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RAPID ELECTROCHEMICAL DETECTION OF CARBENDAZIM IN VEGETABLES BASED ON CARBOXYL FUNCTIONALIZED MULTI-WALLED CARBON NANOTUBES

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At present, the commonly used methods for the detection of benzimidazole fungicides include high performance liquid chromatography (HPLC), liquid chromatography-mass spectrometry (LC-MS), fluorescence spectrometry and so on. These methods have high sensitivity and accurate results, but they have disadvantages such as complicated pretreatment, long time consuming, expensive equipment and professional operators. Electrochemical sensor detection method has the advantages of high sensitivity, simple operation, low cost and easy on-site inspection, etc., which has attracted extensive attention in the field of pesticide residue detection and analysis.

In order to realize the rapid detection of carbendazim content in vegetables, an electrochemical rapid detection method was established by using Carboxyl Functionalized Multi-Walled Carbon Nanotubes (MWCNTs-COOH) modified glassy carbon electrode. In this study, MWCNTs-COOH with special functional groups and large specific surface area were used to modify electrodes to improve the adsorption and enrichment of CBZ on the electrode and amplify the electrochemical signal, aiming to establish a highly sensitive electrochemical rapid detection technology for CBZ.

The results showed that: the modified electrode functionalized with MWCNTs-COOH could significantly improve the electron transfer rate on the electrode surface, which made the detection sensitivity of carbendazim higher. The linear range of detection was 0,3 μM~20 μM, and the detection limit was determined as low as 0,06 μM.

In this study, MWCNT-COOH with better conductivity, adsorption and stability was used to modify electrode, and constructed the MWCNT-COOH/GCE, which improved the adsorption and accumulation of CBZ, effectively promoted the electron transfer on the surface of the electrode, accelerated the response speed of the electrode and improved the current response, to realize the rapid and sensitive detection of trace CBZ in vegetables. This method had high sensitivity, good anti-interference, and detection stability. It was of great significance to detect carbendazim in vegetables.

Key words: *Carbendazim, pesticide residuals, electrochemical sensor, MWCNTs-COOH.*

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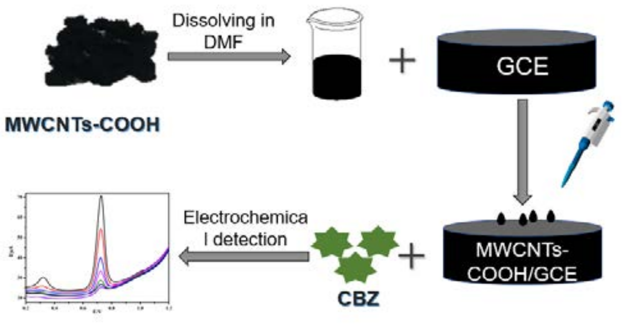
Introduction. Carbendazim (CBZ), as a broad-spectrum fungicide, is widely used for preventing and controlling vegetable diseases and pests (Addrah, 2020; Liu et al., 2021; Ding et al., 2019; Singh et al., 2016). CBZ residues in agricultural products and the environment poses a serious threat to human health due to the stable structure and slow degradation rate of benzimidazole ring (Tao et al., 202). Therefore, accurate, rapid and convenient CBZ detection and analysis methods in agricultural products are very important to protect human health and environmental safety. At present, the commonly used methods for the detection of benzimidazole fungicides include high performance liquid chromatography (HPLC) (Huang et al., 2020; Li et al., 2020), liquid chromatography-mass spectrometry (LC-MS) (Chu et al., 2020; Li, et al., 2020), fluorescence spectrometry (Yang et al., 2018; Yu et al., 2017; Yuan, et al., 2020) and so on (Su et al., 2020; Wang et al., 2020; Zhai al., 2021). These methods have high sensitivity and accurate results, but they have disadvantages such as complicated pretreatment, long time consuming, expensive equipment and professional operators. Electrochemical sensor detection method has the advantages of high sensitivity, simple operation, low cost and easy on-site inspection, etc., which has attracted extensive attention in the field of pesticide residue detection and analysis (Ghorbani et al.; Tu et al., 2020 ; Kumar et al., 2015; Zhao et al., 2015; Al-Hamry et al., 2019; Migliorini et al., 2020; Noori et al., 2021; Sakdarat et al., 2019).

Chen (Chen et al., 2021) successfully developed a high-performance nitrogen-doped holey graphene (N-HG) electrochemical sensor for determination of methyl parathion based on a hierarchical macro and nanoporous 3-D architecture. The influence of various N-configurations on electron transfer kinetics and the sensing performance of the N-HG modified electrode was investigated systematically through combined practical and theoretical studies. It was found that N-HG with a high pyrrolic-N content exhibited the largest electron transfer rate and the best sensing performance(ultralow detection limits: 3,5 pg ml^{-1}; wide linear range: 1 ng ml^{-1}–150 μg ml^{-1}). Renganathan (Renganathan et al., 2020) developed a simple strategy for construction of palladium nanoparticles (Pd NPs) adorned on the boron nitride (BN) heterojunction (HJ) for electrochemical detection of paraoxon ethyl (PXL). It is found that the Pd NPs/BN HJ electrocatalyst exhibited an outstanding performance for PXL detection due to the synergetic effect, large surface area, high electrical conductivity, and numerous active sites. The fabricated Pd NPs/BN HJ modified electrode can detect trace level of PXL from 0,01–210 μM with low detection limit of 0,003 μM and sensitivity of 2,23 μA $μM^{-1}$ cm (−2).

In this study, MWCNTs-COOH with special functional groups and large specific surface area were used to modify electrodes to improve the adsorption and enrichment of CBZ on the electrode and amplify the electrochemical signal, aiming to establish a highly sensitive electrochemical rapid detection technology for CBZ (Karimi-Takallo et al., 2021; Liu et al., 2021; Zeng et al., 2021; Zou et al., 2016. The construction process of the electrochemical sensor is shown in the Scheme 1.



Scheme 1. The fabrication process of the MWCNTs-COOH/GCE sensor for the determination of CBZ

Materials and Methods

Reagents and Instruments. MWCNTS-COOH: Shanghai Aladdin Biochemical Technology Co., Ltd., inner diameter 5–12 nm, outer diameter 30–50, length 10–20 μm; The other reagents used were all analytical grade. The experimental water was secondary distilled water.

Chi 660 E electrochemical workstation: Shanghai Chenhua Instrument Co., Ltd., three electrode system. The working motor is MWCNTS-COOH / GCE or glassy carbon electrode, pair electrode is platinum wire electrode, reference electrode is extremely saturated calomel electrode; CNC ultrasonic cleaning instrument: kunshan ultrasonic instrument co., LTD.

Electrode processing. Surface pretreatment of glassy carbon electrode: The glassy carbon electrode with a diameter of 3mm was polished on the polishing cloth with aluminum oxide powder with a particle size of 1,0, 0,3 and 0,05 μm, followed by ultrasonic cleaning in anhydrous ethanol and deionized water for 2 min successively. After infrared lamp drying, 10 mg MWCNTS-COOH was dissolved in 5 ml DMF and dispersed for 30min with the aid of ultrasonic instrument. A black uniform modified suspension is obtained. Then keep it at room temperature. The MWCNTS-COOH /GCE modified electrode was prepared after the suspension of 5 μL MWCNTS-COOH was dropped on the surface of the dry bare electrode with a pipetting gun and baked with an infrared lamp.

Detection method. A three-electrode system consisting of MWCNTS-COOH/GCE, a saturated calomel electrode and a platinum wire electrode was inserted into the solution containing pesticides. The cyclic voltammetry curves (CV) and differential pulse curves (DPV) of CBZ on the modified electrode under different conditions were recorded.

Results.

Electrochemical properties of $MWCNT_S$-COOH / GCE. A 5 mM $K_3[Fe(CN)_6]$ solution containing 0,3 M KCl was used as an electrochemical probe to test the alternating current impedance (IMP) in the frequency range of 1~105 Hz. The impedance changes before and after electrode modification were shown in the Fig. 1 (A). The electron transfer resistance of the modified electrode (R_{ct}-was estimated using the diameter of the semicircle. When MWCNTS-COOH was modified to GCE, the diameter of the semicircles was greatly reduced, indicating that MWCNTs-COOH/GCE formed a good electron conduction path between the electrode and electrolyte and had good ionic conductivity, which significantly improved the diffusion of $K_3[Fe(CN)_6]$ to the electrode interface.

In addition, in order to further investigate the electrochemical performance of the modified electrode, cyclic voltammetry experiments were carried out in a 5 mM $K_3[Fe(CN)_6]$ solution containing 0,3 mM KCl. As shown in the Fig. 1 (B), all the modified electrodes have a good pair of reversible REDOX peaks. Compared with the bare electrode, the potential difference between the oxidation peak and the reduction peak on $MWCNT_S$-COOH / GCE is reduced, and the response current is larger than that on the bare electrode, which may be due to the rapid electron transfer ability of the highly conductive $MWCNT_S$-COOH.

Electrochemical behavior of CBZ. By comparing CV detection results of GCE and MWCNTs-COOH /GCE (Show as

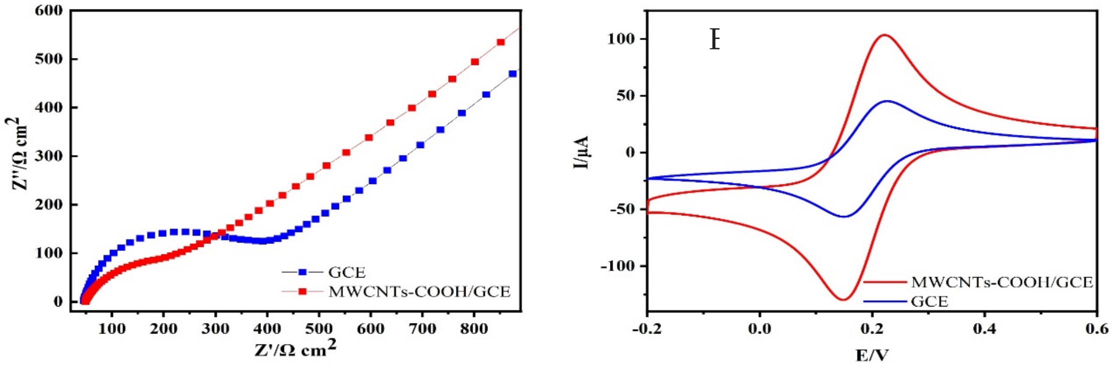


Fig. 1. (A) Electrochemical impedance spectroscopy (EIS) of different electrodes: GCE and MWCNTs-COOH/GCE in 5 mM K_3 [Fe (CN)$_6$] solution containing 0.3 M KCl. (B) CVs of different electrodes: GCE and MWCNTs-COOH/GCE in 5 mM K_3 [Fe (CN)$_6$] solution containing 0.3 M KCl. Scan rate: 50 mV/s

Fig. 2), the oxidation peak current of CBZ at MWCNTs-COOH modified electrode reached 15,92 μA, which was significantly higher than that of GCE, indicating that MWCNTS-COOH had a strong enrichment effect on CBZ, and its large specific surface area could enrich CBZ on the electrode surface to increase the response signal of CBZ. So that the oxidation reaction can be carried out at a lower position, which is consistent with the reports in the literature (Ertan et al., 2016).

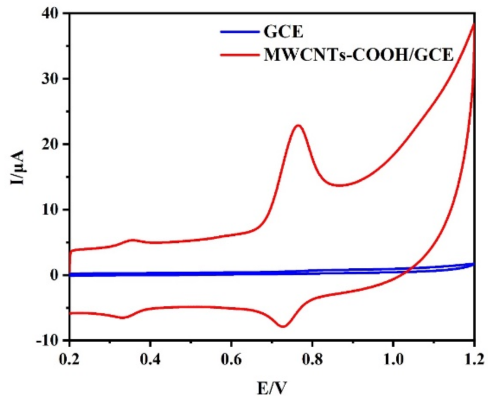


Fig. 2. CVs of 50 μM CBZ in PBS (pH = 7) at GEC and MWCNTs-COOH. Scan rate: 50 mV/s

The results showed that MWCNTS-COOH was successfully modified in GCE, and the sensitivity of the electrode was significantly improved, which was conducive to the rapid detection of low concentration substances. MWCNTs-COOH has a unique molecular structure, high surface volume ratio, good electronic and mechanical properties, as well as good biocompatibility and chemical stability (Saeed & Ibrahim, 2013). It can be used to modify electrodes to construct electrochemical sensors, which can give play to its excellent conductivity, adsorption, and stability (Kumar & Yadav, 2019).

The optimization of detection conditions:

The influence of scanning speed. The control type of electrode reaction can be known by the relation between oxidation peak current and scanning speed. The cyclic voltammetry curves of 50 μM CBZ at different scanning speeds were recorded respectively (show as Fig. 3.).

The results show that there is a good linear relationship between the oxidation peak current and the reduction peak current when the scanning speed at 60–380 mV/s, and the correlation coefficients are $I_O = 0{,}2908x + 13{,}776\ (R^2 = 0{,}9958)$ and $I_R = -0{,}2048x + 10{,}972\ (R^2 = 0{,}988)$ respectively.

The influence of pH. In this experiment, the variation of CV detection peak current at pH from 5 to 9 in Na_2HPO_4-

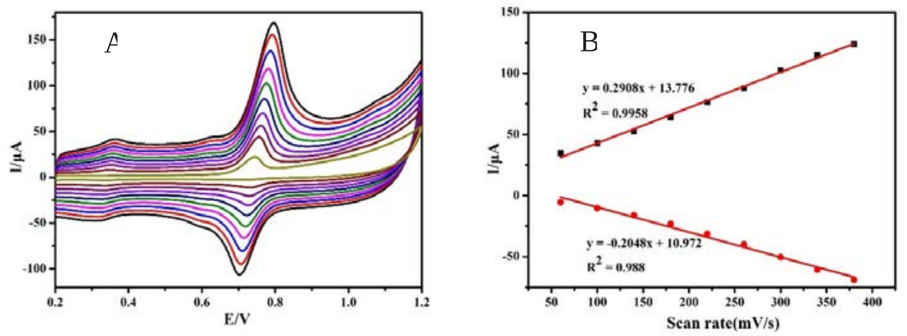


Fig. 3. (A) CVs of 10 μM CBZ at MWCNTs-COOH with different scan rates: 60,100,140,180,220,260,300,340 and 380. (B) The relationship between peak currents and scan rates

NaH_2PO_4 system containing 10μM CBZ solution was investigated. As can be seen from the Fig. 4, when the pH value is between 5 and 7, the peak current response will increase positively with the constant increase of pH. When pH is 7, the peak current response reaches the maximum value, and then the peak current response decreases with the increase of pH. Therefore, pH = 7,0 was selected as the best pH value for CBZ detection. The relation between the oxidation peak current (Ip) and oxidation peak potential (Ep) and the pH value is shown in the Fig. 4 (A) and (B) respectively. Ep decreases with the increase of pH value. The relation is as follows: Ep (V) = −0,0632x + 1,1784 (R2 = 0,9994). The slope of the equation 0,0632 is close to the ideal value of 0,585 V / pH, indicating that the proton and electron transfer numbers are equal in CBZ electrochemical reaction.

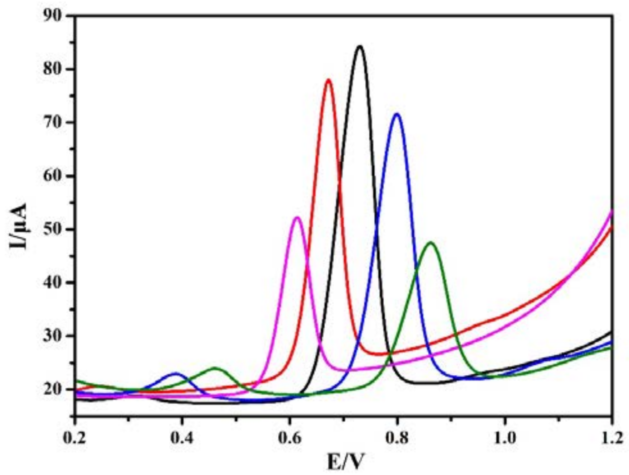


Fig. 4. Effect of pH on the DPV curves of 10 μM CBZ at the MWCNTs-COOH/GCE sensor

Analytical performance of MWCNTS-COOH / GCE sensor. In this study, a series of different concentrations of CBZ standard solutions were measured using DPV. The prepared CBZ standard solution was diluted into multiple concentrations of CBZ solution with PBS buffer at pH = 7. Under optimal conditions, a series of concentrations of CBZ solutions were detected by MWCNTS-COOH/GCE. The results are shown in Fig. 6.

Reproducibility, stability and selectivity. 5 MWCNTS-COOH/GCE tests were repeated in CBZ standard solution with concentration of 1 μMol, and the relative standard deviation (RSD) of 5 separate tests was 4,81 %, indicating that WMCNTS-COOH/GCE had good reproducibility. CBZ was detected for 10 consecutive times on each modified electrode, and the RSD of the detection results was 3,5 %. The results show that MWCNTS-COOH has good stability.

Under the optimal experimental conditions, the selectivity of WMCNTS-COOH/GCE was evaluated by interference experiments. The interference substances were Methyl Parathion, Paraquat, Niclosamide and other inorganic substances with 5 times concentration, respectively. The change of peak current of CBZ was less than 5 % (95,2–104,4 %), indicating that the modified electrode had a good selectivity.

CBZ detection in vegetable samples. Due to the preparation of WMCNTS-COOH/GCE has good sensitivity, stability and selectivity, and this electrochemical sensor can be used for vegetable sample analysis. Recycling experiments were carried out by adding different amounts of CBZ to different vegetables-Cabbage, Cucumber and Potato. Before testing, the vegetables are weighed, juiced, and centrifuged. The experimental results are shown in the Table 1. The recovery rate is approximately between 93,6 % and 104,4 %, indicating that the prepared sensor can still be used for the analysis of CBZ residues in vegetable samples without sample purification process. The results show that this method is accurate, appropriate, and effective for the detection of CBZ in actual samples.

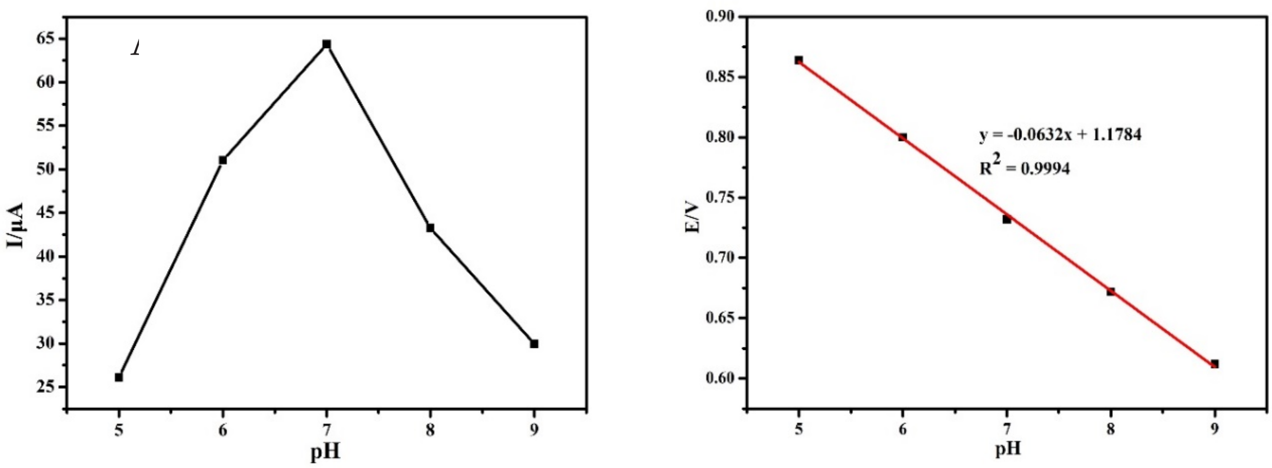


Fig. 5. (A) The relation between the oxidation peak current (Ip) and the pH value. (B) The relation between the oxidation peak potential (Ep) and the pH value

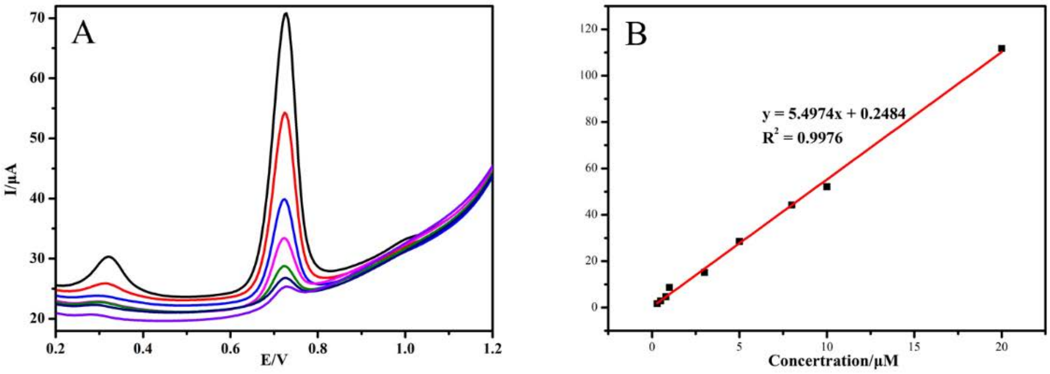


Fig. 6. DPV curves of different concentrations of CBZ at MWCNTS-COOH/GCE. CBZ concentrations (from bottom to top): 0,3, 0,5, 0,8, 1, 3, 5, 8, 10, 20 μM

Table 1

The determination results of CBZ in vegetable samples (n = 3)

Vegetable sample	Added (μM)	Found (μM)	Recovery (%)	RSD (%)
Cabbage	1	1,039	103,9	4,46
	5	5,18	103,6	2,99
	10	9,54	95,4	1,95
Cucumber	1	0,968	96,8	4,78
	5	4,72	94,4	3,21
	10	9,36	93,6	2,39
Potato	1	0,95	95	2,1
	5	5,11	102,2	4,44
	10	10,44	104,4	2,05

Conclusion. In the detection of pesticide residues, the introduction of electrochemical sensors is conducive to the simplification of the previous complex pre-processing, and can achieve convenient, fast, low-cost, qualitative, and quantitative rapid detection. In this study, MWCNT-COOH with better conductivity, adsorption and stability was used to modify electrode, and constructed the MWCNT-COOH/GCE, which improved the adsorption and accumulation of CBZ, effectively promoted the electron transfer on the surface of the electrode, accelerated the response speed of the electrode and improved the current response, to realize the rapid and sensitive detection of trace CBZ in vegetables.

References:

1. Addrah, M.E., Zhang, Y. Y., Zhang, J., Liu, L., Zhou, H. Y., Chen, W. D., & Zhao, J. (2020). Fungicide Treatments to Control Seed-borne Fungi of Sunflower Seeds. Pathogens, **9**(1).

2. Liu, Z.Y., Chen, Y., Han, J. H., Chen, D., Yang, G. Q., Lan, T. T., & Zhang, K. K. (2021). Determination, dissipation dynamics, terminal residues and dietary risk assessment of thiophanate-methyl and its metabolite carbendazim in cowpeas collected from different locations in China under field conditions. Journal of the Science of Food and Agriculture.

3. Ding, H., Zheng, X. Z., Zhang, J., Zhang, Y. S., Yu, J. H., & Chen, D. L. (2019). Influence of chlorothalonil and carbendazim fungicides on the transformation processes of urea nitrogen and related microbial populations in soil. Environmental Science and Pollution Research. 26(30), 31133–31141.

4. Singh, S., Singh, N., Kumar, V., Datta, S., Wani, A. B., Singh, D. & Singh, J. (2016). Toxicity, monitoring and biodegradation of the fungicide carbendazim. Environmental Chemistry Letters, 14(3). 317–329.

5. Tao, H.P., Bao, Z. W., Jin, C. Y., Miao, W. Y., Fu, Z. W., & Jin, Y. X. (2020). Toxic effects and mechanisms of three commonly used fungicides on the human colon adenocarcinoma cell line Caco-2. Environmental Pollution. 263.

6. Huang, S.M., Hu, Y. F., Chen, Y. L., Li, G. K., & Xia, L. (2020). Magnetic Solid-phase Extraction Coupled with High-Performance Liquid Chromatography for Pesticide Residues Analysis in Citrus Sample. Chinese Journal of Analytical Chemistry, 48(10). 1392–1399.

7. Li, P.L., Sun, P. Y., Dong, X. L., & Li, B. H., Residue analysis and kinetics modeling of thiophanate-methyl, carbendazim, tebuconazole and pyraclostrobin in apple tree bark using QuEChERS/HPLC-VWD. Biomedical Chromatography, 2020. 34(9).

8. Chu, Y., Tong, Z., Dong, X., Sun, M. N., Gao, T. C., Duan, J. S., & Wang, M. (2020). Simultaneous determination of 98 pesticide residues in strawberries using UPLC-MS/MS and GC-MS/MS. Microchemical Journal. 156.

9. Li, Y.H., Hu, J., Yao, Z. L., Wang, Q., & Zhang, H. (2020)., Transfer assessment of carbendazim residues from rapeseed to oil production determined by HPLC-MS/MS. Journal of Environmental Science and Health Part B-Pesticides Food Contaminants and Agricultural Wastes, 55(8), 726–731.

10. Yang, Y.X., Huo, D. Q., Wu, H. X., Wang, X. F., Yang, J. S., Bian, M. H., & Hou, C. J., N, P-doped carbon quantum dots as a fluorescent sensing platform for carbendazim detection based on fluorescence resonance energy transfer. Sensors and Actuators B-Chemical, 274. 296–303.

11. Yu, Q.W., Sun, H., Wang, K., He, H. B., & Feng, Y. Q. (2017). Monitoring of Carbendazim and Thiabendazole in Fruits and Vegetables by SiO2@NiO-Based Solid-Phase Extraction Coupled to High-Performance Liquid Chromatography-Fluorescence Detector. Food Analytical Methods, 10(8), 2892–2901.

12. Yuan, Y.Y., Wang, S. T., Liu, S. Y., Cheng, Q., Wang, Z. F., & Kong, D. M. (2020). Green approach for simultaneous determination of multi-pesticide residue in environmental water samples using excitation-emission matrix fluorescence and multivariate calibration. Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy, 228.

13. Su, L.T., Wang, S., Wang, L. M., Yan, Z. Y., Yi, H. Y., Zhang, D. W., & Ma, Y., Fluorescent aptasensor for carbendazim detection in aqueous samples based on gold nanoparticles quenching Rhodamine B. Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy, 2020. 225.

14. Wang, S.Y., Shi, X. C., Liu, F. Q., & Laborda, P. (2020).Chromatographic Methods for Detection and Quantification of Carbendazim in Food. Journal of Agricultural and Food Chemistry, 68(43), 11880–11894.

15. Zhai, Y., T., Wu, Y. P., Guo, X. Y., Ying, Y., Wen, Y., & Yang, H. (2021). Metal-organic-frameworks-enforced surface enhanced Raman scattering chip for elevating detection sensitivity of carbendazim in seawater. Sensors and Actuators B-Chemical. 326.

16. Ghorbani, A., Ojani, R., Ganjali, M. R., & Raoof, Direct voltammetric determination of carbendazim by utilizing a nanosized imprinted polymer/MWCNTs-modified electrode. Journal of the Iranian Chemical Society.

17. Tu, X.L., Gao, F., Ma, X., Zou, J., Yu, Y. F., Li, M. F., & Lu, L. M. (2020). Mxene/carbon nanohorn/beta-cyclodextrin-Metal-organic frameworks as high-performance electrochemical sensing platform for sensitive detection of carbendazim pesticide. Journal of Hazardous Materials, 396.

18. Kumar, P., K.H. Kim, & A. Deep (2015) Recent advancements in sensing techniques based on functional materials for organophosphate pesticides. Biosensors & Bioelectronics, 70, 469–481.

19. Zhao, H.Y., Ji, X. P., Wang, B. B., Wang, N., Li, X. R., Ni, R. X., & Ren, J. J. (2015). An ultra-sensitive acetylcholinesterase biosensor based on reduced graphene oxide-Au nanoparticles-beta-cyclodextrin/Prussian blue-chitosan nanocomposites for organophosphorus pesticides detection. Biosensors & Bioelectronics, 65, 23–30.

20. Al-Hamry, A., A., Ega, T. K., Pasti, I. A., Bajuk-Bogdanovic, D., Lazarevic-Pasti, T., Rodriguez, R. D., & Kanoun, O. (2019) Electrochemical Sensor based on Reduced Graphene Oxide/PDAC for Dimethoate Pesticide Detection. in 5th International Conference on Nanotechnology for Instrumentation and Measurement (NanofIM). Sfax, TUNISIA.

21. Migliorini, F.L., Sanfelice, R. C., Mercante, L. A., Facure, M. H. M., & Correa, D. S. (2020). Electrochemical sensor based on polyamide 6/polypyrrole electrospun nanofibers coated with reduced graphene oxide for malathion pesticide detection. Materials Research Express, 7(1).

22. Noori, J.S., J. Mortensen, & A. Geto (2021). Rapid and Sensitive Quantification of the Pesticide Lindane by Polymer Modified Electrochemical Sensor. Sensors, 21(2).

23. Sakdarat, P., Chongsuebsirikul, J., Phongphut, A., Klinthingchai, Y., Prichanont, S., Thanachayanont, C., & Ieee., (2019). Copper Oxide Nanorods Pesticide Sensor For Methyl Parathion Detection. in IEEE 19th International Conference on Nanotechnology (IEEE-NANO). Macau, PEOPLES R CHINA.

24. Chen, Z.F., Zhang, Y., Yang, Y. Q., Shi, X. R., Zhang, L., & Jia, G. W. (2021). Hierarchical nitrogen-doped holey graphene as sensitive electrochemical sensor for methyl parathion detection. Sensors and Actuators B-Chemical, 336.

25. Renganathan, V., Balaji, R., Chen, S. M., & Kokulnathan, T. (2020). Coherent design of palladium nanostructures adorned on the boron nitride heterojunctions for the unparalleled electrochemical determination of fatal organophosphorus pesticides. Sensors and Actuators B-Chemical, 307.

26. Karimi-Takallo, A., S. Dianat, & A. Hatefi-Mehrjardi (2021). Fabrication and electrochemical study of K(1,10-(1,4 Butanediyl) dipyridinium)(2) PW11O39Co(H2O) /MWCNTs-COOH nanohybrid immobilized on glassy carbon for electrocatalytic detection of nitrite. Journal of Electroanalytical Chemistry, 886.

27. Liu, Y., Cao, B., Zhang, X., Luo, R., Luo, C. H., Lin, H. C., & Peng, H. (2021). Preparation of alpha-Co(OH)(2)@MWCNTs-COOH nanocomposites and their application for supercapacitors. Journal of Materials Science-Materials in Electronics.

28. Zeng, W.J., Li, C., Feng, Y., Zeng, S. H., Fu, B. X., & Zhang, X. L. (2021). Carboxylated multi-walled carbon nanotubes (MWCNTs-COOH)-intercalated graphene oxide membranes for highly efficient treatment of organic wastewater. Journal of Water Process Engineering, 40.

29. Zou, N., Yuan, C. H., Liu, S. W., Han, Y. T., Li, Y. J., Zhang, J. L., & Pan, C. P. (2016). Coupling of multi-walled carbon nanotubes/polydimethylsiloxane coated stir bar sorptive extraction with pulse glow discharge-ion mobility spectrometry for analysis of triazine herbicides in water and soil samples. Journal of Chromatography A, 1457, 14–21.

30. Ertan, B., Eren, T., Ermis, I., Saral, H., Atar, N., & Yola, M. L., Sensitive analysis of simazine based on platinum nanoparticles on polyoxometalate/multi-walled carbon nanotubes. Journal of Colloid and Interface Science, 2016. 470: p. 14–21.

31. Saeed, K. & Ibrahim. (2013). Carbon nanotubes-properties and applications: a review. Carbon Letters, 14(3), 131–144.

32. Kumar, U. & B.C. Yadav. (2019). Development of humidity sensor using modified curved MWCNT based thin film with DFT calculations. Sensors and Actuators B-Chemical, 288, 399–407.

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Швидке електрохімічне визначення карбендазиму в овочах на основі карбоксильних функціоналізованих багатостінних вуглевих нанотрубок, модифікованих скляним вуглевим електродом

Нині широко використовуються такі методи виявлення фунгіцидів похідних бензимідазолу, як: високоефективна рідинна хроматографія (ВЕРХ), рідинна хроматографія – мас-спектрометрія (РХ – МС), флуоресцентна спектрометрія. Ці методи мають високу чутливість та результати, але мають і недоліки, як-от складна *попередня підготовка, тривалий час аналізу, дороге обладнання та наявність професійних операторів. Метод виявлення за допомогою електрохімічних датчиків має такі переваги: високу чутливість, простоту експлуатації, низьку вартість робіт, простоту перевірки на місці тощо, що привернуло велику увагу в області виявлення й аналізу залишків пестицидів.*

Для швидкого визначення вмісту карбендазиму в овочах створено електрохімічний метод швидкого виявлення за допомогою скловуглецевого електрода, модифікованого скловуглецевим електродом із карбоксильними функціональними багатостінними вуглецевими нанотрубками (MWCNTs-OOH). У цьому дослідженні MWCNT-COOH зі спеціальними функціональними групами та великою питомою поверхнею використані для модифікації електродів, покращення адсорбції та збагачення CBZ на електроді, посилення електрохімічного сигналу з метою створення високочутливої електрохімічної технології швидкого виявлення CBZ.

Результати досліджень показали, що: модифікований електрод, функціоналізований MWCNTs-COOH, міг значно покращити швидкість перенесення електронів на поверхні електрода, що підвищило чутливість виявлення карбендазиму. Лінійний діапазон виявлення становив 0,3 мкм ~ 20 мкм, а межа виявлення була визначена на рівні 0,06 мкм.

У цьому дослідженні MWCNT-COOH із кращою провідністю, адсорбцією та стабільністю використовувався для модифікації електрода, був побудований MWCNT-COOH/GCE, який покращив адсорбцію та накопичення CBZ, ефективно сприяв переносу електронів на поверхні електрода, прискорив швидкість реакції електрода та покращив дію на струм, щоб реалізувати швидке та чутливе виявлення слідів CBZ в овочах. Цей метод має високу чутливість, хороший захист від перешкод і стабільність виявлення. Велике значення має виявлення карбендазиму в овочах, особливо в тих, які споживаємо у свіжому вигляді.

Ключові слова: *карбендазим, залишки пестицидів, електрохімічний датчик, MWCNTs-COOH.*

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