Use of vegetable oil refining waste to remove oil products from sewage

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Abstract. The relevance of the research is due to both problems arising from the pollution of surface water with oil products, and the possibility of expanding the range of effective sorbents through the use of industrial waste. The article presents the results on the selection of purification parameters for model effluents containing industrial oils as a type of oil product. Purification was carried out by a sorbent made on the basis of the waste formed during the purification of vegetable oils from waxy impurities. The sorbent was obtained as a result of roasting secondary silica-containing raw materials of oil extraction production in a certain temperature range. It was revealed that the heat treatment of the waste leads to a partial burnout of the organics and the preservation of the paraffin fractions that make up the waxy impurities. Due to this, thermally modified waste becomes hydrophobic and oleophilic; contributes to an increase in oil absorption. In the course of the study, the influence of a number of factors was established, such as the temperature of waste roasting, the duration of contact of the sorbent and the purified medium, the mass of the sorbent, on the efficiency of the process of purifying model solutions from oil products.

1. Introduction

Oil products are the most common toxic polluting ingredients, the source of release to the environment is including the fuel and energy industries.

As a result of the systematic flow of oil and oil products into water bodies, the natural processes of self-cleaning are disrupted, the concentration of toxic products (phenols, naphthols, and other hydroxy derivatives of hydrocarbons) increases, and foaming occurs. This situation requires the use of environmental measures, including technologies for sewage purification from oil products. Numerous methods have been described in the literature for sewage purification from oil and oil products, including those based on sewage components absorption with solids.

At the same time the works of improving the absorption properties of sorbents obtained on the basis of waste, both by mechanical activation and as a result of thermal and chemical modifications are carried out [1-5].

Thermal treatment of plant waste is often used as a modifying agent [6]. The temperature range varies from 150 to 800°C. According to the data for the heat treatment of olive oil squeezing waste in order to obtain a sorbent for oil product removal, the authors selected parameters as temperature 250°C and processing time 60 minutes. The test results of the sorbent showed that the oil capacity was from 6 to 11.6 g/g, depending on the initial oil content in the aqueous medium. The purification efficiency at this ratio of oil to sorbent was 99.9%, which corresponds to the MPC level of 0.3 mg/dm³.
Thermal activation contributes to the appearance of hydrophobic properties of the sorbent, which is important for sewage treatment from oil and oil products. The authors attribute the presence of hydrophobicity to the appearance of –C – C– bonds as a result of the carbonization process [7].

The natural raw materials: for example, clay materials and production wastes, heat-treated defecate – a waste from sugar production were used as inorganic raw materials for oil sorbents [8-10].

Diatomites, gaize and zeolites are the most promising natural materials for sewage treatment containing oil and products of its processing. The content of the main chemical components in natural materials is in the following proportions, %: SiO₂ (45 – 84); Al₂O₃ (3.3 – 11.3); Fe₂O₃ (1.0 – 5.3); MgO, CaO and others 6–8%. The author notes that the sorption ability of materials with respect to petroleum products decreases in the series: modified gaize - f gaize - diatomite - zeolite. Diatomite is an opal-cristoballite rock, consisting in its bulk of numb opal cusps of diatoms and their fragments with macropores ranging in size from 10⁻³ mm [11, 12]. It was shown [13, 14] that when diatomite was ground by mechanical method in order to obtain an adsorbent, it is preferable to use methods based on crushing and grinding with simultaneous drying of the material. Under these conditions, a fraction of 5–45 μm is obtained, which according to the authors, is optimal for imparting sorption properties to the material.

The method of using thermal shock (fast heating at 900 - 1000°C) is often used to increase the porosity of materials and increase sorption capacity. The possibility of using thermally expanded graphite (TEG) as a sorbent for oil products was shown in the article [15, 16]. The technology for producing TEG is described in patent 2142409 of the Russian Federation [17]. TEG was used both as a bulk filter with a loading height of more than 20 mm, and as a floating sorbent. The purification efficiency of the filter with a load weight of 0.1 kg was 97.56% and floating sorbent – 98.8%. It was found that the absorption capacity of the TEG was 1634 kg of oil products per 1 kg of sorbent.

2. Materials and Methods

Model emulsions of concentrations of 50.0; 100.0; 250.0 mg/dm³ was prepared by adding a portion of spindle oil of the I-20 A SN brand to distilled water [18-21].

A sample waste was obtained by gravimmetrical method on a laboratory scale VL-120. The solutions were shaken on an LS-110 mixing device for 24 hours to obtain a stable emulsion. The emulsions were again shaken for an hour before the analysis.

Obtaining thermally modified kieselguhr sludge. To obtain thermally modified kieselguhr sludge (TMKS), used kieselguhr sludge (UKS) was taken, consisting of kieselguhr and organic impurities - oils and waxes [22]. The cup with UKS was placed in a PM-14m type muffle furnace and calcined for 60 min at a given temperature. Then the cup was cooled to room temperature. Calcination was carried out at temperatures: 430, 450, 470, 500, 530, 550, 570, 600, 630, 650 °C.

Method for measuring the mass concentration of oil products.

The concentration of oil products in model solutions and real sewage before and after treatment was determined according to the procedure [23].

Method for the treatment of effluents from petroleum products.

A model solution in a volume of 300 cm³ was poured into a conical flask, where the calculated sample waste of TMKS was then introduced. The contents of the flask were shaken for an hour, and then filtered through a paper filter. The residual quantity of oil products in the purified solution was determined.

3. The received results and their discussion

The absorption capacity of the materials was improved by conducting a thermal effect on the used kieselguhr sludge, based on the fact that the composition of the UKS contains a significant percentage of organic impurities. The content of organic impurities in the composition of UKS is due to the applied technology for the purification of vegetable oils to remove wax-like substances and wax-winterization. This is a gradual cooling technology, as a result of which fats formed the crystals. Then
they are separated from the liquid part using various filters, including those made on the basis of a natural mineral – kieselguhr [24].

High-temperature oxidation of organic impurities in the composition of UKS leads to the burning out of a part of the material, the appearance of additional pores of various diameters, and an increase in the absorption properties. The absorption properties of the material with respect to oil products depend on the characteristics that the material possesses such as hydrophilic or hydrophobic. The presence of these properties can be established by determining the contact angle. Hydrophobicity is indicated by the value of the contact angle $\Theta > 90^\circ$; hydrophilicity $\Theta < 90^\circ$.

Figure 1 shows the dependence of the contact angle on the conditions of thermal action. In the diagram, thermally treated materials with hydrophilic properties are highlighted in blue. This is the initial UKS without heat treatment and samples obtained as a result of roasting at a temperature of 500 °C. They will not be used for further research.

For further study, samples of materials highlighted in yellow, characterized by a contact angle $\Theta > 90^\circ$ and having hydrophobic properties, are of interest.

Along with the determination of hydrophobicity, the oil absorption (figure 2) of the selected material samples was evaluated, which received the symbols TMKS$_{430}$, TMKS$_{450}$, and TMKS$_{470}$.

According to experimental data, the oil capacity of the hydrophobic samples TMKS$_{430}$, TMKS$_{450}$, TMKS$_{470}$ is in the range of $2.7 \div 4.0$ g/g, while for the hydrophilic sample TMKS$_{500}$ it is about $2.1$ g/g and continues to decrease with increasing firing temperature and hydrophilicity of samples.

The authors attribute the increase in the oil capacity of the samples in the temperature range 430–450°C to the development of the porous structure of the samples due to the burning of vegetable oils, wax-like substances and waxes, as well as the achievement of pore sizes commensurate with the molecules of the oil constituents.

The samples TMKS$_{430}$, TMKS$_{450}$, TMKS$_{470}$ were taken to identify the dependence of the cleaning efficiency of model solutions on the conditions of temperature modification of the material. Studies were performed on model emulsions "water-oil" with concentrations of 50.0; 100.0; 250.0 mg / dm³.

The results are presented in figure 3. A purification emulsion with high efficiency up to 86-97% is carried out using samples TMKS$_{430}$, TMKS$_{450}$, TMKS$_{470}$. The use of the hydrophilic sample TMKS$_{500}$ reduces the efficiency of the cleaning process by an average of 9.5 times.
Figure 3. Evaluation of the effectiveness of purification oil emulsions.

An important factor in the practice of sewage treatment is the establishment of an effective amount of material necessary for the removal of pollutants. The samples TMKS_{450} and TMKS_{470} were used for researching as they showed high efficiency in the purification of model oil emulsions. Both model emulsions and sewage from the Belgorod airport were purified. In the experiment, we varied the concentrations of emulsions and the masses of weighed samples of TMKS_{450} and TMKS_{470}. The volume of purified media was constant. The results of experiment are presented in figure 4.

Obviously, an increase in the mass of the added TMKS more than 1.0 g/dm³ does not lead to a significant increase in the purification efficiency and is not cost-effective.

Figure 4. The effect of mass TMKS on the purification efficiency of oil emulsions.

Another factor determining the purification efficiency is the time indicator, i.e., the duration of contact of the reacting components (figure 5). In the experiment, TMKS_{470} was used in an amount of 1.0 g per 1.0 dm³ of the emulsion being purified.

According to the results the process of purification model emulsions using TMKS_{470} occurs within 15 minutes. The increase in the contact time of the components of the emulsion and TMKS does not lead to a significant increase in the efficiency of purification and does not exceed 92-98%.
Figure 5. The dependence of the purification efficiency of emulsions on the duration of mixing.

The established parameters were used for sewage treatment at the Belgorod airport with an oil content of 136.2 mg / l (table 1). As a result of purification an efficiency indicator of 90% was achieved.

Table 1. Own chemical analysis data.

| Indicator                              | Indicator value | MPC of waters |
|----------------------------------------|-----------------|----------------|
| pH                                     | 7,5             | 6,5-8,5        |
| Suspended substances, [mg / m³]        | 0,02            | 0,75           |
| COD, [mg O / dm³]                      | 152,5           | 30,0           |
| Oil products, [mg / dm³]               | 136,2           | 0,3            |

4. Conclusion

It is shown that to ensure energy and resource conservation, the use of industrial wastes in sewage treatment from oil and oil products is relevant;

The main purification mechanism is probably the interaction of the hydrophobic surfaces of the carbon-containing sorbent and drops of emulsified oil. The purification process is based on the retention of oil molecules in the pores and on the surface of the sorbent.

It was found that the maximum purification efficiency of model solutions with a concentration of 50, 100 and 250 mg / l and the analyzed sewage from the territory of the Belgorod airport is achieved with the addition of 1 g TMS470, and reaches 92-98%.

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Acknowledgments.
The article was prepared within development program of the Flagship Regional University on the basis of Belgorod State Technological University named after V.G. Shoukhov, using equipment of High Technology Center at BSTU named after V.G. Shoukhov.