

## ANNOTATION

**of the dissertation for the degree of Doctor of Philosophy (PhD)  
in the specialty 6D060600 – «Chemistry»**

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**on the topic: «Sorption purification of water from Cr (III) and Cr (VI) ions by  
means of cells of microorganisms immobilized on clay carriers»**

**Relevance of the research topic.** Currently, among the main tasks of environmental protection, the search for ways to purify water and air from chromium compounds is one of the urgent problems for Kazakhstan, especially in the western regions. This is due to the fact that our country is ranked 4th among the leading countries in the world in chromium production after South Africa, India and China.

Among the known methods of metal ion extraction from wastewater, sorption is the simplest and most affordable, but the problem lies in the choice of highly effective sorbents. Microbial cells are inexpensive sorbents of heavy metal ions, but their widespread use has some limitations due to the difficulty of separating them from solutions after adsorption. Therefore, the method of immobilization of microbial cells capable of adsorbing Cr(III) and Cr(VI) ions on the surface of solid mineral carriers was used in the work. For the strong fixation of microbial cells on the surface of clay mineral particles, it is very important that they have functional groups capable of interacting with the cell surface. This requires fundamental research on changing the surface of solid carriers, determining the specificity of the interaction of cells and chromium ions, as well as determining the affinity of cells to the functional groups of the solid surface. Zeolites of the Shankanai deposit were used as a carrier of cells. Chitosan, a widespread industrial cationic polymer, was used to modify the solid surface.

**The purpose of the dissertation.** Optimization of conditions for adsorption of Cr(III) and Cr(VI) ions on the surface of algae cells for water purification from chromium compounds.

**To achieve the goal, the following tasks are set:**

1. To determine the effect of the pH of the medium and temperature on the adsorption of Cr (III) and Cr (VI) ions on the surface of the algae *Spirulina platensis* and *Chlorella vulgaris* ZBS1 cells;
2. To process the results of adsorption of Cr(III) and Cr(VI) ions on the surface of *Spirulina platensis*, *Chlorella vulgaris* ZBS1 algae cells within the framework of modern adsorption models and describe them from the point of view of thermodynamics;
3. To determine and substantiate the effect of Cr(III), Cr(VI) ions on the electrokinetic potential of the surface of algae cells;
4. To determine the toxic and coagulating effect of Cr (III), Cr(VI) ions on algae cells;
5. To obtain composite biosorbents by immobilizing algae cells on the zeolite surface;

6. To determine the conditions of desorption of Cr (III) and Cr (VI) ions from the surface of *Spirulina platensis*, *Chlorella vulgaris* ZBS1 algae cells and regeneration of bisorbents.

**Research methods:** X-ray phase analysis, X-ray fluorescence analysis, atomic absorption spectroscopy, FTIR spectroscopy, UV-spectrophotometry, scanning electron microscopy (SEM), optical microscopy (OM), electrokinetic analysis (Z-sizer) and BET method.

**The main provisions submitted for defense:**

1. The adsorption of Cr (III) and Cr (VI) ions on the surface of *Spirulina platensis* and *Chlorella vulgaris* ZBS1 algae cells was evaluated and the results of adsorption were processed within the framework of Langmuir, Freundlich, Dubinin-Radushkevich and Temkin models. Adsorption is mainly determined by non-covalent electrostatic interactions, however, the role of ion exchange, redox processes and donor-acceptor interactions is also important when binding adsorbed ions to functional groups of the cell surface;
2. According to the calculated ( $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$ ) thermodynamic parameters, the adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris* ZBS1 algae cells is endothermic and non-spontaneous, and the adsorption of Cr (III) ions on the surface of *Spirulina platensis* algae cells is exothermic and spontaneous, which is determined by the charge of adsorbed ions and the pH of the medium;
3. At a concentration of  $10^{-3}$  mol/L, Cr (III) ions have a stimulating effect on *Spirulina platensis* cells, and the appearance of new algae cells after 7 days means that they use Cr (III) ions as a nutrient fund. The toxic effect of Cr (VI) ions differs in that they penetrate into the intracellular environment, destroying the protective and hydrated microenvironment of cells;
4. Adsorption of Cr (III) ions on the surface of *Spirulina platensis* cells at a concentration of  $10^{-5}$  –  $10^{-3}$  mol/L leads to their coagulation, which is associated with the neutralization of the negative charge of the cell surface. However, at a Cr(III) salt concentration of  $10^{-1}$  mol/L, coagulation is replaced by stabilization of algae suspensions due to recharging of the cell surface with multicharged Cr (III) ions.
5. Desorption of Cr (III) and Cr (VI) ions from the surface of algae cells reaches 78.5% and 80.3%, respectively, in solutions of 0.1 mol/L HCl and 0.1 mol/L NaOH in 120 minutes. Zeolite-chitosan biocomposites-algae cells can be reused at least 5 times to extract Cr (III) and Cr (VI) ions from water.

**Scientific novelty of the research work:**

1. For the first time, an integrated approach to the study of the adsorption of Cr(III) and Cr (VI) ions on the surface of the algae *Spirulina platensis* and *Chlorella vulgaris* ZBS1 cells was carried out. It was found that the adsorption of Cr (III) ions on the surface of algae cells decreases with increasing temperature, and this process is described by a kinetic model of the pseudo-first order, while the adsorption of Cr (VI) ions increases with increasing temperature and is described by a kinetic model of the pseudo-second order.
2. Thermodynamically, an increase in the negative value of  $\Delta G^\circ$  with an increase in temperature during the adsorption of Cr (III) ions on the surface of *Spirulina*

*platensis* algae cells indicates the favorability of the adsorption process and the increased binding strength of the adsorbent and adsorbate. It is shown that the positive values of  $\Delta G^\circ$  during the adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris* ZBS1 cells are due to the energy consumption to suppress the electrostatic repulsion forces between the anionic groups of the surface of algae cells and Cr (VI) anions.

3. It has been shown that in the region of low concentrations ( $10^{-5} - 10^{-4}$  mol/L), both Cr (III) cations and Cr (VI) anions enhance the negativity of the surface of the algae cells *Spirulina platensis*, *Chlorella vulgaris* ZBS1 and reduce it at high concentrations ( $10^{-3} - 10^{-1}$  mol/L). The effect of Cr (III) cations at low concentrations is associated with the release of additional anionic groups to the surface and the compression of DES at high concentrations: The effect of Cr (VI) anions is to increase the negative charge of the surface at low concentrations and neutralize the negative charge of the surface by their counter ions at high concentrations.

4. Adsorption of Cr (III) ions on the surface of *Spirulina platensis* algae cells leads to coagulation of its suspensions. It was found that the concentration of Cr (III) compounds in  $10^{-3}$  mol/L has a stimulating effect on the cells of *Spirulina platensis* algae, and Cr (VI) ions, on the contrary, have a toxic effect.

5. To separate the cells of algae of high lyophilicity *Spirulina platensis*, *Chlorella vulgaris* from water, it is proposed to immobilize them on the surface of zeolite. To attach negatively charged cells to the surface of a carrier with a negative charge, the surface of the mineral particles was modified with a cationic polymer – chitosan.

#### **Theoretical and practical significance of the research results**

The practical significance of the results of the work lies in the synthesis of biosorbents based on algae cells and clay biocomposites with high sorption properties, and the determination of their adsorption characteristics. The possibility of practical application is based on the production and characterization of highly effective biosorbents capable of purifying industrial wastewater from toxic chromium ions. The economic efficiency of obtaining and using biosorbents and biocomposites is due to the cheapness and availability of raw materials.

#### **Compliance with the directions of development of science or state programs (projects).**

The dissertation work was carried out within the framework of the scientific program "BR05236419 – Creation of functionalized organic substances and materials with the possibility of a wide range of practical applications of high efficiency", funded by the Ministry of Education and Science of the Republic of Kazakhstan (2018-2021).

**Publications.** As a result of the research carried out within the framework of the dissertation work, 13 scientific papers were co-authored, including 2 articles in journals included in the Scopus database: in the journal "Heliyon" (Q1, 82%) and in the journal "Eastern-European Journal of Enterprise Technologies" (Q3, 29%), and also 3 articles in journals included in the list of the Committee for Quality Assurance in the field of Science and Higher Education of the Ministry of Science and Higher

Education of the Republic of Kazakhstan: "Bulletin of KazNU", "Chemical" series, News of the scientific and Technical society "КАНАК", "Промышленность Казахстана", and also in the materials of international and republican scientific conferences.

### **Description of the contribution of the doctoral candidate to the preparation of each publication**

The doctoral candidate was directly involved in obtaining experimental data, processing and discussing the experimental results for the design of the article "Peculiarities of adsorption of Cr (VI) ions on the surface of *Chlorella vulgaris* ZBS1 algae cells" in the journal "Heliyon" ( 2022, V. 8, Issue 9, e10468, Q1).

The doctoral student was directly involved in obtaining experimental data, processing the results obtained for the preparation of the article "Analysis of Cr (III) ions adsorption on the surface of algae: implications for the removal of heavy metal ions from water" in the Eastern-European Journal of Enterprise Technologies" (2021, 4(10) (112), P. 14-23, Q3).

The doctoral student was directly involved in obtaining experimental data, processing and interpreting the results obtained for the design of the article "Adsorption modification of the zeolite surface with chitosan" in the journal "Chemical bulletin of KazNU" (2019, V. 94, No. 4, P. 20-26 ).

The doctoral candidate was directly involved in obtaining experimental data, processing the results obtained for the design of the article «*Chlorella vulgaris* балдыр жасушаларын Cr<sup>3+</sup> иондарының адсорбенті ретінде қолдану» in the journal "КАНАК" (2019, No. 3 (66), P. 85-90).

The doctoral student was directly involved in obtaining experimental data, processing and interpreting the results obtained for the design of the article «*Spirulina platensis*-хитозан-цеолит композиті көмегімен Cr (III) иондарын сулы ерітінділерден бөлу» in the journal "Промышленность Казахстана" (2020, No. 3, P. 40-43).

The doctoral student was directly involved in obtaining experimental data, processing experimental results for the preparation of materials and abstracts of 8 reports at international scientific conferences and forums.