

REVIEW

of the official reviewer for dissertation work

Zhumagaliyeva Assem Nurbergenovna on the theme «Production and testing of carbonized rice husk-based nanocomposites for capturing of carbon dioxide» presented for the degree of Doctor of Philosophy (PhD) in the specialty «6D074000 - Nanomaterials and nanotechnology».

№	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: <u>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)</u>	Dissertation work was carried out on the candidate's own initiative without the framework of a project or target program financed from the state budget, but the final applied results of the work could be led to accomplish the priority direction of the development of science approved by the Higher Scientific and Technical Commission under the Government of the Republic of Kazakhstan for 2021-2023 - "Rational use of water resources, flora and fauna, ecology".
2.	Importance for science	<u>The work makes a significant contribution to science, and its importance is well disclosed</u>	The candidate performed new methods of synthesis nanocomposites based on carbonized rice husk and magnetite nanoparticles and testing its at post-combustion flue-gas conditions.
3.	The principle of independence	<u>Self-reliance level:</u> <u>1) High</u>	Zhumagaliyeva A.N. obtained nanocomposites and nanoporous materials by base-leaching process at laboratory of Institute of Combustion Problems (Almaty) and checked at fixed bed of Institute for Combustion Research at the University of Friedrich Second (Naples). All elaboration were provided by the candidate personally and were published by her in several articles.
4.	The principle of inner unity	<u>4.1 Justification of the relevance of the thesis:</u> <u>1) Justified</u>	Materials with a distinctive surface chemistry could find a large application in adsorption technologies. CO ₂ adsorption by low-cost metal oxide surfaces strongly encourage the possible use as sorbents. Fe ₃ O ₄ - a low cost iron metal oxide, biocompatible, non-toxic for human body, it was applied in a variety of fields including gas sorption. Magnetite, like other metal oxides exhibits active sites exposed at the surface which can interact with gaseous molecules, but the problem of

			<p>predisposition to agglomeration process of the particles is solved by using carbonaceous matrix which helps eliminate this disadvantage. In this work carbonized rice husk was used as carbon matrix or as a support for the preparation of composite materials containing iron oxide particles as active nanomaterials to adsorb CO₂. This material has a great potential for technological applications since it can be converted into different types of fuels and chemicals through a variety of thermochemical conversion processes. The effectiveness of production a new nanocomposite sorbents is primarily driven by economics because it did not implicate significant modifications to the combustion process technologies currently used.</p>
		<p>4.2 The content of the thesis reflects the topic of the thesis: 1) <u>Reflects</u></p>	<p>The topic of the work covers and reflects the content of the defended thesis. Precisely, this work is aims at obtain composite carbon materials with a nanostructure and nanoporous morphology for capturing carbon dioxide under post-combustion flue-gas conditions, without additional pressure and thermochemical effects.</p>
		<p>4.3. The purpose and objectives correspond to the topic of the thesis: 1) <u>correspond</u></p>	<p>The purpose and objectives corresponded to the topic of the thesis. Namely, investigated of carbonized rice husk (cRH) structure used as carbonaceous matrix in nanocomposites; have been synthesized composite materials based on carbonized rice husk coated with magnetite particles; evaluated of optimal parameters for alkaline treatment of cRH and study of CO₂ adsorption capacity depending on surface and structural characteristics; made up evaluation of CO₂ adsorption properties of fabricated materials by breakthrough experiments on a laboratory-scale fixed-bed micro-reactor under post-combustion flue gas conditions.</p>
		<p>4.4 All sections and provisions of the thesis are logically interconnected: 1) <u>completely interconnected</u></p>	<p>Literature review, experimental part and their results and provisions formulated upon discussion of the results show up logical interconnection all part of the defended research. The validity of the set goal follows from the current state of affairs shown in the introduction section. Reaching results and their interpretation with formulation of scientifically proven provisions the candidate shows logical and fully integral approach at conclusion.</p>

		<p>4.5 The new solutions (principles, methods) proposed by the author are reasoned and evaluated in comparison with the known solutions: <u>1) there is a critical analysis</u></p>	<p>The candidate proposes a new approach to the production of nanocomposite sorbents based rice husk and magnetite for gas adsorption, mainly CO₂. A new technological method based on optimal conditions was authorized by the National Institute of Intellectual Property of the Republic of Kazakhstan.</p>
5.	Scientific novelty principle	<p>5.1 Are the scientific results and provisions new? <u>1) completely new</u></p>	<p>The scientific results and provisions are completely new, because first ever nanostructured composite materials were synthesized by coating cRH with magnetite nanoparticles and explored its CO₂ adsorption capacity. on the effect of different alkaline treatments for removal of cRH inorganic components was carried out, also CO₂ capture performances were evaluated. The influence content of magnetite particles in carbonized rice husk composites on CO₂ adsorption capacity was established. Systematic investigation of the CO₂ capture sorption mechanism of the produced composites reported as a function of the breakthrough time and function of the SSA.</p>
		<p>5.2 Are the dissertation findings new? <u>1) completely new</u></p>	<p>The findings in the thesis are completely new in the discovery of the increasing CO₂ sorption properties of produced composite material, modes and methods are selected, the patent is received and an article is written</p>
		<p>5.3 Technical, technological, economic or management decisions are new and reasonable: <u>1) completely new</u></p>	<p>Fundamental research on gas adsorption has been originated since the start industrial revolution. For the sorption of gases, solid sorbents have a lot of advantages, such as great capacity, selectivity, easy handling and reduced energy for regeneration which have long been known. In this dissertation work produced of sorbents for carbon dioxide based on alternative sources and used as a nanocomposite material first time applicate, tested under normal conditions without additional manipulations, it can be concluded that in this work technical, technological and economic solutions are new.</p>
6.	The validity of the main findings	<p><u>All main conclusions are based on scientifically significant evidence or reasonably well substantiated</u></p>	<p>Main conclusions are based on scientifically significant evidence and experimental results, are completely justified and the comparative analyzed with the modern literature data.</p>
7.	The main provisions for the	<p>It is necessary to answer the following questions for each provision separately:</p>	<p>Provision I is new, non-trivial, and has a wide range of applications for investigations of CO₂ solid sorbents, obtained by carbonized material</p>

defense	<p>1. Carbonized rice husk (cRH) has high CO₂ uptake up to 11.26 mg/g under post-combustion flue-gas conditions. The sorption capacity of cRH significantly increases to 29.2 mg/g by leaching with an increase in the concentration of the base NH₄OH to 28% in the aqueous solution.</p> <p>7.1 Is the provision proven? - <u>1) proven;</u> 7.2 Is it trivial? - <u>2) no</u> 7.3 Is it new? - <u>1) yes;</u> 7.4 Application level: - <u>3) wide</u> 7.5 Is it proven in the article? - <u>1) yes</u></p>	<p>matrix and checked under post-combustion flue-gas conditions. The carbonization of rice husk was carried out in auger furnace at 500-800° in an argon atmosphere. the optimal parameters were selected according to the exposure time and concentration in the ammonium hydroxide solution. The increase in trapping, the saturation time of the substrate with obtained sorbent increased linearly. The position was fully proven and published in the rating journal Combustion Science and Technology (Q2, percentile 62%).</p>
	<p>2. Prevention of agglomeration of iron oxide particles in a composite material based on cRH and nanoporous magnetite nFM, in a ratio of 67:33 co-precipitated with TMAOH, effectively increased the sorption capacity to 15.6 mg/g, which exceeds individual indicators of the components by 38% and 13%, respectively. This effect is due to an increase in the volume of microspores up to $3.81 \cdot 10^{-2} \text{ cm}^3/\text{g}$ and a good synergism between the chemisorption of iron oxide nanoparticles and the physical adsorption of carbon in cRH.</p> <p>7.1 Is the provision proven? - <u>1) proven;</u> 7.2 Is it trivial? - <u>2) no</u> 7.3 Is it new? - <u>1) yes;</u> 7.4 Application level: - <u>3) wide</u> 7.5 Is it proven in the article? - <u>1) yes</u></p>	<p>Provision 2 is new, non-trivial, determines the optimal parameters in percentage of nanocomposites components, where nanosized magnetite particles greatly enhanced the uptake capacity of sorbents due to developed produced approach. The data was fully proven and published in the Proceedings of Tenth Mediterranean Combustion Symposium – Naples, Italy (2017), International Conference on Applied Mechanics, Mechanical and Materials Engineering – Xiamen, China (2017)</p>
	<p>3. cRH treated with NaOH solution increases the carbon content up to 80% and the specific surface area of the material up to 431 m²/g, which</p>	<p>Provision 3 is new and non-trivial. Nanoporous material based on carbonized rice husk and precipitated with NaOH was analyzed and proven, exhibits a higher surface area value due to decreasing presence</p>

	<p>enhances physical sorption and increases the sorption capacity up to 21.9 mg/g.</p> <p>7.1 Is the provision proven? - <u>1) proven;</u> 7.2 Is it trivial? - <u>2) no</u> 7.3 Is it new? - <u>1) yes;</u> 7.4 Application level: - <u>2) medium</u> 7.5 Is it proven in the article? - <u>1) yes</u></p>	<p>of ashes. An increase of the volumes of both mesopores and micropores ($V_{\text{tot}}=0,37 \text{ cm}^3_{\text{liq}}/\text{g}$ and $V_{\text{micro}} = 5.32 \cdot 10^{-2} \text{ cm}^3/\text{g}$) after both strong alkaline treatments is also detected, suggesting that the removal of silica particles turns clogged pores into accessible pores. Results of the sorbents characteristics presented in the rating CST journal (IF 1.73).</p>
	<p>4. The sorption capacity cRH of the treated NH_4OH increases to 29.2 mg/g due to chemisorption. This effect refines the saturation time of the sorbent up to 25 s with partial removal of silica, which shows an increase in the saturation time of the sorbent up to 25 s with partial removal of silica.</p> <p>7.1 Is the provision proven? - <u>1) proven;</u> 7.2 Is it trivial? - <u>2) no</u> 7.3 Is it new? - <u>1) yes;</u> 7.4 Application level: - <u>2) medium</u> 7.5 Is it proven in the article? - <u>1) yes</u></p>	<p>Provision 4 is new, non-trivial, determines the influence of the morphological and structural features of carbonized rice husk after base-leaching process on the carbon dioxide sorption capacity. The treatment with a strong alkali solution ($\text{NaOH}/\text{NH}_4\text{OH}$) allowed producing a material with a better sorption capacity. This result is comparable to values obtained in the same experimental conditions by chemisorbent materials, namely sorbents containing reactive sites with high affinity towards CO_2 in their structure. The position was fully proven and patented at QazPatent (#4302, 20.09.2019, bull.#38).</p> <p>Shortcomings/questions:</p> <ol style="list-style-type: none"> 1. What is the reason for the choice of certain hydroxides for synthesis of nanocomposites? Which one presented effective result in CO_2 adsorption process? 2. Did you make additional measurements of sorption of other toxic gases? 3. The percentage efficiency presented in the second provision is not entirely clear. The same can be said about the volume of pores, give a specific explanation for the increase. 4. Explain the influence of the saturation time of the sorbent and the

			characteristics of the sorption mechanism
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	Choice of methodology is justified in accordance with last research requirements, methodology is scrupulously described in the experimental part.
		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	In dissertation work of Zhumagaliyeva A.N. experimental part ensured using modern methods of scientific research, such as X-Ray Diffraction, ICP-MS, SEM, EDAX analysis, FTIR, AFM, TGA, BET analysis. For estimating adsorption capacity of obtained sorbents the candidate using static bed micro-reactor with minimal instrumental error. Interpretation of data represented by using advanced computer programs.
		8.3 Theoretical conclusions, models, identified relationships and patterns have been proven and confirmed by experimental research (for areas of training in pedagogical sciences: 1) yes	All theoretical conclusions, models, identified relations and patterns have been proven and confirmed on the basis of original experimental data.
		8.4 Important statements are confirmed by references to current and reliable scientific literature	Statements in the thesis are consistent with results and analyzes of current research are made up of comparative analysis with literature published in competent scientific journals.
		8.5 Used literature sources are sufficient for a literature review	163 references to the scientific literature are sufficiently enough for completed reviewing.
9	Practical value principle	9.1 The thesis has theoretical value: 1) yes	The theoretical significance of the fundamental investigation relies in determining optimal mass ratio of carbon matrix and nanosized magnetite, which provide a synergistic effect between the two components with the aim of achieving better CO ₂ uptakes. The obtained results were discussed taking into account the influence of the specific surface area, pore size distribution and other structural characteristic to increasing the CO ₂ adsorption by the solid sorbents.
		9.2 The thesis is of practical importance and there is a high probability of applying the results obtained in practice: 1) yes	Production of low-cost CO ₂ solid sorbents starting from carbonized rice husk represents an encouraging possibility to face environmental problems related to the disposal of rice husk, since it is a very abundant and available agricultural waste. Also economically cost-effective will be achieved because using solid sorbents doesn't imply additional

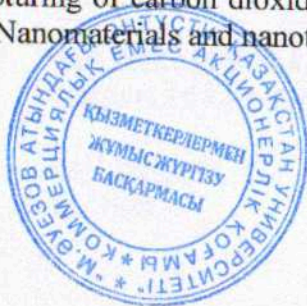
		9.3 Are the practice suggestions new? 1) completely new	equipment for point sources of pollution. The proposed nanocomposites based on carbonized rice husk and nanoparticulate magnetite have been developed and applied under post-burning conditions for the first time.
10.	The quality of writing and design	Academic writing quality: 1) high	Academic writing quality is high. There are grammar and stylistic mistakes in the dissertation work, but this remark does not have a fundamental character

In reviews, official reviewers indicate one of the following solutions:

1) to award the degree of Doctor of Philosophy (PhD) or Doctor of Specialization;

The dissertation work of Zhumagaliyeva Assem Nurbergenovna on the topic: «Production and testing of carbonized rice husk-based nanocomposites for capturing of carbon dioxide» was performed at the appropriate scientific/technical level and author deserves the PhD degree in specialty «6D074000 - Nanomaterials and nanotechnology».

Official Reviewer:



Mamitova

Mamitova Aigul Dzhanabayevna

Candidate of technical sciences,
associate professor of M. Aueзов
South Kazakhstan University.