

CRITIQUE OF OFFICIAL REVIEWER

of the dissertation of KalmakhanovaMarzhanSeitovna, a Ph.D. candidate
from Taraz State University named after M.H. Dulati, specialty 6D060600
"Chemistry", titled: "Application of natural and pillared clays in water
treatment by adsorption and catalytic wet peroxide oxidation"

1. The relevance of the research title and its relationship with general scientific and national programs.

Clays are one of the most common rocks, forming up to 11% of the total volume of the earth's crust. They are traditionally used as raw materials for the production of building materials, as fillers in the manufacture of paper, drilling fluids, etc. One of the unique properties of clays is their high adsorption capacity, which is successfully used for cleaning oils, bleaching fabrics, and also as a natural environmental barrier to combat anthropogenic pollution. The high adsorption capacity of clays is due to the peculiarity of their crystalline structure. Such clay minerals, as montmorillonite, have a sliding crystalline structure. During hydration of such minerals, water molecules and exchangeable cations can penetrate into the interlayer space and significantly increase the interlayer distance, thereby causing a significant increase in the adsorption potential. This remarkable property was used as a basis for the study of M. Kalmakhanova, whose goal was to develop catalysts by modifying natural clays with active metal ions for the oxidation of organic pollutants using liquid peroxidation, and also to obtain an adsorbent for removing heavy metals from wastewater.

The presented work was carried out within the framework of the Polytechnic Institute of Bragança (IPB, Portugal) research project "AIProcMat @ N2020 - NORTE-01-0145-FEDER-000006 (2016-2019), funded by the European and National Research Funds (2016-2019), together with the researchers of Laboratory of Separation and Reaction Engineering-Laboratory of Catalysis and Materials (LSRE-LCM/IPB) of the pole at IPB.

2. Scientific results and their validity.

According to the plan of the thesis, the research was conducted and the following results were obtained:

- Based on the natural clays of the Akzhar, Karatau and Kokshetau deposits (Kazakhstan), pillared clays were obtained by their modification with Zr, Fe-Zn and Fe-Cu-Zr ions.
- The physicochemical properties of the natural and pillared clays were studied by modern methods, namely by FTIR, SEM, TEM, XRD, TGA, adsorption of nitrogen at 77 K and pH_{PZC} determination.
- The catalytic activity of the obtained catalysts was tested in the process of decomposition of H_2O_2 and in the oxidation of 4-nitrophenol with hydrogen peroxide.
- Based on the experimental data obtained, a kinetic model was developed for the oxidation of 4-nitrophenol with hydrogen peroxide on the catalyst surface.

- The adsorption capacity of pillared clays with respect to heavy metals was investigated.

3. The degree of validity and reliability of each scientific result (scientific position), conclusions and conclusions of the applicant, formulated in the thesis.

All scientific conclusions and conclusions formulated in the thesis are confirmed by the results of physicochemical studies performed at a high professional level using modern physicochemical research methods (IR spectroscopy, scanning electron microscopy, transmission electron microscopy, X-ray diffraction analysis (XRD), thermogravimetric analysis, nitrogen adsorption at 77 K, elemental analysis and point zero charge determination). The experimental data given in the thesis are in good agreement with the latest research results in this field.

4. The degree of novelty of each scientific result (position), the conclusion of the applicant, formulated in the thesis.

The method of forming pillared structures in the montmorillonite deposits of Akzhar, Karatau and Kokshetau, by their modification with metal ions (zirconium, iron, copper, zinc) was proposed for the first time, which was confirmed by a positive conclusion about issuing a patent for a utility model (No. 2014/08886.2) of 06.03.2019. The obtained catalysts were tested on a model aqueous solution of 4-nitrophenol and showed a high degree (100%) of the decomposition of the pollutant.

For the first time, natural clays of the Zhambyl region were characterized by the methods of X-ray, SEM, FEM, XRD, TGA and nitrogen adsorption at 77 K, elemental analysis, and point zero charge determination from the point of view of their use as carriers for catalysts. A kinetic model of wet peroxidation of 4-nitrophenol was developed for the first time.

5. Practical and theoretical significance of scientific results.

The developed kinetic model of the catalytic oxidation of 4-nitrophenol with hydrogen peroxide at the active sites of the newly obtained catalysts has an undoubted theoretical significance, since it adequately demonstrates the mechanism of the process and allows one to predict its results.

The practical significance of the research lies in the economic advantage of using cheap natural clays from domestic deposits as feedstock, as well as exceptionally mild conditions of catalyst acquisition. In addition, the result of the deep oxidation of organic pollutants on newly produced catalysts is CO_2 and H_2O , which undoubtedly adds value to the work from an environmental point of view.

6. Comments, suggestions for the dissertation.

According to the results of the thesis there are the following remarks:

1. Referring to the results given in Tables 6 and 7, how can you explain the changes in the content of some metals, such as Ca, Mg, Al, and whether this gives a positive effect on the quality of the catalyst produced.
2. What is the fundamental advantage of the TOC method for evaluating the effectiveness of the oxidation process?

3. Referring to Figure 50 on page 76: explain the shape and the course of the curve in the diagram below.

4. Explain the results of the experiment shown in Figures 19 and 20.

These comments do not affect the overall positive impression of the work read. I believe that in terms of the totality of the results, the research methods used, the conclusions, and publications, the dissertation is a completed research.

7. Confirmation of sufficient completeness of publications of the main provisions, results, conclusions of the thesis.

- 3 articles - in recommended journals of the Education and Science Control Committee of the Ministry Education and Science of the Republic of Kazakhstan

- 1 article - in a journal of the International database Scopus

- 2 articles - in a journal with 1.5 and 3.5 Impact Factors, included in the Thomson Reuters International Database

- 8 abstracts in the published materials of domestic and foreign International conferences

- 1 conclusion on issuing a patent for a utility model

8. Compliance with the content of the thesis in the framework of the requirements of the Rules for the award of scientific degrees.

The thesis of KalmakhanovaMarzhanSeitovna on the topic: "Application of natural and pillared clays in water treatment by adsorption and catalytic wet peroxide oxidation" submitted for the degree of Doctor of Philosophy (PhD) in the specialty 6D060600 - "Chemistry", on the relevance of the problem, volume research, methodological level, novelty of the data obtained, practical significance meets the requirement of the "Rules for the award of scientific degrees" of the Education and Science Control Committee of the Ministry Education and Science of the Republic of Kazakhstan, and its author deserves the award of the PhD degree in the specialty 6D060600 - "Chemistry".

Official Reviewer:

Doctor of Chemical Sciences, professor
of department of Chemistry of the South

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