

## CRITIQUE OF OFFICIAL REVIEWER

of the dissertation of Kalmakhanova Marzhan Seitovna, 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.

The dissertation work of Kalmahanova M.S. was performed in the actual field of creation of catalysts based on natural clays to intensify the processes of purification of waste and natural waters containing organic pollutants based on their deep destruction. The main idea of the research is to create pillared structures of natural clays by modifying them with active metal ions (zirconium, iron, copper, zinc). Currently, pillared clays have received increased interest due to their textural and catalytic properties in various reactions and are used as active catalysts for wastewater treatment. Redox reactions catalysed by materials of this type, allow for the complete destruction of organic substances difficult to oxidize to environmentally friendly products (CO<sub>2</sub>, H<sub>2</sub>O).

The title of the presented work is closely connected with the scientific directions of the Laboratory of Separation and Reaction Engineering-Laboratory of Catalysis and Materials (LSRE-LCM/IPB) of the pole located at the Polytechnic Institute of Braganca (IPB), Portugal. The work was carried out as part of the research project "AIProcMat @ N2020 - NORTE-01-0145-FEDER-000006 (2016-2019), funded by European and Portuguese national research funds (2016 - 2019).

### 2. Scientific results and their validity.

In the dissertation, in accordance with the tasks, comprehensive studies were carried out and the following main scientific results were obtained:

- Pillared clays modified with Zr, Fe-Zn and Fe-Cu-Zr were prepared on the basis of natural clays of Kazakhstan mined at the Akzhar, Karatau and Kokshetau deposits.
- The physical - chemical properties of natural and pillared clays were studied using the methods of FTIR, SEM, TEM, XRD, TGA, adsorption of nitrogen at 77 K and pHPZC determination.
- The catalytic activity of modified clays was investigated in the reaction of decomposition of hydrogen peroxide, as well as in the oxidation of 4-nitrophenol with hydrogen peroxide in aqueous solutions.
- A kinetic model of oxidation of 4-nitrophenol was developed.
- The adsorption capacity of the developed pillared clays with respect to heavy metal ions 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.

The validity and reliability of the scientific conclusions and conclusions formulated in the thesis are not in doubt, since they are confirmed by the

correspondence of the results of a complex of physical and chemical studies to modern literature data, which is confirmed by the corresponding publications.

Scientific results were obtained using modern methods of analysis (IR - spectroscopy, scanning electron microscopy, transmission electron microscope, X-ray diffraction analysis, thermogravimetric analysis, nitrogen adsorption at 77 K, elemental analysis and  $\text{pH}_{\text{PZC}}$  determination).

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

The scientific novelty of the thesis is the development of a new method of producing catalysts by forming pillared structures in natural clays and their use in liquid catalytic peroxidation of 4-nitrophenol, as well as their use for adsorption of heavy metals (nickel). For the first time, catalysts based on the natural clays of Akzhar, Karatau and Kokshetau modified with Zr, Fe-Zn and Fe-Cu-Zr were synthesized in Kazakhstan. For the first time, natural clays of the Zhambyl region were characterized by X-ray, SEM, TEM, XRD, TGA and nitrogen adsorption at 77 K, elemental analysis,  $\text{pH}_{\text{PZC}}$  determination with the aim of studying the possibility of their use as carriers for catalysts. For the first time, a kinetic model of liquid peroxidation of 4-nitrophenol on the catalyst surface was created. As a result of the research, conclusions were obtained on issuing a patent for a utility model (№ 2018/0886.2).

#### **5. Practical and theoretical significance of scientific results.**

The theoretical significance of the thesis lies in the development of the theoretical basis for the preparation of catalysts modified with active metals and an explanation of the mechanism of oxidation of 4-nitrophenol with hydrogen peroxide on the surface of the catalyst obtained. The method of catalyst preparation eliminates high-temperature processes and the use of toxic reagents. The practical significance of the catalysts obtained lies in their high oxidative activity with respect to 4-nitrophenol at a temperature not exceeding 50 ° C and atmospheric pressure under mild conditions. The end products of oxidation are non-toxic carbon dioxide and water.

#### **6. Comments, suggestions for the dissertation.**

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

1. In southern Kazakhstan there is a powerful deposit of bentonite clays, widely used and well-established as adsorbents. They could also be a promising target for this study, along with the montmorillonite clays from the Akzhar and Karatau deposits.
2. It is known that in Kazakhstan many researchers are developing catalysts based on natural clays for use in catalysis. Unfortunately, there are few references to the works of domestic scientists (out of 140 references there are about 7 publications of Kazakhstani scientists).
3. Based on what assumptions were the components chosen from active metals like Zr, Fe-Zn and Fe-Cu-Zr?
4. Why was chosen 4-nitrophenol as the organic pollutant?
5. What useful information can be obtained from such a physical-chemical characteristic as "Point of zero charge"?

