REVIEW
of the dissertation
Kovinchuk Iryna
on the topic "Composites of manganese oxides and oxidehydroxides with halloysite as degradation photocatalysts",
submitted for the degree of Doctor of Philosophy
in the field of knowledge16 Chemical and Bioengineering
in specialty 161 Chemical Technology and Engineering

Relevance of the dissertation topic.

To effectively handle the pollution challenges present in the modern world, the integration of sustainable technologies is essential. However, many existing methods fail to meet current ecological and efficiency standards. Among the most pressing concerns are persistent pollutants such as synthetic polymers and organic dyes, which have become key targets in environmental research. Photocatalytic degradation represents a promising solution, aligning with the principles of sustainable development despite certain inherent limitations. Traditional photocatalysts, primarily titanium dioxide (TiO_2), are restricted by their dependence on ultraviolet (UV) light activation. In contrast, manganese oxides and manganese oxidehydroxides exhibit notable photocatalytic activity under visible light, alongside favourable stability and cost-effectiveness. Further enhancement of photocatalytic performance can be achieved through the formation of composites with materials such as halloysite aluminosilicate nanotubes. Potential strategies for optimisation include the creation of heterojunctions, surface decoration, active component loading, and the effects of structural support.

Given these considerations, this study focuses on evaluating the photocatalytic efficiency of manganese oxide/manganese oxide-hydroxide/halloysite nanotube composites in the degradation of organic contaminants. The research is driven by the critical need to develop advanced, visible-light-responsive photocatalysts for sustainable environmental remediation.

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

The dissertation presents scientifically grounded and experimentally confirmed results that contribute to the field of photocatalysis and environmental chemistry. The scientific novelty of the work lies in the development and comprehensive study of new composite photocatalysts based on manganese oxides/oxidehydroxides and halloysite nanotubes (HNT), as well as the investigation of their application in the degradation of organic dyes and polyethylene films (PE).

For the first time, composite systems were synthesised under different pH conditions (5–7 and 10) in the presence of hydrogen peroxide as an oxidant and ammonium ions as a dopant, which allowed the control of phase composition – resulting in the formation of hausmannite, manganite, and other manganese oxide phases. The study reveals that HNTs act not only as structural supports but also enhance photocatalytic efficiency through decoration and incorporation effects. Electron transfer processes were evaluated using energy band diagrams, which demonstrated a favourable alignment between the conduction and valence bands of the composite and the HOMO–LUMO levels of dyes such as Methylene Blue and Congo Red, explaining their degradation mechanisms under visible light.

The dissertation also provides a detailed analysis of the electrodeposited manganese dioxide from sulfate electrolytes with low Mn^{2+} concentrations, highlighting the influence of NH_4^+ and Cr^{3+} dopants. It was established that ammonium ions significantly affect the morphology and phase composition of the electrodeposited material, yielding structures such as hollandite and birnessite. TEM analysis confirmed the formation of nanoparticles with narrow size distribution and high surface area.

Furthermore, a synergistic photocatalytic effect was observed in PE degradation using a mechanical mixture of anatase TiO_2 and ramsdellite, resulting in significantly higher mass loss (21.3%) than either individual component under UV irradiation.

The reliability of the scientific results and conclusions in the dissertation is ensured by a large volume of experimental data and by the use of modern research methods. Phase composition and crystalline structural characteristics of the synthesised materials were analysed using powder X-ray diffraction. Measurements were performed on two diffractometers: a Rigaku MiniFlex600 (Japan) and a Bruker AXS D4 Endeavor. Elemental analysis was performed using energy-dispersive X-ray spectroscopy (EDS) on a Quanta 22650 scanning electron microscope (Thermo Scientific) equipped with an Oxford Ultim Max 40 detector. The optical properties of both the photocatalyst suspensions and dye solutions were examined by recording UV-Vis absorption spectra on a Specord S600 spectrophotometer (Analytik Jena, Germany). Diffuse reflectance spectra were measured using a Shimadzu UV-3600 spectrophotometer, covering the wavelength range of 200–2000 nm. Fourier-transform infrared (FTIR) spectra were obtained using a Frontier spectrometer (PerkinElmer) within the 400–4000 cm^{-1} range. The morphology and particle size of the synthesised photocatalysts were investigated using a Thermo Scientific Verios G4 HP scanning electron microscope. Dynamic light scattering (DLS) measurements were conducted using a Malvern Zetasizer Nano to assess particle size distribution and zeta potential. The thermal stability of the samples was evaluated via thermogravimetric analysis using a Discovery TGA550 system and a Derivatograph Q1000 (MOM, Hungary). The specific surface area of the materials was determined by nitrogen adsorption using the BET method on a Gemini II 2370 analyser (Micromeritics). Data processing and visualisation were performed using QtiPlot, ImageJ, and Fityk software.

Thus, scientific provisions, conclusions and recommendations can be considered reliable, and their justification - carried out with the necessary completeness.

The research was performed at the Department of Physical Chemistry of the Faculty of Chemical Technology of the National Technical University of Ukraine “Igor Sikorsky Kyiv Polytechnic Institute” (Ukraine) and at the Faculty of Physics and Chemistry of the University of Palermo (Italy) in accordance with the agreement on double supervision of the doctoral dissertation No. 0220/3 dated 28.02.2022.

As a performer, the doctoral student participated in conducting research within the framework of the research project “Physico-chemical foundations of production, functionality and use of multicomponent nanodisperse systems and the use of additives in food and cosmetic products” with state registration number 0117U007592, 2018-2023 and research project “Physical chemistry of nanocomposite and disperse systems for functional purposes”, state registration number 0124U001965, 2024-2026 under the supervision of Professor, Doctor of Chemical Sciences, Professor Sokolsky Georgy Volodymyrovych.

The doctoral student actively participated in mobility programs. Thus, she underwent mobility at the University of Palermo (Italy) within the framework of the Erasmus+ program from 28.02.2022 to 26.02.2023. Part of the experiment was performed at the Department of Advanced Materials of the Jožef Stefan Institute, Ljubljana (Slovenia) in accordance with Work Package 1 of the Marie Skłodowska-Curie Research and Innovation Staff Exchange program “Innovative functional oxide materials for green hydrogen energy production - H-GREEN”.

Thus, the dissertation successfully solved the scientific problem of studying the relationship between the composition, structure and photocatalytic properties of manganese oxide and oxidehydroxide/halloysite composites. The applicant has fully mastered the methodology of scientific research.

Assessment of the dissertation content, its completeness and compliance with the principles of academic integrity.

By its content, the dissertation of Kovinchuk Iryna fully complies with the Higher Education Standard for the specialty 161 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 and testifies presence of the applicant’s personal contribution to the scientific direction of developing photocatalytically active materials that can be used for various purposes.

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 presenting results.

The dissertation is written in English, logically structured, and meets the requirements of the Higher Education Standard for speciality 161, Chemical Technologies and Engineering. The content aligns with the educational and research focus of the relevant program, and the scientific style and terminology used are appropriate and consistent with standards in the field.

The dissertation consists of an introduction, 7 chapters, conclusions, a list of references and appendices. The total volume of the dissertation is 198 pages.

The introduction describes the relevance of the research topic and outlines the purpose and main objectives of the study. It presents the applied research methods, emphasises the scientific novelty and practical value of the results, specifies the author's contribution, links the work to relevant scientific programs and projects, and provides information on the validation of the results.

The first chapter presents a literature review on dyes as water pollutants, including their classification, sources, and environmental impact. It discusses modern methods of water purification, with a focus on photocatalytic degradation, as well as electrochemical and biological approaches. Special attention is given to the role of heterogeneous photocatalysts—particularly manganese oxides, oxidehydroxides, titanium dioxide, and aluminosilicate clays—highlighting their advantages, limitations, and catalytic properties. Additionally, the chapter addresses plastic pollution and current strategies for photocatalytic degradation.

The second chapter outlines the synthesis methods of composite photocatalysts based on manganese oxides/oxidehydroxides and halloysite nanotubes, including electrodeposition techniques and chemical preparation. A method for preparing polyethylene films with embedded photocatalysts is described. It also describes the physicochemical characterisation methods used—such as X-ray diffraction, SEM, IR spectroscopy, and thermal analysis, as well as the spectrophotometric techniques applied to characterise materials and evaluate the photocatalytic activity of the obtained materials.

The third chapter presents a study of the physicochemical properties of manganese dioxide, titanium dioxide, and halloysite nanotubes used to produce composite systems. It details the development of a method for depositing nanomaterials onto polyethylene film surfaces and examines the wettability, thermal stability, and mechanical behaviour of the resulting films. Characterisation was carried out using optical microscopy, contact angle measurements, and thermogravimetric analysis.

The fourth chapter focuses on the physicochemical characterisation of manganese oxides and oxidehydroxides chemically synthesised in the presence of halloysite nanotubes. It describes the influence of pH on phase composition and outlines a method for obtaining these composites. Nanostructural features were analysed using DLS, TEM, and BET surface area measurements. ζ-potential and particle size distribution were determined from aqueous dispersions and TEM images. Phase and elemental composition were studied via Rietveld refinement and EDS. Thermal stability was assessed by thermogravimetric analysis, while DRS was used to evaluate semiconductor properties and band gap values, confirming photocatalytic activity in the visible light range.

The fifth chapter presents the synthesis and characterisation of electrodeposited manganese dioxide materials obtained from low-concentration Mn(II) sulfate electrolytes under varying acidic conditions The influence of NH_4^+ and Cr^{3+} dopants on phase composition and band gap was studied, resulting in the stabilisation of hollandite and birnessite phases. A comprehensive analysis was performed using XRD, BET, EDS, SEM, TEM, TGA, and diffuse reflectance spectroscopy.

The sixth chapter focuses on the photocatalytic properties of manganese oxide and oxidehydroxide composites with halloysite nanotubes in the degradation of organic dyes (Methylene Blue and Congo Red) under UV irradiation and day light. Enhanced activity was observed for HNT-decorated MnxOy samples. The kinetics of dye degradation were analysed, including the determination of rate constants and reaction order. A mechanism of photocatalytic process was proposed based on energy band alignment, using DRS-derived band gap values and Mulliken electronegativity to relate photocatalyst energy levels to dye HOMO/LUMO levels.

The seventh chapter presents the technological implementation of the author's method for synthesising a photocatalytically active composite based. A process block diagram was developed, covering key stages such as dissolution, synthesis, decantation, drying, and grinding. Material and heat balances were calculated for producing 1 kg of the optimal composite, and the exothermic effect of the synthesis was assessed.

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".

Publication 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 article in peer-reviewed scientific journals indexed in the Web of Science Core Collection and Scopus databases, of which 1 articles are in journals classified within the first to third quartiles (Q1) according to the SCImago Journal and Country Rank or Journal Citation Reports. The dissertation results were also presented at 16 academic conferences.

The topics of the credited articles reflect the author’s scientific achievements included in the dissertation. Articles, including those in co-authorship, are performed at a high scientific level and in compliance with the principles of academic integrity, and Kovinchuk I.V.‘s contribution to all publications is decisive.

Thus, the scientific results described in the dissertation work are fully covered in the applicant’s scientific publications.

Shortcomings and remarks on the dissertation work.

1. Section 3.2 of the study presents a study of the wettability of PE films decorated with halloysite, where all samples are considered hydrophobic. At the same time, only surfaces demonstrating a contact angle with water greater than 90° are considered hydrophobic, and surfaces demonstrating a contact angle with water less than 90° are hydrophilic. Thus, conditionally, Samples 1 and 3 should be recognized as hydrophilic.

2. Figure 4.1 illustrates the particle size distribution calculated using ImageJ; however, not all CS samples are displayed. This should be commented on in the text.

3. Section 6.2 uses a reference to Figure 6.4., which was presented on page 138, but it should be Figure 6.6.

4. Tables 6.5 and 6.6 incorrectly indicate the units of measurement for the rate constant of a second-order reaction. This should be $L \cdot mol^{-1} \cdot s^{-1}$.

5. Although Methylene Blue (MB) and Congo Red (CR) are widely used model dyes for evaluating photocatalytic degradation performance, their use has several significant limitations that can lead to misleading or non-reproducible results. Firstly, both dyes are known to undergo direct photolysis under UV and visible light without the involvement of any catalyst, which complicates the accurate assessment of true photocatalytic activity. Secondly, MB is susceptible to photosensitization effects, meaning it can generate reactive species by itself when exposed to light, artificially enhancing apparent degradation rates. Thirdly, both dyes can adsorb strongly onto the surface of photocatalysts, masking the real contribution of catalytic oxidation by simple adsorption effects. Finally, MB and CR do not represent realistic organic pollutants typically found in wastewater and thus provide limited information about practical photocatalytic performance for real-world applications. For these reasons, more environmentally relevant and stable organic contaminants, such as phenolic compounds or pharmaceutical residues, are recommended for reliable evaluation of photocatalytic materials.

6. It should be noted that the energy levels of the dye's frontier molecular orbitals (HOMO and LUMO) were not independently calculated using quantum chemical methods but were instead taken from literature values or estimated by indirect methods. This may introduce uncertainty, as the actual orbital energies can vary depending on solvent effects, dye aggregation, or interaction with the photocatalyst surface. Additionally, the proposed mechanism does not include experimental validation of intermediate reactive species (e.g., via scavenger studies or ESR analysis), which would be necessary to fully confirm the pathway of photocatalytic degradation.

I believe that the expressed remarks are not decisive, do not reduce the overall scientific novelty and practical significance of the results and do not affect the overall positive assessment of the dissertation work.

Conclusion about the dissertation work.

I believe that the dissertation work of the Doctor of Philosophy degree applicant Kovinchuk Iryna Vasylivna on the topic "Composites of manganese oxides and oxidehydroxides with halloysite as degradation photocatalysts" is performed at a high scientific level, does not violate the principles of academic integrity and is a completed scientific study, the set of theoretical and practical results of which solves a scientific task that has significant importance for the field 16 Chemical and Bioengineering. The dissertation work in terms of relevance, practical value and scientific novelty fully complies with the requirements of current legislation of Ukraine, provided in paragraphs 6-9 of the "Procedure for awarding the degree of Doctor of Philosophy and canceling the decision of a one-time specialized academic council of a higher education institution, scientific institution on awarding the degree of Doctor of Philosophy", approved by the Resolution of the Cabinet of Ministers of Ukraine dated January 12, 2022 No. 44.

The applicant Kovinchuk Iryna Vasylivna deserves to be awarded the degree of Doctor of Philosophy in the field of knowledge 16 Chemical and Bioengineering in specialty 161 Chemical Technologies and Engineering.

Reviewer:

Head of the Department of Physical Chemistry, Igor Sikorsky Kyiv Polytechnic Institute, Doctor of Technical Sciences, Professor

Підпис Viсtoria VOROBIOVA

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