REVIEW

of the official reviewer for dissertation work of Bekissanova Zhanar on the topic: "Synthesis, characterization and antibacterial activity study of composites based on natural adsorbents and silver nanoparticles", submitted for the degree of Doctor of Philosophy (PhD) in Educational Program "6D072000 – Chemical technology of inorganic substances"

№	Criteria	Eligibility (one of the options must be checked)	Justification of the position of the official reviewer
1.	The topic of the thesis (as of the date of its approval) corresponds to the directions of development of science and/or state programs	1.1 Compliance with priority areas of science development or government programs:	The dissertation work was carried out within the framework of grant funding from the Ministry of Education and Science of the Republic of Kazakhstan
		1) The thesis was completed within the framework of a project or target program financed from the state budget (indicate the name and number of the project or program) 2) The thesis was completed within the framework of another state program (indicate the name of the program) 3) The dissertation corresponds to the priority direction of the development of science, approved by the Higher Scientific and Technical Commission under the Government of the Republic of Kazakhstan (indicate the direction)	AP05131647 Physical-chemical basis for obtaining multifunctional biomedical materials (nanofilms) with antibacterial and anti-inflammatory properties» AP09561734 Development of conditions for the production of multipurpose antibacterial composite material based on Kazakhstan kaolin AP14972864 Synthesis, characterization, photoluminescent and antibacterial properties of europium/biosilica and silver/biosilica nanomaterials
2.	Importance for science	The work makes/does not make a significant contribution to science, and its importance is well disclosed/not disclosed	The dissertation makes a significant contribution to science, and its importance is well disclosed. Which is confirmed by publications in high level scientific journals: Biomimetics, 9(1), 5. https://doi.org/10.3390/biomimetics9010005 (Q1 WoS) Colloids and Surfaces B: Biointerfaces, 112908.

			https://doi.org/10.1016/j.colsurfb.2022.112908 (Q2 WoS) Materials, 13(15), 2020 , 3409., https://doi:10.3390/ma13153409 (Q2 WoS)
3.	The principle of independence	Self-reliance level: 1) High; 2) Medium; 3) Low; 4) No independence	It is confirmed by the fact that in three publications the applicant is the first author
4.	The principle of inner unity	4.1 Justification of the relevance of the thesis: 1) Justified; 2) Partially justified; 3) Not justified.	There is no doubt about it. The development of new types of antimicrobial materials based on silver nanoparticles and natural matrices is very relevant.
		4.2 The content of the thesis reflects the topic of the thesis: 1) Reflects; 2) Partially reflects; 3) Does not reflect	There is no doubt about it. The content of the thesis fully reflects the topic of the thesis.
		4.3. The purpose and objectives correspond to the topic of the thesis: 1) correspond; 2) partially correspond; 3) do not correspond	The purpose and objectives totally correspond to the topic of the thesis. The purpose and objectives are clearly formulated. All the conducted research is aimed at achieving the purpose and objectives.
		4.4 All sections and provisions of the thesis are logically interconnected: 1) completely interconnected; 2) the interconnection is partial; 3) there is no interconnection	Articles published later have links to previously published articles. Article Bekissanova, Z., Railean, V., Wojtczak, I., Brzozowska, W., Trykowski, G., Ospanova, A., & Sprynskyy, M. (2023). Synthesis and Antimicrobial Activity of 3D Micro–Nanostructured Diatom Biosilica Coated by Epitaxially Growing Ag-AgCl Hybrid Nanoparticles. Biomimetics, 9(1), 5.

			https://doi.org/10.3390/biomimetics9010005 has a reference number 41 which is an article: Kubasheva, Z., Sprynskyy, M., Railean-Plugaru, V., Pomastowski, P., Ospanova, A., & Buszewski, B. (2020). Synthesis and Antibacterial Activity of (AgCl, Ag) NPs/Diatomite Hybrid Composite. Materials, 13(15), 2020 , 3409., https://doi:10.3390/ma13153409 The article Bekissanova, Z., Railean, V., Brzozowska, W., Wojtczak, I., Ospanova, A., Buszewski, B., & Sprynskyy, M. (2022). Synthesis, characterization of silver/kaolinite nanocomposite and studying its antibacterial activity. Colloids and Surfaces B: Biointerfaces, 112908. https://doi.org/10.1016/j.colsurfb.2022.112908 has a reference number 40 wich is an article: Kubasheva, Z., Sprynskyy, M., Railean-Plugaru, V., Pomastowski, P., Ospanova, A., & Buszewski, B. (2020). Synthesis and Antibacterial Activity of (AgCl, Ag) NPs/Diatomite Hybrid Composite. Materials, 13(15), 2020 , 3409., https://doi:10.3390/ma13153409
		4.5 The new solutions (principles, methods) proposed by the author are reasoned and evaluated in comparison with the known solutions: 1) there is a critical analysis; 2) partial analysis; 3) the analysis does not represent one's own opinions, but quotes from other authors	There is no doubt about it. According to Article *Kubasheva, Z., Sprynskyy, M., Railean-Plugaru, V., Pomastowski, P., Ospanova, A., & Buszewski, B. (2020). Synthesis and Antibacterial Activity of (AgCl, Ag) NPs/Diatomite Hybrid Composite. Materials, 13(15), 2020 , 3409.,*

			https://doi:10.3390/ma13153409 before the development of the method for the synthesis of silver nanoparticles, the authors studied 37 literary sources. The article *Bekissanova, Z., Railean, V., Brzozowska, W., Wojtczak, I., Ospanova, A., Buszewski, B., & Sprynskyy, M. (2022). Synthesis, characterization of silver/kaolinite nanocomposite and studying its antibacterial activity. Colloids and Surfaces B: Biointerfaces, 112908. https://doi.org/10.1016/j.colsurfb.2022.112908* contains 98 references to literature sources
5.	Scientific novelty principle	5.1 Are the scientific results and provisions new? 1) completely new; 2) partially new (25-75% are new); 3) not new (less than 25% are new)	Scientific results and provisions are partially new, since the use of silver for antibacterial purposes and the synthesis of silver composites based on natural matrices is known from the literature, however, the matrices used were investigated for the first time.
		5.2 Are the dissertation findings new? 1) completely new; 2) partially new (25-75% are new); 3) not new (less than 25% are new)	Partially new, as they relate to the creation of new analogues of generally known systems.
		5.3 Technical, technological, economic or management decisions are new and reasonable: 1) completely new; 2) partially new (25-75% are new); 3) not new (less than 25% are new)	Partially new, as they relate to the creation of new analogues of generally known systems.
6.	The validity of the main findings	All main conclusions are/are not based on scientifically significant evidence or well-grounded (for qualitative research and areas of training in the arts and humanities)	The validity of the main findings is beyond doubt, since modern research methods and methods of statistical processing of research results are used.

7.	The main provisions for the defense	It is necessary to answer the following questions for each provision separately: **Provision 1** A new composite material with antibacterial properties based on natural diatomite containing (0.71, 4.65, 7.21%) hybrid nanoparticles (1–10 nm) of silver chlorides and metallic silver, (AgNPs/AgClNPs/diatomite) is obtained by formation/immobilization of silver nanoparticles on the surface of a mineral carrier using ion exchange reactions and chemical reduction with an environmentally friendly reducing agent (hydrogen peroxide). The number of silver chloride nanoparticles in the composite is limited by the amount of halite impurity in the diatomite. The synthesized composite exhibits high antibacterial activity against *S.aureus* and *K.pneumoniae* with a minimum inhibitory concentration of the composite of 5 mg/ml and 10 mg/ml, respectively, with a silver content of 0.71% in the composite. 7.1 Is the provision proven? 1) proven; 2) rather proven; 3) rather not proven; 4) not proven 7.2 Is it trivial? 1) yes; 2) no 7.3 Is it new? 1) yes; 2) no 7.4 Application level: 1) narrow; 2) medium; 3) wide	The **Provision 1** is proven in article Kubasheva, Z., Sprynskyy, M., Railean-Plugaru, V., Pomastowski, P., Ospanova, A., & Buszewski, B. (2020). Synthesis and Antibacterial Activity of (AgCl, Ag) NPs/Diatomite Hybrid Composite. Materials, 13(15), 2020 , 3409., https://doi:10.3390/ma13153409 It is not trivial, since a new approach has been applied to the synthesis and research of previously unexplored composites. It is new , because a new type of carrier was used - Mugodzhar diatomite An application level is narrow, since only the antibacterial activity of the obtained composites has been demonstrated

		7.5 Is it proven in the article? 1) yes; 2) no	It is proven in the article: Kubasheva, Z., Sprynskyy, M., Railean-Plugaru, V., Pomastowski, P., Ospanova, A., & Buszewski, B. (2020). Synthesis and Antibacterial Activity of (AgCl, Ag) NPs/Diatomite Hybrid Composite. Materials, 13(15), 2020 , 3409., https://doi:10.3390/ma13153409 ***There is one comment regarding this provision*** According to Table 1 (Page 5, in the article Kubasheva, Z., Sprynskyy, M., Railean-Plugaru, V., Pomastowski, P., Ospanova, A., & Buszewski, B. (2020). Synthesis and Antibacterial Activity of (AgCl, Ag) NPs/Diatomite Hybrid Composite. Materials, 13(15), 2020, 3409., https://doi:10.3390/ma13153409), the original diatomite does not contain sulfur in its composition, whereas the composites contain 0.2-0.4% sulfur. How did it appear there? Calcium, present in the original diatomite, is absent in two out of three developed composites. Where did it disappear? And most importantly, where is hydrogen? According to the results of elemental analysis, neither the original diatomite nor the composites contain hydrogen, while in Section 3-1 of the mentioned article (p.4), the authors point out the presence of characteristic vibrations of Al-OH, Si-OH, and H-OH groups in the IR spectra of the samples.

			Thus, is hydrogen present in your composite and original material or not? And if it is present, then the composition of the composite may not be equal to 0.71%, 4.65%, 7.21% as stated.
		Provision 2 Composite materials based on natural kaolinite containing (0.60, 2.05 and 7.0%) nanoparticles of metallic silver ranging in size from 20 to 50 nm, are obtained by chemical reduction using an environmentally friendly reducing agent - hydrogen peroxide, exhibit antibacterial activity against gram-positive S.aureus and gram-negative K.pneumoniae, E.coli strains of bacteria at a minimum inhibitory concentration of the composite of 10 mg/ml and a silver content of 7% in the composite. 7.1 Is the provition proven? 1) proven; 2) rather proven; 3) rather not proven; 4) not proven	The **Provision 2** is proven in article Bekissanova, Z., Railean, V., Brzozowska, W., Wojtczak, I., Ospanova, A., Buszewski, B., & Sprynskyy, M. (2022). Synthesis, characterization of silver/kaolinite nanocomposite and studying its antibacterial activity. Colloids and Surfaces B: Biointerfaces, 112908. https://doi.org/10.1016/j.colsurfb.2022.112908
		7.2 Is it trivial? 1) yes; 2) no	It is not trivial, since a new approach has been applied to the synthesis and research of previously unexplored composites.
		7.3 Is it new?	It is new, because a new type of carrier

		1) yes; 2) no 7.4 Application level: 1) narrow; 2) medium; 3) wide 7.5 Is it proven in the article? 1) yes; 2) no	was used – kaolinite from Alekseev clay deposits of Kokshetau region (Kazakhstan) and new method for composites preparation was developed. An application level is approximately narrow, since only the antimicrobial assay of silver/kaolinite nanocomposite has been demonstrated The **Provision 2** is proven in article Bekissanova, Z., Railean, V., Brzozowska, W., Wojtczak, I., Ospanova, A., Buszewski, B., & Sprynskyy, M. (2022). Synthesis, characterization of silver/kaolinite nanocomposite and studying its antibacterial activity. Colloids and Surfaces B: Biointerfaces, 112908. https://doi.org/10.1016/j.colsurfb.2022.112908 *The same question concerning to elemental compositions of initial kaolinite and composites based on them. Where is hydrogen?*
		Provision 3 A new 3D micro-nanostructured composite material based on biosilica (AgCl,Ag)NPs/biosilica contains epitaxial hybrid intergrowths of metallic silver and silver chloride in the form of AgCl-Ag hybrid nanoparticles (4.61 and 8.49% silver) with a predominant size from 5 to 25 nm in the form of crystalline twins Axialy Twined (AT) and Layer Twinned (LT). The composites exhibit high antibacterial activity against gram-positive *S.aureus* and gram-negative *K.pneumoniae*, *E.coli* strains of bacteria with a minimum inhibitory concentration of the composite of 1.25 mg/ml and a silver content of 4.61% in the composite.	

		7.1 Is the provision proven? 1) proven; 2) rather proven; 3) rather not proven; 4) not proven	The **Provision 3** is proven in article Bekissanova, Z., Railean, V., Wojtczak, I., Brzozowska, W., Trykowski, G., Ospanova, A., & Sprynskyy, M. (2023). Synthesis and Antimicrobial Activity of 3D Micro–Nanostructured Diatom Biosilica Coated by Epitaxially Growing Ag-AgCl Hybrid Nanoparticles. Biomimetics, 9(1), 5.https://doi.org/10.3390/biomimetics9010005
		7.2 Is it trivial? 1) yes; 2) no	It is not trivial, since a new approach has been applied to the synthesis and research of previously unexplored composites.
		7.3 Is it new? 1) yes; 2) no	It is new, because a new approach of composites preparation was demonstrated by impregnation of diatom biosilica into the aqueous solution of silver nitrate with two different concentrations.
		7.4 Application level: 1) narrow; 2) medium; 3) wide	An application level is approximately narrow, since only the antimicrobial assay of silver/kaolinite nanocomposite has been demonstrated
		7.5 Is it proven in the article? 1) yes; 2) no	The **Provision 3** is proven in article Bekissanova, Z., Railean, V., Wojtczak, I., Brzozowska, W., Trykowski, G., Ospanova, A., & Sprynskyy, M. (2023). Synthesis and

			Antimicrobial Activity of 3D Micro–Nanostructured Diatom Biosilica Coated by Epitaxially Growing Ag-AgCl Hybrid Nanoparticles. Biomimetics, 9(1), 5.https://doi.org/10.3390/biomimetics9010005 *The same question again. The authors (Bekissanova, Z., Railean, V., Wojtczak, I., Brzozowska, W., Trykowski, G., Ospanova, A., & Sprynskyy, M. (2023). Synthesis and Antimicrobial Activity of 3D Micro–Nanostructured Diatom Biosilica Coated by Epitaxially Growing Ag-AgCl Hybrid Nanoparticles. Biomimetics, 9(1), 5.https://doi.org/10.3390/biomimetics9010005) talk about the vibrations of hydrogen-containing functional groups that occur in the IR spectra (p.5 of the article), while the elemental composition shown by them does not contain hydrogen (p. 6 of the article).* . **Provision 4**
		Provision 4 The antibacterial activity of hybrid silver nanoparticles is due to the synergistic effect of two types of nanoparticles, while composites with a predominant content of silver chloride nanoparticles have a greater inhibitory effect compared to metallic silver nanoparticles, both against gram-positive *S.aureus* and gram-negative *K.pneumoniae*, *E.coli* strains of bacteria from the typical collection cultures and clinical isolates (diabetic foot infection and wound isolates). 7.1 Is the provision proven?	The **Provision 4** is proven in articles

		1) proven; 2) rather proven; 3) rather not proven; 4) not proven 7.2 Is it trivial? 1) yes; 2) no	Kubasheva, Z., Sprynskyy, M., Railean-Plugaru, V., Pomastowski, P., Ospanova, A., & Buszewski, B. (2020). Synthesis and Antibacterial Activity of (AgCl, Ag) NPs/Diatomite Hybrid Composite. Materials, 13(15), 2020 , 3409., https://doi:10.3390/ma13153409 Bekissanova, Z., Railean, V., Brzozowska, W., Wojtczak, I., Ospanova, A., Buszewski, B., & Sprynskyy, M. (2022). Synthesis, characterization of silver/kaolinite nanocomposite and studying its antibacterial activity. Colloids and Surfaces B: Biointerfaces, 112908. https://doi.org/10.1016/j.colsurfb.2022.112908 Bekissanova, Z., Railean, V., Wojtczak, I., Brzozowska, W., Trykowski, G., Ospanova, A., & Sprynskyy, M. (2023). Synthesis and Antimicrobial Activity of 3D Micro–Nanostructured Diatom Biosilica Coated by Epitaxially Growing Ag-AgCl Hybrid Nanoparticles. Biomimetics, 9(1), 5.https://doi.org/10.3390/biomimetics9010005 It is not trivial, since a new type of nanocomposites has been applied for combating against different types of gram-positive and gram-negative

		7.3 Is it new? 1) yes; 2) no 7.4 Application level: 1) narrow; 2) medium; 3) wide 7.5 Is it proven in the article? 1) yes; 2) no	microorganisms. It is new, because an antibacterial activity of these composites has been demonstrated for the first time. An application level is medium, since the different type of microorganisms are exposed to the developed composites The **Provision 4** is proven in articles Kubasheva, Z., Sprynskyy, M., Railean-Plugaru, V., Pomastowski, P., Ospanova, A., & Buszewski, B. (2020). Synthesis and Antibacterial Activity of (AgCl, Ag) NPs/Diatomite Hybrid Composite. Materials, 13(15), 2020 , 3409., https://doi:10.3390/ma13153409 Bekissanova, Z., Railean, V., Brzozowska, W., Wojtczak, I., Ospanova, A., Buszewski, B., & Sprynskyy, M. (2022). Synthesis, characterization of silver/kaolinite nanocomposite and studying its antibacterial activity. Colloids and Surfaces B: Biointerfaces, 112908. https://doi.org/10.1016/j.colsurfb.2022.112908 Bekissanova, Z., Railean, V., Wojtczak, I., Brzozowska, W., Trykowski, G., Ospanova, A., & Sprynskyy, M. (2023). Synthesis and Antimicrobial

			Activity of 3D Micro–Nanostructured Diatom Biosilica Coated by Epitaxially Growing Ag-AgCl Hybrid Nanoparticles. Biomimetics, 9(1), 5.https://doi.org/10.3390/biomimetics9010005 *There is one question for all provisions: it is not clear how the particle size distribution was calculated?*
8.	The principle of reliability Reliability of sources and information provided	8.1 Choice of methodology - is justified or the methodology is described in sufficient detail 1) yes; 2) no	All experiments are described in detail and can be repeated
		8.2 The results of the thesis were obtained using modern methods of scientific research and methods of processing and interpreting data using computer technologies: 1) yes; 2) no	The work uses modern research methods such as XRD, SEM-EDX, FTIR, TEM, Zeta-Potential Measurements, Photoluminescence Analysis etc
		8.3 Theoretical conclusions, models, identified relationships and patterns have been proven and confirmed by experimental research (for areas of training in pedagogical sciences, the results have been proven on the basis of a pedagogical experiment): 1) yes; 2) no	All conclusions are confirmed by experimental studies performed in threefold repetition.
		8.4 Important statements are confirmed / partially confirmed / not confirmed by references to current and reliable scientific literature	All statements are confirmed by references to current and reliable scientific literature.
		8.5 Used literature sources are sufficient/not sufficient for a literature review	All articles contain a sufficient number of references to scientific literature to provide comprehensive information about the studied objects.
9	Practical value principle	9.1 The thesis has theoretical value: 1) yes;	The theoretical significance of the work is to expand knowledge of the method of

		2) no	synthesis of hybrid silver nanocomposites using natural matrices and the antibacterial activity of such matrices.
		9.2 The thesis is of practical importance and there is a high probability of applying the results obtained in practice: 1) yes; 2) no	The results obtained have a high potential of applicability for biomedical research.
		9.3 Are the practice suggestions new? 1) completely new; 2) partially new (25-75% are new); 3) not new (less than 25% are new)	Partially, since the antibacterial activity of silver ions and silver-based nanocomposites has been known for a long time, however, the proposed synthesis method is new.
10.	The quality of writing and design	Academic writing quality: 1) high; 2) average; 3) below average; 4) low.	The articles are written in very highly rated journals, in which it is impossible to publish results written with low quality.

I recommend:

1) to award the degree of Doctor of Philosophy (PhD) in Educational Program "6D072000 – Chemical technology of inorganic substances" to applicant Bekissanova Zhanar.

Official Reviewer:
Head of Scientific Center
for Radioecological Researches
of Shakarim University of Semey, PhD

(place of work, academic title)

(signature)

ALEXEY KLIVENKO
(FULL NAME)

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Персоналды басқару және ҚАБ басшысы
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