FEEDBACK

from official opponent, Candidate of Biological Sciences, Associate Professor of the Department of Agronomy and Forestry, Zhytomyr Agrotechnical College, Liudmyla Nemerytska

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 difference of pesticide IMI residue level in different types of leafy vegetables was explored, and high residue and low residue varieties of leafy vegetables were screened by detecting IMI residue in different parts of leafy vegetables. In addition, the study also revealed that the absorption, transportation and accumulation of IMI pesticides in vegetables were affected by the absorption time of IMI.

2) An electrochemical sensor based on MWCNT-COOH/GCE was used to detect CBZ pesticide residues. This innovative approach takes advantage of the unique properties of the hollow conducting carbon structure in MWCNT and the carboxyl functionalization of MWCNT-COOH, which together enhance the sensor's ability to detect CBZ. In order 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 constructed to detect imidacloprid (IMI) pesticide residues. The sensor uses expired soybean as carbon source and has a three-dimensional interconnecting porous structure. The sensor

fully demonstrates the advantages of highly conductive porous carbon network structure and large specific surface area, and performs well in IMI detection performance. The accuracy of SDPC/GCE sensor to detect IMI was verified by high performance liquid chromatography.

4) An electrochemical sensor based on SCB @ ZrO_2/GCE was constructed to detect Methyl Parathion (MP) pesticide residues in vegetables with high sensitivity. The advantage of this method lies in the effective use of the special conductivity of SCB nanoparticles to promote effective charge transfer, and the strong affinity of ZrO_2 nanoparticles for the phosphorus group of MP, which enhances the ability of the sensor to detect MP. Under the synergistic effect of SCB nanoparticles and ZrO_2 nanoparticles, the MP detection ability of SCB@ ZrO_2/GCE sensor is significantly improved. 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) A highly sensitive electrochemical detection method of methyl thiophosphate (MP) based on SJPCS@β-CD/GCE was established. SJPCS was prepared by hydrothermal method and modified by β-cyclodextrin (β-CD). SJPCS has good conductivity, good adsorption performance and large specific surface area. At the same time, combined with the molecular recognition characteristics of β-CD, it ensures the uniform dispersion of SJPCS, which plays a vital role in promoting the recognition and adsorption of MP.

4. Theoretical significance of the dissertation.

The absorption and accumulation of imidacloprid in different leaf vegetable varieties were studied, and the absorption and transfer of imidacloprid in different parts of lettuce plants were explored dynamically. The accumulation and migration of imidacloprid in leafy vegetables were analyzed comprehensively, which provided a theoretical basis for assessing the risk of pesticide residues in leafy vegetables.

In this dissertation, imidacloprid, carbendazim and Methyl Parathion were effectively detected, which provided an important theoretical basis for the construction of electrochemical sensors using composite nanomaterials. Meanwhile, the improved pesticide residue detection method effectively promoted the use of

electrochemical sensing methods based on carbon-based materials.

5. Practical significance of the results of the dissertation.

The difference of imidacloprid residue in different leafy vegetables is mainly due to the difference of imidacloprid absorption and transportation ability among different vegetables. Through hydroponic experiments on various leafy vegetables, we explored the distribution, transfer differences and ways of IMI residues in leafy vegetables and surrounding water systems, which laid the foundation for the safe and reasonable application of imidacloprid and other commonly used pesticides on leafy vegetables.

Based on the molecular structure of pesticides and the potential of functional nanomaterials and composite electrochemical sensing technology, an innovative electrochemical sensor was developed, which was designed to identify pesticide residues quickly, sensitively and accurately. These sensors are specifically targeted at three different pesticides: carbendazim, imidacloprid and methyl parathion. This technological progress has played a key role in ensuring the safety of plant products by providing reliable detection means.

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.

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8. The degree of validity of scientific provisions.

The dissertation is a detailed study completed independently by the applicant to provide a solution for intelligent and precise regulation of the artificial light plant factory environments in the mechanical engineering field of mechanization and automation of agricultural production. The full text is in English.

In summary, these fully demonstrate that the applicant has met the validity of the scientific provisions of the Ukrainian Cabinet Ministerial Resolution (No. 283 dated 03.04.2019 No. 502 dated 19.05.2023).

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. Clause 1.3.3 the full name of all abbreviations should be and supplemented in this part. The authors should check the abbreviations in other sections.

2. Fig. 3-2 Please check the Y-axis, units, and standard curve equation of y = 6265.4x +123.6.

3. Clause 4.2.2 How to obtain the limit of detection? The suthor should explain this point.

4. Table 4.3 Please revise the analysis data to achieve the unification of significant digits. Other tables need careful check and revise if necessary.

5. Clause 5.1.2 The CV curve of IMI detection is necessary for Scheme 5-1. And, the picture of vegetables used in this section should be checked.

6. The authors should check all figure captions and revise some captions if necessary.

7. Some language errors and formatting errors need to be polished.

8. Compared with traditional pesticide analysis methods such as HPLC, the electrochemical sensing analysis method is a simple and novel detection method with low cost, high analysis efficiency, and high sensitivity. This research work is very very important for the development of advanced pesticide analysis technologies. The author should check and present the electrochemical detection mechanism of pesticides in each section.

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 dated 03.21.2022.

Official opponent:
Candidate of Biological Sciences,
Associate Professor of the Department
of Agronomy and Forestry — Liudmyla NEMERYTSKA

Підпис засвідчую
Помічник директора
з кадрової роботи: Савчук Н. І.