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RESEARCH OF STRUCTURE AND SORPTION PROPERTIES OF MONTMORILLONITE MODIFIED WITH HEXADECYLTHYMETHYLAMMONIUM BROMIDE

Об'єктом дослідження є природний шаруватий силікат – монтморилоніт Черкаського родовища (Україна) із загальною формулою $(Ca,Na)(Al,Mg,Fe)_2(OH)_2[(Si,Al)_4O_{10}] \cdot nH_2O$. Хімічний склад мінералу: SiO_2 – 51,9 %, Al_2O_3 – 17,10 %, Fe_2O_3 – 7,92 %, MgO – 1,18 %, Na_2O , K_2O і CaO до 2 % і H_2O – 8,78 %. Монтморилоніт характеризується значною дисперсністю часточок та наявністю великої кількості сорбційних центрів на його поверхні, що здатні до катіонного обміну. Одним з найбільш проблемних місць є те, що монтморилоніт практично не здатен до видалення забруднювачів, що присутні у водах у вигляді аніонів. З метою отримання сорбентів, здатних вилучати аніони важких металів, було проведено модифікування поверхні монтморилоніту катіонною поверхнево-активною речовиною гексадецилтріметіламмоній бромідом.

В ході дослідження для вивчення структури вихідного монтморилоніту і його органомодифікованих форм використовувалися рентгенофазовий аналіз, скануюча електронна мікроскопія, інфрачервона спектроскопія, термічний аналіз. Для вивчення сорбційних властивостей композитів використано спектрофотометричний метод.

У роботі підтверджено, що молекули гексадецилтріметіламмоній броміду сорбуються не тільки на зовнішній поверхні частинок, а й мігрують між алюмосилікатними пакетами шаруватої структури монтморилоніту. Сорбційні дослідження підтвердили, що застосування органомодифікованих форм монтморилоніту дозволило підвищити ступінь вилучення іонів хрому (VI) з 32 % до 96 %. Отримані сорбенти дозволяють очистити забруднену воду з концентрацією хрому (VI) рівній 1 мг/дм^3 до значень гранично допустимих концентрацій. Це пов'язано з тим, що органомодифікування поверхні монтморилоніту має ряд особливостей та дозволяє змінити структуру вихідного мінералу, а також перезарядити поверхню глини від негативної до позитивної. Завдяки цьому забезпечується можливість використання органоглин для видалення неорганічних токсикантів, що знаходяться у аніонних формах. У порівнянні з аналогічними відомими, отримані композити забезпечують видалення навіть слідових кількостей аніонів важких металів з водних середовищ.

Ключові слова: монтморилоніт, органоментморилоніт, рентгенофазовий аналіз, термічний аналіз, сорбція, хром (VI).

Received date: 17.09.2019

Accepted date: 09.10.2019

Published date: 30.12.2019

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1. Introduction

For the extraction of heavy metal ions from aqueous media, especially if they are in trace amounts, sorption methods are promising. In this purification technology, activated carbon and synthetic ionites are most often used, but sorbents based on clay minerals are becoming increasingly important. Such materials are characterized by relative low cost, environmental friendliness and general availability of these raw materials. The high sorption properties of clay minerals are due to the significant dispersion of particles and the presence of a large number of sorption centers on their surface capable of cation exchange. Moreover, the montmorillonite minerals have the highest sorption properties, the large deposits of which are explored and developed in Ukraine. However, clay-based

sorbents are practically incapable of removing pollutants present in waters in the form of anions, which in some cases are the most dangerous (complexes of chromium, uranium, arsenic, etc.) [1]. That is why the development of effective and safe sorbents with high selectivity will ensure the rational use of natural resources, compliance with environmental standards. This determines the relevance of scientific and technological developments to solve the problem of directed synthesis of effective sorbents based on natural silicates with studied properties and structure.

The object of research is a natural layered silicate – montmorillonite of the Cherkasy deposit (Ukraine) with the general formula $(Ca,Na)(Al,Mg,Fe)_2(OH)_2[(Si,Al)_4O_{10}] \cdot nH_2O$. The chemical composition of the mineral: SiO_2 – 51.9 %, Al_2O_3 – 17.10 %, Fe_2O_3 – 7.92 %, MgO – 1.18 %, Na_2O ,

K₂O and CaO up to 2 % and H₂O – 8.78 %. Montmorillonite is characterized by the highest cation exchange capacity (CEC) of 1.0 mmol/g among clay minerals [2].

The subject of research is the structure of montmorillonite and synthesized organomontmorillonites, as well as their sorption properties. The structural cell of montmorillonite during adsorption of vapors of polar substances can increase along the C axis by 0.3–1.4 nm. As a result of the increase in the intermediate package space of layered silicates, gaps can be considered as micropores, the sizes of which can change during adsorption.

The aim of research is investigation of the structure of sorbents obtained on the basis of natural montmorillonite and their sorption properties with respect to heavy metal ions using chromium (VI) as an example.

2. Methods of research

To achieve the aim set in the work, let's use the methods of X-ray phase analysis (XRD), infrared (IR) spectroscopy, scanning microscopy, thermal analysis, as well as a spectrophotometric method for studying the sorption properties of synthesized materials.

Natural montmorillonite was previously converted to the Na form according to the procedure described in [3]. Modifications of Na-montmorillonite (MT) with a cationic surfactant were carried out according to the method described in [4]. Thus, the obtained samples with the ratio of the amount of surfactant in the cation of the exchange capacity of the mineral (surfactant/CEC) are 1 and 2, and are named OMT1 and OMT2, respectively.

To modify the surface of palygorskite, a salt of tetrachlorine-substitution ammonium hexadecyltrimethylammonium bromide (HDTMA) – (C₁₆H₃₃)N(CH₃)₃Br, (Merck) was taken.

X-ray analysis was carried out using a DRON-3M diffractometer (Russian Federation), with a computer scanning system and recording a diffraction pattern. Filtered Cu-K_α radiation was also used.

Microscopic studies were performed on a REM-1061 scanning electron microscope (Ukraine). This microscope receives images of the surface of an object with high spatial resolution and depth of field in reflected and secondary electrons. For research, let's use the samples in a powdered state, with a fraction of $\alpha < 0.1$ mm.

IR spectroscopic studies of the samples were carried out on a Spectrum-One Fourier spectrometer (Perkin-Elmer) in the region of 4000–450 cm⁻¹ with a twenty-fold scan.

Thermogravimetric studies of sorbents were carried out on a derivatograph Q-1500 device (Hungary) of the Paulik-Paulik-Erdey system. Samples were analyzed in a dynamic mode with a heating rate of 10 °C/min to 1000 °C in an air atmosphere. The mass of the samples was 1500 mg. The reference substance is Al₂O₃. In the experiments, a platinum crucible was used. Sensitivity on a scale of change in mass (TG) is 50 mg, on a scale of differential heating (DTA) – 250 μV.

In sorption experiments, a solution of potassium dichromate K₂Cr₂O₇ and weighed portions of the synthesized composites were used. Sorption was carried out under static conditions with continuous shaking of the samples for 1 h (the volume of the aqueous phase was 50 ml, the weight of the mineral was 0.1 g, the concentration of Cr (VI) in the sorption experiments was 1 mg/dm³)

according to the procedure [5]. Ionic strength (0.01 M) of solutions was established using NaCl. After the adsorption equilibrium was established, the aqueous phase was separated by centrifugation (5000 rpm) and the metal equilibrium concentration was determined in it by the spectrophotometric method (UNICO 2100UV, USA) using diphenylcarbazide reagent at a wavelength of 540 nm for chromium. Sorption of chromium ions was studied at pH=6.

3. Research results and discussion

Fig. 1 shows the diffraction patterns of non-oriented samples of montmorillonite and its organically modified form (OMT1). On the X-ray diffraction pattern, which corresponds to the initial montmorillonite (curve 1, Fig. 1), a series of basal reflexes is observed 1.240; 0.315; 0.253 nm and two-dimensional diffraction lines – 0.447; 0.256; 0.224 nm. The presence of the indicated diffraction prints on powder X-ray diffraction patterns is characteristic of smectite [6, 7], and narrow and intense lines with an interplanar distance of 0.425; 0.334; 0.245 nm relate to quartz.

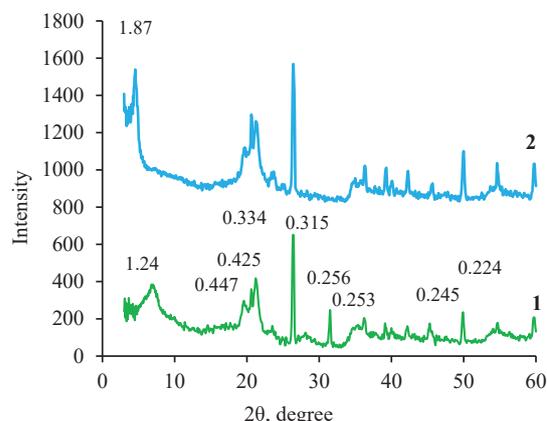


Fig. 1. Diffraction patterns of samples:
1 – montmorillonite (MT); 2 – organically modified form of montmorillonite (OMT1)

The X-ray diffraction pattern of the MT sample (curve 1, Fig. 1) shows a clear basal reflection of 1.24 nm with a peak center of gravity of $2\theta = 6.8^\circ$, which is typical for this mineral in an air-dry state.

After surface modification of the montmorillonite HDTMA (curve 2, Fig. 1), a shift of this reflection towards small angles is observed. In the X-ray diffraction pattern of the OMT1 sample, a peak is not observed at the indicated location, it shifts to the region $2\theta = 4.55^\circ$, which corresponds to an interplanar distance of 1.87 nm. The lid of the structural packets of the mineral occurred as a result of the replacement of exchange cations in the interlayer space of montmorillonite with large volume HDTMA molecules [8–10]. Studies conducted in [3] showed that increasing the ratio of CEC/surfactants to 2 allows to increase the interplanar distance to 2.25 nm.

Montmorillonite and its organically modified form have been electronically studied. Electronic images of the MT surface are shown in Fig. 2, a. In these images, let's observe agglomerates of montmorillonite particles having the form of massive and curved plates. However, clay treated with cationic surfactant has a lower degree of aggregation and a more ordered structure (Fig. 2, b).

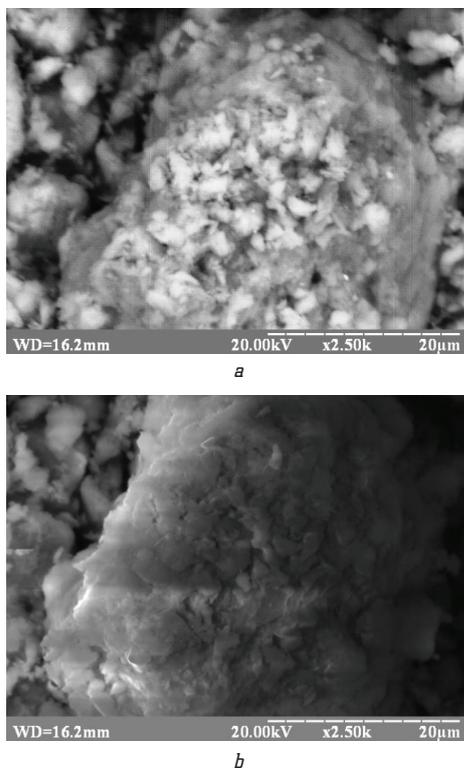


Fig. 2. Results of scanning electron microscopy:
a – montmorillonite (MT); *b* – organomodified form
of montmorillonite (OMT1)

The results of IR spectroscopy of montmorillonite, its organically modified form, and its iron-based composite are presented in Fig. 3. The IR spectra of the starting montmorillonite (curve 1, Fig. 3) have a typical appearance for this mineral with absorption bands at 694, 802, and 1030 cm^{-1} , due to vibrations of Si–O bonds, and bands at 530 and 906 cm^{-1} – vibrations of the Si–O–Al bond. A very intense band at 3625 cm^{-1} refers to stretching vibrations of O–H groups [11]. In the IR spectra of organomodified form montmorillonite (curve 2, Fig. 3), in addition to the main characteristic bands of montmorillonite, new bands appear at 2921 cm^{-1} and 2852 cm^{-1} , which correspond to the groups of (–CH₂–) alkyl chains of HDTMA molecules that are sorbed on the surface of the particles.

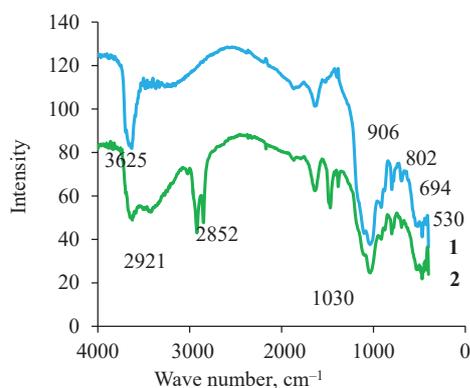


Fig. 3. Infrared spectra of sorbents:
1 – montmorillonite (MT); 2 – organomodified form
of montmorillonite (OMT1)

To determine the nature of the interaction of the applied modifier with the surface of a clay mineral, a thermal analysis was chosen as an additional method that will help to specify the results of XRD. According to the differential thermal analysis (DTA) data for the MT sample (Fig. 4, *a*), three endothermic effects are present on the curve (curve 3, Fig. 4, *a*). The first, an intense, low-temperature effect, is responsible for the release of adsorption and low-pack water, and the next two are responsible for the release of constitutional hydroxyl water [12, 13].

To compare the research results, a thermal analysis of HDTMA is carried out (Fig. 4, *b*). For this sample, in the temperature range 93.9–112.5 °C, an endoeffect is observed without changing the mass of the sample. At this stage, a partial destruction of the structure of HDTMA occurs. At a temperature of 240–255 °C, let's observe an endoeffect, which corresponds to the melting point of HDTMA. With increasing temperature, let's observe the presence of endo and exoeffect. It is impossible to analyze the DTA curve (curve 3, Fig. 4, *b*) in this form, since two opposite processes take place simultaneously:

- 1) melting, which is characterized by a significant absorption of heat (endoeffect);
- 2) combustion, accompanied by a large release of heat (exoeffect).

Both processes are accompanied by weight loss. In the temperature range of 250–360 °C, a sharp weight loss is observed, which is associated with the burning out of surfactant in the sample. On the thermogravimetric analysis curve (TG) (curve 1, Fig. 4, *b*), each change in the slope (decomposition rate) corresponds to a change in the chemical composition of the substance, which is confirmed by the differential gravimetric analysis (DTG) curve (curve 2, Fig. 4, *b*). It can be argued that in the temperature range there are products of chemical transformation during heating. At a temperature of 595.0 °C, the substance completely burns out.

For the OMT1 sample, according to the DTA data (Fig. 4, *c*), in the temperature range 240–640 °C, let's observe an insignificant end-effect (240–270 °C), which corresponds to melting of the organic component. In the temperature range 270–620 °C, part of the organic component of the composite ignites. This process is accompanied by the appearance of a number of exothermic effects on the DTA curve. This thermal behavior of the samples can be explained by the pyrolysis of HDMA, which is adsorbed on a mineral. On the DTA curves, let's observe broad peaks, as a result of the presence of various forms of the introduced surfactant: monomers, micelles, which were formed as a result of thermal decomposition of HDTMA. In this temperature range, let's also observe the imposition of an endoeffect with a maximum at 452 °C, which corresponds to the allocation of constitutional water. The burnout of organic matter ends at 620 °C.

Thermal analysis of the sample with organomontmorillonite with a twice as high HDTMA content was also carried out as compared with OMT1 (sample OMT2) (Fig. 4, *d*). A comparison of the results of DTA and TG with organomontmorillonite with varying degrees of surface modification of montmorillonite of cationic surfactant allows to state that surfactant molecules are firmly bound to the surface of the mineral. The burning out of the organic component from the composite occurs gradually at a higher temperature than the melting and burning out of HDTMA, equal to 250 °C.

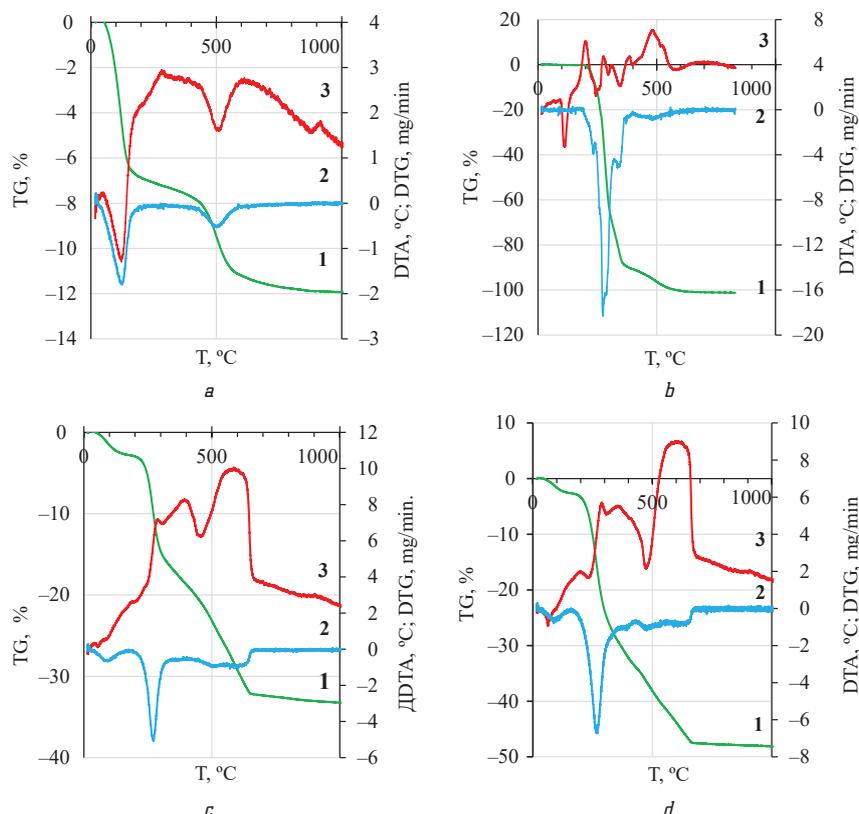


Fig. 4. The results of thermal analysis:

a – montmorillonite (MT); *b* – hexadecyltrimethylammonium bromide (HDTMA); *c* – organomodified form of montmorillonite (OMT1); *d* – organomodified form of montmorillonite with a double content of hexadecyltrimethylammonium bromide OMT2; 1 – mass change curve (TG); 2 – differential mass change curve (DTG); 3 – differential heating curve (DTA)

The DTA curve (curve 3, Fig. 4, *d*) can't be analyzed in this form, since two opposite processes take place simultaneously: melting (endoeffect) and burning (exoeffect). Both processes are accompanied by weight loss. In the temperature range of 250–360 °C, a sharp weight loss is observed, which is associated with the burning out of surfactant in the sample. On the thermogravimetric analysis curve (curve 1, Fig. 4, *d*), sections with different slopes corresponding to a change in the decomposition rate are confirmed by the differential gravimetric analysis (DTA) curve (curve 2, Fig. 4, *d*). It can be argued that in the temperature range there are products of chemical transformation during heating. At a temperature of 595.0 °C, the substance completely burns out.

At a pH close to neutral, which corresponds to natural waters, chromium forms only anionic compounds. So, the dominant form of chromium is CrO_4^{2-} , in the presence of significantly lower amounts of HCrO_4^- ions and $\text{Cr}_2\text{O}_7^{2-}$ ions in trace concentrations. Sorption studies have confirmed that the removal of the anionic forms of Cr(VI) by montmorillonite is negligible. At the same time, for the modified OMT1 and OMT2 samples, a significant increase in the sorption values is observed, which proves their efficiency with respect to Cr(VI) ions compared to the initial sample (Table 1).

The results of checking the effectiveness of the developed sorbent in model waters with a Cr(VI) ion content of 1 mg/dm³ at pH=6 are presented in Fig. 5.

Studies confirm that the purification of aqueous media by synthesized OMT1 and OMT2 composites from Cr(VI) ions reached the maximum permissible concentration (MPC), which is 0.05 mg/dm³ [14].

Table 1

Sorption properties of materials at $C_0=1 \text{ mg/dm}^3$

Sorbent	Adsorption, mg/g	Purification degree, %
MT	0.16	31.77
OMT1	0.47	95.10
OMT2	0.48	96.25

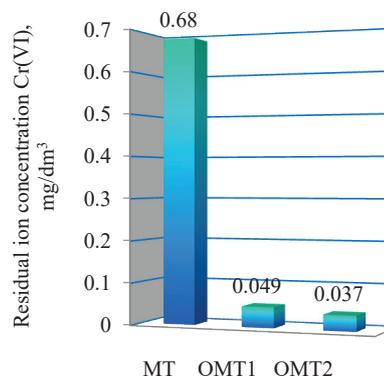


Fig. 5. Residual concentrations of Cr(VI) ions after purification of contaminated solutions with montmorillonite (MT), organomodified form of montmorillonite (OMT1) and organomodified form of montmorillonite with a double content of hexadecyltrimethylammonium bromide (OMT2) at pH=6

4. Conclusions

During the modification of the mineral, cationic surfactant molecules are sorbed not only on the outer surface of the particles, but also migrate between the aluminosilicate packets of the layered structure of montmorillonite, replacing ions of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , etc. in ion exchange positions. This is evidenced by the shift of basal reflexes toward large interplanar distances in the diffraction patterns of the modified samples from 1.24 nm to 1.87 nm.

The results of IR spectroscopy confirmed that the groups of $(-\text{CH}_2-)$ alkyl chains of the HDTMA molecules were successfully sorbed on the surface of montmorillonite particles.

Scanning microscopy results show that montmorillonite treated with cationic surfactant has a lower degree of aggregation and a more ordered structure compared to the starting material.

The study of the thermal properties of organomodified montmorillonite makes it possible to refine the X-ray phase analysis data and confirmed the formation of stable bonds between surfactant cations and the surface of montmorillonite. This makes it possible to carry out directed synthesis of organoclay with certain properties of the mineral surface.

The synthesized organomontmorillonites are capable of removing up to 96.25 % of Cr(VI) ions, which is 3 times higher than the starting montmorillonite and reach the MPC purification levels. Thus, the use of montmorillonite as a raw material for the production of sorbents contributes to a comprehensive solution of environmental issues, resource conservation and technology for the production of sorbents for the extraction of anionic forms of heavy metals from aqueous solutions.

References

- Holembiovskiy, A. O., Kovalchuk, I. A., Kornilovych, B. Yu., Zhdaniuk, N. V. (2011). Vyluchennia spoluk U(VI) z vod iz vykorystanniam orhanohlyny. *Naukovi visti NTUU «KPI»*, 6, 154–158.
- Tarasevich, Iu. I., Ovcharenko, F. D. (1975). *Adsorbciia na glinistykh mineralakh*. Kyiv: Naukova dumka, 351.
- Zhdanyuk, N. (2016). Research of chromium (VI) ion adsorption by montmorillonite modified by cationic surfactants. *Technology Audit and Production Reserves*, 5 (3 (31)), 11–15. doi: <http://doi.org/10.15587/2312-8372.2016.81015>
- Zhdaniuk, N. V. (2017). Kharakterystyka orhanofilizovanoho palyhorskita ta yoho sporidnenist do khromativ. *Visnyk NTU «KhPI». Seriya: Mekhaniko-tehnolohichni systemy ta komplektsy*, 19 (1241), 11–16.
- Prus, V., Zhdanyuk, N. (2016). Investigation of removal of hexavalent chromium and divalent cobalt from aqueous solutions by organo-montmorillonite supported iron nanoparticles. *EUREKA: Physics and Engineering*, 5, 81–88. doi: <http://doi.org/10.21303/2461-4262.2016.00163>
- Brindley, G. W., Brown, G. (1980). *Crystal structure of clay minerals and their X-ray identification*. London: Miner. Soc., 518. doi: <http://doi.org/10.1180/mono-5>
- Frank-Kamenskii, V. A. (Ed.) (1983). *Rentgenografiia osnovnykh tipov porodoobrazuiuschikh mineralov (sloistye i karkasnye sili-katy)*. Leningrad: Nedra, 359.
- Bergaya, F., Theng, B. K. G., Lagaly, G. (2006). *Developments in clay science. V. 1. Handbook of clay science*. Amsterdam: Elsevier, 1224.
- Jiang, N., Li, P., Wang, Y., Wang, J., Yan, H., Thomas, R. K. (2005). Aggregation behavior of hexadecyltrimethylammonium surfactants with various counterions in aqueous solution. *Journal of Colloid and Interface Science*, 286 (2), 755–760. doi: <http://doi.org/10.1016/j.jcis.2005.01.064>
- Hu, Z., He, G., Liu, Y., Dong, C., Wu, X., Zhao, W. (2013). Effects of surfactant concentration on alkyl chain arrangements in dry and swollen organic montmorillonite. *Applied Clay Science*, 75–76, 134–140. doi: <http://doi.org/10.1016/j.clay.2013.03.004>
- Dixon, J. B., Weed, S. B. (1989). *Minerals in soil environments*. Wisconsin: Soil Science Society of America, 1244.
- Ivanova, V. P., Kasatov, B. K., Krasavina, T. N., Rozinova, E. L. (1974). *Termicheski analiz mineralov i gornykh porod*. Leningrad: Nedra, 399.
- Yariv, S., Cross, H. (2001). *Organo-Clay Complexes and Interactions*. New York: CRC Press, 680.
- SANPin 4630-88. *Sanitarnye pravila i normy okhrany poverkhnostnykh vod ot zagriazneniia* (1988). Moscow: Izd. Minzdrava SSSR, 67.

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