

## REVIEW

of the official opponent on 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 knowledge 16 Chemical and Bioengineering

in specialty 161 Chemical Technology and Engineering

### **Relevance of the dissertation topic.**

Among various methods of wastewater treatment from organic compounds of different classes, advanced oxidation processes (AOPs) using heterogeneous catalysts have been widely studied in recent years. The synthesis of photocatalysts and determination of their efficiency attracts significant attention from scientists. Currently, many efforts are being made to develop new photocatalysts with high stability and activity toward the degradation reaction of organic pollutants. The work examines the synthesis, structural, and photocatalytic properties of new composite materials based on manganese oxides and oxidehydroxides with aluminosilicate nanotubes, synthesized by chemical precipitation and electrodeposition methods. In addition, special attention is paid to the possibility of using synthesized composites for the destruction of polyethylene (PE). Therefore, the dissertation topic is relevant.

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

The scientific novelty of the dissertation research results lies in the fact that in accordance with its aim:

- the photocatalytic behavior of both ramsdellite  $\text{MnO}_2$  and anatase  $\text{TiO}_2$ , as well as mechanically mixed  $\text{MnO}_2$  and  $\text{TiO}_2$  in the degradation reaction of PE films was investigated. The composite photocatalyst allowed increasing the degree of destruction to 21.3% compared to pure  $\text{MnO}_2$  (6.5%) and  $\text{TiO}_2$  (14.6%) after 90 hours of irradiation in UV light at  $\lambda = 250 \text{ nm}$ , as evidenced by the  $\text{TiO}_2@\text{MnO}_2$  type 1 heterojunction with faster accumulation of intermediate PE oxidation products;



- composite materials from manganese oxides and oxidehydroxides and halloysite nanotubes (HNT) were synthesized for the first time from solutions at different pH values (5-7 and 10). They have the advantages of a narrow band gap, good stability and high photocatalytic activity of organic substances decomposition under irradiation in the visible light range;

- it was established that composites with halloysite nanotubes demonstrate decoration effects and incorporation of manganese compound into the nanotube, improving functionality due to the role of HNT as a photocatalyst enhancer and improved reagent fixation on the photocatalyst surface;

- it was found that chemically precipitated manganese oxides and oxidehydroxides actively decorate the HNT interface in the presence of cationic forms of  $Mn^{2+}$  in the reaction medium, and incorporation into the HNT lumen is observed during crystallization of negatively charged forms of Mn acid residues of Tutton's salts;

- it was proven that the positive effect of HNT  $Mn_xO_y$  surface decoration on the photocatalytic activity of MB destruction is explained by direct photoelectron transfer from EC of both HNT and  $Mn_xO_y$  and subsequent reduction of MB dye;

- electrodeposition of manganese dioxide under diffusion control was investigated, and the role of doping ions  $NH_4^+$  and  $Cr^{3+}$  was established.

The reliability of the results is confirmed by the use of modern research methods and modern equipment. The phase composition and structure of synthesized samples were studied on a Rigaku MiniFlex600 X-ray diffractometer (Japan), elemental composition was investigated by energy-dispersive spectroscopy using a Quanta 650 Thermal Scientific SEM Oxford detector, optical properties were studied on a Specord S600 spectrophotometer (Analytik, Jena, Germany), Shimadzu UV-3600 UV-VIS-NIR spectrophotometer (200 – 2000 nm) and Frontier FTIR PerkinElmer IR spectrometer (400 – 4000 nm). The morphology and particle size of synthesized photocatalysts were studied on a Thermo Scientific Verios G4HP scanning electron microscope and on a Malvern Zetasizer Nano device. Research results were processed using Microsoft Excel, QtiPlot, ImageJ, Fityk programs.



Thus, the scientific task set in the dissertation work has been fully completed, and the applicant has fully mastered the methodology of scientific activity.

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

In terms of its content, the dissertation work of applicant Kovinchuk I.V. fully complies with the Higher Education Standard for specialty 161 Chemical Technologies and Engineering and the research directions according to the educational program Chemical Technologies and Engineering.

The dissertation work is a completed scientific work and indicates the presence of the applicant's personal contribution to the scientific direction of creating innovative composite photocatalysts based on manganese oxides, oxidehydroxides and HNT.

Having reviewed the similarity report based on the results of checking the dissertation work for text matches, it can be concluded that the dissertation work of Iryna Vasylivna Kovinchuk is the result of the applicant's independent research and does not contain elements of falsification, compilation, fabrication, plagiarism and borrowing. Used ideas, results and texts of other authors have proper references to the appropriate source.

**Language and style of presenting results**

The dissertation work is written in English using generally accepted terminology for the field of knowledge. Research results are structured, presented consistently and accessibly using a scientific style of speech.

The dissertation consists of an abstract, introduction, 7 chapters, conclusions, bibliography and appendices. The total volume of the dissertation is 198 pages.

In the introduction, the relevance of the dissertation topic is substantiated, the aim and main research objectives are formulated, and the scientific novelty and practical value of the results are presented.

The first chapter of the work contains a detailed analysis of dyes and sources of their entry into water sources, features of using advanced oxidation processes for catalytic water treatment. The main heterogeneous photocatalysts are characterized,



including manganese oxides and oxidehydroxides and clays. The advantages and disadvantages of existing photocatalysts are systematically considered.

The second chapter describes methods for synthesizing composite photocatalysts. A description of physicochemical methods for analyzing the obtained materials is provided (diffraction analysis, scanning electron microscopy, IR spectroscopy, derivatography). Methods for studying photocatalytic properties using spectrophotometry are presented.

The third chapter examined the physicochemical properties of manganese dioxide, titanium dioxide, halloysite, which were used as starting materials for obtaining composites. The wettability, thermal and mechanical behavior of PE films with manganese dioxide and titanium dioxide, halloysite were studied. A method for depositing nanomaterials on the surface of PE films by partial surface dissolution and using an adhesive composition was developed. The prepared films were characterized by optical microscopy, contact angle measurement and thermogravimetry methods.

The fourth chapter describes the physicochemical properties of chemically precipitated manganese compounds and their composites with aluminosilicate nanotubes. The influence of the pH of the aqueous medium on the phase composition of the obtained products was clarified. A method for obtaining composites with aluminosilicate nanotubes was developed. DRS measurements were used to evaluate the semiconductor properties of the samples. The obtained samples are effective photocatalysts that can be excited by visible light photons, including HNT composites with band gap values in the range of 1.99 - 2.7 eV.

The fifth chapter examines the synthesis of a series of electrodeposited  $\text{MnO}_2$  samples using band engineering principles. By diffusion control of electrodeposition and doping with Cr(III) ions, the task of improving sample dispersity and reducing the band gap was solved. The regulation of phase composition by adding  $0.5\text{M NH}_4^+$  ions and  $\text{H}_2\text{SO}_4$  was also investigated (hollandite and birnessite structures were stabilized by  $0.5\text{M NH}_4^+$  ions).

The functional properties of the obtained composites and some standard materials were studied. A binding effect was established during the degradation of polyethylene film containing a mechanical mixture of  $\text{TiO}_2$  and  $\text{MnO}_2$ . The general



ability of  $\text{MnO}_2$  and other manganese compounds to be a catalyst for the degradation process regardless of the presence of light for the destruction of PE films, MB and CR dyes was established. The adsorption of MB and CR dyes on HNT (Aldrich Sigma) was investigated and parameters such as maximum molar capacity and molecule surface area according to the Langmuir isotherm were determined.

In the sixth chapter, the kinetics of degradation of organic dyes MB and CR under UV irradiation was investigated. Increased photocatalytic activity of MB degradation was established for samples with HNT  $\text{Mn}_x\text{O}_y$  decorated surfaces. The reaction rate constant and reaction order of dye destruction were established. Using diffuse reflectance spectroscopy measurements of the semiconductor band gap together with the Mulliken electronegativity of the photocatalyst, a scheme for constructing the photocatalyst band gap width for the degradation process was proposed, which involves combining the  $E_c$ ,  $E_v$  energy levels with the HOMO/LUMO levels of the target molecule.

In the seventh chapter, the technological parameters of synthesis of a photocatalytically active composite based on hausmannite,  $\text{Mn}_3\text{O}_4$  and halloysite nanotubes were evaluated. A block diagram was compiled that includes the stages of dissolution, vacuuming, synthesis, decantation, drying, grinding and subsequent storage. Material and heat balances were calculated for the production of 1 kg of the most active composite (45%  $\text{Mn}_3\text{O}_4$ , 15%  $\text{Mn}_2\text{O}_3$ , 12%  $\text{MnO}_2$ , 28% halloysite). The thermal effect of the exothermic synthesis process was calculated.

The dissertation work is formatted in accordance with the requirements of the order of the Ministry of Education and Science of Ukraine dated January 12, 2017, No. 40 "On approval of requirements for dissertation formatting".

### **Publication of dissertation results.**

The scientific results of the dissertation are presented in 19 scientific publications of the applicant, including: 2 articles in scientific publications included on the date of publication in the list of scientific professional publications of Ukraine; 1 article in a periodical scientific publication indexed in the Web of Science Core Collection and/or Scopus databases, belonging to the first quartile (Q1) according to



the SCImago Journal and Country Rank or Journal Citation Reports classification. Also, the dissertation results were presented at 16 scientific professional conferences.

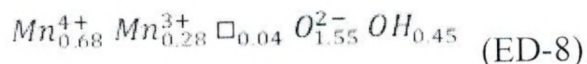
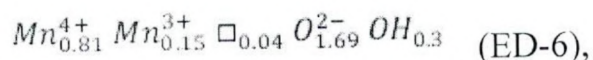
Thus, the scientific results described in the dissertation work are fully presented in the applicant's scientific publications.

### **Shortcomings and remarks on the dissertation work.**

The overall assessment of the dissertation work is positive, however, there are a number of remarks:

1. Chapter 3 describes in detail the composite components, but does not provide microscopic analysis of nanotubular halloysite, which is very important considering the peculiarities of particle shape.

2. On the pages 5, 124, formulas of compounds



are given which are not electroneutral.

3. Figures 6.9 and 6.10 do not show the experimental conditions (time, initial dye concentration, etc.). The absorption spectra of methylene blue with photocatalysts do not contain information about the photocatalysis conditions (Appendix E).

4. It was established that for the degradation reaction of Congo red dye, the dominance of a second-order reaction under UV radiation is demonstrated. It is known that degradation reactions are usually described by first-order reactions. To clarify the reaction order, experiments are conducted at several initial dye concentrations. There is no explanation for the obtained result in the dissertation text

5. In Chapter 1, Figure 1.3 is missing, Figures 5.5 and 5.6 and Figures 6.4 and 6.5 appear twice.

6. The calculation of material and heat balances would preferably be presented in the appendices. In addition, the result of the heat balance is the determination of water consumption for cooling, which is not provided.



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

**Official opponent:**

Professor of the Department of  
Technology of Inorganic  
Substances UDUNT, Doctor of  
Technical Sciences, Professor



Liliya FROLOVA

*Zachigryno*  
*Генерал*



*Генерал* 2025