

REVIEW

of the official opponent on the dissertation

KOVINCHUK IRYNA

on the topic “**Composites of manganese oxides and oxyhydroxides with halloysite as degradation photocatalysts**”,

submitted for the degree of Doctor of Philosophy

in the field of knowledge 16 Chemical and Bioengineering

in specialty 161 Chemical Technology and Engineering

Relevance of the dissertation topic. The topic of Ms. Iryna Kovinchuk's dissertation addresses a significant global issue: finding new environmentally and economically viable methods for the destruction of organic dyes and plastic materials. The importance of this research is underscored by the volume of scientific publications on the subject and various draft laws from the European Union aimed at mitigating the environmental impact of human activities. The focus of Ms. Kovinchuk's research is on composite systems based on manganese compounds, including oxides and oxyhydroxides of different crystallographic forms. These compounds, which are synthesized using chemical and electrochemical methods, are further modified with halloysite nanotubes to explore their potential as dual-purpose photocatalysts. The dissertation includes a comprehensive investigation of how synthesis parameters – such as the composition and concentration of auxiliary substances, as well as the pH level—affect the phase composition, structure, and morphology of these materials, as well as their photocatalytic activity toward organic dyes and polyethylene. The dissertation topic includes the investigation of the physicochemical properties of composite materials. Considerable attention was paid to the study of the optical properties of composites, in particular, the band gap, surface properties, etc. The activity of photocatalytic materials was studied via the destruction of cationic (Methylene Blue) and anionic dyes (Congo Red) from model solutions, as well as the degradation of polyethylene films under the influence of UV and Vis light irradiation.

Consequently, the thesis topic is current and relevant in the context of up-to-date research methodology for creating novel composite systems of photocatalytic action to ensure effective destruction of toxic environmental pollutants containing organic dyes, as well as decomposition of polyethylene films into biosafe components.

Evaluation of the scientific validity, reliability, and novelty of the dissertation results.

When choosing the relevance of the work, the goals and objectives of the research, the object and subject of study, the setting of the experimental part of the work, and the analysis of the obtained material, the author is guided by modern scientific findings on the development of composite

materials for functional purposes. The materials discussed in this dissertation have been published and presented to the international scientific community at various specialized conferences. All claims made in the dissertation are thoroughly substantiated in line with strategies to address these issues. The results were received using a comprehensive range of modern physicochemical research methods, carried out on high-precision equipment at scientific institutions in the European Union, specifically in Slovenia and Italy.

The scientific novelty of this work lies in the development of a method for creating composite systems that combine polymorphic phases of manganese oxides and oxyhydroxides modified with titanium dioxide and halloysite nanotubes for photocatalytic purposes. These composite systems are intended for the photocatalytic decomposition of organic dyes and polyethylene films. For the first time, a composite material was developed that includes compounds of the ramsdellite (manganese dioxide) and anatase (titanium dioxide), and its effectiveness in the photocatalytic decomposition of polyethylene films was investigated, as evidenced by the 1st type of heterojunction $\text{TiO}_2@\text{MnO}_2$, with a faster accumulation of PE oxidation intermediates. Composites of manganese oxides and oxyhydroxides with halloysite nanotubes in neutral and weakly alkaline ammonium hydroxide solutions were synthesized for the first time. The inclusion of manganese compounds in the structure of aluminosilicate halloysite nanotubes (HNT) enhances the functionality of the composite, resulting in high stability and photocatalytic activity in the degradation of organic substances under visible light irradiation. The study found that decorating the HNT surface with manganese oxides increases the photocatalytic activity of the composite during the degradation of Methylene Blue (MB) dye. This enhancement is attributed to the potential for direct photoelectron transfer between the electrons from both the HNTs and the manganese oxides (Mn_xO_y), which facilitates the subsequent reduction of the MB dye. Additionally, for the anionic dye Congo Red (CR), it was observed that rapid direct oxidation can occur through holes from the valence band of the photocatalyst produced by chemical deposition. This study examines the role of doping ions of ammonium and chromium(III), in the formation of nanoscale structures during the diffusion-controlled electrodeposition of manganese dioxide. For the first time, the phase composition and morphology of the resulting structures have been analyzed, and the impact of the doping substances on these properties has been emphasized. Thus, the scientific objective set in the dissertation was fully accomplished, and the candidate has thoroughly mastered the methodology of scientific research.

Assessment of the dissertation content, completeness, and adherence to the principles of academic integrity. By its content, the dissertation of Ms. Kovinchuk Iryna fully complies with the Higher Education Standard for the specialty¹⁶¹ Chemical Technology and Engineering and the research areas according to the educational program Chemical Technology and Engineering.

The dissertation is a complete scientific work and attests to the personal contribution of the candidate to the scientific field of Chemical and Bioengineering. After reviewing the similarity report resulting from the textual analysis of the dissertation, it can be concluded that the dissertation of Kovinchuk Iryna is the result of the candidate's independent research and contains no elements of falsification, compilation, fabrication, plagiarism, or misappropriation. Ideas, results, and texts of other authors are properly cited.

Language and style of presentation of the results. The dissertation is written with a good level of English, is clear and logically constructed, sufficiently accompanied by figures and tables, and includes an appropriate number of bibliography sources. The dissertation consists of an introduction, 7 chapters, conclusions, a list of references, and appendices. The total length of the dissertation is 198 pages.

The introduction reveals the justification for choosing the research topic, the purpose, methods, and objectives of the research, the scientific novelty of the obtained results, and the practical significance of the results. It includes the personal contribution of the applicant, the connection of the work with scientific programs, plans, topics, and approval of the results of the dissertation, publications.

The first Chapter reviews the relevant scientific publications and reveals the current state of development concerning the problem of environmental pollution by organic substances and methods for their removal.

The second Chapter is devoted to the consideration of objects, methods of synthesis of composites, and methodology of their research. The conditions of experimental research and the algorithms of calculations of the obtained data are given.

The third Chapter presents the results of the study of the physicochemical and mechanical properties of standard materials. The characterization of titanium and manganese dioxides, immobilized HNTs was carried out using XRD, TG-DTA, FT-IR, and SEM analysis. Wettability and tensile strength were studied for PE films, and PE/Ti(IV) oxide and PE/TiO₂&MnO₂ composites. TG-DTA was used when characterizing PE films decorated with halloysite nanotubes, and hydrophobic and optical properties were studied.

The physicochemical properties of manganese compounds and their composites with HNTs chemically deposited in alkaline and neutral environments are described in the fourth Chapter. The main phases formed in alkaline environments were low-valent hausmannite and manganese(III) oxide phases. Higher-valent MnOOH and manganese dioxide predominated in neutral environments. The effect of decorating nanotubes and loading their lumens with chemical deposition products was revealed. It was found that all samples are photocatalysts that can be

excited by visible light photons, including composites with HNTs with bandgap values in the range of 1.99 - 2.7 eV. The samples CS-1 and CS-2 exhibit maximum E_g values of 2.52 and 2.7 eV, respectively, in contrast to other composites containing HNTs (CS-6, CS-7).

Electrodeposition of manganese dioxide (Chapter five) was carried out at the lowest concentrations of Mn^{2+} in combination with a high current density, which together ensured diffusion control and, as a result, the maximum possible particle dispersion. The maximum acidity regulated by the introduction of sulfuric acid contributes to the disproportionation of Mn(III)-ions and the formation of phases with various morphologies. At pH 3.5–4.0, an increase in the content of δ/α - MnO_2 polymorphs occurred. The addition of ammonium ions contributed to the formation of the hollandite phase. Analysis of the results of determining the band gap width of some traditional electrodeposited samples of γ - and α -polymorphs confirmed their prospects as photocatalysts for water splitting. It is assumed that there are such directions for correcting electrodeposited MnO_2 to photocatalysis by increasing the contribution of Mn(II) and Mn(III)-ions states. It is possible to use heterojunctions with low-valent manganese oxides, titanium dioxide, and add dopants such as Fe(III) or Cr(III)-ions.

In the sixth Chapter, the functional properties of composites and some standard materials were studied. The binding effect was established for the degradation of a PE film containing a mechanical mixture of titanium and manganese dioxides. The general ability of manganese dioxide and other manganese compounds to be a catalyst for the degradation process, regardless of the presence of light, for the degradation of PE film, MB, and CR dyes, was established. The adsorption of MB and CR dyes on highly filled Aldrich Sigma nanotubes was studied, and such parameters as the maximum molar capacity, the surface area of the molecule were determined using the Langmuir isotherm. The kinetics of the degradation of organic MB and CR dyes under the action of UV irradiation were studied.

The seventh Chapter evaluates the technological parameters of the synthesis of a photocatalytically active composite based on hausmanite Mn_3O_4 and high-carbon nanotubes (HNTs). The research is summarized, and its prospects for implementation in the technological schemes of operating enterprises are shown.

The dissertation is formatted in accordance with the requirements of the Order of the Ministry of Education and Science of Ukraine No. 40 of January 12, 2017 "On Approval of Requirements for Dissertation Formatting".

Dissemination of dissertation results. The scientific results of the dissertation have been reflected in 19 scientific publications of the candidate, including: 2 articles in scientific journals included, at the time of publication, in the list of recognized academic periodicals of Ukraine; 1

articles in peer-reviewed scientific journals indexed in the Web of Science Core Collection and/or Scopus databases and belonging to the first to third quartiles (Q1—Q3) according to the SCImago Journal and Country Rank or Journal Citation Reports. The dissertation results were also presented at 16 academic conferences. Thus, the scientific results described in the dissertation are represented completely in the candidate's scientific publications.

Shortcomings and comments on the dissertation. Despite the thorough consideration of the dissertation topic, there are points that need further clarification from the reviewer's point of view, such as:

1. The reasons for the manifestation of the photocatalytic activity of a series of photocatalysts for the degradation of dyes are quite interestingly analyzed using the example of energy diagrams, while a similar analysis for the degradation of a PE film is not provided. It would be valuable contribution to the study to introduce similar approaches for PE and explain at this level the series of photocatalysts by their photocatalytic activity for the degradation of PE films.
2. The dissertation contains experimental data on the adsorption of dyes on the studied samples of photocatalysts of a series of chemically synthesized samples. However, the results of processing these data are not detailed enough to conclude which surface of the HNTs is involved in the adsorption (the inner lumen or the outer surface with silanol groups). Nevertheless, from the logical point of view, one can expect a predominant ion-exchange adsorption of cationic dye on the outer surface, while anionic on the inner. Can the author of dissertation confirm this hypothesis with her results/conclusions?
3. Mainly complex oxide/oxidehydroxide composites of manganese of different valence were obtained by chemical synthesis methods in this study. Meanwhile, synthetic chemical methods for the synthesis of almost every known phase of the corresponding compounds are known. Why was this particular path chosen?
4. From the analysis of the appendices of the dissertation, the mechanism of photocatalytic degradation of dyes can be explained in more detail, because the intensities of several peaks change during the process. However, these data were not taken into account in the work.
5. Photocatalytic processes are accompanied by the formation of radicals of various types. The study of radical particles is important to establish the mechanism of the process. It would be advisable to introduce an EPR experiment for a deeper understanding of the mechanism, and/or use appropriate scavengers.

In my opinion, the remarks expressed are not substantial and do not diminish the overall scientific novelty or practical significance of the results and do not affect the positive evaluation of the dissertation.

Conclusion on the dissertation. I can conclude that the dissertation of the candidate for the degree of Doctor of Philosophy Kovinchuk Iryna on the topic “Composites of manganese oxides and oxidehydroxides with halloysite as degradation photocatalysts” was carried out at a high scientific level, does not violate the principles of academic integrity, and represents a completed scientific study whose set of theoretical and practical results addresses a scientific problem of significant importance for the field of study 16 Chemical and Bioengineering. The dissertation fully meets the requirements of the current legislation of Ukraine in terms of relevance, practical value, and scientific novelty, as specified in Sections 6–9 of the “Procedure for the Awarding of the Doctor of Philosophy Degree and Revocation of Decisions of One-Time Specialized Academic Councils of Higher Education Institutions and Research Institutions on Awarding the Doctor of Philosophy Degree,” approved by the Resolution of the Cabinet of Ministers of Ukraine No. 44 dated January 12, 2022. The candidate Kovinchuk Iryna deserves to be awarded the degree of Doctor of Philosophy in the field of study 16 Chemical and Bioengineering and specialty 161 Chemical Technology and Engineering.

Official opponent:

Leading Researcher of the
Department of Functional
Ceramics Based on Rare Earths
of the I. Frantsevich Institute for
Problems of Materials Science of
the NAS of Ukraine,



signature

Olena LAVRYNENKO

Doctor of Chemical Sciences,
Senior Researcher

I certify the signature of Doctor of Chemical Sciences, Senior Researcher Olena Lavrynenko
academy secretary of Frantsevich institute for
Problems of Materials Science of the NAS of Ukraine
2025
Denys Myroniuk

