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APPLYING OF DOMESTIC ALUMINOSILICATE MATERIALS FOR PURIFICATION OF MUSTARD OIL BY SORPTION

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Abstract. *On the basis of X-ray phase analysis data we identified the main structural elements of the solid phase of domestic aluminosilicates of different colours used for the purification of mustard oil by sorption. Also we defined these materials fractional and particle size distribution and realized 60-80% of their particles are 0.3-2.5 μm in size. The study reveals the important role of rock-forming fractions kaolinite and montmorillonite (up to 15%), high dispersion and moderately alkaline surface (pH of 1% aqueous dispersion ≈ 8.40-8.43) of aluminosilicate materials by LLC "PolyServis-M" (Moscow) in oil neutralization and bleaching. By the experiment results introduction of these domestic materials into mustard oil prevents its oxidation.*

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Introduction

Natural aluminosilicates - kaolins, their analogs [1, 2], etc., having Lewis and Brønsted centres on the surface [3-5], are widely used for purification of vegetable oils from impurity ingredients [6] as well as separation of heavy metal cations from waste water.

Both natural [5, 7, 8] and modified [9-11] aluminosilicate materials exhibit enhanced adsorption properties towards compounds of inorganic and organic nature present in various media. The results related to the production of domestic materials based on pilled montmorillonite with a high specific surface area and an impressive total pore volume [12]. On the other hand, it must be considered that there is a strong tendency in the oil industry to use imported and generally expensive aluminosilicate materials, which leads to an increase in the cost of the final refining product (refined oil).

The study dwells on the following issues:

- consider the possibility of replacement of imported sorption materials used for vegetable oil purification (Tonsil, Engelhard etc., cost RUB 100-120 thousand-t^{-1}) with cheaper and more

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effective domestic analogues (≤ RUB 20-30-t^{-1}) having similar mineralogical compositions to the foreign ones;

- analysis of quantitative indicators characterizing sorption efficiency using resource-saving technologies and non-deficient domestic aluminosilicate materials [13], the main impurity ingredients (free fatty acids, peroxides and waxy compounds) from vegetable oils produced in Russia and included in the category of vital goods for the population.

Experimental part

Kaolin clay by LLC Research and Production Enterprise "Promyshlennie materialy" (Samara region), as well as domestic sorbents - blue, green, pink and black clays (LLC "PolyServis-M", Moscow) were chosen as research objects for purification of oil-containing media including impurities (free fatty acids, peroxides, waxes).

For purification we used mustard oil produced by CJSC "MARGCOM", the Nizhny Novgorod region, Kstovo (GOST 8807-94).

Kaolin (natural aluminosilicate) is a white powder with various shades of colour. According to Certificate of Quality No. 40 dated 21.07.2004 of LCC Research and Production Enterprise "Promyshlennie materialy"(Samara region); meets the requirements of TU 5729-016-48174985-2003, namely

mass fraction of Fe_2O_3 is not more than 0.02%;
mass fraction of impurities dissolved in HCI is 0.2%;
mass fraction of water-soluble salts is not more than 0.1%;
weight loss on ignition is not more than 13.8%;
mass fraction of moisture is not more than 3.8%;
pH of the 1% aqueous extract is 8.3.

Blue clay, producer LCC "PolyServis-M" (Moscow), TU 9158-003-47308774-00 (natural aluminosilicate) is powder of grey-blue colour; pH of 1% aqueous dispersion is 9.9.

Black clay, producer LCC "PolyServis-M" (Moscow), TU 9158-003-47308774-00 (natural aluminosilicate) is black powder; pH of 1% aqueous dispersion is 8.4.

Pink clay, producer LCC "PolyServis-M" (Moscow), TU 9158-003-47308774-00 (natural aluminosilicate) is powder of pink colour; pH of 1% aqueous dispersion is 8.4.

Green clay, producer LCC "PolyServis-M" (Moscow), TU 9158-003-47308774-00 (natural aluminosilicate) is powder of grey-green colour; pH of 1% aqueous dispersion is 8.9.

Unrefined mustard oil (dark yellow colour); CJSC "MARGCOM", the Nizhny Novgorod region, (GOST 8807-94); is characterized by physico-chemical properties: acid number, mg KOH/g - 0.98 and 2.0 (separate sample for estimation of antioxidant activity); peroxide number, mmol $\frac{1}{2}O_2$-kg^{-1} - 0.15; colour number per 100 ml, mg J2 - 104; wax content, g-kg^{-1} - 4.6;

Ethyl alcohol, GOST R 51652-2000.

Toluene, GOST 5789-51.

Trichloromethane stabilised, TU 2631-066-44493179-01.

0.1 N potassium hydroxide solution (aqueous).

0.01 N sodium thiosulphate solution obtained from crystalline sodium thiosulphate (GOST 244-76).

Ice-cold concentrated acetic acid, "c.p.", GOST 61-75.

Chloroform, GOST 20015-88.

Beeswax is a fat-like substance; it is characterized by physico-chemical properties: acid number, mg KOH - 195; saponification number, mg KOH - 97.8; ether number, mg KOH - 97.2; iodine number, % - 1.06; melting point, K - 351-353; solidification point, K - 349-350; density, g-cm^{-3} at 288 K - 0.94; index of refraction (at 353 K) - 1.4409.

X-ray phase analysis of aluminosilicates

The diffractograms were taken in the region of light scattering angles 2Θ = 10-70° and were compared with the one for kaolin sample. It was previously used for purification of oil-containing media [12, 17].

The complete diffraction profile and wavelength are the input data for X-ray diffraction analysis. At the first stage of analysis we identified the peaks position. The process was based on the maximum $I_{\text{max position.}}$ We calculated the interplanar distances by using the Wolf-Bregg equation. Also we measured the peak intensities and standardized the values obtained. The phases were identified by comparing them with catalogue data (in tables showing interplanar distances for phases, relative intensities as a percentage or fraction of one according to reflex and Miller indices). The experimental diffractogram showed reflexes of a certain interval laying within the specified imaging range (2Θ) at this radiation.

The identification is carried out by distinguishing the 3-5 most intense characteristic peaks of the compound. In such peaks absence we concluded the missing of the phase and tested other compounds.

Determination of grain size distribution and particle size of aluminosilicate materials

The particle size of the imported aluminosilicate materials was determined according to the Instructions for Use of the Fritisx Particle Sizer' analysette 22'; the fixed particle size percentages were estimated taking into account the automatic recording of the linear and integral particle size distribution curves of the fractions.

Treatment of mustard oil at different sorbent rates

We added different aluminosilicate materials of JCB PolyServis-M (Moscow) - pink, blue, green and black clays - in an amount of 0.1-2.0% of oil mass to mustard oil at 20 °C d; stirred the phases during 1 hour with the intensity 80-120 min^{-1}. After 1 hour samples of the treated oil were separated on a filter and the values of the acid, peroxide and colour numbers of the treated oil were measured.

Mustard oil acid number defining

An alcohol-ether mixture is prepared by mixing 2 parts diethyl ether and 1 part ethyl alcohol with 5 drops of phenolphthalein solution added per 50 ml mixture. The mixture is neutralised by 0.1 N KOH alcohol solution until pink colour appearing.

We placed 3-5 g mustard oil (to the second decimal place) into a conical flask, added 50 ml of neutralized solvent mixture, stirred the resulting solution and, while stirring constantly, quickly titrated with 0.1 n alcohol KOH solution until of appearing the slightly pink colour stable for 30 seconds.

The acid number (a.n.) is defined as:

$$\text{a.n.} = 5{,}611\ kv/m, \tag{1}$$

where 5.611 is a coefficient equal to the calculated weight of KOH in 1 cm^3 of 0.1 n. KOH solution. When using NaOH this coefficient is obtained by multiplying the calculated weight of KOH in 1 cm^3 of 0.1 n. solution, (namely 0.4), by 1.4 (56/40, i.e. ratio of molecular weights of KOH and NaOH);

k is a correction to the titre of a 0.1N KOH solution;
v is the volume of 0.1 n KOH solution used for the titration;
m is the weight of the mustard oil sample for analysis, g.

Mustard oil peroxide number defining

The method involves the use of chloroform.

We placed a weighted amount of mustard oil (0.2-1.0 g) into a conical flask. If it is problematic to weigh the flask directly, a sample of oil is weighed in a sample vial and placed in the flask together with the sample.

A flask with the sample is filled with 10 ml of chloroform, the sample is dissolved quickly, 15 ml of glacial acetic acid and 1 ml of a 50-55% KI solution are added. The flask is closed, its content is stirred for 1 min and left for 5 min in the dark place at 288-298 K. Then 75 ml of water is added to the flask, stirred thoroughly and added the starch solution (5 drops) until the appearing of violet-blue colour. The released iodine is titrated with sodium thiosulphate solution ($Na_2S_2O_3$) until the appearing milky white colour stable for 5 seconds.

Control defining (without adding oil to the sample) - carried out in parallel with the main one.

The peroxide value (p.v.) is defined:

$$\text{p. n.} = 100\ (V - V_0)\cdot c/m, \tag{2}$$

in which V is volume of $Na_2S_2O_3$ in the main sample, ml;
V_0 is volume of $Na_2S_2O_3$ in the control sample, ml;
c is the concentration of $Na_2S_2O_3$, mol/l^{-1};
m is the weight of the mustard oil sample for analysis, g.

The resulting peroxide value (p.v.) is expressed in millimoles of active oxygen (mmol ½ O_2) per 1 kg of sample.

To obtain a sodium thiosulphate solution of the required concentrations (0.002 mol/dm^3 and 0.01 mol/dm^3), dilute 0.1 nl before the test. $Na_2S_2O_3$, 50 and 10 times, respectively.

Mustard oil colour value defining

0.26-0.27 g twice resublimed iodine and twiced amount of potassium iodide (0.52-0.54 g KI) are placed into a weighing bottle and dissolved in 10 ml distilled water. The resulting solution is placed into a 250 ml volumetric flask and shaken. The prepared standard solution of iodine has a colour value (c.v.) of 100 mg I_2 and after evaluation of its optical density (relative to distilled water) at λ = 490 nm is used to construct a calibration graph "c.v. - optical density" passing through the zero point on the abscissa and ordinate axes.

The oil is placed in a 20 mm cuvette and the optical density is measured relative to distilled water at λ = 490 nm. The colour indicators corresponding to the measured optical density value are identified according to the graph. It is necessary to define the concentration of the prepared solution of iodine by titration of 0.01 n $Na_2S_2O_3$ solution in presence of starch (iodometric indicator is 1% starch solution).

The starch is prepared as follows: 1 g of the substance is ground in a mortar with 5 ml of distilled water. The mixture is placed into 100 ml of boiling water, boiled for 2-3 minutes and then chilled. The starch solution should give a blue colour with 2 drops of 0.1 n J_2; if the colour turns reddish-brown the solution is unusable.

Defining waxes in mustard oil

The treated oil is poured into a 1 cm cuvette and the optical density is identified by FEC instrument at λ = 490 nm against a sample of oil of waxes were previously isolated by freezing in the refrigerator three times at 277 K. The concentration of waxes in the oil is determined by the calibration curve, which is a relationship of the form $D = f(C_B)$.

Assessment of the antioxidant activity of clays during storage of treated mustard oil

To unrefined mustard oil with a starting a.n. = 2.0 mg KOH/g at 293 K, pink and black clay were added at a material consumption of 10 g-kg^{-1} of clay (PM = 1.0 wt. %) and the phases were stirred with an intensity of 1-2 s^{-1} for 1 h. After 90 days (3 months storage in the container closure system) we separated the samples of the treated oil on a filter and measured a.n. and p.v. of the treated mustard oil.

Results and discussion

The main rock-forming mineral of the comparison sample - kaolin (LCC "Promishlennie materialy", Samara region) is kaolinite $Al_2[Si_2O_5](OH)_4$ (mass content 90-95% wt.); impurity component of kaolin is low-temperature quartz SiO_2 (≤ 5% wt.) (Table 1). At the same time the analysis of diffractograms of samples of other domestic aluminosilicate materials with colour range (blue, pink and black clays, Fig. 1) showed the containing of montmorillonite as rock-forming material: blue clay - 35-40 wt %, black one - not more than 15 wt %, pink one – 5-10 wt % (content is minimum compared with other samples). The latter, however, is kaolinite abandoned (containing 10-15% wt%) among all domestic materials under study. The same native aluminosilicate material includes sufficient amount of saponite $Mg_3(OH)_2[Si_4O_{10}]\cdot nH_2O$ (up to 15% wt.) and maximum amount of β-quartz (65-75% wt.) as compared to other samples. The presence of magnesium and iron (III) cations provides the appropriate colour for this type of material.

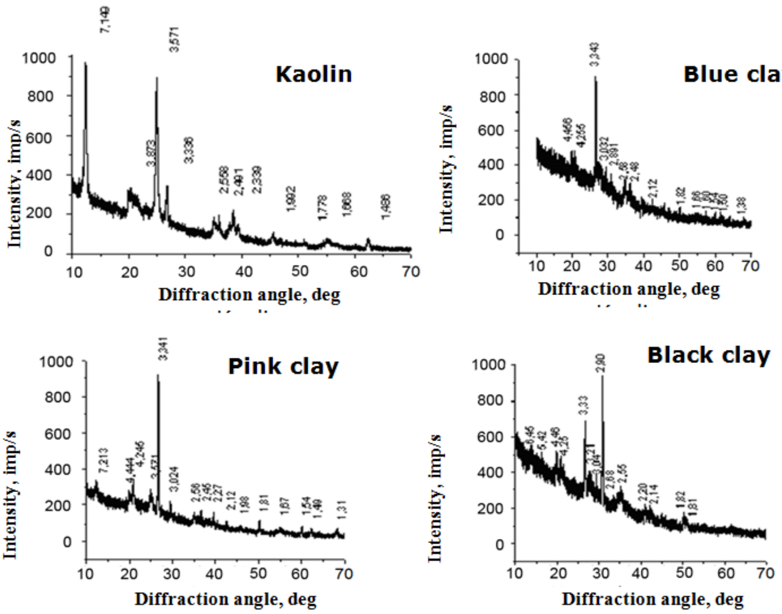

Fig. 1. Diffractograms of clay material samples. Conditions: CuK_α radiation, 40 kV tube voltage, 20 mA current; scanning speed 1 deg/min

The black clay contains significant quantity of hydromica (hydromuscovite content of about 50% wt%) and is apparently abandoned in organic impurities (hydrocarbons). That explains its corresponding colouring.

The blue clay contains β-quartz, montmorillonite, impurities of saponite and hydromica, as well as cobalt and iron (II) cations, in approximately equal proportions (about 6% each).

Table 1. Mineral compositions of domestic aluminosilicate materials in various colours

Sample	Lines	Compliance
Kaolin by LCC Research and Production Enterprise "Promyshlennie materialy"(Samara region) TU 5729-016-48174985-2003	7.149; 3.873; 2.558; 2.491; 2.339; 1.992; 1.778; 1.446	Kaolinite $\mathbf{Al_2[Si_2O_5](OH)_4}$ (90-95%)
	3.338	β-quartz $\mathbf{(SiO_2)}$ (5-0%)
Blue clay by LCC "PolyServis-M" (Moscow)	4.456; 3.343; 1.82; 1.54	β -quartz (SiO_2) (up to 5%)
	4.456; 2.58; 2.48; 2.12; 1.66; 1.60; 1.50; 1.38	Montmorillonite (35-40%) $\mathbf{(Ca, Na)(Mg, Al, Fe)_2(OH)_2[(Si,Al)_4O_{10}]\cdot nH_2O}$
	3.032	Sapovite $Mg_4(OH)_2[Si_4O_{10}]\cdot \mathbf{nH_2O}$ (6-8%)
	2.891	Hydromuscovite (up to 6%) $\mathbf{(K, H_2O)Al_2(OH)_2[(Si_4\ Al)_4O_{10}]\cdot nH_2O}$
Pink clay by LCC "PolyServis-M" (Moscow)	4.245; 3.341; 1.81; 1.54	β -quartz $\mathbf{(SiO_2)}$ (65-75%)
	7.213; 3.024; 2.27; 1.31	Sapovite $\mathbf{Mg_3(OH)_2[Si_4O_{10}]\cdot nH_2O}$ (up to 15%)
	3.571; 2.56; 1.98	Kaolinite $\mathbf{Al_2[Si_2O_5](OH)_4}$ (10-15%)
	4.44; 2.12; 1.67; 1.49	Montmorillonite $\mathbf{(Ca, Na)(Mg, Al, Fe)_2(OH)_2[(Si,Al)_4O_{10}]\cdot nH_2O}$
Black clay by LCC "PolyServis-M" (Moscow)	5.42; 3.21; 3.04; 2.90; 2.55; 2.14	Hydromuscovite $\mathbf{(K, H_2O)Al_2(OH)_2[(Si_4\ Al)_4O_{10}]\cdot nH_2O}$
	4.25; 3.33; 2.68; 2.20; 1.82; 1.81	β -quartz $\mathbf{(SiO_2)}$ (up to 40%)
	6.45; 4.46	Montmorillonite $\mathbf{(Ca, Na)(Mg, Al, Fe)_2(OH)_2[(Si,Al)_4O_{10}]\cdot nH_2O}$

We determined the percentage distribution of blue and pink clay particles by using special sizers and the Fritischer Particle Sizer′ analysette 22′. Analysis of particle size distribution shows the samples of native aluminosilicates the dominant number of particles has a size of 2.5-10.0 μm (Table 2). The black and blue clays are also distinguished by inclusions of fine particles of 0.3-2.5 μm (49.6 and 44.5%, respectively), which probably influences the specific surface area of these materials and affects their sorption properties

Table 2. Percentage distribution of particles by fraction in aluminosilicates

Sample	Dispersion, mkm						
	0,3-1,2	1,2-2,5	2,5-5,0	5-10	10-20	20-30	30-40
Kaolin (reference sample)	3,21	8,84	15,16	23,38	34,77	10,76	3,70
Blue clay	15,06	29,40	25,96	20,87	8,12	0,59	-
Pink clay	7,63	22,20	30,68	30,18	9,31	-	-
Black clay	18,48	31,09	28,21	20,27	1,95	-	-

We made an energy-saving mixing of the solid (pink, black, blue and green clay powders) and liquid phase (mustard oil with a.n. = 0.98 mg KOH) at 298 K and intensity of ≤ 2 s^{-1} for 60 min, varying the low flow rate (PM) between 1-20 g-kg^{-1} oil and then separating the liquid phase from the clay by filtration. The wax compound (WC) content in the untreated oil was fixed (0.5% wt., or 5000 mg kg^{-1} oil): the WC was artificially added to the liquid phase, frozen three times at t = 277 K.

A sample of pink clay (Fig. 2) containing sufficient kaolinite was found to have increased sorption properties against free fatty acids (FFAs) of mustard oil. At 3-5 g kg^{-1} the acid number can be reduced from 0.98 to 0.72 mg KOH (purity of 26.5%). The amount of removed FFAs is $\approx 2.5\cdot10^{-4}$ mol. The other domestic aluminosilicate materials are characterized by the following maximum FFAs release rates:

black clay - $2.0\cdot10^{-4}$ mol FFAs; degree of separation 23.5% at PM = 20 g-kg^{-1};
blue clay - $1.5\cdot10^{-4}$ mol FFAs; degree of separation 15.3% at PM = 20 g-kg^{-1};
green clay - $1.0\cdot10^{-4}$ mol FFAs; degree of separation 13% at PM = 5 g-kg^{-1};

Domestic clay powder materials are ranked by the degree of mustard oil FFAs release as:

$$\underset{\text{increasing of FFAs releasing}}{\underrightarrow{\text{green clay} < \text{blue clay} < \text{black clay} < \text{pink clay}}} \tag{3}$$

For peroxide compounds (PCs) contained in unrefined mustard oil, the dependence of the sorption capacity of these materials as sorbent consumption increases remains similar. The tested domestic materials are ranged in terms of atomic oxygen uptake activity (mol$\cdot10^{-3}$):

$$\underset{\text{the increasing of active oxygen extraction degree.}}{\underrightarrow{\text{blue clay} < \text{black clay} < \text{pink clay.}}} \tag{4}$$

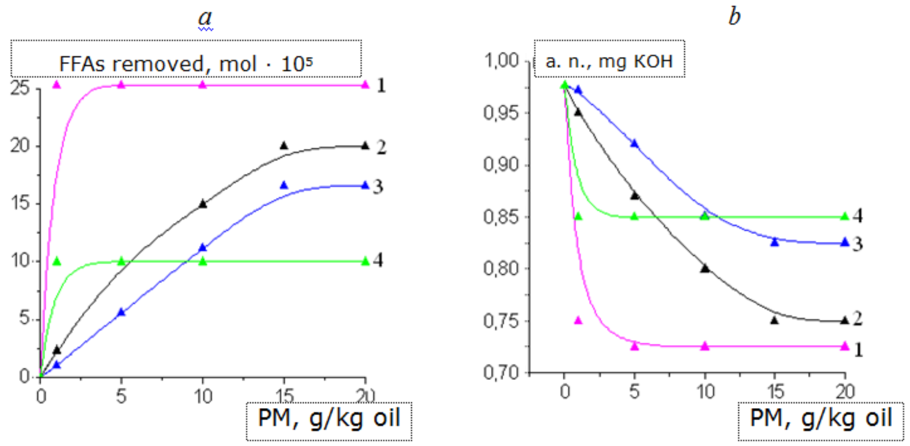

Fig. 2. The native aluminosilicates sorption capacity against free fatty acids of mustard oil (*a)* and change in the acid number of the liquid phase as a function of material consumption (*b*). Conditions: treatment temperature 20 °C, treatment duration 1 hour. Type of domestic aluminosilicate (clay): 1 - pink; 2 - black; 3 - blue; 4 – green

By Fig. 3, the pink clay enables ≈36% peroxides to be extracted from unrefined mustard oil; the p.v. decreases from 0.15 to 0.11 mmol ½ O_2-kg^{-1} already at a low material consumption (1 g-kg^{-1} oil). In this case only green clay cannot compete with other domestic sorbents. No matter of green clay consumption, no more than 10% of the PS can be separated.

But by using a sample of green clay, we obtained the data suggesting a certain degree of affinity of these materials to impurities of a neutral nature - in particular waxes and components of the pigment complex of mustard oil. Thus, while the degree of clarification of domestic green clay in unrefined mustard oil is 9%, for a sample of pink clay it does not exceed 4% (the colour number can be reduced by only 5 units on the iodometric scale). We have to consider it in terms of the surface condition of the sorbent and the pH value of 1% aqueous dispersions of these materials.

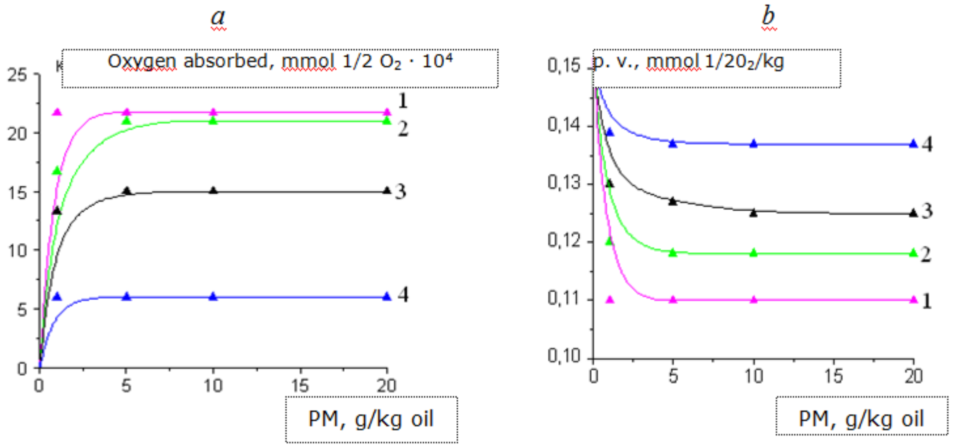

Fig. 3. The native aluminosilicates sorption capacity against peroxide compounds of mustard oil (*a*) and change in the peroxide number of the liquid phase as a function of material consumption (*b*). Conditions: treatment temperature is 293 K, treatment duration is 1 hour. Type of domestic aluminosilicate (clay): 1 - pink; 2 - green; 3 - black 4 – blue

As for the extraction of wax compounds (WC) from mustard oil, all the tested domestic materials have high sorption properties, irrespective of their colour. For example, from 50 g of oil on pink clay, 250 mg WC (i.e. 0.5% impurity of unrefined mustard oil) can be extracted. In samples of black and green clay, these values are 5-8% lower.

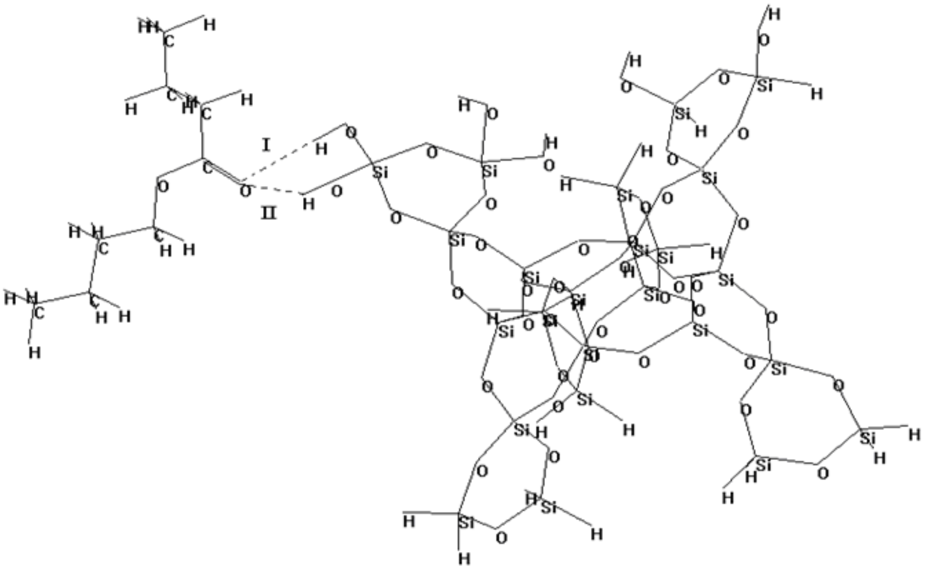

Fig. 4. Scheme of interaction between domestic aluminosilicate and ester waxes component

A positive effect of WC sorption is already achieved at a material consumption of 5 g-kg^{-1}, which is 0.5% of the liquid phase weight.

The data obtained are in agreement with the model of interaction between a typical domestic aluminosilicate material and the ester component of the wax compounds (Fig. 4). On the example of the Volzhskaya silica clay, which has active OH-groups on the surface, it is clearly seen that the interaction involves the end hydrogen atoms of this group and the oxygen atom of the carbonyl of the ester complex component of the WC.

In [14] by semiempirical method PM3 were calculated the lengths of formed hydrogen bonds O...H^1 and O...H^2 (Table 3), which, depending on the empirical number of carbon atoms in the chain, are 2.92-3.09 Å. The presented work is valuable by the discovery of the fact that blue clay has enhanced sorption properties in relation to WC of unrefined mustard oil: its activity level is approximately 20% higher than that of other tested domestic aluminosilicates.

Table 3. Hydrogen bonding parameters for WC-aluminosilicate structure

Number of carbon atoms in the chain	Bond length, Å		Bond valence angle, deg			
	O…H^1	O…H^2	H^1…O=C	H^2…O=C	O…H^1-O^1	O…H^2-O^2
4	3,00	3,04	111,8	127,0	153,0	152,6
9	3,01	3,05	110,9	125,2	153,4	152,5
11	3,01	2,92	105,8	113,6	151,7	155,9
15	3,00	2,90	105,5	112,6	151,4	156,0
18	3,01	2,91	105,4	112,2	151,5	156,3
19	3,03	2,90	104,9	110,9	151,2	159,9
20	3,09	2,92	103,6	107,6	151,1	158,7

The specifics of the interaction between wax molecules and domestic aluminosilicate materials can be simplified by schemes:

waxes (1 molecule) + aluminosilicate material (1 molecule) → complex (1:1); (5)
waxes (2 molecules) + aluminosilicate material (1 molecule) → complex (1:1) + waxes (1 molecule); (6)
waxes (2 molecules) + aluminosilicate material (1 molecule) → complex (2:2). (7)

The extraction of wax compounds from unrefined mustard oil increases the absorption of biologically active ingredients with the ingestion of the oil. This is primarily due to the oil's beneficial impurities - in particular oleic and erucic fatty acids and phytoncides, which have bactericidal, antiviral and immune-stimulating effects The waxes themselves do not have a pronounced negative effect on the organisms.

Conclusions

The possibility of mustard oil energy-intensive refining through the introduction of domestic powder aluminosilicates - pink and black clay containing β-quartz and hydromuscovite fractions with kaolinite, saponite, montmorillonite impurities in the amount of 5-10 g-kg^{-1} oil at mixing the phases for 1 h with the intensity of 1-2 s^{-1} and following phase separation on the filter; characteristic that the process is allowed to perform at room temperature.

The pink clay containing up to 15% kaolinite (exchangeable cation - aluminium) increased sorption properties with respect to free fatty acids and peroxide compounds of mustard oil. With regard to the components of the pigment complex of the oil, green clay has the best brightening capacity (up to 10%). As far as extraction of impurity waxes from the mentioned oil is concerned, all domestic materials of PolyServis-M LCC (Moscow) proved to be excellent regardless of their colour; a high positive effect (≥ 90%) is reached even at a small sorbent consumption rate (5 g-kg^{-1}).

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