

REVIEW

of official opponent on thesis of

Li Che

on the topic «Organo-mineral textured coatings with enhanced water repellency
(Органо-мінеральні текстуровані покриття з підвищеним
водовідштовхуванням)»,

submitted for the degree of Doctor of Philosophy

field of knowledge 16 – Chemical and Bioengineering
specialty 161 – Chemical Technology and Engineering

Relevance of the dissertation topic.

The topic of the dissertation is highly relevant, as it is dedicated to the development of organo-mineral textured coatings with adjustable hydrophobicity—an emerging class of materials with significant potential for industrial implementation. The ability to fine-tune water repellency levels allows adapting surfaces for various functional requirements, ranging from self-cleaning and anti-fouling to condensation control and protection against moisture-induced degradation. The design of such materials is directly aligned with the increasing demand for sustainable and multifunctional coatings in construction, transportation, and energy systems.

Of particular importance is the proposed valorization of red mud waste, which is traditionally considered an environmental burden due to its high alkalinity and large accumulation volumes. The research demonstrates a promising pathway for its conversion into a functional filler with surface inertness suitable for forming stable hydrophobic coatings. This solution not only contributes to environmental remediation but also creates added economic value by integrating industrial by-products into high-performance materials.

The applied approach—based on conventional synthesis and coating methods—ensures technological accessibility and scalability. Unlike complex lithographic or vacuum-based techniques, the use of readily available polymer matrices and dispersive fillers enables the implementation of hydrophobic coatings on large surfaces. Such technological simplicity significantly enhances the chances of transferring laboratory results to industrial practice. Consequently, the topic is fully consistent with the modern trend of developing sustainable materials through resource-efficient and scalable processes.

Assessment of the validity of the scientific results of the dissertation, their reliability and novelty.

The scientific novelty of the dissertation research results lies in the following:

The dissertation presents scientifically novel solutions in the field of functional coatings. A major innovation is the demonstrated possibility of utilizing thermally

treated and organosilane-modified red mud as a texture-forming component in hydrophobic coatings. This is the first evidence that inertization and chemical modification of such industrial waste can produce surfaces with stable high contact angles ($\sim 143^\circ$), enabling its transition from an environmental liability into a value-added material.

Another original result concerns the controlled synthesis of zinc oxide particles with hierarchical architectures. The introduction of TiO_2 and SiO_2 dopants was shown to tailor the particle morphology and significantly enhance the water repellency of coatings. The research also revealed that the hierarchical structure ensures hydrophobic performance across a wide range of compositions, unlike conventional single-phase fillers. In addition, the work proves that TiO_2 -doped ZnO particles possess enhanced photoactivity, increasing by more than sixfold compared with undoped ZnO , which adds multifunctionality to the developed coatings.

The validity and reliability of the results are supported by systematic experimentation and the use of complementary analytical techniques. Structural and phase analyses were carried out by XRD and electron microscopy, while surface chemistry was examined via FTIR and photoluminescence spectroscopy. Wettability measurements were statistically processed, ensuring accuracy and repeatability. The research design included control samples and comparative studies, allowing clear attribution of observed effects to specific structural modifications.

The scientific reasoning is logically built upon established theoretical models of wetting and confirmed by consistent experimental trends. The coherence of results obtained from independent methods and their publication in recognized scientific journals substantiate the credibility and robustness of the conclusions.

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

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

In terms of content, Li Che's dissertation fully complies with the Higher Education Standard for specialty 161 – Chemical Technology and Engineering and research areas in accordance with the Chemical Technology and Engineering educational program.

The dissertation is a complete scientific work and demonstrates the applicant's personal contribution to the scientific field of developing new substances and materials.

Having reviewed the similarity report based on the results of checking the dissertation for text matches, it can be concluded that Li Che's dissertation is the result of the applicant's independent research and does not contain elements of falsification, compilation, fabrication, plagiarism, or borrowing. The ideas, results, and texts of other authors used are properly referenced to the relevant source.

Language, style, and structure of presentation

The dissertation is written in English.

The dissertation consists of an introduction, 6 chapters, conclusions, and a list of references. The total number of pages in the paper is 165, with 133 pages for the main part.

The dissertation is written in grammatically correct and stylistically coherent English, corresponding to the standards of scientific and technical literature in the field of chemical engineering. The presentation is distinguished by consistency, clarity, and accessibility. The author demonstrates the ability to formulate complex scientific ideas in a logically structured manner, ensuring smooth transitions between theoretical concepts, experimental design, and interpretation of results. The text avoids redundancy and ambiguity, while maintaining the necessary level of detail to convey experimental findings convincingly.

The chosen writing style is academic and formal, relying on well-established terminology accepted in the domains of materials science, surface engineering, and polymer technology. The author consistently uses precise definitions and symbols, which promotes unambiguous understanding of key concepts. The discussion is supported by numerical data, illustrative figures, and tables, all properly referenced within the text. The use of modern scientific vocabulary reflects familiarity with international research discourse.

The structure of the dissertation fully complies with the requirements for doctoral theses in chemical technology and engineering. The work consists of an introduction, six chapters, conclusions, a reference list, and appendices. The Introduction substantiates the relevance of the chosen research topic, identifies the object, subject, goal, and tasks, and outlines the scientific novelty and practical significance. It also specifies the connection of the research with state and institutional programs, ensuring contextual completeness.

The first chapter provides a comprehensive review of literature sources on surface wettability, theoretical models such as Wenzel and Cassie–Baxter, and current strategies for producing hydrophobic and superhydrophobic surfaces. The author critically analyzes existing technologies—chemical texturing, plasma modification, nanoparticle coatings—pointing out their scalability limitations and setting the stage for the proposed approach based on organo-mineral systems.

The second chapter is devoted to the experimental methodology. The presentation is logically ordered: it begins with a description of raw materials, proceeds to surface modification methods, and concludes with a detailed list of analytical techniques (XRD, SEM, TEM, FTIR, PL spectroscopy, and goniometric measurements). The precision of methodological descriptions allows reproducibility of the experiments, which is a hallmark of well-structured scientific writing.

The third and fourth chapters report the preparation and characterization of coatings based on red mud and zinc oxide particles, respectively. Each subsection follows a consistent pattern—description of synthesis, structural and morphological analysis, and evaluation of surface wettability. Figures and graphs are clearly labeled, and their discussion is integrated into the narrative, avoiding isolated data presentation.

The fifth chapter synthesizes the obtained results, focusing on the correlation between composition, structure, and functional performance. The author uses logical argumentation supported by theoretical considerations, confirming the soundness of interpretations.

The sixth chapter extends the study to thin organic layers on textured substrates, assessing how they influence wettability and condensation behavior. The exposition is concise and logically connected to previous results, highlighting continuity of research objectives.

The Conclusions succinctly summarize the achieved results and demonstrate their correspondence to the initial aims. They are formulated clearly and reflect both theoretical significance and practical applicability.

Throughout the dissertation, the language remains clear and precise. Each chapter begins with a brief introduction and ends with intermediate conclusions, ensuring a coherent flow of information. References to literature are accurate and formatted according to academic requirements. The structure of the text, the clarity of reasoning, and the consistency of terminology contribute to high readability and comprehension of the research.

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

Presentation of dissertation results

The scientific results of the dissertation are presented in 6 scientific publications by the applicant, including: 4 articles in scientific journals included in the list of scientific professional publications of Ukraine at the date of publication; 2 articles in periodical scientific publications indexed in the Web of Science Core Collection and Scopus databases, of which 2 articles are in publications classified as first and second quartile (Q1–Q2) according to the SCImago Journal and Country Rank or Journal Citation Reports classification.

The results of the dissertation were also tested at 3 scientific conferences.

The applicant's publications are distinguished by their high scientific quality, relevance to the topic of the dissertation, and the current level of development in the field. The works comply with all requirements of academic integrity, and no cases of plagiarism or incorrect citation have been found. The applicant's contribution to joint publications is significant and clearly defined.

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

Shortcomings and comments on the dissertation

1. Throughout several tables (notably Table 3.2 and Table 4.1), the numerical values of contact angles and other measured parameters are presented without specifying standard deviations or confidence intervals. Although the text mentions the reproducibility of experiments, the absence of explicit uncertainty values in the tables may limit the reader's ability to assess statistical significance and compare the stability of results between different samples.
2. Figure 3.2 presents particle size distributions before and after sintering and sieving, but key descriptors (median size D50, distribution width) are not explicitly provided. Without these numerical indicators, it is difficult to quantitatively assess how granulometry influences texture formation and hydrophobic response.
3. While Chapter 4 focuses on the synthesis of ZnO-based particles and Chapter 5 on composite coatings, the transition between these sections could be more explicitly articulated. The relationship between the morphological features of ZnO/TiO₂/SiO₂ particles (Fig. 4.5) and the final coating performance (Fig. 5.3) might benefit from a clearer cross-reference or summary table.
4. In Chapter 5, the relationship between the filler content and the resulting contact angle is presented qualitatively (Fig. 5.2), yet the exact composition–property correlation is not numerically modeled or statistically analyzed. A regression or fitting approach could reveal thresholds of hydrophobicity and clarify whether the dependence is linear or exhibits saturation.
5. While UV stability of ZnO-containing systems is discussed in Chapter 5, the long-term performance of coatings based on modified red mud (Chapter 3) under environmental exposure is not examined. Given the practical relevance of such materials, a short-term aging or water immersion test could provide insight into the stability of their hydrophobicity.
6. Although SEM images in Figs. 4.2 and 4.3 clearly demonstrate the formation of rod-like and flower-like ZnO particles, no shape descriptors (aspect ratio, circularity) or size distributions are reported. Providing these metrics would allow a more rigorous comparison between morphologies synthesized under different conditions.
7. The text mentions that coatings possess sufficient mechanical strength for handling and adhesion (Section 5.3), but no quantitative abrasion or adhesion test results (e.g., cross-cut or tape tests) are included. Such data would be valuable to substantiate the claim of mechanical robustness.

8. A few instances of inconsistent terminology were identified: for example, using the term “superhydrophobic” in Table 3.2 for contact angles below 150°, and alternating references to “contact angle hysteresis” vs. “adhesion angle.” Additionally, some figure captions lack units or scale-bar descriptions (e.g., Fig. 3.5).

I consider that the comments made are not decisive and do not diminish the overall scientific novelty and practical significance of the results, nor do they affect the positive assessment of the dissertation.

Conclusion on the dissertation

I consider that the doctoral dissertation of Li Che on the topic “Organo-mineral textured coatings with enhanced water repellency” has been completed at a high scientific level, does not violate the principles of academic integrity, and is a complete scientific study, the combination of theoretical and practical results of which solves a scientific problem that is of significant importance for the field of knowledge 16 – Chemical and Bioengineering. In terms of relevance, practical value, and scientific novelty, the dissertation fully complies with the requirements of the current legislation of Ukraine, as provided for in paragraphs 6–9 of the "Procedure for awarding the degree of Doctor of Philosophy and revoking 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 Resolution of the Cabinet of Ministers of Ukraine No. 44 of January 12, 2022.

The applicant Li Che deserves to be awarded the degree of Doctor of Philosophy in the field of knowledge 16 – Chemical and Bioengineering specialty 161 – Chemical Technology and Engineering

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