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Sludge Study From Biological Wastewater Treatment After Pyrolysis Processing.

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ABSTRACT

Wastewater treatment leads to the development of sewage sludge at treatment facilities. The resulting waste is almost not amenable to utilization, except for dehydration in silt fields under natural conditions. This method of sludge removal is a long-term process. Besides, sludge deposits occupy huge areas and pose a potential threat to adjacent environments. The storage of sludge can lead to the spread of unfavorable air-gas background, the pollution of soils and groundwaters with toxic components that make up the sediments. The pyrolysis of the sludge to produce a solid residue containing a certain amount of carbon is an alternative. The resulting solid pyrolysis product is a potential sorbent for wastewater treatment from heavy metal ions and petroleum products. In this paper the object of the study is a solid product of sludge pyrolysis. They studied the parameters characterizing the sorption properties of pyrolysis solid product with respect to pollutants contained in surface and waste water - the specific area, surface structure, pore size and their distribution by size. The specific surface, volume and pore radius were determined by capillary condensation of nitrogen. The specific surface area of mud sediment pyrolysis product is 261.7 m2/g. The volume and the radius of pores determined by the t method and BJH method make 0.156 cc/g and 19.6 A, respectively. Scanning electron and X-ray microscopy was used to study the elemental composition and the surface structure of the pyrolysis product. The obtained data indicate the presence of sorption properties. The granulometric analysis showed that the solid product of mud sediment pyrolysis contains predominantly the particles with the sizes from 0.1 to more than 5 mm (82.4%). The values of pyrolysis product bulk density obtained during the determination are not inferior to known adsorbents. And they make 642.8 g/dm3 for sludge. It is established that the removal of sludge by low-temperature pyrolysis makes it possible to obtain a sorption material.

Keywords: pyrolysis, sludge, sorbent, wastewater.

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INTRODUCTION

At present, the current issue is the protection of the environment from pollution, the development of resource-saving and low-waste technologies, the increase of water recycling and reuse system capacity.

The result of domestic and industrial activities of a man is the waste in the form of sewage, which are mainly discharged into the sewer. Sludge is formed during the process of the purification stage passing by sewage waters at sewage treatment plants. Most of sludge is not amenable to any processing, except for dehydration on silt fields under natural conditions. This process is a long-term one and takes huge areas under silt maps. Besides, the storage of sludge leads to the spread of unfavorable gas-air background, the contamination of soils and ground waters with toxic components that make up precipitation [1].

Often the specificity of urban sewage systems is the result of municipal and industrial wastewater mixing. Then, heavy metals compounds, organic compounds such as benz(a)pyrene, pesticides, phenols, etc. can be present in the sediments of biological sewage treatment. And this means that it is not safe to use such sludge to make fertilizers.

Then, the alternative is the pyrolysis processing of sludge as carbonaceous waste (CW), with the production of gaseous, liquid pyrolysis fuels and a solid residue (carbonizate) containing a certain amount of carbon, which is therefore a potential sorbent. The pyrolysis of CW is economically more feasible, since, unlike conventional combustion, CW reduces the negative impact on atmospheric air on one hand, and it allows to obtain a number of products, that can be implemented for partial or full compensation of processing costs on the other.

The pyrolysis of mud sediments at the temperature of 775-825 °C allows to obtain carbonizate with a high specific surface and microporosity. Let's note that during the carbonization of sewage sludge dry matter, the maximum amount of volatile compounds is distilled at 265-330 ºC, and the carbonized precipitate is formed by heating without air access up to 420-655 ºC [1]. It is most expedient to use the obtained material as a sorbent for a deep post-treatment of waste waters that have undergone biological treatment.

Sludge removal by this method allows to get rid of sludge accumulators and to improve the quality of wastewater treatment.

METHODS

In order to determine the bulk density, the test samples were placed in a previously weighed cylinder of 20 ml and the volume occupied by coal was measured before and after shaking. The shaking time is 1 minute [2].

The particle distribution from the solid product of mud sediment pyrolysis by size was determined by sieve analysis and by laser analyzer of particle size "Microsizer 201C" [3].

The moisture content of solid pyrolysis products was determined using ML-50 moisture analyzer, in which the principle of thermogravimetric analysis was implemented [4]. In this analysis, the sample is dried using a halogen lamp and the moisture content (in%) is calculated on the basis of the difference between wet and dry weight.

The mass fraction of ash (mineral part of the residue) was determined as the ratio of mineral impurity weight after sediment calcination and its bringing to a constant mass, to the mass of the dry sample taken for analysis. At that the mass of the dried sample was in the range (1-2.5 g) [5].

To obtain such characteristics as specific surface area, pore size and volume, the studies were carried out by gas sorption on "Quantachrome 4200E" device. Sorption-desorption isotherms were obtained. The determination of the specific surface area and the porous structure was carried out using Brunauer-Emmett-Teller (BET) method.

In order to determine the volume of micropores in the presence of pores of larger diameter, the Halsey t-method was used. The distribution of meso- and macropores by size for the sample was determined by the Barrett-Joyner-Haland method (BJH). The BJH model used to determine the porosity of the sample makes it possible to calculate the pore volume, and also to construct a graph of pore distribution by size in the coordinates "pore radius - pore volume" corresponding to a given radius [6, 7, 8, 9].

RESULTS AND DISCUSSION

The appearance of mud sediment pyrolysis product is shown on Fig. 1.

Figure 1: Solid product of processing of sludge of sewer sewage

Carbonizate is a black powder with a grayish shade without foreign inclusions.

It is known that the adsorption properties of sorbents depend on the value of the specific surface and on the structure, i.e. on pore size and their distribution by size [10]. The structure of the obtained carbonizate affects the rate of the adsorption process, determines the forms of the isotherm and the number of absorbed molecules of various sizes.

For this purpose, they studied the structure and the properties of the potential sorbents obtained as the result of sludge pyrolysis.

The results of the microstructure study using "Jeol JSM-6390 LA" scanning electron microscope indicate that the pyrolysis product of sludge has a porous structure (Fig. 2). The porous structure allows to predict sorption properties.

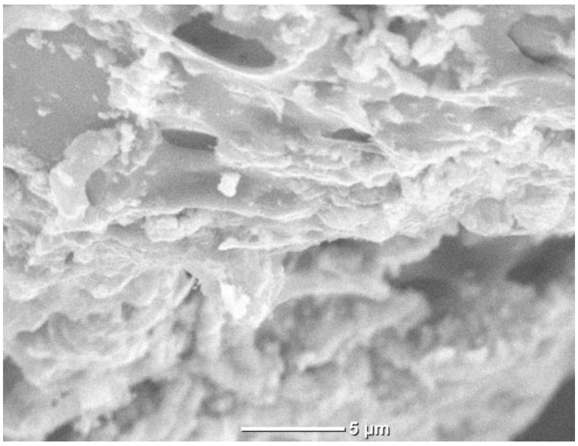

Figure 2: Structure of pyrolysis product of of sludge

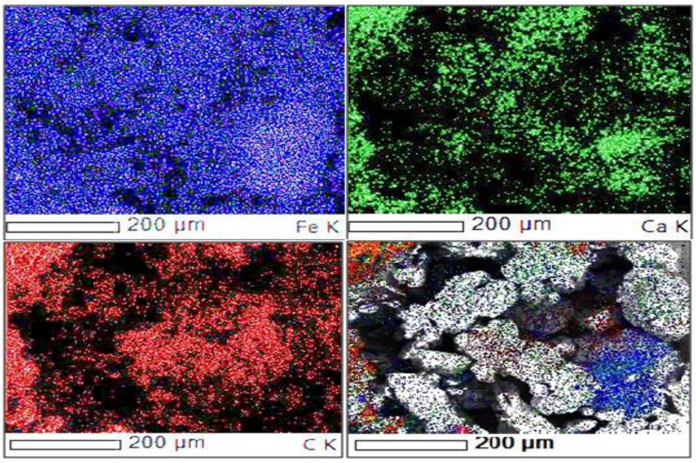

Figure 3: Distribution of elements on the surface of pyrolysis product of sludge (iron, calcium, carbon)

According to X-ray phase analysis, the main components of mud sediment pyrolysis product are carbon, oxygen and nitrogen (Fig. 4). The results are shown in Table 1.

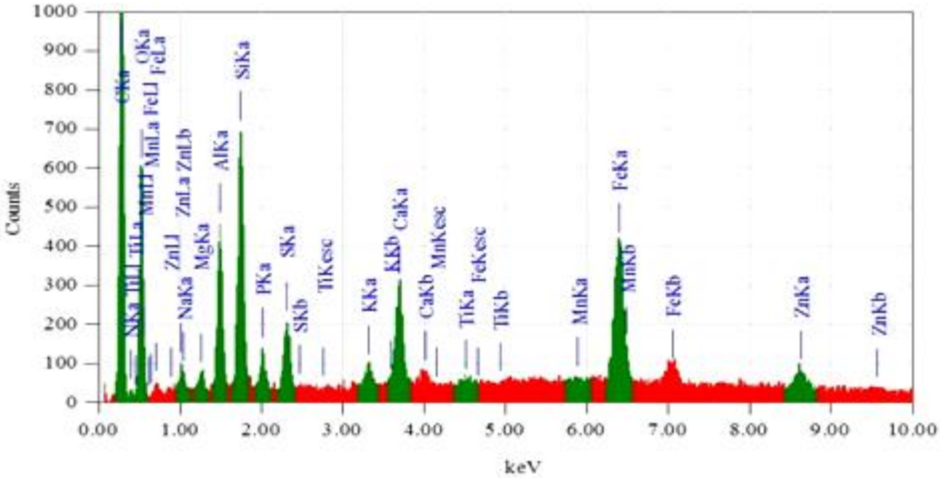

Figure 4: Spectrum obtained by XRF method

Table 1: Elemental composition of the pyrolysis product of sludge

Element	Mass, %
C	38.57
N	18.69
O	25.51
Na	0.02
Mg	0.27
Al	1.46
Si	2.17
P	0.37
S	0.65
K	0.27
Ca	1.36
Ti	0.16
Fe	7.25
Zn	3.25

A high content of organic compounds in the dry matter of sludge causes the total content of these components to be about 83% from the elemental composition of the analyzed pyrolysis product. The mineral part accounts for less than 17% of the elemental composition.

It is important to know the following characteristics for sorbents: specific surface area, volume and pore size. In order to obtain these parameters, the studies have been carried out on the sorption of SPP sludge gas using "Quantachrome 4200E" device.

The sorption-desorption isotherm was obtained, which is shown on Fig. 5.

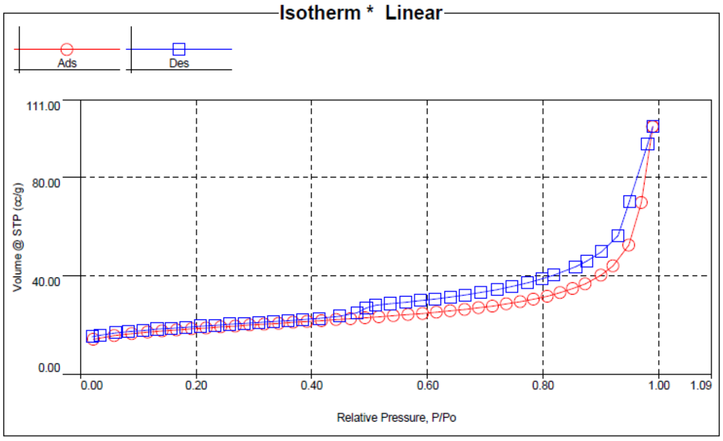

Figure 5: Sorption-desorption isotherm

The adsorption isotherm is used to determine the specific surface area and the porous structure. The most common method is the Brunauer-Emmett-Teller (BET) method. In order to determine the specific surface area, the BET method selects the section of relative pressures, linear in BET coordinates. The BET plot for nitrogen adsorption is shown on Figure 6.

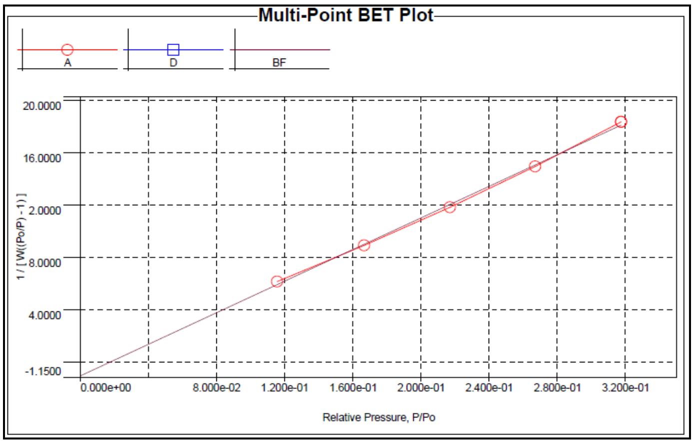

Figure 6: BET plot for nitrogen adsorption

The result of experimental data processing using the BET method shows that the specific surface area of sludge pyrolysis product makes 58.7 m2/g.

The specific surface area of the sample can be determined by the Langmuir method. The results of experimental data processing by Langmuir method are the following ones: 261.7 m2/g. The difference in the results is conditioned by the fact that the BET method can be used to determine the specific surface area of materials that do not contain micropores. Langmuir's method, on the contrary, is suitable to determine the surface area of only microporous substances. For comparison, Table 2 shows the specific surface area values of some sorbents [10].

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Table 2: Surface area of sorbents

parameters	silica gel		aluminosilicate	activated carbon
	fine-pored	coarse-pored		
surface area, m^2/g	450-500	270-350	300-350	600-1700

In order to determine the porosity of the sample, the Halsey t-method was used. T-graph is shown on Figure 7.

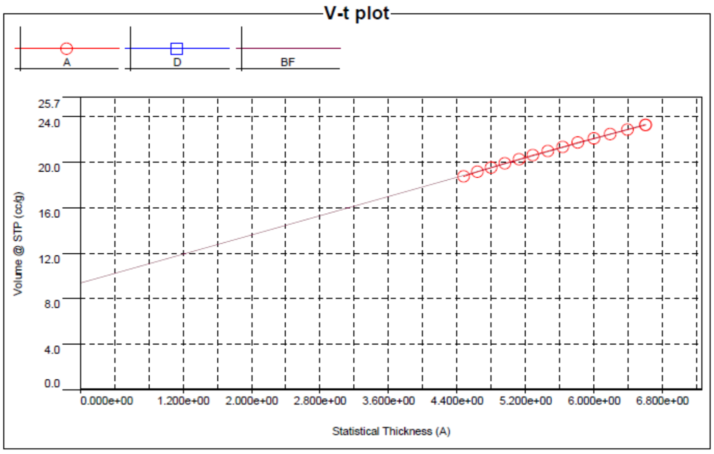

Figure 7: t-plot for nitrogen adsorption of sorbent

The result of the experimental data processing using t-method are the following values: the volume of mud sediment pyrolysis product micropores is 0.015 cm3/g.

The pore distribution by size for a sample with mesopores is determined by BJH method. The model BJH (Barrett-Joyner-Halenda) used to determine the porosity of the sample allows to calculate the pore volume, and also to develop the graph of pore size distribution in the coordinates "the pore radius - the pore volume" corresponding to a given radius (blue graph). The graph is shown on figure 8.

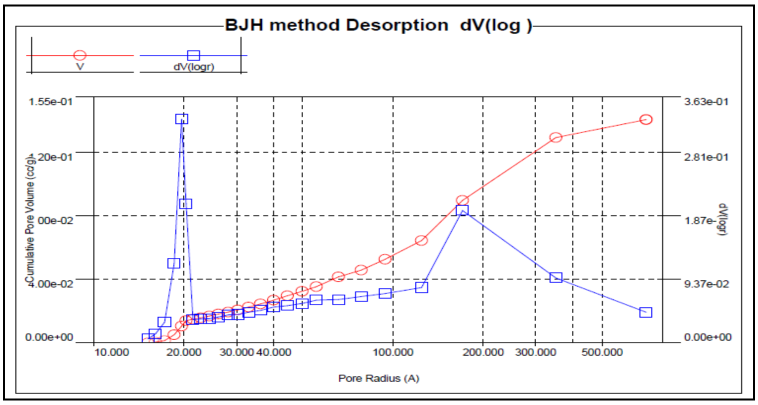

Figure 8: Pore size distribution according to BJH model

The fact that the distribution graph is a thin peak indicates a narrow distribution of pores by size. A wide peak indicates the presence of a small number of larger pores in the sample.

The results of experimental data processing by t-method and BJH method are presented in Table 3.

Table 3: Results of processing of experimental data on a t-method and BJH method

Parameters	pyrolysis product of sludge
micropore volume, cc/g	0.015
meso- and macropores volume, cc/g	0.141
pore size, A	19.6

For comparison: Table 4 shows the indices for some sorbents [10].

Table 4: Volume and pore size parameters

parameters	silica gel		aluminosilicate	activated carbon
	fine-pored	coarse-pored		
pore volume, cc/g	0.280	0.900	0.570	-
pore size, A	5-30	70-100	20-25	less than 70

The characteristics of the obtained mud sediment pyrolysis product are presented in Table 5.

Table 5: Characteristics of pyrolysis product

Sample	color	foreign substance	surface area*, m^2/g	pore volume, cc/g	pore size, A
solid pyrolysis product of sludge	gray-black	no	261.7	0.156	19.6

* - Specific surface area of pyrolysis products by the method Langmuir

The obtained data (specific surface area, pore volume and radius) make it possible to predict the sorption properties of mud sediment pyrolysis products in relation to HMI and petroleum products.
Table 6 presents the results of bulk density measurement concerning mud sediment pyrolysis product.

Table 6: Bulk density of pyrolysis product and activated carbon

Sample	bulk density, g/dm^3
solid pyrolysis product of sludge	642.8

For comparison: Table 7 shows the values of known adsorbent bulk density [10].

Table 7: Bulk density of adsorbents

parameters	silica gel		aluminosilicate	activated carbon
	fine-pored	coarse-pored		
bulk density, g/dm^3	800	500	700	200-600

Proceeding from the obtained results, the following conclusion can be drawn: the values of pyrolysis product bulk density obtained during the determination are not inferior to known adsorbents. And they make up 642.8 g/dm3 for sludge.

The distribution of solid particles from mud sediment pyrolysis products was determined by the method of sieve analysis and using the laser particle size analyzer "Microsizer 201C". The results are shown in Table 8.

Table 8: Particle size distribution (%)

particle size, mm	sludge
> 5	22.3
5-3	20.9
3-1	29.3
1-0.5	9.9
0.5-0.1	12.3
0.1-0.05	1.7
0.05-0.01	1.8
0.01-0.001	1.6
0.001-0.0006	0.1
<0.0006	0.1

According to the granulometric analysis, the solid product of mud sediment pyrolysis contains predominantly the particles with the sizes from 0.1 to more than 5 mm (82.4%). The solid product of sludge processing contains coarser particles with the size of more than 1 mm. This is due to the presence of silt particles in carbonated coal that are not decomposed during the pyrolysis of silt sediments.
The results of the moisture and ash content studies are presented in Table 9.

Table 9: Moisture and mass fraction of ash from solid pyrolysis product

raw materials	moisture, %	mass fraction of ash,%
sludge	0.9	47

The moisture content in carbonated coal is less than the normative value. The standard is 10% in accordance with the GOST 4453-74 "Active clarifying wood powder coal".

Ash content, which characterizes the presence of inorganic substances in the sorbent, is significant and exceeds the ash content of the split graphite sorbent or activated carbon sorbent [10], which a priori indicates the necessity of carbonated coal demineralization in order to improve its adsorption capacity, possibly by the activation with acids or alkali solutions.

CONCLUSIONS

The sludge of biological sewage treatment was treated with low-temperature pyrolysis in production conditions. In this paper, they studied the indicators characterizing the sorption properties of the samples obtained with respect to pollutants contained in surface and waste waters.

Scanning electron and X-ray microscopy was used to study the elemental composition and the structure of carbonated coal surface. According to X-ray phase analysis, the main components of mud sediment pyrolysis product are carbon, oxygen and nitrogen. The pyrolysis product of the sludge has a porous structure.

The result of experimental data processing by the Langmuir method shows that the specific surface area of mud sediment pyrolysis product makes 261.7 m2/g. The volume and the pore radius determined by t-method and BJH method make 0.156 cc/g and 19.6 A.

The obtained data (specific surface area, volume, and pore radius) make it possible to predict the sorption properties of mud sediment pyrolysis products.

According to the granulometric analysis, the solid product of mud sediment pyrolysis contains predominantly the particles with the sizes from 0.1 to more than 5 mm (82.4%). The solid product of sludge processing contains more coarse particles with the size of more than 1 mm. This is due to the presence of silt particles in carbonated coal undecomposed during the pyrolysis of silt particles.

The values of pyrolysis product bulk density obtained during the determination are not inferior to known adsorbents. And they make 642.8 g/dm3 for silt sediments.

The humidity of the sludge after treatment with pyrolysis is less than the standard value and makes 0.9%. The ash content of the obtained pyrolysis product, which characterizes the presence of inorganic substances in the sorbent, is significant, which indicates the need for carbonated coal demineralization in order to improve its adsorption capacity.

SUMMARY

Thus, it is shown that the removal of the sediments of biological wastewater treatment by low-temperature pyrolysis makes it possible to obtain a complex sorption material. The studies of the structure and the properties have shown the possibility of mud sediment pyrolysis product use as a sorption material designed to remove heavy metal ions from aqueous media..

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