

**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 knowledge 16 Chemical and Bioengineering  
in specialty 161 Chemical Technology and Engineering

**Relevance of the dissertation topic**

Modern approaches to combating environmental pollution should include the use of green technologies.

However, not all known methods and technologies meet modern requirements. Waste components such as plastics and organic dyes are essential subjects of modern research.

Promising methods that can decompose such waste, taking into account the requirements of sustainable development and environmental friendliness, are photocatalytic methods despite their limitations.

These methods are based on the use of photocatalysts based on  $\text{TiO}_2$ , but they are limited to ultraviolet radiation wavelengths. Composites with manganese oxides and manganese oxidehydroxides are distinguished by their photocatalytic activity in the visible light range along with stability, low cost, etc. Expanding the capabilities of the photocatalyst lies in the area of using them in the form of composites with other components, such as halloysite aluminosilicate nanotubes. The improvement of photocatalytic ability can be achieved through heterojunctions, decoration effects, loading with active components, and the support function of the photocatalyst. At the same time, the ability of aluminosilicate compounds to destroy organic compounds is known. Therefore, the relevance of the work lies in the need to study the photocatalytic activity of manganese oxide / manganese oxidehydroxide / halloysite nanotube composites for the degradation of organic compounds.

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

The scientific novelty of the dissertation research results is as follows. The work considers for the first time a composite system of manganese oxide/oxidehydroxide with halloysite nanotubes, obtained by chemical synthesis in the presence of hydrogen peroxide in alkaline and near-neutral environments.

The influence of ammonium ions on phase formation in this system is considered. It is shown that hausmannite is the main phase in the product during synthesis in an alkaline environment and MnOOH oxidehydroxide is the main phase during synthesis in the pH range = 5-7. Using the examples of an anionic dye (Congo red) and a cationic dye (Methylene blue), opposite trends in their photocatalytic degradation ability were observed in the series of synthesised samples, primarily related to the average oxidation state of manganese in the composite material and the presence of nanotubes (HNT). The maximum photocatalytic activity of the series samples is explained by the possibility of direct electron transitions from the semiconductor conduction band to the HOMO LUMO levels of the dye.

For the first time, materials based on manganese dioxide were electrodeposited in the presence of ammonium and chromium (III) cations from sulfate electrolytes of different concentrations and low manganese (II) concentrations (0.05 and 0.1 mol/l). The particle size distribution was studied in detail and samples with the narrowest range were established and the phase composition of the product was determined. Samples synthesised in the presence of ammonium cation additives have a hollandite and/or birnessite structure. No effect of chromium(III) cation additive on the phase composition under synthesis conditions was recorded. The potential applications of this series of materials in photocatalytic processes, including water splitting, are demonstrated.

A synergistic photocatalytic effect was established in the photodegradation process of polyethylene films containing a mechanical mixture of TiO<sub>2</sub> (anatase)/ramsdellite, compared to a single-component photocatalyst. This effect was observed when 1% (mass) of photocatalyst was added to the PE film composition. Under conditions of 90-hour UV irradiation ( $\lambda = 250$  nm), the maximum mass loss of the film exceeded 21%.

The results listed above are new and reflected in the author's publications. The novelty is confirmed by the proven main provisions, conclusions and recommendations of the dissertation.

The reliability of scientific results, provisions and conclusions in the dissertation is ensured by a large volume of experimental data and is ensured by the use of modern research methods, including electrochemical polarization measurements, X-ray phase analysis and measurements of structural-crystalline parameters of synthesised samples on Rigaku MiniFlex600 (Japan) and Bruker AXS D4 Endeavor. In the work, the elemental composition was studied by energy dispersive spectroscopy using Quanta 650 Thermo Scientific SEM Oxford, equipped with an Ultim Max 40 detector. The study of optical properties of photocatalyst suspensions, as well as dye solutions was carried out on a Specord S600 spectrophotometer (Analytik, Jena, Germany), differential reflection spectra were recorded on Shimadzu UV-3600, UV-VIS-NIR spectrophotometer

(200 - 2000 nm). Fourier infrared spectra were recorded on a Frontier FTIR PerkinElmer spectrometer (400 - 4000 nm). The morphology and particle sizes of synthesised photocatalysts were studied on a scanning electron microscope from Thermo Scientific, Verios G4HP. Dynamic light scattering for determining particle size and zeta potential was studied using a Malvern Zetasizer Nano device. The temperature stability of materials was determined by thermogravimetric analysis on a Discovery TGA550 thermogravimetric analyzer with TRIOS software and Q1000 derivatograph (MOM, Hungary). The specific surface area was measured using the BET method on a Gemini II 2370 Micromeritics analyzer. The research results were processed using Microsoft Excel, QtiPlot, ImageJ, Fityk programs.

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".

Therefore, in the dissertation work, the scientific task of studying the relationship between phase composition, structure and functional properties of manganese oxides/oxidehydroxides with aluminosilicate halloysite nanotubes in the photocatalytic degradation of polyethylene and aqueous dye solutions has

been fully completed, 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 its content, the dissertation work of the applicant Kovinchuk I.V. fully complies with the Higher Education Standard for specialty 161-Chemical Technologies and Engineering and research areas in accordance with the educational program - Chemical Technologies and Engineering.

The dissertation work is a completed scientific work and testifies to the presence of the applicant's personal contribution to the scientific direction of developing photocatalytically active materials that can be used for various purposes.

Having examined the similarity report based on the results of checking the dissertation work for text matches, it can be concluded that the dissertation work of Kovinchuk Iryna Vasylivna 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 is written in English. The presentation of the material is logical and complies with standards in the field of chemical technologies and engineering. The style of the presented material is scientifically substantiated and contains generally accepted terms.

The main content of the dissertation work is presented in the direction of the description and theoretical analysis of known literature devoted to issues of the chemical nature of manganese oxides and oxidehydroxides, their structural features, physicochemical properties, ability to photocatalysis and dye degradation, features of the structure and properties of halloysite nanotubes, the object and subject of research, formulation based on these results of working hypotheses and their experimental verification and to practical confirmation of the obtained results and formulation of conclusions.

The dissertation consists of an introduction, 7 chapters, conclusions, a list of references and appendices. The total volume of the dissertation is 199 pages.

*The introduction* justifies the choice of research topic and highlights the purpose and objectives of the research. Research methods, scientific novelty of the obtained results, practical significance, personal contribution, connection of

the work with scientific programs, plans, topics, approbation of results are indicated.

*The first chapter* provides a literature review on the characteristics of dyes as water pollutants, their classification by chemical structure and method of use. Theoretical aspects of water purification methods for removing dyes are considered, primarily based on photocatalytic decomposition, electrochemical reclamation, and biological purification, among others. Problems arising from plastic pollution and methods for its degradation to promote environmental purification are described. The role of photocatalysts in modern methods of plastic degradation is highlighted, including titanium dioxide, manganese oxides and oxidehydroxides, catalytic properties of aluminosilicate materials.

*The second chapter* is devoted to the description of research objects, methods of synthesis of manganese oxides and oxidehydroxides with halloysite composite materials, electrodeposition of materials based on manganese dioxide, production of polyethylene films based on metal oxides, halloysite nanotubes. Descriptions of research methods used in performing scientific work are given.

*The third chapter* is devoted to studies of complex composite systems based on manganese dioxides, titanium dioxide and halloysite nanotubes. The results of the wettability, thermal, and mechanical behaviour of polyethylene films with these oxides are presented. The obtained films are characterised using optical microscopy methods, contact angle measurements, and thermogravimetry.

*The fourth chapter* is dedicated to the analysis of the properties of chemically synthesised manganese oxides and oxidehydroxides composites with HNTs. Characterization of manganese oxides and oxidehydroxides composites with HNTs was made from the point of view of their nanodimensions. Colloidal aqueous dispersions of synthesised samples were used to determine  $\zeta$ -potential, and size distribution (DLS, TEM). Surface area was determined by BET analysis. Phase and elemental composition of synthesised composites of manganese oxides and oxidehydroxides with halloysite was studied by the Rietveld refinement method and EDS analysis. Thermogravimetry generally was used to interpret chemical analysis data since samples contain defect position that can be evaluated by the mass loss effects. The diffuse reflectance spectroscopy measurements were applied for the band gap calculation.

*Section 5* introduces the properties of electrochemically synthesised manganese dioxide materials from low-concentrated Mn(II) sulfate electrolytes in 0.031M, 2M H<sub>2</sub>SO<sub>4</sub>. Characterization of electrodeposited manganese dioxide materials was performed using the set of standard methods: XRD Rietveld Refinement, EDS, BET, SEM, TEM, TGA, side distribution, and as final point band gap determination.

*Chapter 6* describes functionalization of samples of manganese system (III, IV). Among other studies attention is paid to photocatalytic activity manganese oxides and oxidehydroxides with halloysite for degradation of dyes in aqueous solutions (Methylene Blue and Congo Red). Mechanism of photocatalytic activity towards aforementioned dyes degradation has been discussed.

*Chapter 7* contains implementation of the author developments as chemical process technology for synthesis of composite photocatalyst. The text describes and introduces the block diagram for synthesis of photocatalytic material with halloysite nanotubes, its material and energy balance.

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 Scopus database, classified by Scopus quartile Q1 according to the SCImago Journal and Country Rank or Journal Citation Reports classification.

Also, the dissertation results were tested at 8 international scientific conferences, including conferences and congresses at European and international levels.

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. The work does not systematically present data on the photocatalytic properties of synthesised samples. For example, chemically synthesised samples were tested on dyes, but not tested for photocatalysis of the polyethylene film degradation process. The initial oxide samples were tested for film degradation, but not tested for the ability to promote dye degradation. And the effect of halloysite nanotubes in the work is well described on the example of

photodegradation of dyes, but not described on the example of degradation of polyethylene films. The experiment with the technology of applying halloysite nanotubes to PE film looks insufficiently logically connected with the topic of photocatalysis.

2. The so-called lifetime prediction of polyethylene films should provide information about the thermostability of films with photocatalyst. However, the trends in changes of this parameter do not correlate with changes in mass loss on TG curves of films and IR spectra of films after irradiation.

3. The work did not conduct comparative studies of the efficiency of the photocatalysis process with different methods of using photocatalysts, namely when introduced on the external surface and into the internal structure of polyethylene film. Is it possible to predict whether the efficiency of the photocatalysis process will change? If so, what exactly will affect it?

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:



Professor, Doctor of Technical  
Sciences, Professor  
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