

Full Paper

Electrochemical Sensor for Sulfite Determination based on a Nanostructured Fe₃O₄ Modified Electrode

Mohammad Hossein Hemmati^{1,*} and Mehri-Saddat Ekrami-Kakhki²

¹*Department of Metallurgical Engineering, Neyshabur Branch, Islamic Azad University, Neyshabur, Iran*

²*Esfarayan University of Technology, Esfarayan North Khorasan, Iran*

*Corresponding Author, Tel.: +985142621946; Fax: +985142615472

E-Mail: mhemmati79@gmail.com

Received: 5 January 2018 / Accepted with minor revision: 15 April 2018 /

Published online: 31 May 2018

Abstract- Fe₃O₄ nanoparticles were synthesized by solvothermal strategy using ethylene glycol (EG). Moreover, a graphite screen printed (SPE) was modified with this Fe₃O₄ nanoparticles by dropping method. The electrochemical behavior and the electrocatalytic activity of this Fe₃O₄/SPE electrode for the oxidation of sulfite were also investigated using cyclic voltammetry, chronoamperometry and differential pulse voltammetry. The results showed that this Fe₃O₄/SPE exhibited high electrochemical activity for the oxidation of sulfite under the synergistic action of Fe₃O₄ nanoparticles. In the differential pulse voltammetry analysis, under optimized experimental conditions, the oxidation peak increased with an increasing concentration of sulfite in the range of 0.5 to 100.0 μM. The calculated LOD value for sulfite was 0.1 μM. At last, the as-prepared modified electrode was successfully used for the determination of sulfite in real samples.

Keywords- Sulfite, Fe₃O₄ nanoparticles, Voltammetric sensor, Screen printed electrode

1. INTRODUCTION

Sulfite is widely used as additive in food, beverages and pharmaceuticals to prevent oxidation and bacterial growth and control of enzymatic reactions during their production and

storage. Sulfite is known to cause some cytotoxic, mutagenic and antinutritional effects [1,2]. It also interacts with some vitamins, i.e. pyridoxal, nicotinamide, thiamine, folic acid leading to reduced nutritional quality of treated food [3-5]. Sulfite oxidase occurs in the mitochondria of all eukaryotes. It oxidizes sulfite to sulfate and transfers the electrons produced, to the electron transport chain via cytochrome c, allowing generation of ATP in oxidative phosphorylation. Lack of functional Sulfite oxidase causes a sulfite deficiency, which leads to neurological disorders, mental retardation, physical deformities, dislocated lenses, degradation of brain and early death. Thus sulfite level in the body must be maintained tightly. Normally, human serum has sulfite concentration in the range of 0–10 μM [6,7]. Therefore, determination of sulfite is important from biological and industrial perspectives.

Various techniques for quantitative determination of sulfite in different types of samples are available such as iodimetry, spectrophotometry, anodic stripping voltammetry, reciprocal oscillographic chronopotentiometry, ion chromatography, enthalpimetry, chemiluminescence, gravimetry, gas chromatography, fluorometry and HPLC [8-11]. However, some of these methods lack sensitivity and precision (e.g. iodimetry, spectrophotometry), while others require time consuming sample preparation, expensive equipments and skilled person to operate [12]. Among these methods, electrochemical detection is most attractive because of its high sensitivity, simplicity, rapid response and inexpensive equipment.

Screen-printed electrodes (SPEs), which are used as economical electrochemical substrates, have gone through significant improvements over the past few decades with respect to both their format and their printing materials [13-19]. If the electrode is bare, the analytes response is weak and we have a high voltage, so we need to correct the electrode surface [20-29]. Modification of electrodes is good and powerful strategy for overcoming of bare electrodes limitation [30-38]. Further, the fabrication and modification of the working electrode with nanoparticles enhances peak current, sensitivity and reproducibility [39-46].

Metal oxides have numerous industrial uses, such as electronic, magnetic, catalytic and sensor applications [47-49]. As an important category of metal oxides, iron oxide (Fe_3O_4) have received considerable attention. Fe_3O_4 nanoparticles (Fe_3O_4 NPs) have attracted an increasing interest in construction of sensors and biosensors because of their good biocompatibility, strong super paramagnetic property, low toxicity, easy preparation and high adsorption ability. Fe_3O_4 with an inverse spinel structure shows ferrimagnetism that originates from magnetic moment of anti-parallel spins between Fe^{3+} ions at tetrahedral sites and Fe^{2+} ions at octahedral sites. The quantitative cytotoxicity test verified that Fe_3O_4 nanoparticles had noncytotoxicity. Moreover, Fe_3O_4 NPs exhibit high surface area and low mass transfer resistance [50-53].

In this work, a screen printed electrode modified with the Fe_3O_4 nanoparticles was used for sensitive voltammetric determination of sulfite and the modified electrode exhibited excellent electrocatalytic activity to sulfite.

2. EXPERIMENTAL

2.1. Chemicals and Apparatus

An Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands) was employed to perform the electrochemical experiments and the system was controlled using a general purpose electrochemical system software.

The screen-printed electrode (DropSens, DRP-110, Spain) consists of three conventional electrodes: graphite counter electrode, a silver pseudo-reference electrode and an unmodified graphite working electrode. pH was measured by a Metrohm 710 pH meter.

Sulfite and all other reagents were analytical grade, and were purchased from Merck (Darmstadt, Germany). For the preparation of buffers, the orthophosphoric acid and its salts were used to provide the pH range of 2.0–9.0.

2.2. Synthesis of Fe₃O₄ nanoparticles

Fe₃O₄ nanoparticles were synthesized in the presence of urea using a solvothermal method. Solution of urea was dissolved in 100 ml of ethylene glycol (EG). Then 10 mL FeCl₃.6H₂O (16 mmol) and 10 mL FeCl₂.6H₂O (8 mmol) were added into the above solution, respectively. The mixed solutions, with stoichiometric 30 molar ratio of urea/Fe³⁺ (with excess urea that form sufficient precipitating ions for metal oxides formation), were magnetically stirred until all the starting materials were totally dissolved at 25 °C. These solutions were further homogenized in an ultrasonic water bath for 15 min and then respectively transferred into Teflon-lined stainless steel autoclave with a capacity of 200 ml in order to keep them at 200 °C for 24 h in an oven. Subsequently, the autoclaves were air cooled to room temperature. The as-obtained precipitates were centrifuged, and then washed with DI water and absolute ethanol for several times to remove the impurities in the products. The resulting products were dried in a vacuum oven at 100 °C for 12 h.

2.3. Preparation of the electrode

The bare screen-printed electrode was coated with Fe₃O₄ nanoparticles according to the following simple procedure. 1 mg Fe₃O₄ nanoparticles were dispersed in 1 mL aqueous solution within 45 min ultrasonication. Then, 5 µl of the prepared suspension was dropped on the surface of carbon working electrodes. It remains at room temperature until becomes dry.

3. RESULT AND DISCUSSION

3.1. Electrochemical profile of the sulfite on the Fe₃O₄/SPE

To study the electrochemical behaviour of sulfite which is pH-dependent, it is necessary to obtain the optimized pH value in order to achieve the accurate results. By performing the

experiments by use of modified electrodes at various pH values ranging from 2.0–9.0, it was revealed that the best results for electro-oxidation of sulfite occur at pH=7.0. The obtained cyclic voltammograms in the presence of 50.0 μM sulfite using the $\text{Fe}_3\text{O}_4/\text{SPE}$ (Curve a) and bare SPE (Curve b) are shown in Fig. 1. According to CV results the maximum oxidation of sulfite on the $\text{Fe}_3\text{O}_4/\text{SPE}$ occurs at 565 mV which is about 250 mV more negative compared with unmodified SPE.

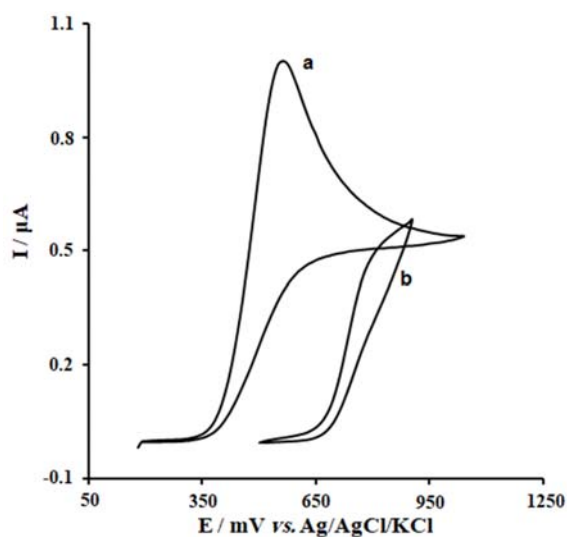


Fig. 1. Cyclic voltammograms of (a) $\text{Fe}_3\text{O}_4/\text{SPE}$ and (b) bare SPE in 0.1 M PBS (pH 7.0) in the presence of 100.0 μM at the scan rate 50 mVs^{-1}

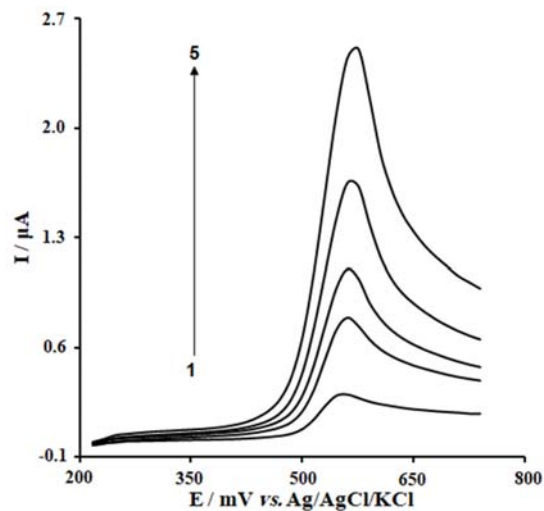


Fig. 2. CVs of $\text{Fe}_3\text{O}_4/\text{SPE}$ in 0.1 M PBS (pH 7.0) containing 100.0 μM sulfite at various scan rates; numbers 1-5 correspond to 10, 30, 50, 100 and 200 mV s^{-1} , respectively

3.2. Effect of scan rate on the results

Increasing in scan rate leads to enhanced oxidation peak current according to the obtained results from the study of the effect of potential scan rates on the oxidation currents of sulfite, Fig. 2. In addition, there is a linear relationship between I_p and the square root of the potential scan rate ($v^{1/2}$) that demonstrates that the oxidation procedure of analyst is in control of diffusion (Fig. 3).

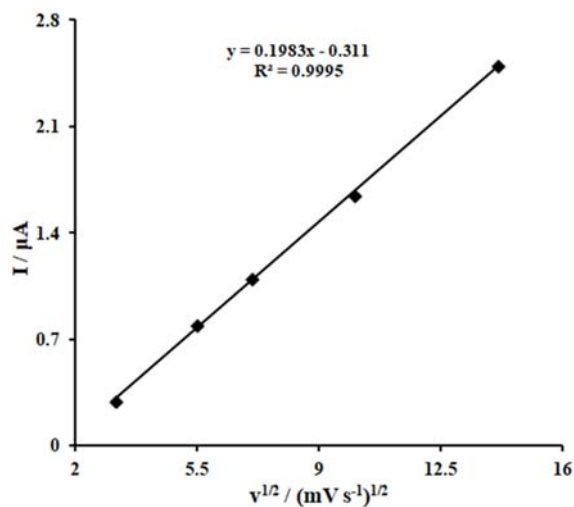


Fig. 3. Variation of anodic peak current vs. $v^{1/2}$ obtained from CVs in Fig. 2

3.3. Chronoamperometric analysis

The analysis of chronoamperometry for sulfite samples was performed by use of $\text{Fe}_3\text{O}_4/\text{SPE}$ vs. $\text{Ag}/\text{AgCl}/\text{KCl}$ (3.0 M) at 0.6 V. The Chronoamperometric results of different concentration of sulfite sample in PBS (pH 7.0) are demonstrated in Fig. 4. The Cottrell equation for chronoamperometric analysis of electroactive moieties under mass transfer limited conditions is as follow [54]:

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2}$$

Where D represents the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), and C_b is the applied bulk concentration (mol cm^{-3}). Experimental results of I vs. $t^{-1/2}$ were plotted in Fig. 5A, with the best fits for different concentrations of sulfite. The resulted slopes corresponding to straight lines in Fig. 5A, were then plotted against the concentration of sulfite (Fig. 5B). The mean value of D was determined to be $1.6 \times 10^{-6} \text{ cm}^2/\text{s}$ according to the resulting slope and Cottrell equation.

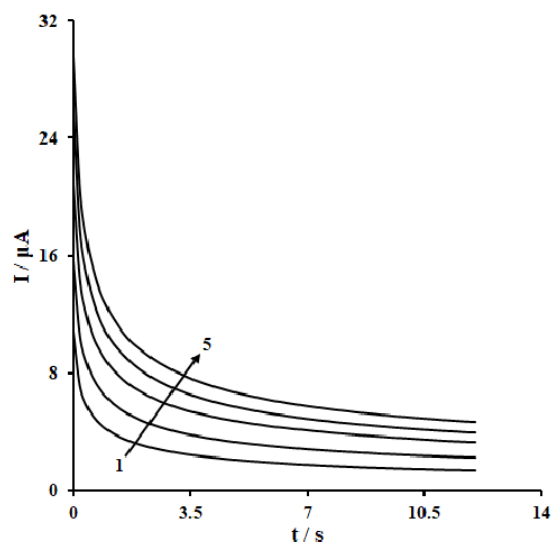


Fig. 4. Chronoamperograms obtained at $\text{Fe}_3\text{O}_4/\text{SPE}$ in 0.1 M PBS (pH 7.0) for different concentration of sulfite. The numbers 1–5 correspond to 0.1, 0.35, 0.75, 1.1 and 1.5 mM of sulfite

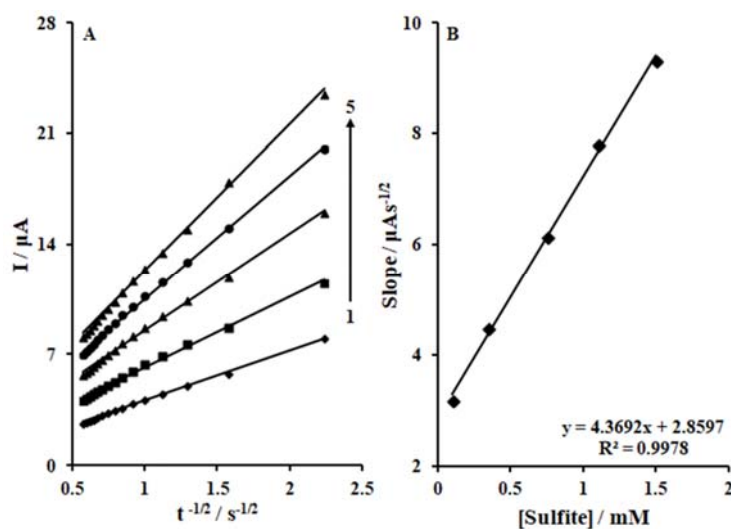


Fig. 5. (A) Plots of I vs. $t^{-1/2}$ obtained from chronoamperograms 1–5. (B) Plot of the slope of the straight lines against sulfite concentration

3.4. Calibration curves

Based on the resulting peak currents of sulfite by use of $\text{Fe}_3\text{O}_4/\text{SPE}$, the quantitative analysis of two targets were done in water solutions. The modified electrode ($\text{Fe}_3\text{O}_4/\text{SPE}$) as working electrode in the range of sulfite concentration in 0.1 M PBS was used in differential pulse voltammetry (DPV) due to the advantages of DPV including the improved sensitivity

and better performance in analytical applications (Fig. 6). According to the results, a linear relationship exists between the peak currents and concentrations of sulfite within the concentration range of 0.5-100.0 μM with the correlation coefficient of 0.997 (Fig. 7). The detection limit was obtained 0.1 μM . Table 1. shows comparison of the analytical figures of merit of the proposed method compared to some other electrochemical techniques for the determination of sulfite.

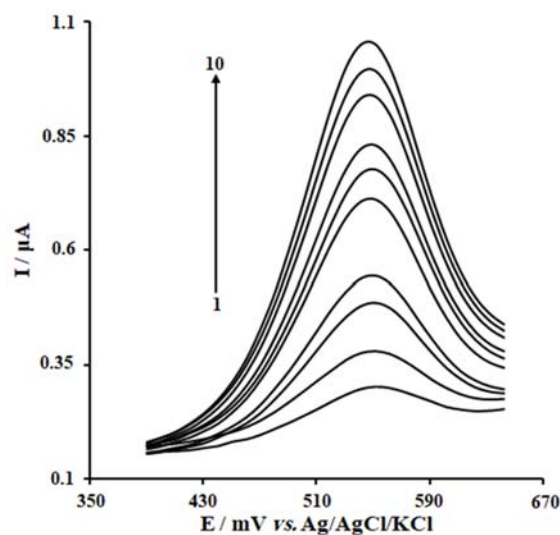


Fig. 6. DPVs of $\text{Fe}_3\text{O}_4/\text{SPE}$ in 0.1 M (pH 7.0) containing different concentrations of sulfite. Numbers 1–10 correspond to 0.5, 7.5, 20.0, 30.0, 50.0, 60.0, 70.0, 80.0, 90.0 and 100.0 μM of sulfite obtained from DPVs in Fig. 6

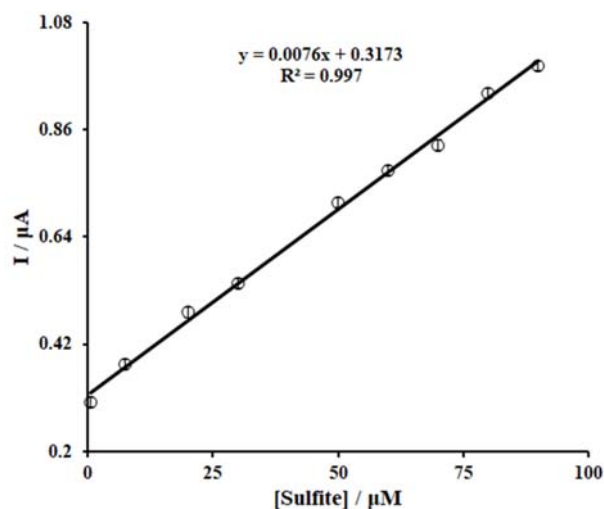


Fig. 7. plot of the electrocatalytic peak current as a function of sulfite concentration in the range of 0.5-100.0 μM

Table 1. Comparison of some electrochemical procedures used in the determination of sulfite.

Electrode	Linear Range	Detection Limit	Ref.
Carbon paste electrodes modified with gold nanoparticles and $\text{Si}_4\text{Pic}^+\text{Cl}^-$	2.54-48.6 mg L ⁻¹	0.88 mg L ⁻¹	[2]
Glassy carbon electrodes modified with films of Prussian Blue	0.0-40.0 mM	80.0 μM	[55]
Glassy carbon electrode modified with electropolymerized Co(II) meso-tetrakis (2-thienyl)porphyrin	0.1-5000.0 μM	-	[56]
Paraffin impregnated graphite electrode modified with nickel aquapentacyanoferrate	2.78-3000.0 μM	0.926 μM	[57]
Graphite screen printed electrode modified with Fe_3O_4 nanoparticles	0.5-100.0 μM	0.1 μM	This Work

3.5. Analysis of real samples

The applicability of this modified electrode in the determination of real samples was assessed through the determination of sulfite in water sample using the described method. In order to perform this analysis, standard addition method was employed and the results are listed in Table 2. Accordingly, the results of sulfite recovery are satisfactory and the reproducibility of the results is proved by the mean relative standard deviation (R.S.D.).

Table 2. The application of $\text{Fe}_3\text{O}_4/\text{SPE}$ for determination of sulfite in water samples (n=5). All concentrations are in μM

Sample	Spiked	Found	Recovery (%)	R.S.D. (%)
Well water	0	-	-	-
	5.0	5.1	102.0	1.6
	10.0	9.7	97.0	2.7
	15.0	14.8	98.7	3.1
	20.0	20.2	101.0	1.9
River water	0	-	-	-
	7.5	7.3	97.3	2.2
	12.5	12.6	100.8	3.3
	17.5	17.3	98.9	2.4
	22.5	23.1	102.7	1.7

4. CONCLUSION

We proposed here a simple and environmental friendly method for the preparation of Fe₃O₄ nanoparticles by using ethylene glycol. In addition, this Fe₃O₄ nanoparticles exhibited high electrochemical activity and some attractive analytical features for the determination of sulfite. The linear working range for the quantitation of sulfite was 0.5–100.0 μM ($R^2=0.997$) with a detection limit of 0.1 μM (3σ of blank). The proposed method was successfully applied to the determination of sulfite in real samples.

REFERENCES

- [1] S. Preecharueangrit, P. Thavarungkul, P. Kanatharana, and A. Numnuam, *J. Electroanal. Chem.* 808 (2018) 150.
- [2] J. P. Winiarski, M. R. de Barros, H. Aparecida Magosso, and C. Luisa Jost, *Electrochim. Acta* 251 (2017) 522.
- [3] H. Yu, X. Feng, X. X. Chen, S. S. Wang, and J. Jin, *J. Electroanal. Chem.* 801 (2017) 488.
- [4] W. Sroysee, K. Ponlakheth, S. Chairam, P. Jarujamrus, and M. Amatatongchai, *Talanta* 156-157 (2016) 154.
- [5] H. Beitollahi, S. Tajik, and P. Biparva, *Measurement* 56 (2014) 170.
- [6] M. Amatatongchai, W. Sroysee, S. Chairam, and D. Nacapricha, *Talanta* 133 (2015) 134.
- [7] L. S. T. Alamo, T. Tangkuaram, and S. Satienperakul, *Talanta* 81 (2010) 1739.
- [8] R. Kaeil, R. Hampp, and H. Ziegler, *Anal. Chem.* 61 (1989) 1755.
- [9] E. Dinckaya, M. K. Sezginurk, E. Akyilmaz, and F. N. Ertas, *Food Chem.* 101 (2007) 1540.
- [10] S. Theisen, R. Hansch, L. Kothe, and R. Galensa, *Biosens. Bioelectron.* 26 (2010) 175.
- [11] B. Doumas, B. Perry, E. Sasse, and J. Straumfjord, *J. Clin. Chem.* 19 (1973) 984.
- [12] C. Zhao, H. Jin, R. Gui, and Z. Wang, *Sens. Actuators B* 242 (2017) 71.
- [13] M. Baniyadi, Sh. Jahani, H. Maaref, and R. Alizadeh, *Anal. Bioanal. Electrochem.* 9 (2017) 718.
- [14] M. Li, Y. T. Li, D. W. Li, and Y. T. Long, *Anal. Chim. Acta* 734 (2012) 31.
- [15] M. R. Ganjali, F. Garkani Nejad, H. Beitollahi, Sh. Jahani, M. Rezapour, and B. Larijani, *Int. J. Electrochem. Sci.* 12 (2017) 3231.
- [16] J. K. Jadav, V. V. Umrana, K. J. Rathod, and B. A. Golakiya, *LWT-Food Sci. Technol.* 88 (2018) 152.
- [17] H. Beitollahi, F. Garkani Nejad, S. Tajik, Sh. Jahani, and P. Biparva, *Int. J. Nano Dimens.* 8 (2017) 197.

- [18] Y. Panraksa, W. Siangproh, T. Khampieng, O. Chailapakul, and A. Apilux, *Talanta* 178 (2018) 1017.
- [19] F. Soofiabadi, A. Amiri, and Sh. Jahani, *Anal. Bioanal. Electrochem.* 9 (2017) 340.
- [20] H. Mahmoudi Moghadam, H. Beitollahi, S. Tajik, I. Sheikhshoae, and P. Biparva, *Anal. Bioanal. Electrochem.* 6 (2014) 634.
- [21] H. Beitollahi, S. Tajik, H. Karimi-Maleh, and R. Hosseinzadeh, *Appl. Organomet. Chem.* 27 (2013) 444.
- [22] M. Khairy, B. G. Mahmoud, C. E. Banks, *Sens. Actuators B* 259 (2018) 142.
- [23] E. Molaakbari, A. Mostafavi, and H. Beitollahi, *Sens. Actuators B* 208 (2015) 195.
- [24] H. Beitollahi, and I. Sheikhshoae, *Int. J. Electrochem. Sci.* 7 (2012) 7684.
- [25] M. Puttaiah, and A. N. Yanjerappa. *Anal. Bioanal. Electrochem.* 9 (2017) 841.
- [26] H. Beitollahi, H. Karimi-Maleh, and H. Khabazzadeh, *Anal. Chem.* 80 (2008) 9848.
- [27] Sh. Jahani, and H. Beitollahi, *Anal. Bioanal. Electrochem.* 8 (2016) 158.
- [28] V. P. Rao, Y. V. Manohara Reddy, K. G. Reddy, C. Madhuri, D. Saritha, and G. Madhav, *Anal. Bioanal. Electrochem.* 9 (2017) 841.
- [29] H. Beitollahi, S. Tajik, and Sh. Jahani, *Electroanalysis* 28 (2016) 1093.
- [30] H. Beitollahi, J. B. Raouf, H. Karimi-Maleh, and R. Hosseinzadeh, *J. Solid State Electrochem.* 16 (2012) 1701.
- [31] E. Nagles, O. García-Beltrán, and J. A. Calderón, *Electrochim. Acta* 258 (2017) 512.
- [32] S. Tajik, M. A. Taher, Sh. Jahani, and M. Shanesaz, *Anal. Bioanal. Electrochem.* 8 (2016) 899.
- [33] H. Mahmoudi Moghaddam, H. Beitollahi, S. Tajik, M. Malakootian, and H. Karimi-Maleh, *Environ. Monit. Assess.* 186 (2014) 7431.
- [34] M. Jin, X. Zhang, Q. Zhen, Y. He, X. Chen, W. Lyu, R. Han, and M. Ding, *Biosens. Bioelectron.* 98 (2017) 392.
- [35] H. Karimi-Maleh, M. Moazampour, H. Ahmar, H. Beitollahi, and A. A. Ensafi, *Measurement* 51 (2014) 91.
- [36] H. Beitollahi, S. Ghofrani Ivary, and M. Torkzadeh Mahani, *Mater. Sci. Eng. C* 69 (2016) 128.
- [37] A. Jirasirichote, E. Punrat, A. Suea-Ngam, O. Chailapakul, and S. Chuanuwatanakul, *Talanta* 175 (2017) 331.
- [38] H. Beitollahi, and F. Garkani-Nejad, *Electroanalysis* 28 (2016) 2237.
- [39] H. Mahmoudi Moghaddam, H. Beitollahi, S. Tajik, Sh. Jahani, H. Khabazzadeh, and R. Alizadeh, *Russ. J. Electrochem.* 53 (2017) 452.
- [40] S. Tajik, M. A. Taher, and H. Beitollahi, *Electroanalysis* 26 (2014) 796.
- [41] H. Beitollahi, and S. Mohammadi, *Mater. Sci. Eng. C* 33 (2013) 3214.
- [42] P. Shaikshavali, T. Madhusudana Reddy, G. Venkataprasad, and P. Gopal, *Anal. Bioanal. Electrochem.* 9 (2017) 940.

- [43] H. Beitollahi, and S. Nekooei, *Electroanalysis* 28 (2016) 645.
- [44] S. Tajik, M. A. Taher, and H. Beitollahi, *Ionics* 20 (2014) 1155.
- [45] H. Beitollahi, S. Ghofrani Ivary, and M. Torkzadeh-Mahani, *Biosens. Bioelectron.* 110 (2018) 97.
- [46] M. Mazloum-Ardakani, H. Beitollahi, B. Ganjipour, and H. Naeimi, *Int. J. Electrochem. Sci.* 5 (2010) 531.
- [47] M. H. Sobhani Poor, M. Khatami, H. Azizi, and Y. Abazari, *Rend. Lincei* 28 (2017) 693.
- [48] F. Sharifi, F. Sharififar, I. Sharifi, H. Q. Alijani, and M. Khatami, *IET Nanobiotechnol.* (2017) doi: 10.1049/iet-nbt.2017.0204.
- [49] E. Zare, S. Pourseyedi, M. Khatami, and E. Darezereshki, *J. Mol. Struct.* 1146 (2017) 96.
- [50] H. E. Ghandoor, H. M. Zidan, M. H. Khalil and M. I. M. Ismail, *J. Electrochem. Sci.* 7 (2012) 5734.
- [51] L. X. Phua, F. Xu, Y. G. Ma, and C. K. Ong, *Thin Solid Films* 517 (2009) 5858.
- [52] M. Khatami, H. Alijani, I. Sharifi, F. Sharifi, S. Pourseyedi, S. Kharazi, M. A. Lima Nobre, and M. Khatami, *Sci. Pharm.* 85 (2017) 36.
- [53] E. Al-Zahrani, M. Tahir Soomro, R. M. Bashami, A. Ur Rehman, E. Danish, I.M.I. Ismail, M. Aslam, and A. Hameed, *J. Environ. Chem. Eng.* 4 (2016) 4330.
- [54] A. J. Bard, and L. R. Faulkner, *Electrochemical Methods Fundamentals and Applications*, second ed, Wiley, New York (2001).
- [55] T. Garcia, E. Casero, E. Lorenzo, and F. Pariente, *Sens. Actuators B* 106 (2005) 803.
- [56] H. Vélez, J. P. Muena, M. J. Aguirre, G. Ramírez, and F. Herrera, *Int. J. Electrochem. Sci.* 7 (2012) 3167.
- [57] S. S. Kumar, and S. S. Narayanan, *Electroanalysis* 20 (2008) 1427.