Review

on the thesis of Ms. Imangaliyeva Ainur Nuralikyzy "Sorption and catalytic characteristics of composite materials based on natural raw materials" submitted for the degree of PhD in the specialty 6D072000– "Chemical technology of inorganic substances"

1. The relevance of the research topic and its connection with general scientific and national programs.

Natural layered silicates (clays) and silicates with skeleton structure (zeolites) possessing a number of unique properties such as ion exchangeability, high cation-exchange capacity, micro- and nanoporous structure, as well as the presence of surface active centers with different nature indicates that these materials are used for a long time as high-performance systems in order to solve a number of problems in many spheres of human activity. A distinctive feature of these minerals is a capacity for reversible inclusion of foreign molecules or groups of molecules into own structure with an expansion of inter-wrapper space for clays or skeleton structure for zeolites with their subsequent release. This property of montmorillonites and zeolites is actively used at the development of sorbents with technical and medical purpose.

The unique catalytic properties of zeolites were discovered in the 60s of last century, and during this time they turned into an important component of industrial catalysts (compared to laboratory conditions) and found a wide application in many branches of chemical industry. At the same time, the natural clay-based minerals, due to their complex and inconstant composition are not widely used in many areas, where the consistency of structural and physicochemical characteristics is necessary, for example, in order to solve a number of urgent catalysis problems. In this regard, the relevance of the thesis "Sorption and catalytic characteristics of composite materials based on natural raw materials", was carried out in the context of grant financing of the Ministry of Education and Science of the Republic of Kazakhstan, is submitted for a doctor's degree in Philosophy and there is no doubt and addressing to solve scientific and practical tasks for obtaining of new sorption and catalytic systems.

2. Scientific results and their relevance.

Thesis work of Imangaliyeva Ainur "Sorption and catalytic characteristics of composite materials based on natural raw materials", is a qualified scientific work and devoted to study of sorption and catalytic properties of modified alumino-silicate containing minerals, where a number of theoretical and practical tasks were solved in natural sequence, that form new ideas on expansion of bentonite clay and zeolites application and aimed to the development of new types of sorbents and catalysts for specific technological processes.

The results and conclusions obtained by candidate during approbation of the methods do not raise any doubts concerning their validity, because the author of thesis work has carried out a very thoughtful analysis of all literary data is known to date as well as applied standardized methods and techniques. Established influence patterns of structural features of selected substances on their further behavior are also believed to be reliable and reasonable due to the fact that theoretical conclusions and statements have been confirmed experimentally. The experimental results are reliable, because were obtained using modern certified equipment at al-Farabi Kazakh National University and Bar-Ilan University (Israel).

The results are statistically processed, reliable and unquestionable.

The analysis of thesis work and published by the author scientific articles and thesis has shown that all main fundamentals, results and conclusions were illustrated in numerous publications and reported at international and republican conferences.

3. Degree of validity and reliability of each scientific result (scientific statement) and conclusions of the applicant formulated in the thesis. Each scientific result and conclusion are defined clearly in order to achieve the main goal of the thesis. The reliability of the results

obtained is beyond any doubt due to the competent choice of modern research methods aimed at solving the tasks set in the thesis.

The results of the PhD investigation presented in 25 publications with 3 articles in journals included in the Web of Science database which ensures the validity and reliability of the scientific results.

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4. The degree of novelty of each scientific result (scientific idea), conclusion of author that were formed in this thesis.

It should be noted the most variable scientific results:

Scientific result 1. Various composites with sorption and catalytic features towards heavy metal ions on the Dinosaur deposit bentonite clay (BT-PEG) and orange (OP-PVP) and mandarin (MP-PVP) peels basis were obtained. The SEM, XRD and BET results analysis points on the successful modification of bentonite structure by PEG.The author of the work suggested optimal conditions for obtaining new polymer-inorganic/organic composite materials with sorption efficiency and catalytic activity, based on natural raw materials. The possibility of using the obtained composite materials in water purification from heavy metal ions by the sorption method is shown for the first time.

Scientific result 2. Cu_2O nanoparticles containing composites (Cu_2O/PEG-BT, Cu_2O/PEG-ZT) were obtained. The clay materials (bentonite, zeolite) were coated by the nanoparticles. The method consists in sequential deposition of the polymer, and then copper (II) ions on the carrier, followed by reduction of the metal of $NaBH_4$in the course of the reduction reaction of 4-nitrophenol. The received materials have a catalytic activity in the reaction of 4-nitrophenol to 4-aminophenol.For the first time, the conditions for obtaining copper-containing composite catalysts are proposed. They are used as catalysts in the reactions of hydrogenation of 4-nitrophenol.

Scientific result 3. New polymer-metallic heterogeneous catalysts based on copper (II) ions and polyvinylpyrrolidone (PVP)/polyethylene glycol (PEG) supported on a carrier were obtained for the oxidation reaction of yellow phosphorus. Based on the analysis of the results of physicochemical studies, the compositions and strengths of the PEG-Cu^{2+} polymer-metal complexes = 2:1 were established.. For the first time, the copper-containing composite catalysts were synthesized. The oxidation of yellow phosphorus to produce orthophosphoric acid and phosphoric acid esters, the composition, stability and thermodynamic characteristics of polymer-metal complexes are established. The author obtained a utility patent for a useful model for the method of obtaining oxidation reaction products, which is also evidence of the novelty of this result.

Scientific result 4. The optimal conditions for the sorption process of lead (II), copper (II) and cadmium (II) ions with the BT-PEG composite material were established. The effect of concentration of the PEG modifier, the amount of sorbent, pH and temperature to the sorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions was shown. The number of adsorbed metal ions increases with increasing pH of the solution. The maximum sorption capacity of BC-PEG towards Pb^{2+}, Cu^{2+} and Cd^{2+} is 22 mg/g, 26 mg/g and 18 mg/g, respectively.

For the first time, optimal conditions for the sorption process of lead (I) and cadmium (II) and copper (II) ions with BT-PEG composite material were recognized. The adsorbed amounts of both metal ions increased with increasing PEG concentration and pH.

5. Practical and theoretical significance of scientific results. The production of CM contributes to the sustainable environmental development. Research conducted in the course of work allows us to open up prospects for the use of the materials obtained as effective, affordable

and cheap sorbents for the purification of wastewater. Moreover, the studied reduction reactions of 4-nitrophenol in the presence of in situ Cu_2O nanoparticles immobilized on natural bentonite and zeolite, functionalized with polyethylene glycol, are highly efficient and inexpensive.

In addition, the study investigated the reaction of oxidative butoxylation of yellow phosphorus in the presence of heterogeneous catalysts — supported $CuCl_2$-PVP. These catalysts due to their high catalytic activity and selectivity can recommended for the synthesis of valuable phosphoric esters directly from yellow phosphorus under mild conditions.

6. Comments, suggestions on the thesis.

1. In accordance with the passport specialty 6D072000– "Chemical technology of inorganic substances there should be considered inorganic systems, but the part of the work is devoted to study of sorption and catalytic properties of the objects based on orange and mandarin peel related to organic substances;

2. Investigation of sorption properties of bentonite clay and catalytic properties of zeolites has received an extended coverage in scientific literature. What is the fundamental difference between earlier studies and the results presented in thesis work;

3. Figure 5 shows the electron scanning microscopy data on sorption of lead and cadmium, the samples of composite material based on bentonite clay is impregnated with polyethylene glycol, and there is made a conclusion on transformation of sorbent crystallinity after sorption. However, it should not be taking about changing of crystallinity degree, but about changing of the surface structure of sorbent;

4. Figure 9 shows the data on boundary changes and particles shape of orange and mandarin peel after modification with a polymeric material. However, these photographs were made with different focal resolutions, and this fact made the author's conclusions incorrect;

5. The presented thesis work for defense has a technological direction, focusing on the development of low-cost sorbents and catalysts based on local raw materials. At the same time, the mentioned technological schemes and the absence of economic calculations do not allow to adequately estimate the degree of economic attractiveness of the composite materials obtained in comparison with applied import analogues;

6. There are some editorial notes, because at page 43 there references to Fig. 2, which does not correspond to the text of thesis work, there is marked non-compliance with the design standards, there are some stylistic and grammatical errors.

All above questions and comments are associated with the interest of the reviewer to research work, they have not fundamental nature and do not reduce the significance of this thesis work.

7. Compliance with the content of the thesis within the requirements of Rules for awarding academic degrees.

Based on relevance, scientific novelty, theoretical and practical significance, I consider that the dissertation work of Imangaliyeva Ainur Nuralikyzy "Sorption and catalytic characteristics of composite materials based on natural raw materials" corresponds to the requirements of "Rules for the award of academic degrees" and author deserves the PhD degree in the specialty 6D072000 - "Chemical technology of inorganic substances".

Reviewer, General Director of
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Doctor of Chemical Sciences, Professor **Tlek Ketegenov**

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