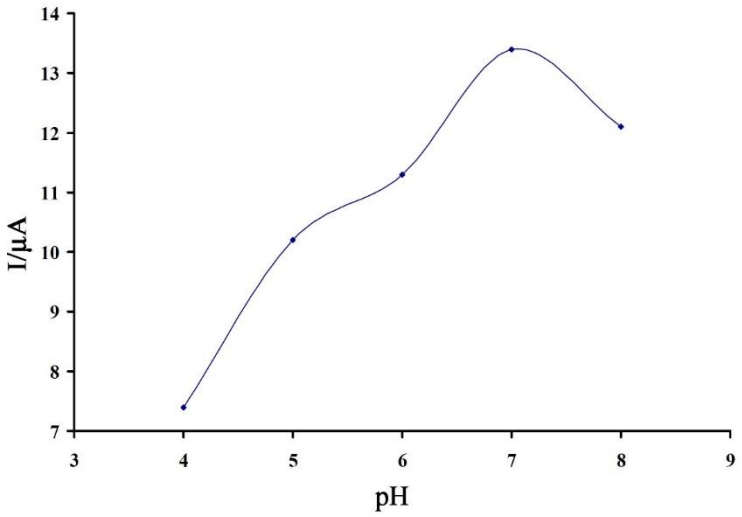


Figure 2. Plot of current vs. pH for the electro-oxidation of 50 μM rutin at surface Ag/NP/1B3MIBr/CPE

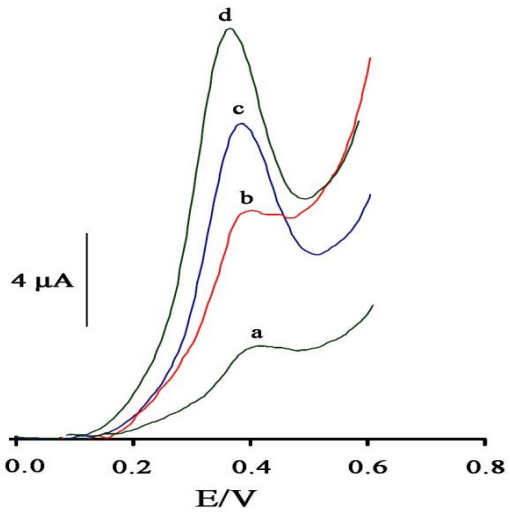


Figure 3. DP voltammograms of (a) CPE, (b) Ag/NP/CPE, (c) 1B3MIBr/CPE and (d) Ag/NP/1B3MIBr/CPE in the presence of 60 μM rutin at pH 7.0, respectively

Voltammmograms showed currents 3.95 μA, 9.68 μA, 13.4 μA and 17.4 μA for the oxidation of rutin at surface of CPE (curve a), Ag/NP/CPE (curve b), 1B3MIBr/CPE (curve c) and Ag/NP/1B3MIBr/CPE (curve d), respectively. In addition, oxidation potential of rutin moved to negative value from 428 mV at CPE to 368 mV at a surface of Ag/NP/1B3MIBr/CPE. These points confirm the high conductivity of Ag/NP and 1B3MIBr after modification of CPE and creating a highly sensitive rutin electrochemical sensor.

The role of the scan rate on redox reaction of rutin was investigated by recording linear sweep voltammograms of 300 μM rutin in the range of 5.0-50.0 mV s^{-1} at Ag/NP/1B3MIBr/CPE (Figuer 4 inset). The positive shift if oxidation potential of rutin with increasing in scan rate confirm a kinetic limitation and also, quasi-reversible behavior for electrooxidation of rutin at surface of Ag/NP/1B3MIBr/CPE. The linear relation with the equation $I = 4.5303\ \nu^{1/2} - 6.1350$ ($R^2 = 0.9975$) was observed for electro-oxidation of 300 μM rutin at surface of Ag/NP/1B3MIBr/CPE that confirm diffusion process for electrooxidation of rutin (Figure 4).

The chronoamprometric signals of 200 μM, 400 μM, and 500 μM rutin was recorded at surface of Ag/NP/1B3MIBr/CPE for

investigation diffusing process of rutin (Figure 5A). Using Cottrell slopes and equation ($I = nFAD^{1/2}C\pi^{1/2}t^{1/2}$) in Figure 5B, the value of the diffusion coefficient was calculated 5.0×10^{-6} cm^2/s.

Linear dynamic range and limit of detection are two major analytical parameters for one new fabricated sensor. Therefore, we used differential pulse voltammetric method for the determination of rutin using Ag/NP/1B3MIBr/CPE as an analytical tool. Results showed a linear dynamic range 0.05 – 320 µM with equation $I = 0.1925\ C_{rutin} + 2.3464$ (R^2=0.9974). In addition, the Ag/NP/1B3MIBr/CPE showed a detection limit 10 nM for determination of rutin at optimum condition.

In the following, for evaluation, the selectivity of Ag/NP/1B3MIBr/CPE, interference of Li^+, Cl^-, Na^+, methionine, glucose and valine were checked with acceptable error 5% and results confirm 1000-fold of these compounds have not any interference for determination of 10 µM rutin.

At the last stage of the project, to evaluate the applicability of Ag/NP/1B3MIBr/CPE, we use this proposed sensor in real food samples such as black tea. After the preparation of black tea, the standard addition method was used for determination of rutin in real samples and results are presence in Table 1. Recorded recovery data confirm the high quality of Ag/NP/1B3MIBr/CPE for the determination of rutin in real samples.

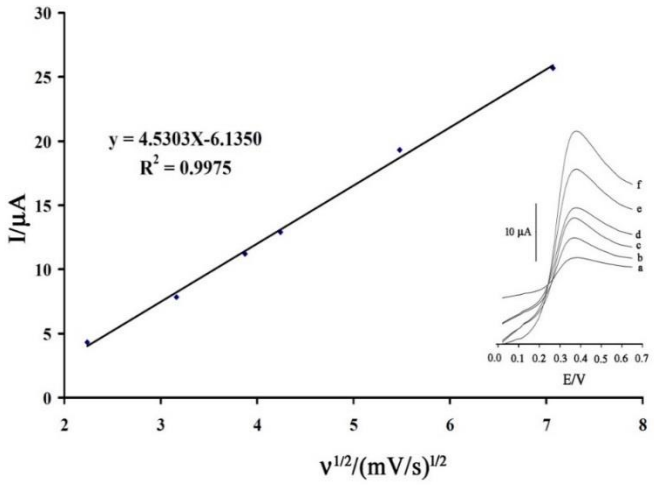


Figure 4. Plot of I_{pa} vs. $\nu^{1/2}$ for the oxidation of 300 µM rutin at Ag/NP/1B3MIBr/CPE. Inset shows linear sweep voltammograms of rutin at scan rates of a) 5.0, b) 10.0, c) 15.0, d) 18.0, e) 30, f) 50.0 mV/s

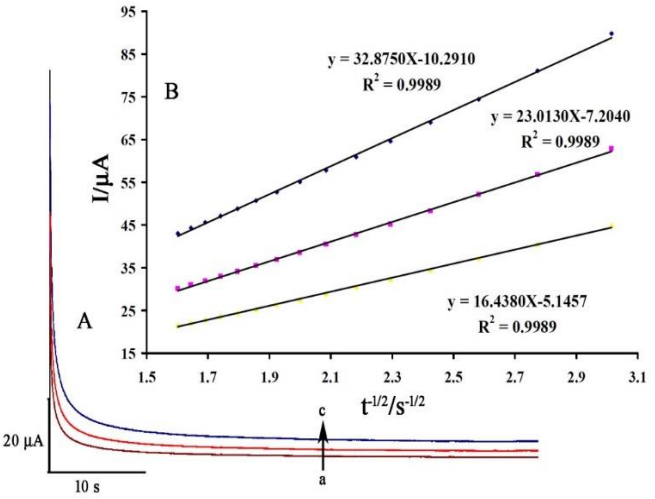


Figure 5. A) Chronoamperograms obtained at Ag/NP/1B3MIBr/CPE in the presence of (a) 200, (b) 400 and (c) 500 µM rutin. B) Relative Cottrell plots

Table 1. Analysis data for determination of rutin in real sample (n=4)

Sample	Added (µM)	Expected (µM)	Founded (µM)	Recovery %
Black tea	---	---	15.22±0.45	--
	10.00	25.22	24.87±0.87	98.61
	20.00	35.22	36.01±0.96	102.24
	30.00	45.22	45.75±1.11	101.17

Conclusion

The aim of this project is to fabricate of a new sensitive electrochemical sensor with a combination of Ag/NPs and 1-buthyl-3-methyl imidazolium bromide to determine the rutin in soy samples. The Ag/NP/1B3MIBr/CPE showed a good linear dynamic range between 0.05 – 320 µM with good limit of detection 10 nM for the determination of rutin using differential pulse voltammetric method. Finally, it has acceptable application in determination of rutin in black tea as a real sample with recovery range 98.61-102.24%.

Disclosure statement

No potential conflict of interest was reported by the authors.

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ORCID

S. A. Shahidi: 0000-0001-5667-2875

A. Ghorbani-Hasan Saraei: 0000-0001-9756-5179

References

[1] D. Stojković, J. Petrović, M. Soković, J. Glamočlija, J. Kukić-Marković, S. Petrović, *J. Sci. Food Agric.*, **2013**, *93*, 3205–3208.

[2] I. Kreft, N. Fabjan, K. Yasumoto, *Food Chem.,* **2006**, *98*, 508–512.

[3] N. Buchner, A. Krumbein, S. Rohn, L.W. Kroh, Effect of thermal processing on the flavonols rutin and quercetin. *Rapid Communicat. Mass Spectrom.,* **2006**, *20*, 3229–3235.

[4] P.H. Cheol, Y.B. Kim, Y.S. Choi, K. Heo, S.L. Kim, *Fagopyrum,* **2000**, *17*, 63–66.

[5] J. Viskupicova, M. Danihelova, M. Ondrejovic, T. Liptaj, E. Sturdik, *Food Chem.,* **2010**, *123*, 45–50.

[6] I. Kreft, N. Fabjan, M. Germ, *Fagopyrum,* **2003**, *20*, 7–11.

[7] B. Gullón, T.A. Lú-Chau, M. Teresa, M. Juan, M. Lema, G. Eibes, *Trend. Food Sci. Technol.,* **2017**, *67*, 220–235.

[8] A. Babazadeh, B. Ghanbarzadeh, H. Hamishehkar, *J. Funct. Food.,* **2017**, *33*, 134–141.

[9] D. Šatínský, K. Jägerová, L. Havlíková, P. Solich, *Food Anal. Method.,* **2013**, *6*, 1353–1360.

[10] R. Crebelli, G. Aquilina, E. Falcone, A. Carere., *Food Chem. Toxicol.,* **1987**, *25*, 9–15.

[11] J. Bretag, D.R. Kammerer, U. Jensen, R. Carle, *Food Chem.,* **2009**, *114*, 151–160.

[12] Z.L. Zhang, M.L. Zhou, Y. Tang, F.L. Li, Y.X. Tang, J.R. Shao, W.T. Xue, Y.M. Wu, *Food Res. Int.,* **2012**, *49*, 389–395.

[13] B.M. Lue, N.S. Nielsen, C. Jacobsen, L. Hellgren, Z. Guo, X. Xu., *Food Chem.,* **2010**, *123*, 221–230.

[14] L. Yang, Q.H. Yan, J.Y. Ma, Q. Wang, J.W. Zhang, G.X. Xi, *Trop. J. Pharm. Res.,* **2013**, *12*, 771–776.

[15] A.M. Danila, A. Kotani, H. Hakamata, F. Kusu, *J. Agric. Food Chem.,* **2007**, *55*, 1139–1143.

[16] V. Kuntić, N. Pejić, B. Ivković, Z. Vujić, K. Ilić, S. Mićić, *J. Pharm. Biomed.,* **2007**, *43*, 718–721.

[17] A. Ćirić, H. Prosen, M. Jelikić-Stankov, P. Đurđević, *Talanta.,* **2012,** *99*, 780–790.
[18] T. Matyushina, E. Morosanova, Y.A. Zolotov, *J. Anal. Chem.,* **2010,** *65*, 308–315.
[19] J.G. da Silva, M.R.L. e Silva, A.C. de Oliveira, J.R. SouzaDe, C.M.P. Vaz, C.S.P. de Castro, *J. Food Compost. Anal.,* **2012,** *25*, 1–8.
[20] V. Arabali, S. Malekmohammadi, F. Karimi, *Microchem. J.,* **2020,** *158*, 105179.
[21] M. Baghayeri, M. Rouhi, M.M. Lakouraj, M. Amiri-Aref, *J. Electroanal. Chem.,* **2017**, *784*, 69–76.
[22] M. Baghayeri, H. Alinezhad, M. Fayazi, M. Tarahomi, R. Ghanei-Motlagh, B. Maleki, *Electrochim. Acta.,* **2019**, *312*, 80–88.
[23] B. Maleki, M. Baghayeri, S.A.J. Abadi, R. Tayebee, A. Khojastehnezhad, *RSC Adv.,* **2016**, *6*, 96644–96661.
[24] Golikand A.N., Raoof J., Baghayeri M., Asgari M., Irannejad L., *Russ. J. Electrochem*., **2009**, *45*, 192–198.
[25] M. Baghayeri, R. Ansari, M. Nodehi, I. Razavipanah, H. Veisi, *Microchim. Acta,* **2018,** *185*, 320.
[26] A. Hojjati-Najafabad, M.S. Rahmanpour, F. Karimi, H. Zabihi-Feyzaba, S. Malekmohammadi, S. Agarwal, V.K. Gupta, *Int. J. Electrochem. Sci.*, **2020**, *15*, 6969–6980.
[27] T. Zabihpour, S.A. Shahidi, H. Karimi Maleh, A. Ghorbani-Hasan Saraei, *Eurasian chem. Commun.,* **2020,** *2*, 362–373.
[28] M. Baghayeri, B. Mahdavi, Z. Hosseinpor-Mohsen Abadi, S. Farhadi, *Appl. Organomet. Chem.,* **2018,** *32*, e4057.
[29] A. Targhoo, A. Amiri, M. Baghayeri, *Microchim. Acta.,* **2018,** *185*, 15.
[30] M. Alizadeh, P.A. Azar, S.A. Mozaffari, H. Karimi-maleh, A.M. Tamaddon, *Front. Chem.,* **2020**, *8*, 677.
[31] A.N. Golikand, J. Raoof, M. Baghayeri, M. Asgari, L. Irannejad, *Russ. J. Electrochem.,* **2009**, *45*, 192–198.
[32] M. Baghayeri, A. Sedrpoushan, A. Mohammadi, M. Heidari, *Ionics.,* **2017**, *23*, 1553–1562.
[33] H. Beitollahi, A. Mohadesi, F. Ghorbani, H. Karimi-Maleh, M. Baghayeri, R. Hosseinzadeh, *Chin. J. Catal.,* **2013**, *34*, 1333–1338.
[34] B. Davarnia, S.A. Shahidi, H. Karimi-Maleh, A. Ghorbani-Hasan Saraei, F. Karimi, *Int. J. Electrochem. Sci.,* **2020**, *15*, 2549–2560.
[35] B. Rezaei, N. Majidi, A.A. Ensafi, H. Karimi-Maleh, *Anal. Method.,* **2011**, *3*, 2510–2516.

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