Study of the Sorption Processes of Petroleum Products in Wastewater using Natural and Modified Bentonite

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Abstract. This study investigates the sorption behaviour of petroleum products from wastewater using natural and modified bentonites, with comparative analysis against activated carbon. Sorption experiments were conducted under static and dynamic conditions using model and real wastewater samples with varying concentrations of petroleum contaminants. The kinetics of sorption revealed that the process reached equilibrium within 2.5–3 hours, and the maximum sorption capacity was directly proportional to pollutant concentration. Thermally, chemically, and thermochemically modified bentonites exhibited 1.5–3 times higher sorption efficiency compared to natural bentonite. Thermochemically modified bentonite demonstrated the highest sorption capacity (up to 5.67 mg/g). Thermal analysis confirmed structural stability up to 400°C, while IR spectroscopy indicated preservation of the mineral framework after modification. Additionally, the study evaluated the synergistic use of bentonite, kaolin, coagulants, and flocculants to improve wastewater treatment efficiency. Regression models describing the sorption dynamics were developed with high predictive accuracy (R2 > 90%). The results validate the suitability of Navbahor bentonite, particularly in modified forms, as a cost-effective and efficient sorbent for oil-contaminated wastewater treatment.

1 Introduction

Currently, great attention is paid worldwide to the development of low-waste or waste-free technologies, as well as energy- and resource-saving technologies. In solving these problems, the degree of purity of substances used in technological processes and obtained as a result plays an important role. The most important requirements for adsorption materials include: high specific surface area, selective activity, and ease of regeneration [1-2]. In addition, bentonite must be inexpensive and safe, not possess corrosive properties, maintain its adsorption characteristics over time, and have high mechanical strength. Among the sorbents used in adsorption processes, sorbents with acid resistance, heat resistance, and acidic properties occupy a special place. The main problem in the production of high-efficiency sorbents is the reduction of their cost and the simplification of the synthesis technology, which is a priority direction for extensive scientific research [3-4].

Study of Sorption Processes and Various Influencing Factors, as Well as the Establishment of Sorption Patterns and the Mechanism of Chemical Adsorption Occurring on the Sorbent Surface, Is Also of Great Importance. Based on the results obtained, it can be concluded that the use of Navbahor bentonite, considered a natural bentonite, as well as its thermally, chemically, and thermochemically modified samples as a highly selective sorbent for the purification of wastewater from petroleum products is advisable [5-6].

At oil refining enterprises, wastewater is generated that contains petroleum products, various cations and anions, suspended solids, and heavy metals.

The wastewater treatment technology implemented at most industrial enterprises provides for sedimentation to separate pollutants into sludge. This approach has a number of serious disadvantages:

– sedimentation partially solves the problem of removing suspended solids from wastewater, but cations and anions mostly remain in the wastewater. As a result, the content of harmful substances in water after treatment facilities can exceed the Maximum Permissible Concentration (MPC) by tens of times.

There are known methods to improve the quality of treated water at enterprises by adjusting the operation of treatment lines. However, it is not possible to improve water quality to MPC levels using such methods [7].

Previous studies have reported that the modification of natural clays and bentonites can substantially enhance their sorption properties. Thermal treatment increases surface area and pore accessibility, whereas acid treatment introduces new active sites and improves cation-exchange capacity [7-8]. Furthermore, combined thermo-chemical modification has been shown to yield synergistic effects, leading to even higher adsorption efficiencies for petroleum-derived contaminants [9]. Activated carbon, although widely applied, remains costly, which motivates the search for alternative, locally available sorbents [10 -11].

In this regard, the scientific and technical hypothesis of this report is to improve the technology of wastewater treatment from suspended solids, various

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cations and anions, as well as heavy metals using coagulants and flocculants.

2 Experimental Part

2.1 Materials and Reagents

Natural bentonite was sourced from the Navbahor deposit in Uzbekistan. Thermally modified bentonite was obtained by heat treatment at 400°C for 3 hours in a muffle furnace. Chemical modification was carried out by treating the bentonite with a 20% aqueous nitric acid (HNO_3) solution under continuous stirring at room temperature for 24 hours, followed by washing and drying. Thermochemical modification involved a sequential combination of the aforementioned thermal and chemical treatments. Commercial-grade activated carbon (BAU-A) was used as a reference sorbent. Analytical-grade reagents including aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$), ferric chloride ($FeCl_3 \cdot 6H_2O$), and sodium carboxymethyl cellulose (Na-CMC) were employed as coagulants and flocculants.

The choice of adsorbents was based on three main criteria: (I) local availability in Uzbekistan, which ensures practical applicability; (II) cost-effectiveness compared to commercial activated carbon; and (III) prior research evidence demonstrating promising sorption capacity for petroleum contaminants. On this basis, nine adsorbents were included in the study, encompassing both natural and modified bentonites, as well as reference materials such as kaolin and activated carbon.

Nine different adsorbents were selected for this study. The choice was guided by their local availability and cost-effectiveness, which makes them practical for large-scale wastewater treatment. Furthermore, the selection was supported by prior literature indicating their adsorption potential for petroleum-based contaminants.

2.2 Model Solution Preparation

Synthetic wastewater was prepared by dissolving petroleum products to achieve initial concentrations of 76 mg/L, 140 mg/L, and 265 mg/L, simulating wastewater effluent from various stages of oil refining. Three 500 mL samples were prepared for each concentration and treated with 10 g of sorbent (natural or modified) at pH 6 and a particle size of 0.5 mm.

2.3 Sorption Procedure

The prepared suspensions were stirred under static conditions for varying durations (2, 4, and 8 hours). Sorption kinetics were evaluated by sampling aliquots at defined intervals and determining residual petroleum content via gravimetric analysis in accordance with standard methodologies.

2.4 Coagulation-Flocculation Studies

For enhanced purification, combined treatments were conducted using bentonite or kaolin (2.0 g/L), aluminum sulfate or ferric chloride (0.5–0.75 g/L), and Na-CMC flocculant (0.15 g/L). Mixing was performed for 20 minutes, followed by sedimentation. Physicochemical parameters such as pH, suspended solids, chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), sulfates, and surfactants were monitored before and after treatment.

2.5 Characterization Techniques

The thermal stability of the sorbents was assessed by thermogravimetric analysis (TGA/DTG) using a derivatograph in the temperature range of 25–1000°C. Fourier-transform infrared (FTIR) spectroscopy was performed on both raw and modified bentonite samples to identify structural and functional group changes. Sorption capacities were statistically evaluated through regression modeling with R^2 values used to assess model reliability and predictive accuracy. Experiments were conducted on a Jar-test laboratory sorption and coagulation-flocculation apparatus (VELP Scientifica JLT6, Italy), operating at 200 rpm for rapid mixing and 40 rpm for slow mixing/sedimentation. Residual oil product content was determined gravimetrically in accordance with the APHA Standard for the Examination of Water and Wastewater (23rd edition, Method 5520B). Synthetic wastewater was prepared by dissolving oil products at concentrations of 76, 140, and 265 mg/L to simulate effluents from various treatment stages. Real wastewater samples were collected at the Bukhara Oil Refinery (Uzbekistan). OriginPro 2024 software (OriginLab Corp., USA) was used for regression modeling and statistical analysis.

3 Result and Discussion

3.1 Kinetics of Sorption Processes on Natural and Modified Bentonites

The purpose of this study is to investigate the processes of chemical treatment of highly mineralized wastewater from oil refining industries and to develop a technology for reducing their salinity to MPC levels using coagulants and flocculants.

To solve the stated tasks, theoretical and experimental studies were carried out on model solutions and real wastewater under laboratory conditions using standard methodologies and licensed software.

Currently, the most commonly used technology for the treatment of highly mineralized wastewater is based on coagulation and flocculation with adjustment of the pH to 7.0–7.5, followed by sedimentation.

Table 1. Physicochemical parameters of wastewater before and after treatment. Values are presented as mean ± SD (n = 3). One-way ANOVA confirmed significant differences between before- and after-treatment values ($p < 0.001$).

Indicator	Before Treatment (Mean ± SD)	After Treatment (Mean ± SD)	ANOVA (F, p)	MPC	Recycled Water Quality Req.
pH	8.72 ± 0.02	7.32 ± 0.05	F=1952.6, p<0.001	7.5	7.2
Suspended solids (mg/L)	317.13 ± 5.16	13.54 ± 0.29	F=10358.7, p<0.001	25.0	20.0
Degree of clarification (%)	–	89.16 ± 0.36	–	85.0	90.0
Sulphates (mg/L)	162.74 ± 2.02	7.14 ± 0.31	F=17321.3, p<0.001	8.2	7.5
Surfactants (mg/L)	66.27 ± 0.79	1.75 ± 0.06	F=19855.9, p<0.001	3.0	2.0
COD (mg/L)	215.31 ± 2.00	41.11 ± 1.28	F=16181.9, p<0.001	45.0	40.0

*COD - Chemical Oxygen Demand

In this case, a mixture of all wastewater streams, which have a similar component composition but differ in pollutant concentrations, pH values, and flow rates, is fed into the treatment plant.

An example is the treatment of wastewater from the Uchaly Mining and Processing Plant, with a characteristic composition for the wastewater under consideration, having a similar component composition but differing in pollutant concentrations, pH values, and flow rates. An example can also be the treatment of wastewater from oil refining enterprises with a characteristic composition for the discussed wastewater (see Table 1). As shown in Table 1, all measured parameters (pH, suspended solids, sulfates, surfactants, and COD) decreased significantly after treatment ($p < 0.001$). The efficiency of treatment was particularly notable for suspended solids and surfactants, with reductions exceeding 90%. The requirements for the quality of technical water established for oil refining equipment are provided.

From the data in Table 1, it is evident that treatment of the examined wastewater with a coagulant result in a low level of purification for nearly all indicators. To improve the quality of treatment, it is necessary to investigate methods for intensifying the sedimentation of wastewater. Flocculation has been adopted as a method for increasing the efficiency of this process, as recontamination of the wastewater by added reagents is unacceptable.

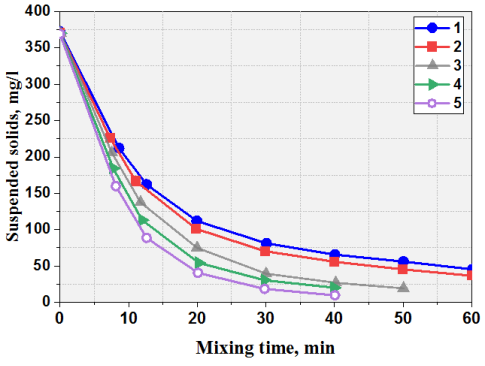


Fig. 1. Dependence of suspended solids content on bentonite concentration and duration of mixing during wastewater treatment. The content of coagulant $Al_2(SO_4)_3 \cdot 18H_2O$ is 0.5 mg/l and flocculant Na-CMC is 0.15 mg/l, Bentonite concentration, g/l: 1-1.0; 2-2,0; 3-3,0; 4-4,0; 5-5,0.

The removal of suspended solids and impurities by coagulants is complicated by their concentration, which in some cases exceeds 40 mg/L. For a more effective approach in the treatment of highly mineralized wastewater, in addition to coagulant and flocculant, it is necessary to introduce highly sorptive bentonite and kaolin.

Experimental data on the treatment of wastewater with initial concentrations of suspended solids and sulfates up to 478 mg/L (Fig. 1) show that the bentonite concentration at which the minimum level of suspended solids is achieved is C = 3.0 g/L. The optimal mixing duration of wastewater with bentonite is 20 minutes, as increasing the mixing time to 30–60 minutes results in negligible changes in the concentration of suspended solids.

Based on the results obtained from the treatment of wastewater from oil refining production, the conclusions made from experiments on model solutions are confirmed. For effective removal of sulfates in each of the two types of wastewaters studied, the simultaneous addition of bentonite, kaolin, coagulant, and flocculant is required with a mixing duration of 20 minutes.

As a result of wastewater treatment by the sorption-coagulation method, a low level of purification is achieved for almost all indicators due to their high concentration. Therefore, the commonly accepted technology for the treatment of highly mineralized wastewater needs improvement in order to reduce salinity levels to meet the requirements of recirculating systems and Maximum Permissible Concentrations (MPC), as well as to obtain sludge suitable for disposal.

In addition, this paper presents the results of the development of a modified method of wastewater treatment with the use of solid compositive reagents, in the sorbent-coagulant-floculant system, which ensures a higher quality of the water to be cleaned with a single timely improvement and satisfaction of its purification process. As a result, cacolin and bentonite were used at a level of 1:1 to 2.0 g/l, as a coagulant of $Al_2(SO_4)_3 \cdot 18H_2O$ and $FeCl_3 \cdot 6H_2O$ at a concentration of 0.5 and 0.75 mg/l, respectively, and the floculant Na-CMC 0.15 mg/l. The establishment of the characteristics of the detectors depending on the conditions of their education, the chemical composition of the floculant and coagulant, and the nature of the parts of the dispersal phase sorbent allowed the goal to develop new companies on the basis of the sorbent, floculant and coagulants, to optimize the conditions for their introduction and to achieve the maximum efficiency of the water treatment process.

In the research process, the effectiveness of wastewater treatment from the supply of additional water was studied. A large measure of the state of illuminated water was carried out from the second report on COD, BOD, control of sulfates, chlorides and phosphates. Fig. 2 clearly demonstrates that the

combined use of sorption, coagulation, and flocculation resulted in the highest removal efficiencies for COD, BOD, and sulfates. The differences among the three treatment approaches were statistically significant ($p < 0.001$).

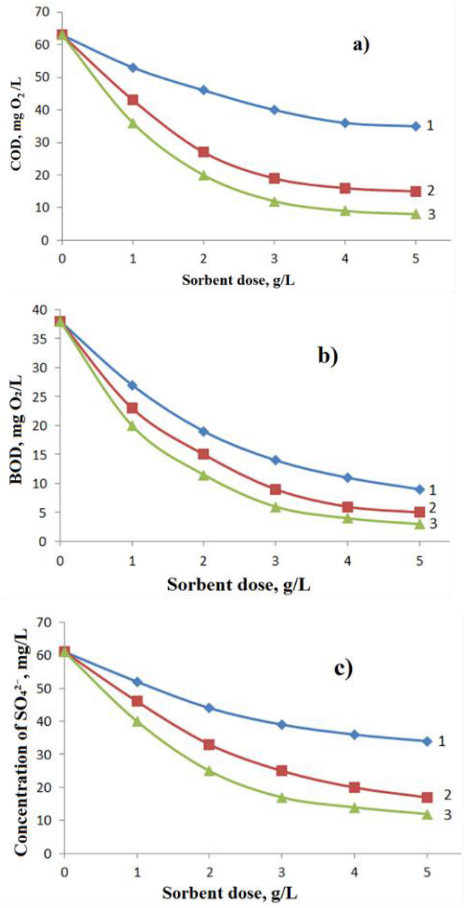
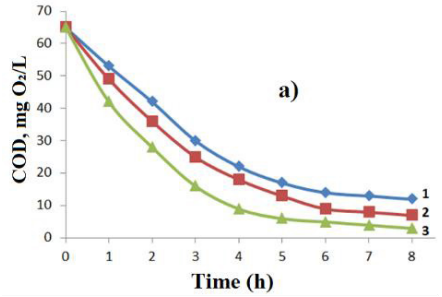


Fig. 2. C Changes in COD (a), BOD (b), and sulfates (SO_4^{2-}) (c) after sorption, sorption–coagulation, and sorption–coagulation–flocculation treatments. Values are mean ± SD (n = 3). ANOVA indicated statistically significant differences among treatments ($p < 0.001$).

The kinetic curves in Figure 3 show that most of the contaminant removal occurred within the first two hours. The sorption–coagulation–flocculation method achieved the most rapid and effective removal, with statistically significant differences compared to the other two methods ($p < 0.001$).



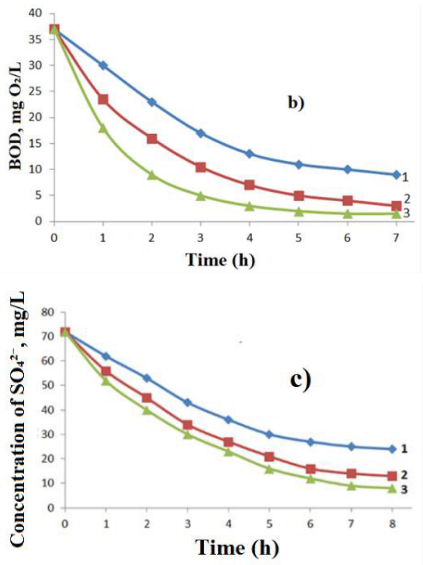


Fig. 3. Kinetics of COD (a), BOD (b), and sulphate (SO_4^{2-}) (c) removal during sorption (1), sorption–coagulation (2), and sorption–coagulation–flocculation (3). Data are mean ± SD (n = 3). ANOVA confirmed significant differences among treatments ($p < 0.001$).

The parameter values determined each hour during the first 2 hours and four hours 6 hours from the beginning of the experiment. The process of coagulation-floculation (3) cleaning is realized in the first 2 hours of the flow water control and the value of the parameters does not change significantly. A sharp decrease in the control of the control of the organic uses of water flow is a sign of the passage of physical activity. The longest reduction is due to biologic oxidation. The kinetic curve of the COD indicator changes shows that in the first 2 hours of the contact with the drainage water, the coagulation treatment proceeds with the maximum interest, which is due to the collection of bioresiscent containers by the sorbent. Intensive cleaning according to the BOD signal; In the first two hours, more than the plane is reduced, since during the complete cleaning, the formation of the bioplate occurs. Effective purification of sulfate ion results in a greater and faster removal of organic applications, the presence of a solid mineral material and a change in the pH value in the side of the biological medium, which affects the intensive growth.

Based on these conclusions, the first phase of the study consisted in studying the regularities of the sorption process on natural bentonite under static conditions in order to determine the sorption capacity and selectivity of the selected sorbents.

To carry out the sorption process, a model solution was prepared, the volume of which was the same for all experiments. The mass of the adsorbent varied in various ratios. The composition of the initial concentration of the solution was adapted in accordance with the components contained in the wastewater of the existing production. With this in mind, the solution was prepared with concentrations of petroleum products of 265, 140 and 76 mg/l, which correspond to the concentrations of the main pollutants in the wastewater generated in various processes of the Bukhara Oil Refinery. The range of concentration fluctuations was

selected based on the analysis of the quality of wastewater after different stages of treatment (after the stage of retention of petroleum products, flotation cleaning and subsequent stages of treatment).

3.2 Efficiency of Sorption-Coagulation-Flocculation in Wastewater Treatment

Three 500 mL volumetric flasks prepared in advance with solutions containing contaminants in wastewater at concentrations of 265, 140 and 76 mg/l obtained 300 mg of solution with 10 g of natural bentonite with a diameter of d=0.5 mm (pH=6). The resulting suspensions were stirred for 2, 4 and 8 hours. The amount of petroleum products in the wastewater before and after the sorption process was determined using the gravimetric method.

In experiments conducted under static conditions, it was found that the sorption process begins in the first 20 minutes, and the maximum sorption value is observed after 2.5-3 hours. In solution models with an initial concentration of petroleum products of 76 mg/l, 140 mg/l and 265 mg/l, the maximum sorption capacity was 0.65 mg/g, 2.15 mg/g and 5.57 mg/g, respectively. The kinetics of changes in the sorption of oil products on natural bentonite depending on the initial concentration of the solution shows that the sorption process reaches its maximum sorption capacity in the first 2.5-3.0 hours, after which the sorption process does not change significantly over time. The results obtained show that adsorption, namely the sorption tank, is proportional to the concentration of pollutants in the wastewater. For example, at a concentration of pollutants in wastewater of 76 mg/l, after 4 hours of mixing, the sorption capacity was 0.76 mg/g, while at a concentration of pollutants of 265 mg/l, the sorption capacity of the adsorbent was 5.83 mg/g.

At the same time, it was found that the sorption capacity of sorbents with high selectivity obtained by thermal, chemical and thermochemical modification of natural bentonite also depends on the method of their modification. We can observe that the sorption capacity of modified bentonite increases by 1.5-3.0 times compared to natural bentonite (Figure 4, a, b, c, d).

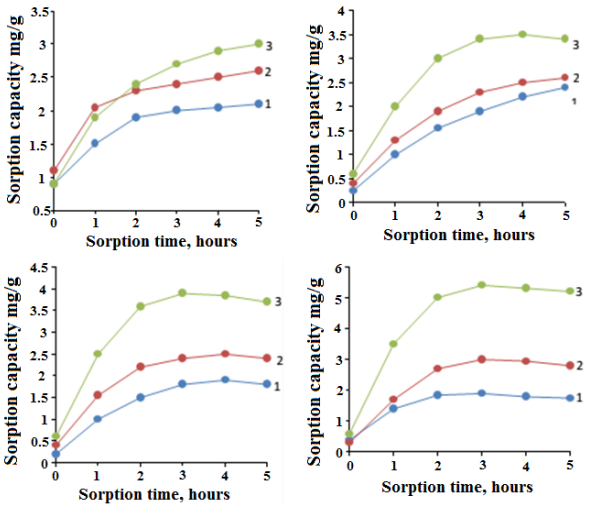


Fig. 4. Dependence of the process of sorption of oil products on natural bentonite on time in the composition of wastewater. Concentration of petroleum products in wastewater; mg/g: 1 – 76 mg/l; 2 – 140 mg/l; 3 – 265 mg/l a) natural bentonite; (b) thermally modified bentonite; (c) chemically modified bentonite; (d) Thermochemically modified bentonite.

The highest sorption capacity in relation to oil products was observed in thermochemically modified bentonite. For example, the sorption capacity of thermally modified bentonite after 4 hours was 1.75 mg/g, chemically modified bentonite was 2.64 mg/g, while the sorption capacity of thermochemically modified bentonite was 5.67 mg/g over the same period of time. Based on the results obtained, it is possible to order the sorbents according to the degree of their selectivity and sorption capacity as follows:

Natural bentonite < thermally modified bentonite < chemically modified bentonite < thermochemically modified bentonite.

In addition, it can be noted that the sorption properties of modified bentonite also differ depending on the method of its modification. The results obtained confirm that natural bentonite from the Navbakhor field has a high sorption activity in relation to the oil products contained in the initial solutions.

It should be noted that in the technological line of wastewater treatment of petrochemical enterprises, sorption filters are usually filled with activated carbon. Therefore, the sorption capacity of Navbakhor bentonite in relation to oil products (AB) was compared with the sorption capacity of BAU activated carbon, which is widely used in wastewater treatment systems (Fig. 5).

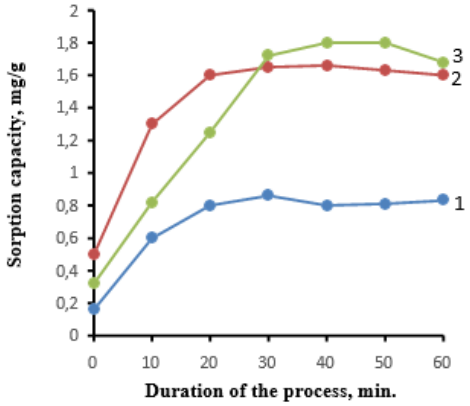


Fig. 5. Kinetics of changes in the sorption tank on natural bentonite, thermochemically modified bentonite and activated carbon during the purification of petroleum products with a concentration of 76 mg/l in the composition of wastewater. Sorbents with a concentration of petroleum products of 76 mg/l: 1 – natural bentonite; 2–thermochemically modified bento-nite; 3 – activated carbon.

The adsorption value was defined as the difference in the concentration of petroleum products in the wastewater before and after the sorption process.

Our findings are in agreement with earlier studies that demonstrated the positive impact of clay modification on sorption performance. For example, Rostami et al. [1] reported improved removal of hydrocarbons using acid-modified clays, while Chokri et al. [2] observed significant increases in sorption

efficiency after combined thermal and chemical treatments. Compared to these works, the thermochemically modified bentonite evaluated in this study showed superior sorption capacities under similar experimental conditions. Moreover, while activated carbon has long been regarded as the benchmark sorbent [12], our results highlight that locally available modified bentonites can achieve comparable or even higher efficiencies, underscoring the novelty and practical value of the present work.

The adsorption of petroleum-derived pollutants onto bentonite and activated carbon is governed by a combination of physical and chemical interactions. Physical adsorption occurs through van der Waals forces and pore filling, which is particularly significant for activated carbon due to its high surface area. Chemical interactions involve hydrogen bonding and ion exchange between the functional groups of the adsorbents (–OH, –COOH, Al–OH, Si–O⁻) and polar components of the contaminants. In addition, electrostatic attraction between negatively charged sites on modified bentonites and cationic pollutants contributes to enhanced sorption efficiency. Hydrophobic interactions also play a role by driving the accumulation of non-polar petroleum molecules onto the sorbent surface. These combined mechanisms explain the superior performance of thermally, chemically, and thermochemically modified bentonites compared to natural bentonite.

3.3 Statistical Modelling of Sorption Capacity and Process Optimization

The results obtained showed that the maximum sorption capacity of modified bentonites is observed for 35-40 minutes, after which their activity begins to decrease. For activated charcoal, the maximum sorption capacity was recorded during the first 30 minutes.

For further analysis and substantiation of the results obtained, statistical processing of the data was carried out, as a result of which a regression dependence was established, which describes the behavior of sorption processes for each sorbent:

$$Amb = 3.2840 - 0.0024 - 0.005\ t2 \quad (1)$$

$$AAK = 2.8563 + 0.02418 - 0.004\ t2 \quad (2)$$

Here, Amb, Aak, respectively, denote modified bentonite clay and activated carbon, their sorption capacity; t is the duration of sorption, min. When choosing approximating functions, the condition for obtaining a high coefficient of determination R^2 was taken into account.

This regression equation makes it possible to determine the value of the sorption capacity of a selective sorbent obtained by thermochemical modification of BAU activated carbon and natural bentonite in the process of sorption of petroleum products for a certain time. It should be noted that, taking into account the time values of the sorption process, which are several tens of minutes, in order to ensure maximum accuracy of calculations, the coefficients were taken with an accuracy of 4 or 5 decimal places. Based on the above equations, Table 2 presents the criteria for statistical significance.

Table 2. Criteria for the statistical significance of regression equations.

Formula	R^2 , %	$R^2_к$, %	DW	δ^2	Δ, мг/ г
(1)	94,26	87,23	2,86	0,082	0,052
(2)	90,32	80,45	2,84	0,124	0,085

R^2 – regression constants

Based on the statistical values calculated from the regression equations, the following conclusions were drawn:

The coefficient of determination (R^2) shows how much of the experimental data is described by this formula. The adjusted coefficient of determination (R^2k) takes into account the insufficiency of data. Each point on the graph represents a factor that expresses the average value of the set of experimental results. The Durbin-Watson (DW) criterion determines the degree to which the results obtained depend on each other. The standard error (β^2) reflects the standard deviation from the regression line. The mean absolute error (Δ) indicates the acceptable ranges of values.

Modified samples of sorbents are used to improve the adsorption properties of natural bentonites and expand the areas of their application. Improving sorption properties through chemical action on natural minerals is important. The range of agregates formed by hydrolysis of coagulants with different bases has matured with an increase in the content of aluminum sulfate and chloride of the iron in the area of the 110–230s-1 coagulant (Fig. 6).

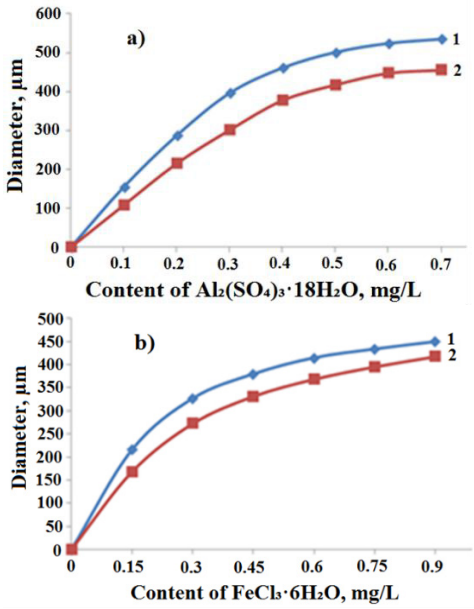


Fig. 6. Dependence of the average diameter of coagulants on the maintenance aluminum sulfate (a) and iron chloride (b). 1- G=110 s^{-1}; 2- G=290 s^{-1}.

It has been established that aluminum sulfate is formed by the largest coa-gulation aggregates, which are more likely to be harvested than iron chloride (seeding speed of 0.004–0.005 m/s and 0.002–0.003 m/s,

respectively). By this fact, it is possible to explain the greater efficiency of the conjugation of aluminum ions in comparison with the microorganisms of the planet in most of the processes of removing pollutants from water.

The parameters of the agregates formed during the hydrolysis of coagulants are also influenced by the conditions of dispersion, which can be.

Large concentrations of iron chloride are obtained at 40s-1 dispersion and aluminum sulfate at 20 s^{-1}. Increasing the dispersion intensity to 270 s^{-1} has led to a reduction in the size of the regions as a result of their mechanical destruction.

3.4 Thermal and Structural Characterization of Modified Bentonites

The modification process leading to surface activation is carried out mainly by physical or chemical methods. Physical modification of natural minerals can be carried out by heat treatment, treatment in colloidal mills under vacuum and high temperature conditions, at high pressure and temperature, and using ultrasonic vibrations. In chemical modification, mineral and organic acids, alkalis, light- and sparingly soluble salts, surfactants, water-soluble polyelectrolytes, organosilicon compounds can be used as chemical reagents. According to scientific and technical sources, thermally modified bentonites have a high adsorption capacity.

Based on the above data, the thermal stability of the sorbent obtained by thermochemical modification of bentonite mined at the Navbahor deposit was studied by thermographic analysis. The assessment of thermal stability revealed two endothermic effects on the thermogram, which are mainly related to the loss of adsorbed (160–240°C) and bound water.

A thermal analysis of bentonite and activated sorbents from the Navbahor deposit was carried out. The results of the derivatographic analysis are presented in Figures 7–8 and Table 3.

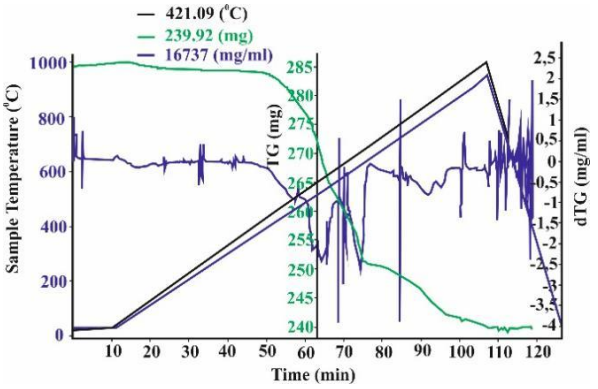


Fig. 7. Derivatogram of Navbahor bentonite.

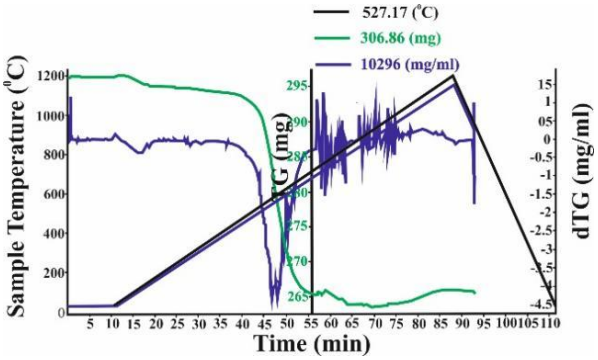


Fig. 8. Navbahor derivatogram (activated bentonite sorbent).

In addition, their aggregate state was studied using derivatographic thermal analysis methods. In the study of the thermal stability of natural and activated clays, it was found that when the temperature rises to 80–280°C, the molecules of adsorbed water contained in clay powders completely evaporate. In the temperature range of 200–660°C , endothermic effects are observed, accompanied by the decomposition of hydrolyzed starch and cellulose compounds. Similarly, on derivatograms of bentonite treated with nitric acid, changes in its constituent components are recorded during thermolysis.

Table 3. On the derivatogram (activated bentonite sorbent), the initial decomposition intervals are manifested in certain temperature ranges.

Bentonite	Weight, %										
Temperature., °C	100	200	300	400	500	550	600	700	800	900	1000
Fragmentation	295	294	293	293	292	286	278	266	266	263	262
95°C	99,7	99,3	98,9	98,9	98,5	96,6	93,9	89,8	89,8	88,8	88,4

3.5. Infrared Spectroscopic Analysis of Sorbents

The exothermic effect that occurs at 800–900°C indicates the destruction of the bentonite structure. The change in the structure of natural bentonite during heat treatment can also be explained by the absorption bands recorded in the IR spectra. To study the main chemical and mineral components of bentonite and its physicochemical properties, the IR spectra of the initial and thermochemically modified solid samples were obtained and analyzed. The vibrational frequencies of the structural components recorded in the spectra are shown in Figures 9–10.

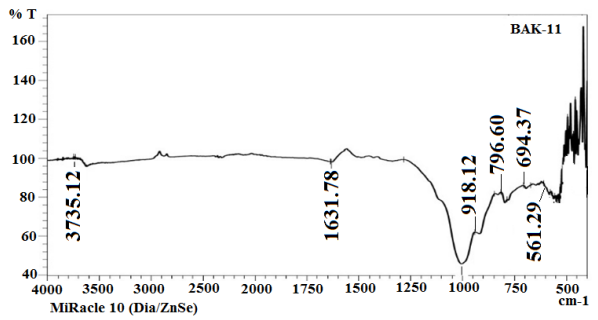


Fig. 9. IR spectrum of natural bentonite Navbahor.

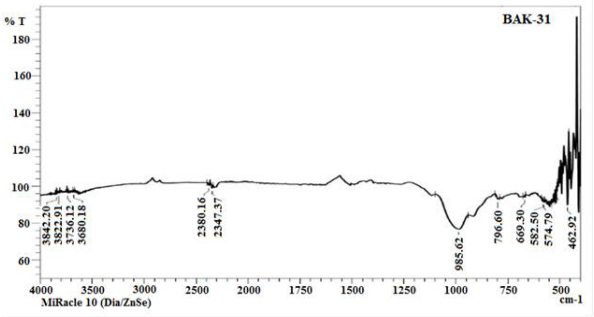


Fig. 10. IR spectrum of heat-treated bentonite (T=300^{0}C).

The IR spectrum of natural bentonite (Fig. 9) shows. In the region of 3626 cm^{-1}, there is a single band of medium intensity, as well as weak absorption bands, indicating the presence of hydroxyl groups associated with various metal ions (HO-Al^{3+}, HO-Fe^{2+}, HO-Mg^{2+}) and absorbed water molecules. Specific water absorption is manifested in the middle region of the spectrum at 1633.71 cm^{-1} in the form of a band of strain oscillation δ(H-O-H). Deformation oscillations δ(H-O-M^{n+}), characteristic of hydroxyl groups, are observed in the form of weak and wide bands in the range of 1510–1450 cm^{-1}.

The main fluctuations associated with SiO_2 and Al_2O_3, which form the basis of bentonite (see para. Table 3) are located in the area of 1100–500 cm^{-1}. The main broad-intensity absorption band is fixed at 983.70 cm^{-1}, and the adjacent bands in the range of 1140–920 cm^{-1} correspond to valence oscillations of Si-O-Si bonds in [SiO_4] tetrahedra. Symmetrical valence and deformation oscillations of Si-O-Al, Al-O-Al, Si-O-M bonds (M = Mg, Ca, Fe) appear in the range of 800–450 cm^{-1} in the form of bands of various low intensity.

Weak absorption bands in the region of 1435 and 860 cm^{-1} in the spectrum indicate the presence of carbonates ($CaCO_3$ – $MgCO_3$), namely oscillations (CO_3^{2-}), δ(CO_3^{2-}), which indicates a low carbonate content in bentonite. The IR spectrum of a bentonite sample subjected to heat treatment at T = 573 K (t = 300°C) (Fig. 10) is almost identical to the spectrum of the original sample, which confirms the preservation of the main chemical and mineralogical components of the "framework". The main difference from the spectrum of the original bentonite is as follows. The band of ν(HO-M) hydroxyl groups shifted by 24 cm^{-1} to the region of 3550 cm^{-1} to a higher frequency. The intensity of this strip decreased by about 40%, which indicates the complete removal of adsorbed water when heated. The absence of the absorption band of 1633 cm^{-1} characteristic of water confirms the process of thermal dehydration.

Hydroxyl (OH^-) groups bound to M ($Fe^{2+/3+}$, Al^{3+}, Mg^{2+}) ions, as well as carbonate (CO_3^{2-}) ions, did not change under the influence of temperature, which is confirmed by the presence of weak absorption bands in the range of 1530–1430.3 cm^{-1}. The absorption range of 1100–460 cm^{-1}, which is typical for aluminosilicate components, has remained unchanged, which proves the stability of the bentonite structure after heat treatment.

After modifying the sample with a 20% solution of nitric acid (HNO_3), no significant changes in the spectrum are observed compared to the original sample. The only difference is the shift of the νas (Si-O-Si) band of oscillations by about 20 cm^{-1} to the higher frequency region.

Bentonite did not show significant sorption activity towards H^+(H_3O^+) and NO_3^- ions from the HNO_3 solution. This is confirmed by the absence of characteristic absorption bands in the following regions: ~3500–3300 $см^{-1}$ (n(H-O) H_3O^+); 1630 $см^{-1}$ (δ(H-O-H) H_3O^+); 1300–1350 cm^{-1} ($\nu_{as}(NO_3^-)$) (Fig. 11).

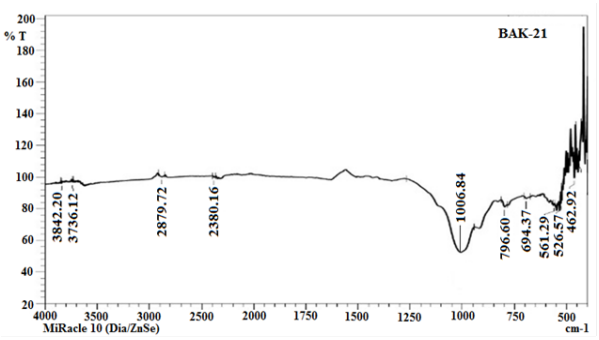


Fig. 11. IR spectrum of chemically modified bentonite.

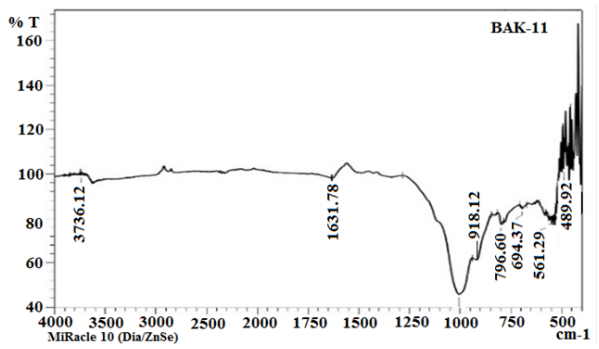


Fig. 12. IR spectrum of thermochemically modified bentonite. (T=300^{0}C, modifier - 20% HNO_3 solution).

This IR spectrum (Fig. 12) belongs to a thermochemically modified bentonite sample. Unlike a heat-treated sample, it more closely resembles the spectrum of the original sample. In the spectrum, changes are observed in the absorption regions: 3660 cm^{-1} – hydroxyl (OH^-) groups and bound water molecules related to the H_3O^+ ion; 1631.78 cm^{-1} – δ(H-O-H) oscillations H_3O^+; 1430 cm^{-1} – ν(CO_3^{2-}); 1100–462 cm^{-1} – vibrations related to aluminosilicate components: ν(Si-O-Si), ν(Si-O-Al), ν(Si-O-M), δ(Si-O-Si), δ(Si-O-Al).

4 Conclusion

This study demonstrated that chemical and thermochemical modifications significantly enhance the sorption capacity of Navbahor bentonite compared to its natural form, with thermochemically modified bentonite showing the highest performance. The combined use of bentonite/kaolin with coagulants and flocculants provided markedly improved removal of suspended solids, sulfates and petroleum-derived contaminants. Regression modelling confirmed the reliability and

predictive power of the sorption process ($R^2 > 0.90$) under the tested conditions. These findings underline the practical applicability of locally available modified clays as cost-effective and efficient sorbents for oil-contaminated wastewater treatment, offering a promising alternative to activated carbon in industrial settings

The maximum sorption capacity of bentonite is achieved by heat treatment at 400 °C. However, when the temperature rises to 600 °C, it decreases sharply. This is due to the fact that at 400 °C, coordinately bound water is removed from the bentonite structure, which leads to an increase in the adsorption surface due to the formation of empty microcapillaries. At 600 °C and above, the destruction of the bentonite crystal lattice leads to a sharp decrease in its adsorption capacity. Based on the thermal data obtained, it can be concluded that the loss of adsorbed and bound water contributes to an increase in the adsorption capacity of bentonite. Therefore, in this work, the effect of thermal modification of natural bentonite on its sorption ability is investigated. This confirms the effectiveness of this method for wastewater treatment from oil products.

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