FEEDBACK

from official opponent, candidate of agricultural sciences, associate professor, head of the department of zoology, entomology, phytopathology, integrated protection and quarantine of plants named after B. M. Litvynova, State Biotechnological University

Serhii Stankevych

for dissertation work of **Li Fang** « **Comparative evaluation of different methods of determining pesticide residues in plant products** », which was submitted for obtaining the scientific degree of Doctor of Philosophy at the one-time special council at Sumy National Agrarian University, branch of knowledge 20 – «Agricultural sciences and food », on specialty 202 Plant Protection and Quarantine.

1. Relevance of the dissertation topic.

The Pesticides are widely used in agricultural production and bring huge economic benefits to society. According to the existing survey, in recent ten years, the problem of pesticide residues is more serious, and crops can absorb and transport pesticides in soil and water, which leads to the hidden danger of pesticide residues exceeding the standard in crops with or without reasonable application of pesticides, and causes great harm to the ecological environment and human health. Therefore, study accurate, rapid and convenient pesticide detection and analysis methods in agricultural products are very important to protect human health and environmental safety.

In this dissertation, the differences of pesticide absorption and transfer in different leaf vegetables were studied, and the dynamic absorption and accumulation rules were explored in hydroponic lettuce. In addition, four kinds of electrochemical sensors were prepared based on carbon-based nanomaterials/composites for the detection of carbendazim, imidacloprid and methyl parathion respectively, and satisfactory results were obtained in vegetable samples. HPLC method was conducted to confirm the accuracy of pesticide residues by electrochemical detection, and those experimental results showed that electrochemical sensing technology can meet the requirements of pesticide residue detection in actual vegetable samples. Moreover, those advantages of simple operation and fast response in electrochemical sensor

provide the possibility for on-site detection of pesticide residues in agricultural products.

Therefore, the research direction of Dr. Li Fang's thesis is to detect pesticide residues in crops by electrochemical sensor method, so as to provide guarantee for the consumption of crops.

2. Connection with scientific programs, topics, plans.

The research work was carried out in accordance with the main direction of scientific research of Sumy National Agrarian University and Henan Institute of Science and Technology within the framework of scientific topics: National Key R&D Program of China (No. 2017YFD0301104), Project of Plant Protection Key Discipline of Henan Province (1070202190011005), and Zhongyuan Thousand Tal-ents Program of Henan Province (ZYQR201810142). The applicant, Li Fang, and his scientific supervisors are the executors of several sections, and the subject of the dissertation is closely related to these programs and plans.

3. Scientific novelty of the obtained results.

1) The differences of pesticide IMI residue levels in different types of leafy vegetables were investigated, and high and low residue varieties of leafy vegetables were screened by detecting the IMI residue levels in different parts of leafy vegetables. In addition, the study also revealed that the absorption, transport and accumulation of IMI pesticides in vegetables are affected by the time of IMI absorption.

2) The electrochemical sensor based on MWCNT-COOH/GCE was used to detect CBZ pesticide residues in vegetables. This innovative method benefits from the unique properties of hollow conductive carbon structure of MWCNT and carboxyl functionalization of MWCNT-COOH, which jointly enhances the detection ability of the sensor. To ensure the accuracy of CBZ detection in vegetable samples, the results obtained by MWCNT-COOH/GCE sensor were cross-verified by high performance liquid chromatography.

3) An electrochemical sensor based on SDPC/GCE was used to detect imidacloprid (IMI) pesticide residues. The sensor uses expired soybeans as carbon source and has a three-dimensional interconnected porous structure. The sensor fully demonstrates the advantages of high conductivity porous carbon network structure and a large number of specific surface areas, and performs well in IMI detection

performance. The accuracy of SDPC/GCE sensor in detecting IMI was verified by HPLC.

4) SCB @ ZrO_2/GCE sensor was used to realize the high-sensitivity electrochemical detection of methyl parathion (MP). This innovative method relies on the special conductivity of SCB nanoparticles to promote effective charge transfer. In addition, ZrO_2 nanoparticles have strong affinity for the phosphorus group of MP, which enhances the ability of the sensor to accumulate MP. The combination of SCB nanoparticles and ZrO_2 nanoparticles improves the MP detection ability of SCB@ ZrO_2/GCE sensor. In order to ensure the accuracy of MP electrochemical detection, the results obtained by the sensor were cross-verified by high performance liquid chromatography.

5) Using SJPCS@β-CD/GCE sensor, another highly sensitive electrochemical detection method for MP was successfully established. SJPCS was prepared by hydrothermal method and modified by β -cyclodextrin (β-CD). SJPCS has good conductivity, good adsorption performance and high specific surface area. At the same time, β-CD with molecular recognition characteristics plays an important role in ensuring the uniform dispersion of SJPCS and promoting the recognition and adsorption of MP.

4. Theoretical significance of the dissertation.

Experiments delved into the absorption and accumulation of imidacloprid across various leafy vegetable varieties, along with a dynamic exploration of imidacloprid absorption and transfer in different parts of lettuce plants. The comprehensive analysis of imidacloprid enrichment and transfer in leafy vegetables establishes a theoretical foundation for assessing pesticide residue risks in this category. Guidance for the judicious application of agricultural production activities is tailored to the distinct characteristics of vegetables and the nature of pesticides.

The enhancement of pesticide residue detection methods prompted the utilization of an electrochemical sensing approach based on carbon-based materials. This method effectively detected imidacloprid, carbendazim, and methyl parathion, offering crucial theoretical insights into the utilization of composite nanomaterials within the realm of sensing detection.

5. Practical significance of the results of the dissertation.

Variations in the presence of Imidacloprid residues within different leafy vegetable types can be ascribed to differences in their ability to absorb and transport this substance. Through the execution of hydroponic experiments involving various leafy vegetable varieties, we were able to initially establish an insight into the distribution, transfer disparities, and patterns of IMI residues within the leafy vegetables and the surrounding water system. This investigation forms the foundational groundwork for the informed and secure application of imidacloprid and other common pesticides in leafy crops.

The utilization of the molecular structure of pesticides and the potential of functional nanomaterials and composite electrochemical sensing technology has culminated in the development of innovative electrochemical sensors, custom-designed for the swift, highly sensitive, and accurate identification of pesticide residues. These sensors were specifically engineered to target three distinct pesticides: Carbendazim, Imidacloprid, and Methyl Parathion. This technological advancement assumes a pivotal role in guaranteeing the safety of plant-based products by offering a dependable means of detecting and monitoring pesticide residues.

6. Number of scientific publications.

Based on the results, a total of 15 academic articles have been published, including 5 Web of Science Core Collection, 4 Ukrainian professional journals, 6 other conference papers.

7. Complete presentation of the dissertation material in scientific publications.

The main material of the dissertation is fully presented in 9 articles published in scientific publications and 6 papers published in international academic conferences with the applicant as the first or corresponding author.

The published works effectively reflect and confirm the results of the studies conducted.

8. The degree of validity of scientific provisions.

The research results of this dissertation are not only based on professional scientific research methods, systematic theoretical research, but also through extensive experimental research and test verification, and the actual fruit and vegetable samples were tested. The validity of scientific regulations is fully reflected

in published scientific publications. This dissertation is a detailed study independently completed by the applicant, aiming to provide a solution for the detection of trace pesticide residues in fruits and vegetables. Full text in English.

Taken together, these fully demonstrate the validity of the applicant's compliance with the scientific provisions of the resolutions of the Cabinet of Ministers of Ukraine (Resolution 283 of April 3, 2019, Resolution 502 of May 19, 2023).

9. The structure and content of the dissertation, its completeness and compliance with the established requirements for design.

The dissertation consists of 9 sections, including Introduction、Section 1“LITERATURE REVIEW ON THE TOPIC AND CHOICE OF RESEARCH DIRECTIONS”、Section 2“ORGANIZATION, SUBJECTS, MATERIALS AND METHODS RESEARCH”、Section 3“THE ABSORPTION AND ACCUMULATION OF IMIDACLOPRID PESTICIDE IN SEVERAL HYDROPONIC LEAF VEGETABLES”、Section 4“DETERMINATION OF CARBENDAZIM IN VEGETABLES BY ELECTROCHEMICAL SENSOR BASED ON MWCNTS-COOH AND EVALUATED BY HIGH PERFORMANCE LIQUID”、Section 5“DETERMINATION OF IMIDACLOPRID IN VEGETABLES BY ELECTROCHEMICAL SENSOR BASED ON SOYBEAN-DERIVED POROUS CARBON AND EVALUATED BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY”, Section 6“DETERMINATION OF METHYL PARATHION IN VEGETABLES BY ELECTROCHEMICAL SENSOR BASED ON SUPERCONDUCTIVE CARBON BLACK@ ZIRCONIA AND EVALUATED BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY”, Section 7“DETERMINATION OF METHYL PARATHION IN VEGETABLES BY ELECTROCHEMICAL SENSOR FABRICATED FROM BIOMASS-DERIVED AND B-CYCLODEXTRIN FUNCTIONALIZED POROUS CARBON SPHERES AND EVALUATED BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY and CONCLUSIONS.

The structure of the dissertation is reasonable and scientific, consistent with standards, clear logical thinking, detailed, systematic and complete. It has a meaningful integrity, consistency and completeness that is entirely consistent with the requirements formulated in the design.

10. Discussion clauses, comments and wishes regarding the content.

There are a few points worth discussing regarding the content of the dissertation:

1.Fig.1-2 The electrochemical sensing analysis method is one kinds of novel analysis technologies. It is suggested to add the schematic diagram of electrochemical workstation and computer monitor in this figure to achieve the better understanding of this sensing analysis method.

2.Fig. 2-1 «Electrochemical Analysis System» may be changed into «Electrochemical Sensing Analysis System». «The determination of pesticide» may be changed into «Three-electrode system».The figure caption «Three-electrode syste» may be changed into «Electrochemical sensing analysis system for pesticide detection»

3.Clause 3.1.2 The IMI concentration (0.2 μM, 0.5 μM, 1 μM, 5 μM, 10 μM, 20 μM, and 30μM) for standard curve should be added in the figure caption of Fig. 3-2.

4.Clause 4.1.1 The characteristic CV curve is important for the analysis of pesticide type based on the electrochemical reaction peaks of pesticide. It is suggested to add the CV curve of CBZ determination in Scheme 4-1.

5.Clause 4.2.2 According to the research about the influence of scan rate, the scan rate has a certain impact on the peak response of CV curve. Please add the scan rate in the figure caption of CV curves in Fig. 4-2(B).

6.Please add the scan rate in the figure caption of CV curves of 50 μM CBZ at the bare GCE and MWCNTs-COOH/GCE sensor in Fig. 4-3.

7.Clause 5.2.6 Please revise the format of Table 5-2 according to the format standard of dissertation. The formats of other tables need check and revise if necessary.

8. The analysis of limit of detection is important for the electrochemical sensing detection of pesticide. It is suggested to check and show the calculation formula limit of detection for the related sections in this research work.

General conclusion

Dissertation work of Li Fang on the topic “Comparative evaluation of different methods of determining pesticide residues in plant products", which was submitted for defense to the specialized academic council for obtaining the degree of Doctor of Philosophy in the field of knowledge 20 Agricultural sciences and food with a

specialty 202 - Plant Protection and Quarantine of agricultural production according to its relevance, scientific and theoretical level, main results of validity, main provisions and the results published in professional publications, the novelty of the formulation and the practical significance meet the requirements of the order of the Ministry of Education and Culture of Ukraine No. 40 of January 12, 2017 "On approval of requirements for the preparation of a dissertation" and Resolution of the Cabinet of Ministers of Ukraine of January 12, 2022 No. 44 "On approval of the Procedure for awarding a degree doctor of philosophy and cancellation of the decision of the one-time specialized academic council of the institution of higher education, scientific institution on awarding the degree of doctor of philosophy" with changes introduced in accordance with Resolution of the Cabinet of Ministers No. 341 dated03.21.2022.

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Підпис С. Станкевича засвідчую:
Т.в.о. начальника відділу кадрів Харевіндова М.