

Nanohybrid-modified working electrodes for electrochemical sensing of chlorpyrifos

S. Sharma¹, S. Mehtab^{2*}, M.G.H. Zaidi², U. R. Mallik¹, R. Singh¹

¹Department of Chemistry, Surajmal Agarwal Pvt. Kanya Mahavidhyalaya, Kichha, Uttarakhand, India

²Department of Chemistry, College of Basic Science and Humanities, G.B Pant University of Agriculture and Technology, Uttarakhand (U.K.), India-263 145

Received: April 12, 2023; Revised: August 10, 2023

Present work demonstrates that development of Nanohybrids (NHs) based working electrodes (WEs) for electrochemical (EC) sensing of chlorpyrifos (CPS). Synthesized c-MWCNT/h-BN NHs in presence of polyvinyl butyral binder in NMP medium was used to modify the surface of stainless-steel plate that worked as working electrode (WE) in EC studies. The EC behavior of CPS was studied by cyclic voltammetry (CV) and square wave voltammetry (SWV) in KCl (0.1 M) at 7.2 pH. SWV data reveals CPS can be quantified upto LOD of 2.62 ng/L and LOQ 7.96 ng/L over WE. The overall result reveals that developed electrode material for EC sensing provides highly sensitive, selective and reproducible estimation of CPS upto nano molar level.

Keywords: Nanohybrid, Electrochemical sensing, Cyclic voltammetry, Chlorpyrifos

INTRODUCTION

Organophosphates (OPs) are a large group of synthetic compounds, including esters, amides, or thiol derivatives of phosphoric, phosphonic, phosphorothioic, or phosphonothioic acids. They are commonly used as insecticides, herbicides, and fungicides, as well as in the production of plastics, gasoline additives, and flame retardants. OPs work by inhibiting the activity of acetylcholinesterase, an enzyme that regulates the transmission of nerve impulses in the body [1]. This leads to the accumulation of acetylcholine, a neurotransmitter in nerve synapses which can result in overstimulation of the nervous system and can be toxic to humans and other animals. Prolonged exposure to OPs can lead to a range of health problems, including nausea, headache, dizziness, confusion, and muscle weakness. In severe cases, OPs exposure can cause seizures, respiratory failure and even death [2]. For such reasons, there is a need of sustainable methodologies for routine, continuous, accurate, reproducible and on spot detection of OPs in real samples. In this context, different chromatographic [3], electrophoretic [4], and electrochemical (EC) [5] techniques were developed for identification of OPs.

CPS (*O,O*-diethyl-*O*-3,5,6-trichloro-2-pyridyl phosphorothioate) is a widely used OPs insecticide that has been used for several decades to control a variety of pests on crops. CPS has a low water solubility and high soil sorption coefficient; these characteristics make it possible so that CPS can

remain in the natural environment for a long time [6]. CPS is absorbed in mammals by all routes wherein, inhalation leads to fastest appearance of symptoms, followed by oral and dermal routes. Prolonged exposure of CPS cause cancer, reproductive and neurological disorders, allergic reactions and neurodevelopmental impairment in growing children [7]. In this context, the quantification of CPS through High performance liquid chromatography (HPLC) [8-10], Thin layer chromatography (TLC) [11], Surface-enhanced raman spectroscopy (SERS) [12], laser-induced breakdown spectroscopy (LIBS) [13, 14], UV spectra [15] and electrochemical (EC) [16, 17] methods have been well established. Recently, EC methods specially based on SWV overcome the problems associated with traditional analytical methods as these are cost effective, highly sensitive, selective and low sample volume, reusable, require less organic solvents and short analysis time. SWV has emerged as most sustainable approach for detection and quantification of OPs [18, 19].

NHs synthesized through dispersion of Nanomaterials over different substrate like MWCNT, graphene can be effectively used in the development of EC sensors. The NHs used for detection of CPS were GO/Fe₃O₄ [20], TiO₂/CA [21], TGO/Uio-66 [22], MWCNT@SiO₂-MIP [23] and PIN-WC [24]. The modification of WE surface by NHs is mainly responsible for the efficiency of EC sensors towards CPS detection. Modification of MWCNT with h-BN has been of interest in attempt to develop the NHs that find their future applications

* To whom all correspondence should be sent:
E-mail: smiitr@gmail.com, mghziaid@gmail.com

in hydrogen energy storage [25], as electrode materials for high temperature supercapacitors and further may be utilized for quantification of CPS [26]. The present work proposed a novel and economical sensor for the trace level EC detection of CPS, using h-BN doped c-MWCNT NHs.

MATERIALS AND METHODS

Materials

Standards of CPS (99.5 %) were procured from Sigma, Aldrich, USA. Poly vinyl butyral (PVB) ($M_w = 3.05 \times 10^4$ g/mol) was procured from Himedia, India and N-methyl-2-pyrrolidone (NMP) was used as solvent was purchased from Loba Cheme. All solutions were prepared in DW (Deionized water) (>18 M Ω -cm). NHs comprising c-MWCNT/h-BN was directly used as provided by Department of Chemistry, G.B. Pant University of Agriculture and Technology, Pantnagar [27]. Rest of the chemicals and solvents (Purity 99.5 %) were used without further purification.

Fabrication of electrodes

WEs were developed according to procedure reported earlier [28]. A series of WEs were fabricated through cast of an electroactive material supplemented with appropriate polymeric binder over current collectors (CC). Prior to deposition, stainless steel plate electrodes (SSPE) were finished through polishing with emery paper, then washed with DW and further ultrasonication in acetone over 10 min. SSPE with mirror like finish were dried and stored at $50 \pm 1^\circ\text{C}/400$ mmHg. Electroactive compositions for deposition over SSPE were prepared through mixing of (35.0 mg) of NHs supplemented with PVB (7.50 mg) in NMP (1 mL) under stirring over 2 h followed by additional ultrasonic treatment over 20 min to afford a slurry. WEs with required thickness were prepared through cast of slurry (125 μL) over SSPE followed by gelation at room temperature for 1 h and then drying it at $50 \pm 1^\circ\text{C}/400$ mmHg. WEs developed by NHs with 5 wt% h-BN were abbreviated as WE-II.

EC characterization

EC studies of fabricated electrodes were performed in a triple electrode cell assembly over Potentiostat-Galvanostat, IVIUM Netherlands in KCl (0.1 M) at optimized pH. Electrode assembly was consist of WE-II, Pt foil (1 cm^2) as auxiliary electrodes and Ag/AgCl as reference electrodes. EC performance of WE-II was examined through CV at scan rate (mV/s) ranging 25 to 150 under compatible current and sweep potential. EC response of OPs over WE-II was optimized under judicious EC conditions. EC data obtained from SWV of standard solutions of CPS were simulated to achieve calibration plots for quantitative estimation of CPS.

RESULTS

EC behavior of WE-II

EC behavior of WE-II was investigated through CV studies in 0.1 M KCl [Fig. 1]. Comparative cyclic voltammograms were obtained for SSPE and WE-II at a common scan rate (SR) of 50 mV/s within potential window of -1.5 to +0.0 V. A pair of well-defined redox peaks was observed on the SSPE and WE-II with the E_{pa} (V) at -0.675 and -0.670, and E_{pc} (V) values of -1.228 and -1.231 respectively. Magnitudes of redox peak current rapidly increased, on modification of SSPE with NHs (5 wt% h-BN) that indicates better EC behavior of WE-II [29]. CV studies was performed in different solvent medium *viz.*, KCl, PBS, H_2SO_4 and KOH and among all KCl showed best response and selected for onwards EC investigations [Fig. 2].

Effect of the scan rate on the EC detection of CPS was examined at different SR of 25, 50, 80, 100, 150 and 200 mV/s. Fig. 3 reflects that, I_{pa} increases from 0.767 to 1.912 mA and I_{pc} reduces from -1.202 to -2.231 mA with linear dependence on SR ranging from 25 to 150 mV/s. Data reveals that fabricated WE-II function as an electron conducting tunnel and releases more electrons with high SR, suggesting a typical surface-controlled electrode process. Further, the polarization of the electrode under high SR attributes to increased potential difference between anodic and cathodic peaks [30].

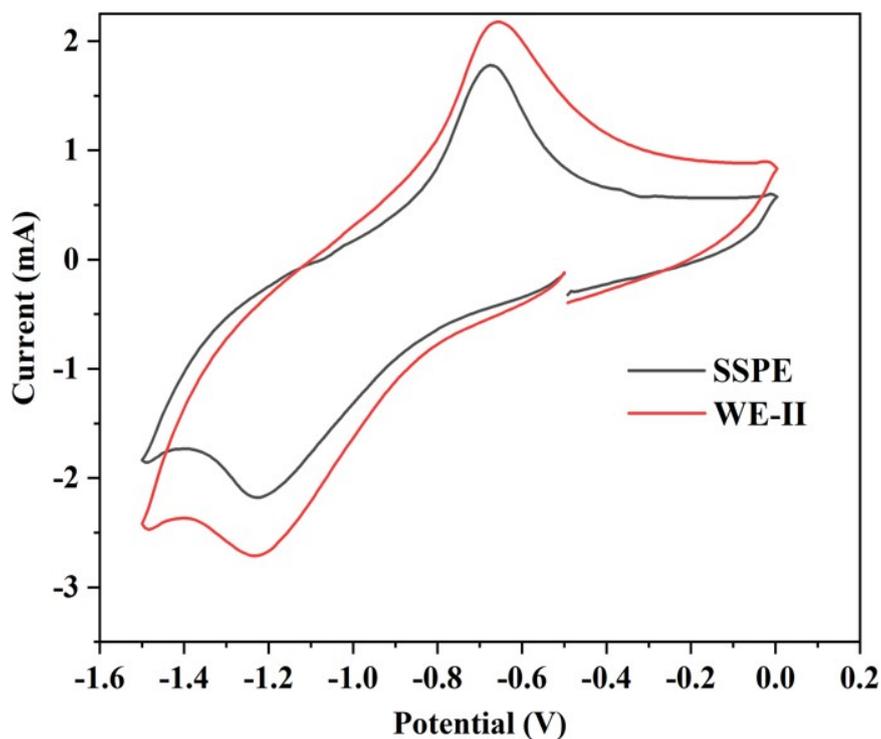


Fig. 1. Comparative CV curves of SSPE and WE-II

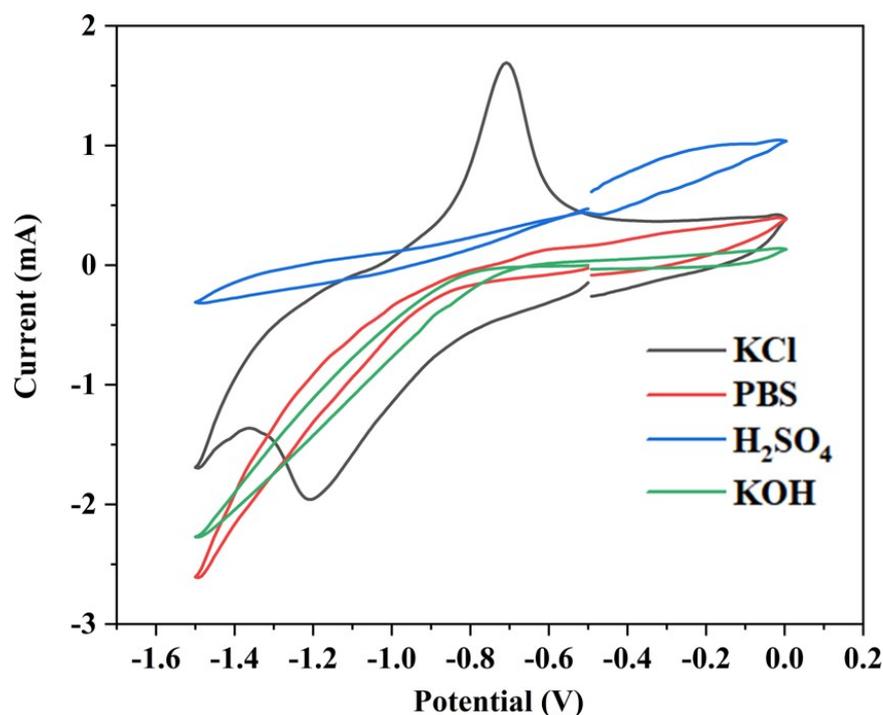


Fig. 2. Electrochemical compatibility of electrolyte media with WE-II

Quantification of OPs through SWV

EC quantification of CPS, was examined through SWV at developed WE-II as sensing device [Fig. 4a]. SWV performed within optimal parameters of potential ranging -2.0 V to 2.0 V, E step of 8 mV @10 Hz pulse amplitude at 100 mV over WE-II.

Calibration curve for CPS was obtained by sequential addition of CPS (10^{-3} M methanolic solution) in KCl (0.1 M aqueous solution, pH 7.4). Calibration graph showed linear relation between I_p (2.79 to 3.61 mA) and successive addition of CPS (5 to 25 ng/L) added with regression coefficient of 0.98

[Fig. 4b]. The LOD and LOQ were estimated from calibration curves using relations, $LOD = 3.3$ (S.D. of intercept/slope) and $LOQ = 10$ (S.D. of intercept/slope) [31]. The proposed EC sensor

demonstrates acceptable quantification of CPS with quite low LOD and LOQ values at WE-II as 2.62 ng/L and 7.93 ng/L, respectively.

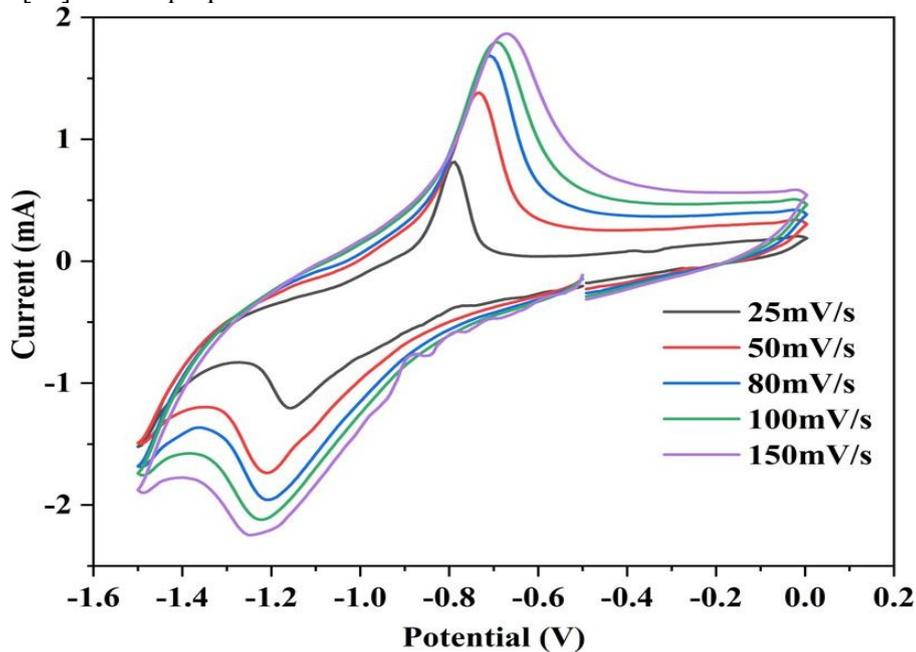


Fig. 3. Effect of SR (mV/s) ranging 25 to 150 on CV of WE-II

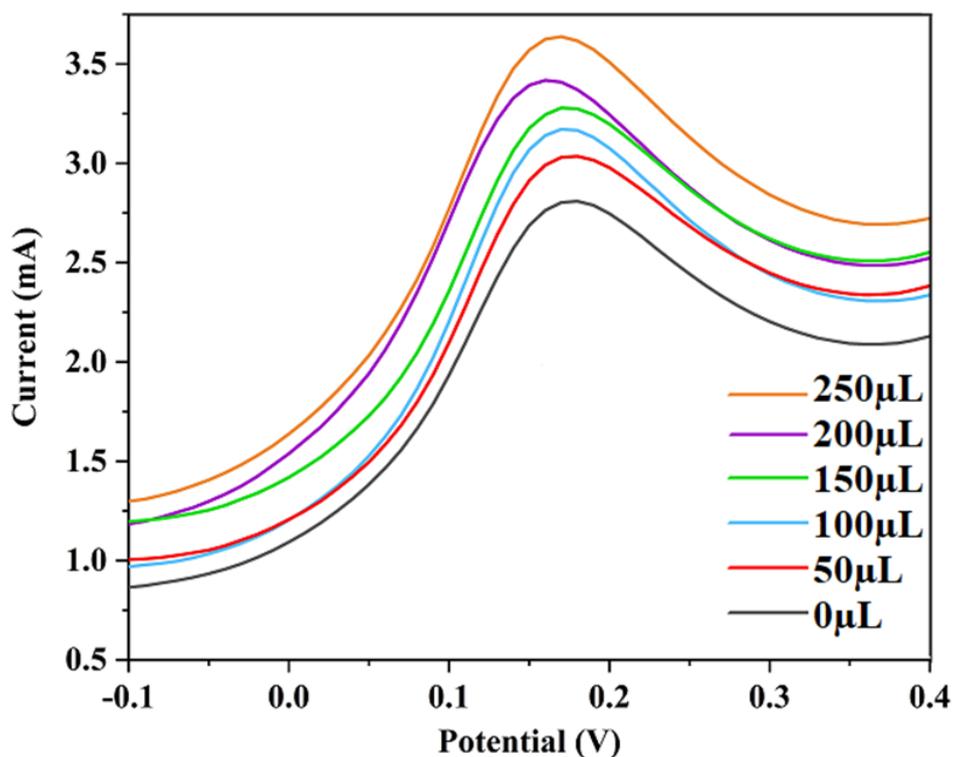


Fig. 4a. Effect of concentration of CPS on current response in SWV at WE-II

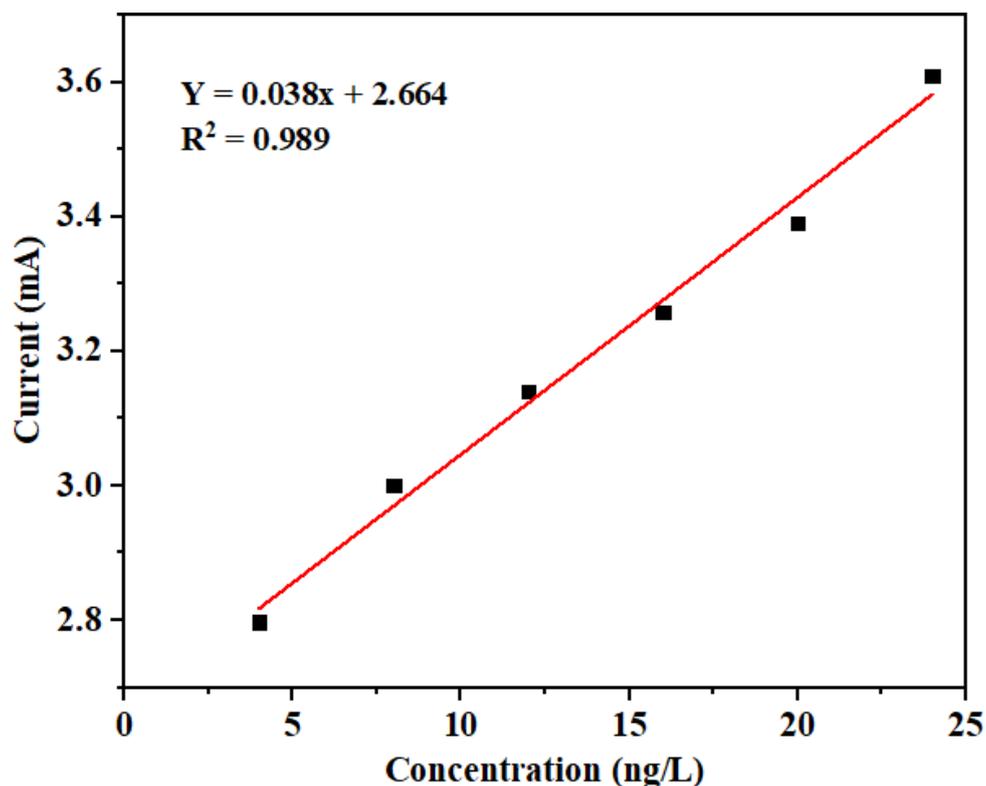


Fig. 4b. Calibration curve drawn from SWV for CPS at WE-II

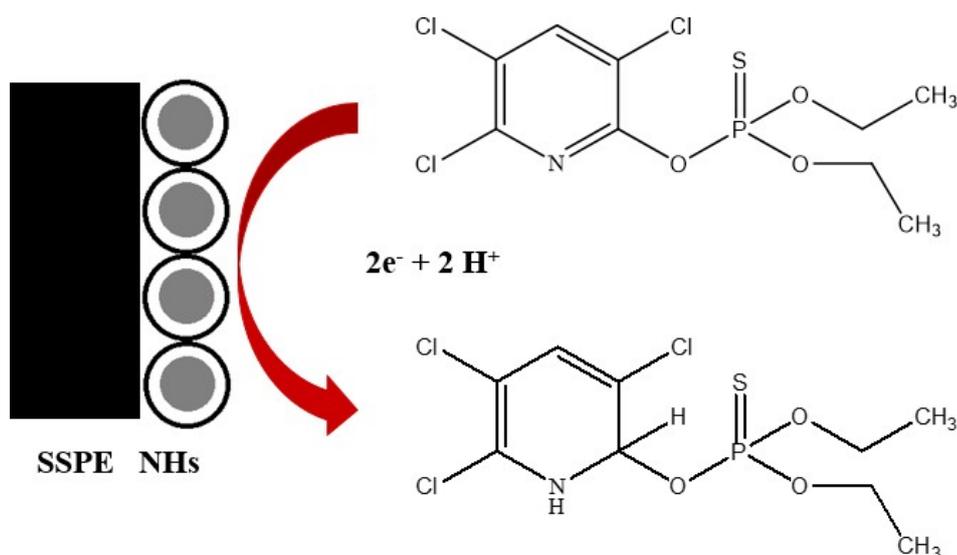


Fig. 5. Mechanism of electro reduction of CPS at WE-II

SWV showed two reductions peaks for CPS, out of them first strong reduction peak was selected for quantification. In SWV, peak appears due to electro-reduction of CPS at pyridine ring ($-C=N-$) via $2e^-/2H^+$ transfer step at pH 7.4 (Fig. 5). Reduction peaks of CPS at ~ -0.1 V and 0.6 V, appeared due to reduction of pyridine nitrogen and carbon ring respectively. Three chlorine atoms attached at pyridine ring facilitate delocalization of electrons at $-C=N-$ bond and thus enhances the reduction of $-C=N-$ bond of pyridine ring at low negative potentials. It revealed that the coated material act as an electron-conducting tunnel and facilitates the

electron transfer kinetics that enhanced EC properties of WE-II. The enhancement in I_p may be attributed to their high surface area of NHs (5 wt% h-BN) and good electrical conductivity of WE-II that increases its sensitivity towards pesticides monitoring [32].

CONCLUSION

The present research has been focused on coating the NHs as potential electrode material for EC detection of CPS. WEs were derived from NHs in presence of PVB binder in NMP. WEs have rendered highly sensitive, selective and reproducible EC

response in KCl 0.1 M. The EC behavior of WE-II was investigated through CV studies under optimized parameters of SR of 50 mVs⁻¹, Estep 8 mV, within the potential window of -1.5 to +0.0 V. CV reveals enhanced redox behavior and EC stability of WEs in KCl at 7.2 pH. EC methods based on SWV reveal immense feasibility of electrodes towards quantification of CPS. SWV data reveals CPS can be quantified upto LOD of 2.62 ng/L and LOQ 7.96 ng/L over WE-II. The developed sensor exhibits high sensitivity, selectivity and shows an excellent recovery that can be employed in real sample analysis.

Acknowledgement: Authors are grateful to Defence Research Development Organization, Ministry of Defence, India, for financial support vide grant No CFEES/TCP/EnSG/CARS/Pantnagar/MOFW/20/20 18 for development of experimental facilities at Pantnagar.

REFERENCES

1. J. Kaushal, M. Khatri, S.K. Arya, *Ecotoxicol. Environ. Saf.*, **207**, 1 (2021).
2. H. Mali, C. Shah, B.H. Raghunandan, A.S. Prajapati, D.H. Patel, U. Trivedi, R.B. Subramanian, *J. Environ. Sci.*, **127**, 234 (2022).
3. X. Guardino, J. Obiols, M.G. Rosell, A. Farran, C. Serra, *J. Chrom. A.*, **823**, 91 (1998).
4. M. Saunders, B.L. Magnanti, S.C. Carreira, A. Yang, U. Alamo Hernández, H. Riojas-Rodriguez, A. Bartonova, *Environ. Health*, **11**, S5 (2012).
5. M.L. Yola, N. Atar, *J. Electrochem. Soc.*, **164**, B223 (2017).
6. R.S. Bhende, U. Jhariya, S. Srivastava, S. Bombaywala, S. Das, N.A. Dafale, *Appl. Biochem. Biotechnol.*, **194**, 2301 (2022).
7. J.N. Seiber, L.A. Kleinschmidt, *J. Agric. Food Chem.*, **59**, 7536 (2011).
8. R.E. Mauldin, T.M. Primus, T.A. Buettgenbach, J.J. Johnston, G.M. Linz, *J. Liq. Chromatogr. Relat. Technol.*, **29**, 339 (2006).
9. Q. Ullah, N. Fatema, A. Mohammad, *JPC-J. Planar Chromat.*, **33**, 533 (2020).
10. V. Kumar, N. Upadhyay, A.B. Wasit, S. Singh, P. Kaur, *Curr. World Environ.*, **8**, 313 (2013).
11. J. Sherma, R. Slobodien, *J. Liq. Chromatogr.*, **7**, 2735 (1984).
12. P. Ma, L. Wang, L. Xu, J. Li, X. Zhang, H. Chen, *Eur. Food Res. Technol.*, **246**, 239 (2020).
13. X. Du, D. Dong, X. Zhao, L. Jiao, P. Han, Y. Lang, *RSC. Adv.*, **5**, 79956 (2015).
14. X. Zhao, C. Zhao, X. Du, D. Dong, *Sci. Rep.*, **9**, 1 (2019).
15. Y. Makino, S. Oshita, Y. Murayama, M. Mori, Y. Kawagoe, K. Sakai, *Trans. ASABE*, **52**, 1955 (2009).
16. N.Y. Sreedhar, M.S. Kumar, K. Krishnaveni, *Sens. Act. B: Chem.*, **210**, 475 (2015).
17. R. Vera, S. Insa, C. Fontas, E. Antico, *Talanta*, **185**, 291 (2018).
18. D. Sharma, A. Nagpal, Y.B. Pakade, J.K. Katnoria, *Talanta*, **82**, 1077 (2010).
19. G.V. Guerreiro, A.J. Zaitouna, R.Y. Lai, *Anal. Chim. Acta.*, **810**, 79 (2014).
20. Y. Jiao, W. Hou, J. Fu, Y. Guo, X. Sun, X. Wang, J. Zhao, *Sens. Actuators B: Chem.*, **243**, 1164 (2017).
21. A. Kumaravel, M. Chandrasekaran, *J. Agric. Food Chem.*, **63**, 6150 (2015).
22. N. Karimian, H. Fakhri, S. Amidi, A. Hajian, F. Arduini, H. Bagheri, *New J. Chem.*, **43**, 2600 (2019).
23. W. Huang, X. Zhou, Y. Luan, Y. Cao, N. Wang, Y. Lu, T. Liu, W. Xu, *J. Sep. Sci.*, **43**, 954 (2020).
24. P. Joshi, S. Mehtab, M.G.H. Zaidi, T. Tyagi, A. Bisht, *J. Nanostructure Chem.*, **10**, 33 (2020).
25. M. Sankaran, B. Viswanathan, S.S. Murthy, *Int. J. Hydrog. Energy*, **33**, 393 (2008).
26. N. Jain, E. Gupta, N.J. Kanu, *Smart Sci.*, **10**, 1 (2022).
27. S. Sharma, S. Mehtab, M.G.H. Zaidi, *Materials Today: Proceedings* **62**, 6494 (2022).
28. S. Sharma, S. Mehtab, M.G.H. Zaidi, *Mater. Chem. Phys.*, **296**, 127278 (2023).
29. M. Amatongchai, W. Sroysee, P. Sodkrathok, N. Kesangam, S. Chairam, P. Jarujamrus, *Anal. Chim. Acta*, **1076**, 64 (2019).
30. B.G.S. Raj, R.N.R. Ramprasad, A.M. Asiri, J.J. Wu, S. Anandan, *Electrochim. Acta*, **156**, 127 (2015).
31. J.C. Miller, J.N. Miller, *Analyst*, **113**, 1351 (1988).
32. N. Karimian, H. Fakhri, S. Amidi, A. Hajian, F. Arduini, H. Bagheri, *New J. Chem.*, **43**, 2600 (2019).