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Article

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Development of Methods to Obtain Composite Materials from Organoclays

The paper presents methods to obtain a bionanocomposite from hydrophobic halloysite with bacteridic properties. During the study using TEM analysis, it was established that Karaganda halloysite has a natural nanostructured material and has a cylindrical in shape (halloysite nanotube HNT). It was shown that bactericidal properties of nanoclays are due to exchange reactions between Ag^+ and with active groups of nanoclay, where free H^+ ions are present. The presence of several peaks characteristic of silver was detected by energy-dispersive X-ray spectroscopy, indicating exchange reactions involving silver. The bactericidal properties of silver-modified halloysite were proven using in situ analysis with live bacteria. The observed displacements of interlayer spaces from values of 9.997 Å to 17.51 Å in the diffraction patterns confirmed the successful intercalation of octadecylamine into the nanohalloisite galleries. Such medicinal bionanocomposite materials can be used as carriers of various vitamins and drugs due to their high adsorption properties. A study to obtain bactericidal oleophilic (hydrophobic) bionanocomposites based on Karaganda halloysite was carried out for the first time and it includes the stages of processing halloysite with silver ions and the stage of hydrophobization of bactericidal halloysite.

Keywords: bionanocomposite, halloysite nanoclay, silver clay, bacteridic properties, hydrophobization, organoclay, silver-modified, composite material.

Introduction

Clays are used as bleaching material in the manufacture of fabrics [1]. In the rubber industry, bentonite clays, along with kaolin, are used as an active filler to give hardness to products, increase their acid resistance and strength. In the soap and cosmetics industry, kaolins are used as filler in the production of cheap soap varieties, in the production of powder, makeup, lipstick, tooth powder, paste and other cosmetics [2]. In the food industry, montmorillonite clays are used to purify water and food products (wine, juices, and vegetable oils). In agriculture, clays are effectively used in the production of animal feed, and in soil reclamation. Montmorillonite clays are used in ceramics as a binder in molding mixtures, in the production of iron ore granules, as well as a waterproofing and adsorption material [3]. In medicine, montmorillonite and halloysites are used in the manufacture of medicines, mainly as a binder in tablets, also have applications in cases as adsorbent of harmful substances in stomach diseases (bioadsorber), ulcers, poisoning with alkaloids, etc. [4].

Halloysite is a clay mineral of the subclass of layered silicates consisting of silicon oxide and aluminosilicates, which is not toxic to living organisms and harmless to the environment. The composition is close to kaolinite, which contains a large amount of water. It crystallizes in monoclinic syngony. The mineral halloysite clay is mainly mined in kaolinite deposits and has a multilayer nanotube structure with an outer diameter of about 50 nm – 700 nm and 2 microns in length. It is a tube-packed kaolin, which finds practical applications in ceramics and polymer composites [1], fabric engineering [1, 3], antimicrobial coatings [2, 5], and microvesicle in cosmetology [3, 5]. It is also used to regulate various strength and mechanical properties of drugs and enzymes. This review summarizes the latest data on the structure of halloysite with an insight into its applications in various fields [4].

Currently, methods of creating a variety of drugs and new forms are daily developing [5–9]. Organomodified bionanocomposites from clay minerals were obtained by the authors [6–8] and as an organically modifiers were used cetyltrimethylammonium bromide, but currently cationic surfactants are not always able to give superhydrophobicity to clay minerals [6, 8]. Medicines and forms of a new type can perform several functional in one, and medicines of this type can be in high demand in production facilities and pharmacology. If the drugs are biodegradable with bactericidal properties, have prolonged effect and high ion exchange capacity, which can sorb from a non-aqueous medium, then such an object is a unique drug. In this regard, the development of technology for the production of multifunctional medicines is an urgent problem today [5–7].

The focus of this work was to obtain a biodegradable nanocomposite based on nanotubes halloysite with prolongation and bactericidal properties, as well as a high sorption capacity, which can be used for ion exchange process to absorb harmful ions from the body [6].

Experimental

Materials

The halloysite clay used in this work has been obtained from the Beloye Glinishche deposit of the Karaganda region. It is known that these halloysite clays are by nature hollow nanotubes [5].

Octadecylamine $C_{18}H_{39}N$ (Sigma Aldrich. CAS No 124-30-1, 99 % chemical pure), a surfactant solution, was used to produce the organomodified clay mineral.

Silver nitrate (Sigma Aldrich. CAS No 7761-88-8, 99,9999 % pure) was used to obtain bionanocomposites from clay mineral.

Methods

X-ray diffractometric analysis was carried out on an automated diffractometer Drone-3 with *CuK* radiation and a β-filter under capturing diffractograms conditions of: U = 35 kV; I = 20 mA; θ-2θ capture; detector 2 grad/min. X-ray phase analysis was performed on diffractograms of powder samples using the method of equal suspensions and artificial mixtures on a semi-quantitative basis.

A scanning electron microscope was necessary to obtain acceptable images of at least 2.5 nm in size and to conduct quantitative and qualitative analysis of objects made of nanomaterials. The images were obtained under vacuum using a Quanta 200 3d scanning electron microscope (FEI Company, USA).

The transmission electron microscopy (TEM) method was used to describe the structure of a material, both in the sample size and on its surface. The morphology of the particle shape of HNTs was studied using transmission electron microscopy, TEM-301 Philips (USA) with an accelerating voltage of 80 kV.

Infrared spectroscopy was used to indicate presence surfactants after hydrophobization of clay minerals by ODA.

To measure the contact angle of water drops with the surface of the samples under study, the Goniometer LK-1 (Russia) was used by the sessile drop measurements method.

Chlorides were determined as a result of titration of the analyzed sample and water with silver nitrate in the presence of potassium chromate is used as an indicator [10].

For indicating bactericidal properties of modified clay samples were put on Petri dish the studying samples of clays and 10 ml of distilled water was added on top and mixed well. In a Petri dish, a test culture of *Escherichia coli* was sowed on a flat surface over a nutritious Agar. Then grooves were made on the agar, as in Figure 6, and 0.2 ml of the studied suspension was poured. Grown in a petri dish at 37 °C thermostat at intervals of 3 days. The bactericidal property of Clay can be found if there is inhibit the growth of the bacterium *Escherichia coli*.

Results and Discussion

The main purpose of this study is to develop a method for creating a multifunctional drug — a self-biodegradable and environmentally friendly drug. Thus, the research will be implemented in the following directions:

- introduction of bactericidal properties into the dosage form halloysite nanotube clays;
- organomodification of HNTs;
- checking and achieving prolongation properties of the modified HNSs;
- characterization of the modified HTNSs to investigate if the initial components for the production of biodegradable nanocomposite are achieved through the use of environmentally friendly products. These are clay nanoparticles, silver ions, organoclay nanoparticles.

In this study, silvered halloysite clay and silvered organohalloysite were obtained from the Beloye Glinishche halloysite deposits.

In the Republic of Kazakhstan there are halloysite deposits in two places. They are halloysite of the Beloye Glinishche deposit near the Karaganda city and the Aizin-Tamarskoye halloysite deposit in the Akmola region [10-12]. The main reason for the selection of halloysite from the Beloye Glinishche deposit is that the mineral of this deposit is very finely dispersed and the main composition is halloysite. Chemical formula is $Al_4[Si_4O_{10}][OH]_8 \cdot 4H_2O$ or $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$. The halloysite mineral does not occur in pure state and is mainly found in nature with kaolinite and quartz, as well as a mixture of other aluminosilicate minerals. In order to determine the composition of the Karaganda halloysite mineral, the mineral was washed, ground and micron-sieved in laboratory conditions by decantation to separate the selected deposit from quartz particles and the composition of the resulting powder was characterized by X-ray diffraction analysis as shown in Figure 1.

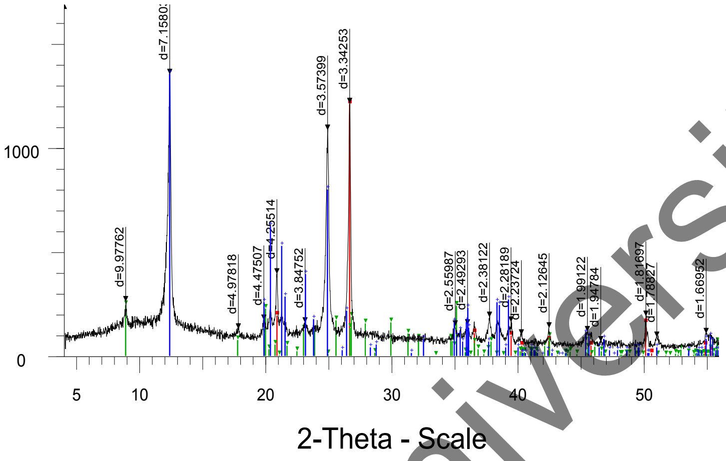


Figure 1. Diffractogram of the halloysite

The analysis of the mineral composition of the sample was carried out according to semi-digital X-ray phase analysis and quantitative indicators were obtained. All diffraction peaks corresponding to different phases shown in Figure 1 are listed in Table 1.

Table 1

Results of semi-digital X-ray phase analysis

Mineral	Formula	Concentration, %
Halloysite	$Al_2(Si_2O_5)(OH)_4$	81.2
Quartz	SiO_2	15.1
Mica	$KAl_2(AlSi_3O_{10})(OH)_2$	3.8

In particular, the mineral halloysite is known to be in the form of rolled sheets [6]. For example, this diagram on below can show 3D structure of halloysites:

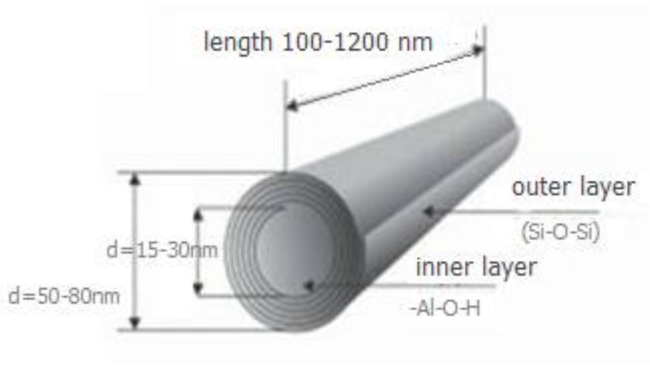


Figure 2. Diffractogram of the halloysite. Adapted and redrawn from [6]

The result of XRD analysis if the Beloye Glinishche deposit), shows that 81.2 % of the bulk of the mineralis is halloysite. Two types of halloysite are known in nature. There are halloysite 10A and halloysite 7A. As a result of this analysis, it is seen that Beloye Glinishche halloysite belongs to the halloysite 10A type, because the interlayer space is equal to 9,997 Å. The next type of analysis of interest is the demonstration of the presence of halloysite nanotubes by scanning electron microscopy, this analysis was ordered to the "National nanotechnological Laboratory of open type" of RSE on Al-Farabi Kazakh National University. The results of the scanning electron microscope (SEM) analysis are shown in Figure 2

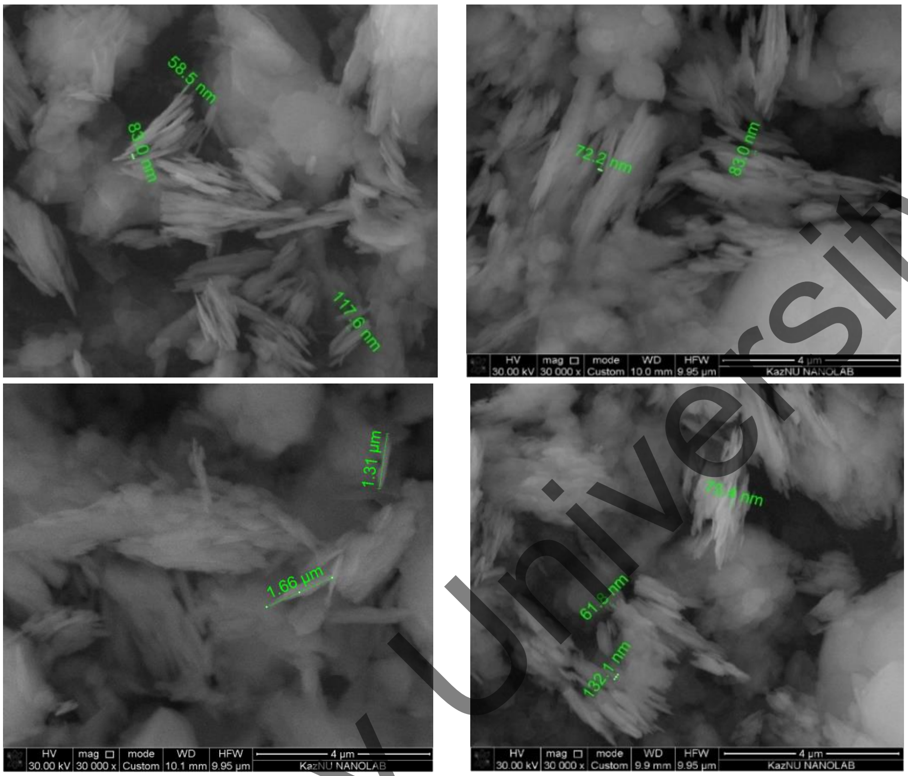


Figure 2. SEM figures of the mineral halloysite

Figure 2 shows SEM-figures of halloysite. It has been observed that the halloysite particles consist of fibrous-shaped particles, the particle length is about 500–1000 nm and the tube diameters fluctuate between 50–80 nm. It is known that halloysite exists in the form of a hollow nanotube [3, 6]. SEM analysis method was able to determine the magnitude of nanotubes, it cannot prove that the tubes are in the form of a hollow tube. Consequently, TEM analysis can show the halloysite particles are a hollow nanotube shape. The TEM analysis was performed in the nanolaboratory of the Kazakh-Japanese innovation center (KJIC) at the Kazakh National Agrarian Research University. The result obtained is presented in Figure 3.

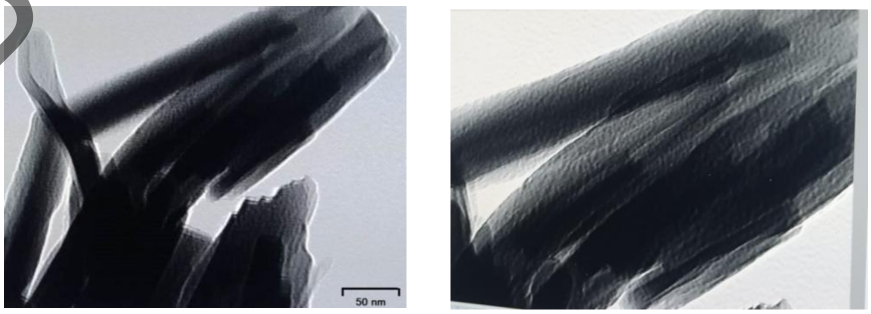


Figure 3. Shape of nanotubes obtained by Transmission Electron Microscopy

Figure 3 shows that the HNTs are in The Shape of spherical tubes wrapped, and each tube has between 20 and 50 nm in diameter. The difference between halloysite and kaolinite is that it contains a small amount of water molecule. Accordingly, halloysite has in their structures two layers and it belongs to the kaolinite group. The scheme of the cristal grid has a 1:1 ratio by type of clays. Therefore, one of them consists of aluminum oxide, the other of silicon oxide [6]. The folding of plates into tubes is carried out due to a sharp difference in the amount of silicon and aluminum ions. In this case, when the tube is folded type, the aluminum oxide layer is inside it, and the silicium oxide layer is located outside. With different ionization of silicium oxide with aluminum oxide, the dielectric properties are different. Aluminum oxide, for example, has a positive charge when placed in a solution with pH=8.5. The presence of different charges in the outer and inner parts of the tubes of halloysite is associated with the possibility of filling the inner parts of the tubes with negatively charged molecules. The peculiarity of using halloysite in comparison with other clays is due to the fact that it has a large surface specific area.

It is known today that silver ions have bactericidal and antiseptic properties and can resist 650 types of bacteria [8]. But when modifying halloysite with silver ions, it was necessary not to change the morphological nature of HNTs. Since the intercalation of a medicinal product into the hollow part of the nanotube has a main future in science and technology the creation of SEM images of silvered halloysite particles has of great interest (Fig. 4).

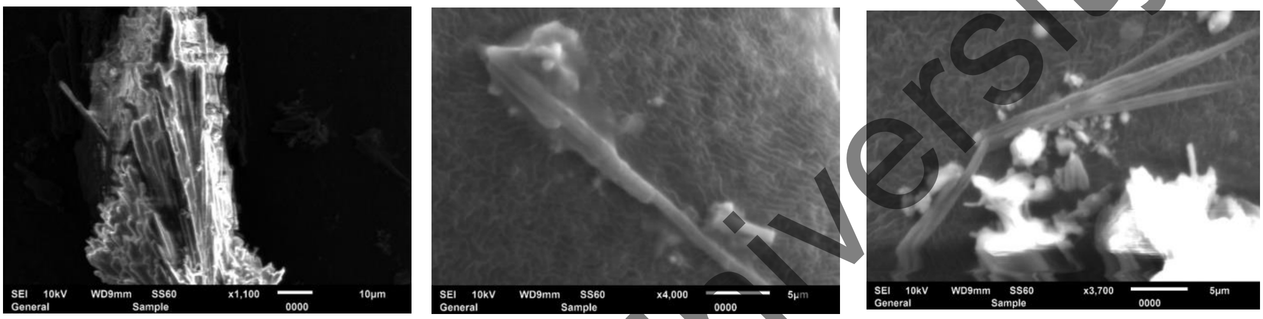


Figure 4. Results of scanning electron microscope analysis of modified clay mineral

Firstly, the halloysite was modified with silver ions. The conversion process was carried out in a simple way. Silver nitrate solutions were prepared with concentration C($AgNO_3$) = 0.4 mg/l. Modification by silver ions of halloysite samples was carried out by static method and left for 24 hours in dark place. The resulting clay sample was washed by the decantation method until a pure solution was obtained. After that, the liquid medium was separated and qualitative and quantitative analyses for silver ions were performed.

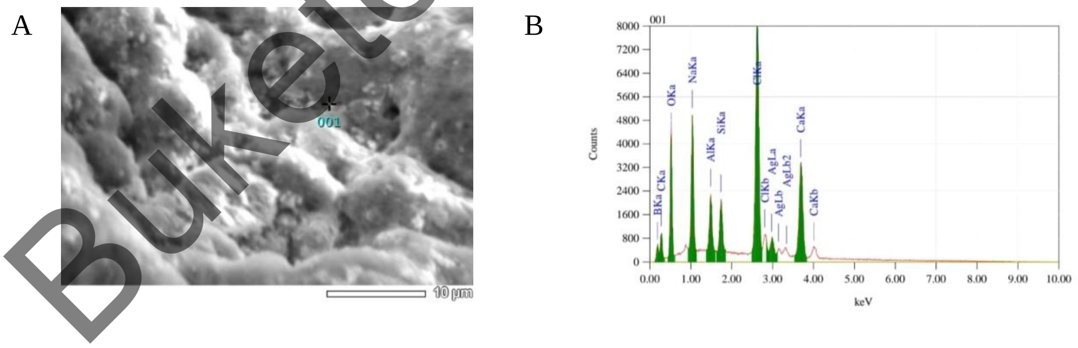


Figure 5. Determination of silver ions by energy dispersive X-ray spectroscopy

As can be seen in Figure 5, halloysite has been proven to contain silver ions using energy dispersive spectroscopy. A SEM image is created first to carry out the process of detecting silver ions. Afterwards the study area is selected (point 001 in Fig. 5A) by placing a dot on any section of the understudy sample and then spectra are obtained on this section. As the Figure 5B shows, the spectra that are colored green are responsible for the clay mineral and the silver ion. It will be right if there is not pay attention to the coal and chlorine signals shown as a result of the analysis, as this also takes into account the composition of the substrate used. Mass fraction of the found ions of the composition is listed in the Table 2.

Table 2

The result of the elemental analysis of the sample

Elements	X-ray energy (keV)	Mass fraction, %	X-ray counts	Deviations, %	Atomic share, %	K
C K_α	0.277	2.61	2972.03	0.01	6.67	1.9354
O K_α	0.525	9.65	27693.86	0.00	18.52	0.7683
Na K_α	1.041	9.71	34731.10	0.01	12.97	0.6167
Al K_α	1.486	4.49	15106.39	0.02	5.11	0.6556
Si K_α	1.739	4.66	15007.89	0.02	5.10	0.6852
Cl K_α	2.621	36.16	79748.70	0.00	31.32	1.0000
K K_α	3.312	1.42	2547.63	0.14	1.12	1.2316
Ca K_α	3.690	21.36	34514.20	0.01	16.37	1.2316
Ag L_α	2.984	9.93	6378.77	0.05	2.83	3.4349
Summary		100.00			100.00	

It is recommended the modified halloysite with silver ions and medicinal preparations from this object to keep away from sunlight, for silver ions oxidize from the sun and turn into silver oxide. For this reason, all the samples obtained were stored in tinted glass containers. The bactericidal properties of the resulting silver halloysite were tested. Testing of bactericidal properties was carried out by order in private enterprise *in vitro* microbiological laboratories of Almaty.

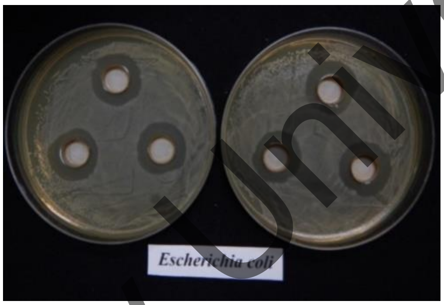


Figure 6. Zones of inhibition of the growth of *Escerichia coli* shoots of silver ion planted clay (21–23 mm)

The bacterium *Escherichia coli* (*E.coli*) was used in this work. As shown in Figure 5, 0.4 g of the studied clay was placed in a test tube and according to the results of the analysis, the bactericidal properties of the silver ion modified clay were revealed.

After organomodification of silvered halloysite, the composition of the study sample should not change, and if the interlayer spaces gallery expandes, it can indicate that large molecules have entered it, that is, either intercalation or exfoliation has occurred. In this regard, after stage of organomodification of silvered halloysite, repeated X-ray diffractometric analysis was performed.

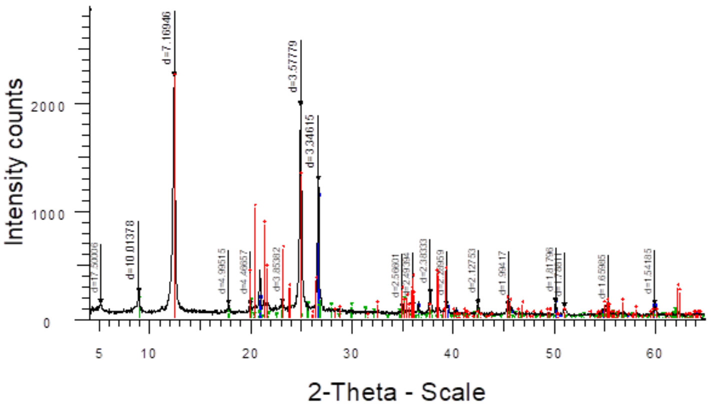


Figure 7. Diffractogram of organomodified halloysite mineral

As a result of the analysis, we observed that the interlayer spaces changed from d =9.98 Å (Fig. 7) to d = 17.50 Å. This is an indicator that adsorption is taking place.

For the hydrophobization of halloysite, it is necessary to have a substance with a diphilic structure in a molecule that should have a long saturated hydrocarbon chain around 17 or 18 carbon atoms or more and in this bond octadecylamine (ODA) was chosen. During organomodification by ODA, the process of flushing the excess ODA was carried out and the amount of ODA could be completely flushed out, as the washing process was performed in three returns. For this reason, using the IR spectroscopy method, ODA molecules were performed in order to prove that they exist on the surface of halloysite.

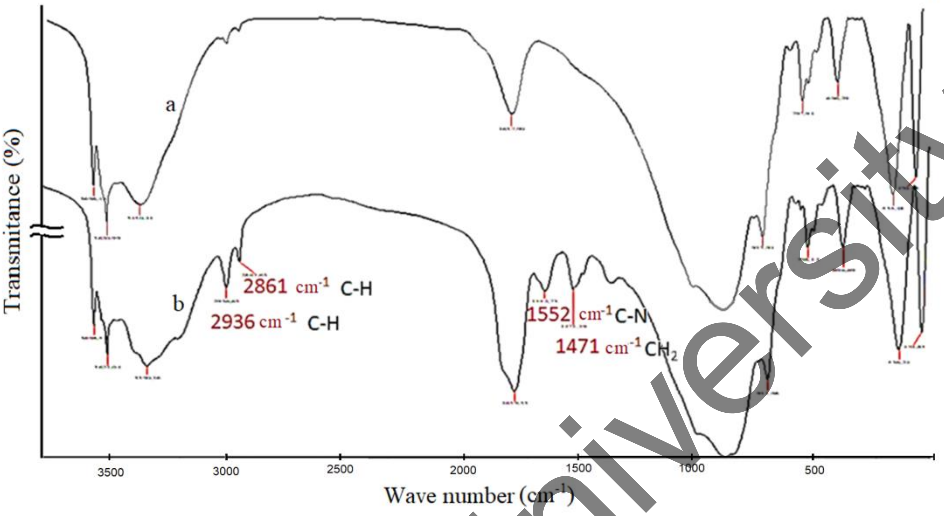


Figure 8. IR-spectra of clay samples. a-halloysite; b-organohalloysite

Data on the IR spectrum of the halloysite clay of the Beloye Glinishche deposit (*a*) and its ODA-modified hydrophobic clay (*b*) are shown in Figure 8. Thus, in halloysite, the peaks from of 3699 cm^{-1} to 3696 cm^{-1} determine the presence of the non free OH-group to which the absorption bands are connected. In the ODA-modified halloysite spectrum in the 3550-3150cm^{-1} region and in the enriched natural halloysite spectrum, the absorption of the free OH-group corresponds to the medium intensity short band frequency of 3620.99–3621.38 cm^{-1}. The location of this band indicates that, according to its nature, an OH-group is strongly linked from the interaction of halloysite [9–16].

In the spectrum of ODA-modified halloysite compound, the absorption of the trans-N-H bond of the secondary amide is determined by 3317.80 and 3323.97 cm^{-1} bands. The absorption band shows moderate intensity, with these bands showing at a very high frequency compared to the ODA-modified halloysite spectrum (*b*), whereas in a halloysite compound these bonds show at a lower frequency (*a*).

In a given region, absorption of the spectra under consideration is observed at very high intensity. The sample is taken in the form of a film (or tablets with KBr), the absorption area of various symmetric C–H bonds in the ODA-modified halloysite spectrum is observed in areas 2936 and 2861 cm^{-1}.

Absorption bands of deformation vibrations of the hydroxyl group in the spectrum of natural halloysite and its modified form with ODA bands are manifested at frequencies 1639.33, 1639.76, 1637.90 cm^{-1}. The CH_2-group in deformation oscillations is in the region of 1500–1300 cm^{-1} of the research spectrum.

The valence oscillations of the natural anti- and symmetrical C–N bond associated with different particles in the molecule are reflected in the absorption band 1129 cm^{-1} and 1150 cm^{-1} in the ODA-modified halloysite spectrum. In the spectrum of enriched natural halloysite, this area is not observed. Thus, from the results of the IR spectrum of natural halloysite and ODA-modified halloysite, the following conclusion is drawn: there is a significant reduction in free O-H bonds in the ODA-modified halloysite. It testifies to a decrease in the number of bands in the corresponding spectrum region, and also indicates the mixing of the remaining bands at a lower frequency. The spectrum picture varies in a known way in the region of 1120–1000 cm^{-1}.

Figure 9 below shows that organomodified halloysite can float on the surface of water, and the first glass is a picture taken at t = 0 sec, and the second glass is a picture taken after t = 120 days.

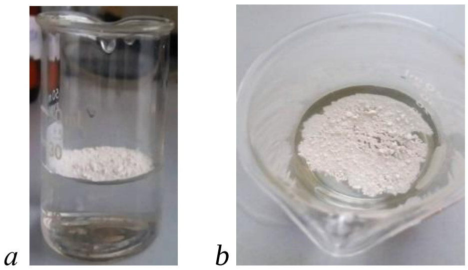


Figure 9. Organoclay powder newly placed on the surface of the water
after *t* = 0 SEC (*a*) and *t* = 120 days (*b*)

The organophilic halloysite obtained from halloysite is hydrophobic and has a stable chemical composition.

Table 3

Values of water absorption angles for samples of organoclay powders obtained at different concentrations of ODA

№	Concentration of ODA spent on modification, mol/L	Angles of incidence, degrees	Oda-modified and bactericidal organoclay names with different concentrations ODA
1	Silvered halloysite	9°	BOMC0
2	0,000625	122°	BOMC1
3	0,00125	129°	BOMC2
4	0,0025	130°	BOMC3
5	0,005	131°	BOMC4
6	0,01	132°	BOMC5

Thus, by modifying silvered halloysite with octadecylamine, as shown in Table 3, 6 type of bactericidal organoclays were obtained and they were assigned the relevant names from BOMC0 to BOMC5. Production facilities will also be provided with this model. Since the oranomodification process is carried out at a certain temperature operation mode, it is important to perform morphological analysis of the particles of the resulting hydrophobic organohalloysite, as it is the most necessary for us to keep the organohalloysite intact in space as a nanotube during the work. Therefore, by the SEM method, a SEM photo of organohalloysite was obtained (Fig. 10).

In order to study the nanotube structure of the mineral organohalloysite, SEM analysis of the mineral sample was carried out and the following results were obtained (Fig. 10).

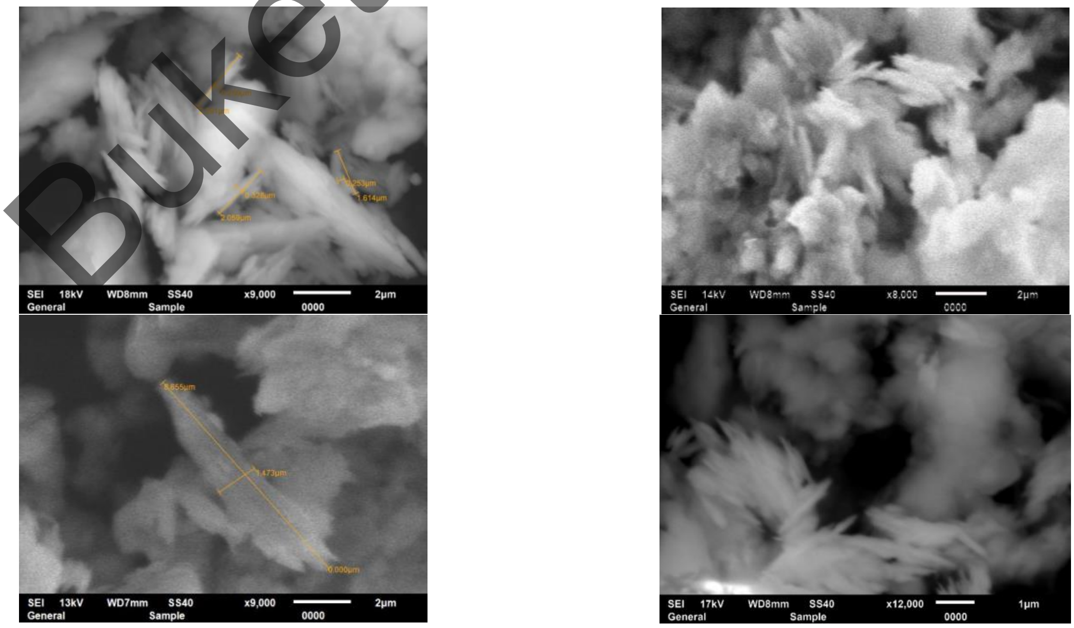
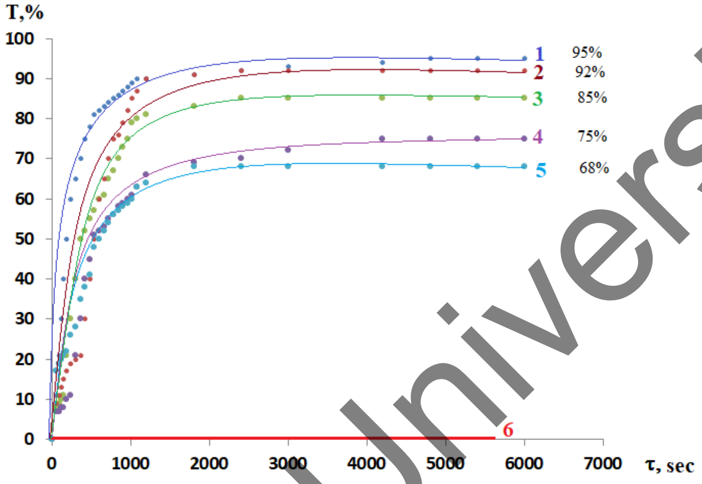


Figure 10. SEM images of organomodified silvered halloysite mineral

SEM analysis measured the width and length of the nanotubes of the halloysite mineral, found that the width is between 10–100 nm, and the length is up to ~1000 nm, and proved not to disturb the type of rolled sheet.

The last step of the performed research work is proving stabilities obtained hydrophobic bionanocomposite in an organic medium. For this reason, sunflower oil was chosen as the organic medium because of its dielectric constant equal to 3.2 and because it is an eco-friendly object for the human body. The kinetics of sedimentation in the sunflower oil medium BOMC0-BOMC5 of the bionanocomposite samples obtained below were studied by the result of a time-dependent change in the amount of light transmittance (T, %). If it considers as a dispersion system, the particles of the dispersed phase begin to settle at the bottom of test tube over time and during the time the light transmittance begins to increase. The results obtained explain if the turbidity stops at one value, there is a certain amount of stability. The results obtained are shown in the Figure 11.



1 — BOMC1; *2* — BOMC2; *3* — BOMC3; *4* — BOMC4; *5* — BOMC5; *6* — BOMC0

Figure 11. Stability of organo halloysite samples in the sunlight oil

As shown in Figure 11, the 6 curves are typical of the non-organomodified halloysite. During the experiment, BOMC0 immediately settles under the test tube and does not show any mechanical interference with the oily medium. Therefore, its light conductivity is equal to 100 percent homogeneous or has no turbidity. From this Figure 11 (curve 5), the lowest value of light transmittance corresponds to BOMC1 and its value equals to T = 65 % and it remains stable of dispersed phase in the medium at this value. It has been proven that this sample can physically interact with BOMC1 sunflower oil, due to which it shows better stability in the oil medium than other (BOMC0-BOMC4) samples. In other words, our samples are recommended to be used as bionanocomposite for a special nonpolar medium. Because currently, the direction of creating bionanocomposite adapted to a polar medium (aquatic medium) has been studied in detail, but the direction of creating bionanocomposite adapted to a nonpolar environment is just being developed.

Conclusions

Thus, recently, the number of works performed as part of the creation of bionanocomposites has been increasing [1–5, 14–17]. The provided results can actually indicate ways to obtain a drug of a new type from a clay mineral, expanding the scope of application of organomodified clay. At the same time, nanotechnology can determine a great scientific direction, creating nanoclays in the direction of science, creating nanobiocomposites based on it and increasing the scope of its application. Thanks to scientific work in this direction, the prospects for the creation and application of nanoclay types are well increasing. The work in this direction is promising and can expand the scope of creating various forms of drugs by creating a form of halloysite with oleophilic and bactericidal properties, structuring and microcapsulating halloysite-based bionanocomposite.

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References

1 Yassin JM, Shiferaw Y, Tedla A. (2022) Application of acid activated natural clays for improving quality of Niger (Guizotia abyssinica Cass) oil. *Heliyon*, 8, (4), e09241. http://dx.doi.org/10.1016/j.heliyon.2022.e09241

2 Amari A., Gannouni H., Khan M.I., Almesfer M.K., Elkhaleefa A.M., Gannouni A. (2018). Effect of structure and chemical activation on the adsorption properties of green clay minerals for the removal of cationic dye. *Appl. Sci.*, *8*(11), 2302; http://dx.doi.org/10.3390/app8112302

3 Parolo, M. E., Pettinari, G. R., Musso, T. B., Sánchez-Izquierdo, M. P., & Fernández, L. G. (2014). Characterization of organo-modified bentonite sorbents: The effect of modification conditions on adsorption performance. *Applied Surface Science*, *320*, 356–363. http://dx.doi.org/10.1016/j.apsusc.2014.09.105

4 Musabekov, K., Zhakyp, B., Tazhibayeva, S., Musabekov, N., & Yergaliyeva, A. (2020).A research of colloidal silver immobilization in bionanocomposites of natural polymers and montmorillonite. *Eastern-European Journal of Enterprise Technologies*, 6 (6–108), 93–101. http://dx.doi.org/10.15587/1729-4061.2020.216995

5 Villegas, Carolina & et al. (2019). PLA/organoclay bionanocomposites impregnated with thymol and cinnamaldehyde by supercritical impregnation for active and sustainable food packaging. *Composites Part B Engineering*, 176, 107336. http://dx.doi.org/10.1016/j.compositesb.2019.107336

6 Kamal, N., Kochkodan, V., Zekri, A., Ahzi, S. (2020). Polysulfone Membranes Embedded with Halloysites Nanotubes: Preparation and Properties. *Membranes*, *10*, 2. http://dx.doi.org/10.3390/membranes10010002

7 Fernández Solarte, A. M., Blanco Massani, M. R., Molina, V. M., Benítez Guerrero, M., & Torres Sánchez, R. M. (2018). Correlating Antimicrobial activity and Structure in Montmorillonite modified with Hexadecyltrimethylammonium and Silver. *International Journal of ChemTech Research*, *11(6)*, 209–223. http://dx.doi.org/10.20902/IJCTR.2018.110627

8 Rhim, J.-W., Park, H.-M., & Ha, C.-S. (2013). Bio-nanocomposites for food packaging applications. *Progress in Polymer Science*, 38(10), 1629–1652. http://dx.doi.org//https://doi.org/10.1016/j.progpolymsci.2013.05.008

9 Pessanha, N. F. N., Kawase, K. Y. F., & Coelho, G. L. V. (2014). Preparation and characterization of silver/organo-clay nanocomposites. *Chemical and Materials Engineering*, *2(8)*, 173–178. http://dx.doi.org/10.13189/cme.2014.020802

10 Korkmaz, D. (2011). Determination of Chloride Ion Concentration by Titration (Mohr’s Method). *University of Cantearbury*, 1-2. Retrieved from https://www.canterbury.ac.nz/media/documents/science-outreach/chloride_mohr.pdf

11 Bakenov, M.M. (2008) Netradicionnye i novye vidy poleznyh iskopaemyh Kazahstana [Unconventional and new types of Kazakhstan’s minerals’] K.I. Satpayev KazNTU: Satbayev University https://www.geokniga.org. Retrieved from https://www.geokniga.org/bookfiles/geokniga-netradicionnye-i-novye-vidy-poleznyh-iskopaemyh-kazahstana.pdf, [in Russian]

12 Isagulov A.Z., Kulikov, V., Kwon, S. S., Shcherbakova, E., Kovaleva, T., & Isagulova D. (2015). Opredelenie frakcionnogo sostava galluazita na fotosedimentometre FSH-6K [Determination of the fractional constituent of halloysite by the photosedimentometer FSX-6K] *Trudy Universiteta — Proceedings of the University*, 3, 29-40. Retrieved from https://www.kstu.kz/tu/2015/trudy_universiteta_3.pdf [in Russian].

13 Sidorina, E.A., Isagulov, A.Z., Kashcheev, I.D. et al. (2022). Production and Development of Superdense Slag-Resistant Aluminosilicate Refractories. *Refractories and Industrial Ceramics*, 63, 280–282. http://dx.doi.org/10.1007/s11148-022-00724-7

14 Arellano, Sofia & et al. (2012). Sorption of Naringin from Aqueous Solution by Modified Clay. *Clays and Clay Minerals*, 60, 153–161. http://dx.doi.org/10.1346/CCMN.2012.0600205

15 Abdullayev, E., Lvov, Y. (2011). Halloysite Clay Nanotubes for Controlled Release of Protective Agents. *Journal of Nanoscience and Nanotechnology*, 11(11), 10007–10026(20). http://dx.doi.org/10.1166/jnn.2011.5724

16 Roy, S., & Chakraborty, C. (2020). Sub-second electrochromic switching and ultra-high coloration efficiency in halloysite nanoclay incorporated metallo-supramolecular polymer nano-hybrid based electrochromic device. *Solar Energy Materials and Solar Cells*, 208, 110392. http://dx.doi.org/10.1016/j.solmat.2019.110392

17 Ahmed, H.B. (2019). Cluster growth adaptor for generation of bactericide Ag-Au bimetallic nanostructures: substantiation through spectral mapping data. *International Journal of Biological Macromolecules*, 121, 774–783. http://dx.doi.org/10.1016/j.ijbiomac.2018.10.088

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