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**FABRICATION OF COMPOSITES BASED ON MODIFIED VERMICULITE AND STUDY OF THEIR SURFACE**

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**Abstract**

Composites based on vermiculite with different modifiers have been fabricated. The composition and structure of the fabricated composites have been investigated by means of the methods of energy-dispersive analysis, X-ray diffraction analysis, and positron annihilation spectroscopy. The adsorption characteristics of the fabricated materials with respect to dye of different nature have been determined, and isotherms of low temperature nitrogen adsorption/desorption have been obtained. It has been demonstrated that for different modifications the composites sorption properties change significantly in dependence on the modifier nature. The possibilities of practical application of sorbents based on vermiculite have been considered. The possibility of using the fabricated sorbents in determination of residual quantities of antibiotics in food products with different matrices has been demonstrated.

**Introduction**

At present, natural and synthetic layered aluminosilicates, including vermiculite, are applied in different fields of industry in the composition of sorbents used, for example, in removal of heavy metals and radionuclides [1–3]. The interest to layered silicates, such as vermiculite and montmorillonite, is concerned with the fact that highly dispersed powders of these inorganic materials having a clearly expressed layered structure appeared to be rather promising in view of application as fillers for different coatings and composite materials [4, 5]. Introduction of polyethylene into a layered silicate results in fabrication of a composite, whose structure depends on the content of this layered silicate. The composite is characterized with high strength due to bimodal distribution of crystallites in it [6]. It was shown that deposition of magnesium, calcium, aluminum, and iron hydroxides on the aluminosilicate surface had a positive effect on the sorption of heavy metal ions [7]. Main results of studies of the adsorption, structure, and surface of layered silicates are presented in a monograph by Yu.I. Tarasevich and F.D. Ovcharenko [8]. At the same time, fabrication of new vermiculite-based composites allowed their application as sorbents characterized with high sorption capacity toward heavy metal ions [9] at decontamination of spent solutions from galvanic baths. In the course of secondary decontamination of spent solutions from galvanic baths, the highest efficiency was demonstrated by the composite based on vermiculite sequentially modified by hydrochloric acid and chitosan [10]. The above sorbents manifest high degrees of decontamination of wastewater streams from food industry plants: in particular, the decontamination factor on proteins attains 68–75 % [11].

Sorbents for determination of residual quantities of antibiotics in food products with different matrices and in aqueous objects were created [12–15].

The method of determination of the chloramphenicol content in food products using the vermiculite-based sorbent was patented [13].

The present work was devoted to modification of vermiculite by different agents (including hydroxide deposition on the surface of vermiculite particles) and studies of the sorption properties of the fabricated materials.

**Experimental**

*Reagents*

The following reagents were used in the present work: hydrochloric acid (analytically pure), ammonia (analytically pure), low-pressure polyethylene, cellulose (ash-free “white tape” filter), and chitosan. Chitosan is a natural polysaccharide with a molecular weight of not higher than 200000 Da: the content of carbon – 41.8 %, the content of nitrogen – 7.5%, the content of water – 8.8 %; the degree of deacetylation – 84.0 %; the viscosity of 1 % solution in 2 % aqueous solution of acetic acid – 88.0 mg/s. The general formula of the natural polysaccharide: (C6O4H11NH2)n.

Vermiculites from the Kovdorskoe (Murmansk Oblast) and Koksharovskoe (Chuguevka District, Primorsky Krai) deposits were used in composites fabrication.

*Equipment*

Measurements of lifetimes and intensities of positron annihilations were carried out using a fast-fast delayed coincidences spectrometer with plastic scintillation detectors of a size of ∅ 25×15 mm and a FEU-87 photoelectric multiplier based on a NOKIA-LP-4840 analyzer.

For X-ray diffraction analysis, an Advance-D8 device with CuKα-radiation (BRUKER) in the angle range 2° < 2q° < 90° was used.

The quantitative analysis element analysis was carried out using an EDX-800-HS X-ray energy-dispersive fluorescence spectrometer.

The sample surface was studied by the method of low-temperature physical nitrogen adsorption using an ASAP 2020 MP analyzer (Micromeritics). The average pore diameter and pore volume were determined from the adsorption/desorption curves obtained by the BJH method.

**Acidic modification of vermiculite:** 100 g of vermiculite of a grain size of 0.10–0.05 mm dried until constant weight at 120–150°C was stirred in 200 ml of 7, 12, 20, and 36.5 % solution of hydrochloric acid for 48 hours. The obtained suspension was filtered and washed with distilled water until neutral reaction on a litmus paper. The composite was dried until constant weight and analyzed on the content of main elements, and its main physical–chemical characteristics were determined: specific surface area, average pore volume, average particle size, positron annihilation parameters, density, and sorption properties toward dyes of different nature.

**Modification of vermiculite-based composite:** 50 g of the acid-modified vermiculite was treated by 75 ml of 2 % solution of chitosan. The suspension was stirred for 1 hour and added with 1–2 ml of 25 % ammonia solution until pH=10. The formed bulky precipitate was filtered, the filtrate was washed with distilled water until neutral reaction, dried, and analyzed for the contents of main elements, and its main physical–chemical characteristics were determined.

**Modification of vermiculite-based composite by ammonia:** To deposit cations transferred to the solution at acid modification, the acidic solution with the vermiculite suspension was added with a precipitation agent (ammonia). The formed gel was structured on the surface of vermiculite particles. The precipitate was filtered, dried until neutral reaction, and analyzed on the main elements contents, and its main physical–chemical characteristics were determined.

**Modification of vermiculite-based composite by cellulose:** Modification was carried out through dispersing using a cavitator at a frequency of 100 Hz. Vermiculite (100 g) was left in a glass of a volume of 800 ml after treatment by 12 % of hydrochloric acid, after which 9 g of cellulose was added (ash-free filter) and dispersed for 30 min. Thereafter, the solution was filtered and dried at 100°C until constant weight. A part of the obtained sample underwent thermal treatment at 600–700°C. Besides, vermiculite modified with cellulose was treated by ammonia according to the above-described technique. A part of the sample obtained upon modification by ammonia underwent thermal treatment at 600–700°C. The fabricated composites were analyzed on the contents of main elements and their main physical–chemical characteristics were determined.

**Modification of vermiculite by polyethylene:** 45 g of vermiculite of a particle size of 2–3 mm was placed into a flask of a volume of 0.8 l equipped with a Dean–Stark trap. 4 or 8 g of polyethylene was placed into 250 ml of xylene upon boiling. The obtained hot solution was added to vermiculite and boiled with a Dean–Stark trap for several hours until the end of water release. The mixture was filtered, and the precipitate was washed with hexane from the excess of polyethylene and dried in air. The obtained material was heated at 350°C for 1 h. Composite materials without thermal treatment and after heating underwent chemical modification through sequential treatment by solutions of HCl and ammonia, as was described above. The fabricated composites were analyzed on the contents of main elements and their main physical–chemical characteristics were determined.

**Results and discussion**

The natural vermiculite from the Kovdorskoe deposit has a general composition of MgFe0,8Ca0,9Al0,4Si3O11,7H2O, while that from the Koksharovskoe deposit – Mg1,43Fe0,68AlCa0,11K0,36Ti0,21Si2,4O10,5·2H2O [16].

The interplane distance for the vermiculite from the Kovdorskoe deposit is 1.43 nm, while that from the Koksharovskoe deposit – 1.01 nm. The vermiculite structure is shown in Fig. 1.

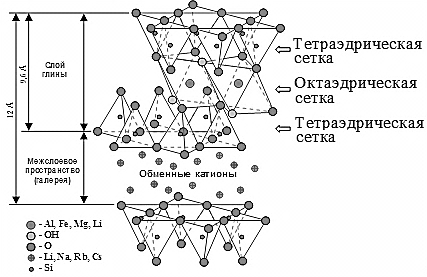


Fig. 1. Structure of vermiculite.

*Results of element analysis*

The compositions of initial and modified vermiculites determined by the method of element analysis are shown in Table 1.

The sample acidic treatment results in destruction of the structure of the natural vermiculite due to release of metal ions to the solution. Destruction is more significant in case of pure vermiculite and less significant – in case of a composite material with PET.

At vermiculite treatment by polyethylene, its composite does not virtually change due to formation of a film on the surface of vermiculite particles, whereas the treatment by acid changes its composition dramatically [6].

Table 1. Compositions of natural and modified vermiculites from Koksharovskoe and Kovdorskoe deposits

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| No. | Sample | Elements contents, % | | | | | | |
| SiO2 | Al2O3 | MgO | CaO | Fe2O3 | TiO2 | C |
| Vermiculites from the Kovdorskoe deposit | | | | | | | | |
| 1 | Initial vermiculite | 42,72 | 11,81 | 24,52 | 5,75 | 8,74 | 0,85 | − |
| 2 | Vermiculite + 7 % HCl | 93,06 | 1,63 | 2,16 | 0,07 | 0,61 | 0,57 | − |
| 3 | Vermiculite + 12 % HCl | 89,63 | 5,18 | 1,06 | 1,01 | 0,34 | 0,17 | − |
| 4 | Vermiculite  + 20 % HCl | 84,26 | 3,64 | 6,74 | − | 4,36 | 0,88 | − |
| 5 | Vermiculite + 36,5 % HCl | 60,61 | 14,81 | 6,95 | 0,74 | 10,83 | 1,06 | − |
| 6 | Vermiculite + 12 % HCl +NH3 | 35,8 | 16,5 | 25,6 | 9,5 | 10,4 | 0,7 | − |
| 7 | Vermiculite + 12 % HCl + chitosan | 95,27 | 1,26 | 1,09 | − | 0,24 | − | − |
| 8 | Vermiculite + 12 % HCl + cellulose | 84,5 | 4,5 | 1,0 | 0,9 | 0,20 | 0,10 | 7,5 |
| 9 | Vermiculite + 12 % HCl + 10% cellulose + NH3 | 56,65 | 14,22 | 16,53 | 0,7 | 10,03 | 0,93 | 9,31 |
| 10 | Vermiculite + 2 % HCl + 10 % cellulose + NH3 + TT at 600–700 °С | 56,84 | 13,90 | 16,54 | 0,52 | 10,41 | 0,89 | 3,78 |
| 11 | Vermiculite + 12 % HCl + cellulose + TT at 600–700°С | 85,6 | 4,8 | 1,1 | 1,0 | 0,25 | 0,10 | 3,4 |
| 12 | Vermiculite + 15 % PET | 29,3 | 8,0 | 17,3 | 4,0 | 14,1 | 0,6 | 19,6 |
| 13 | Vermiculite + 8 % PET, 350 °C | 28,8 | 11,3 | 24,9 | 1,8 | 9,1 | 0,6 | 8,8 |
| 14 | Vermiculite + 8 % PET + 12 % HCl + NH3 | 28,6 | 9,7 | 23,0 | 1,3 | 10,0 | 0,5 | 15,8 |
| 15 | Vermiculite + 8 % PET, 350 °C + 12%HCl + NH3 | 38,5 | 13,2 | 22,7 | 1,3 | 9,6 | 0,5 | 8,2 |
| Vermiculites from the Koksharovskoe deposit | | | | | | | | |
| 16 | Initial vermiculite | 40,60 | 15,63 | 16,03 | 1,73 | 15,47 | 4,73 | − |
| 17 | Vermiculite + 7,2 % HCl | 78,97 | 5,32 | 4,14 | 1,12 | 6,24 | 2,59 | − |
| 18 | Vermiculite + 12 % HCl | 73,05 | 6,24 | 5,9 | 1,23 | 7,63 | 3,16 | − |
| 19 | Vermiculite 2 % HCl + chitosan | 70,77 | 6,18 | 4,13 | 1,57 | 8,34 | 3,23 | − |

At studies of the vermiculite chemical composition, a dependence of changes in the composition on the acid concentration was demonstrated: the higher was the acid concentration, the lower were the contents of all the elements, except silicon. The silicon content increases in comparison with that in initial samples of different vermiculites. However, the silicon content in modified samples decreases along with the increase of the acid concentration. The latter indicates to the fact that, aside from removal of such elements as potassium, calcium, and magnesium, there occurs destruction of the crystal structure of vermiculite, which results in the loss of iron, aluminum, magnesium, and silicon [16,17].

*Discussion of physical–chemical characteristics of the fabricated composites*

The physical–chemical characteristics of the surface of the fabricated samples, such as pore size, surface area, and average particle size, are shown in Table 2.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| No. | Sample | Specific surface area, BET, m2/g | Specific surface area, Langmuir, m2/g | Average pore size, cm3/g | Average pore width, nm | Average pore diameter, nm | Average particle size, nm |
| 1 | Initial vermiculite from Kovdorskoe deposit | 8,79 | 12,88 | 0,0285 | 13,33 | 18,01 | 682,83 |
| 2 | Vermiculite from Kovdorskoe +12 % HCl | 713,97 | 1042,29 | 0,4872 | 2,79 | 3,12 | 8,4 |
| 3 | Vermiculite from Kovdorskoe +12 % HCl | 225,92 | 333,58 | 0,2766 | 5,13 | 4,81 | 26,56 |
| 4 | Vermiculite from Kovdorskoe +12 % HCl | 231,96 | 340,38 | 0,3712 | 6,6 | 6,88 | 25,87 |
| 5 | Vermiculite from Kovdorskoe +12 % HCl | 183,79 | 272,42 | 0,3296 | 7,48 | 7,17 | 32,65 |
| 6 | Vermiculite from Kovdorskoe +12 % HCl | - | 286,0 | 0,130 | - | 2,5-4 | 102,1 |
| 7 | Vermiculite from Kovdorskoe + 20 %HCl +500 С | 225,7 | 333,58 | 0,276 | - | 4,8 | 26,5 |
| 8 | Vermiculite from Kovdorskoe + 8 % PET | 1,86 | 2,78 | 0,0031 | 7,08 | 9,65 | 3219,96 |
| 9 | Vermiculite from Kovdorskoe + 8 % PET + 350 С | 6,48 | 9,32 | 0,014 | 8,78 | 14,05 | 925,34 |
| 10 | Vermiculite from Kovdorskoe + PET + HCl + NH3 | 151,6 | 223,52 | 0,3065 | 8,4 | 8,78 | 39,58 |
| 11 | Vermiculite from Kovdorskoe with high PET content (20-25%) + 350°С | 2,84 | 4,21 | 0,0125 | 18,73 | 38,71 | 2107,13 |
| 12 | Vermiculite from Kovdorskoe + PET + 350°С + 12 % HCl + NH3 | 34,81 | 51,71 | 0,1815 | 21,85 | 20,44 | 172,32 |
| 13 | Vermiculite from Kovdorskoe + 12 % HCl + cellulose + TT at 600–700°С | 52,92 | 76,22 | 0,047 | 3,59 | 5,24 | 113,36 |
| 14 | Vermiculite from Kovdorskoe + 12 % HCl + 10 % cellulose + NH3 | 234,26 | 342,38 | 0,2116 | 3,72 | 4,37 | 25,61 |
| 15 | Vermiculite from Kovdorskoe + 12 % HCl +10 % cellulose + NH3 + TT at 600–700 °С | 224,67 | 332,23 | 0,2248 | 4,17 | 4,54 | 26,71 |
| 16 | Vermiculite from Koksharovskoe + 12 % HCl | 442,29 | 646,28 | 0,3007 | 2,79 | 3,16 | 13,57 |
| 17 | Vermiculite from Koksharovskoe + 12% HCl for 6 days | 442,34 | 642,14 | 0,2951 | 2,72 | 3,19 | 13,56 |

Table 2. Physical–chemical characteristics of the initial vermiculites and composites on their basis

The specific surface area of the vermiculite from the Kovdorskoe deposit modified with 12 % hydrochloric acid is twofold larger than that of the vermiculite from the Koksharovskoe deposit modified through the same method, which could be related to a smaller interplane distance for the latter.

For all the vermiculites under study, one observes trends of the decrease of the specific surface area (both on BET and Langmuir) and the increase of the pore volume along with the increase of the average particle size. Modification of the initial vermiculite by acid significantly increases the specific surface area (Table 2, samples nos. 2–4). As a result, its sorption capacity increases significantly. The largest specific surface area characterizes vermiculite from the Kovdorskoe deposit modified with 12 % hydrochloric acid (Table 2, sample no. 4).

Upon precipitation of the removed aluminum and magnesium ions (Table 2, sample no. 5), the specific surface area somewhat decreases, whereas the internal pore volume increases by 30 %, which indicates to formation of a loose oxide film on the surface of the material particles.

At the vermiculite modification by cellulose (Table 2, sample no. 6), the specific surface area value approaches that of the sample no. 5. Here, the average pore volume decreases significantly, while the particle average size increases. Upon the vermiculite annealing at 600–700°C, its specific surface area, specific volume, pore diameter, and average particle size change insignificantly. The latter indicates to the absence of sintering in the inter-pack space. Moreover, there emerges one more inter-pack space corresponding to the emergence of an extra peak on the X-rai diffraction pattern i.e., the aluminosilicate structuring, rather than its exfoliation, takes place [18].

Upon the vermiculite modification by polyethylene, the particle size increases significantly, while the specific surface area decreases, in comparison with the initial vermiculite. Here, the specific surface area decreases more than 100-fold, while the particle size – up to 400-fold (Table 2, samples nos. 8–12). The most developed surface (>700 m2/g on BET and >1000 m2/g on Langmuir) and the smallest particle size (8.4 nm) characterize the sample no. 2, whereas the lowest specific surface area (<2 m2/g on BET and <3 m2/g on Langmuir) – the sample no. 8 with an average particle size of >3000 nm. Acid treatment of the composite material with subsequent precipitation by ammonia (Table 2, sample no. 10) results in the increase of the specific surface area and the specific volume up to values characteristic of the sample no. 5 (Table 2). Under similar treatment of the sample no. 9 (Table 2, sample no. 12), the specific surface area is 4.3-fold and the specific volume is 2-fold smaller than those for the composite no. 10, which is determined by treatment conditions, as at heating up to 350°C there occurs polyethylene melting on the particle surface, and it fills the interlayer surface, thus blocking the acid percolation.

*Discussion of positron annihilation spectroscopy results*

Physical–chemical properties of vermiculites were studied by positron annihilation spectroscopy (PAS).

The experimental data of positron annihilation spectroscopy of vermiculites from Kovdorskoe and Koksharovskoe deposits are shown in Table 3.

Table 3. Experimental data of positron annihilation spectroscopy of initial vermiculites and those modified by acid

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Sample | Positron annihilation parameters | | | | | | |
| *τ*1, ns | *τ*2, ns | *I*2, % | *τ*3, ns | *I*3, % | *K*2, 1/ns | *K*3, 1/ns |
| Vermiculites from Kovdorskoe deposit | | | | | | | |
| Initial vermiculite | 0,167 | 0,354 | 19,73 | 0,700 | 1,09 | 62,11 | 4,97 |
| Vermiculite + 7 % HCl | 0,161 | 0,310 | 27,82 | 0,891 | 1,36 | 83,06 | 6,91 |
| Vermiculite + 12 % HCl | 0,171 | 0,309 | 30,13 | 1,591 | 4,32 | 78,84 | 22,52 |
| Vermiculite + 20 % HCl | 0,140 | 0,325 | 33,97 | 0,759 | 2,50 | 138,39 | 14,61 |
| Vermiculite + 36,5 % HCl | 0,190 | 0,351 | 20,79 | 0,554 | 1,24 | 50,08 | 4,28 |
| Vermiculite + 12 % HCl + NH3 | 0,204 | 0,331 | 19,75 | 1,953 | 3,77 | 36,76 | 16,49 |
| Vermiculite + 12 % HCl + chitosan | 0,176 | 0,326 | 21,47 | 1,154 | 3,24 | 55,82 | 15,56 |
| Vermiculite + 12 % HCl + cellulose | 0,203 | 0,371 | 29,78 | 1,684 | 1,94 | 65,87 | 8,35 |
| Vermiculite + 12 % HCl + cellulose + TT при 600–700°С | 0,113 | 0,190 | 22,50 | 0,882 | 1,91 | 64,99 | 9,49 |
| Vermiculite + 12 % HCl + 10% cellulose + NH3 | 0,148 | 0,335 | 29,82 | 1,252 | 1,44 | 112,80 | 8,59 |
| Vermiculite + 2 % HCl + 10% cellulose +NH3 + TT at 600–700°С | 0,171 | 0,384 | 20,69 | 0,999 | 1,13 | 66,92 | 5,46 |
| Vermiculites from Koksharovskoe deposit | | | | | | | |
| Initial vermiculite | 0,190 | 0,320 | 16,49 | 0,851 | 1,72 | 35,27 | 7,03 |
| Vermiculite + 7,2 % HCl | 0,194 | 0,312 | 21,32 | 1,322 | 2,28 | 41,53 | 10,03 |
| Vermiculite + 12 % HCl | 0,190 | 0,306 | 24,38 | 1,421 | 3,09 | 48,95 | 14,13 |
| Vermiculite + 12 % HCl + chitosan | 0,161 | 0,343 | 27,29 | 1,353 | 1,75 | 89,78 | 9,57 |

τ1, ns – the lifetime of high-energy positron; τ2, ns – the lifetime of low-energy positron (е+); I2, % – the intensity of positron annihilation (е+); τ3, ns – the positronium lifetime (Ps); I3, % – the intensity of positronium annihilation (Ps); K2, 1/ns – the rate of positron annihilation (е+); K3, 1/ns – the rate of positronium annihilation (Ps).

The results of determination of the concentration of defects and related free volume (Vf) were calculated from models of [19] and shown in Table 4.

Table 4. Calculated data from the free volume

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sample | Параметры | | | | | | | |
| , \*1Е 20 1/cm3 | , \*1Е 20 1/cm3 | trap, Å | trap, Å | , rel. vol. | , rel. vol. | , norm. vol. | , norm. vol. |
| Vermiculites from Kovdorskoe deposit | | | | | | | | |
| Initial vermiculite | 3,71 | 33,54 | 4,49 | 4,34 | 0,141 | 1,152 | 0,110 | 0,890 |
| Vermiculite + 7 % HCl | 5,41 | 44,52 | 4,64 | 4,37 | 0,227 | 1,553 | 0,127 | 0,873 |
| Vermiculite + 12 % HCl | 11,66 | 48,26 | 5,08 | 4,39 | 0,975 | 1,535 | 0,388 | 0,612 |
| Vermiculite + 20 % HCl | 17,74 | 75,79 | 4,61 | 4,34 | 0,479 | 2,599 | 0,156 | 0,844 |
| Vermiculite + 36,5 % HCl | 3,32 | 26,96 | 4,36 | 4,37 | 0,115 | 0,943 | 0,110 | 0,890 |
| Vermiculite + 12% HCl +NH3 | 11,83 | 20,13 | 5,17 | 4,41 | 0,683 | 0,724 | - | - |
| Vermiculite + 12 % HCl + chitosan | 11,79 | 30,75 | 4,79 | 4,37 | 0,543 | 1,077 | 0,335 | 0,665 |
| Vermiculite + 12 % HCl + cellulose | 6,44 | 35,54 | 4,97 | 4,39 | 0,332 | 1,257 | - | - |
| Vermiculite + 12 % HCl + cellulose + TT at 600–700°С | 7,01 | 35,34 | 4,81 | 4,35 | 0,325 | 1,224 | - | - |
| Vermiculite + 12 % HCl + 10 % cellulose + NH3 | 6,20 | 60,60 | 5,01 | 4,34 | 0,327 | 2,079 | 0,136 | 0,864 |
| Vermiculite + 12 % HCl + 10 % cellulose + NH3 + TT at 600–700°С | 3,94 | 36,06 | 4,71 | 4,34 | 0,172 | 1,235 | 0,122 | 0,878 |
| Vermiculites from Koksharovskoe deposit | | | | | | | | |
| Initial vermiculite | 5,33 | 18,90 | 4,53 | 4,39 | 0,208 | 0,671 | 0,237 | 0,763 |
| Vermiculite + 7,2 % HCl | 7,58 | 22,23 | 4,83 | 4,41 | 0,357 | 0,801 | 0,310 | 0,690 |
| Vermiculite + 12 % HCl | 10,93 | 26,21 | 4,89 | 4,42 | 0,537 | 0,947 | 0,361 | 0,639 |
| Vermiculite + 2 % HCl + chitosan | 6,91 | 48,55 | 5,01 | 4,35 | 0,369 | 1,672 | 0,180 | 0,820 |

Nps – the number of positronium annihilations (Рs) in 1 cm3; Ne – the number of positron annihilations (е+) in 1 cm3; Rps – the radius of positronium “trap”; Re – the radius of positron “trap”; Vps, rel. vol. – the relative volume, in which positronium annihilation takes place; Ve, rel. vol. – the relative volume, in which positron annihilation takes place; Vps, norm. vol. – the volume of positronium annihilation in 1 cm3; Ve, norm. vol. – the volume of positron annihilation in 1 cm 3.

The specific free volumes of positronium “traps” are shown in Table 5.

Table 5. Maximal sorption of dyes on initial and modified vermiculites and dependencies of their density and specific volume on the acid concentration at modification

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample | Specific “trap” volume (PAS), Å3 | Dye sorption, mg/g | | Density, g/cm3 |
| Basic | Acidic |
| Vermiculites from Kovdorskoe deposit | | | | |
| Initial vermiculite | 293,9 | 37,0 | 8,8 | 1,597 |
| Vermiculite + 7 % HCl | 235,0 | 50,0 | 14,7 | 0,947 |
| Vermiculite + 12 % HCl | 218,0 | 110,0 | 123,8 | 1,208 |
| Vermiculite + 20 % HCl | 263,0 | 166,0 | 28,6 | 1,235 |
| Vermiculite + 36,5 % HCl | 327,0 | 254,0 | 0 | 1,373 |
| Vermiculite +12% HCl + NH3 | 226 | - | - | - |
| Vermiculite + 12 % HCl + хитозан | 284,0 | 112,0 | 184,0 | 1,289 |
| Vermiculite + 12% HCl + целлюлоза | 324,1 | - | - | - |
| Vermiculite + 12% HCl + cellulose + TT at 600–700°C | 299,2 | - | - | - |
| Vermiculite + 12% HCl + 10 % cellulose + NH3 | 219,3 | - | - | - |
| Vermiculite + 12% HC +10% целлюлоза NH3 + TT at 600–700°С | 309,6 | - | - | - |
| Vermiculites from Koksharovskoe deposit | | | | |
| Initial vermiculite | 443,0 | 28,0 | 2,9 | 1,637 |
| Vermiculite + 7,2 % HCl | 406,0 | 140,0 | 1,92 | 0,888 |
| Vermiculite + 12 % HCl | 331,6 | 62,4 | 0 | 1,098 |
| Vermiculite + 12 % HCl + chitosan | 261,0 | 75,0 | 54,0 | 1,322 |

"–" – parameter was not determined.

Comparison of densities of the vermiculite samples with the concentration of positronium “traps” (Nps) demonstrates that the density decrease results in the increase of the number of “traps”.

The structure of vermiculites from the Koksharovskoe deposit is less susceptible to acid destruction under similar conditions in comparison with those from the Kovdorskoe deposit. The latter must be related to smaller interplane distance in vermiculites from the Koksharovskoe deposit, which is also in agreement with low adsorption capacity of the latter (Table 5).

Thus, vermiculites from the Kovdorskoe deposit are destructed to a much larger degree under effect of acid, as compared to those from the Koksharovskoe deposit. At the same time, more significant destruction of the layered structure of vermiculites from the Kovdorskoe deposit results in fabrication of more efficient sorbents used to remove sorbates of the basic nature.

Along with the increase of the acid concentration at modification, there increases the amount of the sorbed basic dye (Table 5) due to the increase of the number of acidic sites necessary for the sorption. At the same time, the number of “traps” decreases dramatically at the acid concentration of 36.5 % (Table 6), since a positronium competes with a proton in acidic sites.

Table 6. Calculated number of “traps” for initial vermiculites and fabricated composites

|  |  |  |
| --- | --- | --- |
| Sample | Nps\*1Е 20 1/cm3 | Number of positronium “traps” correlating to number of adsorption sites |
| Vermiculites from Kovdorskoe deposit | | |
| Initial vermiculite | 3,71 | 5,2·1013 |
| Vermiculite + 7 % HCl | 5,41 | 6,6·1013 |
| Vermiculite + 12 % HCl | 11,66 | 11,1·1013 |
| Vermiculite + 20 % HCl | 17,74 | 14,7·1013 |
| Vermiculite + 36,5 % HCl | 3,32 | 4,8·1013 |
| Vermiculite + 12% HCl + NH3 | 11,83 | 11,2·1013 |
| Vermiculite + 12 % HCl + chitosan | 11,79 | 11,2·1013 |
| Vermiculite + 12 % HCl + cellulose | 6,44 | 7,5·1013 |
| Vermiculite + 12 % HCl + cellulose + TT at 600–700°С | 7,01 | 7,9·1013 |
| Vermiculite + 12% HCl +10 % cellulose +NH3 | 6,20 | 7,3·1013 |
| Vermiculite + 12% HCl + 10% cellulose + NH3 + TT at 600–700°С | 3,94 | 5,4·1013 |
| Vermiculites from Koksharovskoe deposit | | |
| Initial vermiculite | 5,33 | 6,6·1013 |
| Vermiculite + 7,2 % HCl | 7,58 | 8,3·1013 |
| Vermiculite + 12 % HCl | 10,93 | 10,6·1013 |
| Vermiculite + 12 % HCl + chitosan | 6,91 | 7,8·1013 |

The number of positronium “traps” calculated from the equation 1 correlates to that of reactive sites found on the pyridine adsorption [8].

 (1)

*Discussion of results of low-temperature nitrogen adsorption/desorption*

Measurements of isotherms of low-temperature nitrogen adsorption/desorption enabled us to calculate the values of specific surface areas of the samples of the initial and modified vermiculite samples by Langmuir and Brunauer–Emmett–Teller methods.

Natural vermiculites from Kovdorskoe and Koksharovskoe deposits are characterized with high monodispersitty and small pore volumes.

At treatment of vermiculite from the Kovdorskoe deposit by hydrochloric acid, the quantity of the adsorbed nitrogen increases proportionally to the acid concentration at modification. In case of the initial vermiculite, the sorption capacity is not high (about 20 cm3/g), while for the vermiculite modified with 20 % acid the quantity of the adsorbed nitrogen is about 185 cm3/g, and for that modified with 36.5 % acid this value is about 250 cm3/g (Figs. 2abc). Here, modification of both samples by hydrochloric acid results in the emergence of polydisperse pores (Fig. 3abc), which could be related to changes in the pore volume at washing out of interlayer cations and partial destruction of the aluminosilicate structure in the modification process.

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| --- | --- | --- |
| C:\Users\user\Desktop\рисунки статья\2а, 5а.pngа) | | C:\Users\user\Desktop\рисунки статья\2б.pngb) |
| C:\Users\user\Desktop\рисунки статья\2в.png  c) | | |
| Fig. 2. Isotherms of adsorption/desorption of nitrogen for vermiculite from the Kovdorskoe deposit: a) initial, b) modified with 20 % hydrochloric acid, c) modified with 36.5 % hydrochloric acid. | | |
| C:\Users\user\Desktop\рисунки статья\3а, 6а, 8а, 9а, 10а.png  а) | C:\Users\user\Desktop\рисунки статья\3б.png  b) | | |
| C:\Users\user\Desktop\рисунки статья\3в.png  c)  Fig. 3. Differential curves of distribution of pore volumes on their effective radii for vermiculite from the Kovdorskoe deposit: a) initial, b) modified with 20 % hydrochloric acid, c) modified with 36.5 % hydrochloric acid. | | | |

At modification of vermiculite from the Kovdorskoe deposit, the number of “traps” correlating to the number of reactive sites increases along with the increase of the concentration of acid used in modification, but at the acid concentration of 36.5 % it decreases threefold as compared to the former due to deep destruction of the silicate structure (Fig. 4). Besides, modification with acid of a concentration of 36.5 % induces the formation of a large number positively charged ≡SiOH sites competing with positronium.

Fig 4. Dependence of the number of positronium “traps” on the acid concentration.

In case of vermiculite treated with hydrochloric acid and ammonia, one observes a substantial increase of the quantity of the adsorbed nitrogen: from 20 up to 220 cm3/g, as at modification just by acid (Figs. 5ab). Here, as a result of heterogeneous precipitation of cations transferred to the solution during acid modification, there occur amorphization of the surface of the fabricated composite (Figs. 6ab) and twofold increase of the number of “traps”.

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| C:\Users\user\Desktop\рисунки статья\2а, 5а.png  а) |
| C:\Users\user\Desktop\рисунки статья\5б.png  б)  Fig. 5. Isotherms of adsorption/desorption of nitrogen for vermiculite from the Kovdorskoe deposit: a) initial, b) modified with 12 % hydrochloric acid and ammonia. |
| C:\Users\user\Desktop\рисунки статья\3а, 6а, 8а, 9а, 10а.png  а) | |
| C:\Users\user\Desktop\рисунки статья\6б.png  b) | |

Fig. 6. Differential curves of distribution of pore volumes on their effective radii for vermiculite from the Kovdorskoe deposit: a) initial, b) modified with 12 % hydrochloric acid and ammonia.

The maximal quantity of the adsorbed nitrogen for vermiculite treated by hydrochloric acid and cellulose with subsequent thermal treatment is small (about 30 cm3/g) and close to that for the initial vermiculite (Figs. 7ab). The number of “traps” increases 1.5-fold in comparison with the initial vermiculite, but here one observes a partial surface amorphization (Figs. 8ab).

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Fig. 7. Isotherms of adsorption/desorption of nitrogen for vermiculite from the Kovdorskoe deposit: a) initial, b) modified with 12 % hydrochloric acid and cellulose with subsequent thermal treatment.

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| C:\Users\user\Desktop\рисунки статья\8б.bmp  b) |

Fig. 8. Differential curves of distribution of pore volumes on their effective radii for vermiculite from the Kovdorskoe deposit: a) initial, b) modified with 12 % hydrochloric acid and cellulose with subsequent thermal treatment.

The vermiculite treatment by polyethylene yields changes in the nature of the aluminosilicate surface, which could be related to heterogeneous filling of pores by polyethylene at modification and, therefore, heterogeneous changes in the pore volume (Figs. 9abcd and 10abc).

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| C:\Users\user\Desktop\рисунки статья\9в.png  c) | C:\Users\user\Desktop\рисунки статья\9г.png  d) |

Fig. 9. Differential curves of distribution of pore volumes on their effective radii for vermiculite from the Kovdorskoe deposit: a) initial, b) modified with 8 % polyethylene, c) modified with large amounts of polyethylene (20–25 %) with subsequent thermal treatment, d) modified with 8 % polyethylene with subsequent thermal treatment.

|  |  |
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| C:\Users\user\Desktop\рисунки статья\10в.png  c) | |

Fig. 10. Differential curves of distribution of pore volumes on their effective radii for vermiculite from the Kovdorskoe deposit: a) initial, b) modified with polyethylene, hydrochloric acid, and ammonia c) modified with polyethylene, hydrochloric acid, and ammonia with subsequent thermal treatment.

The maximal quantity of the adsorbed nitrogen decreases significantly for the vermiculite modified with polyethylene in comparison with that of the initial vermiculite (Figs. 11abcd): 10-fold for the vermiculite modified with polyethylene and 1.25 fold for that with high polyethylene content. Upon annealing of the polyethylene-treated vermiculite, the quantity of the adsorbed nitrogen increases 5-fold, but remains still smaller than that for the initial vermiculite.

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| C:\Users\user\Desktop\рисунки статья\11в.png  c) | C:\Users\user\Desktop\рисунки статья\11г.png  d) |

Fig. 11. Isotherms of adsorption/desorption of nitrogen for vermiculite from the Kovdorskoe deposit: a) initial, b) modified with 8 % polyethylene, c) modified with large amounts of polyethylene (20–25 %) with subsequent thermal treatment, d) modified with 8 % polyethylene with subsequent thermal treatment.

In case of the vermiculite modified with polyethylene, at further treatment by acid and ammonia, the maximal quantity of the adsorbed nitrogen increases 100-fold, while at subsequent thermal treatment it decreases down to 125 cm3/g (Figs. 12abc).

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| C:\Users\user\Desktop\рисунки статья\12в.png  c) | |

Fig. 12. Isotherms of adsorption/desorption of nitrogen for vermiculite from the Kovdorskoe deposit: a) initial, b) modified with polyethylene, hydrochloric acid, and ammonia c) modified with polyethylene, hydrochloric acid, and ammonia with subsequent thermal treatment.

The number of “traps” and the nitrogen adsorption value are not correlated, since the nitrogen molecule is neutral, whereas the “trap” has a negative charge and interacts with positron.

At concentrating, one of the methods includes application of natural sorbents, in particular, natural aluminosilicates. The vermiculite modified with 7 % hydrochloric acid (sample no. 2, Table 1) manifests high absorption capacities towards antibiotics: chloramphenicol, tetracycline, ciprofloxacin, and cefazolin: the values of absorption degrees were equal to 73 %, >99 %, >99 %, and 73 %, respectively. Here, the elution degree for chloramphenicol is higher than 75 %, which allows creating concentrating cartridges based on this sorbent. For other antibiotics, the elution degrees are low, which allows application of the vermiculite-based sorbent in decontamination of wastewater and natural water streams from the above antibiotics.

**Conclusions**

1. Natural vermiculites from two natural deposits were modified. At vermiculite modification by hydrochloric acid, a substantial difference between these silicates due to differences in structural parameters has been demonstrated. A less expressed destruction under effect of acid takes place because of the decrease of the inter-pack space. The increase of the number of the adsorption sites and the quantity of the adsorbed nitrogen correlate to the increase of the acid concentration at treatment under similar conditions.
2. At modification of layered natural aluminosilicates by cellulose and polyethylene, the surface nature depends largely on the modifier nature. At treatment by polyethylene, a dramatic decrease of the aluminosilicate surface area due to formation of a dense film takes place. The effect of cellulose is not so significant because of formation of a looser surface structure. The sorption characteristics somewhat improve upon further annealing.
3. Good prospects of application of the fabricated sorbents for antibiotics sorption and analytical determination in food products have been demonstrated.

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