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Abstract

Dissertation topic: Carbon-mineral adsorbents and catalysts for wastewater treatment from surface-active substances

Relevance of the research: One of the most current problems of environmental protection is the treatment of industrial wastewater from toxic organic substances, including surface-active substances (surfactants). The production of surfactants is one of the large-scale enterprises of the petrochemical industry. Most of the produced surfactants are used in the detergents and in the production of fabrics and products based on synthetic and natural resources. Surfactant consumers include the oil and chemical industry, construction industry and a number of others.

In industrial production, wastewater is usually treated before being discharged, but for domestic use of surfactants, it is removed to the sewer without treatment. But even small concentrations of surfactants, when released into natural water bodies, can have a negative impact on living organisms, inhabiting said water bodies, due to a violation of their oxygen metabolism.

Along with this, being in water, surfactants at certain temperatures can form micelles with which other harmful substances are able to solubilize, what contributes to their distribution with water and even more complicates the process of its purification.

There are quite a few methods for wastewater treatment from surfactants. One of the most effective among them is the destructive method, however, when using it, it must be taken into account that the products of breakdown should not be more harmful to the environment than the original substances. In practice, conjugate methods are used: a rough initial and subsequent deeper post-treatment.

Cationic or non-ionic surfactants are substances that are resistant to biological decomposition. For their deep destruction, it is advisable to use strong oxidizers. Among them, the choice of substances that are safe for the environment is preferable. Recently, ozone and hydrogen peroxide have been used as such.

They are highly oxidizing, easy to use, and do not form pollutants when decomposed. However, ozone is more energy-intensive and expensive, so it is most often used to treat relatively low-concentrated wastewater. The process, which uses hydrogen peroxide as an oxidant, is being actively explored as one of the alternative options for treating wastewater with medium and relatively high concentrations of total organic carbon. When using hydrogen peroxide, it is easy to provide the required concentration of this oxidizing agent in water by simply mixing its solution with water.

In addition to oxidizing, sorption methods of wastewater treatment are effective. At the same time, along with traditional types of sorbents, such as absorbent carbon (AC), carburized materials are often used, obtained from cheaper raw materials and even production waste. Waste from the agro-industrial complex, such as cereal straw, buckwheat husks, rice husks, sunflower husks, beet pomace, peanut shells and their other varieties, is increasingly used for wastewater treatment. They also serve as the basis for obtaining sorbents along with cellulose-containing materials in the form of woodworking waste, which include cuttings, shavings, sawdust, chips, wood bark, etc.

Disposal of worn-out car tires is a big problem for the world ecology. The possibilities of using the waste of chemical recycling of automobile tires as a raw material for the carbon sorbents production are being studied today.

There are many types of raw materials available, from which a wide range of carbon-mineral sorbents are produced by various methods. Of practical interest, in particular, is the assessment of the possibility and feasibility of producing carbon-mineral surfactant sorbents and catalysts for the oxidative decomposition of surfactants with hydrogen peroxide based on cheap components in the form of tire crumb and natural clay.

The research objective is to substantiate the choice of raw materials and conditions for the synthesis of carbon-mineral materials based on natural clay and tire crumb; to study their properties that characterize their capabilities as

adsorbents for the removal of surfactants from wastewater, as well as catalysts for the oxidative decomposition of surfactants with hydrogen peroxide.

The research tasks:

1. The choice of raw materials for the production of carbon-mineral materials (CMM), for use as adsorbents and catalysts.

2. Substantiation of rational conditions for modifying natural clays with carbon from tire crumb: the ratio of clay; modifier, pyrolysis temperature, heating rate, holding time at the final temperature, iron additions.

3. Evaluation of crystallinity, textural characteristics and adsorption properties of the obtained CMM for a number of adsorbents (water vapor, benzene, nonionic surfactants).

4. Evaluation of the catalytic properties of the obtained materials: determination of the surface acid sites, the valence state of iron on the surface of clay and CMM, the decomposition efficiency of nonionic surfactants in water solutions by hydrogen peroxide.

5. Development of a technological scheme for obtaining CMM and an indicative feasibility study.

Scientific novelty of the research:

1. Based on the study of the clay characteristics from a number of Kaluga region deposits (yellow montmorillonite clay of the Borshchevskoye deposit, gray and black palygorskite clays of the Kalinovo-Dashkovskoye deposit), the advantage of montmorillonite clay of the Borshchevskoye deposit, which has the best characteristics of the porous structure and contains about 8 wt. % iron, is determined for use in adsorption and catalytic processes for wastewater treatment from organic compounds.

2. A rational ratio of raw material components has been established (natural clay of the Borshchevskoye deposit:tire crumb = 75:25), providing the best adsorption and catalytic characteristics of the obtained carbon-mineral material.

3. The influence of the pyrolysis temperature of CMM samples based on clay of the Borshchevskoye deposit on their physicochemical properties: textural

characteristics, crystallinity, ζ-potential values of CMM colloidal systems, and adsorption properties for water vapor and nonionic surfactant was studied. It has been shown that the best nonionic surfactant adsorbent (for example, neonol AF 9-10), which is not inferior to industrial microporous activated carbons in the region of low concentrations of the organic substrate in water solutions, is CMM pyrolyzed at 650°C. The maximum sorption characteristics of the CMM-650 sample are caused by the optimal ratio of the pore parameters of the resulting material and its crystallinity.

4. The effect of the pyrolysis temperature of CMM samples based on Borshchevskaya clay on the total number of surface acid sites and catalytic properties in the reactions of hydrogen peroxide decomposition and oxidative decomposition of nonionic surfactants (neonol AF 9-10) with hydrogen peroxide was studied. It was found that CMM samples pyrolyzed in the range of 650-750 ^{0}C had the best catalytic properties. The degree of decomposition of hydrogen peroxide under the experimental conditions was 70-80%, the degree of oxidative decomposition of surfactants by hydrogen peroxide was 80%.

5. Using the method of planning the experiment, the conditions for obtaining CMM for adsorption treatment of wastewater from non-ionic surfactants were optimized (for example, neonol AF 9-10): ratio of the Borshchevskoye deposit clay/tire crumb - 75/25, pyrolysis temperature - 650^{0}C, environment - nitrogen.

6. Using the method of planning the experiment, the conditions for the synthesis of CMM are optimized to obtain a catalyst for the oxidative decomposition of nonionic surfactants with hydrogen peroxide.: ratio of the Borshchevskoye deposit clay/tire crumb - 75/25, pyrolysis temperature - 750^{0}C, environment - oxygen-limited air.

Practical significance of the research:

1. A method has been developed for obtaining carbon-mineral material from available natural and technogenic raw materials (natural montmorillonite clay and tire crumb) using standard, simple technological operations, which makes it possible to scale production.

2. The developed CMM is suitable for use both as an adsorbent of nonionic surfactants from water solutions and as a catalyst for the oxidative decomposition of nonionic surfactants by hydrogen peroxide.

3. An equipment-technological scheme for the implementation of the developed technology has been proposed and its tentative feasibility study has been completed.

4. The proposed method of obtaining carbon-mineral materials is one of the possible recycling methods of industrial rubber products which results in the production of high-quality and inexpensive adsorbents and catalysts that are comparable to current developments in this area.