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# INSTRUMENTATION AND FEATURES OF PRODUCING THE OLEOPHILIC SORBENT ON THE PERLITE BASIS*

**Aleksandr Yudakov[1,2], Tatyana Ksenik[1], Oxana Tsybulskaya[1,2]**, Aleksey Kisel[1]**

*[1]Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences, Vladivostok, Russia*
*[2]Far Eastern Federal University, Vladivostok, Russia*

## Abstract

The results of selection and justification for rational instrumentation of the technological process of producing the oleophilic sorbent on the perlite basis are presented. The description of the laboratory and experimental industrial plants is given. The temperature-time modes of the perlite modification process at all its stages are experimentally substantiated. The properties of the natural and modified perlite were investigated. The representativity of the established modes was proved by testing the pilot batches of the oleophilic sorbent in the course of sorption of oil products under laboratory and real conditions.

*Keywords:* adsorption, hydrophobicity, oil products, perlite, porous structure, sorbent

## 1. Introduction

A problem of the waste water treatment and removal of the technogenic pollutions from the water areas is one of the most important and simultaneously intractable technical environmental targets. The oil contamination of water bodies taking place not far from large cities and populated points constitutes a special hazard. So, the largest petroleum products spill took place during emergency in Norilsk on May 29, 2020. The ecologists consider it as the most substantial ecological catastrophe in the Arctic over the last 130 years. On the TPP territory, the concentrated discharge of a high volume of diesel oil has occurred due to loss of reservoir sealing. About 15 thousand tons of the fuel has appeared in the river and its

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** Corresponding author: e-mail: ont55@mail.ru

tributaries while 6 thousand tones in the ground and the environmental plume grew to over 20 km in length. For treatment of the polluted surfaces at the location of emergency, the sorbents of oil products based on the activated carbon, silica-gel, aluminium oxide, silicon dioxide, different ion exchange resins, turf etc. are used (RIA News, 2020). The use of adsorbents allows us to remove promptly the oil products from the surfaces of water and ground and cut the environmental losses.

It is evident that the expanding volumes of production, frequent accidental instantaneous pollutions of water, strengthening of requirements for water quality necessitate the search of more efficient and economically acceptable sorption materials for purification of water bodies from organic impurities.

The authors of (Tsybulskaya et al., 2019a, 2019b) have the experience of investigations and production of the inexpensive and efficient sorbents by way of thermo-chemical treatment of the surfaces of porous inorganic materials by the non-polar hydrocarbons. However, for the further industrial implementation of the processes of producing and applying these sorbents, the scientifically grounded and specific (including with the consideration of specific features of the raw materials) recommendations are necessary.

For this reason, the objective of this study is the development and experimental verification of the rational instrumentation and modes of the technological process of producing the oleophilic sorbent based on perlite and examination of the physical and chemical properties of sorbent.

## 2. Plant, methods, materials

For laboratory testing and study of operating parameters of the modification process, the laboratory plant of small capacity (Fig. 1) was developed. The working chamber of the plant (autoclave 1) represents the cylindrical vessel made of stainless steel (∅260x250x2 mm) with hermetically-sealed cover. At the bottom of autoclave, the spiral heater 2 with the embedded thermocouple and stand with heat reflector are mounted. In the cover of autoclave, the nozzle for spraying the modifier 3 and vacuum valve 4 are placed. The spraying nozzle is connected by the feeding pipe through valve 5 with measuring container 6 with a volume of 10 $cm^3$.

The raw material (perlite) pre-dried in the chamber drier is set in the autoclave. The vacuuming of autoclave to the residual pressure of 0.2-0.5 atm. is carried out using the vacuum pump through the vacuum valve and filter-separator 7. The control over pressure is exercised by the vacuum manometer. Hereafter, the autoclave is heated to material treatment temperature using the heater 2. For the improvement of fluidity, the modifier (fuel oil, oil) is heated in the preparation vessel 9 which is equipped with the metal clamp heater 10 with the embedded thermocouple. The heated modifier in the calculated quantity (1-2% of raw material mass) is fed to the measuring container through the needle valve from the preparation vessel. The valve 5 opening provides a feed of liquid modifier from the vessel to the working volume of autoclave through the drip injector.

A process of autoclave and modifier heating is controlled by the two-channel meter-controller 11. In the autoclave, the gas phase (working gas) of the modifier forms raising the internal pressure to 1.2-1.3 atm. The working gas penetrates the open pores of the material being treated and forms on the walls of pores the continuous organic film which constructs gradually at the expense of cooling of the autoclave without its depressurizing.

The experiments in producing the sorption material using the laboratory plant allowed us to take on creation of the large-sized experimental industrial plant for producing the oleophilic materials. In Fig. 2, the plant with producing capacity of up to 1$m^3$ in a single cycle of material treatment is presented.

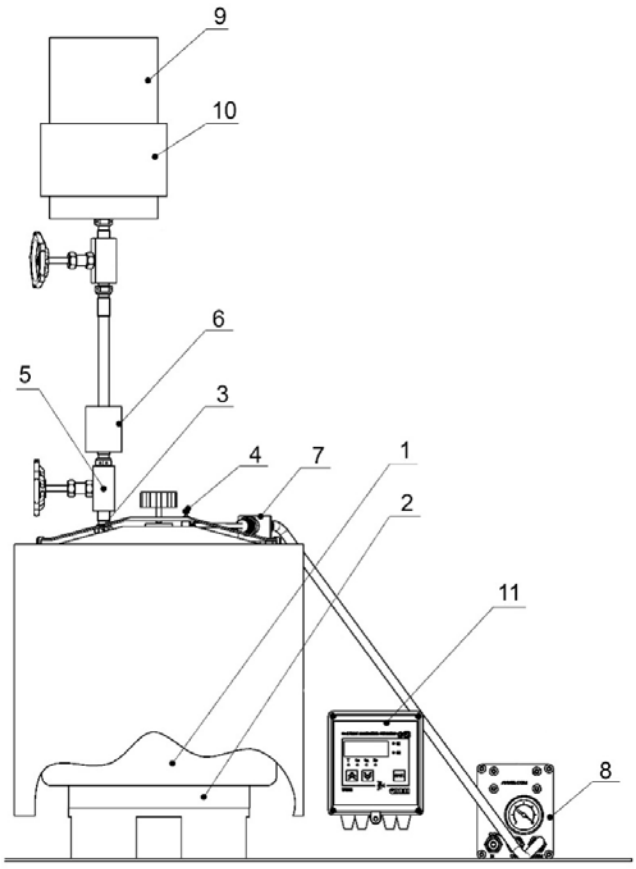


**Fig. 1.** Scheme of laboratory plant for producing the oleophilic materials:
1 – autoclave; 2 – spiral heater; 3 – nozzle; 4, 5 – valve; 6 – measuring container;
7 – filter; 8 – vacuum pump; 9 – vessel for modifier; 10 – clamp heater; 11 – meter-controller

The technological process of raw material processing is realized as follows. The drying and modifying processing are carried out successively in one working chamber. The material in the netted cassette 1 is loaded into the working chamber 3 of the plant using a telpher. The working chamber is pressurized and raw material drying is made by the liquid-fuel burner 4. A removal of water vapor and used heat transfer medium is realized through the output manifold 5. After raw material drying, the depression is created in the receiver with blocked line 8 connecting the working chamber and receiver 7 using the vacuum pump 6. Upon reaching the necessary depression in the receiver, the vacuum pump is cut off and, with the help of check valve 9, the line 8 opens, thereby creating the depression 0.2-0.5 atm. in the working chamber. The previously prepared liquid modifier is fed from the vessel 10 to the heated vacuumized working chamber.

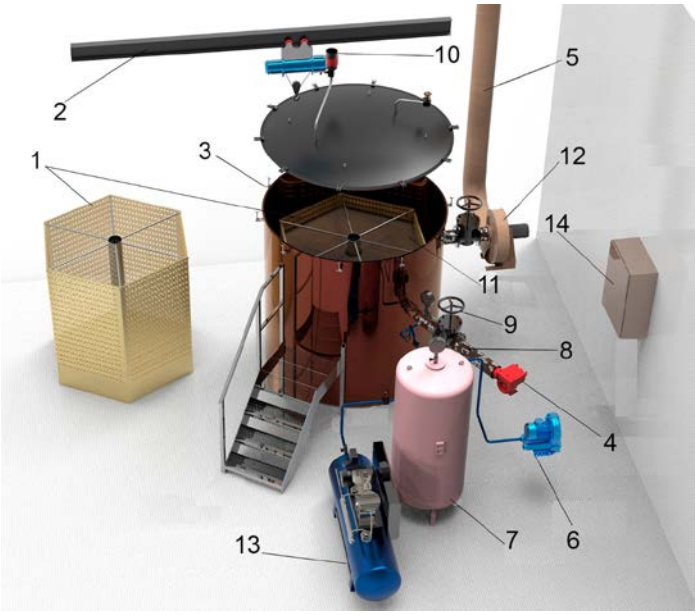


**Fig. 2.** Experimental industrial plant for producing the oleophilic sorbents:
1 – netted cassette; 2 – telpher; 3 – working chamber; 4 – liquid-fuel burner;
5 – output manifold; 6 – vacuum pump; 7 – receiver; 8 – vacuum line;
9 – check valve; 10 – container with heating unit; 11 – raw material (perlite);
12 – fan of hot-gas bleed; 13 – compressor; 14 – control panel

As a result of its evaporation, the increased pressure of gasifying modifier is created in the working chamber. The formation of the oleophilic coating takes place in the course of material cooling without decompression.

For investigation and optimization of the technological modes of producing the oleophilic sorbent on the perlite basis, the samples of the nature alumosilicate – perlite of the Nachikinsky field (Kamchatka Peninsula, Far East of Russia) with the following chemical composition (in % mass) ($SiO_2$ – 68.2; $Al_2O_3$ – 16.83; $Fe_2O_3$ – 0.46; FeO – 0.7; MgO – 0.16; CaO – 0.71; $K_2O$ – 3.18; $Na_2O$ – 3.55; MnO – 0.12; $TiO_2$ – 0.18; $P_2O_5$ – 0.16; $H_2O$ – 1.46) were selected. The basic components forming part and determining the chemical features of the samples' surfaces are predominantly silicon dioxide, aluminum oxide, and potassium and sodium oxides.

## 3. Results and discussion

With the purpose of investigating the raw material characteristics, the physical-chemical studies of the sample of natural perlite were carried out.

The X-ray phase analysis of samples with the use of automatic X-ray diffractometer D8 Advance (Cu – $K_\alpha$-emission) has shown an occurrence of two phases: cristobalite of framework structure and cyanite of isle structure (Fig. 3).

The natural perlite has the branchy mixedly-porous structure and small specific surface. The specific surface of perlite samples computed using the BET method was 9.39 $m^2/g$ while 7.037 $m^2/g$ in case of Greg-Sing method (Perfilyev, 2012) (Perfilyev, 2012). Volume of micropores in the samples is insignificant (0.001 $cm^3/g$). This can point to the fact that meso- and macropores predominate in the perlite samples.

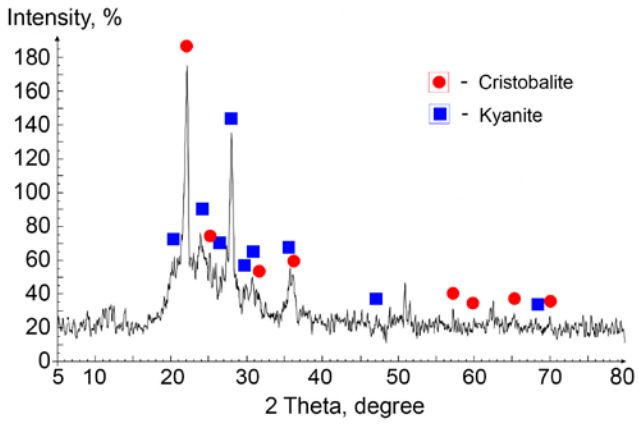


**Fig. 3.** X-ray diffraction pattern of perlite

Total porosity of the perlite samples was determined using the standard technique (ISO 5017:2013, 2013) on the basis of previously measured values of the real and average densities. The porosity was equal to 9.84% vol.

For increasing the specific surface and porosity of the natural perlite and producing the material with developed system of open pores, its thermal modification, i.e. high-temperature treatment (expansion), is necessary. An expansion is the technological operation which consists in the hard firing at which material attains the pyroplastic (plastic-viscous) state and the molecular water is removed from it in the form of vapors as well as other gases ($CO_2$, $O_2$) are evolved. The occurring gases, aiming for exit, expand the particle, i.e. give to it the porous structure. The hydroxyl water is removed from material without destruction of its crystal lattice.

The chemical composition of perlite exerts a significant impact on the expansion process. The presence of alkalies has an effect on the viscosity and surface tension of the softened rock reducing the softening temperature. It is evident that the total content of $Na_2O$ and $K_2O$ in the quantity of 6.73% in the perlite samples from Nachikinsky field will favorably effect on the expansion process.

For the purpose of improving the dynamics of processes taking place when heated perlite, the thermal gravitational analysis of its sample was performed using the derivatograph Q-1500 of F. Paulik, J. Paulik, L. Erdey system. The study was carried out in the open air in platinum crucible at the heating rate of 10°/min to 1000°C (Fig. 4).

An analysis of the thermogram demonstrates that, in case of perlite heating to 580°C, the removal of basic portion of the physically-bounded and hydroxyl water takes place. On the DTA curve, two endothermic effects are observed. The first, vague (with minimum at 330°C) effect was due to dehydration of rocks as a result of evaporation of the physically-bonded water. The second, strongly pronounced (with minimum at 535°C) endoeffect was caused by dehydration as a result of removing the basic mass of hydroxyl water. Total mass loss caused by these processes is 2.30%.

An expansion of perlite samples was carried out in accordance with recommendations of GOST 25226-96. The two-stage mode of thermal modification was chosen, the thermal preparation was preliminarily performed by way of samples' heating at 350°C within 15-20 min. for removal of the excess moisture and, afterwards, the samples were subject to the short-time firing (thermal shock) at 1000 – 1150°C within 30-60 seconds.

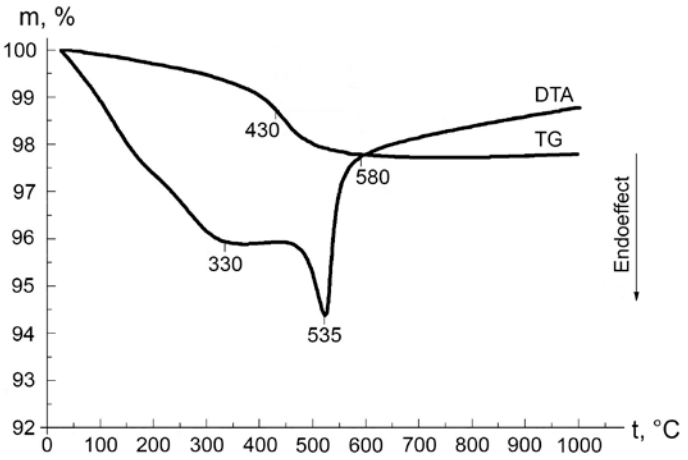


**Fig. 4.** Thermogram of the natural perlite sample

After the perlite samples expansion, their X-ray phase and chemical analyses were performed. The X-ray phase analysis has established the X-ray amorphous character of the structure of all expanded samples of perlite.

The chemical analysis has demonstrated an increase in content of the amorphous $SiO_2$ by 7.41% as well as the redistribution of the contents of other oxides in the composition. The expanded perlite samples were characterized by the following oxides in their compositions (in % mass.): $SiO_2$ – 75.61; $Al_2O_3$ – 12.75; $Fe_2O_3$ – 0.12; FeO – 0.74; MgO – 0.11; CaO – 0.62;$K_2O$ – 4.38; $Na_2O$ – 3.83; MnO – 0.09; $TiO_2$ – 0.12; $P_2O_5$ – 0.1; $H_2O$ – 1.4.

The poured density of the perlite samples after expansion has determined as the ratio of the sample mass to the volume which it occupies. The results are presented in Fig.5.

The optimal values of the poured density (0.18 g/cm$^3$) and, respectively, expansion coefficient were reached after firing of the samples of perlite with the fractional makeup of 3 to 5 mm at 1050°C. The expansion coefficient (extent of increasing the volume of samples) was determined as a ratio of the poured density of sample (g/cm$^3$) before treatment to the poured density after treatment. The dependence is presented in Fig.6.

With rising the firing temperature to 1100÷1150°C, too intensive gas generation and removal of gases from the rocks occur while the sufficient softening of vitreous mass of perlite was not yet reached. For this reason, a partial rock shattering can take place which is accompanied by the decrease in the popping (expansion) coefficient. With increase in fraction of the original perlite, the value of the expansion coefficient rises.

The porosity of perlite after firing has increased 5-10 times (for different conditions of treatment) and reached maximum value of 97% vol. for the expanded perlite samples.

Consequently, after the thermal modification of perlite, the developed porous structure of samples is formed which created the favorable conditions for their thermo-chemical modification and producing the oleophilic materials.

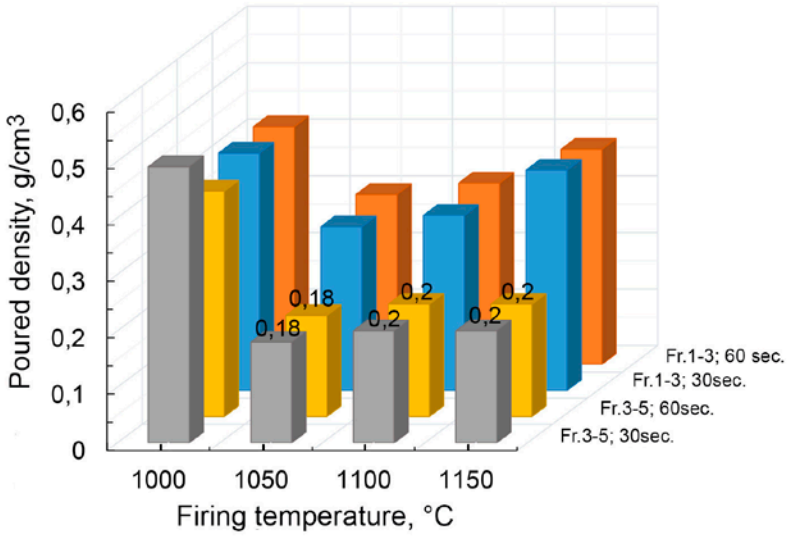


**Fig. 5.** Poured density of the expanded perlite

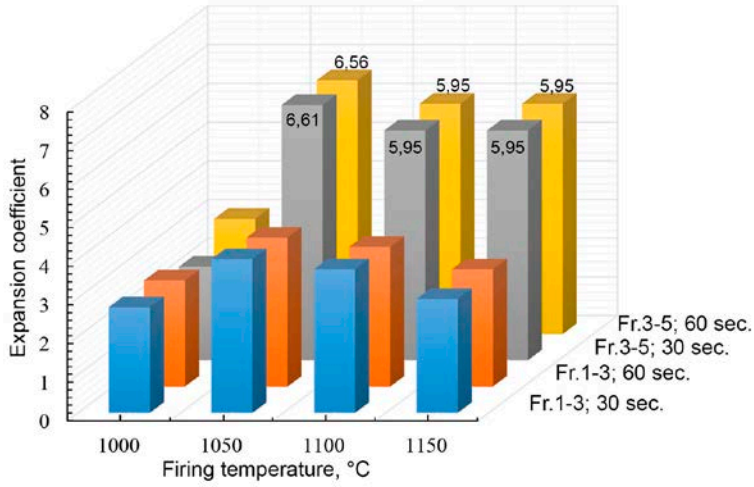


**Fig. 6.** Dependence of perlite expansion on temperature at different values of fraction composition and firing time

For carrying out the thermo-chemical modifying treatment in the experimental industrial plant presented in Fig. 2, the perlite samples characterized by the largest expansion coefficients (6.61) (after firing at 1050°C within 30 sec) were selected.

The essential characteristic of obtained sorbents is the amount of modifier on the surface of particle. Experience has shown that an increase in the modifier consumption to 1.5% mass. is accompanied by increase in mass of fixed substance on the surface of the perlite particles while the further increase in consumption has no a strong effect on increment of sample mass. The optimum consumption of the modifier per unit mass of the expanded perlite was 1-2% mass.

The optimal modes of the technological process were experimentally established. The high-temperature drying is made at 400-450°C within 15-30 minutes with the purpose of

dehydration and preparation of the surfaces of open pores for application of the oleophilic coating. On termination of drying, the working chamber is pressurized and vacuumized to 0.2-0.5 atm. The feed of the modifier is provided and, for this purpose, the fuel oil, diesel fuel and technical oil are used. In the working chamber, the excessive pressure of the gasified modifier is generated. The gasified modifier penetrates the open pores of the perlite granules and forms the continuous organic film on the pore walls. Consequently, the oleophilic coating is formed at the expense of the processes of the chemical and physical adsorption of hydrocarbon compounds from the gaseous environment in the course of material cooling without decompression of the working chamber.

After carrying out the modifying treatment, the characteristics of the produced sorbent were examined.

The investigation of the obtained perlite samples for buoyancy has shown that all samples, due to low poured density, stand at the water surface in the saturated with oil product state within 96 hours which allows to ascribe them to the adsorbents of high buoyancy. The contact angle of wetting for different samples has varied from 89 to 102°.

The water absorption of the oleophilic perlite under static conditions with regard to distilled water was determined as the ratio of mass of water contained in the sample to mass of dry sample. After 48 hours of exposition, the water absorption of the expanded and oleophilic perlite was 75% mass. and 12.5% mass. respectively.

For determining the oil capacity of the natural and modified perlite, the samples were exposed in touch with oil product within 24 hours. The oil capacity in g/g was computed from difference of masses of initial sample and sample saturated with oil product.

The results of comparative investigations of the natural and oleophilic samples of perlite for different types of oil products are presented in Table 1.

As a result of the surface modification, the adsorption capacity of the oleophilic perlite increases by a mean of 72% in comparison with the expanded one.

The adsorption of oil products from aqueous solutions depends not only on properties of the sorbent itself and oil product absorbed by it but also on environmental effects such as temperature, time, pH of environment, pressure and depression. For assessment of external influence, the kinetics of adsorption was investigated using the samples of oleophilic perlite at temperatures of 25°C and 80°C and environmental pH of 6.72. As the simulative oil product, the fuel oil of M-100 grade was used. This fuel oil was applied on the water surface and, afterwards, the fuel oil is covered with the sorbent layer.

At definite time intervals, the sorbent was withdrawn and weighted. The first measurements were performed within 20 min. after beginning of tests. The curves of the sorption kinetics (Fig. 7) show that in 20 minutes the adsorptive saturation is 0.487 g/g for perlite sample at 80°C. The equilibrium in the system is more quickly attained at 25°C (within 120 min.). However, the maximum value of saturation (0.497 g/g) is reached at 80°C in 240 minutes after the beginning of tests.

The measurement of oil products concentration in the water was carried out by method of the IR-spectrophotometry using the concentration meter KN-2m (PEP "Sibekopribor", Russia), the results are presented in Fig. 8.

**Table 1**. Adsorption capacity of perlite samples

| *Perlite sample* | *Adsorption capacity, g/g* | | | |
|---|---|---|---|---|
| | *by fuel oil (MDO; ISO 8217: 2017)* | *by diesel fuel* | *by engine oil (SAE 20)* | *by industrial oil* |
| Natural | 0.01 | 0.01 | 0.01 | 0.01 |
| Expanded | 1.8 | 1.71 | 0.60 | 0.38 |
| Modified | 2.33 | 1.94 | 2.20 | 1.25 |

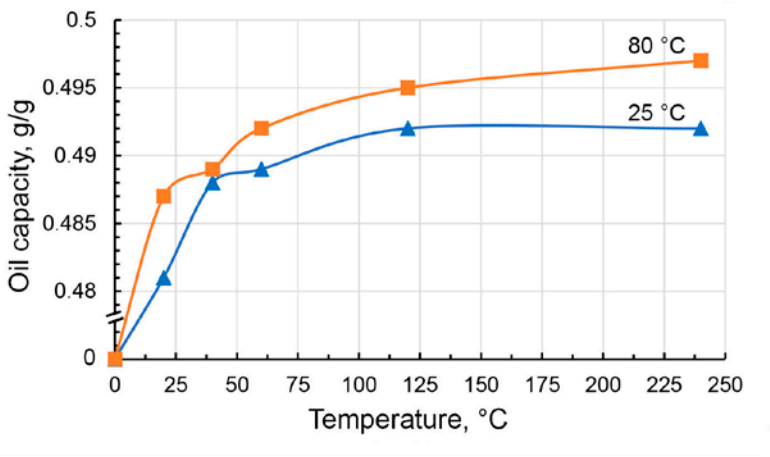


**Fig. 7.** Kinetics of adsorption by the samples
of oleophilic perlite at different environmental temperatures

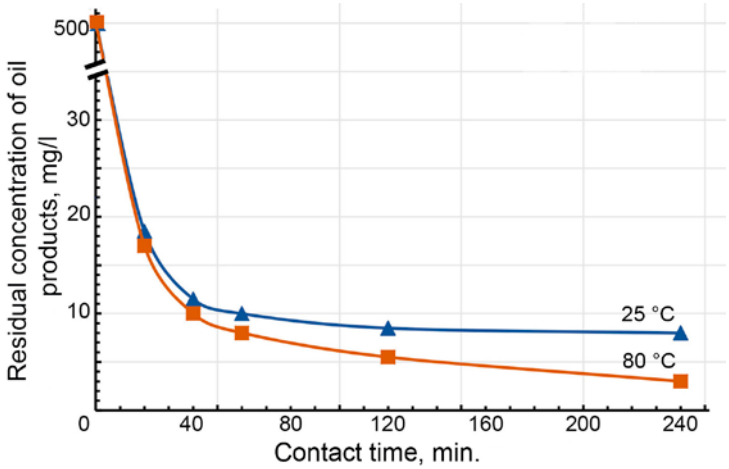


**Fig. 8.** Reduction in concentration of oil product in case of adsorption on the samples of oleophilic perlite at different temperatures

A graph of reduction in oil product concentration in the water demonstrates that the highest extent of purification (99.47%) is reached at the higher environment temperature. The concentration of fuel oil in the water has decreased from 500 mg/l to 2.64 mg/l within 240 min.

As a result, the examination of the physical and chemical characteristics of the oleophilic perlite shows that the obtained material is characterized by low poured density, high porosity, developed surface, buoyancy, low water absorption and satisfactory sorption capacity with regard to the oil products. It should also be noted that the spent sorbent can be refreshed in the developed plant by way of its firing at 500°C and subsequent modification. The technological modes (regimes) of producing the oleohilic sorbent based on perlite from the Nachikinsky field were determined (Fig. 9).

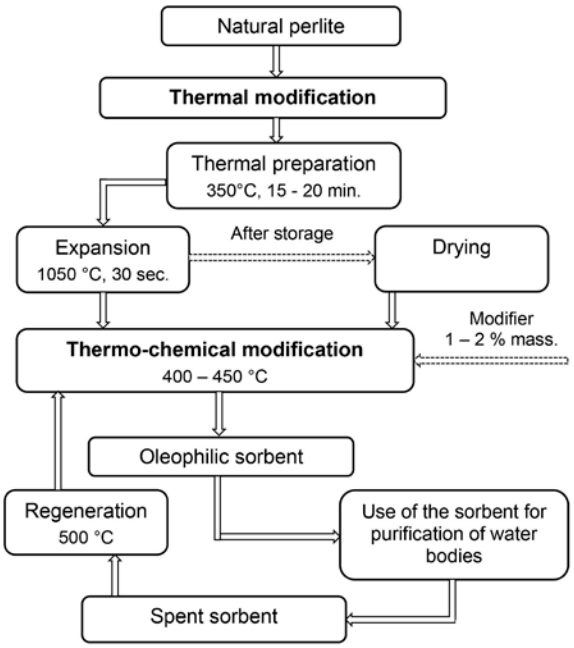


**Fig. 9.** Technological scheme of producing the oleophilic sorbent based on natural perlite

## 4. Conclusions

Hence, the experimental studies have demonstrated that the proposed technological scheme and instrumentation of the process allow us to produce a sorbent on the basis of expanded perlite. The oleophilic sorbent based of perlite satisfies all requirements specified to the sorbents for waste water treatment as well as for recovery of spilled oil products. It should be noted that the accessibility of raw materials, simplicity of the sorbent production technology and possibility of its regeneration make the developed method of sorbent producing technologically attractive. The practicability of the developed technological modes of producing the oleophilic sorbent was proved by production and successful tests of the experimental batches for purification of water from oil products in actual practice.

The results obtained allow us to realize such technologies in all enterprises interested in the production and application of such sorbents.

**Acknowledgements**
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## References

ISO 5017:2013, (2013), Dense shaped refractory products – Determination of bulk density, apparent porosity and true porosity, International Organization for Standardization, ISO 5017:2013, On line at: https://www.iso.org/obp/ui/#iso:std:iso:5017:ed-3:v1:en.

Perfilyev A., (2012), *Production and properties of the organo-mineral hydrophobic adsorbents on the basis of nature aluminosilicates*, Ph.D. thesis in Chemistry Science, (in Russian), Institute of Chemistry Far Eastern Branch, RAS, Vladivostok.

RIA News, (2020), In Norilsk, about 33 thousands square meters of the ground were treated with sorbent, (in Russian), *RIA Newswire*, https://ria.ru/20200609/1572674562.html.

Tsybulskaya O.N., Ksenik T.V., Yudakov A.A., Kisel A.A., (2019a), Development of technology of producing the hydrophobic aluminosilicate sorbents for cleaning of water objects from organic pollutions, *Procedia Environmental Science, Engineering and Management*, **6**, 535-545.

Tsybulskaya O.N., Ksenik T.V., Yudakov A.A., Kisel A.A., Volkov D., (2019b), Method for producing the hydrophobic materials, Patent of Russian Federation 2681017, (in Russian), Vladivostok, Russia.