Evaluating the properties of organic and mineral sludge as a raw material for the production of sorption material

Zh A Sapronova, Yu L Makridina, I V Starostina, M N Spirin and E V Fomina

Belgorod State Technological University named after V.G. Shoukhov, 46, Kostukova Str., Belgorod, 308012, Russia
E-mail: fomina.katerina@mail.ru

Abstract. The comparative investigations of the physical and chemical properties of two large-tonnage organic and mineral wastes of agricultural raw materials processing - carbonate sediment (CS) formed during the processing of sugar beets and diatomaceous sludge (DS), which is a waste product of sunflower oil production were carried out in work. It was found that in both materials during burning, carbonization of organic substances occurs on the surface of the mineral core; heat treatment gives them hydrophobic properties, the pH of the aqueous extract has an alkaline reaction (for DS pH = 10.8, for CS pH = 11.5). The central part of the mineral component of CS is calcium carbonate, and DS is silicon oxide, CS has a more developed specific surface area, which is ensured by the presence of small globular structures. The oil capacity of the materials after heat treatment is 3.5 g/g for DS and 1.13 g/g for CS; dye capacity "methylene blue" for heat-treated CS is 77.9 mg/g, it is 9.5 mg/g for DS. Further research is needed to develop a method for sharing these materials for the effective treatment of multicomponent sewage.

1. Introduction
Processing of agricultural products is inevitably accompanied by the formation of a large amount of waste. In some cases, they are used as secondary raw materials in agriculture [1-5], for the production of building materials and mixtures [6-8], as sorbents for sewage treatment [9-16]. However, a significant part of them remains unclaimed.

Sludge waste is a big problem. Sludge wastes have a complex chemical composition, emit toxic and foul-smelling gases during storage, serve as a medium for the propagation of pathogenic microorganisms, and can be a source of pollution of nearby water bodies [17-23].

Sugar beet, sugar production waste appears at the stage of purification of beet juice from non-sugars with lime milk. It is formed in the amount of 12-13% by weight of the processed plant material, i.e., on average, one sugar factory produces about 190 thousand tons of sludge per year. Its main component is chemically synthesized calcium carbonate; in addition, CS contains nitrogen and nitrogen-free organic compounds (sugar residues, proteins, pectin, calcium salts of organic acids, saponin, minerals) [24].

In the production cycle of refining sunflower oil, there is also a large-tonnage sludge waste - diatomaceous sludge (DS). Diatomaceous sludge is formed as a result of purification of vegetable oil from wax impurities at the stage of winterization. The mineral part of the sludge is represented by diatomite - sedimentary rock formed by siliceous fragments of the frustule of microscopic diatomic
algae - diatoms and radium. The central part of the siliceous frustule (skeleton) is amorphous silica hydrates of various degrees of watering. In essence, varieties of opal of the form mSiO2 • nH2O, the crystalline component is represented by impurities of quartz. Diatomite is a natural nanostructured material with a large specific surface area. The porous structure of native diatomite is represented mainly by macropores: pores with diameters of 140 nm or more make up about 80% of the total volume of all pores. When filtering vegetable oil, unwanted wax impurities contained in it are retained in the pores of diatomite [25].

The study of these wastes is of great interest since it is known that with a specific treatment, they can acquire the properties of sorption materials and can be used in water purification [23, 24]. The creation on their basis of an integrated composite sorption material reduces the technogenic load on the environment. It reduces the cost of the water purification process and improves the ecological situation in the agriculturally developed region as a whole.

2. Materials and methods

The thermal treatment of the sludge test samples has been carried out in the muffle furnace LOIP LF-7/13 in the presence of oxygen.

The analysis of peculiarities of the chemical composition and structure of the samples has been carried out by using the scanning electron microscope of high resolution «TESCAN MIRA 3 LMU».

The pH of water extract was determined after three minutes of 5g dry sludge boiling into 50 sm3 of distilled water. The measurement was conducted with pH-meter (I-500 econometric converter, Akvilon, Russia).

The right density was found in a psychometric way. To determine the bulk density, the method ASTM D2854-70 "Standard method of controlling the apparent density of active carbons was used.

The oil capacity of the samples was determined as follows: 35 ml of the investigated industrial oil (I-20A engine oil, GOST 20799-88) was placed in a Petri dish, then a sample of a sorbent weighing 1 g was poured on top of it. At certain intervals (1 min, 5 min, 15 min, 30 min, 60 min) with the help of brass sieves with a cell of 0.063 mm, the investigated sample of the sorbent with absorbed sorbate was removed. The formula calculated oil capacity:

\[ A = \frac{(m_1 - m_2)}{m_2} \]

where \( m_1 \) is the mass of absorbed oil with sorption material, g; \( m_2 \) is the mass of sorption material, g.

The specific surface of the materials was determined using a TriStar II 3020 automated sorption unit manufactured by Micromeritics using low-temperature nitrogen adsorption. A volumetric version of the sorption method was used in the experiments.

The sorption capacity for the dye "methylene blue" (chemical formula C_{16}H_{18}ClN_{3}S) was determined by constructing adsorption isotherms. The dye concentration was measured photocolorimetrically (spectrophotometer "KFK-3"). The amount of substance sorbed by the solid phase (A, mg/g) was calculated by the formula:

\[ A = \frac{(C_i - C_f) V}{m} \]

where \( C_i \) is the initial concentration of the substance in solution, mg/l; \( C_f \) — the final concentration of the substance in the solution after equilibrium, mg/l; \( V \) is the volume of the solution, l; \( m \) is the mass of the sample, g.

3. Experimental part

The agricultural processing wastes selected for the study have many similar features. They are finely dispersed materials, and both have a mineral "core" with organic components adsorbed on the surface. At the same time, there are significant differences (Tables 1, 2).

As can be seen from the data presented, DS is characterized by a higher content of organic substances, up to 70%, while CS contains only 25%. The oxides that make up the mineral part of DS
are silicon oxide. To a small extent calcium oxide, CS is represented by calcium carbonate, in terms of oxides, it has 49% calcium oxide and 38.24% carbon dioxide.

### Table 1. Some technological properties of waste sludge

| Parameter                        | Value               |
|----------------------------------|---------------------|
| Colour                           | Off-white           |
| Organic matter content (%)       | 70                  |
| Bulk density (kg/m³)             | 450                 |
| Initial density (kg/m³)          | 2750                |
| pH of water extract              | 6.92                |
|                                  | DS                  |
|                                  | CS                  |

### Table 2. The oxide composition of the mineral part of the sludge

| Sludge | SiO₂ | CaO | Na₂O₃ | Al₂O₃ | Fe₂O₃ | MgO | CO₂ |
|--------|------|-----|-------|-------|-------|-----|-----|
| DS     | 86,54| 5,85| 2,9   | 2,4   | 0,89  | 0,54|     |
| CS     | 1,71 | 49,0| 0,32  | 1,7   | 0,68  | 3,83| 38,24|

As organic components, DS contains residues of vegetable oil represented by triglycerides of acids such as linoleic (C₁₇H₃₁COOH), oleic (C₁₇H₃₃COOH), palmiticCH₃(CH₂)₁₄COOH, as well as plant waxes [26,27].

CS contains calcium salts of oxalic (CaC₂O₄), citric (Ca₃(C₆H₅O₇) 2), and malic acids ([OOCCH₂CH(OH)COO]Ca), some amino acids, and pectin [27].

Since the hydrophobicity of the material plays an essential role in the extraction of hazardous substances such as petroleum products from sewage, studies have been conducted to determine the degree of hydrophobicity of the surface of the materials (Figure 1).

![Figure 1](image.png)

**Figure 1.** Determination of the degree of hydrophobicity of the surface by the shape of a drop:

a – hydrophobic (θ> 90 °); b – hydrophilic (θ<90 °) surface

A drop of water was applied to the surface of the test material, and the contact angle of wetting was determined.

The study showed that the initial materials are hydrophilic, while after heat treatment (DS t = 500 ° C; CS t = 600 ° C) both sludges show hydrophobic properties (Figure 2).
During the burning of materials, carbonization of organic substances occurs, which is easily determined by the colour change of the sludge. Moreover, the DS begins to carbonize at lower temperatures than CS (Fig. 3) when the burning temperature of 620–650 °C is reached, the processes of destruction of organic substances begin with their decomposition into CO₂ and H₂O.

The study of the microstructure of materials has demonstrated differences in the structure of their surface. CS is composed of small globular structures, DS has a smoothed surface, which is due to the presence of wax and oil substances in its composition. These differences remain during the burning of materials (Figure 4).

**Figure 2.** The shape of a drop of water on the surface of the initial materials: a – DS, b – CS; heat-treated materials: c – DS, d – CS

**Figure 3.** Change the colour spectrum of materials depending on the burning temperature

**Figure 4.** The microstructure of the initial and heat-treated samples, a – initial CS, b – source DS, c - CS t = 600 °C, d – DS t = 500 °C
CS has a higher specific surface area \( CS_{\text{init}} = 54 \text{ m}^2/\text{g} \), burning at a temperature of 600 °C increases it to 72 m\(^2\)/g. DS has an initial value of the specific surface area of 2.2 m\(^2\)/g, with burning \( t = 500 \text{ °C} \) it increases to 3.9 m\(^2\)/g. When burned, both sludge have an alkaline aqueous extract reaction, \( \text{pH} \text{ DS} = 10.8, \text{pH} \text{ CS} = 11.5 \).

It is known that surface hydrophobicity is a favourable factor in the purification of aqueous media from hydrophobic substances, such as petroleum products.

Studies have been conducted to determine the oil capacity of heat-treated sludge. As a result of studies, it was found that the oil capacity of DS is 3.5 g/g, the oil capacity of CS is 1.13 g/g.

One of the crucial characteristics of industrial sorbents is the sorption capacity for dye "methylene blue." As a result of studies, it was found that CS has a significantly higher methylene blue capacity – 77.9 mg/g, for DS, this indicator is 9.5 mg/g.

Studies have been conducted comparing the efficiency of purification of model waters from copper ions (Fig. 5). Sorbent mass is10 g / dm\(^3\), the initial concentration of Cu\(^{2+}\) ions was 25 mg/dm\(^3\). The reaction temperature of the aqueous medium in all experiments was in the range of 18–20 °C. The content of copper ions in aqueous solutions was determined by the photocolorimetric method.

It was found that both sorption materials are useful sorbents of copper ions. Under these conditions, CS demonstrates slightly higher indicators than DS, but in general, the values of the efficiency of extraction of copper ions are close.

The results obtained are of specific scientific interest since with the general similarity of sorption materials, their sorption capacity for some essential substances is noticeably different. At the same time, based on the physicochemical properties of the materials under study, it seems possible to share them in the treatment of multicomponent sewage containing various groups of pollutants. Presumably, the joint use of two wastes in the composition of the raw material mixture to obtain a composite sorption material is permissible.

Further research in this direction is required to study the possibility of their common use in the treatment of multicomponent sewage with the achievement of high rates of extraction of various groups of pollutants.

4. Conclusion

Thus, a comparison of the physical and chemical properties of the investigated organic and mineral wastes show that they have a number of similar indicators: during burning, carbonization of organic substances occurs on the surface of the mineral core; heat treatment gives them hydrophobic properties, the pH of the aqueous extract has an alkaline reaction. The differences are that the central part of the mineral component of CS is calcium carbonate, in terms of oxides, it has 49% of calcium oxide and 38.24% of carbon dioxide. DS – silicon oxide (86.54%), CS has a more developed specific surface area, which is ensured by the presence of small globular structures.
These wastes are generated, as a rule, in geographically close regions, since the cultivation of agricultural raw materials requires specific climatic conditions and the presence of suitable soils. Their frequent use for sewage treatment from various pollutants is a promising area of research.

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