

APPLICATION OF INTERCALARY SORBENTS AND TECHNOLOGY OF THEIR EXTRACTION

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ABSTRACT

In the study, a solution containing Al₁₃ polycation was prepared by hydrolysis of aluminium chloride. AlCl₃·6H₂O was added dropwise to the solution at room temperature until NaOH [OH⁻]/[Al³⁺]=2,4 at pH 4. 3-4. 7. The solution was then incubated at 60 °C for 24 h to form the Al₁₃ polyhydroxycomplex. Al₃₀ polycation solution was obtained by hydrothermal processing according to the recipe, Al₁₃ preservative was soaked in the solution for 5 hours at a temperature of 115 °C. The molar ratio of Al₂(OH)₅Cl and FeCl₃·6H₂O in a solution mixture of high-volume Al/Fe polyhydroxycomplex solutions in a high-pressure reactor (at 135 °C for 20 hours) by hydrothermal processing is Al: Fe = 15. With respect to Al³⁺, the concentration of the solution (x) is x = 2, 5, 3, 7, 4, 3, 5, 1M (in the case of x > 6M a precipitate is formed). 20 g of bentonite was immersed in 1 litre of distilled water and after 24 h the top layer of the suspension was centrifuged. The separated MM (montmorillonite) fraction particles were dried at 60 with an average size of 2 μm. MM Al₁₃, Al₃₀, and Al/Fe polyhydroxycomplex intercalation were performed by adding an intercalating solution (3mol Al³⁺ /g MM) by ion exchange in a 1% aqueous suspension using a strong magnesium agitator for 2 h at 80 °C. After 12 h, the suspension was washed with Cl⁻ ions at room temperature. Alkaline and Al/Fe polyhydroxycomplex intercalation were performed by ion exchange in a 1% aqueous suspension by adding an intercalating solution (3mol Al³⁺ /g MM) and using a powerful magnesium agitator for 2 h at 80 °C. After 12 h, the suspension was washed with Cl⁻ ions at room temperature. Intercalation of Al₃₀ and Al/Fe polyhydroxocomplexes was performed by ion exchange in a 1% aqueous suspension by adding an intercalating solution (3mol Al³⁺/g MM) and using a powerful magnesium agitator at 80 °C for 2 h. After 12 h, the suspension was washed with Cl⁻ ions at room temperature.

KEYWORDS: Bentonite, Kaolin, Intercalation, Technological Scheme.

INTRODUCTION

Active research in the field of targeted synthesis of new highly efficient functional nanostructured materials for various purposes, for example, for use as catalysts, sorbents, dosage form carriers, membranes, composite fillers, ceramics, etc., continues all over the world [1–5]. Catalytic and adsorption processes are almost impossible to implement without the use of materials with a developed nanoporous structure. Oxide materials containing silicon and aluminium, both natural and synthetic, are widely used and are of considerable scientific interest since it is possible to control their porous structure and composition during synthesis and subsequent modification in order to impart the necessary functional properties [6–8]. The modification of aluminosilicates by introducing metals of variable valence makes it possible to use them in redox catalysis, including for solving environmental problems. Catalytic oxidation of organic substances is an effective method for neutralizing gas emissions from wastewater [9–12].

Pillarization is a special case of intercalation, in which inorganic compounds are introduced into the interlayer space. Regardless of particular features, the modification process can be reduced to three main stages: 1) hydrolysis of metal ions with the formation of polynuclear hydroxo complexes (PNHC) - pillaring solution, 2) ion exchange, 3) heat treatment of the modified material. The process of pillaring layered aluminosilicates. In aqueous solutions, montmorillonite swells, and the distance between the aluminosilicate layers increases. The aluminosilicate is placed in a pillaring solution containing polynuclear metal hydroxylations, and the interlayer clay cations are ion-exchanged for larger polynuclear hydroxo complexes. Polyhydroxy complexes are usually obtained by hydrolysis of cations with NaOH solution.

Aim: Development of physicochemical and technological bases for obtaining, modifying and using nanostructured clays for purification and separation of liquid and gaseous media.

EXPERIMENTAL PART

Natural soils from Karnabota kaolin, Kattakurgan and Navbahor bentonite deposits were used as objects of study [15-22].

The solution containing Al_{13} polycation was prepared by hydrolysis of aluminium chloride. $AlCl_3 \cdot 6H_2O$ was added dropwise to the solution at room temperature until $NaOH [OH^-]/[Al^{3+}] = 2.4$ at pH 4.3-4.7. The solution was then precipitated at 60 °C for 24 h, resulting in the formation of Al_{13} polyhydroxycomplex. By the hydrothermal processing method according to the recipe of the solution containing Al_{30} polycation, Al_{13} was obtained from the solution soaked for 5 hours at a temperature of 1150S. The molar ratio of $Al_2(OH)_5Cl$ and $FeCl_3 \cdot 6H_2O$ in a solution mixture of high-volume Al/Fe polyhydroxycomplex solutions in a high-pressure reactor (at 135 °C for 20 hours) by hydrothermal processing is Al: Fe = 15. With respect to Al^{3+} , the concentration of the solution (x) is x = 2.5, 3.7, 4.3, 5.1M (in the case of $x > 6M$ a precipitate is formed).

20 g of bentonite was placed in 1 litre of distilled water and after 24 h the top layer of the suspension was centrifuged. The separated MM (montmorillonite) fraction particles were dried at 60 °C with an average size of 2 μm . MM Al_{13} , Al_{30} , and Al/Fe polyhydroxycomplex intercalation were performed by adding an intercalating solution (3mol Al^{3+}/g MM) by ion exchange in a 1% aqueous suspension using a strong magnesium agitator for 2 h at 80 °C. After 12 h, the suspension was washed with Cl^- ions at room temperature.

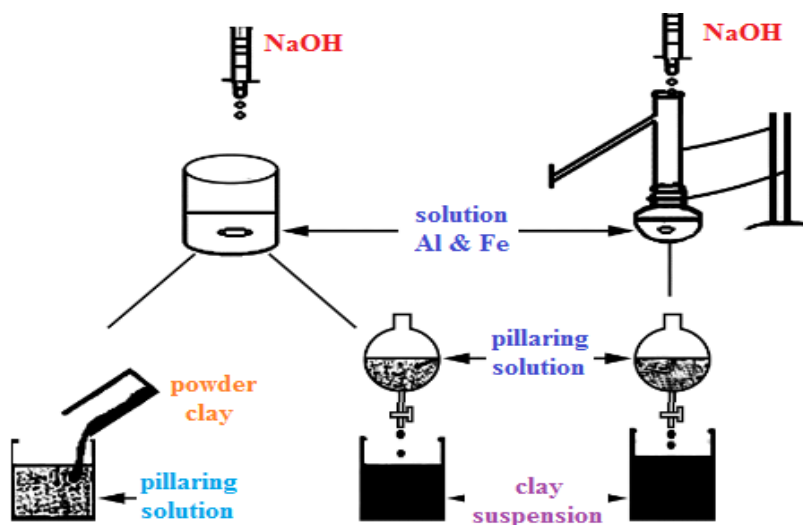


Figure 1. Bentonite intercalation scheme

Methods for testing the adsorption properties. Adsorption experiments were performed as follows: 0.1 g of adsorbent was placed in a 50 mm cylindrical beaker, 20 ml of dye mixture was added to it, and stirred at 20 °C for 15 min to 1440 min at a constant rate of 400 rpm. At the end of the experiment, the adsorbent was separated from the mixture by centrifugation at 8000 rpm for 4 min. The dye concentration in the mixture was studied using a spectrophotometer UF-is U-2001 (“Hitachi”) at the maximum absorption λ wavelength ($\lambda_{\max}=514\text{nm}$ for red acid 17, $\lambda_{\max}=663\text{nm}$ for metallic blue dye). To study the effect of pH on the adsorption process (in the 2.0–13.0 range), the pH was measured using a pH meter by adding HCl (0.1M) or NaOH (0.1M) to the mixture. To obtain the kinetic curve of adsorption, samples were taken from experimental cups at 15, 60, 120, 180, 300, and 1440 min. By analyzing the residual concentration of the dye in the adsorption isotherm, an increase in the content of the dye was obtained in an aqueous solution of 10 to 100 mg/l. The amount of dye in the sample adsorbed during (q_t) is determined from the following equation.

$$q_t = \frac{V(C_0 - C_t)}{m}$$

In this case and (mg/ml) - values of the dye concentration at the initial and t (min) time, V -mixture volume (ml), m - dry adsorbent mass. C_0 and C_t .

Adsorption kinetics. To study the kinetics of the sorption process, the method of adsorption of a solid sorbent in a liquid medium for two well-known kinetic models of mixing anion and cation dyes in water solution MM. The first mode used Lagergren (1 and 3) and the second mode *Ho* and *McKay* (2 and 4):

Nonlinear

$$q_t = q_e (1 - e^{-k_1 t}) \quad (1)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (2)$$

Linear t

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

In this case, q_e - the amount of adsorption dye at a given moment of time in equilibrium and condition; K_1 (min^{-1}) and K_2 ($\text{mg}/(\text{g} \cdot \text{min})$) are the adsorption rate constants of the first and second-order, respectively. q_t, q_e

Adsorption isotherm. The classical interpretations of *Langmyura* (5 and 7) and *Freundlix*a (6 and 8) from the two models of adsorption constants for writing the adsorption isotherm are as follows.

Nonlinear

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

$$q_e = K_F C_e^{1/n} \quad (6)$$

Linear

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (7)$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (8)$$

In this case, the equilibrium of the dye concentration in the Fe-mixture (mg/l); q_m -maximum sorption capacity (mg/g); K_L (mg/g) and Langmuir and Freundlix equilibrium constants; n -heterogeneity factor.

Processing of results. The dynamic adsorption capacity (GV) of water vapour in mg/cm^3 is calculated according to the following formula:

$$\Gamma_v = \frac{(M_2 - M_1 - K)}{(M_1 - M_0)} \cdot \rho, \quad (9)$$

where M_2 is the mass of the adsorber tested with the adsorbent, mg;

M_1 is the mass of the adsorber after regeneration with the adsorbent, mg;

M_0 is the mass of the adsorber without adsorbent, mg;

K - correction for a weight gain of adsorbed moisture, mg;

ρ is the mass density of the adsorbent, mg/cm^3 .

Correction for adsorbed K moisture, mg weight gain is determined by the following formula:

$$K = (M_1 - M_0) \cdot \left(\frac{T - T_1}{T} \right), \quad (10)$$

Where the total time of T-adsorption (from -70 °C to the point of high growth), minutes;
Duration of protective effect up to -70 °C to T1-growth point, minutes.

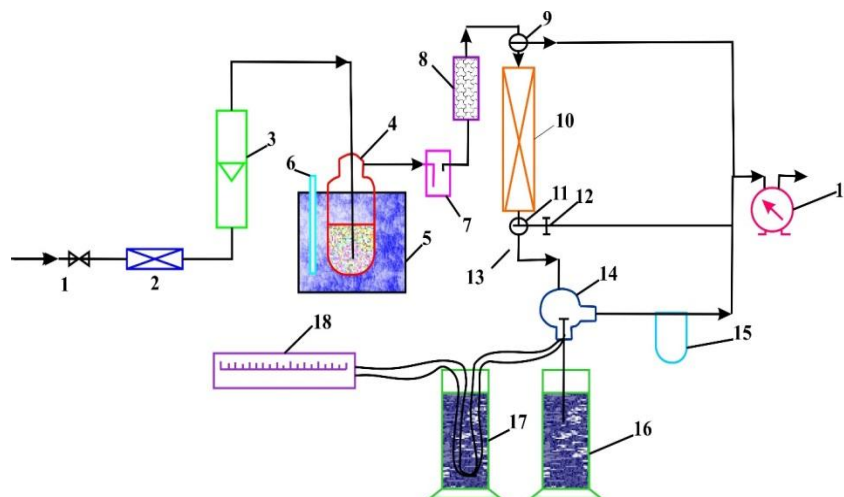


Figure 2. Installation scheme to determine the dynamic adsorption capacity of adsorbents relative to water vapour.

1 - needle valves (ventl); 2 - activated carbon cartridge (cartridge); 3 - rotameter; 4 - Ivitsky tube; 5 - water bath; 6 - thermometer; 7 - trap; 8 - drop separator cartridge (cartridge); 9, 11 - three-way valves (cartridges); 10 - adsorber; 12 - clamp; 13 - copper pipe; 14 - solution flow indicator (EOC) device; 15 - rheometer; 16, 17 - Dewar vessels; 18 - potentiometer; 19 - gas meter.

Dynamic adsorption capacity G for n-heptane vapours, weight% is calculated according to the formula:

$$\Gamma = \frac{\tau_{pr} \cdot Q \cdot C}{G} \cdot 100,$$

where: τ_{pr} - working time of the adsorbent before absorption, hours;

Q is the flow rate of the initial gas mixture, m³/h;

C is the amount of n-heptane in the gas mixture, g/m³;

G is the mass of adsorbent loaded on the adsorber, g;

Conversion factor at 100%.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

The amount of minerals in the studied samples was determined by the intensity of the spectra on the reflex radiograph. The results obtained are presented in Table 1. All studied samples consist of montmorillonite-kaolinite-hydraulic soils. The samples studied show that the Karnab parent soil retained more soil minerals in the enriched state (4 samples). The amount of montmorillonite in Kattakurgan and Navbahor soil samples differs 2 times from natural and enriched ones.

Coallinite and hydro slide are 1. 5 times different. The quartz reflex is clearly visible on the radiograph.

TABLE 1. THE INTENSITY OF X-RAY REFLEXES IN SOIL ORE

Soils	Absolute intensity of reflex, mm					
	Soil minerals			Mixed minerals		
	montmorillonite d-14. 73-14. 56Å	Kaollinite d-7,20- 7,15Å	Hydrosluda d-2. 98Å	Quartz d-3. 34Å	Orthoclase d-3. 20-3. 18Å	Muscovite d-2. 35-2. 34Å
Garnab parent soil						
Natural 1-sample	187	86	44	208	24	-
Enriched 4-sample	191	90	37	93	22	-
Kattakurgan soil						
Natural 2-sample	65	49	35	229	62	-
Enriched 5-sample	158	60	40	217	21	-
Navbahor soil						
Natural 3-sample	67	35	25	318	52	27
Enriched 6-sample	152	62	33	310	41	26

Due to the high content of montmorillonite in the Karnabota soil (sample 4) from the studied natural soils, it was recommended to prepare sorbents and catalysts in them.

The structure of natural soils and the adsorption of modification samples based on them were studied at low temperatures (nitrogen 77K). The presence of hysteresis in the isotherm of natural soils (Fig. 3), i. e. , the presence of a capillary-condensation ring, is a process specific to sorbents.

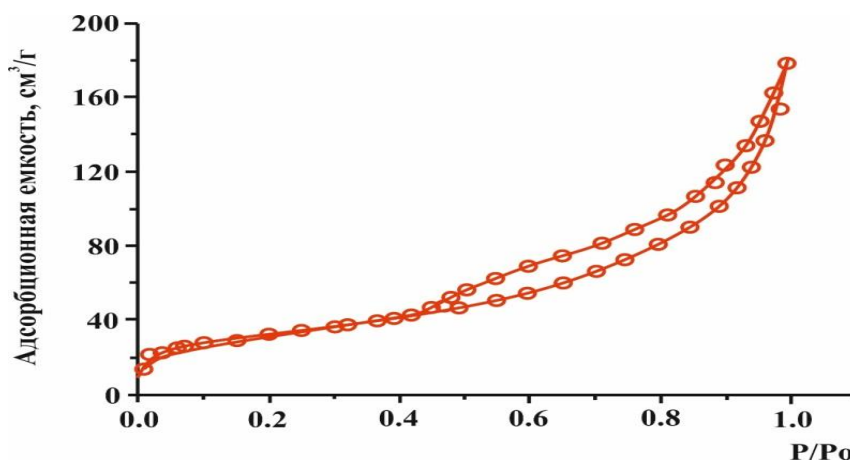


Figure 3. Nitrogen adsorption isotherm in natural soil dried at 110 °C

The hysteresis ring shape belongs to type V and is characteristic of the de Boer classification, which indicates the presence of fissured and flat parallel ores in the soil. The formation of cracks also indicates the presence of a desorption network. Isothermal R/R₀ is close to 1, indicating a sharp rise in the sorption curve. One process also shows the presence of large pores in the soil, i. e. montmorillonite.

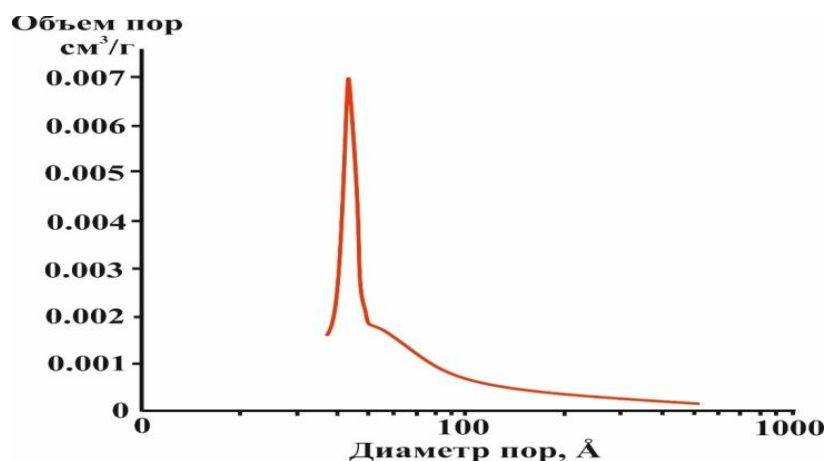


Figure 4. Distribution curve depending on the dimensions of natural soil samples shown at 110 °C

IR spectroscopy also provides information about the structural changes that occur below (Figure 5). Absorption full bands (p. p.) in natural soil IR spectra, this MM. It is a characteristic feature of the structure. 1090 and 1044 cm⁻¹ p. p. corresponds to the valence oscillations characteristic of silicon-oxygen tetrahedra. 580, 425, and 340 cm⁻¹ area p. p. belong to the deformation oscillations in the silicon-oxygen tetrahedron and the aluminium oxygen octahedron.

Comparing the absorption spectra of natural soil and Na-soil, it was observed that for exchangeable cations and sodium cations, 1090 and 1044cm⁻¹ yu. p. the intensity of the silicon-oxygen tetrahedron layer corresponding to the valence oscillation changes significantly (Fig. 5, Spectrum 2). Deformation vibrations in the 580, 425, and 340cm⁻¹ silicon-oxygen tetrahedrons and aluminium oxygen octahedron bands are eliminated and sharply reduced. Such changes in the IR spectrum are associated with structural changes in the tetrahedral and octahedral montmorillonite layer.

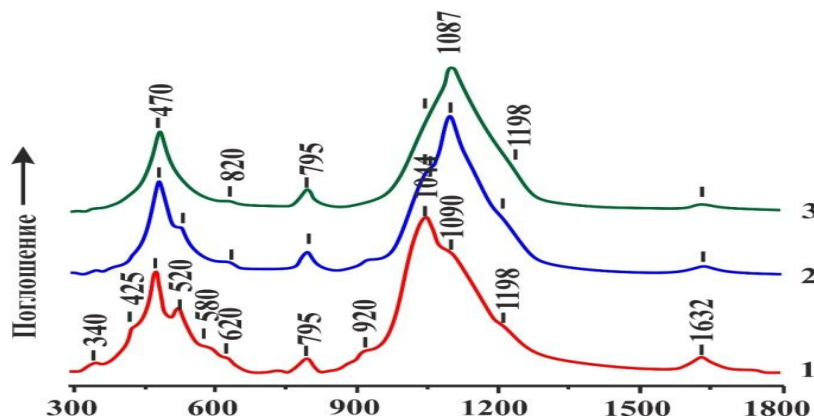


Figure 5. IR spectra of 1-natural soil, 2-Na-soil, 3-Al-soil-1 soils.

An aluminium polyhydroxycomplex is incorporated into the soil, and partial disruption of its structure (Fig. 5, Spectrum 3) can be seen as a maximum shift of the spectra from 1044cm⁻¹ to 1097cm⁻¹. Uznda yu. p. the intensity changes dramatically. It is known that the modification MM disrupts the periodicity of irregular shifts relative to each other in three-layer packages and the breakage of joints in three-layer packages.

Figure 6 shows a diffractogram of a Fe-soil-k sample obtained by adding iron PGK to natural soil. According to RFA, the modification changes the layer structure of the soil when it is heated to 500 °C. Fe-soil-k passes into a layered structure, which in this literature is called the “house of cards”. The diffractogram results in the disappearance of reflexes corresponding to d001 and the appearance of low-intensity diffusion bands, indicating the formation of irregular silicate layers.

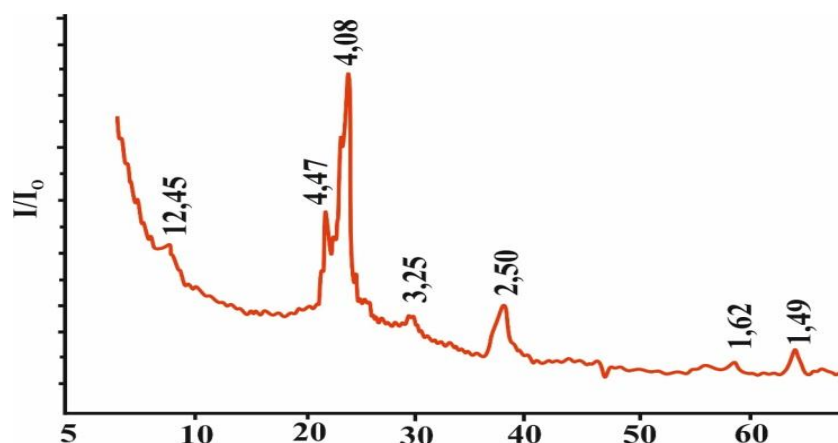
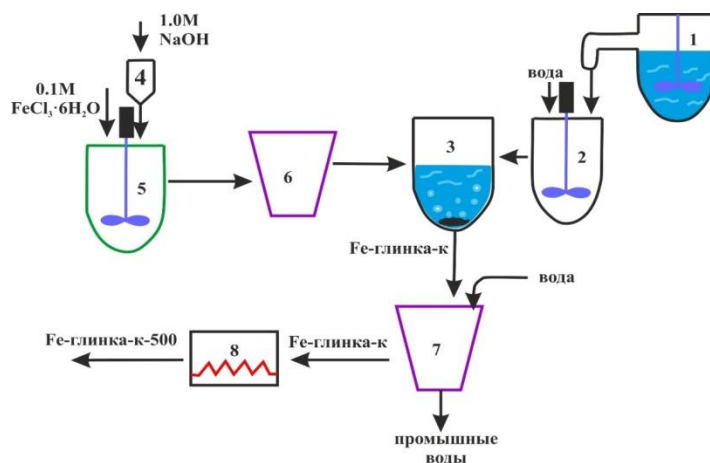


Figure 6. The Fe-soil-k-500 diffraction diagram is given in distances between planes. Å

The results obtained show that the modified specific reference surface, average diameter and ore volume depend on the sampling, polyhydroxylation composition and injection method. Increase in specific surface area in modified samples relative to natural soil. In samples of Al-soil-1, and Fe-soil-0, the average diameters increase less, and in samples of Al-soil-2, Fe-soil-k, Fe-Al-soil-o, Fe-Al-soil-k, it decreases, natural the total volume varies less than the soil.

Fe - soil extraction technology. Soil preparation block 1 Natural soil from the Karnabota deposit contains a fraction of <0.1 μm in size. The pre-washed natural soil is poured into a mixer 2 (Fig. 7), which is filled with water in a ratio of 1:10 = T: J (Q: S) and left to swell at room temperature for 24 hours. The ground suspension is then placed in a 3-mixer and treated with ultrasound at a frequency of 22kGts for 3 minutes.

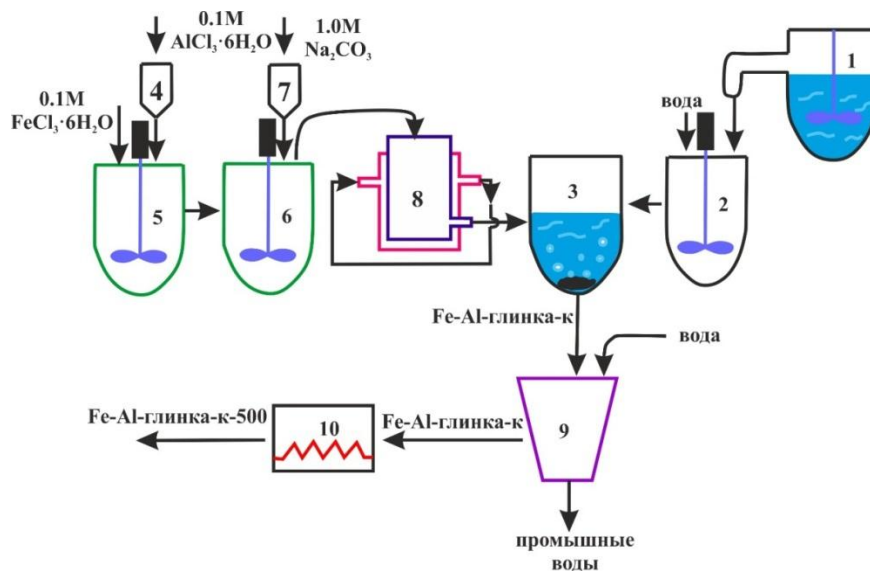
An iron (III) -based chloride mixture is prepared, placed in the 5th mixer and 1 drop of 1,0 M FeCl₃* 6H₂O NaOH is added to the desired concentration from the 4th block. The resulting ash is put on ageing at room temperature for 24 hours. In the hydrolyzed salt of iron, the pH should be around 1.55-1.95. The ash is then added while stirring in a mixer 2 containing the soil suspension. Every 1 kg of soil is filled with 10 litres of ash.



1- soil preparation block, 2- mixer, 3rd mixer, 4- tank, 0

Figure 7. Technological scheme of Fe-soil extraction

Fe - Al - soil extraction technology. The modifying mixture is prepared in a mixer 5, which is removed from the 4th tank by dripping 0,1 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ until it reaches $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. The mixture is then poured into a mixer 6 and 0,1M Na_2CO_3 from tank 7 is mixed. The resulting ash is put at room temperature, to wear for 24 hours. The pH value should be around 4. 00-4. 05. The resulting mixture is then poured into thermostat 8 and allowed to wear for 4 hours at 120 °C and 36 hours at 95 °C. Then the prepared ash is poured into the 2nd mixer with the soil suspension in it, stirring constantly. 10l ash is added to 1kg of soil.



1- soil preparation block, 2- mixer, 3rd mixer, 4- tank, 5. 6-mixer, 7- tank, 8- thermostat, 9th chloride ion washing capacity, 10th oven

Figure 8. Technological scheme of obtaining Fe-Al-soils

Two-stage treatment technology for wastewater treatment.

The two-stage adsorption-catalyst technological scheme of purification of polluted water from organic dyes and SAM is based on sorbents and catalysts obtained from natural soils and iron polyhydroxycomplex, mixed polyhydroxycomplex aluminium experiments.

The high efficiency of this technology has been proven in many experiments, for example, the results of dyeing wool products have been well tested in the scientific laboratory of the East Siberian University of Technology. The training experience of processing this in mixed models in test paints and SAMs was in combo "EKOM". The results show that the oxidation in organic dyes and SAM proves that the catalysts obtained in the future in this technological process have great potential.

REFERENCES

1. Gil, A., Korili, S. A., & Vicente, M. A. (2008). Recent advances in the control and characterization of the porous structure of pillared clay catalysts. *Catalysis Reviews*, 50(2), 153-221.
2. Guerra, D. L., Airoidi, C., Lemos, V. P., & Angélica, R. S. (2008). Adsorptive, thermodynamic and kinetic performances of Al/Ti and Al/Zr-pillared clays from the Brazilian Amazon region for zinc cation removal. *Journal of Hazardous Materials*, 155(1-2), 230-242.
3. McCauley, J. R. (1988). Stable intercalated clays and preparation method: Int. Pat. Appl. PCT/US88/O0567.
4. Наседкин, В. В., & Ширинзаде, Н. А. (2008). Даш-Салахлинское месторождение бентонита. С. 85.
5. Zhu, H. Y., & Ma, Q. (1999). Influence of heat treatments on the pore and adsorption characteristics of sodium doped alumina pillared bentonite. *Journal of Porous Materials*, 6(2), 135-142.
6. Al-Qunaibit, M., & Al Juhaiman, L. (2012). Mechanical modification of Khulays clay; structural and textural effects. *Int. J. Basic Applied Sciences*, 12(6), 205-209.
7. Dunaev, A. M., Motalov, V. B., & Kudin, L. S. (2015). The method of high-temperature mass spectrometry for determining the work function of the electron of ionic crystals: triiodides of lanthanum, cerium and praseodymium. *Russian Chemical Journal*, 59(1-2), 85-91.
8. Lagergren, S. (1898). To the theory of so-called adsorption released substances. *The Royal Swedish Academy of Sciences. Acts*, 24, 1-39.
9. Ho, Y. S., & McKay, G. (1998). Sorption of dye from aqueous solution by peat. *Chemical engineering journal*, 70(2), 115-124.
10. Butman, M. F., Belozerov, A. G., Karasev, N. S., Kochkina, N. E., Khodov, I. A., & Ovchinnikov, N. L. (2015). Structural and textural properties of pillared montmorillonite upon intercalation of large-sized Al- and Al/Ce-polyhydroxo complexes. *Russian Nanotechnologies*, 10(9-10), 36-41.

11. Butman, M. F., Ovchinnikov, N. L., & Karasev, N. S. (2017). Electrical conductivity of Li+-doped pillared montmorillonite. *News of higher educational institutions. Chemistry and Chemical Technology*, 60(9), 82-91.
12. Butman, M. F., Karasev, N. S., Ovchinnikov, N. L., & Vinogradov, A. V. (2019). Al30-pillar montmorillonite with improved textural properties due to pre-machining. *Izvestiya Vysshikh Uchebnykh Zavedenii. Seriya Khimiya i Khimicheskaya Tekhnologiya*, 62(12).
13. Motalov, V. B., Karasev, N. S., Ovchinnikov, N. L., & Butman, M. F. (2017). Thermal emission of alkali metal ions from Al30-pillared montmorillonite studied by mass spectrometric method. *Journal of Analytical Methods in Chemistry*, 2017.
14. Butman, M. F., Ovchinnikov, N. L., Karasev, N. S., Kapinos, A. P., Belozerov, A. G., & Kochkina, N. E. (2017). Adsorption of anionic and cationic dyes on pillar montmorillonite. *Surface Physicochemistry and Materials Protection*, 53 (4), 361-367.
15. Mamadoliev, I. I., Khalikov, K. M., & Fayzullaev, N. I. (2020). Synthesis of high silicon of zeolites and their sorption properties. *International Journal of Control and Automation*, 13(2), 703-709.
16. Mamadoliev, I. I., & Fayzullaev, N. I. (2020). Optimization of the activation conditions of high silicon zeolite. *International Journal of Advanced Science and Technology*, 29(3), 6807-6813.
17. Ibodullayevich, F. N., Yunusovna, B. S., & Anvarovna, X. D. (2020). Physico-chemical and texture characteristics of Zn-Zr/VKTS catalyst. *Journal of Critical Reviews*, 7(7), 917-920.
18. Omanov, B. S., Fayzullaev, N. I., & Xatamova, M. S. (2020). Vinyl acetate production technology. *International Journal of Advanced Science and Technology*, 29(3), 4923-4930.
19. Fayzullayev, N. I., & Umirzakov, R. R. (2005). To obtain acetone by spontaneous hydration of acetylene. In *ACS National Meeting Book of Abstracts* (pp. PETR-71).
20. Fayzullayev, N. I., Umirzakov, R. R., & Pardaeva, S. B. (2005). Study of acetylating reaction of acetylene by gas chromatographic method. In *ACS National Meeting Book of Abstracts* (pp. PETR-66).
21. Xudoyberdiyevich, X. S., & Murodovich, M. R. (2022). Catalytic Synthesis of Liquid Hydrocarbons. *Eurasian Journal of Engineering and Technology*, 4, 46-54.
22. Aslanov, S. C., Buxorov, A. Q., & Fayzullayev, N. I. (2021). Catalytic synthesis of C₂-C₄-alkenes from dimethyl ether. *arXiv preprint arXiv:2104.03173*.