ANNOTATION

to the dissertation for the degree of doctor of Philosophy (PhD) in the educational program

“6D074000 – Nanomaterials and nanotechnologies”

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on the topic “The modified carbon nanomaterials of porous graphite and rice husk”

General description of work. In the presented dissertation work, nanostructured porous carbon samples of graphite and rice husk were obtained and studied. These studies made it possible to develop low-cost technologies for the synthesis of nanostructured porous samples modified by high-temperature heat treatment by direct oxidation. Studies have shown that these methods provide controlled synthesis of nanostructured samples with desired morphology and properties. Physicochemical properties, morphological structure, processing parameters and sorption properties of modified samples were studied.

Relevance of the research topic.

The problems of creating low-cost technologies for the synthesis of multifunctional nanostructured porous products are attracting attention. When synthesizing nanostructured porous samples, wide possibilities open up for controlling the structure and these samples to take into account size effects visible in the nanometer region and the contribution of the specific surface area to the properties of the samples. Potential developments are high using oil sorbents based on nanostructured porous samples such as graphite and rice husk.

Oil production increases every year, which is accompanied by significant environmental pollution. Oil is included in the list of ten main pollutants of the biosphere. Pollution of surface water bodies with petroleum hydrocarbons occurs not only during emergency oil spills, but also during transportation, drilling and storage, which increases the anthropogenic load on the ecosystem. There are five types of oil impacts on aquatic ecosystems:

- direct poisoning of living organisms resulting in death;
- disruption of the physiological activity of aquatic organisms;
- direct shell of petroleum products of a living organism;
- the occurrence of diseases caused by the intake of carbohydrates into the body;
- negative changes in the environment.

Currently, the creation of oil sorbents with special morphology and characteristics is one of the most important tasks due to their unique chemical and physical properties.

In this regard, the task is to create an economical oil sorbent with high sorption properties for the rapid removal of oil contaminants from the water surface. An urgent task to solve this problem is the search for nanostructured porous samples containing carbon, suitable for the production of sorbents for capturing oil from water surfaces and purifying industrial wastewater.

The main requirements for an optimal carbon sorbent for collecting oil and oil products from the surface of water are: high oil sorption properties, the possibility of regeneration with utilization of collected oil, low cost, etc. The basis of such substances is organosilicon compounds such as rice husks, as well as graphite, which has high sorption properties. Thus, the purpose of this scientific dissertation is to search for highly effective oil sorbents, such as modified nanostructured carbon porous samples based on graphite and rice husk.

The goal of the work – obtaining highly porous samples of a modified nanostructure based on graphite and rice husk with determination of their oil sorption properties.

To achieve this goal it is necessary to complete the following **tasks:**

1. development of technology for the synthesis of modified carbon nanostructured porous samples of graphite and rice husk;
2. determination of effective parameters and modes of structural modification by heat treatment methods;
3. characterization of synthesized thermally expanded graphite and carbonized rice husk by chemical composition, structural features, particle sizes and morphological properties;
4. assessment of oil absorption capacity and optimization of the absorption process of thermally expanded graphite and carbonized rice husk.

Objects of research: nanostructured porous materials based on rice husk and graphite, porosity, metal nanoparticles in mixtures of 20%graphite/ 80%$Zn(NO_3)_2 \cdot 6H_2O$ and 30%graphite/70%$FeCl_3 \cdot 6H_2O$, sorption properties.

Research methods

The following research methods were used in the work: low-temperature nitrogen adsorption analysis, scanning electron and optical microscopic analysis, energy dispersive X-ray microanalysis, Raman spectroscopic analysis, X-ray phase analysis, infrared spectroscopic analysis, spectrophotometric analysis, sorption capacity and leaching method.

Subject of research: determination of synthesis conditions using the method of heat treatment of target materials, the degree of swelling necessary to study the nanopores of the obtained samples and ensure complete completion of the process, as well as effective phase separation of the samples to obtain a porous nanostructured sorbent.

Main provisions submitted for defense:

1. Heat treatment of mixtures of 20% graphite/80%$Zn(NO_3)_2 \cdot 6H_2O$ and 30%graphite/70%$FeCl_3 \cdot 6H_2O$ at a temperature of 800 ^{0}C for 5 minutes makes it possible to obtain nanostructured porous materials with an average pore diameter of 13.3 nm and 10.7 nm. their swelling coefficients were 70.1 cm^3/g, 50.2 cm^3/g. Carbonization of rice husk at 900 0C for 60 minutes in the presence of propane-butane led to the formation of a nanostructured porous material with an average pore diameter of 11 nm and a carbon content of 73.2%.
2. According to Scanning Electron Microscopy of samples of Thermally expanded graphite TEG-1 and TEG-2, under the influence of particles of zinc (Zn) and iron (Fe) 3-4 nm in size obtained as a result of modification of graphite and the

pores of carbonized rice husk (CRH-900) imparts samples new properties, according to Raman spectra, the Id/Ig ratio was equal to 0.75-0.87, which indicated an increase in structural disorder and graphitization of the structure of heat-treated samples

3. Nanoporous samples obtained by heat treatment of mixtures of 20%graphite/80%$Zn(NO_3)_2 \cdot 6H_2O$ and 30%graphite/70%$FeCl_3 \cdot 6H_2O$ showed an oil absorption capacity of 90 g/g and 79 g/g, the highest part of these samples consists of mesopores, which are very suitable for the adsorption of large organic molecules and contribute greatly.

4. The resulting heat-treated samples with a ratio of 20% graphite/ 80% $Zn(NO_3)_2 \cdot 6H_2O$ and 30% graphite/ 70% $FeCl_3 \cdot 6H_2O$ by combustion in an oil layer on the surface of water showed a sorption capacity for oil of -58 g/g zhen 45 y/y, this is explained by the influence of external factors, such as wave height, wind speed and oil layer thickness.

Scientific novelty of the work.

1. For the first time, methods and optimal technological conditions have been proposed for the production of carbon nanostructured porous materials by heat treatment of mixtures of 20%graphite/ 80%$Zn(NO_3)_2 \cdot 6H_2O$ and 30%graphite/ 70%$FeCl_3 \cdot 6H_2O$ and carbonized rice husks.

2. The degree of graphitization of the disordered structure was determined by the pore size and I_D/I_G ratio of thermally expanded graphite samples TEG-1, TEG-2 and CRH-900.

3. It was revealed that the sorption capacity of nanostructured porous sorbents developed on the basis of thermally expanded graphite is 90 g/g, this is explained by the fact that most of these samples consist of mesopores.

Practical significance.

Samples of heat-treated sorbents based on graphite and agricultural waste processing residues make nano-sized modified nanostructured porous samples more active. The resulting nanostructured porous samples and samples based on them, due to their high oil sorption and retention properties, are promising for use as sorbents for eliminating oil and oil product spills on the water surface.

Relationship with research work.

The dissertation work was carried out according to the plan of the research project of the Institute of Combustion Problems “Development of innovative technology for decontamination of the consequences of emergency oil spills on the water surface” within the framework of the grant funding program of the Republic of Kazakhstan (state registration No. 0115 RK 0085).

The author of this dissertation personally took part.

The goals and objectives of the dissertation work were created jointly with the PhD supervisor Kenes Kakimovich Kudaibergenov. All experimental work on the production of nanostructured porous materials was carried out by the author independently. Surface morphology, Raman spectra, microscopic and optical characteristics, structural properties, study of surface morphology, elemental analysis of thermally treated samples were carried out with the help of

technological personnel staff of the national open-type nanolaboratory of the Al-Farabi Kazakh National University.

The pore size and specific surface area of the samples were analyzed using a TriStar II Plus analyzer (Micromeritics) at the Laboratory for Advanced Research in Materials and Laser Technologies, Nazarbayev University, Astana. Infrared spectroscopic analysis, spectrophotometric analysis, sorption parameters and methods for determining the alkalinity of the obtained samples were performed at the Combustion Research Institute in Naples, Italy.

The results obtained by the dissertation student were discussed with the scientific advisor, Doctor of Philosophy (PhD) K.K. Kudaibergenov and foreign consultant Doctor of Philosophy (PhD), Professor Roberto Di Capua, as well as Doctors of Philosophy (PhD) M. Alfe and V. Gargulio during a foreign internship at the Combustion Research Institute in Naples, Italy.

The author was directly involved in writing scientific articles together with a scientific supervisor and testing the results of the work by participating in seminars and conferences. The author is the first or correspondent of all major scientific articles written based on the results of the work performed.

Approbation of work. The dissertation materials were presented and discussed at the following international scientific conferences and symposia:

The research results were presented at the international conference of young students and scientists "Farabi world" (Almaty, 2016).

IX International Symposium "Combustion and Plasma Chemistry", (Almaty, 2017),

FMHIHC, IOP Conference Series: Materials Science and Engineering, (Dubai, United Arab Emirates, 2018),

7th International Conference on Carbon Dioxide for Energy Conservation and Environmental Protection (ESCO'17), (Lyon, France, 2017).

Publications.

According to the main results of the dissertation, there are 23 publications, including 1 article in scientific journals included in the 3rd quarter quartile of the CiteScore index 36% percentile in the Scopus database, 7 articles in scientific journals recommended by the Committee for Quality Assurance in Education of the Ministry of Education of the Republic of Kazakhstan, 9 articles in international scientific journals and 4 theses - in collections of international conferences and 2 patents on utility models of the Republic of Kazakhstan "Method of obtaining graphite sorbent" No. 2235 dated 21.06.2016 and No. 2713 dated 26.06.2017.

Structure and scope of the dissertation.

The dissertation consists of an introduction, four chapters, a conclusion, a list of domestic and foreign literature containing 124 publications. The dissertation is written on 105 pages, including 67 figures,12 tables, 31formulas and 2 appendices.