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STUDY OF THE COMPOSITION AND PROPERTIES OF VERMICULITE TREATED UNDER MECHANOCHEMICAL ACTIVATION IN THE PRESENCE OF ACID PHOSPHATE ($NA_2H_2P_2O_7$)

Abstract. The conditions of MX-treatment of vermiculites without additives and in the presence of salt ($Na_2H_2P_2O_7$) were established. The methods of BET Sorbtometer M and laser analyzer SALD 7071 show that specific surfaces and particle sizes, indicating spontaneous aggregation of particles depending on the time and multiplicity of MX-treatment, lead to a decrease in the degree of sorption.

The results of the research conducted on MX-treatment of vermiculites both in the presence of acidic phosphate of the taken salts and without them contributes to an increase in sorption properties. First of all, the type of activator is centrifugal or planetary, of the two mills, the planetary mill is more efficient, because the measurement of particle size showed the smallest particle size, the specific surface area of the largest (11.921 m^2/g). In the case of a planetary mill, the dependence of the increase in sorption properties associated with the participation of grinding bodies (Fe) in the transformation of vermiculite was revealed.

The results of wheat germination with samples of vermiculite processed in a centrifugal mill showed a low growth of the shoot and root system, in comparison with the planetary mill, which is associated with the degree of particle grinding due to the difference in the mechanism of action during MX-processing.

Studies of the effect on the germination of wheat seeds showed the greatest efficiency of modified vermiculites without salt during mechanochemical activation in a planetary mill (root 110.52%,growth104.41%).

Key words: vermiculite, mechanochemical treatment, planetary mill, sorption, specific surface area.

Introduction. Vermiculite is a large lamellar crystals of golden yellow or brown color. Worm-shaped columns or threads of golden or silver color are formed from the plates with transverse division into the thinnest scales (expanded vermiculite) when heated [1,2]. Calcined masses of vermiculite float freely on the surface of the water. Upon transition to the vaporous state, the volume of vermiculite increases greatly, so that the resulting expanded vermiculite becomes up to ten times larger than its original state. It is this property that has given the mineral such widespread use [3-5].

The sorption efficiency of natural vermiculites is low [6-8]. Therefore, it is very relevant to study the physicochemical properties of Kampirsai vermiculites under the conditions of mechanochemical treatment in the presence of acid phosphate ($Na_2H_2P_2O_7$) [9].

EXPERIMENTAL PART

Characteristics of starting materials and methods of chemical and physico-chemical studiesa) the chemical composition of vermiculite (Kempirsai deposit) with the approximate formula $(Mg^{+2},Fe^{+2},Fe^{+3})_3[(AlSi)_4O_{10}]\cdot(OH)_2\cdot 4H_2O$.b) Sodium dihydrogendiphosphate anhydrous ($Na_2H_2P_2O_7$).

The distribution of vermiculite particles was determined using the laser analyzer SALD 7071 (BSU, UFA), which allows real-time studies.X-ray fluorescence analysis was performed at Focus-M (KazNU named after al-Farabi, Almaty). The specific surface and pore volume of the modified vermiculites were determined on a SorbtometerM instrument; IR-spectra were recorded using a Spectrum 65 spectrometer in the frequency range from 400 to 4000 cm -1, in tablets with KBr. X-ray phase analysis was carried out on a DRON-3M and DRON-7 diffractometer (KazNU named after al-Farabi, Almaty).

The initial solutions of heavy metal salts with a concentration of 1 g / l were prepared by dissolving weighed portions in distilled water, from which solutions of the required concentration of 10, 15, 30, and 100 μr / ml were prepared by successive dilution. 100 ml of the resulting solution is mixed with 1 g of modified vermiculite and shaken for 1 hour. The solid phase is separated from the liquid phase to determine the content of Mn^{2+}, Cu^{2+}, Cr^{6+}.

The degree of sorption (α) is calculated by the formula (1):

$$\alpha = (C_{\text{initial solution}} - C_{\text{solution}}) * 100 / C_{\text{initial solution}} .$$

RESULTS AND DISCUSSION

Since the purpose of the work is to obtain sorbents from natural silicates modified with an acidic salt of sodium phosphate ($Na_2H_2P_2O_7$), a mechanochemical treatment of the original vermiculites and a mixture with the indicated salt was carried out.

Vermiculite - $Na_2H_2P_2O_7$. To establish the optimal conditions for obtaining modified vermiculites in the presence of salt, the dependences on:

1) from the multiplicity of processing in a centrifugal mill of vermiculite and vermiculite with salt;

2) comparison of planetary and centrifugal mills.

One ratio of vermiculite mass to salt mass was taken to be 1: 1, and the processing time at the planetary mill was 30 minutes. The results of studying the change in the degree of sorption of Mn2 + ions depending on the rate of processing of vermiculite with salt and without salt are presented in figure 1.

The dependence of the degree of sorption on the multiplicity of processing in a centrifugal mill as well as in a planetary one is inconsistent (it decreases, then increases). Since changes are observed not only in the mixture, but also vermiculite, it can be argued that changes in the degree of sorption is not associated with the use of salts, which confirms the possibility of aggregation during MX-processing.

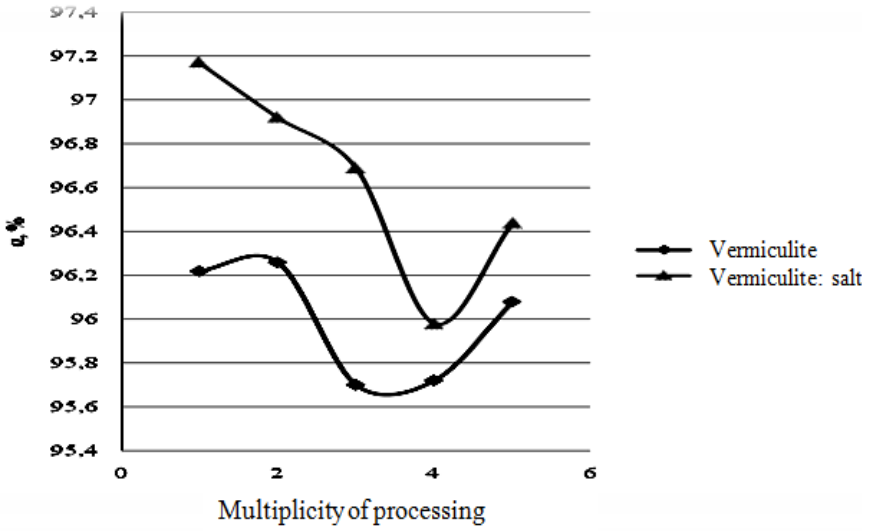


Figure 1 – Dependence of the degree of sorption of Mn2+ cations
on the multiplicity of processing in a centrifugal mill of vermiculite with and without$Na_2H_2P_2O_7$

Next, it was necessary to compare the centrifugal and planetary mill. For this purpose, a diagram (figure 2) was constructed on the degree of sorption by modified vermiculite of Mn^{2+}, Cu^{2+}, Cr^{6+} ions at a concentration of the initial solution of 100 mcg/ ml.

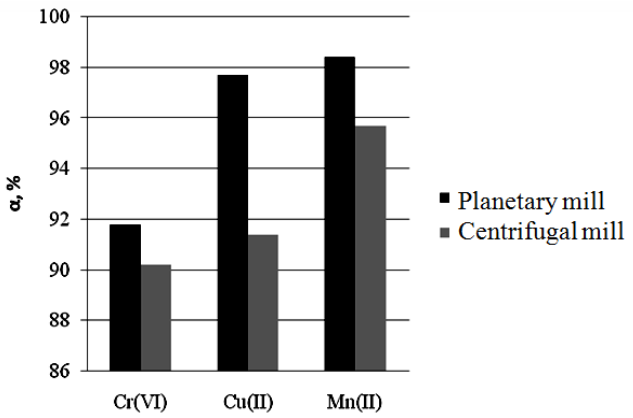


Figure 2 – Dependence of the degree of sorption of modified vermiculite
in centrifugal and planetary mills

As can be seen from the data obtained, the sorption capacity of modified vermiculite on a planetary mill is higher in comparison with a centrifugal mill. This is because the layered structure of vermiculite, when exposed to a free impact in a centrifugal mill, absorbs destructive forces due to the free space between the layers

of particles, in contrast to a planetary mill, where the destructive effect is a constrained blow.

The effect of modified vermiculites on wheat germination is investigated. Wheat is soaked for 2 days in a thermostat at a temperature of 25°C. 15 grains of wheat are placed in a Petri dish on a bed of filter paper, three cups for each concentration of the mixture (33 g / l, 166 g / l), then 6 ml of the mixture are added. The control is 6 ml of distilled water. According to the growth of the seedling and root system in relation to the control, the effect of modified vermiculites is judged.

Figures 3, 4 show the results of studies on the effect of vermiculite with and without salt on the germination of wheat seeds.

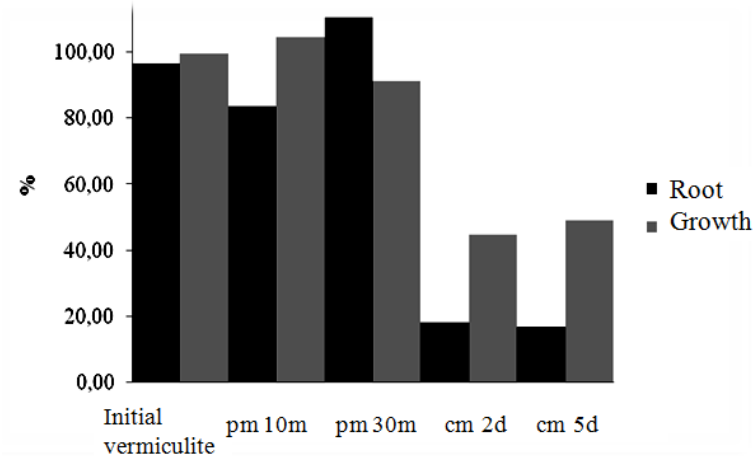


Figure 3 – The effect of salt-free vermiculites processed on a planetary mill for 10 and 30 minutes (pm 10m, pm 30m) and a centrifugal mill 2- and 5-fold (cm 2d, cm 5d) on the germination of wheat seeds

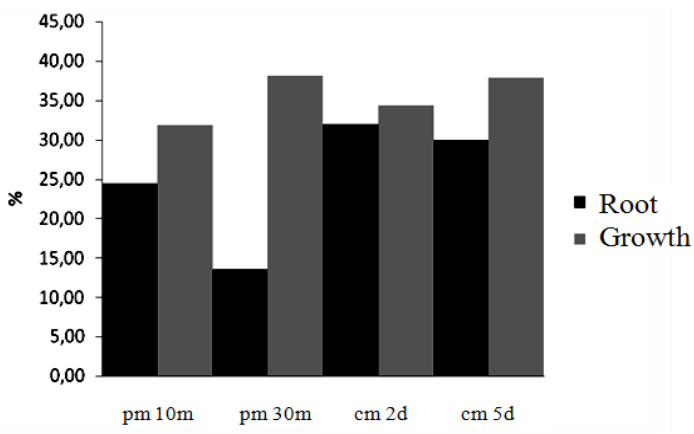


Figure 4 – Effect of modified vermiculites with $Na_2H_2P_2O$ on a planetary mill (pm 10m, pm 30m) and centrifugal mill (cm 2d, cm 5d) on the germination of wheat seeds

As can be seen from figures 3, 4, vermiculites processed in a planetary mill with $Na_2H_2P_2O_7$ showed a low result in comparison with vermiculite without additives, which is possibly associated with an increase in the acidity of the medium, which affects the germination of wheat, limiting the access of trace elements to the plant. At the same time, the changes in the centrifugal mill are insignificant, which is possibly associated with the destruction of salt into monophosphate and the separation of water, because the salt has a crystalline structure, and the mechanism of action of free impact has a more pronounced form.

The results of wheat germination with vermiculite samples processed in a centrifugal mill showed a low increase in shoot and root system, compared with a planetary mill, which is possibly related to the degree of particle grinding due to the difference in the mechanism of action during MX-processing [10].

Further, the influence of modified vermiculite with precipitated Cu^{2+} ions on the germination of wheat grains was studied, the concentration of 16 g/l was taken, the results results are shown in table 1.

Table 1 – Effect on the growth of wheat modified vermiculite with copper ions deposited on it

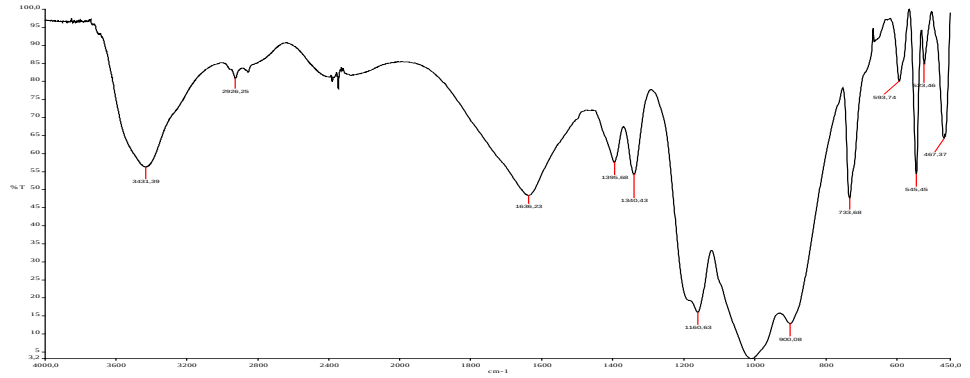
Mixture	ProcessingConditions	Growth	Root
Vermiculite	Withouttreatment	60,30	91,38
Vermiculite	Planetarymill 30 minutes	69,92	97,43
Vermiculite	Centrifugalmill 5 timesprocessing	39,65	71,35
Vermiculitewith$Na_2H_2P_2O_7$	Centrifugalmill 5 timesprocessing	63,34	84,99

As can be seen from the table, the best result was shown by a sample with deposited copper of modified vermiculite without salt treated in a planetary mill for 30 minutes.

The most effective results were shown by MX-processing in a planetary mill with a concentration of 33 g / l with a processing time of 30 minutes, the effect on the root, 10 minutes on the growth.

The results of the IR analysis of the processing of vermiculites with $Na_2H_2P_2O_7$ processed in a centrifugal mill are shown in figure 5.

The IR spectrum during the modification of vermiculites with the $Na_2H_2P_2O_7$ salt in a centrifugal mill, the absorption band disappears in the frequency range 670 cm^{-1}, which corresponds to the stretching vibrations of the Si – O bond, which appears after 5-fold treatment (663 cm^{-1}). Also, after 2-fold and further processing, the absorption band at 2926 cm^{-1}, associated with stretching vibrations ofH_2O and PO-H bonds, disappears. Also, after a single treatment, the absorption band of 492 cm^{-1} disappeared, caused by vibrations of theHPO_4^{2-} anions, then it appears already after a double treatment. Despite the layered structure of vermiculite, along with changes in the absorption bands corresponding to the salt, changes in the absorption bands of the mineral are observed, which is consistent with theX-ray phase analysis results.



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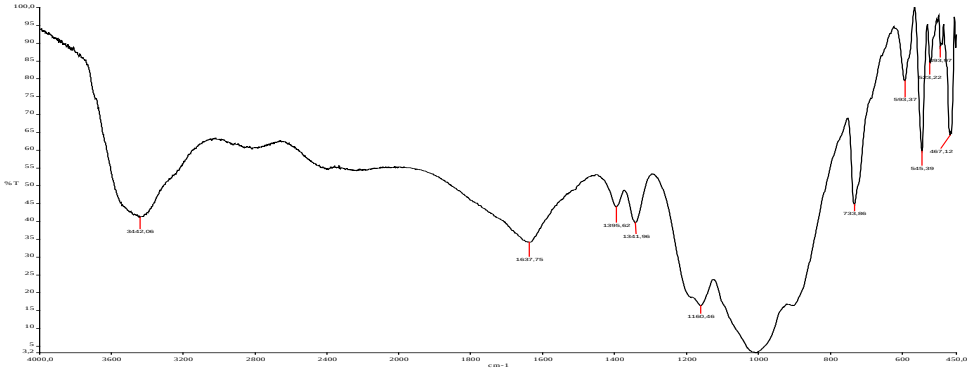

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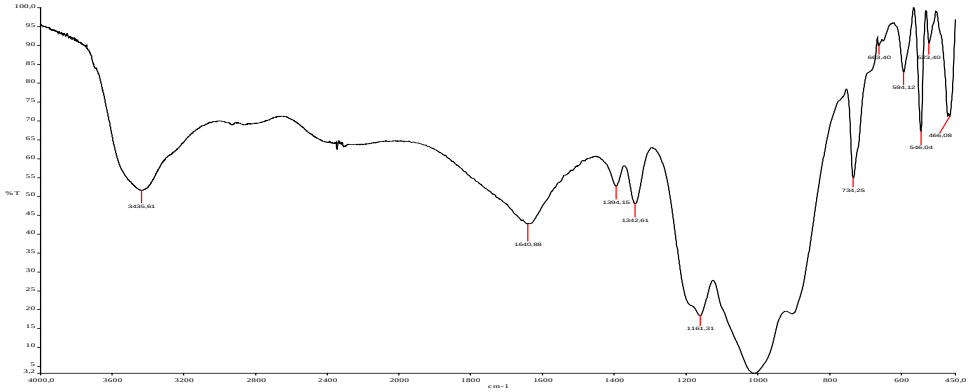

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Figure 5 – IR spectrum of vermiculite
with $Na_2H_2P_2O_7$ treated 1(1);2(2);5(3)-multiple on centrifugal mill

The specific surface was measured by the single-point BET method, the specific pore volume from the maximum filling. The measurement results are summarized in table 2.

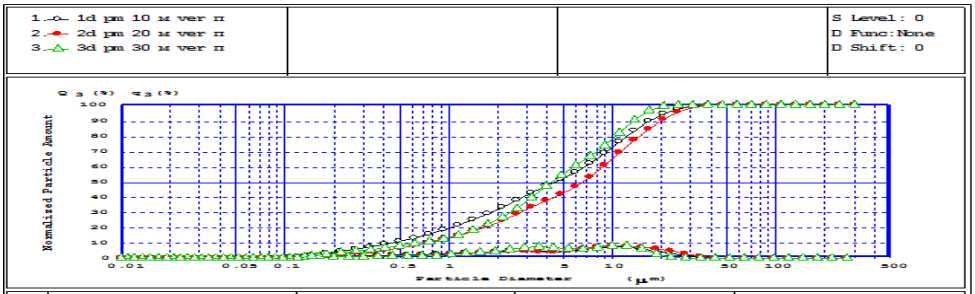
Table 2 – Specific surface and pore volume of modified vermiculites

Sample composition	Processing conditions	Specific surface area, m^2/g	Specific pore volume, cm^3/g	Average-poresize, nm
Vermiculite	Withouttreatment	10,565	0,005	1,717
Vermiculite	Planetarymill 30 minutes	11, 921	0,005	1,721
Vermiculite	Centrifugalmill 1timesprocessing	11,577	0,005	1,721
Vermiculite	Centrifugalmill 3timesprocessing	7,304	0,003	–
Vermiculite	Centrifugalmill 5 timesprocessing	10,784	0,005	1,720
Vermiculite: $Na_2H_2P_2O_7$	Centrifugalmill 1 timesprocessing	5,369	0,002	–
Vermiculite: $Na_2H_2P_2O_7$	Centrifugalmill 3 timesprocessing	3,972	0,002	–
Vermiculite: $Na_2H_2P_2O_7$	Centrifugalmill 5 timesprocessing	5,825	0,003	–

When using a centrifugal mill, the specific surface, depending on the processsing ratio, increased or decreased, which can be explained by the process of aggregation of individual particles of material with the formation of flakes, intergrowths and other neoplasms, which significantly reduce the contact surface area of the material. This fact explains the results of sorption in terms of multiplicity, because when studying the degree of sorption by multiplicity, the degree of sorption first decreased, and then increased again. Because according to the results of sorption, modified vermiculites with $Na_2H_2P_2O_7$ have better sorption ability, it was assumed that the specific surface area will be larger in comparison with the initial one. Comparing the type of activator, the planetary mill 11.921 m^2/g showed the best result on the specific surface.

The results of particle size measurements of modified vermiculites are shown in figures 6–8.

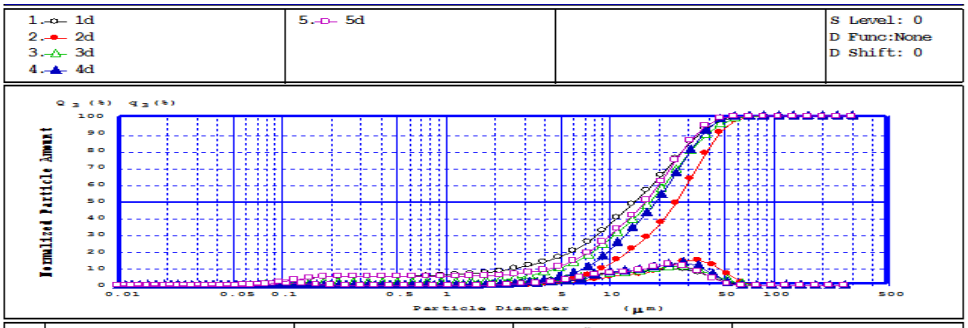
Particle size measurements showed that the average particle size of the powder, depending on the processing conditions on a planetary mill for vermiculite with $Na_2H_2P_2O_7$, was from 4.3 to 6.6 micrometers (figure 6), after a centrifugal mill for vermiculite from 14.3 to 25.7 micrometers (figure 7) and for vermiculite with $Na_2H_2P_2O_7$ from 27.4 to 45.5 micrometers (figure 8). It follows that the results of the BET analysis correlate with the results of the study of sorption properties and confirm the presence of aggregation processes during mechanochemical processing.



	File Name	Sample ID	Sample #	R Index
1	1d pm 10 м ver n			1.55-1.00i
2	2d pm 20 м ver n			1.55-1.00i
3	3d pm 30 м ver n			1.55-1.00i

	Median D	Modal D	Mean V	Std Dev	25.0%D	50.0%D	75.0%D
1	4.506	9.993	3.507	0.602	1.386	4.506	10.750
2	6.640	9.993	4.862	0.553	2.167	6.640	12.910
3	4.295	12.281	3.625	0.514	1.959	4.295	9.314
4							

Figure 6 – Integral and differential distribution of particles of vermiculite processed in a planetary mill with $Na_2H_2P_2O_7$ 1-10 minutes, 2-20 minutes, 3-30 minutes in size in microns



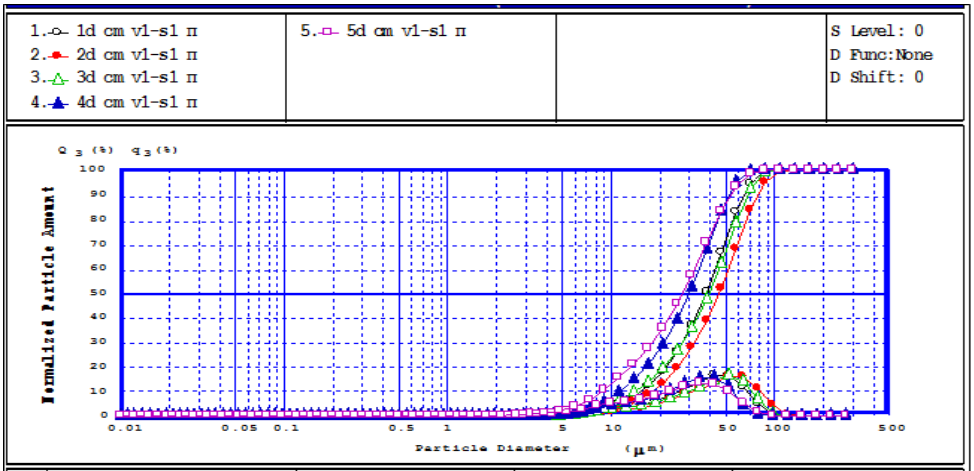
	File Name	Sample ID	Sample #	R Index
1	1d			1.55-1.00i
2	2d			1.55-1.00i
3	3d			1.55-1.00i
4	4d			1.55-1.00i
5	5d			1.55-1.00i

	Median D	Modal D	Mean V	Std Dev	25.0%D	50.0%D	75.0%D
1	14.292	22.795	10.379	0.596	7.133	14.292	25.160
2	25.672	34.429	22.571	0.277	14.985	25.672	36.479
3	17.725	28.014	14.575	0.440	9.270	17.725	28.549
4	19.181	28.014	17.145	0.291	11.040	19.181	28.817
5	16.522	22.795	11.779	0.574	8.745	16.522	25.611

Figure 7 – Integral and differential distribution of vermiculite particles processed in a centrifugal mill 1-,2-,3-, 4- and 5-fold processing (1d, 2d, 3d, 4d and 5d respectively) in size in microns

The results of x-ray fluorescence analysis are shown in figures 9, 10.

The spectrum of x-ray fluorescence analysis showed an increased iron content of up to 70% relative to the initial composition. The reason could be the metal casing of a centrifugal mill, grinding jars and steel balls used when working on a planetary mill. The increase in iron content according to XRD results in the formation of biotite, which contributes to an increase in α-sorption. So, when using a planetary mill, the iron content is higher in comparison with centrifugal, corresponding to a high degree of sorption when using a planetary mill.



	File Name	Sample ID	Sample #	R Index
1	1d cm v1-s1 n			1.55-1.00i
2	2d cm v1-s1 n			1.55-1.00i
3	3d cm v1-s1 n			1.55-1.00i
4	4d cm v1-s1 n			1.55-1.00i
5	5d cm v1-s1 n			1.55-1.00i

	Median D	Modal D	Mean V	Std Dev	25.0%D	50.0%D	75.0%D
1	38.020	52.001	34.267	0.245	24.607	38.020	52.218
2	45.542	52.001	40.839	0.253	28.968	45.542	63.108
3	39.619	52.001	34.886	0.263	24.239	39.619	55.348
4	29.999	42.313	26.872	0.254	18.661	29.999	42.068
5	27.373	34.429	24.154	0.301	15.450	27.373	41.048

Figure 8 – Integral and differential distribution of vermiculite particles processed in a centrifugal mill with $Na_2H_2P_2O_7$ 1-,2-,3-,4- and 5-fold processing (1d, 2d, 3d, 4d and 5b respectively) in size in microns

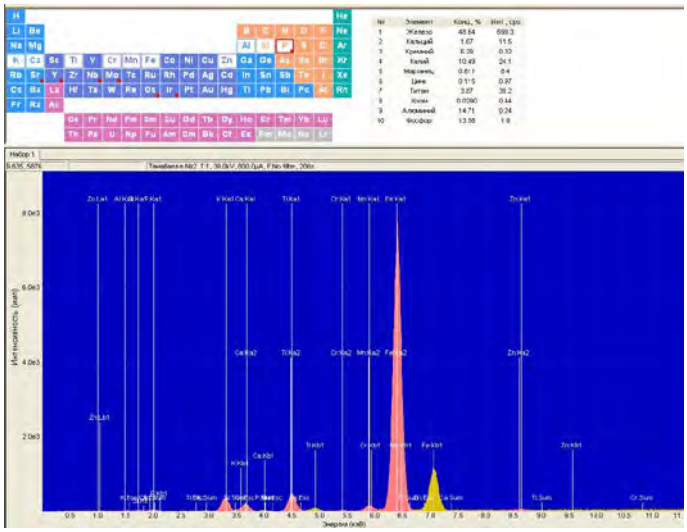


Figure 9 – The spectrum of processed 5-fold vermiculite in a centrifugal mill

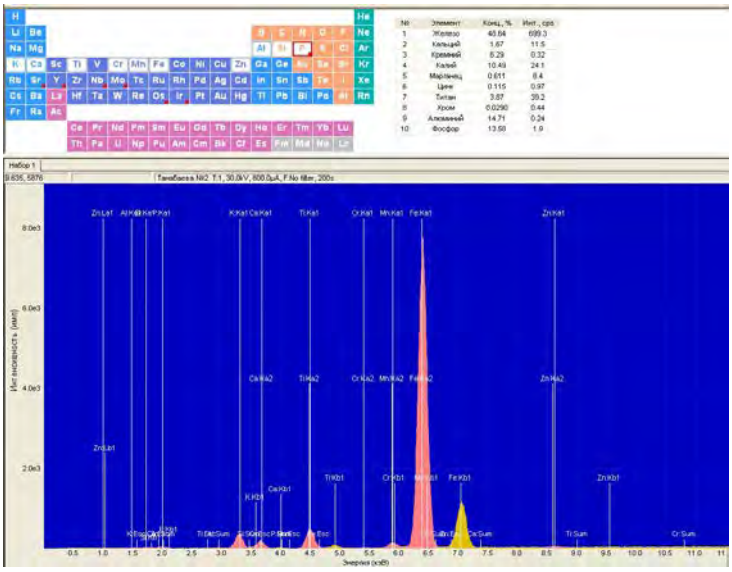


Figure 10 – The spectrum of treated 5-fold vermiculite with $Na_2H_2P_2O_7$ in a centrifugal mill

Modified vermiculites can be used with respect to all the studied ions Mn^{2+}, Cu^{2+}, Cr^{6+}, so the lowest result was the degree of sorption with respect to chromium 90.2%, and the best with manganese 98.43%.

Conclusions.

1. The results of studies of MX processing of vermiculites, both in the presence and without acid phosphate of salts taken, contribute to an increase in sorption properties. First of all, the type of activator is centrifugal or planetary, of two mills, the planetary mill is more effective, because particle size measurement showed the smallest particle size (average particle size from 4.3 to 6.6 μm depending on the processing time), the specific surface area was the largest (11.921 m2 / g). In the case of a planetary mill, the dependence of an increase in sorption properties associated with the participation of grinding media (Fe) in the vermiculite transformation was revealed.

2. Studies have shown the effect on the germination of wheat seeds showed the greatest effectiveness of modified vermiculites without salt during mechanochemical activation in a planetary mill.

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Резюме

Б. Д. Балғышева, И. А. Масалимов, Ф. Х. Уракаев, Д. Ғ. Балтабаева

ҚЫШҚЫЛ ФОСФАТ ($NA_2H_2P_2O_7$) ҚАТЫСУЫМЕН МЕХАНОХИМИЯЛЫҚ АКТИВТЕНДІРУ ЖАҒДАЙЫНДА ӨҢДЕЛГЕН ВЕРМИКУЛИТТІҢ ҚҰРАМЫ МЕН ҚАСИЕТТЕРІН ЗЕРТТЕУ

Вермикулиттерді қоспасыз және тұздың ($Na_2H_2P_2O_7$)қатысуымен МХ-өңдеу шарттары белгіленген. БЭТ Sorbtometer M және SALD 7071 лазерлік анализаторы әдістерімен МХ-өңдеу уақыты мен еселігіне байланысты бөлшектердің өздігінен агрегациясы туралы куәландыратын бөлшектердің үлестік беті мен өлшемдері сорбция дәрежесінің азаюына алып келеді.

Алынған тұздардың қышқыл фосфатының қатысуымен де, онсыз да вермикулиттерді МХ-өңдеудің жүргізілген зерттеулерінің нәтижелері сорбциялық қасиеттердің артуына ықпал етеді. Бірінші кезекте екі диірменнен ортадан тепкіш немесе планетарлық активатор түрі әсер етеді, планетарлық диірмен тиімдірек, себебі бөлшектердің өлшемін өлшеу бөлшектердің ең аз мөлшерін көрсетті, ал ең үлкенін (11,921 $м^2$/г) меншікті бетін өлшеу көрсетті. Планетарлық диірмен жағдайында борлы денелердің (Fe) вермикулитіне трансформациялануына байланысты сорбциялық қасиеттердің ұлғаюы арасындағы тәуелділік анықталды.

Центрден тепкіш диірменде өңделген вермикулит үлгілерімен бидайды өсіру нәтижелері планетарлық диірменмен салыстырғанда өркен мен тамыр жүйесінің төмен өсуін көрсетті, бұл МХ-өңдеу кезіндегі әсер ету механизмінің айырмашылығынан бөлшектердің ұсақтау дәрежесіне байланысты.

Бидай тұқымдарының өнімділігіне әсер ету зерттеулерімен планетарлық диірменде механохимиялық активтендіру кезінде тұзсыз модификацияланған вермикулиттердің барынша тиімділігі көрсетілген (тамыр 110,52%, өркен 104,41%).

Түйін сөздер: вермикулит, механохимиялық өңдеу, планеталық диірмен, сорбция, меншікті бет.

Резюме

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ИССЛЕДОВАНИЕ СОСТАВА И СВОЙСТВ ВЕРМИКУЛИТА, ОБРАБОТАННЫХ В УСЛОВИЯХ МЕХАНОХИМИЧЕСКОЙ АКТИВАЦИИ В ПРИСУТСТВИИ КИСЛОГО ФОСФАТА ($NA_2H_2P_2O_7$)

Установлены условия МХ-обработки вермикулитов без добавки и в присутствии соли ($Na_2H_2P_2O_7$). Методами БЭТ Sorbtometer M и лазерного анализатора SALD 7071 показано, что удельные поверхности и размеры частиц, свидетельствующие о самопроизвольной агрегации частиц в зависимости от времени и кратности МХ-обработки, ведут к уменьшению степени сорбции.

Результаты проведенных исследований МХ-обработки вермикулитов как в присутствии кислого фосфата взятых солей, так и без них способствуют увеличению сорбционных свойств. В первую очередь влияние оказывает тип активатора центробежный или планетарный, из двух мельниц, планетарная мельница более эффективна, так как измерение размеров частиц показало наименьшие размер частиц, удельная поверхность наибольшей (11,921 $м^2/г$). В случае с планетарной мельницей выявлена зависимость увеличения сорбционных свойств, связанное с участием в трансформировании вермикулита мелющих тел (Fe).

Результаты проращивания пшеницы образцами вермикулита, обработанного на центробежной мельнице, показали низкий прирост побега и корневой системы, в сравнении с планетарной мельницей, что связано со степенью измельчения частиц из-за разницы механизма воздействия при МХ-обработке.

Исследование влияния на всхожесть семян пшеницы показало наибольшую эффективность модифицированных вермикулитов без соли при механохимической активации на планетарной мельнице (корень 110,52%, побег 104,41%).

Ключевые слова: вермикулит, механохимическая обработка, планетарная мельница, сорбция, удельная поверхность.