JOURNAL of THE TURKISH CHEMICAL SOCIETY SECTION: A CHEMISTRY

TURKISH CHEMICAL SOCIETY

Comparison of Polyacrylonitrile-and Polypyrrole-based Electrochemical Sensors for Detection of Propamocarb in Food Samples

Selcan Karakuş[1*], Cihat Taşaltın[2], İlke Gürol[2], Barbaros Akkurt[3], Gülsen Baytemir[4], Nevin Taşaltın[4,5*]

[1]Istanbul University-Cerrahpasa, Department of Chemistry, Istanbul, Turkey.
[2]TUBITAK Marmara Research Center, Institute of Materials, Gebze, Kocaeli, Turkey.
[3]Istanbul Technical University, Department of Chemistry, 34469 Istanbul, Turkey
[4]Maltepe University, Department of Electrical & Electronics Engineering, Istanbul, Turkey.
[5]Maltepe University, Department of Basic Sciences, Istanbul, Turkey.

Abstract: Food safety is a crucial issue; all countries have struggled against pesticides for years. In this study, Polypyrrole (PPy)- and Polyacrylonitrile (PAN)-based non-enzymatic electrochemical sensors were investigated to detect the pesticide propamocarb (PM) in food samples. Under the experimental conditions, the proposed strategy exhibited a high selectivity of the disposable PPy-based and PAN-based sensors for the determination of propamocarb pesticide in the concentration of 1 μM with a rapid detection within 1 min at pH 7.4 and 25 °C. We demonstrated the detection of PM residues on cucumber and tomato samples with good electrochemical performances towards the real-time usability on real food samples. PAN-based non-enzymatic electrochemical sensor has good sensitivity, higher selectivity, and stability than PPy-based non-enzymatic electrochemical sensor. The prepared PAN-based non-enzymatic electrochemical sensor is a potential candidate to be used in devices which perform food safety in agricultural products.

Keywords: Food safety; pesticide; electrochemical sensor; Polypyrrole; Polyacrylonitrile.

Submitted: March 14, 2022. **Accepted:** April 21, 2022.

Cite this: Karakuş S, Taşaltın C, Gürol İ, Akkurt B, Baytemir G, Taşaltın N. Comparison of Polyacrylonitrile-and Polypyrrole-based Electrochemical Sensors for Detection of Propamocarb in Food Samples. JOTCSA. 2022;9(3):801–8.

DOI: https://doi.org/10.18596/jotcsa.1087096.

*Corresponding authors. E-mails: nevintasaltin@maltepe.edu.tr , selcan@iuc.edu.tr.

INTRODUCTION

Food safety is one of the significant issues for human beings and environment due to constant population growth and industrial development (1,2). The use of pesticides and fungicides have toxic effects, which are extensively common to kill or control insects, mollusks, weeds, fungi, and bacteria in agriculture (3,4). Due to the use of these chemicals at global scale, their residues become a vital issue to protect the natural environment (5). From this perspective, rapid, sensitive, and portable detection of these chemicals in food products, soil and water in low concentrations has gained momentum in research (6–8).

Sensitive, portable, and low-cost biosensors have started to be preferred with nanotechnological approach instead of expensive and not-easy-to-apply methods such as gas chromatography (GC), mass spectrometry (MS), and high-performance liquid chromatography (HPLC) (9,10). In previous studies, ultra-highly sensitive nanostructure-based biosensors with different shapes, structures, and sizes were produced and their effectiveness in sensor applications was investigated for environmental pollutants (11,12). In this regard, the performances of these sensors have been developed using different structures such as Ag_2O-ZnO composite nanocone (13), Pr_2O_3-ZnO nanocomposites (14), V_2O_5-doped ZnO nanocomposites (15), CuO nanocomposites (11), TiO_2 nanoparticles/ molybdenum disulfide (MoS_2) nanosheets (16), iron oxide (Fe_3O_4) nanoparticles (17), reduced graphene oxide nanosheets - gold nanoparticles (18), reduced graphene oxide-wrapped silver nanoparticles (19), and polypyrrole (PPy) nanotubes (20). However, there are numerous studies in literature that reported novel non-enzymatic electrochemical biosensors to give some information in development of the sensitive pesticide sensors. For instance, Zhai et al. developed a highly selective and recyclable sensor for the electroanalysis of phosphothioate pesticides using silver - doped arrays of ZnO nanorods (21). Cesana et al. reported the synthesis and application as electrochemical sensor of the pesticide fenitrothion with fluorescent Cdots(N)-Silica composites (22). Chen et al. investigated the fluorometric determination of pesticide ferbam using the organic-inorganic manganese(II) halide hybrids-based paper sensor (23). Dissanayake et al. developed a highly sensitive plasmonic metal nanoparticle-based sensors for the detection of organophosphorus pesticides (24). Recently, PPy and PANI are commonly used as the preferred conductive polymers due to their unique electrical, electrochemical, and optical properties in diagnostics, food, and environmental applications (25–31). PPy, which is known to be a conductive organic polymer, has superior properties such as the mobility of charge carriers and fast electron transfer rate, can be used in electronics, optical, biological, and biomedical applications (32,33). Also, polyaniline (PANI) is another kind of conductive polymer which is prepared using the electrochemical oxidation of aniline in acidic medium (34). To the best of our knowledge, polyacrylonitrile (PAN) and PPy-based non-enzymatic electrochemical sensors have not been reported for the ultra-sensitive detection of the pesticide propamocarb in food samples. Furthermore, a clear proof of the existence of conductive polymers and their non-enzymatic-sensing mechanism for propamocarb pesticide needs to be experimentally clarified in food samples. Therefore, the highlight of this study was to use the electrochemical activities of PPy and PAN towards PM detection in tomato and cucumber samples. The goal of this study was to demonstrate a sensing platform based on non-enzymatic electrochemical polymers for low-cost, selective, and rapid detection of PM in real samples.

MATERIALS AND METHODS

Materials

Turkish tomatoes (Solanum lycopersicum) and cucumbers (Cucumis sativus L.) were purchased from a local supermarket (İstanbul, Turkey). All samples were harvested from Antalya (Turkey) on July and were stored at 15 °C until use. PPy (average Mw ~12,000 g/mol) and PAN (average Mw~150,000 g/mol) were purchased from Sigma Aldrich Company (Germany). N-N-Dimetylformamide (DMF) (purity (GC), ≥ 99.8 %) and ethanol (purity (GC), ≥ 99.9 %) were purchased from Merck Company (Germany). Propamocarb (PESTANAL®, analytical standard, formula:$C_9H_{20}N_2O_2$, molecular weight: 188.27 g/mol), a carbamate pesticide, was obtained from Sigma Aldrich Company (Germany). Electrochemical transducers were purchased from Ebtro Electronics. All chemicals and reagents were used without further purification.

Fabrication of PPy and PAN-based electrodes

2 mg of PPy powder was dissolved in 5 mL of ethanol, 2 mg of PAN powder was dissolved in 5 mL of DMF for 30 min via high stirring at 25 °C. The gold (Au) electrochemical transducers were rinsed with ethanol, distilled water, and dried with nitrogen. The electrochemical transducers were coated with PPy solution and PAN solution by drop casting, and then the sensing films were dried at 40 °C. All electrochemical sensor measurements were performed using Ebtro Electronics voltammetric electrochemical workstation. 1 μM of PM analyte was prepared. All sensor measurements were carried out at room temperature.

RESULTS AND DISCUSSION

There is a growing concern about extremely hazardous chemical pesticides and their influence on human health and the environment (35–37). For this purpose, in this study, it was aimed to selectively detect different pesticides such as malathion, deltamethrin, cypermethrin, and propamocarb (PM) by comparing them with different PPy and PAN-based sensors in food samples (tomato and cucumber). Measurements of PPy- and PAN-based non-enzymatic electrochemical sensors were performed at [−1, +1] V with a scanning rate of 50 mV/s. Comparative current density-voltage graphs of PPy and PAN-based non-enzymatic electrochemical sensors against pesticides were presented (see Figure 1). Figure 1 showed the non-enzymatic electrochemical responses of the PPy- and PAN-based non-enzymatic electrochemical sensors for the presence of 1μM pesticides (malathion, deltamethrin, cypermethrin, and PM) at a scanning rate of 50 mV/s.

The peaks seen in Figure 1a-b are attributed to redox reactions resulting from interactions between the polymers and PM. According to experimental results, the PPy and PAN-based non-enzymatic electrochemical sensors did not show a noticeable response in the presence of malathion, deltamethrin, and cypermethrin; however, the prepared sensors were only selective against PM. The results were statistically significant when compared with the experimental results. Both PPy- and PAN-based non-enzymatic electrochemical sensors have high selectivity against 1 μM PM within 1-minute cyclic voltammetry measurement. Additionally, the experimental results were confirmed by the selective pesticide detection-based assessment of the vegetable, and therefore proving the sensor’s application potential for the rapid detection for the vegetable quality.

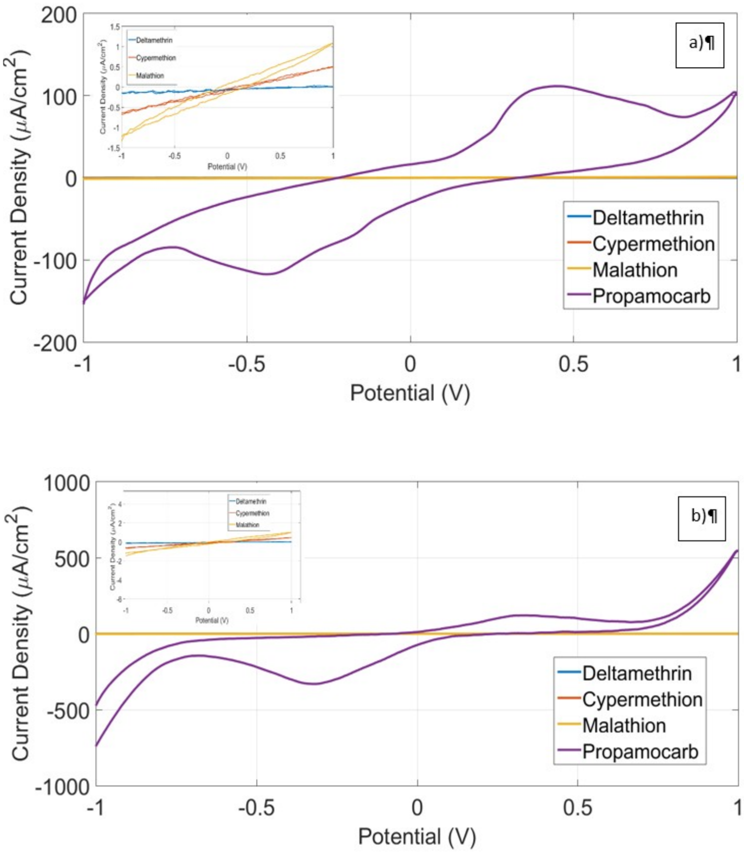

Figure 1: **(a)** Current density-voltage graphs of PPy-based non-enzymatic electrochemical sensor, and **(b)** Current density-voltage graphs of PAN-based non-enzymatic electrochemical sensor against pesticides.

PPy and PAN polymer--based PM sensors have not been previously reported in the literature. This is the first report presenting the preparation and PM tests of PPy and PAN-based non-enzymatic electrochemical sensors. The sensors are facile, selective, low-cost, and repeatable for agricultural usage. For food safety in agriculture this study highlighted the application of the sensor in detection of the pesticide PM on real cucumber and tomato samples. Current density-voltage graphs of repeated 2 tests of PPy- and PAN-based non-enzymatic electrochemical sensors against 1 μM PM applied real cucumber and tomato samples are presented (see Figure 2).

Various studies in literature have proven that biosensors had an excellent electrochemical performance against pesticides. We compared these experimental results with previous studies reported based on non-enzymatic/ enzymatic electrochemical sensors for pesticide determination in Table 1. The experimental results showed that the fabricated PAN-based electrodes had unique electrochemical properties and these results were appreciable from the comparison with the results of previous reports in the literature (Table 1). The proposed PAN-based sensor showed good sensitivity for rapid detection of PM. Moreover, the proposed sensor has different advantages such as easy to prepare, disposable, and portable.

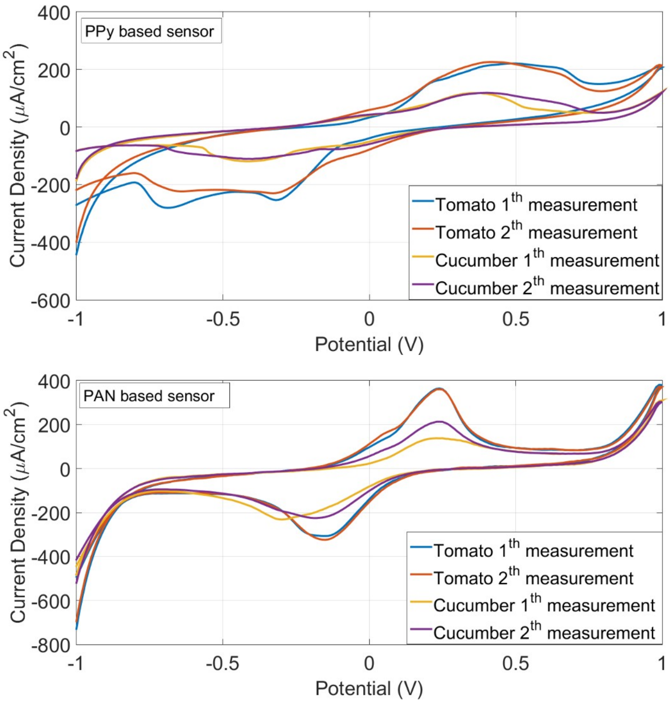

Figure 2: **(Top)** Current density-voltage graphs of PPy-based non-enzymatic electrochemical sensor, and **(bottom)** PAN-based non-enzymatic electrochemical sensor against 1 μM PM applied cucumber and tomato.

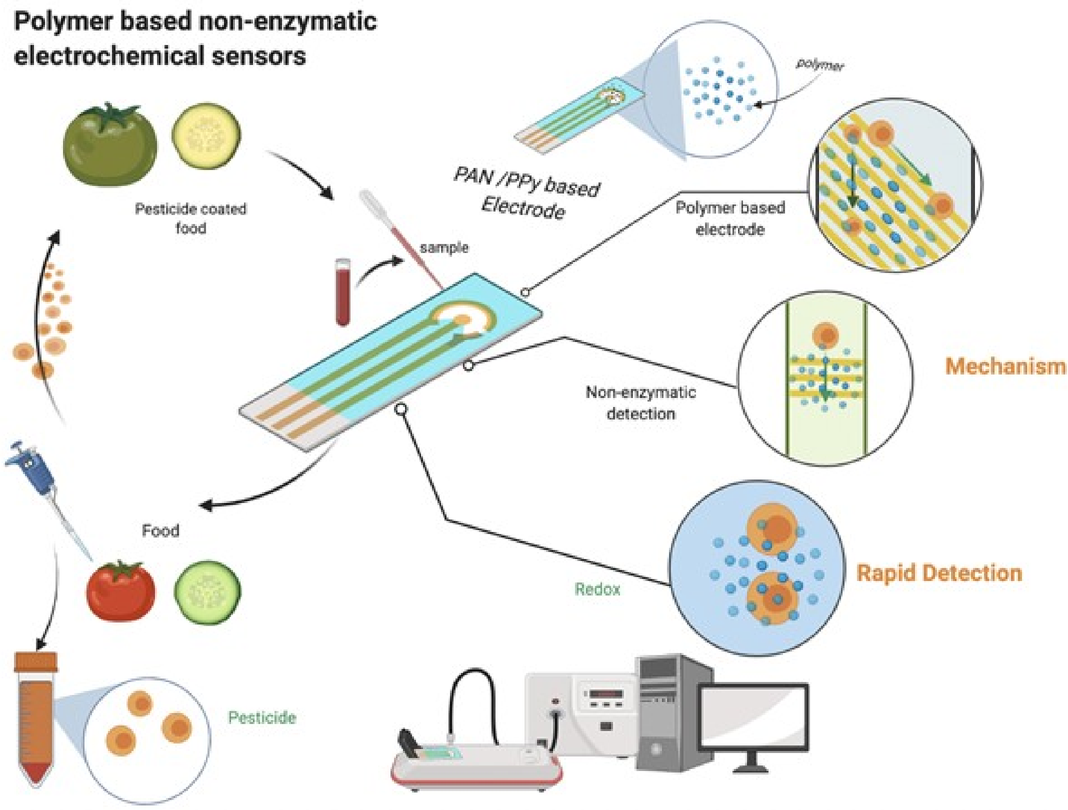

Figure 3: The schematic diagram of polymer-based non-enzymatic electrochemical sensors for the detection of pesticides from foods.

In Figure 3, the schematic diagram of polymer-based non-enzymatic electrochemical sensors for the detection of pesticides from foods was presented.

Table 1: The comparison of electrochemical experimental results of various biosensors for the detection of pesticide.

Sample	Analyte	Platform	References
Tyrosinase/poly(2-hydroxybenzamide)-modified graphite electrode	Fenitrothion	Enzymatic, electrochemical	(38)
PPy nanocomposite	Carbaryl Pesticide	Enzymatic, electrochemical	(39)
Boron dipyrromethene-phthalocyanine-single walled carbon nanotube hybrid	Methyl Parathion, Deltamethrin, Chlorpyrifos and Spinosad	Non-enzymatic, electrochemical	(40)
CuO microspheres	Endosulfan	Non-enzymatic, electrochemical	(41)
Reduced graphene oxide decorated on Cu/CuO-Ag nanocomposite	Carbaryl And Fenamiphos Pesticides	Non-enzymatic, electrochemical	(42)
Boronic acid functionalized nanocomposites	Glycoside Toxins	Non-enzymatic, electrochemical	(43)
Nickel oxide modified screen-printed electrodes	Parathion Pesticide	Non-enzymatic, electrochemical	(44)
Cu nanoparticles	Phorate	Non-enzymatic, electrochemical	(45)
PPy and PAN-based electrodes	Malathion, Deltamethrin, Cypermethrin, And Propamocarb	Non-enzymatic, electrochemical	This study

PPy- and PAN-based non-enzymatic electrochemical sensors detected 1 μM PM residue on real cucumber and tomato samples. Figure 2a-b shows the result of the sensor tests, the sensors detected 1 μM PM residue on food (cucumber and tomato) samples within a 1-minute cycle. PAN-based non-enzymatic electrochemical sensor has higher stability. PAN-based non-enzymatic electrochemical sensor has a significant potential in the field of the PM pesticide detection. According to the experimental results, we can provide the basis study for the selective and efficient processing of the polymer--based sensor with excellent electrochemical performances with food analytical methods for the monitoring of food safety and quality. Future studies will focus on integrating advanced sensor applications using the latest analytical methods to design and optimize the conductive polymer--based sensors for the monitoring of pesticide residues in food samples.

CONCLUSION

In this study, PPy and PAN-based non-enzymatic electrochemical sensors were investigated to detect the pesticide propamocarb (PM) in food samples. The PPy-based sensor and PAN-based sensor detected 1 μM propamocarb pesticide on cucumber and tomato with high selectivity within 1 min. We demonstrated the detection of PM residues on cucumber and tomato samples with good electrochemical performances towards the real-time usability on real agricultural samples. PAN-based non-enzymatic electrochemical sensor has good sensitivity, and higher selectivity and stability than PPy-based non-enzymatic electrochemical sensor. The prepared PAN-based non-enzymatic electrochemical PM sensor may be used in a portable detector kit for detection of PM type pesticide in food samples.

ACKNOWLEDGMENT

This study was supported by TUBITAK (Grant number 120N816).

CONFLICT OF INTEREST

All authors declare that they have no conflict of interest.

REFERENCES

1. Popp J, Pető K, Nagy J. Pesticide productivity and food security. A review. Agron Sustain Dev. 2013 Jan;33(1):243–55. <DOI>.

2. Rastogi S, Kumari V, Sharma V, Ahmad FJ. Gold Nanoparticle-based Sensors in Food Safety Applications. Food Anal Methods. 2022 Feb;15(2):468–84. <DOI>.

3. Tang FHM, Lenzen M, McBratney A, Maggi F. Risk of pesticide pollution at the global scale. Nat Geosci. 2021 Apr;14(4):206–10. <DOI>.

4. Wei X, Anfeng Z, Ali T, Zhang Z, Davis KF, Wu F. China's Food Security and Water, Fertilizer, Pesticide, and GHG Saving through Crop Redistribution [Internet]. Department of Agricultural Economics, Purdue University, West Lafayette, IN: Global Trade Analysis Project (GTAP); 2020. Available from: <URL>.

5. Sharma A, Shukla A, Attri K, Kumar M, Kumar P, Suttee A, et al. Global trends in pesticides: A looming threat and viable alternatives. Ecotoxicology and Environmental Safety. 2020 Sep;201:110812. <DOI>.

6. Dong J, Yang H, Li Y, Liu A, Wei W, Liu S. Fluorescence sensor for organophosphorus pesticide detection based on the alkaline phosphatase-triggered reaction. Analytica Chimica Acta. 2020 Sep;1131:102–8. <DOI>.

7. Fan L, Wang F, Zhao D, Peng Y, Deng Y, Luo Y, et al. A self-penetrating and chemically stable zinc (ii)-organic framework as multi-responsive chemo-sensor to detect pesticide and antibiotics in water. Appl Organomet Chem [Internet]. 2020 Dec [cited 2022 May 21];34(12). <DOI>.

8. Rasheed Z, Vikraman AE, Thomas D, Jagan JS, Kumar KG. Carbon-Nanotube-Based Sensor for the Determination of Butylated Hydroxyanisole in Food Samples. Food Anal Methods. 2015 Jan;8(1):213–21. <DOI>.

9. Lu Y, Tan Y, Xiao Y, Li Z, Sheng E, Dai Z. A silver@gold nanoparticle tetrahedron biosensor for multiple pesticides detection based on surface-enhanced Raman scattering. Talanta. 2021 Nov;234:122585. <DOI>.

10. Ge X, Zhou P, Zhang Q, Xia Z, Chen S, Gao P, et al. Palladium Single Atoms on TiO2 as a Photocatalytic Sensing Platform for Analyzing the Organophosphorus Pesticide Chlorpyrifos. Angew Chem. 2020 Jan 2;132(1):238–42. <DOI>.

11. Liu X, Sakthivel R, Liu WC, Huang CW, Li J, Xu C, et al. Ultra-highly sensitive organophosphorus biosensor based on chitosan/tin disulfide and British housefly acetylcholinesterase. Food Chemistry. 2020 Sep;324:126889. <DOI>.

12. Cheng Y, Ma B, Tan CP, Lai OM, Panpipat W, Cheong LZ, et al. Hierarchical macro-microporous ZIF-8 nanostructures as efficient nano-lipase carriers for rapid and direct electrochemical detection of nitrogenous diphenyl ether pesticides. Sensors and Actuators B: Chemical. 2020 Oct;321:128477. <DOI>.

13. Chakraborty U, Bhanjana G, Kannu, Kaur N, Sharma R, Kaur G, et al. Microwave-assisted assembly of Ag2O-ZnO composite nanocones for electrochemical detection of 4-Nitrophenol and assessment of their photocatalytic activity towards degradation of 4-Nitrophenol and Methylene blue dye. Journal of Hazardous Materials. 2021 Aug;416:125771. <DOI>.

14. AlAbdulaal TH, AlShadidi M, Hussien MSA, Vanga G, Bouzidi A, Rafique S, et al. Enhancing the electrical, optical, and structure morphology using Pr2O3-ZnO nanocomposites: Towards electronic varistors and environmental photocatalytic activity. Journal of Photochemistry and Photobiology A: Chemistry. 2021 Sep;418:113399. <DOI>.

15. Alam MM, Asiri AM, Rahman MM. Fabrication of phenylhydrazine sensor with V2O5 doped ZnO nanocomposites. Materials Chemistry and Physics. 2020 Mar;243:122658. <DOI>.

16. Singh AP, Balayan S, Gupta S, Jain U, Sarin RK, Chauhan N. Detection of pesticide residues utilizing enzyme-electrode interface via nano-patterning of TiO2 nanoparticles and molybdenum disulfide (MoS2) nanosheets. Process Biochemistry. 2021 Sep;108:185–93. <DOI>.

17. Wang L, Huang X, Wang C, Tian X, Chang X, Ren Y, et al. Applications of surface functionalized Fe3O4 NPs-based detection methods in food safety. Food Chemistry. 2021 Apr;342:128343. <DOI>.

18. Yan L, Yan X, Li H, Zhang X, Wang M, Fu S, et al. Reduced graphene oxide nanosheets and gold nanoparticles covalently linked to ferrocene-terminated dendrimer to construct electrochemical sensor with dual signal amplification strategy for ultra-sensitive detection of pesticide in vegetable. Microchemical Journal. 2020 Sep;157:105016. <DOI>.

19. Minh PN, Hoang VT, Dinh NX, Van Hoang O, Van Cuong N, Thi Bich Hop D, et al. Reduced graphene oxide-wrapped silver nanoparticles for applications in ultrasensitive colorimetric detection of Cr(vi) ions and the carbaryl pesticide. New J Chem. 2020;44(18):7611–20. <DOI>.

20. Ding S, Lyu Z, Li S, Ruan X, Fei M, Zhou Y, et al. Molecularly imprinted polypyrrole nanotubes based electrochemical sensor for glyphosate detection. Biosensors and Bioelectronics. 2021 Nov;191:113434. <DOI>.

21. Zhai X, Xu F, Li Y, Jun F, Li S, Zhang C, et al. A highly selective and recyclable sensor for the electroanalysis of phosphothioate pesticides using silver-doped ZnO nanorods arrays. Analytica Chimica Acta. 2021 Apr;1152:338285. <DOI>.

22. Cesana R, Ferreira JHA, Gonçalves JM, Gomes D, Nakamura M, Peres RM, et al. Fluorescent Cdots(N)-Silica composites: Direct synthesis and application as electrochemical sensor of fenitrothion pesticide. Materials Science and Engineering: B. 2021 May;267:115084. <DOI>.

23. Chen S, Gao J, Chang J, Zhang Y, Feng L. Organic-inorganic manganese (II) halide hybrids based paper sensor for the fluorometric determination of pesticide ferbam. Sensors and Actuators B: Chemical. 2019 Oct;297:126701. <DOI>.

24. Dissanayake NM, Arachchilage JS, Samuels TA, Obare SO. Highly sensitive plasmonic metal nanoparticle-based sensors for the detection of organophosphorus pesticides. Talanta. 2019 Aug;200:218–27. <DOI>.

25. Ragazzini I, Gualandi I, Selli S, Polizzi C, Cassani MC, Nanni D, et al. A simple and industrially scalable method for making a PANI-modified cellulose touch sensor. Carbohydrate Polymers. 2021 Feb;254:117304. <DOI>.

26. Lv D, Shen W, Chen W, Tan R, Xu L, Song W. PSS-PANI/PVDF composite based flexible NH3 sensors with sub-ppm detection at room temperature. Sensors and Actuators B: Chemical. 2021 Feb;328:129085. <DOI>.

27. Matindoust S, Farzi G, Nejad MB, Shahrokhabadi MH. Polymer-based gas sensors to detect meat spoilage: A review. Reactive and Functional Polymers. 2021 Aug;165:104962. <DOI>.

28. Kumar V, Mirzaei A, Bonyani M, Kim KH, Kim HW, Kim SS. Advances in electrospun nanofiber fabrication for polyaniline (PANI)-based chemoresistive sensors for gaseous ammonia. TrAC Trends in Analytical Chemistry. 2020 Aug;129:115938. <DOI>.

29. Oh WC, Fatema KN, Cho KY, Biswas MRUD. Microwave-assisted synthesis of conducting polymer matrix based thin film NaLa (MoO4)2-G-PPy composites for high-performance gas sensing. Surfaces and Interfaces. 2020 Dec;21:100713. <DOI>.

30. Hien HT, Van Tuan C, Anh Thu DT, Ngan PQ, Thai GH, Doanh SC, et al. Influence of surface morphology and doping of PPy film simultaneously polymerized by vapour phase oxidation on gas sensing. Synthetic Metals. 2019 Apr;250:35–41. <DOI>.

31. Dai H, Cao P, Chen D, Li Y, Wang N, Ma H, et al. Ni-Co-S/PPy core-shell nanohybrid on nickel foam as a non-enzymatic electrochemical glucose sensor. Synthetic Metals. 2018 Jan;235:97–102. <DOI>.

32. Ding A, Wang J, Ni A, Li S. Ageing of sandwich composites with E-glass fibre/vinylester skins and PVC foam core in synergistic environmental agents. Composite Structures. 2018 Oct;202:253–60. <DOI>.

33. Kannan A, Radhakrishnan S. Fabrication of an electrochemical sensor based on gold nanoparticles functionalized polypyrrole nanotubes for the highly sensitive detection of l-dopa. Materials Today Communications. 2020 Dec;25:101330. <DOI>.

34. Shen Y, Qin Z, Li T, Zeng F, Chen Y, Liu N. Boosting the supercapacitor performance of polyaniline nanofibers through sulfonic acid assisted oligomer assembly during seeding polymerization process. Electrochimica Acta. 2020 Oct;356:136841. <DOI>.

35. Delińska K, Yavir K, Kloskowski A. Ionic liquids in extraction techniques: Determination of pesticides in food and environmental samples. TrAC Trends in Analytical Chemistry. 2021 Oct;143:116396. <DOI>.

36. Kumar M, Yadav AN, Saxena R, Paul D, Tomar RS. Biodiversity of pesticides degrading microbial communities and their environmental impact. Biocatalysis and Agricultural Biotechnology. 2021 Jan;31:101883. <DOI>.

37. Zaynab M, Fatima M, Sharif Y, Sughra K, Sajid M, Khan KA, et al. Health and environmental effects of silent killers Organochlorine pesticides and polychlorinated biphenyl. Journal of King Saud University - Science. 2021 Sep;33(6):101511. <DOI>.

38. Alves M de F, Corrêa RAM de S, da Cruz FS, Franco DL, Ferreira LF. Electrochemical enzymatic fenitrothion sensor based on a tyrosinase/poly(2-hydroxybenzamide)-modified graphite electrode. Analytical Biochemistry. 2018 Jul;553:15–23. <DOI>.

39. Loguercio LF, Thesing A, Demingos P, de Albuquerque CDL, Rodrigues RSB, Brolo AG, et al. Efficient acetylcholinesterase immobilization for improved electrochemical performance in polypyrrole nanocomposite-based biosensors for carbaryl pesticide. Sensors and Actuators B: Chemical. 2021 Jul;339:129875. <DOI>.

40. Köksoy B, Akyüz D, Şenocak A, Durmuş M, Demirbas E. Sensitive, simple and fast voltammetric determination of pesticides in juice samples by novel BODIPY-phthalocyanine-SWCNT hybrid platform. Food and Chemical Toxicology. 2021 Jan;147:111886. <DOI>.

41. Rathnakumar SS, Noluthando K, Kulandaiswamy AJ, Rayappan JBB, Kasinathan K, Kennedy J, et al. Stalling behaviour of chloride ions: A non-enzymatic electrochemical detection of α-Endosulfan using CuO interface. Sensors and Actuators B: Chemical. 2019 Aug;293:100–6. <DOI>.

42. Hashemi P, Karimian N, Khoshsafar H, Arduini F, Mesri M, Afkhami A, et al. Reduced graphene oxide decorated on Cu/CuO-Ag nanocomposite as a high-performance material for the construction of a non-enzymatic sensor: Application to the determination of carbaryl and fenamiphos pesticides. Materials Science and Engineering: C. 2019 Sep;102:764–72. <DOI>.

43. Shi Z, Lu Y, Chen Z, Cheng C, Xu J, Zhang Q, et al. Electrochemical non-enzymatic sensing of glycoside toxins by boronic acid functionalized nano-composites on screen-printed electrode. Sensors and Actuators B: Chemical. 2021 Feb;329:129197. <DOI>.

44. Khairy M, Ayoub HA, Banks CE. Non-enzymatic electrochemical platform for parathion pesticide sensing based on nanometer-sized nickel oxide modified screen-printed electrodes. Food Chemistry. 2018 Jul;255:104–11. <DOI>.

45. Fu J, An X, Yao Y, Guo Y, Sun X. Electrochemical aptasensor based on one step co-electrodeposition of aptamer and GO-CuNPs nanocomposite for organophosphorus pesticide detection. Sensors and Actuators B: Chemical. 2019 May;287:503–9. <DOI>.