



Original scientific paper

Electroanalysis of tert-butylhydroquinone in food products using a paste electrode enlarged with single wall carbon nanotubes as catalyst

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Abstract

In this study, an electrochemical sensor was introduced as a simple and fast electro-analytical tool to monitor and sensing of tert-butylhydroquinone (TBHQ) in food products. The suggested electrochemical sensor is fabricated by modification of paste electrode (PE) by single wall carbon nanotubes (SWCNTs) as nanocatalyst. The oxidation current of TBHQ was improved by about 2.62 times and its oxidation potential was reduced by about 50 mV after using SWCNTs as conductive catalyst on a carbon paste matrix. The oxidation current of TBHQ showed a linear dynamic range of 0.05 to 390 μ M in the sensing process using SWCNTs/PE as the electroanalytical sensor. On the other hand, SWCNTs/PE successfully monitored TBHQ with a detection limit of 10 nM at optimum conditions. The real sample analysis data clearly showed a recovery range of 97.2 to 104.3 %, which is very interesting for a new analytical tool in the food-sensing process.

Keywords

Food analysis; electroanalysis; modified electrode; carbon paste; voltammetry

Introduction

Monitoring food additives is one of the best methods for investigating quality food products and checking the presence of prohibited substances [1-7]. For this purpose, different measurement methods have been reported in food samples [8-13]. In the meantime, attention to electrochemical methods has grown significantly due to many advantages and low cost [14-18]. By presenting various solutions for modification in electrochemical sensors, various reports have been presented

for the use of these sensors in the construction of measuring instruments [19-24]. High overpotentials and low redox signals of electroactive materials and, especially, food additives are the main problems to trace level monitoring of them in real samples [25-29]. Therefore, conductive catalysts were suggested for the fabrication of highly conductive and sensitive electrochemical sensors [30-33].

It is important to check the concentration of food additives and especially antioxidants widely used in the food industry to determine the food quality [34]. The tert-butylhydroquinone (TBHQ) is one of the phenolic-type antioxidants with a wide range of applications in many edible animal fats and vegetable oils [35]. High concentrations of TBHQ can be harmful to the human body and create some problems, such as vision disturbances and neurotoxic effects [35]. Therefore, many research works focused on monitoring them in food products [36,37]. However, efforts are still being made to provide simpler and more sensitive solutions.

Carbon nanotubes (CNT) are one of the main and useful carbon nanocatalysts widely used in different branches of science, especially in sensors and energy majors [38-40]. Easy modification and high surface area with good electrical conductivity have introduced them as a unique catalyst [41,42]. On the other hand, according to the literature, single wall carbon nanotubes (SWCNTs) showed more advantages than other carbon-based nanomaterials as catalysts for the fabrication of electrochemical sensors due to high electrical conductivity and good surface area and were selected for this work [43].

In this research work, a carbon paste electrode (PE) was modified with single-walled CNTs (SWCNTs) as conductive catalysts and a fabricated sensor was used to determine TBHQ in food products. The results clearly showed the powerful ability of SWCNTs/PE in trace analysis of TBHQ with acceptable recovery data in real sample analysis.

Experimental

Instrument and materials

A potentiostat/galvanostat (Metrohm Company) was used to record redox signals of TBHQ in an aqueous solution. All potentials were recorded using Ag/AgCl/KCl_{sat} as a reference electrode. Pt wire was used as a counter electrode and SWCNTs/PE as the working electrode. The TBHQ (99 %) was purchased from ACROS Company and a stock solution of TBHQ was prepared by dissolving 0.0166 g TBHQ in PBS (pH 7.0) + ethanol (1:1 v/v) (10 mL) under ultrasonication to 10 min. SWCNTs were purchased from Sigma-Aldrich Company and used to fabricate SWCNTs/PE electrodes. The orthophosphoric acid (85 %) was purchased from Merck Company and used to prepare phosphate buffer solution (PBS, 0.1 M).

Fabrication of SWCNTs/PE

The ratio of SWCNTs was prepared by mixing 0.15 g SWCNTs + 0.85 g graphite powder in the presence of paraffin oil as a binder. The powder dissolved in 10 mL diethyl ether solution and then stirred at 25 °C to evaporate the solvent. Then paraffin oil was added dropwise and the sample was hand-mixed for 45 min. The SWCNTs/PE was added to the end of the glass tube and an electrical connection was established by a copper wire.

Real sample preparation

Orange and apple juices and soybean oil were selected as real samples to study the capability of SWCNTs/PE in monitoring TBHQ. The orange and apple juices were centrifuged for 20 min at 4000 rpm

and then the solution was filtered to preparation of pure sample and diluted by PBS (pH 7.0). The soybean oil was extracted with 50 mL ethanol for 1 h and then was filtered to prepare a pure sample and diluted by PBS (pH 7.0). The standard addition was used as an analytical method.

Results and discussion

Optimization of SWCNTs

The ratio of SWCNTs catalyst to graphite powder is one of the important factors in the fabrication of SWCNTs/PE as a new sensor. Therefore, the oxidation signal of 200 μM TBHQ was recorded at the surface of the carbon paste electrode (CPE) modified with 0, 5, 10, 15 and 20 wt.% SWCNTs. The results showed maximum sensitivity in the presence of 15 wt.% of SWCNTs in SWCNTs/PE matrix (Figure 1).

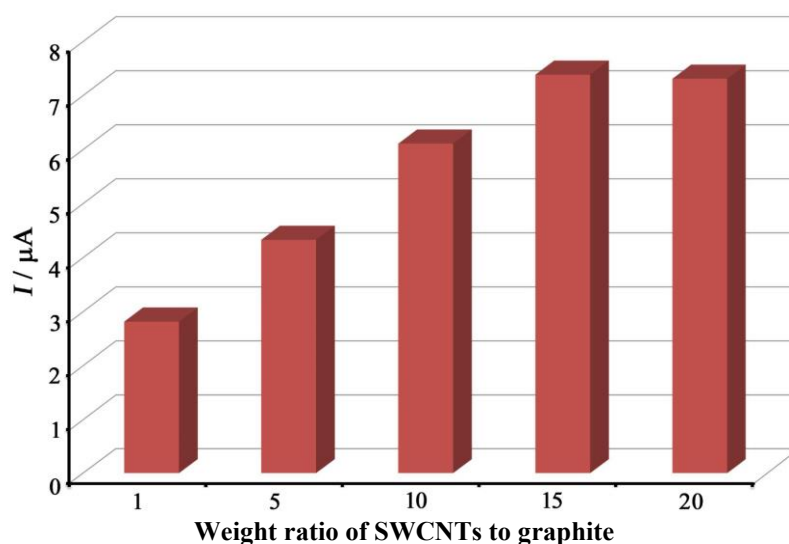


Figure 1. Recorded oxidation current of TBHQ at surface of paste electrode modified with different percentage of catalyst

Electrochemical investigation

The oxidation signal of TBHQ was recorded at a pH range of 5.0 to 9.0 and results showed in Figure 2 inset. The plot of the oxidation current of TBHQ vs. pH is shown in Figure 2 and clearly confirms maximum sensitivity at neutral conditions. On the other hand, the plot of the oxidation peak potential vs. pH follows the linear equation $E = -0.057 \text{ pH} + 0.784$ ($R^2 = 0.9942$) (not shown). Therefore, the reaction mechanism shown in Scheme 1 was suggested for the redox reaction of TBHQ at the surface of SWCNTs/PE [44].

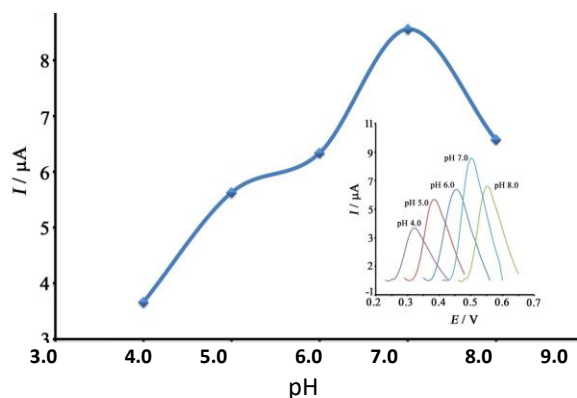
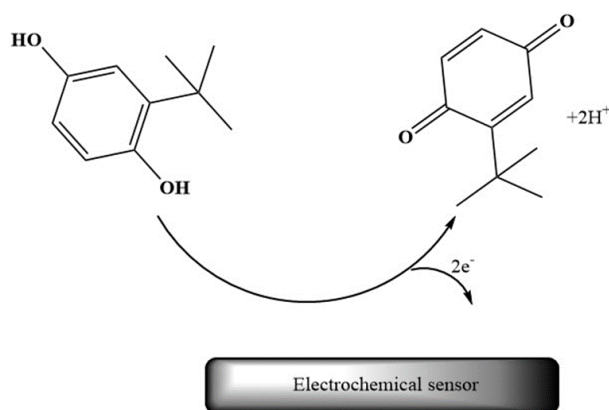


Figure 2. *I*-pH curve for electrooxidation of 220 μM TBHQ at surface of SWCNTs/PE. Inset: DPV of 220 μM TBHQ at surface of SWCNTs/PE in pH range 4.0 to 9.0



Scheme 1. TBHQ electrooxidation mechanism

The oxidation signal of 200 μM TBHQ was recorded at the surface of PE (Figure 3 curve a) and SWCNTs/PE (Figure 3 curve b), respectively. The increase in current from 2.816 to 7.386 μA and the decrease in potential from 550 mV to 500 mV are the main advantages of SWCNTs as catalysts at the surface of the paste electrode. On the other hand, the active surface area of PE and SWCNTs/PE were calculated at about 0.13 and 0.19 cm^2 , respectively. This issue clearly confirms the high electrical conductivity of SWCNTs as a catalyst for the electrooxidation of TBHQ.

A positive shift was observed in the oxidation potential of TBHQ with the increase in the scan rate (see Figure 4 inset), revealing kinetic limitations and quasi-reversible behavior in the redox reaction of TBHQ at the surface of SWCNTs/PE. In addition, a linear dependence of the current peak height and the square root of the scan rate was observed, $I = 1.5580 v^{1/2} + 2.6282$, confirming a diffusion-controlled electrooxidation process (Figure 4) [45].

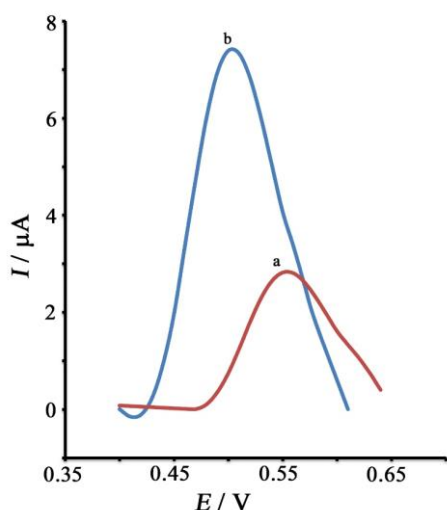


Figure 3. DPV 200 μM TBHQ at surface of PE (a) and SWCNTs/PE (b)

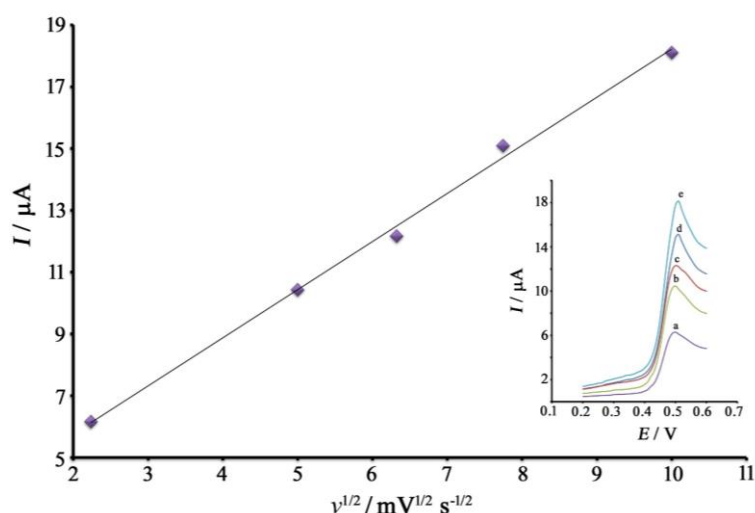


Figure 4. $I-v^{1/2}$ curve to redox reaction of TBHQ at the surface of SWCNTs/PE. Inset: linear sweep voltammograms TBHQ at scan rates a) 5; b) 25; c) 40; d) 60 and e) 100 mV s^{-1}

The stability of SWCNTs/PE in monitoring 200 μM TBHQ was investigated over 70 days. Results are shown in Figure 5 and data showed good stability of SWCNTs/PE in monitoring TBHQ in an aqueous solution after 60 days.

The differential pulse voltammograms (DPV) of TBHQ in the concentration range 0.05 to 390 μM were recorded at the surface of SWCNTs/PE and results are shown in Figure 6 inset. Results displayed a linear equation $I = 0.0325C + 0.8047$ ($R^2 = 0.9974$) where C is concentration. The limit of

detection 10 nM ($Y_{LOD} = 3S_b/m$ where S_b is the standard deviation of blank solution and m is sensitivity or slope of LDR plot) was calculated for SWCNTs/PE as a new sensor.

In the final step, the standard addition results relative to monitoring of TBHQ using SWCNTs/PE are shown in Table 1. The experiments were repeated three times and mean values were displayed in the table. Results clearly confirm the powerful ability of SWCNTs/PE in sensing TBHQ in orange juice and soybean oil samples.

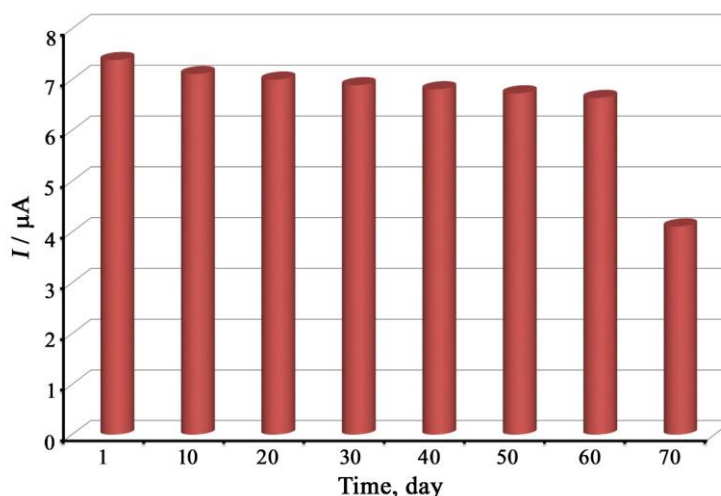


Figure 5. Diagram of oxidation current of 200 μM TBHQ in period of 70 days at the surface of SWCNTs/PE

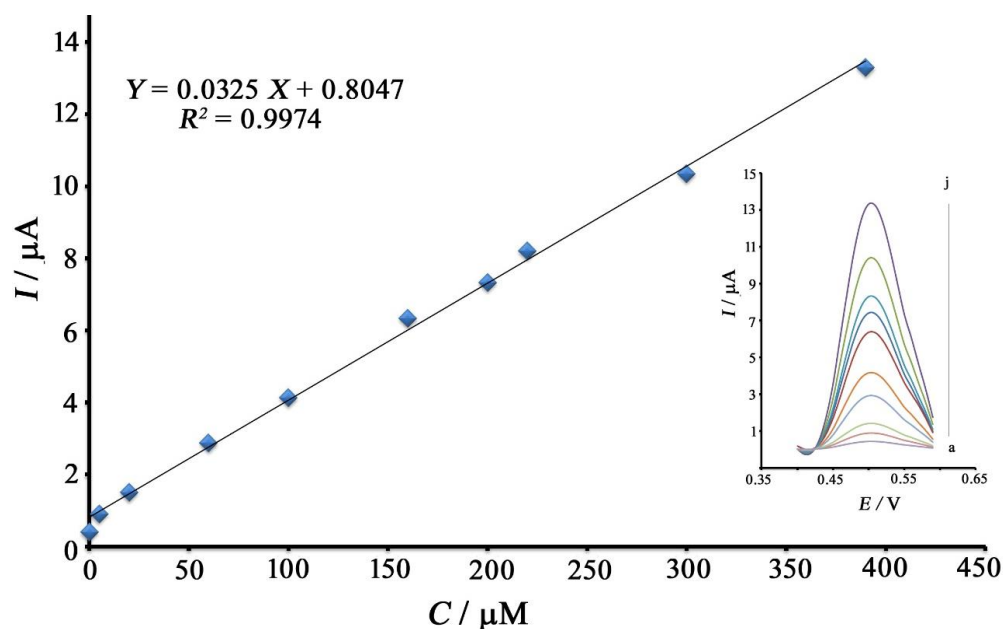


Figure 6. LDR plot to sensing of TBHQ using SWCNTs/PE as sensor. Inset: DP voltammograms TBHQ in the concentration range 0.05 to 390 μM (from a to j)

Table 1. Monitoring of TBHQ in food samples

Sample	Amount of TBHQ, μM			Recovery, %
	Added	Expected	Found by proposed method	
Soybean oil	---	---	1.86 ± 0.22	---
	5.00	6.86	6.98±0.44	101.74
Orange juice	---	---	<LOD	---
	10.00	10.00	9.72±0.73	97.2
Apple juice	---	---	<LOD	---
	20.00	20.00	20.86±0.99	104.3

Conclusions

The present study suggested a very attractive and capable electroanalytical sensor to monitor TBHQ in food products. The new sensor was fabricated using the modification of a paste electrode with SWCNTs as a conductive and powerful catalyst. The SWCNTs/PE showed catalytic activity to sensing of TBHQ by reducing 50 mV oxidation potential and increasing the 2.62-time oxidation potential of antioxidants compared to the unmodified electrode. The SWCNTs/PE showed a good limit of detection (10 nM) for monitoring TBHQ in an aqueous solution that is sufficient for sensing this antioxidant in real samples. The SWCNTs/PE showed a recovery range of 97.2 to 104.3 % to sensing of TBHQ in food products.

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References

- [1] M. Ghalkhani, N. Zare, F. Karimi, C. Karaman, M. Alizadeh, Y. Vasseghian, Recent advances in Ponceau dyes monitoring as food colorant substances by electrochemical sensors and developed procedures for their removal from real samples, *Food and Chemical Toxicology*, (2022) 112830. <https://doi.org/10.1016/j.fct.2022.112830>
- [2] S. Cheraghi, F. Shalali, M.A. Taher, Kojic acid exploring as an essential food additive in real sample by a nanostructure sensor amplified with ionic liquid, *Journal of Food Measurement and Characterization* **17** (2023) 1728-1734. <https://doi.org/10.1007/s11694-022-01738-y>
- [3] J.A. Buledi, A.R. Solangi, A. Mallah, Z.-u.-H. Shah, S.T. Sherazi, M.R. Shah, A. Hyder, S. Ali, Electrochemical monitoring of isoproturon herbicide using NiO/V₂O₅/rGO/GCE, *Journal of Food Measurement and Characterization* **17** (2023) 1628-1639. <https://doi.org/10.1007/s11694-022-01733-3>
- [4] H. Karimi-Maleh, M. Ghalkhani, Z.S. Dehkordi, M. M. Tehran, J. Singh, Y. Wen, M. Baghayeri, J. Rouhi, L. Fu, S. Rajendran, MOF-enabled pesticides as developing approach for sustainable agriculture and reducing environmental hazards, *Journal of Industrial and Engineering Chemistry* **129** (2023) 105-123. <https://doi.org/10.1016/j.jiec.2023.08.044>
- [5] F. Khademi, S.N. Raeisi, M. Younesi, A. Motamedzadegan, K. Rabiei, M. Shojaei, H. Rokni, M. Falsafi, Effect of probiotic bacteria on physicochemical, microbiological, textural, sensory properties and fatty acid profile of sour cream, *Food and Chemical Toxicology* **166** (2022) 113244. <https://doi.org/10.1016/j.fct.2022.113244>
- [6] S.N. Raeisi, H.B. Ghodduji, E.J. Boll, N. Farahmand, B. Stuer-Lauridsen, E. Johansen, J.P. Sutherland, L.I.I. Ouoba, Antimicrobial susceptibility of bifidobacteria from probiotic milk products and determination of the genetic basis of tetracycline resistance in *Enterococcus* species after *in vitro* conjugation with *Bifidobacterium animalis* subsp. *lactis*, *Food Control* **94** (2018) 205-211. <https://doi.org/10.1016/j.foodcont.2018.07.016>
- [7] F. Fazeli, S.M.S. Ardabili, Z. Piravivanak, M. Honarvar, N. Mooraki, Optimization of extraction conditions for polycyclic aromatic hydrocarbons determination in smoked rice using the high performance liquid chromatography-fluorescence detection, *Journal of Food Measurement and Characterization* **14** (2020) 1236-1248. <https://doi.org/10.1007/s11694-020-00372-w>
- [8] K.N. Waliszewski, V.T. Pardio, S.L. Ovando, A simple and rapid HPLC technique for vanillin determination in alcohol extract, *Food Chemistry* **101** (2007) 1059-1062. <https://doi.org/10.1016/j.foodchem.2006.03.004>
- [9] R. Rebane, I. Leito, S. Yurchenko, K. Herodes, A review of analytical techniques for determination of Sudan I–IV dyes in food matrixes, *Journal of Chromatography A* **1217** (2010) 2747-2757. <https://doi.org/10.1016/j.chroma.2010.02.038>

- [10] Q. Xiang, Y. Gao, Y. Xu, E. Wang, Capillary electrophoresis-ampereometric determination of antioxidant propyl gallate and butylated hydroxyanisole in foods, *Analytical Sciences* **23** (2007) 713-717. <https://doi.org/10.2116/analsci.23.713>
- [11] N. Ermis, N. Zare, R. Darabi, M. Alizadeh, F. Karimi, J. Singh, S.-A. Shahidi, E.N. Dragoi, M.B. Camarada, M. Baghayeri, Recent advantage in electrochemical monitoring of gallic acid and kojic acid: a new perspective in food science, *Journal of Food Measurement and Characterization* **17** (2023) 3644-3653. <https://doi.org/10.1007/s11694-023-01881-0>
- [12] S.-A. Shahidi, Effect of solvent type on ultrasound-assisted extraction of antioxidant compounds from *Ficaria kochii*: Optimization by response surface methodology, *Food and Chemical Toxicology* **163** (2022) 112981. <https://doi.org/10.1016/j.fct.2022.112981>
- [13] S.M. Razi, A. Motamedzadegan, L. Matia-Merino, S.-A. Shahidi, A. Rashidinejad, The effect of pH and high-pressure processing (HPP) on the rheological properties of egg white albumin and basil seed gum mixtures, *Food Hydrocolloids* **94** (2019) 399-410. <https://doi.org/10.1016/j.foodhyd.2019.03.029>
- [14] M. Vardini, N. Abbasi, A. Kaviani, M. Ahmadi, E. Karimi, Graphite electrode potentiometric sensor modified by surface imprinted silica gel to measure valproic acid, *Chemical Methodologies* **6** (2022) 398-408. <https://doi.org/10.22034/chemm.2022.328620.1437>
- [15] S. Saghiri, M. Ebrahimi, M.R. Bozorgmehr, Electrochemical amplified sensor with MgO nanoparticle and ionic liquid: A powerful strategy for methyldopa analysis, *Chemical Methodologies* **5** (2021) 234-239. <https://doi.org/10.22034/chemm.2021.128530>
- [16] W.H. Danial, N.A. Norhisham, A.F. Ahmad Noorden, Z. Abdul Majid, K. Matsumura, A. Iqbal, A short review on electrochemical exfoliation of graphene and graphene quantum dots, *Carbon Letters* **31** (2021) 371-388. <https://doi.org/10.1007/s42823-020-00212-3>
- [17] Y.F. Mustafa, G. Chehardoli, S. Habibzadeh, Z. Arzehgar, Electrochemical detection of sulfite in food samples, *Journal of Electrochemical Science and Engineering* **12** (2022) 1061-1079. <https://doi.org/10.5599/jese.1555>
- [18] M. Akbari, M.S. Mohammadnia, M. Ghalkhani, M. Aghaei, E. Sohoul, M. Rahimi-Nasrabadi, M. Arbabi, H.R. Banafshe, A. Sobhani-Nasab, Development of an electrochemical fentanyl nanosensor based on MWCNT-HA/Cu-H₃BTC nanocomposite, *Journal of Industrial and Engineering Chemistry* **114** (2022) 418-426. <https://doi.org/10.1016/j.jiec.2022.07.032>
- [19] R.M. Mohabis, F. Fazeli, I. Amini, V. Azizkhani, An overview of recent advances in the detection of ascorbic acid by electrochemical techniques, *Journal of Electrochemical Science and Engineering* **12** (2022) 1081-1098. <https://doi.org/10.5599/jese.1561>
- [20] H. Medetalibeyoğlu, An investigation on development of a molecular imprinted sensor with graphitic carbon nitride (g-C₃N₄) quantum dots for detection of acetaminophen, *Carbon Letters* **31** (2021) 1237-1248. <https://doi.org/10.1007/s42823-021-00247-0>
- [21] G. Li, J. Li, Z. Yang, An electrochemical sensor based on graphene-chitosan-cyclodextrin modification for the detection of *Staphylococcus aureus*, *Carbon Letters* (2023) <https://doi.org/10.1007/s42823-023-00518-y>
- [22] S. Ariavand, M. Ebrahimi, E. Foladi, Design and construction of a novel and an efficient potentiometric sensor for determination of sodium ion in urban water samples, *Chemical Methodologies* **6** (2022) 886-904. <https://doi.org/10.22034/chemm.2022.348712.1567>
- [23] A.R. Umar, K. Hussain, Z. Aslam, M.A.U. Haq, H. Muhammad, M.R. Shah, Ultra-trace level voltammetric sensor for MB in human plasma based on a carboxylic derivative of Calix [4] resorcinarene capped silver nanoparticles, *Journal of Industrial and Engineering Chemistry* **107** (2022) 81-92. <https://doi.org/10.1016/j.jiec.2021.11.024>
- [24] B. Muthukutty, J. Ganesamurthi, T.-W. Chen, S.-M. Chen, J. Yu, X. Liu, A novel high-performance electrocatalytic determination platform for voltammetric sensing of eugenol in acidic media using pyrochlore structured lanthanum stannate nanoparticles, *Journal of*

- Industrial and Engineering Chemistry* **106** (2022) 103-112.
<https://doi.org/10.1016/j.jiec.2021.10.015>
- [25] B.B. Mulik, A.V. Munde, R.P. Dighole, B.R. Sathe, Electrochemical determination of semicarbazide on cobalt oxide nanoparticles: Implication towards environmental monitoring, *Journal of Industrial and Engineering Chemistry* **93** (2021) 259-266.
<https://doi.org/10.1016/j.jiec.2020.10.002>
- [26] A.R. Cherian, L. Benny, A. George, A. Varghese, G. Hegde, Recent advances in functionalization of carbon nanosurface structures for electrochemical sensing applications: tuning and turning, *Journal of Nanostructure in Chemistry* **12** (2021) 441-466. <https://doi.org/10.1007/s40097-021-00426-5>
- [27] A. John, L. Benny, A.R. Cherian, S.Y. Narahari, A. Varghese, G. Hegde, Electrochemical sensors using conducting polymer/noble metal nanoparticle nanocomposites for the detection of various analytes: a review, *Journal of Nanostructure in Chemistry* **11** (2021) 1-31.
<https://doi.org/10.1007/s40097-020-00372-8>
- [28] B. Davarnia, S.-A. Shahidi, H. Karimi-Maleh, A. Ghorbani-HasanSaraei, F. Karimi, Biosynthesis of Ag nanoparticle by peganum harmala extract; antimicrobial activity and ability for fabrication of quercetin food electrochemical sensor, *International Journal of Electrochemical Science* **15** (2020) 2549-2560. <https://doi.org/10.20964/2020.03.70>
- [29] H. Karimi-Maleh, R. Darabi, M. Baghayeri, F. Karimi, L. Fu, J. Rouhi, D.E. Niculina, E.S. Gündüz, E. Dragoi, Recent developments in carbon nanomaterials-based electrochemical sensors for methyl parathion detection, *Journal of Food Measurement and Characterization* **17** (2023) 5371-5389. <https://doi.org/10.1007/s11694-023-02050-z>
- [30] P. Ebrahimi, S.-A. Shahidi, M. Bijad, A rapid voltammetric strategy for determination of ferulic acid using electrochemical nanostructure tool in food samples, *Journal of Food Measurement and Characterization* **14** (2020) 3389-3396. <https://doi.org/10.1007/s11694-020-00585-z>
- [31] H. Sadeghi, S.-A. Shahidi, S.N. Raeisi, A. Ghorbani-HasanSaraei, F. Karimi, Electrochemical determination of vitamin B6 in water and juice samples using an electrochemical sensor amplified with NiO/CNTs and Ionic liquid, *International Journal of Electrochemical Science* **15** (2020) 10488-10498. <https://doi.org/10.20964/2020.10.51>
- [32] F. Karimi, E. Demir, N. Aydogdu, M. Shojaei, M.A. Taher, P.N. Asrami, M. Alizadeh, Y. Ghasemi, S. Cheraghi, Advancement in electrochemical strategies for quantification of Brown HT and Carmoisine (Acid Red 14) From Azo Dye stuff class, *Food and Chemical Toxicology* **165** (2022) 113075. <https://doi.org/10.1016/j.fct.2022.113075>
- [33] M. Alizadeh, E. Demir, N. Aydogdu, N. Zare, F. Karimi, S.M. Kandomal, H. Rokni, Y. Ghasemi, Recent advantages in electrochemical monitoring for the analysis of amaranth and carminic acid food colors, *Food and Chemical Toxicology* **163** (2022) 112929.
<https://doi.org/10.1016/j.fct.2022.112929>
- [34] A. L. Branen, P. M. Davidson, S. Salminen, J. Thorngate, *Food Additives*, CRC Press, 2001.
<https://doi.org/10.1201/9780367800505>
- [35] G. Van Esch, Toxicology of tert-butylhydroquinone (TBHQ), *Food and Chemical Toxicology* **24** (1986) 1063-1065. [https://doi.org/10.1016/0278-6915\(86\)90289-9](https://doi.org/10.1016/0278-6915(86)90289-9)
- [36] W. Cao, Y. Wang, Q. Zhuang, L. Wang, Y. Ni, Developing an electrochemical sensor for the detection of tert-butylhydroquinone, *Sensors and Actuators B* **293** (2019) 321-328.
<https://doi.org/10.1016/j.snb.2019.05.012>
- [37] Y. Pan, K. Lai, Y. Fan, C. Li, L. Pei, B.A. Rasco, Y. Huang, Determination of tert-butylhydroquinone in vegetable oils using surface-enhanced Raman spectroscopy, *Journal of Food Science* **79** (2014) T1225-T1230. <https://doi.org/10.1111/1750-3841.12482>

- [38] S.S. Siwal, A.K. Saini, S. Rarotra, Q. Zhang, V.K. Thakur, Recent advancements in transparent carbon nanotube films: chemistry and imminent challenges, *Journal of Nanostructure in Chemistry* **11** (2021) 93-130. <https://doi.org/10.1007/s40097-020-00378-2>
- [39] A. Mohammadnavaz, F. Garkani-Nejad, Voltammetric determination of hydrochlorothiazide at a modified carbon paste electrode with polypyrrole nanotubes, *ADMET and DMPK* **11** (2023) 293-302. <https://doi.org/10.5599/admet.1706>
- [40] A. Hosseini-Roudsari, S.-A. Shahidi, A. Ghorbani-HasanSaraei, S. Hosseini, F. Fazeli, A new electroanalytical approach for sunset yellow monitoring in fruit juices based on a modified sensor amplified with nanocatalyst and ionic liquid, *Food and Chemical Toxicology* **168** (2022) 113362. <https://doi.org/10.1016/j.fct.2022.113362>
- [41] S. Salmanpour, A. Sadrnia, F. Karimi, N. Majani, M.L. Yola, V.K. Gupta, NiO nanoparticle decorated on single-wall carbon nanotubes and 1-butyl-4-methylpyridinium tetrafluoroborate for sensitive raloxifene sensor, *Journal of Molecular Liquids* **254** (2018) 255-259. <https://doi.org/10.1016/j.molliq.2018.01.105>
- [42] Q. Zhao, Z. Gan, Q. Zhuang, Electrochemical sensors based on carbon nanotubes, *Electroanalysis* **14** (2002) 1609-1613. <https://doi.org/10.1002/elan.200290000>
- [43] A. Ambika, N. Navya, S. Kiran Kumar, B. Suresha, Electrochemical determination of paracetamol by SWCNT-modified carbon paste electrode: a cyclic voltammetric study, *Carbon Letters* **32** (2022) 1287-1295. <https://doi.org/10.1007/s42823-022-00354-6>
- [44] S. Zheng, J. Fan, F. Yin, J. Chen, Z. Hui, J. Tang, X. Wang, J. Guo, Electrochemical determination of tert-butylhydroquinone by ZIF-67@ TiO₂ derived hierarchical TiO₂/Co/NCNTs, *New Journal of Chemistry* **47(33)** (2023) 15569-15578. <https://doi.org/10.1039/D3NJ02149A>
- [45] M.-H. Karimi-Harandi, M. Shabani-Nooshabadi, R. Darabi, Cu-BTC metal-organic frameworks as catalytic modifier for ultrasensitive electrochemical determination of methocarbamol in the presence of methadone, *Journal of The Electrochemical Society* **168** (2021) 097507. <https://doi.org/10.1149/1945-7111/ac2468>

