The use of vegetable oil waste for the sewage purification from dyes

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Abstract. Currently, the search for new methods of wastewater treatment is an urgent task. In this work, investigation was carried out on the treatment of sewage containing dyes using modified waste generated during the refining of oils. During the research, the influence of various physical and chemical factors on the efficiency of sewage containing dyes was investigated. As a result of investigation on model sewage, it was found that when using modified waste, the maximum cleaning efficiency reaches 98%. At the same time, the following environmental problems are being solved simultaneously: reducing the amount of man-made waste and, as a result, reducing the area for its storage and treatment of waste water containing dyes.

1. Introduction
Vegetable oils are products extracted from plant materials and consisting of triglycerides of fatty acids and related substances (phospholipids, free fatty acids, waxes, styrenes, coloring agents, etc.) [1]. Currently, at the regeneration of mineral oils the adsorption method is most often used. When carrying out adsorption refining, pigments and soap stock residues are extracted after the neutralization process. Bleaching (adsorption refining) is carried out with the use of special sorbents that are able to interact with and retain pigments. In subsequent filtration, the bleaching powders are separated from the oil together with the absorbed coloring matter. As an adsorbent, bleaching clay is often used.

Bleaching clay is a product of weathering of igneous rocks and their decomposition under the influence of water and other factors. As a result of this effect, more loose and porous structures with good sorption properties are formed. They are able to retain asphalt-resinous substances, acidic components and other undesirable impurities formed as a result of oil aging processes on their surface. Bleaching clays belong to bentonite clays, as a rule of montmorillonite composition [2,3]. To improve the sorption properties, bleaching clays are often subjected to special treatment with acids.

Bleaching clay has a specific surface area of 100-300 m² / g. The effectiveness of its action during the regeneration of oils is affected by the structural features of the crystal lattice and the origin of the material. The main advantage of bleaching clays is their relative cheapness [4].

Purification with bleaching clays can be used both as an independent method and in conjunction with other approaches. The complex effect increases the efficiency of regeneration.
The spent bleaching clay containing oil, after the development of its sorption capacity, is a hazard class IV waste according to the Federal Waste Classification Catalog. Spent bleaching clay in its composition contains from 30 to 50% fat. The danger of this waste is that it is able to ignite spontaneously. Spontaneous combustion can occur due to the oxidation of adsorbed vegetable oil. Currently, most of the bleaching clay generated at the enterprises is located at the municipal solid waste landfill. Clay comes into contact with oxygen for the first time when unloading from a filter. At this point, the temperature of the spent clay is from 90 °C to 130 °C. Self-ignition is possible only when the spent bleaching clay can react with oxygen in sufficient quantities, therefore, it is necessary to ensure the minimum possible contact between the clay containing oil and oxygen in the air. For this reason, spent bleaching clay should not be in drafts; if possible, it should be stored in an inert gas atmosphere. If the spent bleaching clay is left in the open air on a hot day, spontaneous combustion will occur within a few hours. Wastes of this type from one enterprise per year range from 300 to 550 tons. Moreover, the enterprise pays money for the disposal of this waste.

Currently, this waste is used in the production of expanded clay, brick, drying oil, astringents, as well as in various areas of agriculture. When analyzing the literature data, it was found that the adsorbents currently used for sewage treatment from fats, vegetable oils and other organic substances are of high cost. In this regard, there is an acute problem with the search for new materials that will have high sorption properties for sewage treatment. Currently, as a result of the growth of industrial production, a large amount of waste is generated, which can be regenerated and modified with subsequent use as secondary raw materials. The use of waste will not only significantly reduce the human impact on the environment, but also reduce the cost of sewage purification measures [5,6].

In this work, investigation was carried out on the treatment of sewage containing dyes using thermally modified waste generated during the refining of oils.

2. Theoretical part
For the preparation of model solutions, the dye "methylene blue" was used. During the experiment, model solutions with concentrations of 25 and 50 mg/dm³ were used.

The thermal method is the processing of spent bleaching clay in a muffle furnace. To obtain the material, the waste was calcined in a muffle furnace at temperatures from 100 °C to 700 °C. When burning, the mass of the test material decreases. This indicates the burnout of the organic part of the waste and the formation of a carbon layer on the surface of the material particle. The transition of the color from dirty white to black indicates the process of carbonization of the organic substances of the material that are contained in the waste after bleaching the oil, but the transition from black to white shows the burnout of the carbon layer. As a result of heat treatment, a material was obtained on the surface of which there are products of various degrees of carbonization of the organic component of the waste - thermally modified bleaching clay (TMBC) (table 1).

| Burning temperature, (°C) | Color change of TMBC | Initial density, (kg/m³) | Bulk density, (kg/m³) |
|--------------------------|----------------------|-------------------------|----------------------|
| 100                      | Off-white            | 2680                    | 1210                 |
| 150                      | Gray                 | 2690                    | 1220                 |
| 200                      | Brown                | 2700                    | 1230                 |
| 250                      | Dark brown           | 2710                    | 1250                 |
| 300                      | Dark grey            | 2715                    | 1280                 |
| 350                      | Black                | 2720                    | 1320                 |
| 400                      | Dark grey            | 2790                    | 1390                 |
| 450                      | Light gray           | 2860                    | 1430                 |
| 500                      | White gray           | 2890                    | 1470                 |
| 550                      | White gray           | 2910                    | 1490                 |
| 600                      | Off-white            | 2930                    | 1510                 |
| 650                      | White                | 2960                    | 1540                 |
| 700                      | White                | 3100                    | 1570                 |
The data obtained show that during burning of the source material, an increase in bulk (24.7%) and true density of the waste (9.3%) occurs. This can be explained by grinding conglomerates of the studied material.

For a more complete study of the waste, we studied the chemical composition and basic physical and chemical properties. The research results are presented in table 2, 3.

**Table 2.** The chemical composition of the initial clay, (%).

|      | SiO₂   | Al₂O₃ | TiO₂ | Fe₂O₃ | MgO | CaO | Na₂O | K₂O | P₂O₅ |
|------|--------|-------|------|-------|-----|-----|------|-----|------|
| %    | 51,08  | 16,39 | 2,29 | 17,10 | 2,29| 0,95| 0,44 | 8,81| 0,35 |

**Table 3.** Properties of bleaching clay are presented in table.

| №   | Name of indicator                              | Data obtained | TC norms     |
|-----|-----------------------------------------------|---------------|--------------|
| 1   | Moisture content, [%]                         | 7,2           | No more than 15 |
| 2   | The residue after dispersion using a sieve with a mesh size | 0,16          | No more than 5 |
| 3   | Oil capacity, [%]                             | 60,8          | -            |

To confirm the possibility of using the material as an adsorbent, we carried out some experiments studies to study the microstructure [7]. The surface microstructure of the samples was studied using a TESCAN MIRA 3LMU scanning electron microscope (Poland). Figure 1 shows the surface of the studied material at multiple magnification. In microphotographs it is seen that the waste presents particles of a complex structure with protrusions, cracks, channels, which indicates a strong defect in their surface and high surface energy of the system as a whole, which is a positive factor for the occurrence of adsorption processes.

![Figure 1. The microstructure of the surface of the investigated material particles (burning temperature 350 °C).](image)

When studying the quantitative composition of TMBC using an X-ray phase [8,9] and X-ray fluorescence analysis Blok Station Arl-9900, it was found that the waste contains 69% organic and 31% inorganic matters.

When conducting studies of the inorganic part [10] of the waste, it was found that a significant proportion is represented by the following substances: CaO (50.29%), K₂O (23.08%), MgO (5.23%), SiO₂ (4.72%) and P₂O₅ (3.87%), Al₂O₃ (2.68%), RuO₄ (2.40%), SO₃ (2.24%), Cl (1.62%), PdO (0.772%), Na₂O (0.770%), Fe₂O₃ (0.742%), Rh₂O₃ (0.692%), Ag₂O (0.167%), MoO₃ (0.141%), TiO₂ (0.120%), I (0.073%), TeO₂ (0.067%), MnO (0.0643%), H₂O₂ (0.052%), ZnO (0.0466%), WO₃ (0.039%), Gd₂O₃ (0.029%), CdO (0.029%), Lu₂O₃ (0.026%), SrO (0.0193), Bi₂O₃ (0.0101%).
In the energy dispersive spectrum [11,12] of Figure 2, it can be seen that the great part of thermally modified clay (TMBC) is carbon, which confirms the presence of a significant proportion of the organic component in the material.

![Figure 2. Energy dispersive spectrum of TMBC.](image)

Due to the fact that the properties of the material [13] under study can change under the influence of temperature, it was necessary to find out the optimal temperature of thermal modification. Samples of the initial waste were pyrolyzed at temperatures from 50 to 700 °C, with interval of 50 °C. The resulting materials were used to clean model methylene blue dye solutions; the weight of TMBC additive was 1 g / 100 ml. The research results are presented in Figure 3. The studies were carried out with model dye solutions [14] with concentrations of 25 and 50 mg / dm³.

![Figure 3. Dependency chart of the cleaning efficiency on the temperature of the heat treatment of the initial material.](image)

From Figure 3, it can be concluded that at the firing temperature of 50°C, the cleaning efficiency is not high and is 40 and 57%, but with an increase in the heat treatment temperature, the cleaning efficiency increases at the firing temperature of 350 °C. Since it is 94-97%. Further, with an increase in temperature of more than 350°C, the cleaning efficiency of model solutions decreases, which is associated with the burning of the carbon layer on the surface of the modified waste particles [15-17]. It is obvious that the possibility of interaction is higher the larger the surface area.

An important parameter in sewage purification [18] is the determination of the optimal amount of adsorbent required for purification. The experimental results are presented in Figure 4.
Figure 4. Dependency chart of the cleaning efficiency on the mass of added material.

It was found that the maximum purification efficiency of model solutions with a concentration of 25 and 50 mg / l is achieved by adding 1 g of adsorbent and reaches 92-98%. An analysis of the obtained dependences showed that, depending on the mass of the adsorbent, the purification efficiency of model solutions from a given dye to a certain value also increases.

In the course of physical and chemical processes at the phase boundary (for example, liquid – solid), the surface area of the phase interface or the contact surface area of reacting substances is of great importance [19, 20]. In this case, interaction occurs only if the particles in solution can approach a solid surface and react with substances on it. Obviously, the greater the possibility of interaction is the larger the surface area is.

Since the total surfaces of dispersed particles, which are burned waste particles in this system, the higher the smaller their diameter, it is of interest to study the dependence of the purification efficiency on the particle size of the sorbent. The study was carried out with of studied material TMBC.

The study on the dependence of cleaning efficiency on the particle size of the sorbent was carried out with fractions: 0.2-1; 0.063-0.2 and <0.063 mm. The research results are presented in Figure 5.

The experimental results shown in Fig. 6 show that the purification efficiency increases (up to 98%) with increasing dispersion of the material and reaches maximum values for the most finely dispersed fraction of TMBC.

Therefore, we can conclude that the thermal modification of the waste is advisable, since it significantly increases its sorption characteristics.

3. Conclusion

Studies have been conducted on the thermal modification of the waste, its basic physical and chemical properties. Pyrolysis at various temperature conditions showed a change in the color of the initial material, which indicates the process of carbonization of the organic substances of the material. Microphotographs confirmed the heterogeneity of the surface of the material particles, which indicates the presence of sorption centers capable of participating in intermolecular interactions.
Thus, our studies have shown the possibility of using our proposed waste from the production of vegetable oil for sewage purification from dyes, which will reduce the amount of man-made waste and expand the raw material base of adsorption materials.

The reliability of the results obtained is ensured by the application of proven experimental techniques and metrological characteristics and their satisfactory coincidence with production results. It was found that the degree of sewage purification from the dye methylene blue using TMBC reaches 96-98%. The optimal conditions of the adsorption process using TMBC are established. As a result of the experiments, it was found that the optimum temperature of the heat treatment of the initial waste is a temperature of 350 °C.

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