Apparatus and technological design of the production process of activated highly porous carbon material

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Abstract. The possibility of developing activated highly porous carbon materials with a maximum specific surface area is shown. Their classification, the main stages of research and the results obtained are considered. A schematic diagram of the production of a material with a BET specific surface in the range of 2400 - 3600 m² / g is presented. The main stages in the production of an activated highly porous carbon material have been determined, including the preliminary carbonization of carbon raw materials, its alkaline activation and post-processing of the resulting material (from the pre-preparation of the components and the preparation of the reaction mixture to the subsequent isolation and drying of the finished product). The composition of the equipment and the possibility of a large-scale transition of the instrumental and technological design of the production process from laboratory to pilot industrial have been established. The obtained activated highly porous carbon material can be used as sorbents in gas media purification systems and in gas accumulators, as well as for solving various environmental problems.

Carbon materials with a developed surface and porosity have found wide application in various fields of modern industry: chemical, pharmaceutical, radio electronics, etc. They are used as sorbents for purification of liquid and gaseous media from harmful organic and inorganic substances, for absorption of radionuclides, for purification of liquid media from harmful bacteria, viruses, biologically active substances and for neutralizing these agents, in order to eliminate the consequences of oil spills, as hemo- and enterosorbents in medicine, as catalysts and their carriers for various chemical processes, electrode materials for chemical current sources, in particular, fuel cells, supercapacitors, etc. Carbon materials with a developed surface can be characterized and classified according to a number of parameters: surface characteristics and porosity; semi-empirical characteristics of adsorption properties in terms of the ability to adsorb various substances; molecular structure; isotropy or anisotropy of the structure and properties of the material; the characteristic size of structural elements or particles of the material; the presence on the surface of particles or pores of a carbon material of heteroatoms, chemically grafted functional groups, non-carbon layers, clusters, nanoparticles; electrophysical, thermal, mechanical, tribological properties and many others [1-3].

For most applications, the most effective materials are those containing meso- and micropores with a high specific volume and specific surface area. The term "nanoporous material" is also widely used, for which the range of pore sizes is not standardized, but usually ranges from one to several nanometers, that is, overlaps with the range of mesoporosity. Nanoporous carbon material is a material, one of the key characteristics of which, determining the effectiveness of its application, is its porous structure,
namely, the average pore size, their shape, pore size distribution, specific pore volume, specific surface of pore walls available for the sorbed substance.

The most promising in this direction can be considered activated highly porous carbon materials, which have a developed system of micro- and mesopores and have found their application in technological processes associated with the separation, isolation and concentration of various gaseous media. For this application, it is necessary that the material has the following characteristics: a large specific pore volume, the size of which is required for the penetration of molecules of adsorbed substances and a sufficiently large specific surface corresponding to the available pores; the material must also have large (transport) pores, ensuring the rapid diffusion of molecules of adsorbed substances in the bulk of the material; must be chemically inert under the conditions of use, the material must be free of impurities or chemical groups that are not stable under conditions of adsorption or other influences [4-9].

To obtain nanoporous carbon materials, various carbon raw materials are carbonized, and then activated with liquid-phase or gas-phase reagents, for example, water vapor, carbon dioxide, nitric acid, potassium hydroxide, etc [10-13].

It can be noted that the authors of numerous works, presenting their results on the synthesis of activated carbon materials, rely on laboratory studies that do not lend themselves well to a large-scale transition to industrial conditions of production - technologies and equipment, or paying attention only to individual properties of carbon materials and individual parameters of production processes, obtain materials with obviously the worst key indicators. In a number of works, the results of mathematical modeling are presented, which are of a private nature and, by and large, are poorly supported by experimental research [14-18]. However, without an integrated approach, knowledge of the relationship between the initial characteristics of raw materials and the resulting highly porous carbon materials, as well as hardware and technological support of the production process, it is impossible to carry out a high-quality full-fledged transition from laboratory research to industrial production [19-20].

The study of the relationship between the characteristics of an activated highly porous carbon material and the instrumental and technological parameters of the synthesis process seems to be a rather complex complex task, which was divided into several intermediate stages.

The first stage included experimental studies aimed at determining the main parameters of the synthesized activated carbon material - the surface parameters and porosity, calculated from the adsorption-desorption isotherms according to one or another theoretical model. Most often, calculations of the surface and porosity of various materials are carried out according to the BET, BJH and DFT models, which, as a rule, are included in the programs of modern devices for adsorption measurements. For different types of materials and size ranges, one or another model is better suited. In our case, the parameters were determined by nitrogen adsorption; specific surface area according to the multipoint BET method; pore size distribution and specific pore volume - by the DFT method, which are most adequate for the materials under study. Preliminary studies have shown that these physicochemical characteristics depend, first of all, on the initial components used to obtain carbon-containing substances (carbonizates), as well as on the activation modes (mass ratio, for example, potassium hydroxide to the activated material, temperature and time activation, gas exchange mode in the reaction zone). In particular, it was found that the addition of graphene to the initial carbonized carbon material significantly changes the macrotexture. Thus, a material without graphene is built of cells, the size and wall thickness of which reaches several micrometers. The walls of the cells have secondary porosity (mesopores), a large thickness of the walls of the cells slows down the diffusion of ions and molecules into the working pores (mesopores), and this worsens the efficiency of such a material in adsorption and electrochemical applications. The addition of graphene radically changes the texture - the mesoporous carbon is distributed in a thin layer on the surface of the graphene layers, making the mesopores easily accessible. An increase in its content to a certain level enhances the effect of improving the macrotexture, however, with a further increase in its content, the specific surface area begins to decrease, since it is only a structure-forming component and by itself does not make a significant contribution to the development of the surface and mesoporosity. And some parameters of the synthesis and the initial
composition can lead to the production of activated carbon, the specific surface of which is predominantly micropores, that is, inaccessible for large ions and molecules [12, 21].

The second stage is aimed at characterizing the physical and mechanical properties of the obtained nanoporous carbon materials. In laboratory studies, these parameters, as a rule, are not given due attention, however, they are very important in industrial conditions. Determination of the initial characteristics (size of particles and agglomerates, coefficients of internal and external friction, slope angles, etc.) was carried out in accordance with GOST. These results will also be in demand at other stages of the work, since they will help to establish the relationship between the characteristics of the obtained material and the instrumental and technological design of the pilot industrial production process.

Studies of the mutual influence of the properties of raw materials, operating parameters of equipment on the synthesis process (third stage) were carried out on the existing laboratory setup. The design allows changing all the main parameters of the process, both carbonation and subsequent activation. The research was based on the hypothesis that as a result of carbonization of carbon raw materials, including carbon nanomaterials (carbon nanotubes or graphene) and subsequent alkaline activation, an activated highly porous carbon material will be obtained that combines an efficient ordered macroscopic structure, high specific surface area and specific volume of mesopores.

The final evaluation of the efficiency of the obtained activated highly porous carbon material (fourth stage) was evaluated based on the results of experimental studies of the actual sorption capacity (sorption/desorption) of real gases, for example, hydrogen, methane, etc., on existing prototypes. At the same stage, a study was carried out to optimize commercial industrial forms of the obtained material.

At the current stage of the research, the authors have worked out the principle technological scheme of production, which has the possibility of further scaling, selection and testing of the general layout of equipment. For the convenience of implementing the technological process and solving layout issues, it is advisable to divide the production line of the activated highly porous carbon material into several stages (according to the technological operations carried out):

1) pretreatment (heat treatment) of the initial carbon substance containing phenol-formaldehyde resin (PFR), graphene (GNP) or carbon nanotubes (CNT), dextrin or carboxymethyl cellulose (CMC) - as a result, a carbonized carbon substance is obtained;

2) mixing carbonated carbon material with potassium hydroxide granules to obtain a uniform reaction mixture;

3) heat treatment of the reaction mixture at the activation temperature - high-temperature alkaline activation, which is carried out by heating the powdered carbonized carbon material with potassium hydroxide with a gradual increase in temperature to 750 °C and holding for a specified time, while an inert environment is maintained in the reactor;

4) carrying out the first stage of post-processing of the activated mixture - which consists in soaking and holding the resulting material with the formation of potassium hydroxide, as well as dissolution of potassium carbonate contained in the activated substance in water. Next, an alkaline aqueous suspension of activation products is transferred to a filter. Filtration and washing with water is carried out on a filter with a filtering layer made of non-woven polypropylene material until the pH of the wash water leaving the filter reaches 7-8;

5) carrying out the second stage of post-processing of the activated mixture - soaking and holding the activated material in acid - is carried out to purify the carbon material from residues of alkali and potassium carbonate, as well as to dissolve impurities of iron compounds that could get into the product at the activation stage. After that, the acidic suspension is washed on a filter with a polypropylene filtering layer to neutral pH of the washing water flowing out of the filter;

6) the drying of the activated highly porous material is carried out in a ventilated drying cabinet at a temperature of 110 °C.

7) packing the dried activated highly porous carbon material into a sealed polyethylene non-transparent container.

The placement of equipment in the schematic diagram should correspond to the sequence of processing of raw materials in technological processes - from pre-preparation of components and
obtaining carbonated material to its chemical activation, and subsequent post-processing - with washing and drying of the resulting finished product. This placement determines the types and number of devices, directions of technological flows, possible grouping of equipment and its distribution in accordance with the main technological chain.

The line for the production of activated highly porous carbon material includes a set of equipment for the implementation of the technological stages of the production of the finished product. The choice of a specific type of equipment is directly influenced by the type of technological process taking place in it, the reaction medium and a number of other processes, such as typification and standardization of structural elements (Figure 1).

Figure 1. Schematic diagram of the production of activated highly porous carbon material.
RC - reactor for carbonization of the original carbon substance; B1 - bunker for potassium hydroxide; B2 - bunker for carbonated carbon matter; B4 - bunkers for the original carbon material; M - mixer for obtaining a pre-reaction mixture; R - reactor for high-temperature alkaline activation; B3 - cylinders for argon; C1 - container for the first stage of post-processing; F1 - apparatus for filtering and washing alkaline suspension; C2 - container for the second stage of post-processing; F2 - apparatus for filtering and washing acidic suspension; DD - drying oven for drying the obtained carbon material; PM - packing machine

To implement the presented production scheme, standard equipment was used - pipelines, shut-off valves, instrumentation, etc. The mixer, tanks and hoppers used in the activated highly porous carbon material production line are typical designs that differ only in volume. An exception are carbonization and alkaline activation reactors, the design and volume of which meet the performance requirements, taking into account the working medium, the need for heating and cooling the reaction volume, supply and removal of inert gas and chemical reaction products.
The technological process includes the following stages and production sequence. Initial carbon materials from bunkers B4 are loaded in a predetermined ratio into the RC carbonization reactor for heat treatment. After that, the powdered carbonated carbonaceous substance and potassium hydroxide and bunkers B1 and B2 are fed with the help of dispensers into the mixer-disperser M for mixing and grinding to obtain a homogeneous reaction mixture. Next, the resulting mixture is loaded into the chemical activation reactor R, into which at the same time the supply of inert gas - argon from the cylinders B3 begins, controlled by a gas meter. In the reactor, the above-mentioned components undergo activation - heat treatment, stepwise, at 400° C and 750° C for several hours [6]. After activation, the resulting product is transferred to the vessel C1 for soaking and holding and is filled with distilled water from the vessel C4. In the C1 container, the material settles for 12-24 hours. Next, the alkaline suspension is fed into the F1 filter, where it is washed with distilled water until neutral. The washed material is fed into the C2 tank, where acid (for example, hydrochloric acid) is also fed from the C3 tank using a liquid dispenser. The mixture remains in the container for 12-24 hours. Then the reaction products - the acidic suspension enters the F2 filter, where they are washed to neutral acidity. After the filter, the material is placed in an DD drying cabinet, where it is dried at 110° C for 4-7 hours, depending on the weight. After that, the obtained activated highly porous carbon material is crushed in the dispenser D and transferred to the PM packing machine for filling and packaging.

Depending on the feedstock used and the activation process modes (temperature, heating rate, holding), activated nanoporous carbon materials with a highly developed porous surface with a predominance of micro- or mesopores were obtained [21]. Physicomechanical and physicochemical characteristics (surface parameters and porosity) were determined by nitrogen adsorption using a surface and porosity analyzer Nova Quantachrome E1200; specific surface area was determined by the multipoint BET method; pore size distribution and specific pore volume - according to the DFT method (Figure 2).

Figure 2. An example of the analysis result of an activated highly porous carbon material carried out on a Nova Quantachrome E1200 analyzer.
As a result, nanoporous carbon materials were obtained with the following characteristics: BET specific surface area - 2400-3600 m² / g, DFT specific pore volume - 2-3.6 cm³ / g, of which for mesopores ≈ 80%, average pore diameter - 2-4.5 nm (table 1).

Table 1. Examples of characteristics of the obtained activated highly porous carbon material

| Initial carbon raw material | S specific surface area by BET, m²/g | S specific surface by DFT, m²/g | Specific pore volume by DFT, cm³/g | Average pore diameter according to DFT, nm |
|-----------------------------|-------------------------------------|---------------------------------|-----------------------------------|------------------------------------------|
| PFR + CMC                   | 2479                                | 1610                            | 2.49                              | 4.5                                      |
| PFR + CMC + CNT             | 2566                                | 2365                            | 2.87                              | 3.55                                     |
| PFR + dextrin               | 2517                                | 1590                            | 3.07                              | 4.15                                     |
| PFR + sugar                 | 3078                                | 1899                            | 2.02                              | 3                                         |
| PFR + dextrin + GNP         | 3200                                | 1780                            | 3.63                              | 1.97                                     |
| PFR + dextrin + GNP         | 3202                                | 2043                            | 2.49                              | 3.63                                     |
| PFR + dextrin + CNT         | 3616                                | 2337                            | 2.61                              | 3.62                                     |

* - The mass ratio of the initial components and the technological parameters of activation (temperature, heating rate and holding) were varied.

Conclusions
Analyzing the results obtained at this stage of research, we can make an unambiguous conclusion that the task set by the authors of the development of an activated highly porous carbon material with the maximum possible specific surface area and specific volume of mesopores has been successfully solved. Despite some ambiguity and insufficient experimental data, it is possible to draw a number of conclusions:
- Highly porous carbon materials were considered and classified, their key characteristics and parameters were determined;
- the necessary research stages for obtaining a highly porous carbon material have been determined and their description has been given;
- established the main stages and features of the production of activated highly porous carbon material, including carbonization of the original carbon raw material, alkaline activation and post-processing of the resulting material;
- it was found that the parameters of the specific surface area and porosity depend, first of all, on the initial components used to obtain carbon-containing substances and their percentage, as well as on the technological modes of activation;
- a schematic diagram of the production of activated carbon material is presented, the basic composition of the equipment is determined, and the possibility of a large-scale transition of the instrumental and technological design of the production process from laboratory to pilot industrial is established;
- the resulting activated highly porous carbon material, according to its characteristics and parameters, can be used as sorbents in systems for purifying gaseous media, in gas accumulators and solving various environmental problems.

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