PREPARATION OF VERMICULITE AND POLYPOLYACRYLONITRILE COMPOSITE AND ITS MODIFICATION WITH DIETHANOLAMINE

S.A. Kholmurodova[1]*, Kh.Kh. Turaev[1], R. Alikulov[1], A.Kh. Tashkulov[1], B.A. Xolnazarov[1], S.G. Yuldashova[2], Kh.E. Eshmurodov[3]

[1]*Faculty of Chemistry, Termiz State University, Termiz, Uzbekistan*
[2]*Tashkent Research Institute of Chemical Technology, Tashkent, Uzbekistan*
[3]*Department of Medical and Biological Chemistry, Termez branch of Tashkent Medical Academy, Termez, Uzbekistan*
**e-mail: xolmurodovasaboxat84@gmail.com, (ORCID:0000-0003-0002-7054).*

Received 10.06.2024
Accepted 11.08.2024

Abstract: *This article studied the characteristics of vermiculite sourced from the Tebinbulok mine situated within the borders of the Republic of Uzbekistan, as well as the most favorable conditions for its activation through heating and treatment. A 7% solution of hydrochloric acid was used for activation. Activated vermiculite was modified using maleic anhydride and polyacrylonitrile dissolved in acetic acid solution. The properties of the resulting composite were studied. To further increase its sorbent properties, diethanolamine with an amine functional group was added to the composite. A laboratory study of the obtained organic-inorganic composite is presented. The research was carried out in the state connected to the reflux cooler, at a temperature of 60-70°C, with constant stirring. The properties, microstructure, porosity, thermal tolerance, and composition of the samples were analyzed using traditional and empirical methods of physical and chemical analysis, respectively, and IRTracer-100 SHIMADZU (Japan), infrared IR-Fourier, MIRA 2 LMU scanning electron microscope (SEM), elemental analysis, thermogravimetric (TGA and DTA) analysis, and X-ray phase analysis were studied. The results showed that after activation, vermiculite, which is almost chemically stable, was bound to polyacrylonitrile through the OH^{-} bonds formed in it, and maleic anhydride acted as a modifier in the binding, polyacrylonitrile vermiculite polymerized in solution It was proved by analysis that it formed one composite with OH- bonds formed on its surface. To further increase the sorption capacity of this composite with maleic anhydride as a binder, diethanolamine containing an amine functional group was added to it.*

Keywords: *Vermiculite, activation, polyacrylonitrile, maleic anhydride, modification, sorption, desorption.*
DOI: 10.32737/2221-8688-2025-1-3-19

1. Introduction

In recent years, there have been endeavors to develop contemporary and exceptionally efficient sorbents designed for extracting toxic metal ions from diverse industrial waste streams. It is a challenge to manufacture sorbents that would be efficient concerning various pollutants. [1, 2]. "Salt in a porous matrix" composites based on expanded vermiculite are widely used for their properties such as high sorption and heat retention [3]. In a broader sense, the proposed approach helps to accelerate the sorption of methanol, water, and ammonia in composites based on macroporous matrices [3].

Several experiments have shown that mineral sorbents such as zeolite and vermiculite are more effective than organic sorbents for nickel, cobalt, strontium, and other metals under static conditions, and they can be used as high-efficiency filters with high sorption capacity [4]. As the level of pollution in water and land increases due to climate change around the world, ions are created that affect global food security. In 2022 research conducted based on FGBOU HE SPbGUVM, 45 Guppy aquarium fish were taken as research subjects, and when the natural vermiculite sorbent mixture was added to the feed of these fish in the amount of

4%, the amount of lead in the fish body was reduced. showed a significant decrease in the amount [5]. It has also been revealed that up to 45% of waste antibiotics can be removed using vermiculite treated with 7% hydrochloric acid [6]. In addition, the increase in the mechanochemical activation level of vermiculite can change the hydration state of vermiculite, and it can change from its hydration state to a single or bilayer state. This indicates that the level of sorption of oil product waste is high [7]. One such study conducted by Russian scientists obtained composite materials based on resorcinol-formaldehyde polymer of vermiculite and phosphorous vermiculite, and their sorption characteristics were studied in the example of methylene blue adsorption and strontium extraction from aqueous solutions under static conditions [8]. In the following research work, vermiculite-based sorbents showed the best results for cleaning hexachlorobenzene, one of the persistent organic pollutants that can have harmful effects on humans and other living organisms [9, 10]. The technology of cleaning highly concentrated solutions using activated vermiculite and granular serpentine sorbent was used to clean soils contaminated by the wastes of copper-nickel production from vermiculite mineral (Monchegorsk, Murmansk region) [11]. A vermiculite-based sorbent was also used to clean Cr (VI) ions and humic acid in the soil [12, 13].

The purpose of research. Determining the composition and properties of Tebinbulok vermiculite. Obtaining a composite based on vermiculite and polypolyacrylonitrile and obtaining sorbents by modifying it with diethanolamine, studying their physico-chemical sorption properties.

2. Experimental part

2.1. Obtaining a vermiculite composite. To obtain a polyacrylonitrile-modified vermiculite composite, Tebinbulok mine vermiculite meeting the requirements of GOST 12865-67 (Table 1), polyacrylonitrile in the technical state GOST 11097-86, pure maleic anhydride meeting the requirements of GOST 11153-75 in the technical state, and TY 2423 were included to bind the amine functional group. A-151-00203335-2003 type of diethanolamine with 98%, which meets the requirements of GOST, was used.

Table 1. Chemical composition of Tebinbulok mine vermiculite

Component	**SiO_2**	**MgO**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**Na_2O**	**K_2O**	**FeO**	**TiO_2**	**MnO**	**SO_3**	**other**
The amount; % mass	38-49	20-23.5	12-17.5	5.4-9.3	0.7-1.5	0.8	5.2-7.9	1.2	1.5	0.1-0.3	1.5	2.04

(a) (b)

Fig. 1. View of vermiculite from Tebinbulok mine in natural (a) and porous (b) state

Washed, cleaned and dried vermiculite in distilled water was burnt in a Digital Muffle Furnace FHX-05 at a temperature of 900°C in an airless environment. In this case, hydration water between the layers of vermiculite is released [14-15]. The layers of vermiculite swell up again and turn yellow with a beautiful metallic sheen (Fig. 1).

When the temperature exceeds 150°C, the condensed water between several layers of vermiculite starts to evaporate. This situation, which occurs in chemically more stable vermiculite, can be understood by analyzing its structure (Fig. 2).

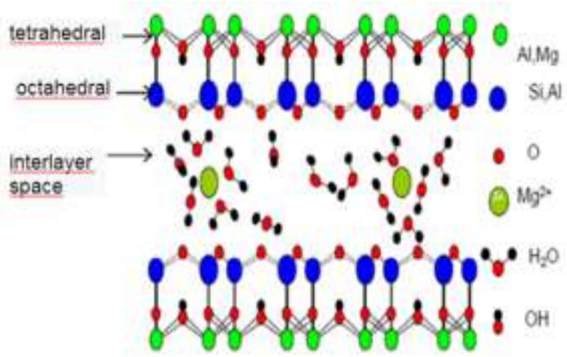
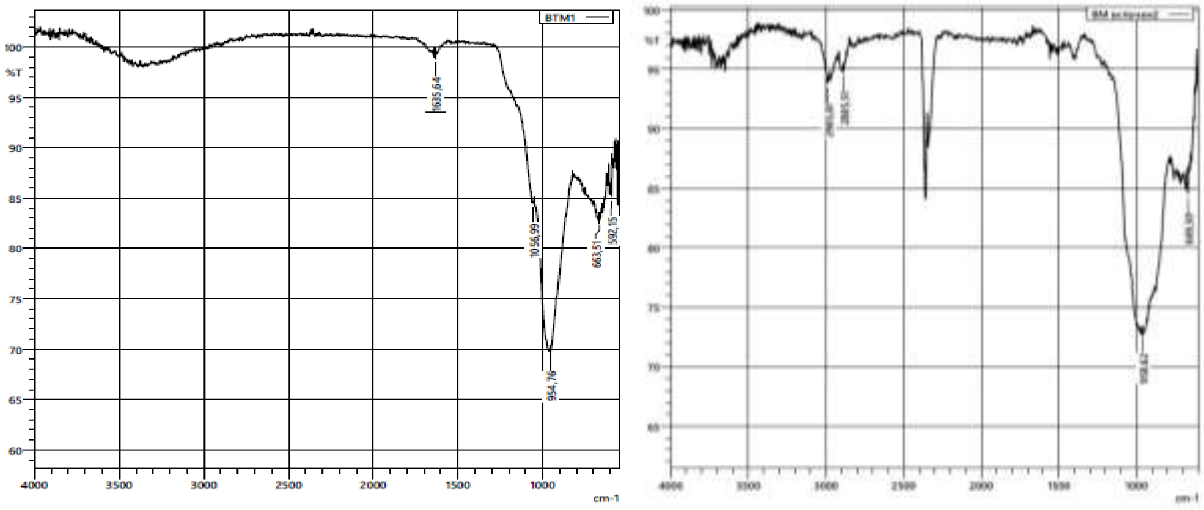


Fig. 2. The structure of vermiculite.

Vermiculite consists of hydrated aluminum and magnesium silicate, and when heated to 150-1000 °C, it expands 8-30 times compared to its original volume due to the vaporization of constituent waters in vermiculite layers. After cooling, expanded vermiculite retains its new volume. Expanded vermiculite particles are seen as thin plates separated by air spaces. Their shape, color, brightness, and composition are closely related to the original raw materials. The water absorption capacity of vermiculite increased dramatically as the bulk density and particle size varied from 64 to 160 kg/m^3. As a result, vermiculite has several properties such as low thermal conductivity, high fire resistance, and strong sound absorption [14].



(a) (b)

Fig. 3. IR spectra of Tebinbulok mine vermiculite, natural (a) and porous (b)

In our research, we have studied the activated methods with solutions of hydrochloric acid of different concentrations and performed acidic thermal treatment with hydrochloric acid in the following order. 10 mg of crushed Tebinbulok mine vermiculite, porous at 900 °C, was placed in a flask with a flat bottom, 250 ml capacity. and 100 ml of 7% HCl acid solution was added and stirred in a magnetic stirrer at a speed of 650 rpm. The process was carried out in a reflux condenser with the temperature control adjusted to 65-70°C. The mixture was filtered and the remaining acid residue was neutralized with low low-concentration sodium hydroxide solution. The resulting salts were decanted. In all the above cases, vermiculite was washed and cleaned, and dried in a drying oven at a temperature of 80-95 °C for one day. The resulting product is a dark yellow, porous, small granular substance [16] (Fig. 3). The reaction yield is 91%.

In Fig. 4, we can see the analysis of infrared spectra obtained after processing and activating Tebinbulok mine vermiculite in 15% sulfuric acid and 7% hydrochloric acid. Deep peaks in the 3361.93 cm^{-1} vibrational regions of hydrochloric acid-treated vermiculite, shown in black lines, and 3384.11 cm-1 vibrational regions in the IR spectra of sulfuric acid-treated vermiculite, represented in red lines, increase the degree of hydration during activation in the outer layers of vermiculite. appeared to belong to the resulting H-bonded, valence-vibrating, extensive, and intense OH bonds. The presence of Si-O- valence bonds was seen in the vibration fields of 1060.85 cm-1 in black lines and 1039.63 cm^{-1} in red lines.

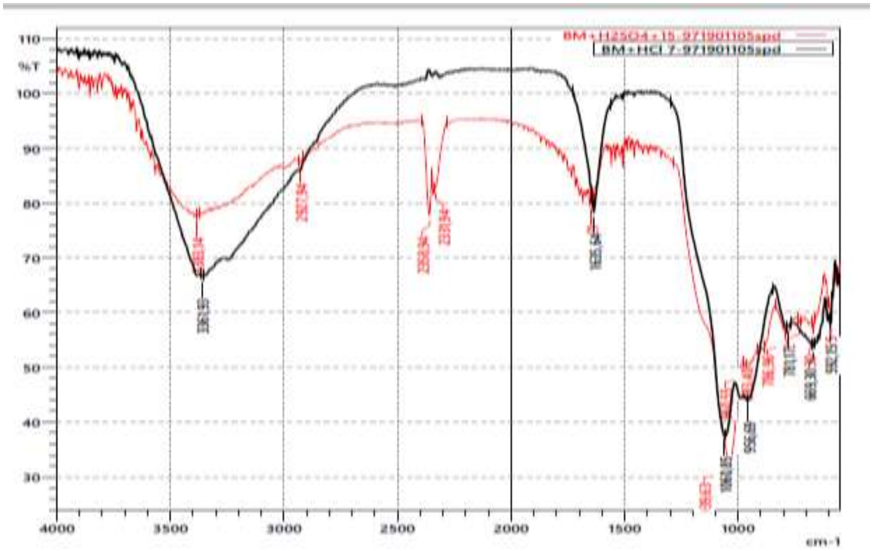


Fig. 4. IR spectroscopy analysis of vermiculite activated with 15% sulfuric acid (red lines) and 7% hydrochloric acid (black lines).

2.2. Porous and activated vermiculite was modified using polyacrylonitrile. Maleic anhydride was used to etch polyacrylonitrile and vermiculite composite. Maleic anhydride dissolved in acetic acid easily enters and intercalates between layers of vermiculite. Polyacrylonitrile is polymerized with the help of maleic anhydride and forms a whole composite with vermiculite. The initiation of solution polymerization was initiated after adding a small amount of initiator [17]. The experiment was carried out in a magnetic stirrer at a temperature of 348 K with distillation with a deflegmator connected and under constant stirring. Polymerization first occurs in water and precipitates as the molecular weight increases. After the polymerization was completed, it was filtered and dried in a drying oven at 70°C for one day [15].

2.3. The sorbent properties of the obtained composite were studied. Vermiculite, which is a natural sorbent, has a SAS value of 0.8 mg-eq/g, while this composite has a value of 4 mg-eq/g. This value was determined by the sorption of copper ions from a 0.1 N solution of $CuSO_4$. 30 mg of ionite was taken and placed in 10 ml of solution. The concentration of the solution left for one day was measured in a UF spectrometer. The standard solution, that is, the solution without ionite, and the solution that was in the sorbent for one day, were examined. By putting the results into the following formula, the value of ionite sorption amount was determined.

$$q_e = \frac{V_{0,i} \cdot (C_{0,i} - C_i)}{m}$$

Here: q_e is the amount of ion absorbed by the ionizer; mmol/g
$V_{0,I}$ – solution volume; l
C_{0i}- initial concentration of the solution; mmol/l
C_{0i}- equilibrium concentration; mmol/l
m- dry ionite mass; g.

Based on this formula, the amount of Cu(II) ions and Zn(II) ions absorbed into the sorbent was found. The highest reaction yield and static exchange capacity were obtained when the ratio of starting materials, vermiculite: polyacrylonitrile: maleic anhydride - 1:2:0.5 was obtained. It was determined that the amount of ions absorbed by the obtained sorbent is equal to qe=4.1 in the solution containing Cu (II) ion, and q_e=3.01 in the solution containing Zn(II) ion [16]. The results of the study of the physico-chemical properties of the obtained sorbent are presented in Table 2.

Table 2. The influence of the mole amounts of the initial substances on the physico-chemical properties of the obtained sorbent

Vermiculite, Polyacrylonitrile and Maleic Anhydride	Reaction product, %	Static exchange capacity in 0.1 N solution, mmol/g	
		$CuSO_4$	$ZnSO_4$
2:2:0.5	78%	2.6	2.1
1:1:1	80%	3.5	2.9
1:2:0.5	94%	4.1	3.01

To further increase the sorption capacity of the obtained sorbent, an amine functional group was added to this sorbent. For this, diethanolamine containing an amine group was exposed to a sorbent in a mass ratio of 1:0.2. The reaction was carried out in a fume hood at a temperature of 338 K with continuous mechanical stirring. When the mixture became tar-like, we poured it into a large porcelain container, dried it with the help of artificial wind, and crushed it. The obtained product is a solid, porous substance of light brown color. The static exchange capacity of the sorbent modified with diethanolamine was studied. This value was found to be equal to qe=10. Initial and final solutions of ionic solution of Cu (II) were examined in the UF spectrophotometer of the Japanese company SHIMADZU [17, 18]. Zn(II) ion was detected by complexometric titration using the optical densities of the standard and test solution to determine the amount of static exchange in the available solutions. This value was equal to qe=5.5. The investigation was carried out at temperatures of 338 K, 353 K, and 318 K. The best optimum temperature for reaction yield was found to be 338 K. The reaction yield at this temperature was 95.5%. Table 3 presents the results of the study of the synthesis of vermiculite-based sorbent modified with polyacrylonitrile and diethanolamine (VT-PANDEA) on the dependence on temperature and other physicochemical processes [19].

Table 3. Dependence of VT-PANDEA sorbent on physical and chemical conditions

Temperature, K	Reaction product, %	Static exchange capacity in 0.1 N solution, mmol/g	
		$CuSO_4$	$ZnSO_4$
318	82	7.5	5.3
338	**95.5**	**10**	**6.5**
353	85	6.3	4.5

3. Results and its discussion

3.1. Raman spectroscopy analysis. To study the composition of vermiculite-based composite sorbent modified with polyacrylonitrile and diethanolamine, Raman IR-spectroscopy analysis was conducted (Fig. 5). Analyzes were performed on a Japanese Shimadzu instrument in the 0 to 3500 cm^{-1} field.

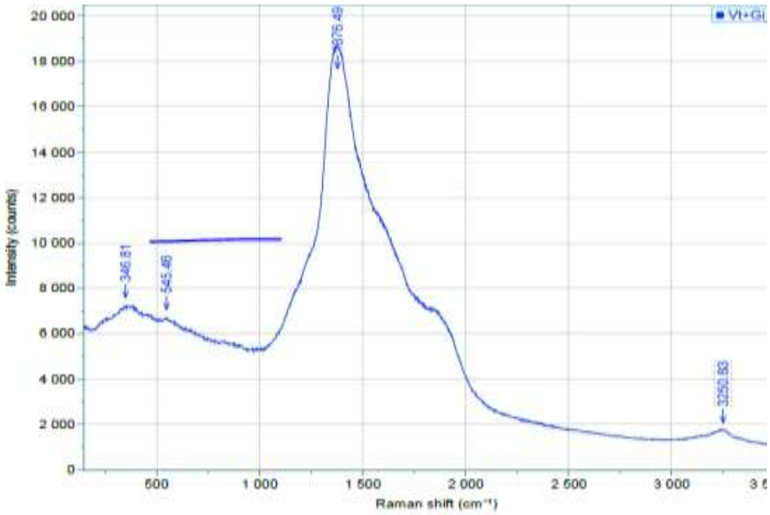


Fig. 5. A novel spectroscopy analysis of the VT-PANDEA ionite.

In the curve of Raman spectroscopic analysis of the vermiculite-based composite ionite modified with polyacrylonitrile and an amine group introduced through diethanolamine, the highest and broadest peak was recorded in the vibration region of 1376.49 cm^{-1}. These vibrational fields belong to strongly intensively bound OH ions. It leads to the conclusion that the bonds between -OH ions formed on the surface of vermiculite mineral and -COOH carboxyl groups in the polymer of polyacrylonitrile formed in the presence of maleic anhydride caused the peaks in this area. 3250.83 cm^{-1} represented the valence vibrational peaks given by O-H bonds, formed by crystal waters in the composite and a wide and intense H-bond [20].

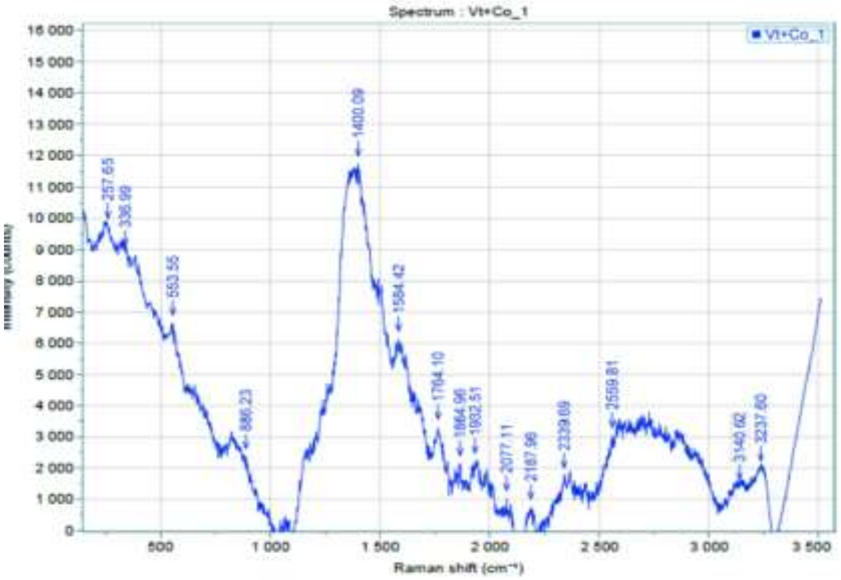


Fig. 6. Novel spectroscopic analysis of VT-PANDEA ionite sorbed Cu(II) ions from 0.1 N solution.

3.2. Novel spectroscopic analysis of VT-PANDEA composite sorbent. The VT-PANDEA composite sorbent, which absorbed Cu(II) ions from a 0.1 N solution of CuSO$_4$*5H$_2$O, was dried at room temperature, crushed, and analyzed by Raman spectroscopy (Fig. 6).

The novel spectra of the sorbent absorbing Cu(II) ions were obtained in the field range from 0 to 3500 cm^{-1}. VT-PANDEA ion analysis (Fig. 5) and Raman spectrum analysis of the same ionite that sorbed Cu(II) ions from solution (Fig. 6) were compared. From the analysis, it can be seen that the device recorded several broad and intense peaks resulting from the absorption of Cu(II) ions into the VT-PANDEA composite. Several intense peaks were noted in the analysis, Men(CO)m in the vibrational region of 1932.51 cm^{-1} and 1864.96 cm^{-1} in three intense regions, formed between the Cu(II) ion and ionite with valence vibration [20]. We can observe the gardens of the complex. Bonds of R-COO- anion and C=O group were formed in 1400.05 cm^{-1} vibration areas of scanning and 1764.40 cm^{-1} areas. The peak of moderately intense valence-bonded -NH$_2$ groups were recorded at the widths of 2077.11 cm^{-1} and the vibration fields of 2187.96 cm^{-1}. In the region of 2339.69 cm^{-1} of the analysis, there are moderately intensive, valence-vibrating –C=N group bonds. At 3140.62 cm^{-1}, the peaks of highly intense, valence-vibrating –N-H bonds, and at 3237.602 cm^{-1} peaks of broad and intense, valence-vibrating –OH groups forming H bonds were recorded. These -OH bonds were formed on the surface of polyacrylonitrile composite and vermiculite [21-22].

3.3. SEM analysis of VT-PANDEA sorbent. Using a scanning electron microscope (SEM) and elemental analysis, the 10μm, 50μm, and 100μm surface sections of polyacrylonitrile and vermiculite composite modified with diethanolamine were compared and analyzed and percentages of elements are shown in Table 4.

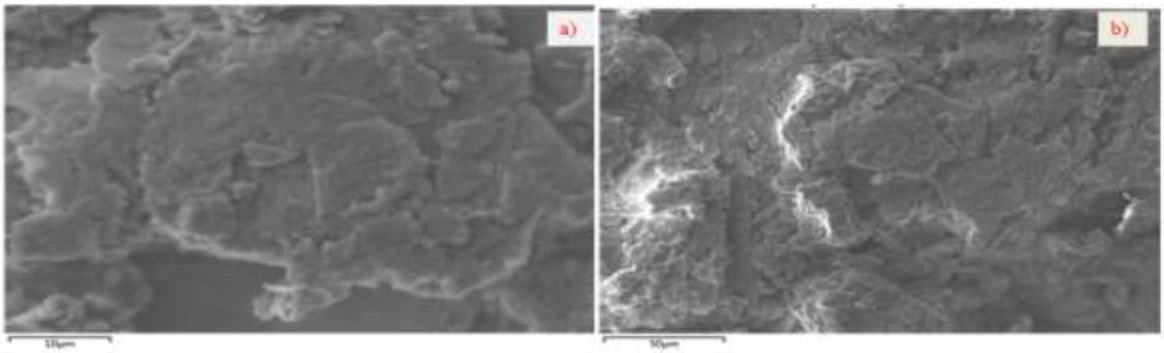


Fig. 7. SEM analysis of polyacrylonitrile and vermiculite composite ionite (VT-PANDEA) modified with diethanolamine a)10μm b)50μm and energy dispersive spectroscopy.

It can be observed from the 10μm and 50μm magnified images of the VT-PANDEA composite sorbent and the energy dispersive spectroscopy analysis that the surface morphology of the substances did not show the remains of the initial substances.

It is visible that the silicate layers of the vermiculite, which formed the basis of the sorbent, and the pores between the layers were not damaged. Fig. 7(a) SEM images show mega layers of vermiculite and particles of polyacrylonitrile and diethanolamine attached to it [23].

In the 100 μm magnified images of the analysis of the sorbent surface morphology taken from four different focal points (Fig. 7), the pores on the surface and between the layers are visible. Fig. 7(a) SEM images show mega layers of vermiculite and particles of polyacrylonitrile and diethanolamine attached to it [24].

3.4. Elemental analyses of VT-PANDEA sorbent. During SEM scanning of VT-PANDEA sorbent, analysis of chemical elements was obtained from the sorbent surface area. Spectra of chemical element analysis of VK-PANDEA sorbent were obtained together with 10 μm magnification and 100 μm SEM images.

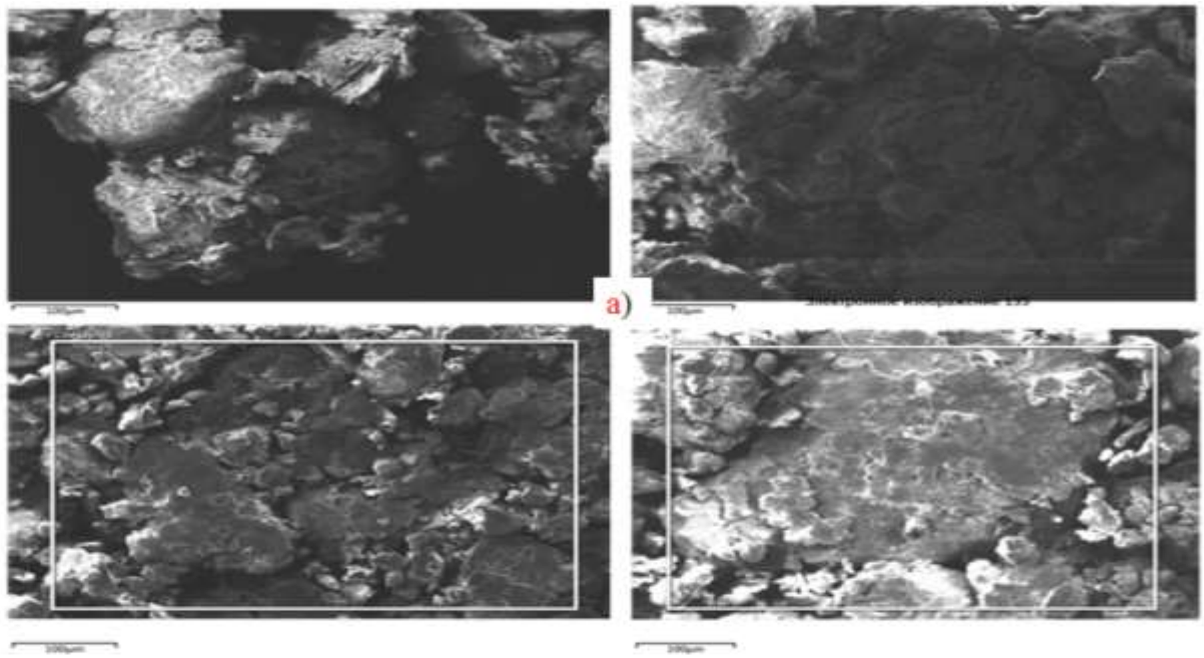


Fig. 7. SEM analysis of diethanolamine-modified polyacrylonitrile and vermiculite composite ionite (VT-PANDEA): 100 μm magnified image (taken from four different focuses).

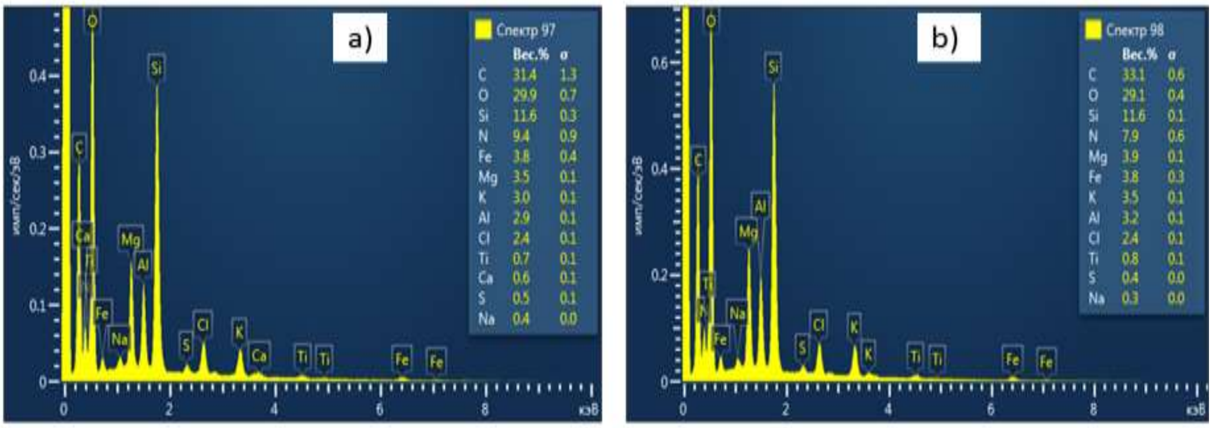


Fig. 8. Element analysis analysis of VT-PANDEA a)10μm b)100μm.

We can see that the difference between the amount of elements in chemical element analysis is not very big (Fig. 8). According to the analysis, the highest mass fractions are C; and O; which belong to Si. It seems that the highest percentage of the substance belongs to element C. It is known that this is due to polyacrylonitrile in the investigated sorbent, maleic anhydride inserted as a polymer binder between it and vermiculite, and diethanolamine included in the composition to attach the amine group. The O element, which made up more than 29% of the mass of the substance, corresponded to O in oxides, OH groups, and maleic anhydride and OH groups in diethanolamine in vermiculite. In several areas, the metals contained in vermiculite, namely Mg; No; We can see peaks corresponding to metals such as K, Al, Fe^{+3}; Fe^{+2}. Cl, which is more than 2% in the composition of the sorbent, belongs to the residues of Cl in the activation of vermiculite [25]. Quantitative proportions of elements in the sorbent are presented in Table 4.

From the analysis of the results, it can be seen that the porosity of the polyacrylonitrile and vermiculite composite ionite (VT-PANDEA) modified with diethanolamine is high, that is, the starting materials are completely connected. It can be seen that the elements are connected and that there are no additives in the composition of the substances. Also, in the elemental analysis of ionite, it was shown that the percentages of elements presented in the 10 μm and 100 μm SEM images have almost the same index [26].

Table 4. The results of the analysis of elements in the VK-PANDEA ionite (in percentages)

Elements	**C**	**O**	**Si**	**N**	**Mg**	**Fe**	**K**	**Al**	**Cl**	**Ti**	**S**	**Na**
Weight. % 100μm	33,1	29,14	11,63	7,85	3,95	3,81	3,45	3,19	2,38	0,81	0,42	0,32
Weight. % 10μm	31,4	29,9	11,63	9,42	3,46	3,76	3,00	2,90	2,40	0,71	0,51	0,36
Sigma Weight. % **100μm**	0,60	0,40	0,10	0,60	0,10	0,30	0,10	0,10	0,10	0,10	0,01	0,01
Sigma Weight % **10μm**	1,30	0,70	0,26	0,90	0,10	0,40	0,10	0,10	0,10	0,13	0,06	0,05

3.5. X-ray phase analysis of VK-PANDEA sorbent. From the X-ray diffraction (XRD) of VT-PANDEA composite sorbent, we can observe that the vibrational peaks of the formed compounds moved along a line and gave clear peaks. To obtain diffractograms in XRD, CuKa 1=1.5406 Å, CuKa 2=1.54443Å; CuKb =1.39225 Å in the radiation mode and the current mode was set to 40 mA and tube voltage 45 kV, respectively.

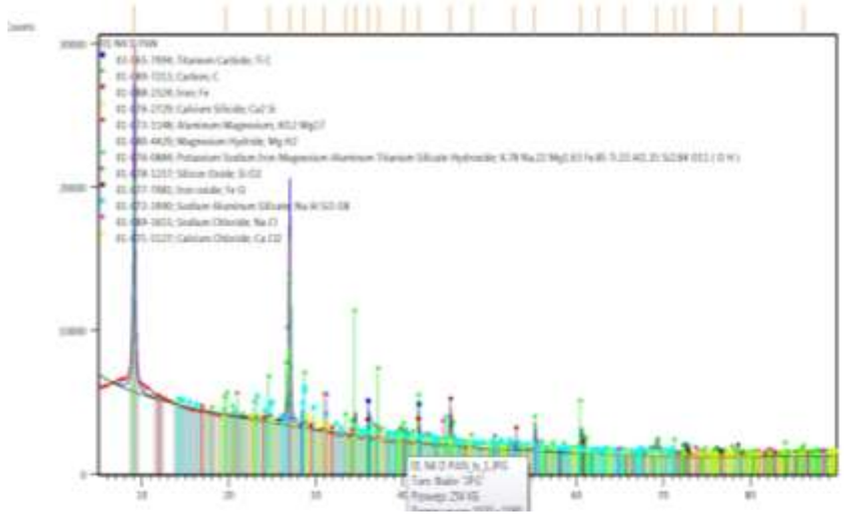


Fig. 9. Graphic analysis view of X-ray phase analysis of vermiculite-based VT-PANDEA composite ionite modified with polyacrylonitrile and diethanolamine

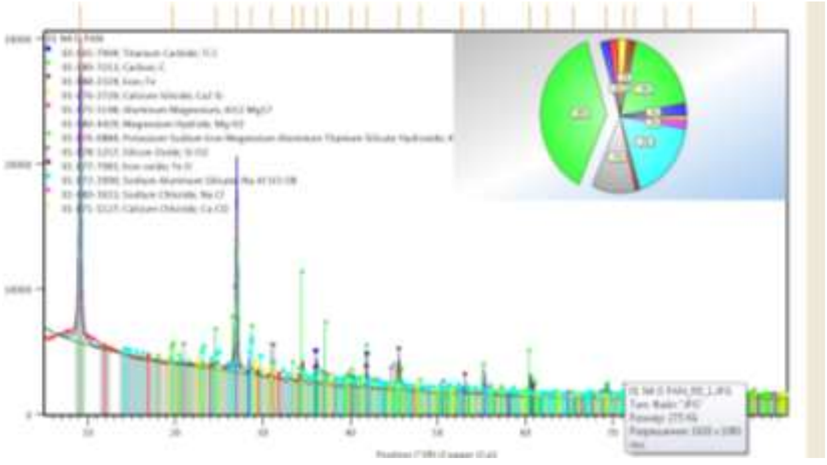


Fig. 10. X-ray phase analysis of VT-PANDEA sorbent: main graph and donut diagram analysis view

Scanning was applied with a K-A2 / K-A1 ratio of 0.50000, a detector step of 0.020 for 96.3900 c at a constant rotation rate of 4 deg/min (overlap ω/2θ), and the scan angle was varied from 00 to 900. A rotating camera was used to record the experiments, and its rotation speed was 30 rpm. The analysis was carried out on a continuous-type goniometer with a radius of 240 mm and a divergence crack radius of 100 mm, with a divergence crack size of °0.4354, with the participation of 10 mm samples [27]. Graphs of the spectra resulting from scanning to determine the X-ray phase composition of VT-PANDEA sorbent are presented in Fig. 9-11. The results and calculations of the spectrum peaks in these graphs are shown in Table 4.

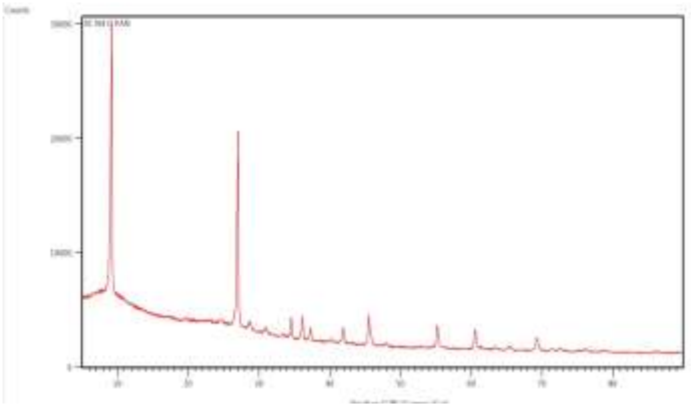


Fig. 11. X-ray phase analysis of VT-PANDEA sorbent: analysis results obtained in a Cu anode goniometer with a voltage of 45 keV

Table 5. Results of VT-PANDEA X-ray spectra analysis

Pos. [°2θ]	**Height [cts]**	**FWHM Left [°2θ]**	**d-spacing [Å]**	**Rel. Int. [%]**
9.1057	15029.73	0.2494	9.70409	100.00
19.6480	206.23	0.0825	4.51464	1.37
24.6300	381.03	1.7070	3.61157	2.54
26.9628	13155.16	0.1640	3.30417	87.53
28.6795	498.21	0.4359	3.11016	3.31
30.9617	272.20	0.3583	2.88592	1.81
33.3619	54.69	0.1677	2.68357	0.36
34.5303	1160.99	0.1977	2.59540	7.72
36.0949	1303.72	0.2027	2.48640	8.67
37.2388	587.96	0.1965	2.41261	3.91
40.0960	103.46	0.0942	2.24703	0.69
41.8705	879.69	0.2458	2.15581	5.85
45.4995	1789.37	0.2730	1.99195	11.91
47.9537	306.49	0.0746	1.89557	2.04
52.7637	125.32	0.3014	1.73354	0.83
55.1802	1690.30	0.2621	1.66320	11.25
60.5226	1393.79	0.3166	1.52854	9.27
62.5045	137.98	2.5941	1.48475	0.92
65.4266	285.67	1.5593	1.42533	1.90
69.2279	933.23	0.4356	1.35605	6.21
71.3319	187.34	0.7295	1.32114	1.25
72.5146	218.14	1.0774	1.30247	1.45
75.9630	195.41	1.4466	1.25169	1.30
78.8649	130.85	2.6229	1.21275	0.87
86.1379	128.77	0.2878	1.12802	0.86

From the X-ray diffractograms of the sorbent samples, we can see that the peak output of the X-ray spectrum was observed at °2θ = 5.0131°, the end of the spectrum was 2θ = 89.9811°.

According to the data obtained as a result of X-ray phase scanning of the sorbent, the compounds present in the sample and their information are presented in Table 6.

Table 6. X-ray phase analysis data of compounds in polyacrylonitrile-modified vermiculite and diethanolamine composite ionite

Ref.Code	Score	Compound Name	Displ.[°2θ]	Scale Fac.	Chem. Formula
03-065-7994	59	Titanium Carbide	0.197	0.078	Ti C
01-089-7213	24	Carbon	0.509	0.331	C
01-088-2324	31	Iron	-0.306	0.096	Fe
01-076-2729	14	Calcium Silicide	-0.342	0.027	Ca_2 Si
01-073-1148	25	Aluminum Magnesium	0.092	0.029	Al_{12} Mg_{17}
01-080-4429	20	Magnesium Hydride	0.438	0.041	Mg H_2
01-076-0884	51	Potassium Sodium Iron Magnesium Aluminum Titanium Silicate Hydroxide	0.275	0.472	K.78 Na.22 Mg1.63 Fe.85 Ti.33 Al1.35 Si2.84 O11 (OH)
01-078-1257	17	Silicon Oxide	-0.162	0.219	SiO_2
01-077-7981	41	Iron oxide	-0.272	0.045	Fe O
01-073-3990	14	Sodium Aluminum Silicate	0.062	0.084	$NaAlSi_3O_8$
01-089-3615	10	Sodium Chloride	0.141	0.075	NaCl
01-071-5127	11	Calcium Chloride	-0.230	0.014	$CaCl_2$

3.6. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of VK-PANDEA composite ionite. The thermal stability of VT-PANDEA composite sorbent is an important indicator reflecting its efficiency. Through this TGA analysis, the onset and termination temperatures of mass loss effects of polyacrylonitrile-based vermiculite were determined. The TGA and DTA parameters of the sorbent were calculated using the combined curves of peaks reflecting temperature changes [28]. Results of a thermogravimetric experiment for polyacrylonitrile-modified vermiculite The results of the thermogravimetric experiment for vermiculite-based polyacrylonitrile and diethanolamine-modified composite ionite 4.88 mg sample was studied in an argon environment, in the temperature range of 20-800 °C (Fig. 12).

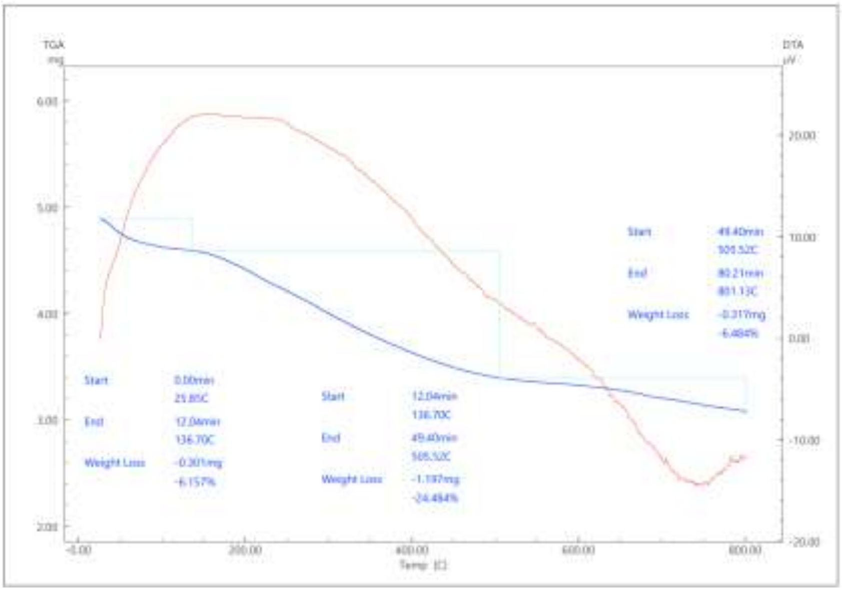


Fig. 12. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of polyacrylonitrile-modified vermiculite and diethanolamine composite ionite (VT-PANDEA).

In the DTA analysis of vermiculite-based sorbent modified with polyacrylonitrile and diethanolamine, the mass loss occurred in three stages, and one exothermic and one endothermic process occurred. The first mass loss started at 25.85°C and continued to 136.7°C in 12.04 minutes [29]. A mass loss of 0.301 mg or 6.157% was observed. At this stage, the release of hygroscopic water vapor was observed. The second stage lasted until 49.40 minutes of temperature increase, i.e. up to 505.52°C, and the mass loss during this interval was 1.197 mg, i.e. 24.484%. Carbon (II) oxide was released as a result of the decomposition of carboxyl groups in this range of temperatures. The third stage is the main decomposition stage, starting at 440.31°C and ending at 877.7°C, 4.648 mg, 43.458% mass loss was observed. In this case, from the decomposition of organic compounds, the decomposition of oxides from the amino group of nitrogen and some other organic compounds was observed. In the DTA analysis of the synthesized product, it can be seen that 2.751 mg or 25.725% of residual substances remained at 802.34°C in the endothermic process. At this stage, it can be observed that the remains of metal salts remain.

3.7. Analysis of adsorption isotherms and pore sizes of VT-PANDEA sorbent. Textural properties of VT-PANDEA sorbent samples were studied by benzene vapor adsorption using an Mc-Ben-Bakra sensitive quartz spiral setup [30]. The benzene was first stripped under vacuum, cooled until its vapor pressure reached the vapor pressure given in the table for pure benzene, and degassed. Before measuring the adsorption of benzene vapor on adsorbents, each adsorption system was vacuumed until the residual pressure was $1.33 \cdot 10^{-3}$ Pa and heated at 473 K for 6 hours, then adsorption isotherms were obtained (10-12 figures).

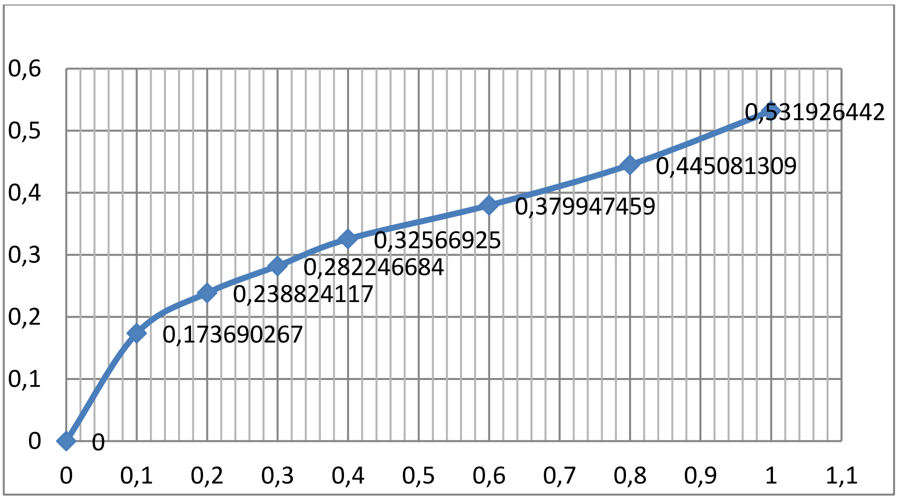


Fig. 13. Benzene vapor adsorption isotherm in VT-PANDEA ionite

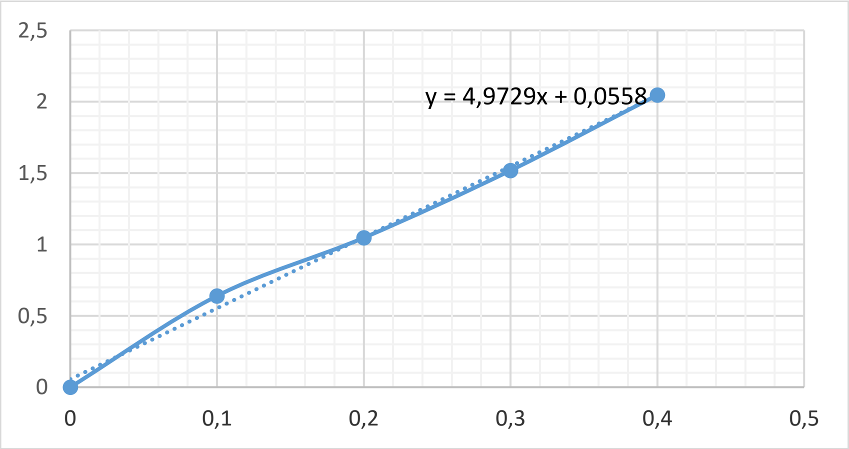


Fig. 14. Benzene vapor adsorption isotherm in VT-PANDEA ionite

It was calculated that the adsorption of vermiculite and diethanolamine composite ionite modified with polyacrylonitrile to benzene vapor is high. According to the amount of benzene adsorbed on ionite increases sharply from zero relative pressure to P/Ps =0.1 and approaches full saturation at P/Ps =1 (Fig. 13). The obtained isotherm belongs to the type I according to the IYUPAK classification, and 70-75% of the sorbent consists of micropores [31-32].

Table 7. VT-PANDEA composite ionite adsorption isotherm calculations

P/Ps	a	1-P/Ps	a*(1-P/Ps)	(P/Ps)/a*(1-P/Ps)
0	0			0
0,1	0,174	0,9	0,1563212	0,639708333
0,2	0,239	0,8	0,1910593	1,046795455
0,3	0,282	0,7	0,1975727	1,518428571
0,4	0,326	0,6	0,1954016	2,047066667
G=2.04496; A=0.0558				

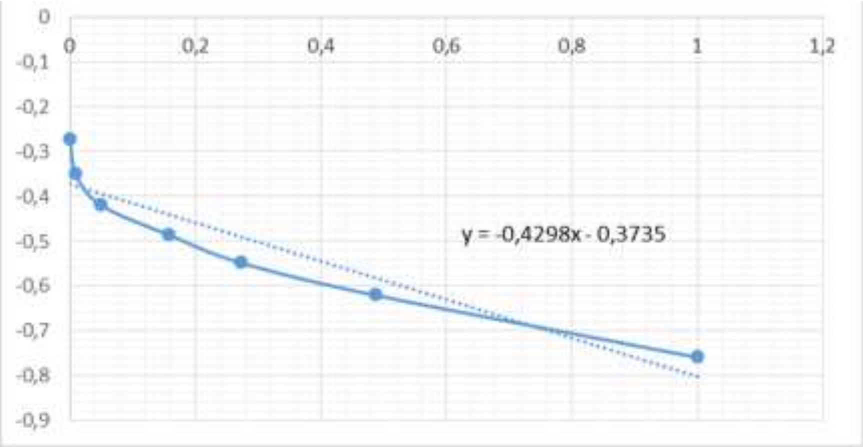


Fig. 15. Benzene vapor adsorption isotherm in VT-PANDEA ionite

Table 8. VT-PANDEA composite ionite adsorption isotherm

P/Ps	a	log(a)	PS/P	LOG(Ps/P)	(logPs/P)2	
0.1	0.1737	-0.760224518	10	1	1	-0.760224518
0.2	0.2388	-0.621921819	5	0.698970004	0.488559067	-0.621921819
0.3	0.2822	-0.549371152	3.333333333	0.522878745	0.273402182	-0.549371152
0.4	0.3257	-0.487223246	2.5	0.397940009	0.158356251	-0.487223246
0.6	0.3799	-0.420276456	1.666666667	0.22184875	0.049216868	-0.420276456
0.8	0.4451	-0.351560644	1.25	0.096910013	0.009391551	-0.351560644
1	0.5319	-0.27414842	1	0	0	-0.27414842

Table 9. Sizes of VT-PANDEA composite ionite adsorbed benzene

Mr	density	max mol/kg	Substance density	A	G	B	lga	a	Vm
78	0,88	0.532	40	0.0558	2.04496	5.1124	-0.3735	0.42315551	0.088636

The density of VT-PANDEA composite ionite in water (Mr-18g/mol; r=1 g/m^3) is 10.8 g/m^3 and in benzene (Mr=78g/mol; r=0.88g/m^3) it is 40 g/m^3 was founded. The following results can be noted during the study of the mentioned adsorption isotherms and calculations (Fig. 14, 15). Porous and benzene sorption parameters of VT-PANDEA ionite are presented in Table 10.

Table 10. Sizes representing porosity properties of VT-PANDEA composite sorbent

a (monolayer capacity)	S (comparative surface)	Micropore W_o	Saturation volume Vs	Mesa poreW_{me}	Pore radius
0.193mol/kg	46.59m^2/g	0.037507	0.0471545	0.01	20.2 Å 2.02nm

4. Conclusions

The following results were obtained from the results of the research conducted based on Tebinbulok mine vermiculite in this research work:

I. The chemical composition of Tebinbulok mine vermiculite was studied by the elemental analysis method. The natural vermiculite was heated in an incinerator to expel the bound water, thus increasing the volume and porosity of the vermiculite several times. To increase the surface area of vermiculite and its activity, it was activated with 7% hydrochloric acid.

II. Porous and activated vermiculite was modified using polyacrylonitrile and diethanolamine. Reaction conditions and optimal temperatures of the synthesized composite were studied. The static exchange capacity of the sorbent was calculated following the requirements of GOST 20255.1-8. Sorption was carried out against Cu(II) and Zn(II) ions. The experiment conducted at a temperature of 338 K was found to be the most optimal temperature, and the reaction yield was 95.5%. The SAS value of Cu(II) is 10 mmol/g and that of Zn(II) is 6.5 mmol/g.

III. Roman spectrum analyzes of the composite sorbent and Cu(II) ion absorbing state were obtained. In the novel spectroscopy analysis, the highest and broadest peak was recorded for intensively bonded -OH bonds in the vibrational region of 1376.49 cm^{-1} and Men(CO) in the vibrational region of 1932.51 cm^{-1} and 1864.96 cm^{-1} We were able to observe metal ions with m valence vibrations, intensively bound, sorbed to VT-PANDEA and the bonds of the complex formed between ionite.

IV. Using scanning electron microscope (SEM) and elemental analysis, the images of the surface morphology of polyacrylonitrile and vermiculite composite modified with diethanolamine at sizes of 10μm, 50μm, and 100 μm were studied. In the scanner images magnified by 10 μm and 50 μm, it was found that the remains of the initial substances were not visible on the surface of the composite and pores were noticeable. Scan images of the composite sorbent were taken at 100 μm magnification from four different focal points. Analysis of these images confirmed the descriptions given to the specimen.

V. During SEM scanning of VT-PANDEA sorbent, analysis of chemical elements was obtained from the sorbent surface area. Spectra of chemical element analysis of VT-PANDEA sorbent were obtained together with 10 μm magnification and 100 μm SEM images. From this analysis, the amount of elements in the composite sorbent corresponds to theoretical calculations. It turned out that the only foreign element in the composition is Cl, and it is a residue left in the composition during the activation of vermiculite. Quantitative proportions and σ masses of the elements in the sorbent were given.

VI. X-ray phase analyses of the compounds formed were obtained from X-ray diffraction (XRD) of polyacrylonitrile and vermiculite composite ionite (VTPAN-DEA) modified with diethanolamine. From the X-ray diffractograms of the sorbent samples, the spectra related to the TiC compound, i.e., the peak output of the X-ray spectrum was observed at °2θ = 5.0131°, and the end of the spectrum was 2θ = 89.9811° (Figures 9-11). The results of the VK-PANDEA X-ray spectra analysis and the indicators of compounds in the sample are given in the tables.

VII. To determine the thermal stability of VT-PANDEA composite ionite, thermogravimetric and differential thermal analyses were conducted. The starting and ending temperatures of mass loss effects of vermiculite modified based on polyacrylonitrile were determined. The TGA and DTA indicators of ionite were calculated using the combined curves of peaks reflecting temperature changes. During the analysis, there was a mass loss in three stages one exothermic and one endothermic process.

VIII. Textural properties of VT-PANDEA sorbent samples were studied by benzene vapor adsorption using an Mc-Ben-Bakra sensitive quartz spiral setup. The sample was heated at 473 K for 6 h, then adsorption isotherms were obtained. Based on adsorption isotherms, parameters such as monolayer capacity, specific surface area, saturation volume, micropore, mesopore level, and pore radii of the sorbent were calculated.

IX. A method of synthesizing a new sorbent based on vermiculite modified with polyacrylonitrile and diethanolamine was developed and a new organic-inorganic sorbent was synthesized. The reaction conditions of the obtained sorbent were studied. Experiments on the sorption of Cu(II) and Zn(II) ions by the sorbent were conducted. The amount of these ions adsorbed on the surface of the sorbent was calculated and the SAS value was calculated. This amount represented a high sorption capacity. The thermal stability of the sorbent was determined based on DTA and TGA analyses. Adsorption isotherms and physical properties of such a sorbent were obtained using the Mac-Ben-Bakra apparatus. It can be concluded that the sorbent has sufficient surface area based on the porosity level and pore radii.

References

1. Melnikov A.A., Gordina N.E., Sinitsyn A.P., Gusev G.I., Gushchin A.A., Rumyandsev R.N. Investigation of the influence of mechanochemical effects on the structure and properties of vermiculite sorbents. *J. Solid State Chem. Academic Press,* 2022, Vol. **306**, p. 122795. https://doi.org/10.1016/j.jssc.2021.122795
2. Dubus J., Leonhardt N., Latrille C. Multi-cation exchanges involved in cesium and potassium sorption mechanisms on vermiculite and micaceous structures. *Environ. Sci. Pollut. Res*. 2023, **Vol. 30(1)**, p. 1579-1594. https://doi.org/10.1007/s11356-022-22321-4.
3. Matveeva V., Danilov A., Pashkevich M. Treatment of multi-tonnage manganese-containing waste water using vermiculite. *J. Ecol. Eng*, 2018, Vol. **19(1)**, p. 125733. https://doi.org/10.1016/j.energiya.2022.125733.
4. Popova O.S., Baryshev V.A. Use of sorption premixes in fish farming as a prevention of nutritional toxicosis. *Leg. Regul. Vet. Med*, 2023, Vol. **109(4)**, p. 2782. https://:10.52419/issn2782-6252.2022.4.109.
5. Galchenko D.S., Smirnova M.G., Sokolova L.I. Using natural aluminosilicate (vermiculite) sorbent for purifying waste water from antibiotics. *XXI Century. Technosph. Saf*, 2022, Vol. **6(4)**, p. 387-394. https:// : 10.21285/2500-1582-2021-4-387-394
6. Shapkin N.P., Surkov V.M., Tutov M.V., Xalchenko I.G., Fedorets A.N., Sharshena E.A., Razov V.I., Tokar E.A., Papinov E.K. Organo-Inorganic Composites Based on Phosphorus Vermiculite and Resorcinol–Formaldehyde Polymer and Their Use for Sorption of Nonradioactive Strontium from Solutions. *Russ. J. Inorg. Chem*, 2022, Vol. **67(2)**, p. 221-230. https://10.1134/S0036023622020152.
7. Böhm L., Granchich P., Sholtzova E., Benjamin J.H., Rolf A.D., Yan S., Gerzabek M.H., Tunega D. Adsorption of the hydrophobic organic pollutant hexachlorobenzene to phyllosilicate minerals. *Environ. Sci. Pollut. Res*, 2022, Vol. **30(2)**, p. 36824-36837. https://:10.1007/s11356-022-24818-4.
8. Syrmanova K.K., Suleymanova M.T., Kovaleva A.Y., Butaboyev A.N., Kaldebekova A.N., Vermiculite absorption capacity increasing by acid activation. *Orient. J. Chem*, 2017, Vol. **33(1)**, p. 509–513. https://:10.13005/ojc/340241.

9. Ivanova T.K., Sliskovskaya M., Mosends I., Krasavtseva E.A. Modified materials based on layered minerals as ameliorants for the remediation of podzol in the industrial barren. *Rudn J. Agron. Anim. Ind.*, 2021, Vol. **16(4)**, p. 370-388. https://:10.22363/2312-797x-2021-16-4-370-388.
10. Huang H.L., Lin P., Vang H., Huan S., Chao H.V. Ionic liquid extraction behavior of Cr(VI) absorbed on humic acid–vermiculite. *Molecules*, 2021, Vol. **26(24)**, p. 14203049. https://: 10,3390/molekulalar26247478 ISSN : 14203049
11. Cho S.B., Chang J.H. Vermiculite-polyethylene hybrid packaging films for keep-freshness of bananas with enhanced oxygen and water–vapor permeability. *J. Korean Ceram. Soc*, 2021, Vol. **58(2)**, p. 212-218. https://:10.1007/s43207-020-00091-4
12. Shapkin N.P., Khal’chenko I.G., Matskevich A.I. Method for Modification of Vermiculite with Copper Ferrocyanide for Selective Extraction of 137 Cs from Liquid-salt Media. *Radiochemistry*, 2021, Vol. **63(2)**, p. 345–352. https://doi.org/10.1134/S1066362221030127.
13. Shapkin N.P., Khal’chenko I.G., Yudakov A.A., Sergienko V.I., Panasenko A.E., Maiorov V.Yu., Leont’ev L.B. Synthesis of a nanocomposite based on polyethylene and modified vermiculite. *Inorg Mater*, 2017, Vol. **53(2)**, p. 1091–1096. https://doi.org/10.1134/S0020168517100120.
14. Hamidova J.Sh., Kazemzade L.K., Hasanova E.I., Isakov E.U., Babayev S.S. Synthesis of allylcaprylate-styrene copolymers with styrole and their research as a viscosity additive to lubricant oils. *Chemical Problems*, 2020, Vol. **18(2)**, p.158-163. https://doi.org/10.32737/2221-8688-2020-2-158-163.
15. Huseynov K.Z., Aliyev P.A., Mirzoyeva M.A., Eyvazova I.M., Aliyev N.A.. Synthesis of alkoxycarbonylmethyl esters of thioacetic and thiobenzoic acids and their investigation as additives to lubricating oils. *Chemical Problems*, 2023, Vol. **21(3)**, p. 294-300 https://doi.org/10.32737/2221-8688-2023-3-294-300.
16. Nazirov Sh..S., Turaev Kh.Kh., Kasimov Sh.A., Normurodov B.A., Jumaeva Z..E., Nomozov A.K.. Spectrophotometric determination of copper(II) ion with 7-bromo-2-nitroso-1-oxinaphthalene-3,6-disulphocid. *Indian J of Chem*, 2024, Vol. **63(5)**, p. 500-505. https://doi.org/10.56042/ijc.v63i5.9289.
17. Froehner S., Scurupa M.K., Falcão F. Adsorption of Dibenzothiophene by Vermiculite in Hydrophobic Form, Impregnated with Copper Ions and in Natural Form. *Water Air Soil Pollut*, 2010, Vol. **209(8)**, p. 357–363. https://doi.org/10.1007/s11270-009-0204-8.
18. Froehner S., Furukawa W., Maceno M. Water Remediation by Columns Filled with Micelle–Vermiculite Systems. *Water Air Soil Pollut*, 2009, Vol. **202**, pp. 161–168. https://doi.org/10.1007/s11270-008-9966-7.
19. Shaymardanova M.A., Mirzakulov Kh.Ch., Melikulova G., Khodjamkulov S.Z., Nomozov A.K., Shaymardanova Kh.S. Study of processe of obtaining monopotassium phosphate based on monosodium phosphate and potassium chloride. *Chemical Problems*, 2023, Vol. **21(3)**, p. 279-293. https://doi.org/10.32737/2221-8688-2023-3-279-293.
20. Lee T. Removal of Heavy Metals in Storm Water Runoff Using Porous Vermiculite Expanded by Microwave Preparation. *Water Air Soil Pollut*, 2012, Vol. **223(3)**, p. 3399–3408. https://doi.org/10.1007/s11270-012-1119-3.
21. Krysenko D.A., Tarasevich Y.I., Dolenko S.A. Sorption of Octyl-, Decyl-, and Dodecyltrimethylammonium Cations from Premicellar Solutions onto the Na-Form of Vermiculite. *Theor Exp Chem*, 2018, Vol. **54(8)**, p. 210–216. https://doi.org/10.1007/s11237-018-9564-8.
22. Johns C.A., Martos-Villa R., Guggenheim S. Structure Determination of Trimethylsulfoxonium-Exchanged Vermiculite. *Clays. Clay. Miner*. 2013, Vol. **61**, p. 218–230. https://doi.org/10.1346/CCMN.2013.0610305.

23. Maiti S., Jain N., Malik J. Light Weight Plasters Containing Vermiculite and FGD Gypsum for Sustainable and Energy Efficient Building Construction Materials. *J. Inst. Eng. India Ser. A* 2023, Vol. **104**, p. 603–614. https://doi.org/10.1007/s40030-023-00736-7.
24. Gordeeva L.G., Moroz E.N., Rudina N.A., Aristov Yu.I. Formation of Porous Vermiculite Structure in the Course of Swelling. *Russian Journal of Applied Chemistry*, 2002, Vol. **75**, p. 357–361. https://doi.org/10.1023/A:1016165915362.
25. Nomozov A.K., Beknazarov Kh.S., Khodjamkulov S.Z., Misirov Z.Kh. Salsola Oppositifolia acid extract as a green corrosion inhibitor for carbon steel. *Indian Journal of Chemical Technology*. 2023, Vol. **30**, p. 872-877. https://doi.org/10.56042/ijct.v30i6.6553.
26. Muzaffarova N.Sh., Nurkulov F.N., Khaydarova Z.N., Abdirazokov A., Bozorova M.I., Abdimalikov I.I. Synthesis of fire retardant with phosphorus and metal for preservation and reach of reduction of flammability of textile materials. *Chemical Problems,* 2024, Vol. **22(3)**, p. 290-302. https://doi.org/10.32737/2221-8688-2024-3-290-302.
27. Muratov B.A., Turaev Kh.Kh., Umbarov I.A., Kasimov Sh.A., Nomozov A.K., Studying of Complexes of Zn(II) and Co(II) with Acyclovir (2-amino-9-((2-hydroxyethoxy)methyl)-1,9- dihydro-6H-purine-6-OH). *Int. J of Eng. Trends and Tech*, 2024, Vol. **72(1)**, p. 202-208. https://doi.org/10.14445/22315381/IJETT-V72I1P120.
28. Turaev Kh.Kh., Shavkatova D., Amanova N.A., Shadhar M. H., Berdimurodov E., Bektenov N. Application of Sulfur-2,4-dinitrophenylhydrazine as Modifier for Producing an Advantageous Concrete. *Baghdad Sci. J.* 2023, Vol. **20(6)**, p. 2414. https://bsj.uobaghdad.edu.iq/index.php/BSJ/article/view/9038.
29. Turayev Kh.Kh., Eshankulov Kh.N., Umbarov I.A., Kasimov Sh.A., Nomozov A.K., Nabiev D.A. Studying of Properties of Bitumen Modified based on Secondary Polymer Wastes Containing Zinc. *Inter. Journal of Eng. Trends and Tech*, 2023, Vol. **71(9)**, p. 248-255. https://doi.org/10.14445/22315381/IJETT-V71I9P222.
30. Mammadli S.B., Amirov F.A., Alamdarly A.V., Orucaliyeva U.B., Nurullayeva D.R. Synthesis of an optically transparent copolymer on the basis of n-vinyl carbazole and styrene. *Chemical Problems*, 2022, Vol. **20(4)**, p. 374-380. https://doi.org/10.32737/2221-8688-2022-3-374-380.
31. Umirova G.A., Turaev Kh.Kh., Alimnazarov B.K., Kasimov Sh.A., Jalilov A.T., Ibragimov B.T., Ashurov J.M. Crystal structure and Hirshfeld surface analysis of 8-azaniumylquinolinium tetrachloridozincate (II). *Crystallographica Section E: Crystallographic Communications*, 2023, Vol. **79(11)**, p. 856-860. https://doi.org/10.1107/S2056989023007466.
32. Kholnazarov B.A., Turaev Kh.Kh., Djalilov A.T. Synthesis of Superabsorbent Hydrogels Based on Starch Copolymer/Minerals Powder. *International Journal of Engineering Trends and Technology*. 2022, Vol. **70(12)**, p. 351-358. https://doi.org/10.14445/22315381/IJETT-V70I12P234.