Modified Bleaching Clay as a Sorption Material

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Abstract. In the process of refining vegetable oils, bleaching clays are often used, which leads to the formation of organic mineral solid waste. In the work, the possibility of neutralizing waste bleaching clay by the thermal method and its subsequent use for sewage treatment from dyes was investigated. As a result of the waste heat treatment, a finely dispersed powder was obtained, on the surface of which there were products of various degrees of carbonization of organic substances. To substantiate the theoretical possibility of using the studied material as an adsorbent, the structure of its structure was studied. The obtained micrographs showed that the particles of the modified material are a loose bulk surface 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. Studies on model solutions of the dye "methylene blue" allowed us to establish that the optimum temperature for roasting is 350 °C and to achieve a cleaning efficiency of 96%.

1. Introduction

Refined vegetable oils are used in food around the world. One of the stages of refining is the bleaching process, which allows you to extract dyes from vegetable oils.

Activated bleaching earth is the most common adsorbent used in edible oil bleaching [1, 2].

During the adsorption bleaching of oils, special bleaching powders are used, which have the ability to absorb dyes dissolved in oils and hold them on their surface. During subsequent filtration, the bleaching powders are separated from the oil together with the absorbed coloring matters. In the process of adsorption refining, a highly effective sorbent is widely used i.e. bleaching clay, which meets all the requirements of the quality of oil purification from coloring substances [1, 3-5].

Bleaching clays are represented by bentonite clays of usually montmorillonite composition or siliceous rocks (diatomite, tripoli, siliceous marl) [4,6,7]. Bentonite clays are a product of centuries-old oceanic sediment and they are formed about 25 million years ago during the period when the surface of the deposit was covered with water. Special treatment of bleaching clays with acids (activation) increases their sorption properties several times.

Bentonites are finely dispersed, highly plastic clays with binding, toxotropic and sorption properties. They consist mainly of the minerals such as montmorillonite [Al₂O₃·4SiO₂·H₂O] and bedelite [Al₂O₃·3SiO₂·H₂O]. These minerals are characterized by the layered structure of the crystal lattice, the ability to exchange bases and absorb water, accompanied by a sharp increase in volume [8,9].

It has been estimated that around 2 million metric tons of spent bleaching clay are produced yearly worldwide [5].

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Currently, clay produced at enterprises is located at waste landfills [3,6,11]. The neutralization of bleaching clay involves the elimination of such dangerous properties of clay as self-ignition. Therefore, the search for ways to utilize this waste is an urgent task.

The development of new sorbents is of great practical interest in connection with the widespread increase of volumes in industrial production, and, as a result, an increase in the volume of sewage requiring purification [12]. The use of various wastes for these purposes can significantly reduce the negative anthropogenic impact on the environment, and is also economically viable [13-20].

In this work, the possibility of neutralizing waste bleaching clay (WBC) by the thermal method and its subsequent use for the sewage treatment from dyes was investigated.

2. Materials and methods

To obtain a material suitable for use in water purification, WBC was roasted in a LOIP LF-7/13 muffle furnace at various temperatures.

A bowl with dry, crushed waste was placed in a preheated muffle furnace and calcined for 30 minutes at a given temperature. Then the bowl was cooled in air to room temperature. Calcination was repeated at temperatures from 100 to 600 °C with an interval of 50 °C.

The pH of the aqueous extract was measured using a pH meter (I-500 ionometric converter, Akvilon, Russia).

The analysis of peculiarities of the chemical composition and structure of the sample has been carried out by using the scanning electron microscope of high resolution "MIRA 3 LMU" produced by "TESCAN", Czech Republic.

The dye “methylene blue”, the chemical formula C₁₆H₁₈ClN₃S, was used as a model pollutant, as a compound widely used to study the sorption properties of sorbents.

Purification of aqueous media from the dye was carried out as follows: 100 ml of the solution was placed in a conical flask, and then a sample of sorption material was added and mixed by electronic stirrer for 20 minutes. After that the contents of the flask were left for sedimentation for 15 minutes.

Clarified water was examined for the dye concentration using photocolometric method by apparatus KFK-3 produced by "ZOMZ", Russia;

The purification efficiency (E) was calculated according to the formula:

$$E = \frac{(C_1 - C_2)}{C_1} \times 100\%$$

where $C_1$ and $C_2$ - the concentrations of substances before and after of water purification, respectively.

3. Results and discussion

To obtain more complete information about the studied material, we obtained data on the chemical composition of bleaching clay and the main physical and chemical properties (tables 1, 2)

| SiO₂ | Al₂O₃ | TiO₂ | Fe₂O₃ | MgO | CaO | Na₂O | K₂O | P₂O₅ |
|------|-------|------|-------|-----|-----|------|-----|------|
| 51,38 | 16,39 | 2,29 | 17,10 | 2,29 | 0,95 | 0,44 | 8,81 | 0,35 |

| Name of index | Data obtained |
|---------------|---------------|
| Moisture content, % | 7,2 |
| The residue after sifting on a sieve with mesh No.008, % | 0,16 |
| Bulk density, g/cm³ | 0,63 |
| pH of the aqueous extract | 6,8 |

A change in the color of the material from gray to black (Table 3) indicates the process of carbonization of organic substances contained after oil purification; and the further process of reducing the intensity of the black color indicates the burnout of the carbon layer. Thus, as a result of
heat treatment of WBC, a finely dispersed powder was obtained, on the surface of which products of various degrees of carbonization of organic substances were contained.

Table 3. Change in the color and density of WBC depending on the roasting temperature.

| Roasting temperature, °C | Color        | Initial density, kg/m³ | Bulk density, kg/m³ |
|--------------------------|--------------|------------------------|---------------------|
| 100                      | Off-white    | 2680                   | 1210                |
| 150                      | Grey         | 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 grey   | 2860                   | 1430                |
| 500                      | White grey   | 2890                   | 1470                |
| 550                      | White grey   | 2910                   | 1490                |
| 600                      | Off-white    | 2930                   | 1510                |

The data obtained show that during roasting of the original material, there is a slight increase in the bulk and initial density of bleaching clay, which can be explained by grinding the waste particles.

To justify the theoretical possibility of using the studied material as an adsorbent, it was necessary to study the structure of its compound. Figure 1 shows a thermally modified waste at multiple magnifications.

The micrograph shows that the particles of the modified WBC are a loose bulk surface 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.

![Micrograph of the surface of particles of modified WBC.](image)

Due to the fact that the composition of the waste can change under the influence of various temperatures, it was of interest to find out the most optimal temperature regime of roasting. For this, samples weighs of the initial waste of about 50 g each were subjected to pyrolysis at various temperatures from 50 to 700 °C, in increments of 25 °C. The thermal exposure period for all samples was 60 minutes. Roasted samples were used to purify model methylene blue dye solutions; the weight of the additive of modified WBC was 1 g /100 dm³.
As it follows from figure 2, at the initial stages, the purification efficiency is low and is 40 and 57% for a dye solution with concentrations of 25 and 50 mg/dm³. However, with an increase in the roasting temperature, a significant increase in the purification efficiency occurs. In the roasting temperature range from 200 to 350 °C, it increases by 72 and 71%, while at a temperature of 350 °C there is a maximum of efficiency. Over the period from 350 to 800 °C, the purification efficiency decreases which is probably due to carbon burnout. The maximum purification efficiency (96%) is achieved at a roasting temperature of 350 °C.

Thus, from the obtained results it follows that the temperature 350 °C is optimal for roasting.

4. Conclusion

Studies have been conducted on the modification of WBC by the thermal method. Processing at various temperature conditions showed a change in the color of the material from gray to black what indicates the occurrence of the process of carbonization of organic substances contained after cleaning the oil; and a further process of reducing the intensity of the black color indicates the burnout of the carbon layer. The obtained micrographs demonstrated the heterogeneity of the surface of the particles of the material, which indirectly indicates the presence of sorption centers capable of participating in intermolecular interactions.

The purification of model solutions with the obtained material allowed us to determine the optimal heat treatment temperature of 350 °C, while the efficiency of dye removal of 95% is achieved.

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