Ecobiotechnology in the process of industrial wastewater treatment of the closed mining enterprise as a guarantee of environment safety

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Abstract. The report presents the results of long-term studies of the problem of ecological and chemical assessment of the impact of mineral processing waste in the form of pulp on the ecosphere, including aquatic ecosystems, and the development of bioengineering technologies (bioremediation) aimed at reducing their negative impact on the environment in the Primorsky territory. In the last century at the concentrating plant of the closed Khrustalnensky GOK mining enterprise a chemical method was used to treat industrial wastewater, a degree of which was no more than 75%. It is shown that pollutants discharged into water bodies after chemical treatment, which have a general toxic, carcinogenic and mutagenic effect, still pose a great threat to the ecological balance of natural systems. The studies show that there was intense pollution of ground and surface water, soil and vegetation, exceeding the regional background indicators up to 9 or more times within the boundaries of the anthropogenic system impact. Therefore, in the study area it is necessary to ensure environmental and social safety of industrial effluents by improving their treatment technology. In this regard, the aim of the research was not only to assess the extent of the negative impact of beneficiation mineral toxic wastes in the form of pulp to the ecosphere, but also in the development of ecologically safe biotechnological method of purification industrial wastewater by biodegradation, biooxidation and biosorption from solutions using the metabolic potential of biological systems (hydrophytic plants). Based on the purpose, the following tasks are defined: 1. To analyze and summarize the literature on the problem of industrial wastewater treatment using biological methods; 2. To study the composition and properties of industrial wastewater in the form of pulp and assess their impact on the environment; 3. To investigate ecological and biological features of little Duckweed as a possible concentrator of heavy metal compounds; 4. To develop a biotechnological solution for industrial wastewater treatment using bioremediation (higher aquatic vegetation, Duckweed). Experimental studies have proved the effectiveness of the biological systems metabolic potential (little Duckweed) to ensure the normative quality of treated wastewater by the example of a closed mining enterprise in the Primorsky territory (Khrustalnensky GOK). The scientific novelty of the proposed method is confirmed by a Patent of the Russian Federation (2014).

1. Introduction
The functioning of the material world is due to the destruction of the lithosphere areas and the subsequent use of the substances obtained [1-3]. Considering the environmental impacts of the increasing rate of mining in Russia and the Primorsky Territory, in particular, it should be noted that
Large amounts of toxic waste have been extracted on the day surface simultaneously. They include not only solid material, but also liquid pulp, containing pollutants (heavy metal ions, suspended mineral particles, etc.), which pose an environmental hazard [4-5]. Industrial wastewater undertreated at the processing plant by chemical method, in which, in addition to heavy metal compounds (HM) such as Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, As^{3+}, Fe^{3+}, Mn^{4+}, Co^{2+}, Ni^{2+}, Sn^{2+}, Sb^{3+} etc., residues of highly toxic reagents used in the minerals processing contained, are dumped into water objects and taken out of the production area. As a result, there was a large-scale technogenic pollution not only of the hydrosphere, but also atmosphere, soils and vegetation, exceeding the regional background values by up to 9 times or more within the boundaries of the impact of the natural mining technogenic system[6]. Their dumping into natural reservoirs has a negative impact on the processes taking place in them, contributes to the disruption of biological equilibrium and thus, complicating rational water use. The discharge of untreated industrial runoff has a negative impact on oxygen mode, color and transparency of water, its acidity. This leads to a decrease in the productivity of the reservoirs and disruption of self-cleaning processes[7-9]. When industrial wastewater enters natural water sources, the chemical composition, temperature and acidity of the water object changes, which leads to death of some plants and organisms and mutation of others. The waters become unsuitable for household use. There are also changes in the near-water space (the flora and fauna are changing) [9]. It is obvious that protection from technogenic pollution of the air basin, biota, soil, surface and groundwater is an urgent environmental task in the area under study. Biological methods of industrial wastewater treatment are now quite widely used in mining. It is known that both charophytes and higher aquatic plants are used [10-14]. Higher aquatic plants (hydrophytes) have a beneficial effect on the processes of water quality formation [10-16]. They adapt better to toxic and non-toxic substances than microorganisms. Therefore, they can be used to treat highly concentrated wastewater without diluting with fresh water. In this regard, the purpose of the study was not only to assess the negative impact of mineral processing toxic waste in the form of pulp on the ecosphere, but also to develop an environment friendly biotechnological method of industrial wastewater treatment by biodegradation, biooxidation and biosorption from solutions using the metabolic potential of biological systems (hydrophytic plants). Based on the goal, the following objectives are formulated: 1. To analyze and summarize literary sources on the problem under study; 2. To study the composition and properties of industrial wastewater in the form of pulp as a source of the ecosphere pollution and to determine its impact on environment condition; 3. To assess the environmental and biological features of little duckweed (Lemna minor) as a possible concentrator of heavy metal compounds; 4. To develop innovative proposals to ensure the environmental safety of tin waste processing in the form of pulp.

2. Materials and Methods

The research was carried out within the boundaries of the impact of the Khrustalnensky GOK closed mining enterprise in the Primorsky Territory. The object of the study was natural mining system, formed in the last century by its economic activity. It consists of processing waste in the form of pulp, stored in the tailings dump, as well as environment objects (water from local watercourses, Zerkalnaya river, snow cover, soil, vegetation, bottom sediments and little duckweed (Lemna minor). The methodological basis of the study was Academician V.I. Vernadsky doctrine and the main provisions set out in the Program and Methods for studying technogenic biogeocenoses by B.P. Kolesnikov and L.V. Motorina [17]. The paper uses conventional modern physical-chemical, chemical, biological and mathematical-statistical methods, as well as: the analytical summary of the results of the study of the assessment of environment impact of solid and liquid waste; the analysis of soil, plants, and industrial wastewater samples; laboratory tests; pilot semi-industrial advanced wastewater treatment tests.

3. Results and discussion

Literary and patent searches have shown that the toxic wastes accumulated in the last century in the course of tin ore development, in the form of pulp including, containing a large amount of HM and arsenic compounds, have a negative impact on ecosphere [18, 19, et al]. However, according to the
literary data, in the mining enterprises of the Far Eastern Federal District, the problem of ecosphere protection almost was not given due attention. Here, still insufficiently treated industrial wastewater is drained to natural water facilities, polluting all components of the biosphere on a large scale [20, 21]. Large volumes of pulp, formed as a result of the operation of mining and processing plants are dumped in tailings ponds, creating huge artificial reservoirs, with large areas of open water surface, which contributes to active evaporation of water containing compounds of harmful chemical components [22, 23]. Hypergenic and technogenic processes occurring in tailings dumps lead to oxidation of sulphides. The presence of a gas component in them, namely, sulphur dioxide and hydrogen sulfide, etc., entering the atmosphere, cause its technogenic pollution. The significant removal of the solid material (in the form of dust), formed by fine, loose, incoherent material from the surface of tailings ponds occurs also [24, 25]. Liquid and solid pollutants, spreading over considerable distances, fall in the form of precipitation or dust formations, which leads to chemical contamination not only of adjacent, but also remote areas. According to the actual content of chemical compounds: zinc, nickel, copper, lead, cadmium, cobalt, antimony, arsenic compounds, etc., the waste stored in the tailings dump, is highly toxic (2 class of hazard). Undoubtedly, the ions of chemical elements contained in industrial wastewater (in the form of pulp) are the main source of environment objects pollution. This is evidenced by the study of geochemical and mineralogical features of tin-ore waste, allowed to establish a high ecological toxicity of waste, which undoubtedly contributes to intensive pollution environment (table 1).

Table 1. Average content of chemical compounds in the tailings dump of the closed Khrustalnensky GOK mining enterprise.

| Chemical compounds | Concentration, mcg/dm$^3$ |
|--------------------|-------------------------|
| Cr$^{3+}$          | 69.24                   |
| Co$^{2+}$          | 102.57                  |
| Ni$^{2+}$          | 225.79                  |
| Cu$^{2+}$          | 1827.88                 |
| Zn$^{2+}$          | 720.49                  |
| As$^{5+}$          | 1532.17                 |
| Sb$^{2+}$          | 0.49                    |
| Cd$^{2+}$          | 258.53                  |
| Pb$^{2+}$          | 9.53                    |

Soils and vegetation in a closed mining enterprise are enriched by HM compounds due to sulphides oxidation, which get into them as a result of spreading of waste decomposition products by the wind [26] and especially near the tailings dumps. Thanks to wind transportation, sulphides enter the soil and, interacting with water, air oxygen, carbon dioxide, etc., highly concentrated microporous solutions are formed, from which the pollutants enter plants through the roots. According to our research, higher vegetation accumulates HM compounds in quantities exceeding regional-background indicators. The patterns of technogenic pollution of environment objects were revealed and their negative impact on the components of the biosphere was assessed (excess of MPC and background values in soils ranged from 1.5 to 36 times). Mine waters, around the clock for many decades, carry large amounts of pollutants into the ecosphere, including water facilities. The concentration of the main elements of sulphides and the enclosing rocks of technogenic water entering the Zerkalnaya River and further the Zerkalnaya Bay of the Sea of Japan, exceeds the background values and MPC$_{fish-farm}$ in dozens, hundreds, and even thousands of times. The mine and sludge waters within the boundaries of the study area are enriched with the following HM compounds (Sn$^{2+}$, Cu$^{2+}$, Pb$^{2+}$, Zn$^{2+}$, Fe$^{3+}$, Mn$^{2+}$, Sb$^{2+}$, Cd$^{2+}$, Sr$^{2+}$ etc.), as well as arsenic. Abnormal amount of suspended solids in the water of the Zerkalnaya River is associated with the mining technogenic component of the river runoff.

Based upon the concentration ratios (K$_c$ equal to 23) and the total pollution index of heavy metal compounds ($Z_c$ – about 200), which does not correspond to the acceptable category of soil pollution, it can be argued that tin waste is the greatest threat to the environment. The negative impact of HM compounds on living organisms was defined, which is manifested in metabolism changes, in violation of morphology of biological communities populations, reproductive activity, which is expressed in increase of pollen grains sterility and causes low seed germination. Pollen sterility increased to 23-25% on contaminated soils. As pollution increases, pollen sterility increases. The use of a complex of physical, chemical and biological methods allowed to assess the ecological state of the research area within the boundaries of the impact of technogenic system of the closed Khrustalnensky GOK mining.
enterprise as critical at a distance up to the 10-12 km, unsatisfactory – up to 15-18 km and partially satisfactory – 20 km.

The large volume of pollutants accumulated in the last century as a result of the Khrustalnensky GOK activities, including industrial wastewater, and its transportation to the ecosphere demonstrates the need for urgent (as soon as possible) environmental measures. In order to reduce the technogenic burden on natural complexes, it is necessary to create new environment friendly biotechnological technologies [27], so-called ecobiotechnologies, providing for the latest approach to protect and preserve the environment, namely the use of metabolic potential of biological systems in the process of wastewater treatment (bioremediation). In this regard, we have continued, started in 2014, experimental research on the wastewater treatment of the closed Khrustalnensky GOK mining enterprise using Lemna minor. Based on previously developed principles for ensuring the environmental safety of tailings dumps containing toxic mineral waste during 2014-2017 in the laboratory an experiment was set up to purify industrial wastewater by its advanced treatment with hydrophytes, namely little duckweed (Lemna minor). The essence of the experiment was as follows (starting on July 7 – finishing on September 6): 4 liters vegetative vessels were filled with the study samples in triple replication, namely, with waste industrial water from the Fabrichny tailings damp of the Khrustalnensky GOK closed mining enterprise. On July 7, 2016, Lemna minor was planted in them. Then, the chemical analysis of samples from each container was made for every 10 days to determine the residual concentration of chemical elements. The experiment was finished on September 6. The data obtained during the experiment showed that the degree of advanced treatment of the tailings dump using Lemna minor was high. At the same time, based on the results, it can be concluded that the process of Lemna minor accumulation was not stable and ambiguous for different polluting elements. A steady decrease in the content of arsenic, cadmium and antimony compounds has been detected over time. At the same time, the concentration of compounds of such elements as chrome, cobalt, nickel, copper, zinc and lead, showed the frequency of their decline and some increase and decrease again (as they saturate Lemna minor and then their return the aquatic environment). The results of the experiment showed that the process of absorption of chemical element compounds by Lemna minor was quite active and the accumulating abilities of hydrophyte are very high.

Below, there are the results of analytical studies of changes in the chemical compounds concentration in the technological effluents of the Fabrichnoe tailings dump during the experiment (figure 1, 2). A high degree of industrial wastewater treatment using Lemna minor is shown. Virtually, all compounds of toxic chemical elements contained in industrial wastewater (zinc, cobalt, nickel, cadmium, iron, manganese, lead, etc.) were completely absorbed by the hydrophyte. Ninety-five per cent of the pollutants extraction has been achieved.

**Figure 1.** Zinc content, mcg/dm³.

**Figure 2.** Arsenic content, mcg/dm³.

Thus, the results of the laboratory study proved the possibility of effective use of little duckweed (Lemna minor) for the treatment of sludge, drainage and mine waters, which for many decades being unrestricted around the clock carry a large amount of pollutants into the ecosphere, including water
facilities. The novelty of the proposed ecobiotechnology has been confirmed by the Patent of Russian Federation (2014) [28]. Ecobiotechnology is the guarantor of the environmental safety of tin waste processing in the form of pulp. A system is currently being developed for year-round biological advanced treatment of industrial wastewater (in the form of pulp) in treatment modules using Lemna minor and common reed grass (Phragmites australis).

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