

The processing of kieselguhr sludge with obtaining a new end product as reserve for reducing resources consumption of vegetable oil manufacture

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Abstract. The article presents the research findings of processing kieselguhr sludge – a waste product of refined sunflower oil production, generated at winterization stage, when vegetable waxes, waxlike substances and other components, which crystallize at low temperatures and cause the oil turbidity, are removed. The resulting waste product is a sludge stock of organo-mineral composition with organic matter content 65-70%. This sludge is virtually not recycled, but dumped at municipal solid waste disposal sites. This results in the environment pollution and non-recoverable losses of high-quality mineral stock and valuable organic components. It has been determined that after thermal modification of sludge waste the organic substances in it are partially oxidized with the formation of carbon layer on the surface of diatomite particles. The resulting product is a thermally modified kieselguhr sludge, which is characterized with mesoporous structure, high water repellency, and oil-receptivity and can be used as an adsorption material for purifying wastewaters from emulsified petroleum products in dynamic conditions. The secondary use of kieselguhr sludge would allow reducing the amounts of waste accumulation and improving the efficiency of raw material resources utilization.

1. Introduction

Vegetable oil extraction is one of the most intensively developing branches of food industry. There are four major producers of vegetable oil in the world market - Ukraine, Russia, European Union and Argentina, which account for about 70% of the global oil production. In the structure of global vegetable oil production the palm oil prevails - 38%, while the soya oil ranks second in popularity, its share amounting to 33% in 2016. The sunflower and colseed oils, produced mostly in the countries of the Eurasian Economic Union (EAEU), make up 10 and 16% of the global production, respectively (figure 1).

The vegetable oil market in the Russian Federation has its own pronounced specifics: the largest share of production and consumption accounts for sunflower oil. In 2016 the amount of its production was 3.8 mln tons. To obtain the high-quality cooking oils they are refined – i.e. purified from related substances, mechanical impurities, phosphatides, vegetable waxes, waxlike substances and other components [1-3], which crystallize at low temperatures and cause the oil turbidity.

Refining means a complicated multi-stage process, which consists of such individual operations as hydration, neutralization, bleaching, winterization and deodorization. Waxes and waxlike substances are removed by means of low-temperature fractionation method, which is called winterization or freezing-out.



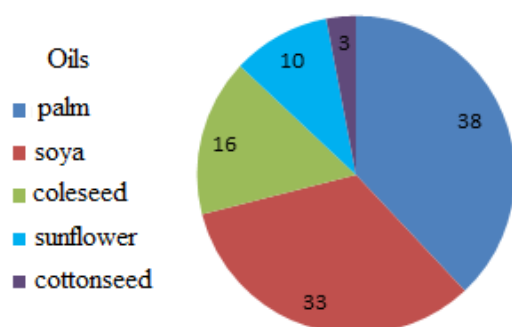


Figure 1. Global vegetable oil production structure in 2016, %

This method consists in the slow cooling of oil to the waxes' crystallization temperature (8-12°C) and exposure to this temperature with the subsequent filtration [3].

Then the organic impurities are removed in pre-coat filtration systems, in which as a filtering element the natural sorption materials are used – kieselguhr, perlite, bleaching clay and others. The sorption materials consumption makes up from 0.1 to 1% of the weight of the oil. As a result, the refined oil is obtained and the waste products are formed, which are called paste-like filter masses or waste sludges.

Together with the extracted impurities, a certain amount of oil is also removed at filtering. The total content of organic impurities in waste sludge can amount to 70%, and the waxlike impurities can make up from 1.5 to 12% depending on the properties of the vegetable oil to be refined. The wax content in the raw sunflower oil depends on the species and varieties of the oil-bearing crop, as well as on the location of the growing area, temperature and oil treatment technology, and can vary from 0.02 to 0.35% [4, 5]. After refining, the content of waxes and waxlike substances is reduced to 0–0.06% [6-8].

Unfortunately, the amounts of generated filter masses at oil-extraction industry enterprises are virtually not accounted by statistics. But, bearing in mind that the average yield of waste sludge can reach 150 kg per 1 ton of refined oil [9], we can calculate the volume of such waste generation at this or that enterprise (table 1).

Table 1. Approximate volume of filter masses generation at some fat-and-oil enterprises of the Russian Federation.

Enterprise	Oil production, mln tons per year	Filter masses formation volume, thousand tons per year
J-SC «Aston»	3.3	490
GC «Sodruzhestvo»	2.9	420
GC «Yug Rusi»	2.8	400
LLC «Solnechnye producty»	1.6	240

The «EFKO» company alone, which ranks second in the Russian Federation in terms of sunflower seeds processing, produces 500 tons of sunflower oil a day, and, consequently, generates up to 70 tons of waste kieselguhr sludge a day.

Filter masses, according to waste classification catalogue, belong to low-hazardous wastes (hazard category 4), which allows the enterprises dumping them at municipal solid waste disposal sites. This results in considerable non-recoverable losses of high-quality mineral stock and valuable organic components.

The problem of rational utilization of oil-extraction industry waste sludges has been paid great attention. They are known to be used as fat components, minor-nutrient elements and biologically active substances in mixed feed formulas for laying hens, as added fat in raising broiler chickens and cattle milking herds [10]. This helps increasing the productivity of animals by 10-20%.

There are technologies of extracting from the waste filter masses vegetable waxes and oils, which can be used for drying oil production. By using saponification method of waste sludge, the bar soap and soapy pastes were obtained [11]. Filter masses are known to be used as vulcanization activators in industrial rubber goods production technologies [12]. In Europe the oil-extraction industry waste sludges, due to their high energy content, are used as alternative sources of energy instead of the costly hydrocarbon fuel at brick and cement factories. A water-repellent emulsion for protecting construction products and structures from adverse external factors etc. can be also obtained from this waste [13].

There is a method of extracting vegetable wax from the waste sludge [14]. The greater part of oil (up to 80%), contained in the sludge, is removed by water-and-soap solution treatment with the subsequent centrifuging, and the wax particles are extracted with a solvent. The pureness of the obtained wax amounts to 96%.

The oil-contaminated diatomite is known to be used together with galvanic sludge and glass scrap in ceramic materials production [15]. It has been demonstrated that the obtained samples of ceramic bricks have the adequate compressive strength, low water adsorption and no heavy metal leaching, which determines the economic attractiveness of such materials.

The usage of oil-extraction industry waste kieselguhr sludge as a sorption material for removing various pollutants from wastewater is not given much coverage in literature. Chinese scientists have carried out research concerning the usage of waste diatomite as a sorption material for removing herbicides and dyestuffs from water media [16, 17], but they considered the diatomite waste of wine-making industry.

But the above-mentioned variants of using waste sludge don't solve the problem of recycling the whole amount of the generated waste. Besides, it should be taken into account that the permanent storage of filter masses, having high specific surface and organic matter content, at the open area can result in the intensive biodeterioration of impurities, oxidation of hydrocarbonic components with the formation of highly-toxic compounds, or spontaneous combustion of waste and the occurrence of fire-hazardous and explosion-hazardous situations at disposal sites.

Taking into account the growing rates of oil-bearing crops processing and the increasing amounts of vegetable oil, especially sunflower oil, production, the generation and accumulation of sludge wastes is going to increase. This circumstance makes it necessary to rapidly recycle such wastes. So, searching for the new areas of refined vegetable oil production waste filter masses utilization is a crucial task.

The purpose of this work is obtaining on the basis of refined oil production waste sludge a new end product – a carbonaceous sorption material to use it in industrial wastewater purification from petroleum products.

2. Materials and Methods

As an object of research the oil extraction industry waste kieselguhr sludge (WKS) of the «EFKO» plant, Alekseevka city, Belgorod region, Russia, was used. Waste kieselguhr sludge is a dingy-white slow stock with organic impurities content up to 70%. The mineral part of the sludge is represented with diatomite – sedimentary rock, formed by siliciferous frustules of microphytic diatomic algae – diatoms and radiolarians. The main component of the siliciferous frustule (skeleton) is presented with amorphous siliceous hydrates of various hydration degree – opal varieties of the type $m\text{SiO}_2 \cdot n\text{H}_2\text{O}$; the crystalline component is presented with quartz impurities.

The chemical composition is characterized with the following oxides content, wt. %: CaO – 5.85, Na_2O_3 – 2.9, Al_2O_3 – 2.4, Fe_2O_3 – 0.89, MgO – 0.54, K_2O – 0.36, TiO_2 – 0.14, P_2O_5 – 0.13, SO_3 – 0.06.

The thermal modification of WKS was carried out in an electrical furnace SNO 25/12 within 1 hour, in conditions of low oxygen.

3. Results and Discussion

The research findings, presented in the earlier work, have demonstrated [18], that at the heat treatment of WKS at temperatures from 430 to 600°C within 1 hour in conditions of low oxygen the organic im-

purities are partially oxidized, with the formation of soot-graphite compositions on the surface of the principal mineral – diatomite – and the generation of a new product – the carbonaceous thermally-modified kieselguhr sludge (TKS). The obtained material has shown high efficiency of extracting heavy metal ions from wastewaters.

This paper considers the possibility of using TKS for removing emulsified petroleum products from wastewaters. It should be mentioned that the heat treatment changes the color of the end product – from brownish gray (at 430°C) through black (at 450-550°C) to dingy white (at 600°C and more). The color of the obtained TKS correlates with the carbon content, forming on the surface of kieselguhr (diatomite) particles (figure 2), and water adsorption of the formed surface (table 2).

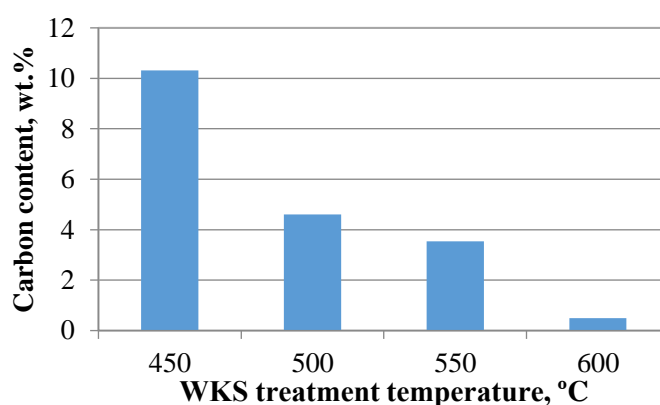


Figure 2. The influence of WKS treatment temperature on the carbon content in TKS.

Table 2. Water adsorption of TKS, obtained at various temperatures.

Parameter	Measuring unit	WKS modification temperature, °C				
		Initial	450	500	550	600
Water adsorption	g/g	0.7	2.0	12.2	21.6	24.2

The highest carbon content – 10.31% is formed at temperature 450°C, which provides the lowest water adsorption. Increasing the temperature up to 600°C results in the disrupting of carbon – it is oxidized to CO₂ and its content is reduced to the lowest value – 0.49% (figure 2). As a result, the hydrophilic properties of the obtained material are increased – water adsorption reaches 24.2 %.

Further on, analyzing the influence of WKS heat treatment on the chemical nature of the resulting products' surface was of interest. The qualitative analysis of functional groups was carried out by means of infrared spectroscopy, and the quantitative analysis – by means of selective neutralization according to [19-21]. The infrared spectra of WKS, treated at temperatures 450 and 500°C and designated TKS₄₅₀ and TKS₅₀₀, respectively, are presented in figure 3. At the infrared spectra the bands with high intensity at 471, 791 and 1088-1092 cm⁻¹ are registered, which can refer to siloxane groups of Si-O-Si type, which is in agreement with natural diatomite research findings [3].

The absorption bands are found, which can refer to phosphates (1000-1100 cm⁻¹), and to C-OH groups [22]. The band at 791 cm⁻¹ can be associated with valence vibrations vs(Al-O) of clay impurity minerals, contained in diatomite. The high-intensity bands at 2926, 2853 cm⁻¹, which corresponds to the range (2850 – 3000 cm⁻¹), can refer to valence vibrations, and the medium-intensity band at 1470 cm⁻¹ – to bending vibrations of methylene groups, characterizing the presence of Csp³-H bond on the carbonaceous surface of TKS₄₅₀. With the increase of the treatment temperature up to 500°C their intensity goes down to zero, which indicates the burning-out of the surface carbon forms, containing fragments of C-H.

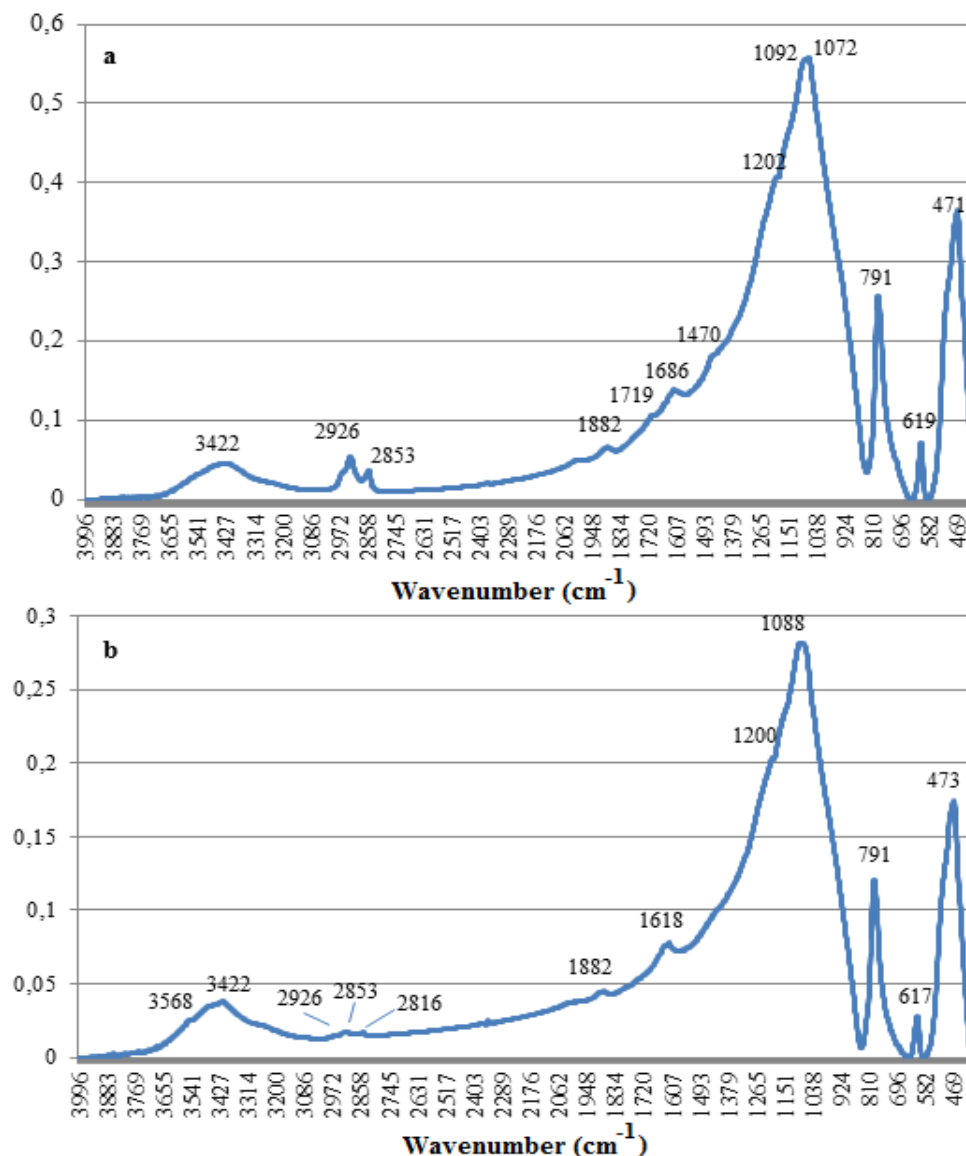


Figure 3. Infrared spectra of carbonaceous materials - TKS₄₅₀ (a) and TKS₅₀₀ (b).

The valence vibrations at 1719 cm⁻¹ characterize the C=O bonds in compound ethers, contained in vegetable waxes and waxlike substances [23, 24], which provides TKS₄₅₀ with high surface hydrophobicity – water adsorption is no more than 2% (table 2). In figure 4 we can see that at applying water on the surface of the compacted material a sitting drop is formed, while petroleum soaks in. So, the material has oleophilic properties.

Increasing the kieselguhr sludge modification temperature up to 500°C results in decomposition of waxlike substances, which influences the infrared spectrum – the valence vibrations in the range 1700-1750 cm⁻¹ are not registered, and the hydrophobicity degree of TKS₅₀₀ particles surface is reduced – water adsorption amounts to 12.2% (table 2).

The infrared spectrum range 3100-3700 cm⁻¹ characterizes the valence vibrations of various types of hydroxyl groups, including those in the water molecules, adsorbed on hydroxyl groups. The band 3422 cm⁻¹ can probably refer to both C-O-H groups, and to silanol groups Si-O-H [22], which can effectively bind heavy metals by the ion exchange mechanism [21].



Figure 4. Interaction of the compacted TKS₄₅₀ layer with petroleum (a) and water (b).

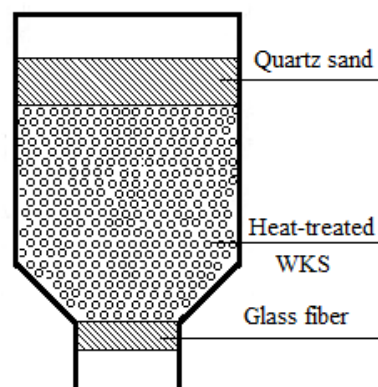


Figure 5. Scheme of the filtration plant.

The quantity of functional groups was studied by the Boehm method [19]; the results are presented in table 3.

Table 3. Functional groups content on the surface of TKS, obtained at various temperatures (10^{-3} mg eq/g).

Temperature of WKS treatment (°C)	Carboxyl groups	Total carboxyl and lactonic groups	Lactonic groups	Total carboxyl, lactonic and hydroxyl groups	Hydroxyl groups
450	4.967	7.336	2.369	8.775	1.439
500	0.503	1.147	0.644	3.477	2.330

Low concentrations of functional groups are typical for activated coals and determine the similarity of the carbonic part of sorption materials, obtained at temperatures 450 and 500°C, with activated coals.

So, the carried-out research of the chemical composition of the obtained carbonaceous materials, based on waste kieselguhr sludge, indicates the presence of carbon and various functional groups on the particles surface. Such materials, having adsorption centers of various natures, would exhibit activity to both polar and nonpolar substances.

Then the possibility of using the obtained carbonaceous materials TKS₄₅₀ and TKS₅₀₀ as sorbents for extracting nonpolar substances – emulsified petroleum products – from wastewaters was analyzed. The sorption properties of TKS₄₅₀ and TKS₅₀₀ to petroleum products were studied in dynamic conditions by filtering model emulsions through a stationary bed of a sorbing agent. For this purpose a filtration plant was prepared, the scheme of which is presented in figure 5.

Sand and adsorbents were placed in a column 30 mm in diameter; the lower layer of the absorption material was 40 mm thick, and the upper sand layer - 2 mm thick. The necessity of using sand as a weight is explained by the high buoyancy of the sorbents under study. The sand was preliminarily washed in distilled water and tempered in muffle furnace at temperature 500°C within 3 hours. The absorption materials - TKS₄₅₀ and TKS₅₀₀ were used in fractions 0.63-1 mm.

As a model wastewater, the petroleum products emulsion with concentration 15 mg/dm³ was prepared, by mixing a precisely weighed quantity of industrial oil I-20A with density 0.818 g/dm³ and the distilled water within 48 hours.

The flow of model wastewater in the filter was performed from top downward with throughput rate 2.5 cm³ per min.

The efficiency of model wastewater purification from emulsified petroleum products was evaluated by the alteration of emulsions turbidity.

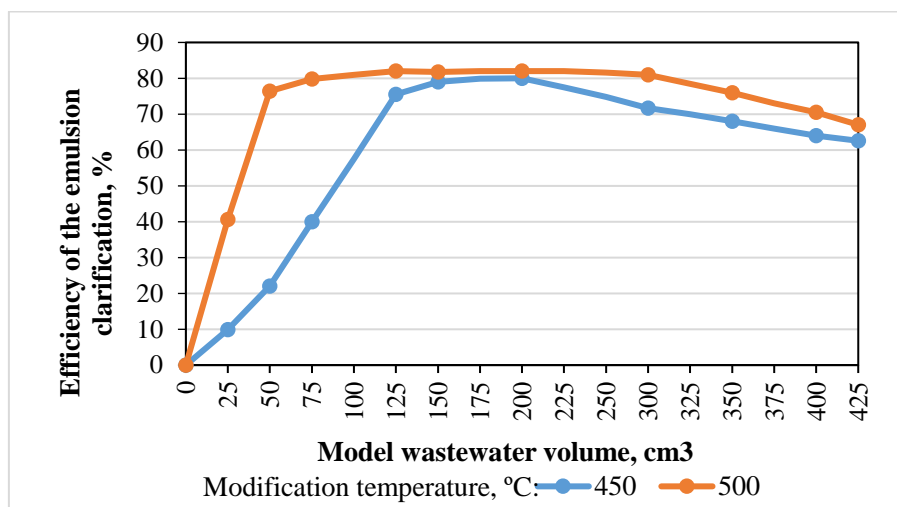


Figure 6. The influence of WKS modification temperature on the efficiency of extracting emulsified petroleum products in dynamic conditions.

The research findings, presented in figure 6, have shown that the temperature of WKS modification has no substantial impact on the maximum efficiency of extracting emulsified petroleum products. This characteristic amounted to 80% and 82% for TKS₄₅₀ and TKS₅₀₀, respectively. But when using TKS₅₀₀ the adsorption filter reaches its efficient mode after the throughput of 75 ml of model wastewater, and when using TKS₄₅₀ the high purification efficiency (79%) is reached after wastewater throughput in amount of 150 ml.

So, the thermally-modified oil-extraction industry waste kieselguhr sludge can be used as a carbon-containing sorbent for wastewater purification from petroleum and petroleum products in dynamic conditions. The highest sorption properties to emulsified petroleum products are demonstrated by the materials, obtained at temperatures 450 and 500°C, designated TKS₄₅₀ and TKS₅₀₀, respectively.

The secondary use of kieselguhr sludge would allow reducing the amounts of waste accumulation, decreasing the anthropogenic load on the environment and improving the efficiency of raw material resources utilization.

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