

USE OF CLAYS AS ADSORBENTS FOR BLEACHING USED MOTOR OILS

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Abstract

This article examines current environmental issues related to the disposal and regeneration of used motor oils. Modern motor oils are alloyed lubricants, typically containing several alloying additives that significantly improve the performance properties of the resulting motor oils. During use, motor oils undergo degradation processes as a result of thermochemical reactions, which lead to oil aging and a decrease in its quality. The processes occurring in oils can be divided into thermal transformations, oxidation, and sedimentation. Изменения состава масла обусловлены окислением, термическими превращениями и потерей коллоидной стабильности. As a result, used oils contain numerous undesirable impurities, including asphaltene-resinous and organometallic components. Therefore, when regenerating used motor oils, it is necessary to bleach the used oils using appropriate adsorbents. The paper presents the results of scientific research on the feasibility of using new adsorbents obtained from local mineral resources in the bleaching and purification of used motor oils. The study examined the physicochemical and adsorption properties of natural mineral deposits. Turkestan Region, and conducted scientific experiments on the regeneration of waste oils using natural minerals. The results demonstrated the potential and economic feasibility of using clays from Turkestan Region deposits for bleaching waste motor oils.

Based on a study of the chemical composition of local clays, the authors showed that the high content of aluminosilicates – silicon oxides (up to 58.4%) and aluminum (up to 16.03%) – is an indicator of their high adsorption activity. It has been established that local clays are valuable raw materials for use after appropriate processing for adsorption purification of mineral oil and can be an alternative to imported bleaching clays.

Keywords: Used motor oils, clays, adsorbents, natural minerals, base oil, tar, recycling, regeneration.

Introduction

The problem of used motor oil processing is highly relevant for our republic, considering the annual growth in the number of motor vehicles, especially in megacities. The disposal and processing of used motor oil is not only a reduction in environmental pollution volumes, but also a decrease in the consumption of primary resources and energy. In practice, when changing engine oil in automobiles, large volumes of used motor oil accumulate at service stations, which must be collected for disposal or processing and reuse. Modern motor oils are alloyed lubricating materials. They necessarily contain several alloying additives - supplements that



significantly improve the properties of the oil or give it completely new, extremely necessary properties. The base of motor oil consists of base oil, which is obtained from processing residues of atmospheric oil refining, the so-called fractions that boil at temperatures above 350°C. During vacuum distillation of fuel oil, oil distillates are obtained, which form the basis of base oil, which after appropriate selective purification and dewaxing can be used as commercial oil. During the operation of an internal combustion engine, qualitative changes occur in motor oil - aging, due to its operation under conditions of high thermal and dynamic loads. This is accompanied by factors that cause deep physicochemical changes in material properties and deterioration of their operational indicators. Despite obvious successes and improvements in modern methods of used oil regeneration, a significant problem remains the high cost of the process. Until now, very often used motor and transmission oils that remained during replacement in engines and units of automobiles, tractors, and ships were often drained into special storage facilities. Used motor and industrial oils, as a rule, do not meet established standards for flash point temperature. Mainly they are accepted as mixtures of used petroleum products at a price 4 times lower than the price of furnace fuel. It is known that about half of the lubricating oils used are irretrievably lost during operation, that is, evaporates, burns in internal combustion engines, spills, etc. The remaining oil is subject to changes (temperature and others) during operation and subject to replacement [1]. It should be noted that according to the Law of the Republic of Kazakhstan of 2016 "On Amendments and Additions to Certain Legislative Acts of the Republic of Kazakhstan" on issues of the country's transition to a "green economy," amendments were made to the Environmental Code of the Republic of Kazakhstan, providing for a ban on the burial of used motor and other oils [2,3]. During the operation of motor oils, various oxidation products, contaminants, and other impurities accumulate in them, which sharply reduce the quality of oils. During regeneration, used oils are collected and subjected to regeneration in order to save significant raw materials, which is economically interesting. Per year, about 530,000 tons of oils are collected on the territory of the Republic of Kazakhstan, only about 12-14% are processed. Depending on the regeneration process, 2-3 fractions of base oils are obtained, from which commercial oils (motor, transmission, hydraulic, plastic lubricants) can be prepared by compounding and introducing additives. The average yield of regenerated oil from used oil containing about 2-4% solid contaminants and water, up to 10% fuel, is 70-85% depending on the regeneration method used [4]. Various technological processes based on physical, physicochemical, and chemical patterns are used to restore used oils and consist of cleaning the oil in order to remove aging and contamination products from it. Natural substances (bleaching clays, bauxites, natural zeolites) and artificially obtained substances (silica gel, aluminum oxide, aluminosilicate compounds, synthetic zeolites) are used as adsorbents [1,2]. Let us recall that regeneration is the comprehensive processing of used oil in order to remove undesirable components from the oil, in particular, with the removal of asphaltenes and resins, petroleum acids, coke, etc. from the oil. Regeneration involves, in addition to physical, chemical, adsorption, combined, and other purification methods. The main purification of used oil occurs during physical purification. Among the accompanying substances removed at the adsorption refining stage are pigments. The nature and structure of coloring substances in mineral oils are different, however, they all have a certain degree of



polarity, therefore, polar adsorbents with sufficient selectivity and activity are usually used for adsorption refining of oils. For this purpose, special adsorbents are used - activated bleaching earths, traditionally obtained from natural bentonite earths (aluminosilicates), activated by mineral acids, less often - activated carbons [1,5,6].

Adsorbents used for oil purification must meet the following requirements: have high adsorption capacity and activity so that with a smaller amount of adsorbent, a high effect can be achieved during bleaching; have a developed surface (porosity) and a significant number of active centers; have low oil capacity (the amount of oil, in percent, retained by the adsorbent); not enter into chemical interaction with acids and phenols of oils; easily separate from oil by filtration, have a high filtration rate; not impart foreign smell and taste to the oil. One of the stages of obtaining oils is adsorption purification of oils, which is based on the ability of adsorbents to selectively extract resinous and sulfur compounds, unsaturated and polycyclic aromatic hydrocarbons, as well as organic acids, residues of sulfuric acid solvents from oil. As a result of purification, the color of the oil, its stability, viscosity index, and coking ability improve. Natural clays (bleaching earths) are used as adsorbents in oil purification, as in fuel purification [7]. One of the main indicators of oil quality is the viscosity index, a very important parameter by which one can preliminarily assess the quality of the resulting base oil. Another important indicator evaluating the quality of purification is the clarification of used motor oils. Oil bleaching is the process of interaction of adsorbents with oil, as a result of which the oil is clarified by removing substances that give the oil a dark color. Clarification (bleaching) of motor oils is one of the most important stages of used oil regeneration, and oil clarification technologies should maximally meet the requirements of resource and energy saving, as well as environmental safety. One effective method of bleaching and purification from mechanical impurities and water is filtration. It allows the removal of mechanical impurities and resinous compounds by passing used oil through partitions of special filters. In order to improve the quality of purification, multi-stage filtration (coarse and fine) can be used [8-10]. Currently, Kazakhstan's need for lubricating oils is increasing due to increasing needs for them in transport communications and energy facilities, therefore, an increase in demand for lubricating materials is expected. It should be said that Kazakhstani lubricating oil manufacturers cover only 30% of the market; all the rest of their consumed volume is imported from abroad (Russia, Germany, Korea, China, Japan, etc.), moreover, with large costs for acquisition and transportation. It should be noted that Kazakhstan has unique raw materials for the production of mineral oils, which include: Mangyshlak, Uzen, Zhetybai, Kumkol oils, characterized by high potential oil and paraffin content [11]. The problem of increasing waste petroleum products from motor transport and used motor oil is relevant for the country. Disposal and processing of used petroleum products is not only a reduction in environmental pollution, but also a reduction in the consumption of primary resources and energy. On the one hand, certain costs are required for the extraction and processing of crude oil, and in practice, used motor oil accumulates at enterprises. For example, to produce 1 liter of new high-quality lubricating oil requires 67.2 liters of crude oil and only 1.6 liters of used oil. Modern motor oils are alloyed lubricating materials. They necessarily contain several alloying additives - supplements that significantly improve the properties of the oil base or give it completely new, extremely necessary properties.



During engine operation, qualitative changes occur in motor oil - aging, due to its operation, which occurs under conditions of high thermal and dynamic loads and is accompanied by factors that cause deep physicochemical changes in material properties and deterioration of their operational indicators. As a result, at a certain point in time, the quality indicators of the oil go beyond the limits of tolerances, contamination with dust, wear products, fuel combustion products occurs, and depending on the temperature, sludges, varnishes, and carbon deposits are formed, leading to complete oil replacement in the oil system [12,13]. According to GOST 6370-2018, used petroleum products can be used as follows: motor oils - as raw materials for regeneration; industrial oils - as raw materials for regeneration and purification; mixtures of petroleum products - as petroleum flushing fluids, oils for heat treatment of metals, cylinder, transmission; oil and liquid petroleum fuels extracted from treatment facilities - for processing at refineries mixed with oil and as a component of boiler fuel. It is known that if used oils are used as a fuel component, economic efficiency increases on average by an order of magnitude. Existing mini-installations for processing used oils, whose action is based on thermal cracking and distillation processes, transform "waste" into full-fledged furnace fuel, diesel fuel, as well as coke, bitumen, etc. [14]. **The purpose of this work** is to investigate the possibility of obtaining adsorbents from a mixture of various minerals from Kazakhstan deposits, which will allow the development of technology for regeneration of used motor oils using activated sorbents. The authors carried out the selection and activation of clay samples from the Turkestan region in order to establish the possibility of their use as sorbents for bleaching base oil. **Clay samples for activation:** bentonite clay; white kaolin clay (Saryagash, Darbaza); Yellow clay (Badam). Activation of clay for processing used motor oil was carried out in accordance with the requirements of GOST 21046 - 2021. Used oils contain many undesirable components: asphalt-resinous components and additives, organometallic components in the form of rust inhibitors, antioxidants, detergent-dispersing and antifoam substances, polymeric synthetic depressants, and substances that increase the viscosity index. Used oils also contain lead, iron, calcium, phosphorus, sulfur, zinc, etc. Also, as a result of the operation of an internal combustion engine, the formation of soot, coke (carbon deposits), varnish, and sludge is observed in oils. In addition to the formation of deposits during engine operation, an increase in the thickness and viscosity of the oil is possible, due to the polymerization of oxygen-saturated products and the presence in the oil of insoluble products of incomplete fuel combustion. Such features of the composition and structure of used oils pose the most important task of selecting adsorbents during oil regeneration, because it is of great importance to preserve the base of the oil and the active part of the additives. Previously, we conducted research work to study the adsorption activity of the proposed minerals from Kazakhstan deposits when bleaching used motor oils, and determined the chemical composition, physicochemical, and structural-sorption properties of adsorbents [15,16]. To study the possibilities of using local mineral raw materials, several samples of bleaching clay extracted from deposits in the Turkestan region were investigated. Table 1 shows the chemical compositions of the studied clay samples.



Table 1 - Chemical composition of clay samples from deposits in the Turkestan region, %

Name	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	CO ₂	P ₂ O ₅
Bentonite clay, Saryagash	57,28	16,03	6,25	0,11	0,18	1,25	0,28	1,57	2,07	0,18	0,14
White kaolin clay, Darbaza	58,4	15,5	3,54	0,30	2,40	1,45	1,12	2,08	1,39	0,03	0,04
Yellow clay, Badam	51,4	12,3	4,03	0,28	2,03	1,52	0,75	1,87	1,53	0,07	0,06

Studies of the chemical composition of clays showed high content of aluminosilicates – silicon oxides (up to 58.4%) and aluminum (up to 16.03%), which is an indicator of their high adsorption activity. IR spectra of initial and activated clays were obtained using a Shimadzu IRPrestige-21 Fourier Transform IR spectrometer equipped with an attenuated total reflectance (ATR) Miracle attachment from Pike Technologies.

Data from IR spectral analysis of the studied clay samples (before activation) are shown in Figures 1 and 2. For spectroscopic studies, clay samples were ground and dried at a temperature of 75-80°C to constant weight. Key Technical Terms Translation:

This passage describes the analytical methodology used to characterize the clay samples through infrared spectroscopy, which is a standard technique for identifying the molecular structure and functional groups present in the materials. Claude is AI and can make mistakes. Please double-check responses. Sonnet 4.5

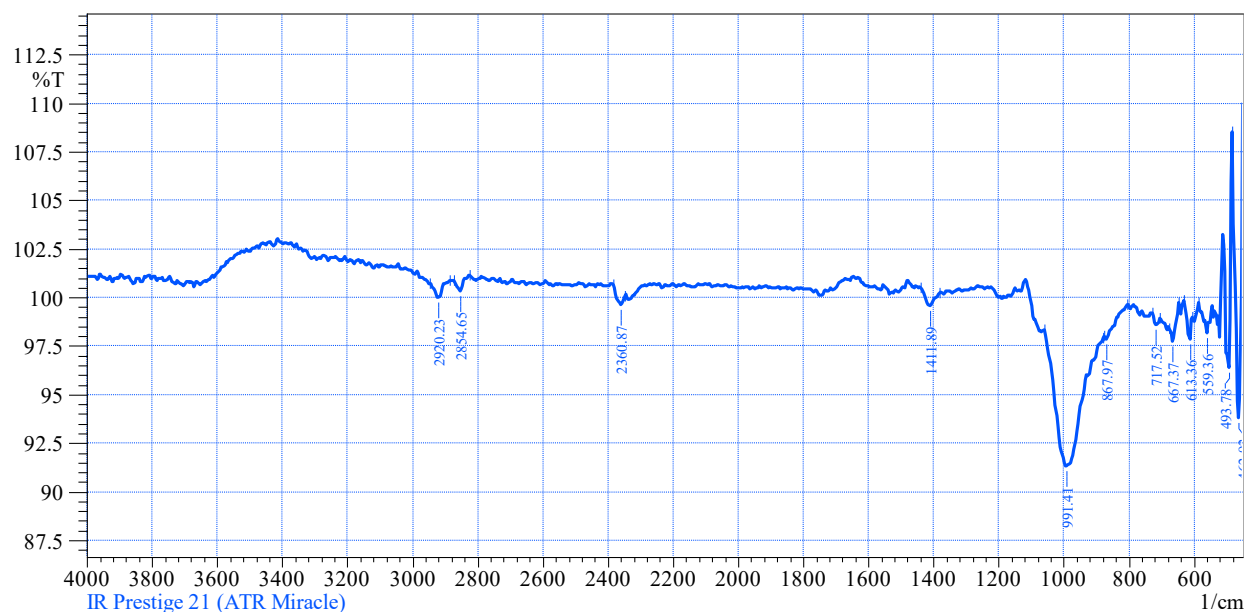


Figure 1. - IR spectra of activated bentonite clay (Saryagash).

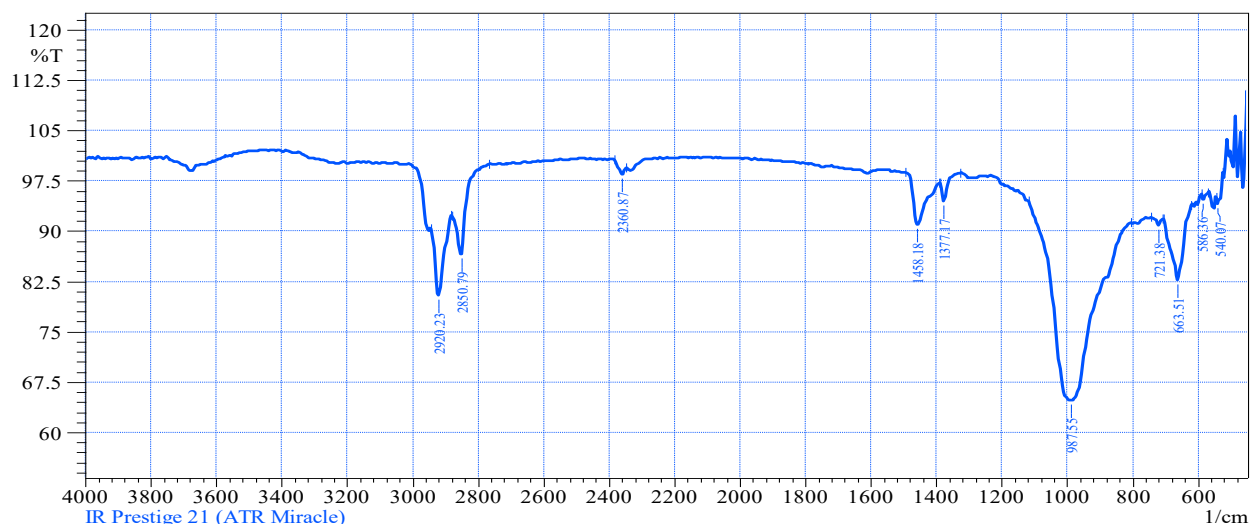


Figure 2. - IR spectra of activated white clay kaolin (Darbaza).

In the presented IR spectra, there are differences between samples that confirm the presence of amorphous silica. Peaks (around 1000 cm^{-1}) suggest a crystalline structure of the samples along with an amorphous component related to stretching vibrations of Si-O silicates. In the region of $3000\text{-}4000\text{ cm}^{-1}$, there are bands of stretching vibrations of hydroxyl groups associated with octahedral cations, as well as H_2O molecules associated by strong hydrogen bonds. The second region of $1800\text{-}800\text{ cm}^{-1}$ reveals the silicate structure. Due to the fact that the tested clay samples are layered silicates, when ions exit from the crystal lattice structure and cavities between layers, pore enlargement occurs. And as a consequence of this process, there is an increase in the number of acidic centers, and therefore an increase in sorption volume. Therefore, the studied clays exhibit high adsorption activity.

Preliminary tests showed the regenerating effects of the presented clays during regeneration of used oils in terms of the basic physical and colloidal properties of the obtained oils.

We used bleaching clays of 4 samples as adsorbents. By selecting adsorbents with pores of a certain size, it is possible to carry out selective adsorption of certain compounds of asphaltene and resinous substances, alkenes, and polycyclic arenes. From such purification, the oil becomes lighter, therefore this process is called oil clarification. Laboratory studies showed that optimal yield of clarified oil was obtained at a sorbent layer height of 5.8 cm. Further increase in layer height led to insignificant improvement in yield, while at levels less than 3.5 cm, yield decreased significantly.

At HILL Corporation LLP, regeneration of used oils is carried out on a modern installation, whose equipment and technology supplier is the German company FLUID SOLUTIONS. Dehydrated used oils are fed to the Plasma Tube Reaktor (PTR) installation, where under deep vacuum and temperature up to 600°C , oil fractions are obtained by distillation (40 in total), as well as bottom residue. The most in-demand and valuable products are fractions 1 and 2 (if necessary - fraction 3). These fractions differ from each other in kinematic viscosity and are filtered separately, resulting in base oils N80, 150, 240, and others.

For clarification (bleaching) of these fractions, Spanish-manufactured bleaching clay is used for contact purification on filters. To study the possibilities of using local mineral raw materials,

several samples of bleaching clay extracted from quarries of Kazakhstan deposits were studied. Studies were conducted in the accredited testing laboratory of HILL Corporation LLP to determine the bleaching capacity of oil fractions by clays from local quarries. The testing process consisted of the following stages:

To 500 g of fraction 1, clay is added in the amount of 7%, i.e., 35 g.

The mass is thoroughly mixed and heated to 150-160°C.

The mass is filtered through a filter with selectivity of 1 µm.

The obtained filtrate is analyzed.

Test conditions: temperature 24.3°C, relative humidity 75%, pressure 93.3 kPa (Table 3)

Table 3 Test results using samples of various natural adsorbents

№	Indicator Name	Sample №1	Sample №2	Sample №3	Sample № 4
1	Kinematic Viscosity at 100°C, mm ² /sec	6,47	6,45	6,51	6,5
2	Kinematic Viscosity at 40°C, mm ² /sec	47	46,1	46,7	47
3	Viscosity Index	83	85	85	84
4	Mechanical Impurity Content, % (mass)	0,005	0,005	0,005	0,005
5	Open Cup Flash Point, °C	222	224	220	224
6	Density at 20°C, g/cm ³	0,866	0,866	0,866	0,866
7	Color, CNT units	3,9	2,4	3,3	1,9
8	Ester Content, %	0,07	0,08	0,09	0,11
9	Fatty Acid Content, %	0,23	0,17	0,20	0,18

Here's the English translation:

When testing the first sample (Sample #1) "Bentonite clay, Saryagash," clarification was observed from 6.5 units to 3.9 units. The next sample (#2) "White kaolin clay, Saryagash (Darbaza)" showed clarification of the first fraction from 6.5 units to 2.4 units. Sample #3 "Yellow clay (Badam)" showed that clarification of the first fraction was observed from 6.5 units to 3.3 units. And finally, sample #4, clay used at HILL Corporation LLP, manufactured in Spain, showed clarification of the first fraction from 6.5 units to 1.9 units.

According to the results of the conducted studies among the tested samples shown in Table 1, it can be seen that the main technical characteristics of oils, such as kinematic viscosity at 100°C and at 40°C, as well as viscosity index, after bleaching in all four samples are practically the same, but the best results are obtained when bleaching oil with sample #2, i.e., white kaolin clay from the Darbaza deposit (Saryagash).

Thus, studies on the possibility of using adsorbents from local raw materials according to the main technical indicators (viscosity and bleaching) of regenerated motor oils showed that the best result was obtained using "White kaolin clay." After testing, base oil was obtained that complies with regulatory documentation (base oil SN-350, with a color indicator up to 2.5

units). It is recommended to carry out measures to activate this clay to enhance adsorption properties. The use of this clay after appropriate activation in production conditions at HILL Corporation LLP can significantly affect the production cost and provide additional economic benefit.

Studies of the chemical composition of local clays showed high content of aluminosilicates - silicon oxides (up to 58.4%) and aluminum (up to 16.03%), which is an indicator of their high adsorption activity. We believe that local clays are valuable raw materials for their use after appropriate treatment for adsorption purification of mineral oil and can serve as an alternative to imported bleaching clays.

The white kaolin clay from Darbaza showed the most promising performance among local clays and represents a cost-effective alternative to imported bleaching clays.

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1. Here's the English translation of the references:

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