ABSTRACT

of the dissertation submitted for the degree of Doctor of Philosophy (PhD) in the specialty 6D072000 – "Chemical technology of inorganic substances"

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Development of sorption remediation methods of Kazakhstan's water basins from heavy metals

General characteristics of the work. Dissertation work "Development of sorption methods of remediation of reservoirs of Kazakhstan from heavy metals" is devoted to the development of technology for producing activated carbons based on cheap non–traditional raw materials of plant origin - Miscanthus plants grown on the territory of Kazakhstan. Methods of purification of water bodies with developed activated carbons are proposed.

Relevance of the research topic. The Republic of Kazakhstan, as well as the whole world, is characterized by increasing trends of urbanization and industrialization, which cause deterioration of the ecosystem. Currently, the rivers and lakes of Kazakhstan continue to be intensively polluted by mining, metallurgical and chemical industries, municipal services of cities, posing a real environmental threat to the biosphere and water security of the Republic. Despite the significant work being done to improve the condition of the country's water bodies, water pollution continues to grow, in particular, as the data showed, with heavy metal ions: lead, zinc, copper.

Reducing the content of heavy metal ions in water to values that are safe for human use, as well as reducing the damage caused by humans to the environment in the course of economic activity, is a priority task for the country. One of the widely developing technologies for the treatment of wastewater and natural waters from the most harmful components – heavy metal ions is the use of adsorption technologies based on activated carbons. Sorption purification from metal ions has become widespread due to efficiency, the absence of secondary contaminants, as well as environmental and economic efficiency.

In this regard, the search for new sorbents and the development of sorption technologies is an important stage in the technology of restoration of the polluted

natural aquatic environment. To solve this problem, it is necessary to choose an inexpensive, but effective material suitable for sorption processes.

In this work, the plant Miscanthys x giganteus (miscanthus), which is a promising, renewable plant raw material with good sorption properties, was selected as a raw material for the production of activated carbons (AC). Miscanthus is a highly productive triploid perennial cereal. It grows well in waterlogged areas, adapted to cold climatic conditions. Interest in miscanthus has increased worldwide due to the ability of its roots to accumulate heavy metal ions, and aboveground biomass can be used for various purposes, in particular, to obtain AC. Kazakh scientists are actively studying the possibility of growing this plant on the territory of Kazakhstan, while examining soils contaminated with heavy metals and organic pollutants.

Obtaining AC from miscanthus straw will make it possible to obtain economically profitable and effective sorbents from renewable raw materials grown on the territory of Kazakhstan, ensuring the integrated use of the plant to solve environmental problems associated with contamination of soils and water bodies from heavy metal ions. All of the above determines the relevance of the development of technologies to prevent pollution of the biosphere and methods of purification of aquatic environments from TM by sorption method using an AC based on miscanthus straw, as one of the stages of a comprehensive technology for the purification of both natural reservoirs and wastewater.

The purpose of the study: To develop a technology for producing activated carbons from plant raw materials "miscanthus giganteus" and their use for cleaning reservoirs of Kazakhstan from toxic metals.

Research objectives:

1. To obtain activated carbons based on miscanthus straw (ACM) grown in the field by carbonization with subsequent activation by superheated water vapor.
2. To study the structure, physico-chemical properties of the obtained ACM.
3. To investigate the adsorption properties of ACM from aqueous solutions containing TM ions under static conditions.
4. To conduct a comparative analysis of the method of obtaining ACM with the methods of obtaining coals from various raw materials by the partial order method.
5. To develop an environmentally friendly technology for obtaining new ACM for adsorption purification of aqueous solutions contaminated with TM ions, calculation of the material balance of production, basic technological equipment and economic justification.
6. To develop a technology for cleaning reservoirs using ACM.

Objects of research: miscanthus straw, activated carbons based on miscanthus straw, heavy metals, aqueous solutions.

Subject of research: activated carbons based on miscanthus straw and the development of technology for producing activated carbons and methods for cleaning contaminated water.

Scientific novelty of the research. In this paper, for the first time, a method for obtaining activated carbons from the straw of a miscanthus plant grown in Kazakhstan is proposed by a two-stage method: carbonation followed by activation with superheated water vapor. It is shown that the use of miscanthus straw as a basis for the production of AC is advisable, since, as is known, the plant itself is used to clean the soil from TM. It is known that its roots effectively absorb heavy metals, and the aboveground part of the biomass can find effective use as a material for the production of sorbents.

Optimal conditions were found for obtaining AC with a high specific area of the sorbent, which exceeded 500 m^2/g and a specific pore volume of 0.232 cm^3/g. The features of purification of aqueous solutions of AC based on miscanthus straw from TM ions have been established.

A basic technological scheme for the production of activated carbons from miscanthus straw has been developed, laboratory regulations for their production have been developed, the material balance of production per 100 kg of products, the productivity of the main equipment and the main economic indicators of production have been calculated. It is established that the cost of manufactured products is 73 tenge per 1 kg of ACM.

A technology for cleaning reservoirs using new activated carbons from miscanthus straw has been developed.

The new AU obtained showed good sorption capabilities with respect to TM ions in solutions with a pH of 4 for lead ions and 6 for zinc and copper ions. The results of the studies revealed a high sorption capacity of the studied AU with respect to Cu^{2+}, Zn^{2+} and Pb^{2+} ions. It is shown that the AU obtained by us removes up to 90% of Zn^{2+}, Cu^{2+} and 99.8% Pb^{2+} ions at an initial content of 50 mg/l for 60 minutes.

Scientific and practical significance of the study.

The possibility of obtaining sorption-active carbon materials based on cheap non–traditional raw materials of plant origin - miscanthus plants grown on the territory of Kazakhstan is shown.

The straw of the miscanthus plant, provided by the Institute of Biology and Biotechnology of the KN of the Ministry of Education and Science of the Republic of Kazakhstan (Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan) within the framework of the NATO international project “New Biotechnology for Cleaning Contaminated Military Sites” [23], which studies the bioremediation of contaminated TM soils of Kazakhstan using Miscanthus, was used as a feedstock. Accordingly, by growing Miscanthus to clean soils contaminated with TM ions, the aboveground part of the straw can be used to obtain productive AC for use in methods of water purification from TM ions, thereby simultaneously solving the issue of disposal of the aboveground part of the dried straw.

The technology of production of AC for purification of reservoirs from TM ions is described.

Methods of purification of water bodies with the obtained sorbent are described.

The inclusion of coal treatment methods for water purification will lead to a decrease in the content of TM ions, they can also be used as sorption materials in various industries due to their cheapness.

The developed technological schemes for obtaining AC, as well as the proposed methods for cleaning reservoirs using the obtained AC can be used to purify waters contaminated not only with TM, but also with other pollutants.

The obtained results and scientific data on the dissertation work will contribute to the development of new technologies aimed at solving international and regional environmental problems related to the metallurgical and mining industries of Kazakhstan and other countries. The work is aimed at using renewable and cheap environmentally friendly sorption materials, which will allow developing cost-effective technologies for water purification by sorption methods.

Research methods.

The following research methods were used in the work: mass spectrometry, atomic absorption spectrometry, microscopy, X-ray fluorescence analysis, IR spectroscopy, thermogravimetry, Raman spectrometry, elemental analysis, porometric analysis.

Validity and reliability of the data obtained.

The conclusions are formulated on the basis of experimental data obtained on devices authorized by state bodies. The data obtained by us correlate with the data of previously done work by scientists around the world on the study of activated carbons of various origins. Special licensed computer programs were used to process experimental data. Thus, the results of the work carried out are reliable and justified. The use of methods of statistical processing of results serves as an additional basis for the reliability of the conclusions drawn and the results obtained.

Part of the work, as well as some articles, were written under the supervision of the foreign scientific supervisor Professor Lars Carlsen (Lars Carlsen, Denmark, Roskilde).

Description of the contribution of the doctoral student to the preparation of each publication.

The doctoral student was directly involved in the preparation of activated carbons, obtaining experimental data, processing and interpretation of experimental results, and also took part in the performance of physical and chemical studies for the design and writing of scientific publications.

The main provisions submitted for protection.

1. The maximum yield of coal up to 29% with a carbon content of 85% by weight for the straw of the miscanthus plant grown in Kazakhstan is achieved by its carbonation at 500 ^{0}C for 30 minutes.

2. The specific surface area of the sorbent 542 ± 9 m^2 / g with a specific pore volume of 0.232±0.004 cm^3 / g is achieved by activating carbons from miscanthus straw with superheated water vapor at 800 ^{0}C for 60 minutes.

3. The technology of obtaining AU from miscanthus by carbonation at 500 ^{0}C for 30 minutes and subsequent activation by superheated water vapor at 800 ^{0}C for 60 minutes, makes it possible to obtain a sorbent with high adsorption capacity to TM ions: up to 90% Zn^{2+} ions, 90% Cu^{2+} and 99.8% Pb^{2+} in an initial concentration of 50 mg/l.

4. The price of ACM obtained according to the technological scheme, which includes the carbonation stage at 500 ^{0}C for 30 minutes and the activation stage by superheated water vapor at 800 ^{0}C for 60 minutes, is 73 tg for 1 kg of products, which is 13 times less than the cost on the market of known adsorbents such as BAU.

The connection of the topic with the research plan and various Government programs.

The work was carried out within the framework of the project funded by the KN MES RK 3655/GF4. Topic: "Cost-effective remediation of freshwater basins of Kazakhstan polluted with heavy metals" on the priority "Rational use of natural resources, processing of raw materials and products"

The main material – Miscanthus straw was provided by the Institute of Biology and Biotechnology of the KN of the Ministry of Education and Science of the Republic of Kazakhstan, studied within the framework of the NATO international project G 4687 “New Biotechnology for Cleaning Contaminated Military Sites” on the development of phytoremediation technology of heavy metal-contaminated soils of Kazakhstan, with the help of giant miscanthus.

Approbation of work and publications.

The results of the work performed are reflected in 12 scientific papers, including:

- in 2 articles published in international scientific publications that have a non-zero impact factor according to the Thomson Reuters information database (ISI Web of Knowledge, Thomson Reuters), or are included in the Scopus database;
- in 4 articles published in journals recommended by the Committee for Control in the Field of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan;
- in 5 materials and abstracts of international, republican scientific symposia and conferences, 3 of them in the materials of foreign conferences.
- in 1 material for one of the chapters of the book.

Personal contribution of the dissertation.

The results presented in the dissertation of K. E. Abit were obtained by the author himself, under her supervision or with her direct participation.

The structure and scope of the dissertation.

The dissertation is presented on 125 pages, consists of an introduction, 4 main sections, a conclusion, a list of used sources from 217 titles and includes 29 tables, 22 figures and 2 diagrams.

Based on the results of the dissertation research, the following conclusions were made:

1. In the course of the work, a technological scheme was developed for obtaining sorption-active carbon materials based on cheap non–traditional raw materials of plant origin - miscanthus plants grown in Kazakhstan by carbonation with subsequent thermal activation by superheated water vapor. The method is economically and environmentally sound.

2. The most optimal carbonization temperature regime for Miscanthus straw is: firing at a temperature of 500 ^{0}C for 30 minutes, which results in a sample with a carbon content by weight of 73%.

3. The physicochemical composition and technological characteristics of the obtained AU are established. Activation by superheated water vapor of coals obtained at 800 ^{0}C for 60 minutes makes it possible to obtain activated carbon with a specific surface area of 542 ± 9 m^2/g, an adsorption volume of 0.232 ± 0.004 cm^3/g.

4. The resulting activated carbons have a high sorption capacity with respect to Cu^{2+}, Zn^{2+} and Pb^{2+} ions. AUM removes up to 90% of Zn^{2+}, Cu^{2+} and 99.8% Pb^{2+} ions at an initial concentration of 50 mg/l. As can be seen from the analyses carried out, activated carbons from miscanthus are most easily removed from aqueous solutions of Pb^{2+} ions.

5. The beginning of the sorption of TM ions by activated carbons obtained from aqueous solutions from pH 4 for lead, as well as from pH 6 for zinc and copper with concentrations of initial solutions of 10 mg / l.

6. A comparative analysis of the method of obtaining ACM with methods of obtaining coals from various raw materials by the partial order method showed that this method is a good alternative for the production of AC from vegetable raw materials.

7. Technological schemes of AC production have been developed. It is shown that the cost of production of AC from miscanthus straw is 13.7 times less than the cost of coal on the market of Kazakhstan AC from other types of vegetation on the example of BAC.

8. The technology of purification of reservoirs with the use of AC from miscanthus straw as a sorbent has been developed. The inclusion of coal treatment in the complex of technological schemes for water purification will lead to a decrease in the content of heavy metal ions, they can also be used in various industries, while reducing costs compared to expensive sorption materials from non-renewable raw materials.