Temperature modification of diatomite sludge of oil extraction production at obtaining a sorbent

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Abstract. One of the most widely used methods of water treatment is adsorption. The use of agricultural waste is of great interest in obtaining economical and efficient sorption materials. In this paper, the features of temperature modification of diatomite sludge are studied. Diatomite sludge is a multi-tonnage waste of oil extraction production formed during the purification of sunflower oil with diatomite. The kinetics of thermal activation of diatomite sludge at temperatures of 450, 500, and 600 °C was studied. It was found that the temperature of 450 °C is optimal for thermal modification of waste. In this case, part of the organic compounds is preserved, as with a further increase in temperature, they completely disintegrate into gaseous products. IR spectra and energy dispersion analysis were analyzed, and the structure and physical and chemical properties of diatomite and diatomite sludge were studied before and after heat treatment. It was found that the water extract of the samples, both initial and thermomodified, has a pH close to neutral. With an increase in the firing temperature, a small suspension effect is observed, which means the presence of a charge in the DSH particles in the aqueous medium, which can intensify the convergence of molecules with a positive charge with the surface of the sorbent. The development of methods for the secondary use of agricultural raw material processing waste for wastewater treatment allows solving comprehensively the problems of reducing the anthropogenic load on natural ecosystems, is an urgent task of modern society for environmental protection, and has scientific and practical significance.

1. Introduction

Currently, waste that requires recycling or disposal is generated everywhere. Many scientists consider the term “waste” obsolete, as each waste can become a valuable secondary raw material in some technological process [1, 2].

In the process of processing agricultural raw materials, large amounts of organic and organomineral waste are generated. As the volume of food production is steadily increasing (due to the continued growth of the world’s population), waste is generated in large quantities every year [3, 4]. Most of it is not used, but is taken to landfills for storage. This leads to environmental pollution and alienation of valuable territories.

Global production of oils and fats is about 2.5-3 million tons/year, 75% of which is obtained from plants. During the separation of oils from oilseeds and subsequent cleaning of the resulting oils, a large amount of waste is generated, for which disposal is an urgent problem [5, 6].
An example of such waste is diatomite sludge (DS). Diatomite is a sedimentary rock formed by silica fragments of the shells of microscopic diatoms – diatoms and radiolarians. The main part of the siliceous carapace (skeleton) is amorphous silica hydrates of various degrees of water content – varieties of opal of the mSiO$_2$·nH$_2$O type, the crystal component is represented by quartz admixtures [7, 8]. Natural diatomite is subjected to thermochemical stabilization, treated with solutions of alkalis, calcined at a temperature of about 1000 °C, and then used as a filter material in the food industry, in particular, in brewing and oil extraction production [7, 9]. DS formed during the purification of vegetable oils is non-toxic, however, during its long-term storage, air and water bodies are polluted with aldehydes, ketones, oxide compounds and other substances - products of decomposition of organic components [10]. Taking into account the high specific surface area of sludge particles and the significant content of adsorbed vegetable oil, the risk of self-ignition is possible when the waste comes into contact with air oxygen [11].

Sunflower is a traditional oilseed crop for Russia and Eastern Europe. It is also grown in small quantities in India, the United States, and other countries [12, 13]. Table 1 shows data on the share of sunflower oil consumption in the world out of the total amount of vegetable oils, % [14, 15].

| Oil      | Consumption in the world, % | Oil      | Consumption in the world, % |
|----------|-----------------------------|----------|-----------------------------|
| Palm     | 33.1                        | Cotton   | 4.3                         |
| Soybean  | 24.2                        | Palm kernel | 3.6                        |
| Rapeseed | 15.2                        | Coconut  | 2.9                         |
| Sunflower| 8.5                         | Olive    | 2.7                         |
| Peanut   | 5.1                         | Corn     | 0.4                         |

In small quantities DS can be used as a feed additive after oil purification, however, this product is very perishable [16], which makes it difficult to use it widely.

The main brand of diatomaceous earth used in the fat and oil industry and allowing achieving high filtration rates is “Celite 545 VO”. Diatomite is used to extract waxes and sticky impurities from sunflower oil that degrade consumer qualities.

It is known that many organic and organomineral wastes are suitable raw materials for the production of sorption materials that can be used in water treatment [17-21]. This makes it possible to reduce significantly the cost of wastewater treatment and at the same time dispose of waste, which leads to a comprehensive reduction in the anthropogenic load on natural ecosystems.

One of the most frequently used methods of modifying such materials is carbonation, which allows forming a sorbing carbon layer and neutralizing simultaneously organic compounds that are subject to oxygen and bacterial decomposition.

To develop a sorption material based on DS, it is necessary to conduct a set of studies to assess the physical and chemical changes that occur during heat treatment.

2. Materials and methods

As an object of research, we used the spent DS formed during the purification of sunflower oil with diatomite of the Celite 545 VO brand in the conditions of EFKO LLC, Alekseevka, Belgorod region, Russia. DS is an oily paste-like mass with an organic content of up to 70%. The mineralogical composition is mainly represented by cristobalite, quartz is present in small quantities, and clay minerals in an amorphous state are noted. The bulk density is 450 kg/m$^3$, the true density is 2750 kg/m$^3$. The composition of substances adsorbed on the surface of diatomaceous earth during the filtration of vegetable oils also includes vegetable waxes, the content of which is 1.3-12 % [22].

Thermal modification of the DS was performed by heating the average sample without oxygen in an electric furnace of the SNOL 25/12 brand with holding at the maximum temperature for 1 hour.
Infrared spectra were obtained using the Vertex 70 instrument (USA), and then decoded using reference and scientific literature [23–25].

Energy dispersion analysis was performed using a scanning electron microscope TESCAN MIRA LMU (Czech Republic).

The pH values of water extracts were measured on the pH meter I-500 “Aquilon” (Russia).

3. Results and discussion

DS samples were fired at various temperatures, after which their structure and physical and chemical properties were studied.

In the course of research, it was found that at temperatures of 300-450°C, organic substances are not completely oxidized. The intermediates formed as a result of heat treatment settle on the surface of the diatomaceous earth particles in the form of a carbon layer. To determine the optimal conditions for the modification of the DS, it is necessary to obtain information about the transformations of the substances that make up its composition during heat treatment.

The results of studies of samples of materials in the IR spectrum are shown in figures 1,2.

![Figure 1. IR-spectrums: a – diatomite; b – DS.](image)

In the region of 1300-400 cm\(^{-1}\), minerals show bands of stretching and bending of Si-O bonds and bands of bending of O-H bonds. The shape and position of the bands depend very much on the location inside the layers.

If the majority of octahedral positions are occupied by divalent central atoms, the O-H bending bands are shifted towards smaller wave numbers in the range of 700-600 cm\(^{-1}\) [23].

The initial diatomite has expressed peaks of 1092 cm\(^{-1}\) and 473 cm\(^{-1}\), which are related to Si-O bond fluctuations. Peaks of 3452 cm\(^{-1}\) show the presence of bound water; peaks of 791 cm\(^{-1}\) and 619 cm\(^{-1}\) can be attributed to the O-H of water molecules affected by hydrogen bonds [24]. In addition, the band at 791 cm\(^{-1}\) can be associated with valence vibrations of the \(\nu_s\) (Al-O) clay impurity minerals that are part of the diatomite.

Crystallization water is often characterized by peaks in the range of 1670-1600 cm\(^{-1}\), which is marked by a peak of 1620 cm\(^{-1}\) on the IR spectrum of diatomite [24].

The DS sample clearly shows a peak of 2924 cm\(^{-1}\), which indicates the presence of asymmetrically attached CH\(_2\) radicals, a peak of 2853 cm\(^{-1}\) can be attributed to a CH\(_3\) bond with symmetric bonds, and a peak of 3009 cm\(^{-1}\) indicates -CH\(_3\). A blurred peak in the range of 3600-3200 cm\(^{-1}\), related to chemically bound water, still stands out. The intense peak of 1746 cm\(^{-1}\) is defined as C=O bond. Similar peaks can be noted in the IR spectra of linseed oil and vegetable wax (Table 2) [25].
Table 2. Characteristic peaks for vegetable wax and linseed oil.

| Range, cm⁻¹ | Bond between molecules | Type of oscillations                  |
|-------------|------------------------|--------------------------------------|
| 3600-3200   | O -H                   | Band of valence vibrations            |
| 3000-2800   | C-H                    | Band of valence vibrations            |
| 1780-1700   | C=O                    | Band of valence vibrations            |
| 1480-1300   | C-H                    | Bands of deformation vibrations       |
| 1300-900    | C-O                    | Band of valence vibrations            |
| 750-700     | C-H                    | Bands of rotational vibrations        |

The peak of 1464 cm⁻¹ probably belongs to the deformation vibrations of C-H (1480-1300 cm⁻¹), similar to the IR spectrogram of linseed oil. The peaks of 1377 cm⁻¹, 1236 cm⁻¹, and 1163 cm⁻¹ fall within the range of 1300-900 cm⁻¹, which corresponds to the presence of C-O bonds [23]. They can determine the peaks characteristic of pure diatomite: 1099 cm⁻¹, 476 cm⁻¹.

Further, samples that were heat-treated at 450 °C were examined (DS₄₅₀), when organic substances were not fully destroyed, and at 500 °C (DS₅₀₀), when most of the organic compounds decomposed.

According to the results of the IR analysis shown in Figure 2, after heat treatment, the peaks related to vibrations in organic molecules become less expressed, and the peaks indicating the presence of silicon compounds (1092 cm⁻¹,1090 cm⁻¹, 471 cm⁻¹) are more expressed. However, the peak of 1090-1092 cm⁻¹ in both DS₄₅₀ and DS₅₀₀ is more intense than in the original diatomite. Presumably, it is enhanced by fluctuations in oxygen organic products of partial destruction of waxes and vegetable oil, and the presence of C-O-C (1270-1060 cm⁻¹) and C-O (1150-1000 cm⁻¹) bonds is possible.

There are no peaks characteristic of C=O bonds (1900-1550 cm⁻¹), which are among the first to be destroyed during heat treatment.

The intense bands at 2926 cm⁻¹ and 2853 cm⁻¹, which corresponds to the region of 2850-3000 cm⁻¹, can be attributed to valence vibrations, and the medium intensity band at 1470 cm⁻¹ can be attributed to deformation vibrations of methylene groups and characterize the presence of a Csp³-H bond on the carbon surface of DS₄₅₀.

With an increase in the processing temperature to 500 °C, their intensity decreases to zero, which indicates the burnout of surface forms of carbon containing C-H fragments.

The valence fluctuations at 1719 cm⁻¹ in DS₄₅₀ correspond to the carbonyl group (C=O) of esters or lactone that are part of vegetable waxes and waxy substances, which explains the presence of hydrophobic properties of this material. The IR range of 3100-3700 cm⁻¹ characterizes the valence vibrations of various types of hydroxyl groups, including in water molecules adsorbed on hydroxyl groups. Siloxane groups Si-O-Si are characterized by intense peaks of 1111-1000 cm⁻¹ [24, 25].

Thus, it can be seen that the IR spectrograms of diatomite and DS₅₀₀ are very similar to each other, the latter slightly differs in the intensity of the peaks, and their general shape and location are almost
identical for the samples. Therefore, the temperature of 450 °C is the threshold for the heat treatment of DS, when a part of organic compounds is preserved, as with a further increase in temperature they completely break down into gaseous products.

The results of energy-dispersive studies are in good agreement with IR spectroscopy data (Figure 3). It can be noted that at a temperature of 450 °C, a significant amount of carbon is retained in the material. The ratio of oxygen and carbon changes already at a temperature of 500 °C – the processes of destruction of the bulk of organic compounds occur. The sample obtained at a temperature of 600 °C contains a small amount of carbon. The maximum peak of oxygen, which is obviously part of the inorganic oxides, is clearly recorded.

Previously, it was found that the source material has a significant hydrophobicity, as it contains a large amount of oil and wax residues. As the firing temperature increases, the hydrophobicity decreases markedly [26] due to the decomposition of organic substances. The hydrophobic properties of the sorption material are a positive factor in the recovery of hydrophobic pollutants, such as petroleum products. At the same time, such a sorption material will be ineffective when treating wastewater from heavy metal ions, dyes, and other ions and compounds with hydrophilic properties. The presence of a charge on the surface of the latter particles can be a positive factor when interacting with oppositely charged ions and polarized molecules.

![Energy dispersion analysis of DS](image)

**Figure 3.** Energy dispersion analysis of DS: a – DS; b – DS_{450}; c – DS_{500}; d – DS_{600}.

To determine the presence of charge on the surface of the sorption material, the suspension effect was studied.

It was found that the water extract of samples, both initial and heat-treated, has, in general, close to neutral pH (Table 3). With an increase in the firing temperature, a small suspension effect is observed, which means the presence of a charge in the DS particles in the aqueous medium. As the suspension has a more acidic reaction than the filtrate, therefore, the particles have a small negative charge. Despite the fact that the charge of the particles is very small, its presence can facilitate the convergence of molecules with a positive charge with the surface of the sorbent. In particular, this applies to heavy metal ions.
Table 3. pH of suspension and filtrate of water extract DS.

| Sample | pH of suspension | pH of filtrate |
|--------|-----------------|----------------|
| DS     | 6.44            | 6.45           |
| DS400  | 6.89            | 6.92           |
| DS450  | 6.90            | 6.93           |
| DS500  | 6.85            | 6.99           |
| DS550  | 6.81            | 7.3            |
| DS600  | 6.79            | 7.2            |
| DS650  | 6.77            | 7.3            |

The information obtained is of great interest, as the DS processed at different temperatures can serve as a sorption material for hydrophobic substances (firing temperature 400-450 °C) or positively charged ions, such as heavy metals or dyes (firing temperature 500-550 °C).

4. Summary
Studies were conducted to determine the optimal conditions for modifying the DS. The analysis of the IR spectra of diatomite and diatomite sludge of various degrees of modification allowed establishing that the temperature of 450 °C is optimal for the heat treatment of DS, when a part of organic compounds is preserved, as with a further increase in temperature they completely disintegrate into gaseous products. The results of energy-dispersive studies are in good agreement with IR spectroscopy data.

When the firing temperature increases, there are small changes in the pH of the water extract and a suspension effect occurs, due to the appearance of a negative charge around the sludge particles. Despite the fact that the charge of the particles is very small, its presence can facilitate the convergence of molecules with a positive charge with the surface of the sorbent. In particular, this applies to heavy metal ions. Thus, by processing at different temperatures, it is possible to obtain a sorption material that is more effective in extracting hydrophobic or hydrophilic pollutants.

5. References
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Acknowledgments
This work was supported by a grant from the President of the Russian Federation for state support of young Russian scientists – candidates of sciences and doctors of sciences and leading scientific schools of the Russian Federation, application number MD-1249.2020.5. The work is realized in the framework of the Program of flagship university development on the base of the Belgorod State Technological University named after V.G. Shukhov, using equipment of High Technology Center at BSTU named after V G Shukhov.