Abstract:

In this work, the specific features of formation of a composite material consisting of a mixture of low-melting ground glass and waste active sludge, which is used for sewage purification, have been considered. It has been established that, after low-temperature (600–700 °C) short-term (30–60 min) treatment, specimens consist of a porous glass shell and a core saturated by carbon form. With change in temperature treatment conditions, the thickness and porosity of the shell and the size of the carbonized core change, leading to different absorption and adsorption properties. Due to the presence of a carbon-containing core, specimens absorb efficiently methylene blue (MB) from aqueous solution.

Keywords: Waste active sludge; Glass powder; Temperature treatment.

1. Introduction

Waste glass and waste active sludge are classified as large-scale anthropogenic waste, which are processed into a new type of materials in insufficient volumes. At the same time, it is well known that porous glass is one of the most promising environmentally friendly materials that can be used in various branches of technology [1-4]. At present, foam glass obtained from different types of cullet [5-9] is finding increasing application as a building material having good heat-insulating, sound-insulating, mechanical, and even micro-wave absorption properties [10-17]. Foam (cellular) glass is usually obtained in the process of sintering of glass powder and foaming agent. Inorganic compounds that decompose to form gaseous/vapor products (e.g., CaCO$_3$, Na$_3$PO$_4$, NaCl, Na$_2$SiO$_3$, C, SiC, coal fly ash, etc.) during sintering can be used as foaming agents. Recently, organic compounds that readily form CO$_2$/CO as a foaming agent during temperature treatment were used [6, 17-20]. Therefore, it was interesting to find an organic foaming agent that transforms readily into carbon and requires disposal. Waste activated sludge can be one of the most promising materials used for waste water treatment.

The urgency of recycling waste activated sludge is as follows. For storage of residues formed in purification of household sewage, the large specially equipped territories are allotted [21]. As a result, the formation of ecologically dangerous objects, which are
characterized by a high degree of negative influence on the environment and human health, occurs. However, the processing and recycling of stockpiled waste are not practically performed. Nevertheless, there exists a series of methods of using this type of waste [22]:

a) disinfection and detoxication of deposits with obtaining organic-mineral fertilizers and composts;

b) anaerobic destruction and disinfection of used deposits of sewage;

c) temperature treatment including burning in furnaces of different design and low-temperature pyrolysis with obtaining liquid fuel and active carbon.

Taking into account that, during thermodestruction of organic compounds under conditions of oxygen deficiency, not only the release of CO and CO$_2$, but also the formation of carbon occurs [22-24], the aim of the present investigation is to investigate the process of formation of a composite material based on porous glass and active carbon possessing sorption properties. It was assumed that the use of low-melting glass will help to find regimes of temperature treatment in air in which the appearance of glass melt will prevent the active interaction of formed carbon with oxygen of air. The formulation of this problem differs significantly from the problem of synthesis of only porous glass and is actually reduced to the development of the synthesis of samples consisting of a porous glass shell and carbonized core.

2. Experimental Technique

Briquettes with sizes 25×25×25 mm were compacted from a mixture consisting of 50 wt.% ground glass and 50 wt.% waste activated sludge. Since briquettes had a high humidity, they were subjected to natural drying in air for different times: from 1 to 7 days. The temperature treatment (sintering) of specimens was performed in the temperature range ($T_{tr.}$) 600–700 °C for $t_{tr.} = 10-120$ min. Glass powders with a size ($d_{glass}$) of ≤ 90 μm, ≤ 125 μm, and ≤ 250 μm were used.

The specimens were investigated by the X-ray diffraction (XRD) method in Cu $K_α$ radiation (a Siemens D-500 diffractometer). An electron microscopy study and electron-probe microanalysis were performed with a LEO 1450 VP type scanning electron microscope. An electron paramagnetic resonance spectroscopy (EPR) investigation was carried out on an EPR spectrometer (Jeol JES TE-300, Tokyo, Japan), operated in the X-band mode at a modulation frequency of 100 kHz, at room temperature under a pressure of 10$^{-2}$ mm Hg. An IR spectroscopy study was performed with an FSM 1202 Fourier spectrometer. UV-Vis measurements were carried out with an Ocean Optics USB4000-XR1 spectrometer. Water absorption was determined on primary specimens by standard methods and calculated by the formula: $W (%) = 100 - [(P_f - P_0)/ P_0] 100$, where $P_0$ is the initial weight of a specimen and $P_f$ is the weight of this specimen after water absorption. For all other investigations, the internal parts (cores) of preliminarily destroyed specimens were analyzed.

3. Results and discussion

3.1. Characterization of raw materials

The composition of waste active sludge (WAS) is presented in Tab. I, and the composition of ground glass is presented in Tab. II. The main component of the WAS is an organic material. Moreover, in the WAS, clay and sand impurities, and a number of nitrogen-containing and inorganic compounds are present. In the work, low-melting glass with a melting point of 700–800 °C was used.
Tab. I Composition of waste active sludge.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH</td>
<td>6.7</td>
</tr>
<tr>
<td>Organic matter, %</td>
<td>80.20</td>
</tr>
<tr>
<td>Clay + Sand, %</td>
<td>19.80</td>
</tr>
<tr>
<td>Type of soil</td>
<td>Organic mud in sewage</td>
</tr>
<tr>
<td>Texture</td>
<td>Smoke slimy sand</td>
</tr>
</tbody>
</table>

Tab. II Content of oxides in used ground glass (wt.%).

<table>
<thead>
<tr>
<th>Type of oxides</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content of oxides</td>
<td>72.03</td>
<td>1.989</td>
<td>7.006</td>
<td>1.0</td>
<td>1.001</td>
<td>13.964</td>
<td>0.005</td>
</tr>
</tbody>
</table>

3.2. Weight loss of waste sludge

The temperature treatment of biowaste in air is accompanied by mass loss (Fig. 1) and a change in the color of the material from gray to brown, which is typical of red clay at the corresponding sintering temperatures (see the upper part of Fig. 1). The treatment in air is accompanied by fast burning of the organic component for the first 10 min. After 60 min treatment, the solid residue constitutes at most 3.75 %.

![Fig. 1](image)

Fig. 1. Weight loss of waste sludge during heat treatment in air at $T_{tr} = 600$ °C and change in the color of specimens (upper part of the figure).

3.3. XRD data

The X-ray diffraction pattern of dried biowaste is a broad line, which corresponds to the amorphous form of the product (Fig. 2a). On this broad line, a number of weak narrow lines, which can be assigned to silicon oxide (SiO$_2$) in the form of quartz and cristobalite, silicates
similar to feldspars, and a number of broadened peaks of montmorillonite are present. The presence of these inorganic compounds is characteristic of sewage after the second stage of purification [25].

**Fig. 2.** Fragments of X-ray diffraction patterns of sludge specimens heat treated in air for different times (a) and intensities of relevant peaks in different specimens (b): (1) for cristobalite with $d = 0.4133$ nm; (2) for quartz with $d = 0.3239$ nm; (3) for feldspar with $d = 0.3273$ nm; (4) halo. $T_{ir} = 600 \, ^\circ C$. $d_{glass} \leq 90 \, \mu m$. 
After temperature treatment of biowaste in air at 600 °C, a typical X-ray diffraction pattern of partially dehydrated montmorillonite with peaks of quartz, cristobalite, and feldspar was obtained [26-29]. The differences in the intensities of diffraction peaks of these phases indicate their different contents in the chosen specimens. The regular weakening of the intensity of halo with increase in the temperature treatment time (Fig. 2b, peak 4) is due to the thermodestruction of the organic component and its burning.

After temperature treatment of specimens prepared from the glass–biowaste mixture, the intensity of the halo increases substantially and, in the specimens having a black core, it exceeds the intensity of the halo in glass (Fig. 3 and Fig. 4). The size of the core and the thickness of the white shell depend on the temperature treatment regime of specimens.

Changes in the intensity of the halo (of the thermodestruction product of the organic component of the sludge) and in the intensity of the peak of cristobalite with \( d = 0.4133 \) nm (the inorganic component of the sludge) with change in the conditions of preparation of specimens from the glass–biowaste mixture and treatment regime are shown in Fig. 5. As is seen in Fig. 5a, with increase in the treatment (sintering) time of specimens at \( T_{\text{tr}} = 700 \) °C, the intensity of the halo changes substantially. After treatment for 120 min, the halo disappears. Schematically, these changes are shown in Fig. 5a’. Correspondingly, the intensity

**Fig. 3.** Fragments of X-ray diffraction patterns (a) and change in the intensity of the halo (b) in different specimens after temperature treatment at \( T_{\text{tr}} = 700 \) °C for \( t_{\text{tr}} = 60 \) min. \( d_{\text{glass}} \leq 90 \) μm.
of the halo decreases for products obtained from glass with a larger particles size (Fig. 5b). The drying time of specimens also influences the intensity of the halo (Fig. 5c). Note that, in all treatment regimes and for all particle sizes of glass, the intensity of the diffraction peak of cristobalite changes insignificantly.

**Fig. 4.** Fractures of specimens obtained from the glass–biowaste mixture treated at $T_{tr} = 700 \degree C$ for $t_{tr} = 60$ min. For (a) $d_{glass} \leq 125 \mu m$ after 5 days of drying; (b) $d_{glass} \leq 125 \mu m$ after 6 days of drying; (c) $d_{glass} \leq 90 \mu m$ after 1 day of drying; (d) $d_{glass} \leq 90 \mu m$ after 2 days of drying; (e, f) $d_{glass} \leq 90 \mu m$ after 6 days of drying.

**Fig. 5.** Change in the intensity of the halo (1) and in the intensity of the diffraction line of cristobalite with $d = 0.4133$ nm (2) with the sintering time of specimens (a), size of glass particles (b) and drying time (c). $T_{tr} = 700 \degree C$, $t_{tr} = 60$ min. In the right part of the figure, simplified schemes of processes are presented. In (a, b), after 6 days of drying. In (a, c), $d_{glass} \leq 90 \mu m$. 

$d_{glass} \leq 90 \mu m$. 

The obtained data enable us to conclude that, in the used treatment regime of the binary mixture (inorganic component–biowaste), glass particles play the role of a “filler” and do not take part in the processes of interaction with inorganic components contained in biowaste (dehydrated montmorillonite, silica, and feldspar). At the same time, substantial changes in the intensity of the halo indicate the burning out of the organic component of biowaste through the stage of formation of carbon [30-33]. From this viewpoint, the decrease in the intensity of the halo with increase in the particle size of introduced glass can be explained by the simplified penetration of oxygen from air into the pore space of the specimen and the release of oxidation products (CO↑ and CO₂↑) (see Fig. 5b’). In its turn, with increase in the drying time of specimens, the evaporation of water vapor occurs, and the pore space, into which oxygen subsequently enters, changes. In the stage of short-term drying, much water is still present in the specimens. In temperature treatment of these specimens, the evolution of H₂O and release of CO₂ simultaneously occur, the porosity increases, and, as a consequence, the burning out of carbon is intensified. With decrease in the water content in the specimens after 4 days of drying, their initial porosity decreases. Therefore, the penetration of O₂ into pores is hindered, the evolution of CO₂ decreases, and the amount of carbon in specimens increases. In long-term drying, predominantly the processes of burning of carbon and evolution of CO₂ set in (see Fig. 5c’).

3.4. IR spectroscopy data

In investigation of specimens treated at 700 °C, it was established that, after short-term treatment (tₜ, ~ 30 min) of the binary mixture, absorption bands of the organic and inorganic component were present in the IR spectrum (Fig. 6, Tab. III). In view of the overlap of the regions of manifestation of vibrations characteristic of the inorganic and organic components, the unambiguous interpretation of the assignment of absorption frequencies presents difficulties. Nevertheless, the investigated range of frequencies can be divided into several characteristic regions: at ν ~ 450–1200 cm⁻¹, vibrations of Me–O (where Me is Si, Na, etc.), Si–O–Al, Si–O–Si, and H–O–Al bonds, which characterize the inorganic component of the mixture, manifest themselves. In the frequency range ν ~ 1200–1800 cm⁻¹, vibrations of the C=O, C=C, C–C, C–H, C–N, and N–H bonds of the organic component of the mixture manifest themselves. The frequency range ν ~ 2800-3600 cm⁻¹ is typical of vibrations of the C–H and O–H bonds.

Tab. III IR absorption bands in investigated specimens treated at 700 °C.

<table>
<thead>
<tr>
<th>tₜ, min</th>
<th>ν, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>462 w.</td>
</tr>
<tr>
<td></td>
<td>541 s.wd.</td>
</tr>
<tr>
<td></td>
<td>610 w.</td>
</tr>
<tr>
<td></td>
<td>640 w.</td>
</tr>
<tr>
<td></td>
<td>719 m.</td>
</tr>
<tr>
<td></td>
<td>794 m.</td>
</tr>
<tr>
<td></td>
<td>849 m.</td>
</tr>
<tr>
<td></td>
<td>912 sh.</td>
</tr>
<tr>
<td></td>
<td>1045 m.</td>
</tr>
<tr>
<td></td>
<td>1018 sh.</td>
</tr>
<tr>
<td></td>
<td>1093 m.n.</td>
</tr>
<tr>
<td></td>
<td>1187 m.</td>
</tr>
<tr>
<td></td>
<td>1232 w.</td>
</tr>
<tr>
<td></td>
<td>1274 w.</td>
</tr>
<tr>
<td></td>
<td>1307 w.</td>
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<tr>
<td></td>
<td>1350 w.</td>
</tr>
<tr>
<td></td>
<td>1401 m.</td>
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<tr>
<td></td>
<td>1458 m.</td>
</tr>
<tr>
<td></td>
<td>1510 m.</td>
</tr>
<tr>
<td></td>
<td>1578 w.</td>
</tr>
<tr>
<td></td>
<td>1630 s.</td>
</tr>
<tr>
<td></td>
<td>1730 m.</td>
</tr>
<tr>
<td></td>
<td>2856 m.n.</td>
</tr>
<tr>
<td></td>
<td>2926 m.n.</td>
</tr>
<tr>
<td></td>
<td>2960 sh.</td>
</tr>
<tr>
<td>60</td>
<td>460 s.wd.</td>
</tr>
<tr>
<td></td>
<td>570 sh.</td>
</tr>
<tr>
<td></td>
<td>610 w.</td>
</tr>
<tr>
<td></td>
<td>640 w.</td>
</tr>
<tr>
<td></td>
<td>677 w.</td>
</tr>
<tr>
<td></td>
<td>764 m. wd.</td>
</tr>
<tr>
<td></td>
<td>882 s.w d.</td>
</tr>
<tr>
<td></td>
<td>930 sh.</td>
</tr>
<tr>
<td></td>
<td>1015 m.</td>
</tr>
<tr>
<td></td>
<td>1087 m.</td>
</tr>
<tr>
<td></td>
<td>1380 m.</td>
</tr>
<tr>
<td></td>
<td>1510 w.</td>
</tr>
<tr>
<td></td>
<td>1555 w.</td>
</tr>
<tr>
<td></td>
<td>1620 m.</td>
</tr>
<tr>
<td></td>
<td>3417 w.wd.</td>
</tr>
</tbody>
</table>

Notes:
s is strong; m is middle; w is weak; wd is width; n is narrow; sh. is shoulder.

Frequency assignment.
According to [38]:
bands at: (1650–1630) cm\(^{-1}\) belongs to aromatic C=C, C=O - in amide (I), ketone and quinone groups;
(1540–1550) cm\(^{-1}\) in amide (II);
(1460–1380) cm\(^{-1}\) belongs to CH\(_3\), OH groups of phenols, COO\(^{-}\) ortho-distributed aromatic rings;
(1265–1223) cm\(^{-1}\) belongs to amides or ethers;
a broad band between (1120–980) cm\(^{-1}\) with sharp peak centered at ~1034 cm\(^{-1}\) belongs to aromatic ethers, and also carbohydrates and silicates.

According to [39]:
bands at: 1650 cm\(^{-1}\) assigned to amide (I), carboxylates, C=C from aromatic group and alkenes;
band near 1376 cm\(^{-1}\) belongs to vibration on N–O stretching;
1270 cm\(^{-1}\) belongs to C–O stretching of aryl ethers;
near 1123 cm\(^{-1}\) aromatic ring bends, symmetric bending of aliphatic CH\(_2\), OH and C–O stretching of various groups;
near (1030–1040) cm\(^{-1}\) belongs to C–O stretching of alcohol, sulfoxides, carbohydrates or polysaccharides-like substance, or Si–O of silicates.

According to [40]:
bands at: 1723 cm\(^{-1}\) belongs to aromatic ring; 1505 cm\(^{-1}\) belongs to aromatic C–C stretching;
1453 cm\(^{-1}\) belongs to C–H bending; 1408 cm\(^{-1}\) and 1339 cm\(^{-1}\) belong to deformation C–H alkane; 1234 cm\(^{-1}\) belongs to asymmetric C–C–O stretching involving the carbon in aromatic ring; 1128 cm\(^{-1}\) and 1091 cm\(^{-1}\) belong to O–C–C asymmetric stretching; 871.5cm\(^{-1}\) belongs to aromatic C–H out of plane bending; 721.8 cm\(^{-1}\) belongs to aromatic C–H wagging.

According to [41]:
Glass Na\(_2\)O – Al\(_2\)O\(_3\) – SiO\(_2\): 1160 cm\(^{-1}\); 980 cm\(^{-1}\); 800 cm\(^{-1}\); 580 cm\(^{-1}\); 480 cm\(^{-1}\).
Montmorillonite: 1639.8 cm\(^{-1}\); 1088.24 cm\(^{-1}\); (1045 –1030) cm\(^{-1}\);1036.7 cm\(^{-1}\);  915.6 cm\(^{-1}\); 841.5 cm\(^{-1}\); 794.6 cm\(^{-1}\); 623.3 cm\(^{-1}\); 519.9 cm\(^{-1}\).
Glass+Montmorillonite after \(T_0\) = 600 °C: 1626 cm\(^{-1}\);1095 cm\(^{-1}\); 872 cm\(^{-1}\); 795 cm\(^{-1}\); 691 cm\(^{-1}\); 611 cm\(^{-1}\); 599 cm\(^{-1}\); 475 cm\(^{-1}\).

After treatment for 60 min, the IR spectrum changes substantially. The broadening of bands characteristic of the inorganic component of the mixture in the frequency ranges \(\nu \sim 450-600\) cm\(^{-1}\) and 800-1100 cm\(^{-1}\) occurs. The intensities of the absorption bands in the frequency ranges \(\nu \sim 1350-1750\) cm\(^{-1}\) and 3200-3500 cm\(^{-1}\) decrease, and the bands in the frequency ranges \(\nu \sim 1200-1350\) cm\(^{-1}\) and 2800-2960 cm\(^{-1}\), which are typical of the organic component of the mixture, disappear. All narrow absorption bands are located on the broad band. The formation of the broad band indicates the formation of carbon (carbon black) [34-37]. These changes characterize the carbonization process proceeding with increase in the treatment time. This manifests itself particularly clearly in temperature treatment of specimens preliminarily dried for different times (Fig. 7a, b). It can be seen that, with increase in the predrying time, subsequent temperature treatment is accompanied by the more rapid dehydration of specimens and their carbonization, which, in turn, is accompanied by a
decrease in the intensity of all narrow IR bands (Fig. 7c). This effect indicates that the carbon-containing material shields (covers) particles of the inorganic component of the formed composite. From the investigation of the carbonization process in specimens with different size of glass particles it is obvious that this process is leveled with increase in the size of glass particles (Fig. 8) because more active burning, i.e., removal of carbon from the composite, occurs (see the scheme shown in Fig. 5b’).
Fig. 7. IR spectra of sludge–glass specimens after different drying times (a, b) and change in the intensity of bands of Si–O bonds (1) and H\textsubscript{2}O (2). T\textsubscript{tr.} = 700 °C for t\textsubscript{tr.} = 60 min. d\textsubscript{glass} ≤ 90 μm.

Fig. 8. IR spectra of sludge–glass specimens after treatment at 700 °C for 60 min (a, b) and change in the intensity of bands (c) with the size of glass particles. In (c): (1) intensity of the Si–O absorption band at ν ~ 1120 cm\textsuperscript{-1}; (2) intensity of halo (carbon).

3.5. EPR data

EPR investigations showed that the spectrum of heat treated specimens is a
superposition and is represented by a weak signal with \( g \sim 4.3 \) (in Figs. 9, 10, it is denoted by *) , an intensive broad signal with \( g \sim 2.3 \), and a narrow signal with \( g \sim 2.01 \). The signal with \( g \sim 2.3 \) is a superposition. The signals with \( g \sim 4.3 \) and \( g \sim 2.3 \) are assigned to Fe\(^{3+}\) ions in the lattice of the clay mineral, products of its dehydration, and glass and iron oxides contained in clay minerals [44-46]. The narrow signal with \( g \sim 2.01 \) is assigned to carbon (thermodestruction products of the organic part of biowaste) (free radicals) [47-50]. In temperature treatment, the shape of the wide EPR signal somewhat changes, which indicates a certain reconstruction in the inorganic component of the biowaste–glass system. At the same time, the narrow signal with \( g \sim 2.01 \) disappears during temperature treatment in air (Fig. 9b), which testifies to the burning of carbon, beginning from the most active radical forms of carbon.

Thus, the XRD, IR spectroscopy, and EPR data indicate the formation of weakly ordered carbon in thermodestruction of waste sludge with simultaneous burning during treatment of specimens in air. The burning rate of the carbon component and the degree of its conservation in the specimen depend on the following technological parameters: the burning temperature, burning time, and dispersity of the introduced glass.

![Fig. 9](image1.png)

**Fig. 9.** EPR spectra of specimens treated at different temperatures (a, a’) and change in the intensity of the narrow signal with the treatment temperature (\( g = 2.002 \)) (b). \( t_{tr.} = 30 \text{ min.} \)

![Fig. 10](image2.png)

**Fig. 10.** Change the form of the broad ERR signal in specimens with change in the treatment time. \( T_{tr.} = 700 \, ^\circ\text{C} \).
3.6. SEM–TEM–EDS investigations

SEM images of the carbonized core presented in Fig. 11 a, b show the formation of different types of products: fibers, aggregates of small particles, spherical particles, and large particles with melting traces. An EDS analysis indicates the inhomogeneous distribution of carbon and elements such as O, Si, Na, Ca, and Al, which are characteristic of glass (see Fig. 11c, d, e). As a rule, the carbon content is high in fibers and aggregates of small particles. Moreover, in the largest glass particles, carbon is inhomogeneously distributed (see Fig. 11b, d, e).

![Fig. 11](image)

**Fig. 11.** Micrographs of the material of the core (a, b) and contents of elements in different parts of the core (c, d). $T_{tr.} = 600^\circ C$, $t_{tr.} = 30$ min.

![Fig. 12](image)

**Fig. 12.** SEM micrograph of the surface of a particle in a specimen obtained at $T_{tr.} = 700^\circ C$ for $t_{tr.} = 60$ min. $d_{glass} \leq 90$ μm (a, b), and contents of elements in the region shown in (c), which is framed in (a). The drying time is 7 days.
Fig. 13. STEM micrograph of the surface of a particle in a specimen obtained at $T_{tr} = 700$ °C for $t_{tr} = 60$ min. $d_{glass} \leq 90 \mu$m. The drying time is 7 days (a, b).

An investigation of the surface of glass particles showed (Figs. 12a, b, c) that, on their surface, a layer that is not strong and, along with elements typical of silicates, carbon is present (Fig. 12d). It can be concluded that this layer formed on glass particles as a result of the thermodestruction of biowaste. A STEM investigation revealed (Fig. 13) that this layer consists of nanoparticles that can be represented by both carbon and dehydrated particles of the clay mineral. Note that attempts to obtain a TEM image failed because the burning of carbon occurred under the electron beam.

3.7. Absorption of water

Since it was established that, during treatment in air of specimens consisting of ground glass and biowaste, the formation of amorphous carbon and its burning occurs, the sintered specimens must have porosity. The performed investigations of water absorption showed that, with increase in the treatment temperature and with movement into the region of active glass melting, the open porosity of specimens decreases (Fig. 14a, b). Accordingly, the porosity of the specimens is influenced by the time of preliminary drying (Fig. 14c) because the water contents in them turn to be different (see Fig. 5c, c’). In specimens with smaller glass particles, in which carbon is contained and is “encapsulated” (see Fig. 5b, b’), for the burning out of carbon, longer time and passage of CO$_2$↑ through the melt are required. As a result, the porosity of these specimens turns to be larger than that for specimens with large particles.

Fig. 14. Change in the absorption of water by carbonized glass with the sintering temperature of glass–biowaste mixtures (a, b) and the drying time of glass-biowaste mixtures (c). In (a): (1) $t_{tr} = 30$ min., (2) $t_{tr} = 360$ min., for $d_{glass} \leq 125 \mu$m, 5 days of drying. In (b): (1) $t_{tr} = 30$ min., (2) $t_{tr} = 360$ min., for $d_{glass} \leq 90 \mu$m, 6 days of drying. In (c): $T_{tr} = 700$ °C, $t_{tr} = 60$ min., for $d_{glass} \leq 90 \mu$m.
The established features of formation of specimens enable us to represent their structure in different stages of temperature treatment (Fig. 15). According to the model shown in Fig. 15, specimens with a carbon core and without it must exhibit different properties and have different application. Taking into account that nanodisperse carbon has adsorption properties [51-55], experiments on adsorption of MB from aqueous solutions were carried out.

![Fig. 15](image)

**Fig. 15.** Simplified scheme of transformations in specimens of foam glass under different sintering conditions.

### 3.8. Adsorption properties of carbonized specimens

An investigation of the adsorption properties of specimens showed that specimens obtained at 600–650 °C for 30 min of treatment have the best adsorption properties (Fig. 16a, b). Moreover, the size of glass particles must not exceed 90 μm (Fig. 16c). With increase in the treatment temperature to 700–750 °C, when glass melts, and the content of open pores diminishes, the absorption of MB decreases (see Fig. 16a). In specimens prepared from the mixtures of biowaste with large glass particle, the indicated processes are retarded, and this is why they have better adsorption properties (see Fig. 16d). Thus, all adsorption changes agree with the XRD, IR spectroscopy, and EPR data and schemes of formation of the composites presented in Fig. 5 and Fig. 15.
Fig. 16. Change in the concentration of MB in solution with the sintering temperature (a), sintering time (b) of specimens, and with change in the size of glass particles in the glass–biomass mixtures. In (a): $t_{tr} = 30$ min. In (b): $T_{tr} = 600 ^\circ C$, $d_{glass} < 90 \mu m$. In (c): $T_{tr} = 650 ^\circ C$. In (d): $T_{tr} = 700 ^\circ C$. The exposure time is 1 day.

4. Conclusions

The performed investigations have shown the following.

• The temperature treatment of a composite consisting of a 50 wt.% ground glass–50 wt.% waste active sludge mixture in air in the temperature range 600–700 °C for 30-60 min is accompanied by the formation of specimens of complex structure: a porous glass shell and a carbonized core. With change in the drying regime and temperature treatment regime, the size of the core, the thickness of the shell, and its porosity change.

• Waste active sludge is a composite consisting of an organic component (bacteria, microorganisms, etc.) and particles of minerals contained in sewage (montmorillonite, silica, and feldspars).

• Carbonized biowaste consist of nanocarbon particles (similar to carbon black), nanoparticles of dehydrated montmorillonite, silica particles, and particles of feldspars.

• During temperature treatment of the biowaste–glass mixture, the carbon components from both on the surface of glass particles and between them.

• Specimens having a carbon core and open porosity in the external glass shell exhibit good adsorption properties.

• Porous specimens without a carbon core are foam glass and can be used as a heat-insulating and sound-insulating material.
5. References

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У овом раду су разматрани одређени аспекти формирања композитног материјала који се састоји од смеше млевеног стакла са ниском тачком топљења и отпадног материјала, који се користи за пречишћавање канализационих вода. Утврђено је да, после краткотрајног (30-60 мин) третmana на релативно ниској температури (600-700 °C), узорак се састоји од порозне стаклена опне и језгра које се састоји највећим делом од угљеника. Променом температуре термичког третмана долази до промена у дебљини и порозности стаклена опне и величини угљеничног језгра, због чега долази до промена у њиховим адсорпционим својствима. Због присуства угљеничног језгра, узорци добро адсорбују метилен-плаву из воденог раствора.

Кључне речи: отпадни материјал; млевено стакло; термички третман.

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