

Modern Technologies for Producing Foamed Phosphate Glass for Oil Sorbents

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Abstract. The paper considers applications of foamed glassy phosphate materials as carriers of biologically active substances. The atomic layer deposition method allowed chemically synthesizing surface-modified composite materials based on graphite and carbon fibers, which maximally preserved the activity of enzymes and biologically active substances. The synthesis process of a mono-layer titanium-containing coating on the surface of graphite and carbon fibers by processing them with TiCl₄ vapors is considered. The main characteristics of the graphite surface before and after modification and characteristics of the porous structure and surface of carbon fibers are obtained. Biologically active substances by adsorption from a solution to the surface of both the original and modified carriers were applied. biological activity and temperature stability of the obtained composite materials were studied. It is shown that the activity of a biologically active substance depends on the chemical composition and state of the surface of carbon-based carriers.

Introduction

Environmental problems have now acquired a global character and are expressed in irreversible changes in the conditions of human existence. In this regard, there are tasks of eliminating oil spills, products of condensation of exhaust gas aerosols in megacities, cleaning and restoration of technogenically destroyed territories, which include auto enterprises, technology parks, garages and parking lots, territories adjacent to highways and tunnels.

The solution of the above problems is possible by using the technology of complex biological cleaning of territories from oil pollution [1].

Currently used technologies for cleaning territories and eliminating oil spills have a number of disadvantages: firstly, the toxic effect of sorbents on the soil, and therefore the need to collect the sorbent from the surface to be cleaned and its disposal, and secondly, the mandatory implementation of a number of measures for additional soil restoration [2].

Taking into account these shortcomings and on the basis of previously performed studies [3], the biosorbent "BIAVA" was developed and patented, which is a porous sorbent carrier on the surface of which there are microorganisms-destructors of hydrocarbons and catalysts of biooxidation processes [4].

Methods

A foamed glassy phosphate material (foam glass) (Fig.1, a) with micro-additives of boron, cobalt, iron, copper, manganese, and molybdenum, which provide optimal conditions for the vital activity of microorganisms for a long time, was chosen as the carrier sorbent. The internal porous structure of the sorbent is shown in the photo (Fig.1, b) obtained using an electron microscope. Glasses for



biosorbents were synthesized in the system at 1200-1300°C in the system (K₂O-CaO-MdO-P₂O₅) from the charge in quartz crucibles for one hour with stirring. Good results of cooking in gas-heated pot furnaces were achieved by using a liquid charge obtained from orthophosphoric acid.

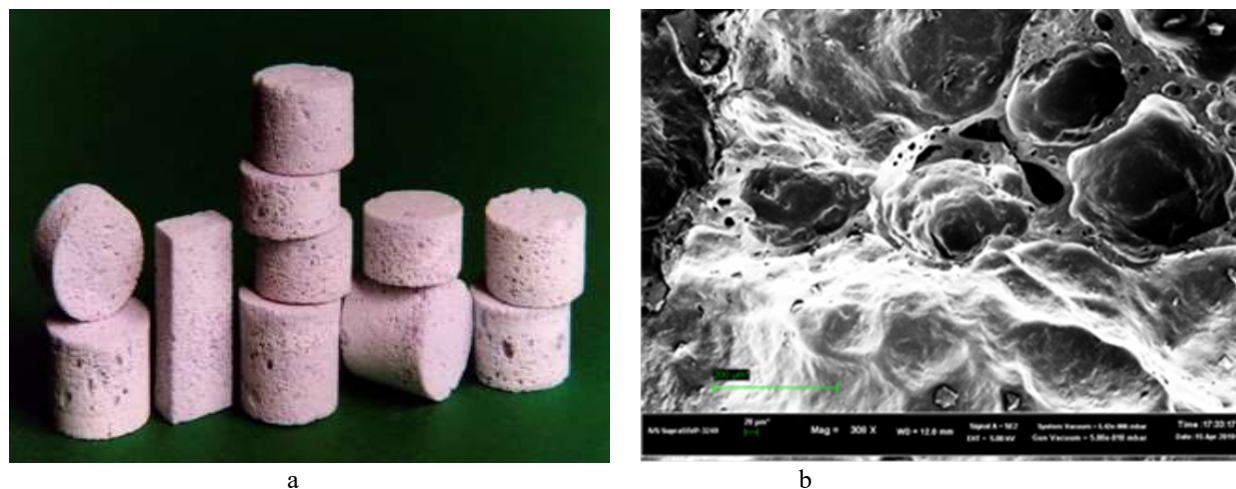


Fig. 1. foamed glassy phosphate material (a), internal porous structure of the sorbent (b)

Also, the main raw materials used were magnesite concentrate, potassium carbon dioxide with a K₂CO₃ content of at least 98 wt.%, and apatite concentrate. The charge was loaded at a temperature of 1100-1150°C in portions. Each new portion was loaded onto the charge that had been boiled and was already in the crucible. Heating was carried out at a temperature of (1200-1250 °C). The production of glass was carried out on metal plates and it's cooled in the air.

For the foaming of glass, a laboratory device was made, including a horizontally arranged tubular furnace, the temperature along the axis of which varies in the range of 150 – 700 – 150°C. The foaming of the pellets inside the furnace was carried out in a "fluidized bed" with the tilt of the furnace, ensuring the continuous movement of the pellets at the desired speed. To maintain the pellets in a suspended state, a pipe was introduced into the working area of the furnace, through which air was blown from the compressor. During the research, the foaming temperature in the furnace varied within 520-620 °C with an interval of 20 °C.

When obtaining foamed samples based on phosphate glasses under laboratory conditions, the initial mixture was a mixture containing 66.7 wt.% of the phosphate glass powder fraction ≤ 1.25 microns and 33.3 % of the foaming agent. The mixture obtained in this way was moistened, and granules of 5-8 mm in size were pressed from it. Foaming was carried out in a gradient furnace, which was heated to 650 °C (at the inlet-220°C, at the outlet-200 °C) (Fig. 2) .

The production of foam glass granules includes the following stages:

- preparation of the initial mixture for foaming;
- forming of pellets;
- foaming of pellets.

The initial components of the mixture (glass powder and foaming agent) were ground in a ball mill to obtain a specific surface area of 1000-4000 cm² / g. The specific surface area was calculated based on the determination of the air permeability of the porous material. The analytical composition of the glasses was determined by the atomic emission method with inductively coupled plasma. It is shown that the difference in the compositions of glasses synthesized in both laboratory and industrial conditions does not exceed 1.0 – 1.5 %.

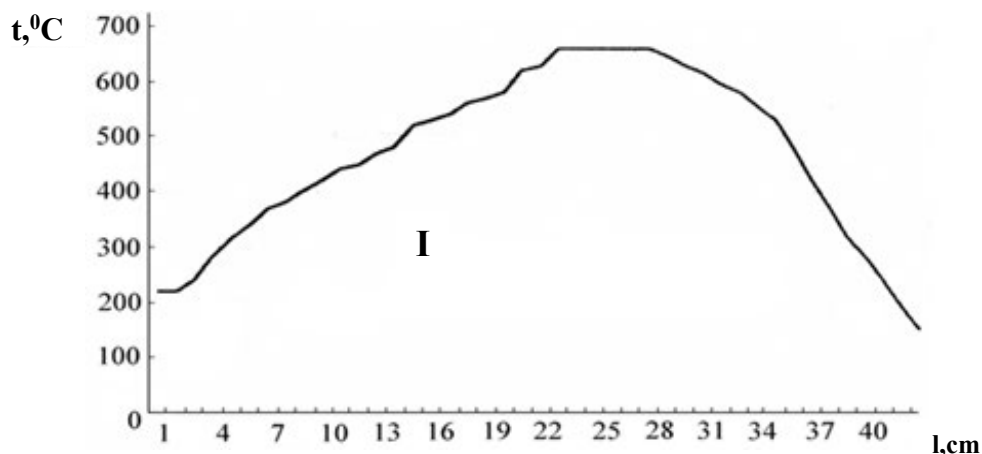


Fig. 2. Calibration curve: 1 - drying zone; 2 - hot zone; 3 - annealing zone

In order to change the chemical nature of the graphite surface, we synthesized monolayer coatings based on elemental layers of titanium and zirconium. One of the effective methods for their synthesis is the atomic layer deposition (ALD) method [5 - 10]. The main advantages of the ALD technology are: control the thickness of the resulting film (a coating of several nanometers), reagents don't interact with each other until they reach the substrate, obtaining a uniform film thickness on the substrate.

The route allows forming covalently-bound monolayer coatings on the substrate surface. Importantly, the synthesis process allows depositing a self-assembled element oxychloride monolayer, since the treatment time required to achieve a maximum coverage is determined by exhaustion of the active surface sites. As a result, a highly reproducible and conformal coating can be obtained [11].

The proteolytic enzyme trypsin was chosen as a model system of biologically active substances. Trypsin is an enzyme preparation with a proteolytic effect, has pronounced anti-inflammatory and decongestant properties, is able to break down dead tissue, fibrinous formations, viscous secrets and exudates. In relation to healthy tissues, the enzyme is inactive and safe. This drug can be used as a part of coatings of artificial organs, vessels during implantations. Immobilization of trypsin on a carrier will allow maintaining the enzyme activity at a sufficiently high level, prolonging its action and increasing resistance to destabilizing factors.

Trypsin immobilization on the surface of carbon materials was carried out by adsorption. The catalytic activity of trypsin was determined spectrophotometrically from the decomposition products of casein.

Results and discussion

Evidently (Table 1), the concentration of oxygen-containing functional groups increases significantly after oxidation and slightly decreases as a result of successive cycles of formation of titanium oxide layers.

The studied carbon fibers are characterized by a small volume of macropores and a specific surface area of not more than 50 m²/g (table 2). These results indicate a low sorption activity of the studied carbon fibers.

The changes in the surface characteristics of the initial and modified graphite correspond to the dependence of the immobilized trypsin amount on the number and chemical composition of the

titanium and zirconium oxide layers (Fig. 3, curves 1' and 2'). With an increase in the number of cycles of graphite surface treatment by the ALD method, the number of active functional groups of the surface decreases, which leads to a decrease in the amount of adsorbed enzyme.

Table 1. Characteristics of the surface of original and modified graphite

Sample	Static exchange capacity for NaOH [$\mu\text{mol}/\text{m}^2$]	Specific surface [m^2/g]
Original graphite	70	16.0
Oxidized graphite	3.00	17.0
Graphite modified with titanium oxide groups (after 1. Treatment cycle)	2.85	15.5
Graphite modified with titanium oxide groups (after 2. Treatment cycle)	2.80	15.3
Graphite modified with titanium oxide groups (after 3. Treatment cycle)	2.65	15.2
Graphite modified with titanium oxide groups (after 4. Treatment cycle)	2.50	14.9

Table 2. Characteristics of the porous structure and surface of carbon fibers

Sample of carbon fibers	Heat treatment temperature [K]	pore volume, m^3/g	Static exchange capacity for NaOH [$\mu\text{mol}/\text{m}^2$]	Specific surface [m^2/g]
gralen	2073	02	05	15
uglen	1173	16	12	50
licron	773	03	03	18

At the same time, samples modified with titanium and zirconium oxide layers show an increase in the activity of the immobilized enzyme (Fig. 3, curves 1 and 2). Obviously, samples based on graphite modified after 4 cycles of sequential deposition of zirconium oxide layers with an enzyme activity of about 80% were obtained (Fig. 3, curve 1).

As a result of surface modification of carbon fiber uglen by zirconium containing coatings, composite materials with the following surface characteristics were obtained (Table 3).

Table 3 shows that it was impossible to significantly increase the biological activity of carbon fiber-based composite materials. Apparently, the interaction of the enzyme molecule with the surface of the carbon fiber changes the tertiary structure of the molecules, which leads to a decrease in catalytic activity. The main reason for the decrease in catalytic activity is usually the formation of associates of enzyme molecules on the surface and blocking of the active center of the enzyme.

Table 3. Characteristics of the surface of original and modified carbon fibers uflen

Sample of carbon fibers	Zirconium content in the sample [$\mu\text{mol}/\text{m}^2$]	Specific surface [m^2/g]	Biological activity A [%]
original uflen	0	50	32
uglen modified with zirconium oxide groups (after 1st treatment cycle)	4	47	39
uglen modified with zirconium oxide groups (after 2nd treatment cycle)	9	38	45
uglen modified with zirconium oxide groups (after 3ed treatment cycle)	1.3	30	47
uglen modified with zirconium oxide groups (after 4th treatment cycle)	1.7	25	49

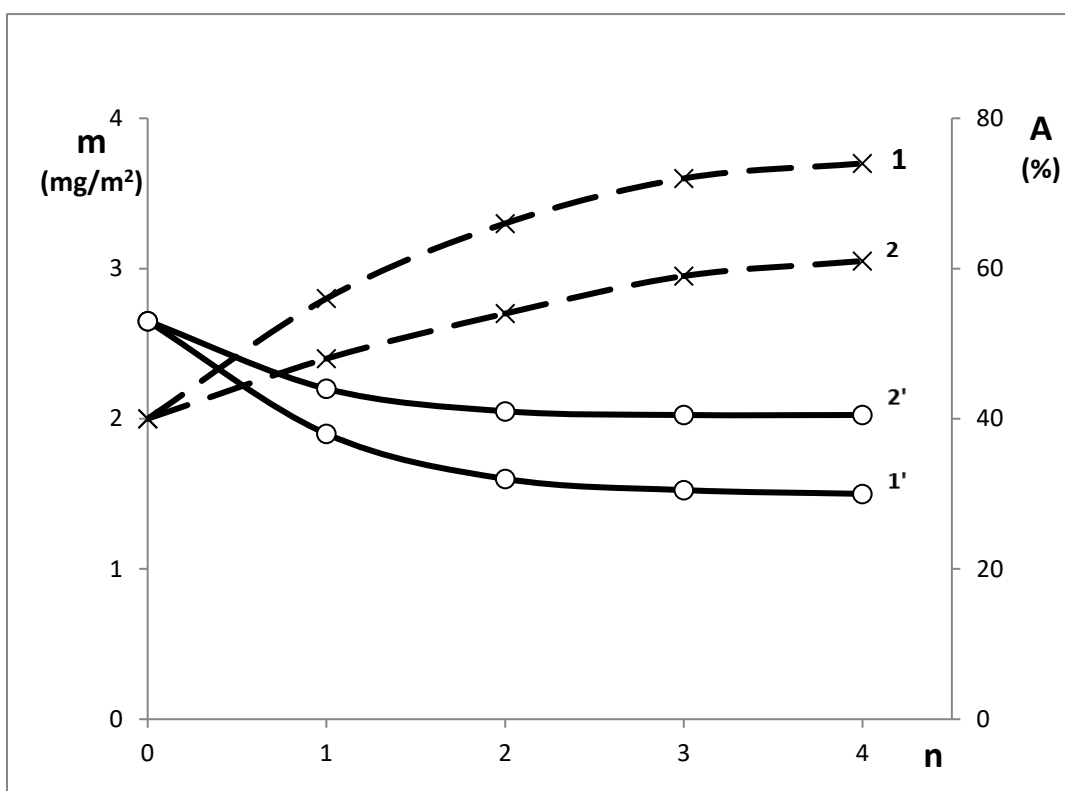


Fig. 3. Dependences of the amount of immobilized trypsin m (1', 2') and biological activity A (1, 2) on the number and chemical composition of element-oxide layers n

Summary

Thus, the decrease in trypsin activity during adsorption on carbon carriers can be due to two factors: the influence of the chemical nature of the active surface centers, as well as the formation of inactive surface associates of the enzyme at high degrees of filling of the carrier surface.

When trypsin was immobilized on a graphite surface with a zirconium-containing coating, samples were obtained with biological activity of about 80 % of the activity of the free enzyme in solution, possessing resistance of the biologically active substance to elevated temperature and pH, the capability of repeated use, which enables further use of these composite materials for the production of electrochemical biosensors.

Thus, changing the chemical nature of the graphite surface by modifying the surface with monolayer titanium and zirconium-containing coatings allows for directional control of the adsorption activity of the surface and production of materials with predictable properties and high catalytic activity for biomedical sensors and other industrial purposes.

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