

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.

Composite materials (CMs) are widely used in medicine, construction, shipbuilding, sorption, catalysis, as well as in many other branches of science and technology.

Consequently, there is a need to create new effective composite materials with practical characteristics. Recently, world countries are increasingly faced with the problem of utilizing pollutants, both inorganic and organic, from drinking, natural and industrial waters. For instance, it is known that heavy metals are a major environmental problem due to their toxicity and prevalence. Nitrophenols (NP) are among the most refractory water pollutants with carcinogenic character and high toxicity.

In addition, CMs are actively used in various catalytic reactions. Kazakhstan has extensive reserves of phosphate ores. In this regard, obtaining phosphorus-containing products is a priority for the country. Inorganic product of oxidation of yellow phosphorus as phosphoric acid is used in the production of various technical salts, organophosphorus compounds, including insecticides, semiconductors, ion exchange resins, as well as to create protective coatings on metals. In addition, the synthesis of valuable phosphoric acid esters is widely used as plasticizers, flame-retardants, solvents, complexing agents, heat carriers, and effective extractants of rare and transuranic elements.

Therefore, the research topic seems relevant, due to the great need for the synthesis of new materials with high sorption and catalytic properties.

The dissertation work was held within the framework of the project "Development of scientific basis of phosphorus containing compounds based on the technogenic raw materials" - 2015-2017 (№ 0115PK00515), initiated by MES RK.

2. Scientific results and their validity

Scientific result 1. Optimal conditions for the sorption of Cu^{2+} and Ni^{2+} ions by composites - OP-PVP and MP-PVP were determined. Freundlich model describes the sorption of copper and nickel ions by composites based on orange and mandarin peel; the modification of citrus with PVP polymer leads to an increase in their sorption properties.

Scientific result 2. Composites $\text{Cu}_2\text{O/PEG-BT}$ (ZT) showed high catalytic activity in a model reduction reaction of 4-NP to 4-AP. Zeolite showed the best catalytic and kinetic characteristics than bentonite, as a substrate. The rate constants

of the 4-NP reduction reaction are $1.22 \times 10^{-2} \text{ s}^{-1}$ and $1.79 \times 10^{-2} \text{ s}^{-1}$ in the presence of $\text{Cu}_2\text{O}/\text{PEG-BT}$ and $\text{Cu}_2\text{O}/\text{PEG-ZT}$, respectively.

Scientific result 3. The optimal conditions for the reaction of butoxylation of yellow phosphorus in the presence of a polymer-metal complex of copper (II) supported on carriers and the molar ratio of reagents were established: temperature 60°C in the presence of a catalyst $10\% \text{ Cu (II)-PVP}/\gamma\text{-Al}_2\text{O}_3$.

Scientific result 4. Optimal conditions for the reaction and a good yield of phosphoric acid are achieved at 70°C and $P_{\text{O}_2} = 1 \text{ atm}$ with a molar ratio of reagents $[\text{Cu (PEG)}_2\text{Cl}_2]: [\text{P}_4] = 11:1$.

Scientific result 5. Technology scheme of synthesis of composite materials based on natural raw materials has developed. A preliminary assessment of the economic efficiency of obtaining composite materials with sorption and catalytic properties in comparison with known sorbents and catalysts were carried out.

3. Degree of validity and reliability of each scientific result (scientific statement) and conclusions of the applicant formulated in the thesis.

The author of the dissertation carried out an adequate selection of up-to-date research methods aimed at solving the problems posed in the thesis. Adequate interpretation of the results obtained on the basis of modern views in the field of chemistry and chemical technology, allows to judge the high degree of validity of the conclusions on the thesis. Obtained data published in 25 publications including 3 articles in international journals with impact factors and peer-review, which ensures the validity and reliability of the scientific statements.

4. The degree of novelty of each scientific result (statement) and conclusions of the applicant formulated in the thesis.

Scientific result 1. For the first time, the possibility of using the obtained CM in water purification from Cu^{2+} and Ni^{2+} ions by composites - OP-PVP and MP-PVP was shown.

Scientific result 2. The first time copper-containing CMs are investigated as catalysts in the hydrogenation reactions of 4-nitrophenol.

Scientific result 3. The optimal conditions for the reaction of butoxylation of yellow phosphorus in the presence of a polymer-metal complex of copper (II) supported on carriers were investigated for the first time.

Scientific result 4. The author proposed a new approach in the development of optimal conditions for the synthesis of new polymer-inorganic composite materials. The first time the copper-containing CMs were investigated as catalysts in the oxidation reactions of yellow phosphorus to produce orthophosphoric acid.

Scientific result 5. For the first time scheme of synthesis of new composite materials based on natural raw materials was developed

5. Practical and theoretical significance of scientific results.

The catalytic reactions are priorities in the production of organic and phosphorous compounds.

The experimental data obtained in the course of the work allowed to open up views for using the achieved materials as effective, affordable and cheap sorbents for the purification of industrial wastewater. In addition, the oxidation of yellow phosphorus with obtaining valuable phosphorus inorganic (phosphoric acid) and organic (butyl esters of phosphoric acid) in the presence of homogeneous and heterogeneous catalysts directly from yellow phosphorus under mild conditions were found reasonable.

It should be noted that the obtained results can make a theoretical contribution in the field of physical chemistry (thermodynamics and kinetics of heterogeneous processes: sorption, catalysis), chemistry of coordination compounds.

6. Comments, suggestions on the thesis.

1) The catalytic effect of $\text{Cu}_2\text{O}/\text{PEG-BT}$ (ZT) composites on the reaction rate were discussed. How does the effect of these composites on the purity and yield of the final product? In addition, the formation of the product by the absorption region on the UV spectrum was not shown; control was carried out only by the initial nitrophenol and intermediate product.

2) P. 60 statement "The selection of PEG with concentration 0.1 % was fine for adsorption of heavy metal ions". However, at 0.1 % concentration, the adsorption is minimum as compared to other concentrations. How was chosen as optimum?

3) In work on Figure 24 provides sorption data in mg/g of sorbent. What is the degree of removal of metal ions as a percentage unit from original solution?

4) Adsorbent dose is 10 g/L. This is quite high. How was chosen as optimum?

5) There are stylistic errors, punctuation inaccuracies and typographical errors, the correction of which will improve the quality of this dissertation work.

These comments are suggestive and do not reduce the significance of the work. Author wrote the dissertation work in a worthy way, so as a reviewer I recommend this dissertation work for further consideration by dissertation council.

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

Based on the above, I believe that thesis of Imangaliyeva Ainur Nuralikyzy "Sorption and catalytic characteristics of composite materials based on natural raw materials" submitted for the degree of Doctor of Philosophy in the specialty 6D072000– "Chemical technology of inorganic substances" was conducted at high level, meets all requirements of theses and Imangaliyeva Ainur deserves a PhD degree.

**Reviewer, Candidate of Chemical
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LLP "Institute of High Technology"**



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