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ADSORPTION TREATMENT OF WASTEWATER FROM PETROLEUM PRODUCTS WITH PLASMA TREATED VERMICULITE

G. I. Gusev, A. A. Gushchin, V. I. Grinevich, E. M. Baburina, T. V. Izvekova

Grigory I. Gusev, Candidate of Chemical Sciences, Senior Lecturer; **Andrey A. Gushchin**, Candidate of Chemical Sciences, Associate Professor; **Vladimir I. Grinevich**, Doctor of Chemical Sciences, Professor; **Ekaterina M. Baburina**, Student; **Tatiana V. Izvekova**, Candidate of Chemical Sciences, Associate Professor
Ivanovo State University of Chemical Technology, Ivanovo, Russian Federation, grisha.gusev.05@mail.ru

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Abstract. *The paper presents the results of studies of wastewater treatment processes from petroleum products using vermiculite before and after treatment in dielectric barrier discharge plasma. During the experiment we determined the time of reaching equilibrium in the heterophase system "sorbent - aqueous solution of petroleum products", is 30 min. The kinetic sorption curves are processed in first- and second-order linear coordinates. We found that the kinetics of petroleum product sorption by vermiculite is most adequately described by a second-order kinetics model, indicating an ion-exchange adsorption process. The article describes the processes of external and internal mass transfer of petroleum products in the presence of vermiculite obtained under different conditions. When treating the sorption kinetics in Boyd-Adamson coordinates we found that the adsorption process proceeds in an inward diffusion regime. Treatment of the sorbent, after use in the wastewater treatment process, in dielectric barrier discharge plasma leads to a slight decrease of sorption characteristics, but results in its regeneration. We studied the morphology of vermiculite obtained under different conditions. The sample is a micro-heterogeneous material with a particle size of 0.4-0.7 μm. The total pore volume obtained from the linear coordinates of the micropore volumetric filling theory is 0.21 cm^3/g. All microphotographs reflect the characteristic morphology of the vermiculite mica packet. The results of the study of the sorption properties evaluated by the method of low-temperature inert gas adsorption made it possible to construct isotherms of adsorption/desorption of liquid nitrogen on the sorbent surface, the BET treatment of which showed that the specific surface area of the sorbent is 7 m^2/g.*

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Introduction

One of environmental problems today is the pollution of water bodies and the deterioration of the quality of water resources, which leads to a reduction of the amount of available drinking water. One of the priority pollutants of the hydrosphere is petroleum products (PPs) and their derivatives. The pollution level is increasing every year and becoming global. Therefore, improving existing as well as developing new technologies for the removal of such compounds, which should meet the modern requirements of being as accessible, convenient, environmentally friendly and economically viable as possible, is a priority [1, 2]. The adsorption method is one of such methods of treating wastewater from organic compounds [3, 4]. The advantages of the method are the high efficiency (up to 95%), the possibility to treat multicomponent wastewater, and the possibility to recover adsorbed substances [5-7].

Traditionally, natural sorbents such as zeolites [8] and diatomites [9] as well as industrial wastes such as drilling waste [10], felt production waste [11] and sawdust [12] are used to remove various pollutants from water. In order to obtain higher characteristics, the sorbents are subjected to various kinds of modification: chemical [13], thermal [14], ultrasonic [15], mechanical activation [13, 16-17], etc. High-energy chemistry techniques, including various types of discharges, can also be used for these purposes [18].

Thus, the purpose of this work is to study physical and chemical regularities of the process of sorption of petroleum products from aqueous solutions onto vermiculite modified in dielectric barrier discharge (DBD) plasma.

Materials and methods

We used aqueous solutions of petroleum products (M8-B motor oil) as model pollutants. The choice of this object for research is due to its widespread use in industry, resulting in its ubiquitous occurrence in environmental media, as well as its high toxicity for natural ecosystems. Petroleum products are persistent to natural degradation processes [19], therefore the search for methods to treat NP-contaminated water is urgent.

The concentrations of petroleum products in aqueous solutions were selected on the basis of data on their content in real industrial effluents. The model petroleum product solution is prepared by mixing the required volume of M-8B engine oil with distilled water.

A schematic view of the experimental unit for the treatment of adsorbents is shown in Fig. 1, the main element of which was the dielectric barrier discharge reactor. The primary voltage was monitored with a D 5015 voltmeter. We determined the input power by integrating the product of the voltage and current signals over a period. The average voltage value in the experiments was 16.5 kV, with a discharge current of 13.1 mA. The frequency of the AC voltage applied to the electrodes was 800 Hz.

The volumetric power invested in the discharge (P, W/cm^3) was 8.6 W/cm^3 and was calculated using the formula:

$$W = \frac{U \cdot I}{V_p}\ , \qquad (1)$$

where I is the current strength of the secondary circuit, A; U is voltage, V; V_d is discharge zone volume, cm^3, calculated according to the formula

$$V_p = S_{\text{сеч.}} \cdot L_{\text{р.з.}}\ , \qquad (2)$$

where S_{csa} is the cross-sectional area of the discharge zone, cm^2; L_{dz} is the length of the discharge zone, cm.

The volume of the discharge zone of the DBD reactor was 25 cm^3. In all experiments we used technical oxygen as plasma-forming gas, with a flow rate of 500 ml/min (8.33 ml/s).

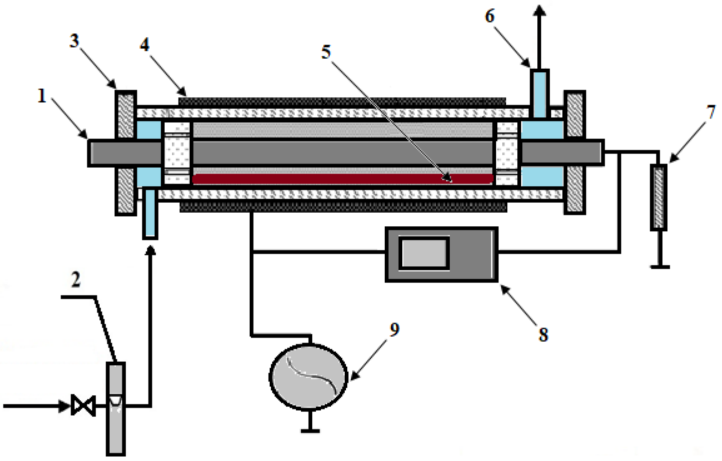

Fig. 1. Schematic view of experimental setup: 1 - inside electrode 2 - gas bottle with flow meter; 3 - teflon insert; 3 - flow meter; 4 - inside electrode; 5 - treated sorbent layer; 7 - 100 Ohm resistor; 8 - GW Instek GDS-2072 digital dual channel oscilloscope; 9 - power supply unit

In our work we study the vermiculite sorbent (SiO_2 (37.2%), Al_2O_3 (6.2%), CaO (15.3%), Fe_2O_3 (19%), MgO (13.1%)). The main characteristics of the sorbent are the specific surface area, the sorption capacity, the adsorption coefficient b_i and the adsorption limit value a_m. We determined these values using the standard method in linear Langmuir isotherm [20]. In addition, we have determined the value of Henry's constant H_i, which in its physical sense coincides with the thermodynamic distribution coefficient of adsorbate at low concentrations of solute. As part of the formal treatment, we calculated the maximum surface coverage θ_i for the sorbent from the value of the total adsorption a_i and the limiting adsorption a_m.

The equilibrium values of adsorption are usually measured by changes in concentration of one of the components, which is established by prolonged contact of the solution with the adsorbent. Adsorption values are calculated with the Gibbs excess method, as surface excesses from the difference in contents of a component in a volume near the surface and in the same volume of solution away from the surface. If we neglect the change in volume of the solution during adsorption, the Gibbs adsorption value a_i of component i, expressed, for example, in mol/g of adsorbent, is

$$a_i = \frac{V_0 \cdot (C_{0,i} - C_i)}{m}, \tag{3}$$

where V_0 is the volume of the solution, l; m is the mass of the adsorbent, g; $C_{0,i}$ and C_i are its initial and final equilibrium concentrations, mol/l.

Conversion per surface unit A results in an excess adsorption value G_i:

$$\Gamma_i = \frac{V_0 \cdot (C_{0,i} - C_i)}{m \cdot A}. \tag{4}$$

In order to obtain the necessary range of equilibrium concentration values to obtain the isotherm, we have reduced equation (4) to the form

$$C_i = C_{0,i} - \frac{\Gamma_i \cdot m \cdot A}{V_0}. \tag{5}$$

From equation (5), it follows that in addition to $C_{0,i}$, the m/V_0 ratio can be the varying parameter. Thus, the modelling of the petroleum product adsorption isotherm for the sorbent under study involved the following stages:

1) preparation of a model aqueous solution containing the test substance at a given concentration;

2) weighing and transferring the sorbent sample;

3) mixing the set volume of the model solution with the sorbent. Stirring parameters for all samples were constant (we conducted the experiment on the sorption of petroleum products from aqueous solutions under static conditions, stirring and thermostatting at 298 K. The kinetics of petroleum product sorption were investigated in a limited volume solution);

4) measuring the concentration of a substance in a solution;

5) determination of the sorption capacity of the tested sorbent sample (mg/g) according to the formula

$$q_\tau = \frac{C_0 - C_\tau}{m} \cdot V , \tag{6}$$

where q_τ is the sorption capacity of the sorbent, mg/g; V_0 is the sample volume of the model solution, l; C_0 and C are the initial and final concentrations of the substance, respectively, mg/l; m is the mass of the sorbent sample, g.

In order to obtain an adsorption isotherm, the initial concentration - C_0, the volume of solution - V_0 and the mass of the sorbent - m are varied.

6) Drawing an adsorption isotherm in the coordinates: O_x (equilibrium concentration of the test substance, mg/l) - O_y (sorption capacity of the sorbent, mg/g).

Conditions for the experiment to determine the adsorption capacity are: initial concentration of petroleum products (C_0 - 10-2100 mg/l), volume of petroleum product solution (V_0) - 100 ml, mass of sorbent (m) - 2 g.

We defined the water absorption of the sorbent as the ratio of the mass of water absorbed to the mass of sorbent spent on sorption:

$$Wa = m_{ads.} - m_{Sorb.} / m_{ads}, \tag{7}$$

where m_{Wa} is the mass of the sorbent with absorbed water, g; m_{sorb} is the mass of the sorbent material, g; Wa is the water absorption, g/g.

We determined the moisture content of the sorbent according to the method of GOST 12597-67 [21] by drying a product sample in a desiccator to a constant mass and defined the product weight reduction. The mass fraction of water is expressed as a percentage.

We studied the surface morphology and elemental composition of vermiculite using a Tescan VEGA 3 SBH scanning electron microscope (Czech Republic) equipped with an Oxford Instruments X-Act energy dispersive X-ray analysis [22].

We obtained surface microphotographs at the following parameters:

- accelerating voltage: $U = 5$ kV,
- focal distance: $l = 15$ mm.
- beam diameter: $D = 80$ nm.

We used the following mode of operation to determine the elemental composition:

- accelerating voltage: $U = 20$ kV,
- focal distance: $l = 7$ mm,
- beam diameter: $D = 120$ nm.

Energy-dispersive spectra were recorded from a scanning area of 90×90 μm [22].

We studied the specific surface area by low-temperature noble gas adsorption on a Sorbi MS instrument, which makes it possible to plot isotherms of adsorption/desorption of liquid nitrogen on the vermiculite surface and determine the specific surface area and total pore volume [23].

We processed the kinetic curves of petroleum product sorption with first-order models (8) and second-order models (9):

$$\lg(q_e - q_\tau) = \lg q_e - k_1\tau\,, \tag{8}$$

$$\frac{\tau}{q_\tau} = \frac{1}{k_2 \cdot q_e^2} + \frac{\tau}{q_e}\,, \tag{9}$$

where k_1 is the rate constant of the sorption process by the first order model, min^{-1}; k_2 is the rate constant of the sorption process by the second order model, mg-min-g^{-1}; q_e is the sorption capacity at equilibrium, mg/g; q_τ is the sorption capacity at a given time.

We used Boyd-Adamson diffusion models to identify the limiting stage of the sorption process. Within the Boyd-Adamson model, when external diffusion is limited, the kinetic curve must be linear in the coordinates $-\ln(1-F) = f(\tau)$, where F is the degree of equilibrium in the system, calculated using the equation

$$F = \frac{q_\tau}{q_e}\,, \tag{10}$$

where q_τ and q_e are the sorption capacities at the present time and at the time of reaching adsorption equilibrium, respectively, mg/g.

If the limiting process stage is sorption in the sorbent phase (internal diffusion), the linearity of the kinetic curves must be observed in the coordinates $F = f(\tau^{1/2})$.

Weber-Morris internal diffusion is described by the equation

$$q_\tau = k_{id} \cdot \sqrt{\tau} + c\,, \tag{11}$$

where k_{id} is the rate constant of intra-porous diffusion; c is a parameter related to the thickness of the boundary layer.

To obtain the sorption characteristics of the process we treated the adsorption isotherms of petroleum products in the linear coordinates of the Langmuir (12), Freundlich (13) models:

$$\frac{C}{A} = \frac{1}{A_m} \cdot C + \frac{1}{A_m K_L}\,, \tag{12}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \cdot \ln C\,, \tag{13}$$

where C and C_τ equilibrium and current petroleum product concentration, respectively, mol/l; q_τ and q_e are the sorption capacities at the present time and at the time of reaching adsorption equilibrium, respectively, mg/g; A and A_m are equilibrium and maximum sorption capacity, mol/kg; $1/n$ is the characteristic constant that determines the favourable process of adsorption;

K_L is the concentration constant of sorption equilibrium which describes the intensity of adsorption, l/mol; K_F is Freundlich constant, (mg/g)(l/mg)$^{1/n}$.

We determined the concentration of petroleum products by the method based on extraction of petroleum products from the sample with a low-polarity solvent (hexane) and measuring the fluorescence intensity of the extract on a "Fluorat-02" device [24].

We assessed the functional groups in the petroleum products by infrared spectroscopy (Nicolet Avatar 360 spectrophotometer, USA). Thus, for motor oil M8-B we found that in the spectrum (Fig. 2) there are mainly bands characteristic of functional groups of CH, CH_2 and CH_3, linear hydrocarbons - in the area of wave numbers (2890±10), (2853±10) and (2872±10) cm^{-1} there are three bands due to the presence of structural groups of CH_3, CH_2 and CH in hydrocarbons respectively [25].

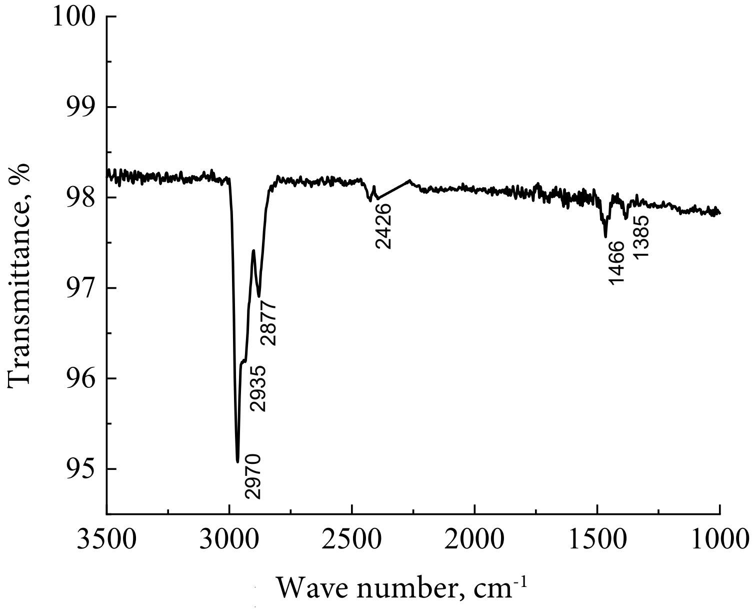

Fig. 2. Infrared spectrum of M8-B oil

It is also possible that essential groups (1465 cm^{-1}) are present in small quantities in the oil composition. Therefore, M8-B consists mainly of a set of linear hydrocarbons.

In order to determine the approximate molecular weight of petroleum products, we used an empirical relationship - Craig's formula for petroleum fractions [26]:

$$M = 44.29 \cdot \rho^{298}/(1.03 - \rho^{298}), \tag{14}$$

where ρ^{298} is oil density (905 kg/m^3) at 298 K; M is the molar mass (g/mol).

Calculation by this ratio gives an approximate formula for M8-B oil – $C_{22}H_{38}$ и M = 302 g/mol.

We estimated the cleaning efficiency α (%) of aqueous solutions from petroleum products using the formula

$$\alpha = \frac{C_н - C}{C} \cdot 100, \tag{15}$$

where C_{in} and C are the initial and final concentration of the test compound in the aqueous solution (mg/l).

Main body

The morphology of the vermiculite we obtained under different conditions is shown in Fig. 3. The sample is a micro-heterogeneous material with a particle size of 0.4-0.7 μm. The individual particles are shaped like a rhombic dodecahedron.

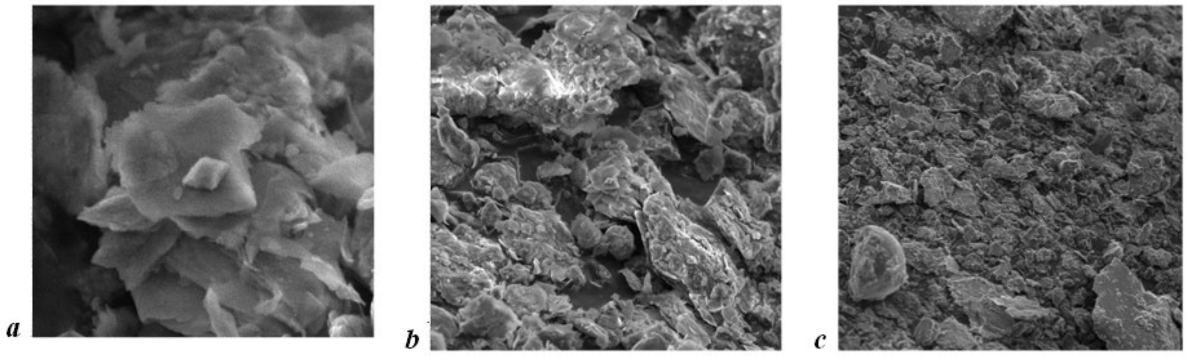

Fig. 3. Microphotographs of vermiculite samples: *a* - scale of 1 μm; *b* - scale of 20 μm; *c* - scale of 100 μm, after treatment in DBD

The total pore volume obtained from the linear coordinates of the micropore volumetric filling theory is 0.21 cm^3/g. All microphotographs reflect the characteristic morphology of the vermiculite mica packet. The surface has a layered structure in the form of flake and lobed aggregates tightly adhering to one another and forming a single framework with numerous macropores acting as transport channels during heterogeneous processes. As the scanning length decreases, the globular structure of individual surface areas with fragments of crystalline inclusions becomes apparent. Vermiculite is characterised by a fairly high dispersibility, it contains particles of regular lobe shape and the mica pack is consistent with understanding of this mineral given in the general literature.

Results of the study of sorption properties of vermiculite estimated by the specific surface area by low-temperature inert gas adsorption method made it possible to construct adsorption/desorption isotherms of liquid nitrogen on vermiculite surface (Fig. 4); BET processing showed that specific surface area of the sorbent is 7 m^2/g, which is quite a low value as compared to activated carbons (540–580 m^2/g) [27].

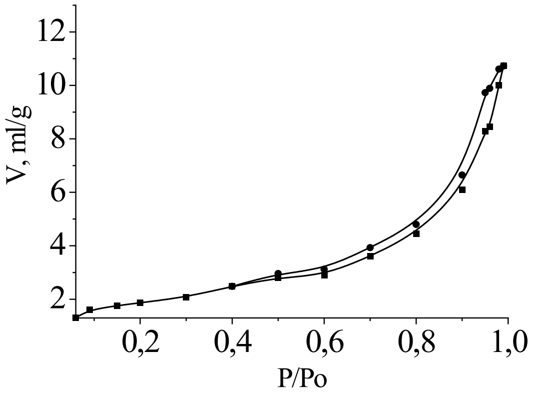

Fig. 4. Adsorption isotherms of liquid nitrogen on vermiculite

Vermiculite has a large number of pores belonging to the mesopores (Fig. 5). However, the larger mica packages have very thin macropores.

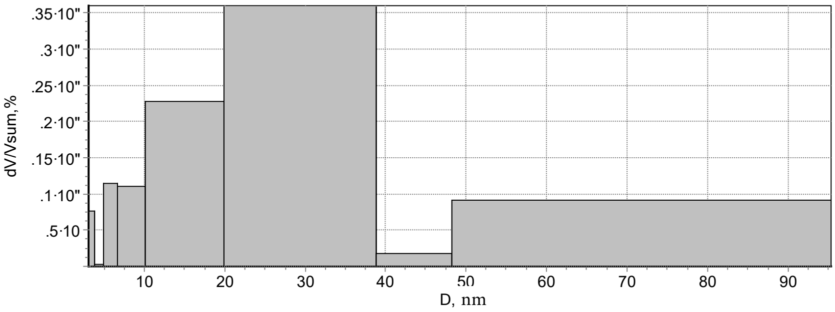

Fig. 5. Distribution of pores in relation to their total volume on the initial vermiculite

The main stage of the work determines the effectiveness of mesoporous vermiculite samples in petroleum product sorption processes. The change in values of sorption capacity at different times (Fig. 6) shows the reaching of the equilibrium in the system "vermiculite - petroleum product" for all three samples at the contact time with a solution in the range of 30-100 min.

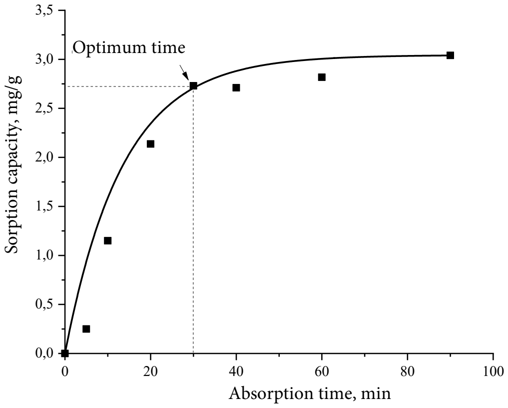

Fig. 6. Kinetic curves of petroleum product sorption on vermiculite

We processed the kinetic data of the sorption of petroleum products onto vermiculite in first- and second-order coordinates. All kinetic parameters are determined graphically (Fig. 7, 8) and summarized in Table 1.

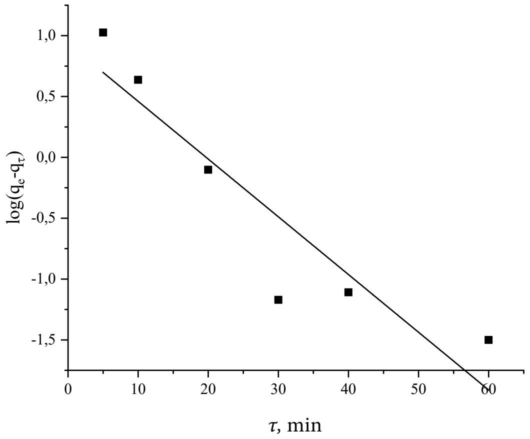

Fig. 7. Processing the kinetics of petroleum product sorption in first-order coordinates

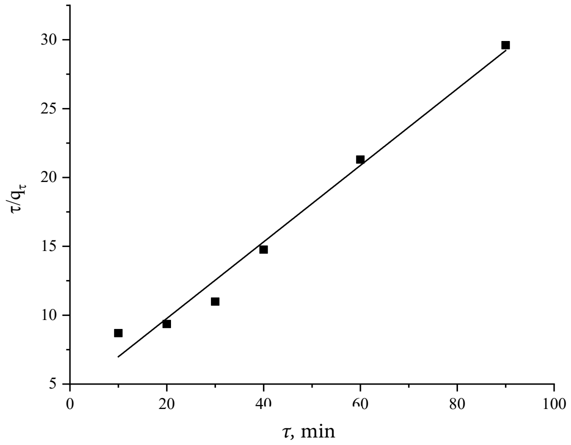

Fig. 8. Processing the kinetics of petroleum product sorption in second-order coordinates

Table 1. Rate constants and theoretical equilibrium adsorption capacities determined in first- and second-order coordinates

q_τ, mg/g	First order			Second order		
	q_e, mg/g	k_1, min^{-1}	R^2	q_e, mg/g	k_2, g/mg·min	R^2
3.04	3.04	0.047	0.85	3.034	6.145	0.99

The correlation coefficients in first- and second-order linear coordinates are 0.85 and 0.99, respectively. Thus, the adsorption of the petroleum product on the vermiculite surface is best described by a second-order equation. The value of the equilibrium sorption capacity q_e calculated in second order coordinates is 3.034 mg/g and is close to the experimental value (3.04 mg/g). The rate constant of the petroleum product adsorption process, derived from second-order linear coordinates, is 6.145 g/mg·min. Thus, the stage determining the speed of the petroleum product sorption process is the formation of covalent bonds through electron exchange between the adsorbent and the adsorbate.

The structure of the porous body can greatly influence the adsorption kinetics. When adsorbing on porous bodies, a stage of intra-pore transfer occurs, which is mainly characterised by the diffusion mechanism. This stage often determines the time of establishment of adsorption equilibrium [28].

The process of diffusion of petroleum products from the bulk phase of the solution into the volume of the sorbent was studied in the framework of Boyd-Adamson models. If linearity is realised in coordinates $-\ln(1-F) = f(\tau)$, then the external mass transfer stage is limiting, and if linearity in coordinates $F = f(\tau^{1/2})$ is observed, the transfer of petroleum product from the sorbent surface to its bulk phase is limiting. From the dependencies shown (Fig. 9) the internal diffusion stage is uniquely limiting throughout the adsorption process, which is probably due to a constant pore radius distribution in the volume. Thus we observe diffusion-controlled mass transfer.

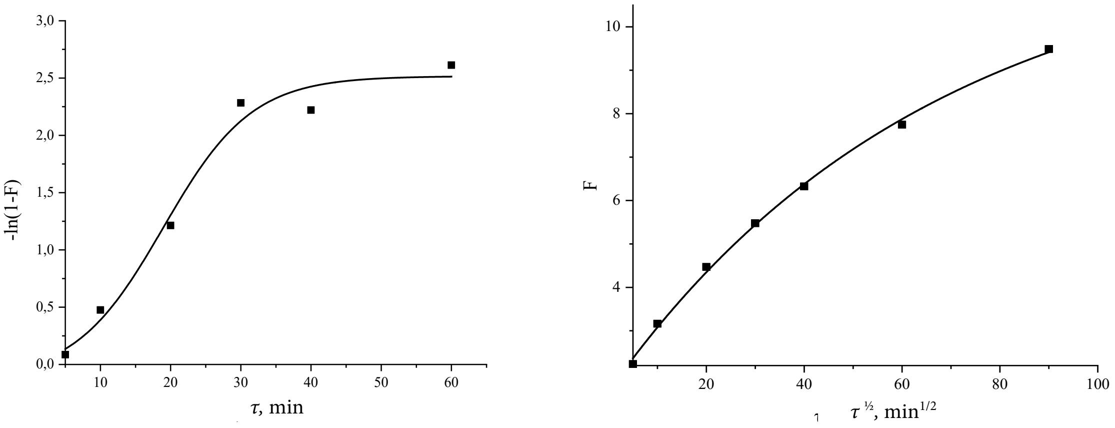

Fig. 9. Petroleum product sorption kinetics represented in Boyd-Adamson diffusion model coordinates

The resulting adsorption curve for the sorption of petroleum products (Fig. 10) is a type I curve, and is characteristic of the adsorption process occurring on solids with a relatively small proportion of the outer surface. Therefore, when processing the adsorption curves in linear Langmuir isotherm coordinates, the value of the coefficient of determination (R^2) varied in the range 0.07~0.5, all further calculations of the sorption characteristics of the process were performed in the linear coordinates of the Freundlich model (Fig. 10).

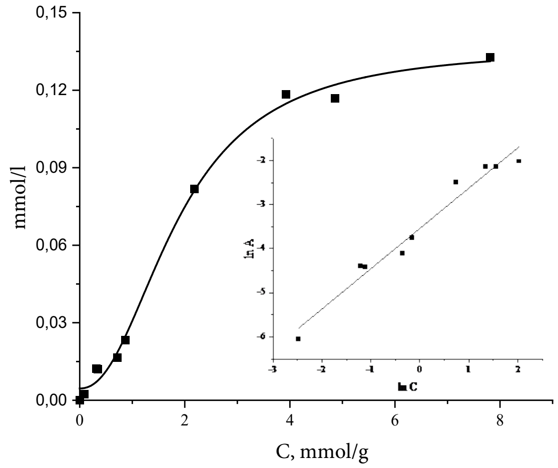

Fig. 10. Adsorption capacity of vermiculite for petroleum products and linearisation of petroleum product adsorption isotherms in Freundlich isotherm coordinates

Actually, measurement of the specific surface area by low-temperature adsorption of liquid nitrogen on the surface of vermiculite, as well as surface analysis of the samples using a scanning electron microscope, confirm this fact.

An important stage of the work was to determine the effect of treatment in DBD plasma on the surface properties of the vermiculite adsorbent. The specific surface of the catalyst was measured by the method of low-temperature adsorption of liquid nitrogen and it was determined that the treatment in DBD plasma reduced the specific surface area of the catalyst to 0.9 m^2/g, which is 6 times lower than that of the initial catalyst. However, the calculation of the ultimate adsorption capacity as well as the maximum fill level (Table 2) showed that these values, although decreasing, were less significant. The loss of ultimate sorption capacity after treatment is no more than 30% of the initial capacity (Fig. 11). As in the case of the initial vermiculite, the treated vermiculite is described satisfactorily ($R^2 = 0.96$) within the Freundlich model (see Fig. 11).

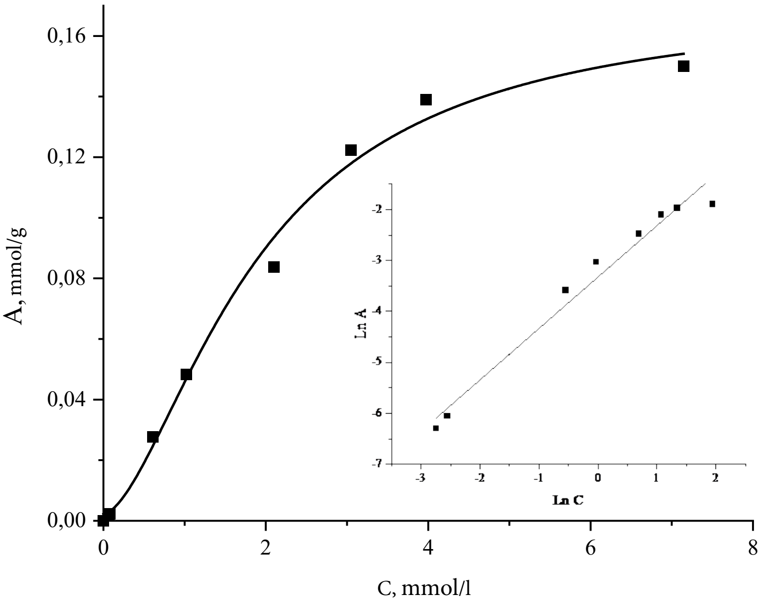

Fig. 11. Adsorption capacity of vermiculite for petroleum products and linearisation of petroleum product adsorption isotherms in Freundlich isotherm coordinates

Table 2. Petroleum product adsorption process constants for modified samples

No	A_m, mmol/g	Distribution coefficient K_d, l/g	θ	Langmuir	Freundlich			α, %
				R^2	$1/n$	K_F, $(mg/g)/(l/mg)^{1/n}$	R^2	
Initial vermiculite	0.132	0.03	0.43	0.44	3.54	2.484	0.96	79.5
Vermiculite, DBD treatment	0.094	0.027	0.54	0.41	3.65	2.612	0.90	67.4

Thus, both while the DBD treatment and in the initial sorbent, the linearization of the experimental data on adsorption of petroleum products is achieved in linear coordinates of the Freundlich isotherm ($R^2 = 0.91 \sim 0.97$), which confirms the course of adsorption in the volume of an energetically heterogeneous porous adsorbent.

From the linear coordinates of the Freundlich isotherm, describing the adsorption process on energetically heterogeneous surfaces, we obtain the values of the characteristic constants K_F and $1/n$. In particular, linear least squares and linearly transformed equations are widely used to correlate sorption data, where $1/n$ is the heterogeneity parameter, whereby the smaller $1/n$ is, the greater the expected heterogeneity. This expression reduces to a linear adsorption isotherm at $1/n = 1$. If n is between one and ten, this indicates a favourable sorption process [29]. It follows from the data in Table 2. By Table 2, the average value of $1/n$ is 3.5 ~ 3.65 for both the initial vermiculite and the vermiculite treated in DBD, which means that adsorption proceeds successfully.

The results of processing the obtained adsorption isotherm presented in Table 2 also show that the distribution coefficient (K_d, l/g), found as a ratio of C to A_i, for vermiculite is 0.03 and for the treated - 0.027, which are quite low values, and also indicates the course of adsorption by the competitive mechanism.

We observe a similar pattern when analyzing the maximum surface filling: the surface is filled to around 43–54%. It should be noted that for the samples the determined values of Θ_i are consistent with the assumption of monolayer adsorption.

The value of the adsorption limit is 0.132 mmol/g sorbent. The value obtained corresponds with the experimental data on the sorption capacity of vermiculite, when adsorbing petroleum products from emulsion under dynamic conditions, found in [30].

The maximum recovery of petroleum products from the solution is 79.5% under optimum experimental conditions, and is commensurate with the data obtained in [31]. However, the results obtained by linearising the adsorption isotherms of petroleum products on the modified samples in Freundlich isotherm coordinates, as well as the calculated values of the distribution coefficients and the degree of surface filling indicate the competitive mechanism of adsorption proceeding. In order to improve the properties of the treated vermiculite samples, additional surface hydrophobation, e.g. with organosiloxanes, is required [31].

Conclusions and recommendations

We studied the adsorption of petroleum products from solution by vermiculite sorbent (both initial and modified in dielectric barrier discharge plasma) under static conditions. During the experiment we determined the time of reaching equilibrium in the heterophase system "sorbent - aqueous solution of petroleum products", which is 30 min. The kinetic sorption curves are processed in first- and second-order linear coordinates. We found that the kinetics of petroleum product sorption by vermiculite is most adequately described by a second-order kinetics model (correlation coefficient 0.99), indicating an ion-exchange adsorption process. The article describes the processes of external and internal mass transfer of petroleum products in the presence of vermiculite obtained under different conditions. When treating the sorption kinetics in Boyd-Adamson coordinates we found the proceeding of adsorption process at inward diffusion regime. The obtained curves of dependence of the sorption capacity of the sorbent on the initial concentration are type I curves and are characteristic for the adsorption process proceeding on microporous solids with a relatively small fraction of the outer surface. Since in the treatment of the adsorption curves in linear Langmuir isotherms $R^2 = 0.44$, we performed all further calculations of the sorption characteristics of the process in the linear coordinates of the Freundlich model. The ultimate adsorption value for vermiculite was 0.132 mmol/g sorbent and 0.094 for DBD treated. The value obtained corresponds with the experimental data on the sorption capacity of vermiculite, when adsorbing petroleum products from emulsion under dynamic conditions. The maximum degree of recovery of petroleum products from the solution by vermiculite is 75.5%. The results obtained by linearising the adsorption isotherms of petroleum products on the modified samples in Freundlich isotherm coordinates, as well as the calculated values of the distribution coefficients and the degree of surface filling indicate the fact that adsorption proceeds by a competitive mechanism. In order to improve the properties of the treated vermiculite samples, additional surface hydrophobation, e.g. with organosiloxanes, is required.

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