UNIVERSITY OF BELGRADE - FACULTY OF PHYSICAL CHEMISTRY
ACADEMIC COUNCIL

At the 9th regular meeting of the Academic Council of the Faculty of Physical Chemistry, University of Belgrade, held on June 13th, 2024, we were appointed as members of the Committee for the review and evaluation of the doctoral dissertation of candidate Vedran Milanković, MSc in Physical Chemistry, under the title:

"Novel carbon materials obtained by thermochemical conversion of biowaste as adsorbents for the removal of malathion and chlorpyrifos from water"

Based on the decision of the Academic Council of the Faculty of Physical Chemistry, University of Belgrade, the preparation of a doctoral dissertation under the above-mentioned title was approved.
After reviewing and analyzing the doctoral dissertation of the candidate, we hereby submit the following

R E P O R T

1. Overview of the dissertation content
The doctoral dissertation of candidate Vedran Milanković is written in English, on 128 pages of A4 format typed text (Times New Roman font, size 12 pt, and single spacing). The dissertation is prepared according to the instructions for formatting doctoral dissertations at the University of Belgrade. The dissertation consists of 7 chapters: **Chapter One - Introduction** (1 page), **Chapter Two – Theoretical Foundations** (15 pages), **Chapter Three – Aim of the doctoral dissertation** (1 page), **Chapter four - Experimental** (5 pages), **Chapter five - Results and discussion** (80 pages), **Chapter six – Conclusions** (2 pages), and **References** (6 pages). In addition to the mentioned content, the dissertation includes the English Title Page (1 page), Serbian Title Page (1 page), List of Mentors and Defense Committee Members (1 page), Acknowledgments (1 page), Summary in English (1 page), Summary in Serbian (2 pages), Table of Contents (3 pages), Candidate's Biography with Bibliography (4 pages), and Attachments prescribed by the University rules for submitting doctoral dissertations for approval (4 pages). The dissertation contains 48 figures (3 in Chapter Two – Theoretical Foundations, 1 in Chapter four – Experimental, and 45 in Chapter Five - Results and Discussion) and 34 tables (1 in Chapter four – Experimental, and 33 in Chapter Five - Results and Discussion), of which 45 figures and 33 tables represent the candidate's research.

Chapter One - Introduction
In Chapter One - Introduction, the Author provides an overview of the research's subject matter and outlines the study's objectives. The introduction sets the context for the thesis by discussing the global challenge of biowaste and pollution, its environmental, health, and economic impacts, and the importance of innovative recycling technologies. The chapter emphasizes the significant role of pesticides in reducing food biowaste and their negative effects and highlights the specific challenge of managing spent coffee grounds (SCG). It introduces the innovative use of biowaste-derived carbon materials for environmental applications, particularly in water purification, addressing the dual issues of biowaste accumulation and pesticide pollution.

Chapter two – Theoretical foundations

In Chapter Two – Theoretical Foundations, the Author addresses the emerging problem of biowaste and its potential solutions through thermochemical conversion and various activation methods, including chemical, physical, and physicochemical processes. The chapter includes discussions on the properties and environmental impact of organophosphorous pesticides, particularly malathion and chlorpyrifos, to underscore their significance in this context. The principles of adsorption are explored in depth, with explanations of key concepts such as kinetic models (pseudo-first order, pseudo-second-order, Elovich, Intraparticle), isotherm models (Freundlich, Langmuir, Temkin, Dubinin-Radushkevich), and thermodynamics, all of which will be used further in the study. Emphasis is placed on the previous applications of carbon materials derived from biowaste as effective adsorbents for these pesticides. By laying this theoretical groundwork, the chapter equips readers with the necessary background to understand the subsequent experimental investigations and methodologies for pesticide remediation.

Chapter three – Aim of the doctoral dissertation

In Chapter Three – Aim of the doctoral dissertation, the Author explains the main and specific objectives of this doctoral dissertation. The Author aims to explore the use of thermochemical conversion and activation processes to address the environmental impact of SCG, a widespread food biowaste. Specifically, the main objective is transforming SCG into valuable activated carbon materials capable of adsorbing organophosphorus pesticides, malathion, and chlorpyrifos. The specific objectives include optimizing SCG adsorbent production by investigating different thermochemical conversion temperatures (400°C, 650°C, 900°C) and activation methods (KOH, H_3PO_4, CO_2, KOH/CO_2, H_3PO_4/CO_2), characterizing the resulting materials using various physicochemical techniques, and studying the mechanisms of malathion and chlorpyrifos adsorption. Through detailed kinetic, isotherm, and thermodynamic studies, the Author aims to assess the adsorption efficiency and subsequently further characterize the most promising materials to deepen understanding of material properties. One of this doctoral dissertation's specific aims is to assess neurotoxicity reduction after adsorption. Finally, the dissertation aims to evaluate the economic, environmental, and practical implications of SCG-based adsorbents to provide insights into their feasibility for pesticide remediation applications.

Chapter four – Experimental

In Chapter Four – Experimental, the Author begins by detailing the synthesis of 21 materials derived from SCG using thermochemical conversion and chemical, physical, and physicochemical activation methods. This includes precise temperature selection based on thermogravimetric analysis (TGA), ensuring optimal yield and stability during thermochemical conversion. Characterization of these materials follows with a comprehensive suite of techniques: Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) coupled with Energy-Dispersive X-ray Analysis (EDX), X-ray Diffraction (XRD) for crystal phase identification, Infrared Spectroscopy with Fouier transormation (FTIR), Raman spectroscopy for vibrational modes, Boehm titrations for oxygen functional groups, Zeta potential measurements for surface charge analysis, and Brunauer-Emmett-Teller (BET) analysis for assessing surface area and pore volume. This chapter proceeds with a detailed account of the adsorption experiments, encompassing both batch and dynamic conditions to evaluate the efficiency of synthesized materials in removing organophosphate pesticides. Additionally, assessing acetylcholinesterase (AChE) activity inhibition using the modified Ellman procedure provides insights into the physiological impacts of pesticide exposure. This comprehensive chapter lays the groundwork for understanding the experimental methodologies crucial for interpreting subsequent research findings.

Chapter five - Results and discussion

Chapter Five – Results and discussion extensively evaluate synthesized adsorbents for removing organophosphate pesticides, employing detailed adsorption kinetics under batch and dynamic conditions alongside comprehensive physicochemical characterization. This chapter's findings underscore the materials' efficacy in environmental remediation, emphasizing their potential applications and underlying mechanisms in mitigating pesticide-related risks. Chapter five is divided into 8 sections: Screening test, Spent coffee grounds (SCG) – baseline material, Material obtained by chemical activation of SCG with KOH – SCG material K, Materials obtained by thermochemical conversion of SCG at 400°C – SCG 400 materials, Materials obtained by thermochemical conversion of SCG at 650°C – SCG 650 materials, Materials obtained by thermochemical conversion of SCG at 900°C – SCG 900 materials, SCG material 900PC, and Comparative analysis of materials obtained by thermochemical conversion of SCG for MLT and CHP removal. In the first section-Screening test, the Author describes the screening test procedure and presents the results based on which materials will be investigated and which are the most promising materials chosen. In Sections 2-7, the Author gives a detailed characterization of the materials and the results obtained through kinetic, isotherm (at 25, 30, and 35°C), and thermodynamic studies. The discussion on malathion and chlorpyrifos adsorption onto corresponding materials is given at the end of each section. Finally, in Section 8, the Author discusses and compares the materials obtained by thermochemical conversion of SCG regarding their physicochemical properties, economic environmental, and practical aspects of their application, with a focus on the cost of materials production and their adsorption efficiency.

Chapter Six – Conclusions

The final Chapter Six – Conclusions, summarizes the findings and conclusions drawn from the research. It presents a concise overview of the main results, discusses their significance in the context of the research objectives, and highlights the study's implications. The primary conclusion of this thesis is that SCG can be effectively converted through thermochemical processes and activated to produce high-performance adsorbents for removing organophosphate pesticides from water. The research demonstrates that SCG-derived materials exhibit favorable adsorption capacities and kinetics influenced by factors such as specific surface area, pore volume, and surface functional groups introduced during activation. This study highlights the environmental sustainability of using SCG, a widely available biowaste, to develop carbon-based materials suitable for mitigating pesticide pollution in water systems. Considering all processes investigated in this doctoral dissertation, it is concluded that this contribution supports and advances the UN's sustainable development goals, in particular SDG 6 (Clean Water and Sanitation) by remediation of OPs, SDG 12 (Responsible consumption and production) and SDG 13 (Climate action) by using climate-harmful biowaste (SCG) in production of carbon materials.

Overall, the thesis structure provides a logical progression from introducing the research topic to presenting the experimental methods and results and, finally, drawing meaningful conclusions from the obtained data.

2. Short overview of the thesis results

The main thesis results can be overviewed as follows:

Material Synthesis and Characterization

The study successfully synthesized 20 materials from spent coffee grounds (SCG) through thermochemical conversion at 400°C, 650°C, and 900°C, with various activation methods (KOH, H_3PO_4, CO_2, KOH/CO_2, H_3PO_4/CO_2). Characterization using SEM, EDX, FTIR, BET, and Zeta potential demonstrated that thermochemical conversion significantly impacts the carbon and oxygen content. At the same time, activation methods affect the surface area, porosity, and functional groups. Characterization using XRD, Boehm titrations, and Raman spectroscopy was performed additionally for the most promising material to investigate its physicochemical properties further.

Optimization of Synthesis Parameters

The study highlights the critical role of synthesis parameters, including temperature and activation methods, in developing effective adsorbents for organic pollutant removal. The comprehensive analysis of adsorption mechanisms, kinetics, and thermodynamics underscores the need to optimize these parameters to balance economic, environmental, and practical aspects for sustainable applications.

Adsorption Efficiency and Mechanisms

The adsorption behavior of MLT and CHP onto SCG-based materials varied. MLT generally showed faster adsorption kinetics due to its aliphatic structure, and CHP exhibited higher adsorption capacities influenced by its aromatic nature. The adsorption process was predominantly driven by surface interactions and influenced by molecular structure.

Impact of Activation Methods

Physical activation using CO_2 generally enhances the specific surface area and total pore volume. In contrast, chemical activation, especially with KOH, introduces oxygen-containing functional groups, which further improve adsorption properties but at the cost of increased production complexity and cost. Materials activated at higher temperatures exhibited improved adsorption kinetics and capacities, emphasizing the importance of activation processes in optimizing SCG-based adsorbents.

Environmental and Economic Considerations

The thermochemical conversion and activation of SCG reduced biowaste and enhanced pesticide remediation. While higher temperature and chemical activation improve adsorption efficiency, they also increase production costs and may involve environmentally harmful chemicals. Therefore, materials like 400 offer a cost-effective and environmentally friendly alternative with reasonable adsorption capacities. On the other hand, despite higher production costs for materials like 900PC, their superior performance in adsorption efficiency and reusability justifies the investment for specific applications. After the adsorption of pesticides, the inhibition of AChE activity decreased, indicating that no more toxic products were formed during the interaction.

Sustainable Development Goals (SDGs)

The research supports the United Nations' SDGs, particularly SDG 6 (Clean Water and Sanitation) by improving water quality through pesticide remediation, SDG 12 (Responsible Consumption and Production) by valorizing biowaste, and SDG 13 (Climate Action) by utilizing SCG, a climate-harmful biowaste, in the production of carbon materials.

In summary, the thesis findings represent a significant contribution to the field of environmental remediation and sustainable materials development. By synthesizing and characterizing 20 innovative SCG-based adsorbents, the thesis provides valuable insights into optimizing synthesis parameters to enhance adsorption efficiency for organic pollutants like MLT and CHP. The study underscores the critical role of thermochemical conversion and activation methods in developing effective adsorbents, balancing economic, environmental, and practical aspects. This research supports UN Sustainable Development Goals by improving water quality, reducing biowaste, and promoting climate action. For practical application of the thesis results, further investigations should focus on exploring additional activation methods and synthesis parameters to optimize adsorption performance. Assessing the environmental impact of production processes and scaling up the synthesis for industrial applications will ensure practical and sustainable solutions for water pollution control and biowaste valorization.

3. Comparative analysis of the thesis results with previously published data

The thesis results support and extend the existing literature on biomass-derived carbon materials for environmental remediation, specifically focusing on their application in removing organophosphorus compounds such as MLT and CHP. Repurposing spent coffee grounds (SCG) aligns well with the principles of a circular economy, effectively minimizing environmental impact by converting waste into valuable resources [1]. This approach not only reduces greenhouse gas emissions from decomposing coffee grounds in landfills but also simultaneously addresses the challenges of biowaste disposal and water pollution [2]. SCG-derived carbon materials provide a versatile solution for environmental cleanup, utilizing their diverse morphological characteristics and adjustable porosity to absorb pollutants from water sources [3] efficiently.

There has been limited investigation of biowaste-derived carbon materials for removing MLT and CHP, and no studies have conclusively shown a reduction in AChE activity inhibition during the remediation process presented in this thesis [4, 5]. Previous studies have demonstrated varying adsorption capacities depending on the biomass precursor, carbonization, and activation methods used, highlighting the significant influence of activation techniques on material effectiveness [6-8]. This thesis demonstrates the adsorption rate and capacity that are far higher than previously reported for biomass-derived carbon materials used as adsorbents for MLT and CHP.

This thesis contributes significantly to understanding the adsorption kinetics and mechanisms for MLT and CHP on SCG-derived materials. MLT, characterized by its aliphatic structure, exhibits faster adsorption kinetics, while aromatic CHP demonstrates higher adsorption capacities due toπ-π interactions with the carbonaceous surface. This differentiation in adsorption behavior aligns with previous research [9, 10]. The comparative analysis underscores the unique advantages of SCG-derived materials, highlighting their morphological diversity and adjustable porosity, which are crucial for optimizing adsorption performance against specific contaminants.

Additionally, this thesis investigates the environmental, economic, and practical aspects of SCG-based materials production and application, taking into account the use of harmful chemicals, energy consumption, and application in dynamic conditions. Continued research should focus on scaling up production processes, evaluating long-term adsorption efficiency, and exploring multifunctional applications of SCG-derived materials in sustainable environmental practices.

References

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4. Scientific results

4.1. Articles published in international scientific journals of significance (M20)

4.1.1. Articles in leading international journals of category M21a

1. **Milanković, V.**, Tasić, T., Brković, S. M., Potkonjak, N. I., Unterweger, C., Bajuk-Bogdanović, D. V., Pašti, I. A., & Lazarević-Pašti, T. (2024). Spent coffee grounds-derived carbon material as an effective adsorbent for removing multiple contaminants from wastewater: A comprehensive kinetic, isotherm, and thermodynamic study. Journal of Water Process Engineering, 63, 105507–105507. https://doi.org/10.1016/j.jwpe.2024.105507

4.1.2. Articles in leading international journals of category M21

1. **Milanković, V.**, Tasić, T., Pejčić, M., Pašti, I., & Lazarević-Pašti, T. (2023). Spent Coffee Grounds as an Adsorbent for Malathion and Chlorpyrifos—Kinetics, Thermodynamics, and Eco-Neurotoxicity. Foods, 12(12), 2397–2397. https://doi.org/10.3390/foods12122397

4.2. Proceedings of international scientific conferences (M30)

3.2.1. Papers presented at internationally significant conferences published as a whole – M33

1. **Milanković, V.,** Tasić, T., Mitrović, S., Brković, S., Perović, I., & Lazarević-Pašti, T. (2022). Spent Coffee Grounds as an Adsorbent for Malathion and Malaoxon. Physical Chemistry 2022 - 16th International Conference on Fundamental and Applied Aspects of Physical Chemistry: Proceedings.
2. **Milanković, V**., Tasić, T., Brković, S., & Lazarević-Pašti, T. (2023). Remediation of Organophosphorous Pesticides Using Spent Coffee Grounds – Kinetics and Neurotoxicity. 1st International EUROSA Conference: Proceedings. Novi Sad: University of Novi Sad, Faculty of Technical Sciences.

3.2.2. Paper presented at an internationally significant conference published as an abstract – M34

1. **Milanković, V**., Tasić, T., Brković, S., & Lazarević-Pašti, T. (2023). Effect of temperature for chlorpyrifos adsorption onto carbon material derived from spent coffee grounds. DISC2023: 3rd DIFENEW International Student Conference: Abstract Book. Novi Sad: Faculty of Technical Sciences.
2. **Milanković, V**., Tasić, T., & Lazarević-Pašti, T. (2023). Removal of chlorpyrifos and malathion using spent coffee grounds – isotherm study. ISC 2023: 8th International Student Conference on Technical Sciences: Book of Abstracts. University of Belgrade: Technical Faculty in Bor.
3. **Milanković, V**., Tasić, T., Brković, S., Pašti, I., & Lazarević-Pašti, T. (2023). The impact of thermal treatment on spent coffee grounds for chlorpyrifos removal from water. 21st Young Researchers' Conference Materials Sciences and Engineering: Program and the Book of Abstracts. Belgrade: Institute of Technical Sciences of SASA.
4. **Milanković, V.**, Tasić, T., & Lazarević-Pašti, T. (2022). Non-Treated Biowaste Material as Adsorbent for Malathion. 2nd DIFENEW International Student Conference - DISC2022. Novi Sad: Faculty of Technical Sciences.

5. Plagiarism check

The verification of the doctoral dissertation's originality was conducted in accordance with the Regulations for the Procedure of Checking the Originality of Doctoral Dissertations Defended at the University of Belgrade ("Official Gazette of the University of Belgrade" No. 204 dated June 22, 2018). Using the iThenticate software, the originality check of the candidate's doctoral dissertation titled "**Novel carbon materials obtained by thermochemical conversion of biowaste as adsorbents for the removal of malathion and chlorpyrifos from water**" revealed a similarity index of 0%. The identified degree of similarity originates from the use of citations, personal names, bibliographic data of referenced literature, common phrases and data, as well as previously published results of the candidate's research included in the dissertation, which is consistent with Article 9 of the aforementioned Regulations. Based on the above findings, the Committee has determined that the doctoral dissertation of candidate Vedran Milanković is original and fully complies with academic citation rules, thereby allowing the prescribed procedure for its defense to proceed.

6. Conclusions

Based on the presented content, it can be concluded that the results of candidate Vedran Milanković's thesis represent an original and significant scientific contribution to the field of physical chemistry, particularly materials and environmental control and protection. A part of the thesis results has been published in scientific journals, including two papers in leading international journals (categories M21a and M21). The Committee acknowledges that the candidate fulfills all the requirements for accepting a completed doctoral dissertation as prescribed by the University of Belgrade and the regulations defined in the Faculty of Physical Chemistry's Doctoral Dissertation Rules and Evaluation.

Based on the presented content, the Committee provides a positive evaluation of the doctoral thesis titled: "**Novel carbon materials obtained by thermochemical conversion of biowaste as adsorbents for the removal of malathion and chlorpyrifos from water**" by Vedran Milanković and recommends the Academic Council of the Faculty of Physical Chemistry, University of Belgrade, to accept this evaluation, thereby fulfilling all the conditions for approving the public defense of the doctoral dissertation and granting the title of Doctor of Physical Chemistry.

In Belgrade, 8th July 2024.

Committee members:

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