EVALUATION REPORT

on the doctoral thesis

SORPTION PURIFICATION OF WATER FROM Cr (III) AND Cr (VI) IONS BY MEANS OF CELLS OF MICROORGANISMS IMMOBILIZED ON CLAY CARRIERS

elaborated by Doctoral student: Zhadra A. Tattibayeva (6D060600 – Chemistry), Al-Farabi Kazakh National Universit, Kazakhstan

I, Dr.habil.chem. Laura Bulgariu, professor at the Department of Environmental Engineering and Management, "Cristofor Simionescu" Faculty of Chemical Engineering and Environmental protection, "Gheorghe Asachi" Technical University of Iasi, Romania, appointed, based on the Order of the Dissertation Council no. 27-03-09-481/14.07.2023, as a member of the analysis committee for the public defense of the doctoral thesis with the title: "Sorption purification of water from Cr (III) and Cr (VI) ions by means of cells of microorganisms immobilized on clay carriers" elaborated by Doctoral student: Zhadra A. Tattibayeva, I analyzed the thesis and found the following:

1. The scientific importance of the doctoral thesis topic

Environmental pollution, especially of water sources, is one of the most important problems that are becoming more significant and widespread, as industrial activities expand. Pollution control, especially, in the industrial sectors, requires more concentrated efforts, due to the large number and variety of contaminants that are used, but also to the large number of companies operating in this industrial field. Therefore, this Ph.D. thesis addresses a very important and current issue, both nationally and internationally, considering that the development of industrial activities, which are so beneficial for to increase the quality of human life, has inevitable determined the increase of environmental pollution degree. Due to the seriousness of the health problems that are generated by the release of industrial effluents, it is considered that environmental pollution due to the industry is one of the most serious problems, in this century. It is well known that water sources (such as lakes, rivers, seas and oceans) provide significant economic and social benefits. Therefore, maintaining the quality of these ecosystems is a real challenge in today's society, where rapid industrial development is required. That is why it is unanimously accepted that treating industrial effluents before their discharge into the environment is the most effective way to control environmental pollution. Particular attention is paid to the removal of chromium ions (Cr(III) and Cr(VI)), which, due to their economic importance (in various industrial sectors) significantly contribute to the increase in environmental pollution and the degradation of the quality of the ecosystems.

In this context, the Ph.D thesis: "Sorption purification of water from Cr (III) and Cr (VI) ions by means of cells of microorganisms immobilized on clay carriers" elaborated by Doctoral student: Zhadra A. Tattibayeva, aims to identify a novel, efficient and cost-effective treatment method for the removal of Cr(III) and Cr(VI) ions from aqueous effluents.

The results included in this thesis indicate that the cells of the microalgae (*Spirulina platensis* and *Chlorella vulgaris ZBS1*), in raw form or deposited on a zeolitic support, can be successfully used for the effective removal of Cr(III)/Cr(VI) ions from aqueous media, and the quantitative parameters calculated for each sorption system, allow highlighting the usefulness of these materials in environmental decontamination processes. Such a method will reduce the number of treatment steps required to treat industrial effluents and will minimize investments and operating costs.

2. Objectives and the structure of Ph.D. thesis

The overall objective of this Ph.D thesis is the optimization of sorption conditions for the removal of Cr(III) and Cr(VI) ions, using raw microalgae (*Spirulina platensis* and *Chlorella vulgaris ZBS1*) and microalgae deposited on zeolitic support, from aqueous media, to identify an efficient and cost-effective method for the treatment of industrial effluents containing chromium compounds. Starting from a rigorous study of the literature, the thesis reviews the most important methods used to treat industrial effluents. The most important advantages and disadvantages of these methods are highlighted, which are useful for identifying the best opportunities, both in terms of process efficiency and implementation costs.

The specific objectives that have been followed up under this thesis and allow the proposed theme focused on the following issues:

1. The study of the effect of the initial concentration of chromium compounds, the solution pH and the temperature on the sorption of Cr(III) and Cr(VI) ions on the surface of the microalgae cells (*Spirulina platensis* and *Chlorella vulgaris ZBS1*);

2. Identifying and substantiating the effect of Cr(III) and Cr(VI) ions on the electrokinetic potential of the surface of algae cells;

3. Isotherm and kinetic modeling of the experimental results obtained for the sorption of Cr(III) and Cr(VI) ions on the surface of the microalgae cells (*Spirulina platensis, Chlorella vulgaris ZBS1*);

4. Determination of toxicity and coagulation effects of Cr(III) and Cr (VI) ions on algae cells;

5. Obtaining composite biosorbents by immobilizing algae cells on the surface of the zeolite;

6. Determination of the conditions for the desorption of Cr(III) and Cr(VI) ions from the exhausted microalgae sorbents (*Spirulina platensis* and *Chlorella vulgaris ZBS1*) and their regeneration.

These specific objectives are detailed presented and discussed along of four chapters, including a chapter of Conclusions. In all experiments, the materials were rigorously characterized, the optimal experimental conditions were established, and the obtained experimental data were modeled and detailed discussed.

3. Appreciation on original contributions presented in Ph.D. thesis

The Ph.D thesis: "Sorption purification of water from Cr (III) and Cr (VI) ions by means of cells of microorganisms immobilized on clay carriers" elaborated by Doctoral student: Zhadra A. Tattibayeva, is

well structured and argued, in accordance with the academic criteria. In addition, the thesis is actual and brings important contributions in the field of chemical and environmental engineering, where due to intensification of industrial activities, finding suitable materials and methods for the efficient removal of chromium ions from industrial effluents is still an open topic.

In this context, the studies performed by **Doctoral student: Zhadra A. Tattibayeva** are welcome, as they follow the use of microalgae (raw or deposited on zeolitic support) to find the most appropriate uses as sorbents with applications in the treatment of aqueous effluents containing chromium compounds. By the way the Ph.D. thesis was addressed **Doctoral student: Zhadra A. Tattibayeva** has proven to posses high researcher skills coupled with a good ability to use various methods for experimental investigation.

The Ph.D. thesis is elaborated at a high scientific level and contains an impressive amount of original data (over 70 % of thesis content), valuable both from theoretical standpoint, but also in terms of practical solutions, because identify the possible uses of new sorbent materials in the decontamination processes of the aqueous effluents containing chromium compounds. The scientific importance of the thesis is proved through a series of arguments, the most important being:

) theoretical studies, but especially experimental ones aimed at conducting a critical analysis of the state of knowledge and research conducted worldwide on the use of low-cost materials as sorbents for heavy metal ions removal, to develop efficient and ecological methods for their preparation and characterization;

) an evaluation of the performance of the microalgae sorbents (*Spirulina platensis* and *Chlorella vulgaris ZBS1*), in raw form or deposited on zeolitic support, used in this research to test the sorptive properties of these materials in the removal of Cr(III) and Cr(VI) ions from aqueous media. These studies were conducted to establish the potential applications of such materials in the decontamination processes of industrial effluents containing chromium compounds;

) detailed characterization of the materials selected as sorbents, both in terms of chemical composition and structural particularities. All these results were then adequately used to highlight the possibility of their application in the treatment of the artificial effluents;

) the experimental studies were carried out rigorously and meticulously, in accordance with the methodology presented in the literature. For each individual case, optimal experimental conditions (solution pH, initial Cr(III)/Cr(VI) concentration, contact time and temperature) were established and kinetic and equilibrium data were modeled and detailed discussed;

) special attention was given to economic aspects of the treatment processes, because these are an important argument for practical implementation;

) careful analysis of the Cr(III) and Cr(VI) removal efficiency for each case, and comparison of the performance efficiency of analyzed systems.

I would have one more thing to add. The experimental results included in this Ph.D. thesis are rigorously obtained and valuable. It's a shame **Doctoral student: Zhadra A. Tattibayeva** couldn't put them to better use by now. The 5 papers published in prestigious Journals (2 papers in ISI Ranked Journals (1 paper in Q1 Journal) and 3 papers in Scientific journals recommended by the committee of the Ministry of Education and Science of the Republic of Kazakhstan), and the publication of 8 papers in the proceedings of national and international

conferences, are the most important evidences related to the scientific importance of the experimental data included in this doctoral thesis.

Considering all the aspects mentioned above and the results presented in the thesis "Sorption purification of water from Cr (III) and Cr (VI) ions by means of cells of microorganisms immobilized on clay carriers" elaborated by Doctoral student: Zhadra A. Tattibayeva, meet all the conditions required for granting the Ph.D. title.

la i, 29.08.2023

Prof.dr.habil.chim. Laura BULGARIU

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