Original Article

Obtaining of Organo-Inorganic Sorbent by Modification of Vermiculite and Hydrolyzed Polyacrylonitrile Composite with Melamine

Kholmurodova S.A.[1*], Turaev Kh.Kh.[1], Alikulov R.V.[1], Toshkulov A.Kh.[1], Kulbosheva Kh.Kh.[1], Toshev M.E.[1]

[1]*Faculty of Chemistry, Termez State University, Termez 190111 Uzbekistan.*

*Corresponding Author : xolmurodovasaboxat84@gmail.com

Abstract *- This work synthesises samples of organic-inorganic polymer sorbents and analyses their properties. To obtain an organic-inorganic sorbent exhibiting high sorbent properties, the method of obtaining a composite of 0.7 grade hydrolyzed polyacrylonitrile (GIPAN) and expanded and activated vermiculite (KFV) and the modification of this composite with melamine (MA) were presented. Vermiculite from Tebinbulok mine, a local mine, was used in the research. The sorption and desorption properties of the organic-inorganic ionite obtained as a result of the study were investigated. The experiment was conducted at 65 °C with a reflux condenser. The properties of the resulting composite were studied. Based on the IR-spectroscopic analysis of the synthesized sorbent, its composition was determined. According to the analysis of the obtained thermal stability, it was found that the sorbent does not change its composition at temperatures up to 262 °C. The structural and sorption properties of the organic-inorganic sorbent were analyzed using the Brunauer, Emmett and Teller (BET) method based on water vapour absorption at low pressure. It was found that the obtained sorbent has a high sorption property and a mesoporous structure. As a result of the research, it was found that the modified sorbent based on melamine with an amine group has the highest capacity in the study of the static exchange capacity of sorbents synthesized based on GIPAN-KFV.*

Keywords *- Vermiculite, Hydrolyzed polyacrylonitrile, Melamine, Organic-inorganic, Microstructure, Desorption, Static capacitance.*

1. Introduction

All over the world, industrial development leads to pollution of wastewater sources. This could soon lead to drinking water shortages. Therefore, the use of minerals from natural layers in wastewater treatment is one of the most promising methods. Vermiculite, a naturally layered clay mineral, is a sorbent with excellent properties [1]. Several sorbents based on LiCl, i.e. silica gel (LiCl-SG_30) and expanded vermiculite (LiCl-EVM_45), were obtained, and their sorption levels were studied. According to the results, sorption isobars showed that the degree of sorption of LiCl-SG_30 depends on the combination of LiCl crystals. When the sorption rate was studied, Microporous Siegel showed the highest sorption rate, followed by LiCl-SG_30 and LiCl-EVM_45[2] Vermiculite-CaCl$_2$ was adopted as a working material due to its high energy density, good cycling ability, and low cost, and its efficiency was used as a sorbent with high [3]. From natural minerals, Montmorillonite sorbent was obtained from the alkaline bentonite deposit located in Navbahor District, Navoi Region, Uzbekistan, and this sorbent is considered the most effective adsorbent for water purification; its surface area is 450 m^2/g, and vermiculite is

450- 500 m^2/g [4]. The composition and sorption properties of vermiculite obtained from the Mugodzhari mine (Kazakhstan) were studied. The sorption properties of modified vermiculite were studied in the presence of acidic sodium phosphate, Na$_2$HPO$_4$ 12H$_2$O, and mechanical-chemical properties. The results of the experiments showed that the sorption level of activated vermiculite to Mn^{2+} is higher than to Ni^{2+}, and Cu^{2+}. The sorption results show that the sorption capacity properties are improved when vermiculite is treated with Na$_2$HPO$_4$·12H$_2$O to form an amorphous phase. grows with Na$_2$HPO$_4$·12H$_2$O in the following sequence Mn^{2+}> Ni^{2+}>Cu^{2+} (Mn = 99.8 %, Ni = 99.3 %, Cu = 99.0 %). As a result of research, a new effective sorbent was obtained from natural vermiculite by mechanical activation in the presence of sodium hydrogen phosphate Na$_2$HPO$_4$·12H$_2$O [5].

Today, laboratory research on nitrogen group compounds removal from wastewater of the enterprise based on Arctic iron ore with the help of various sorbents: zeolite, sistof, and thermovermiculite [6]. The following natural sorbents were used for the experiments: bentonite clay with carbonate addition, dense, slightly porous rocks consisting of the

smallest particles of biogenic silicon, diatomite, glauconites - iron mica, calcined vermiculite. The ability of these natural sorbents to sorb heavy metals such as copper, zinc, lead, cadmium, nickel, chromium and arsenic were studied. Experiments have shown that copper in the form of a bivalent cation is well sorbed by all sorbents, while chromium in the form of a complex anion (in the hexavalent form) is not practically sorbed [7-9].

Vermiculite is impregnated with alkaline polysulfides and thiosulfates, which can be used to adsorb mercury. Unlike other sorbents, vermiculite maintains high thermal stability in air, allowing its use even at temperatures of 180 °C [10,11]. The natural mineral vermiculite was expanded using an aqueous solution of H_2O_2 and used to obtain oil sorbent [12]. This study used porous at 400 ºC vermiculite, which was produced for agricultural and construction purposes in the markets of Uzbekistan. The composition of vermiculite from the Tebinbuok mine fully corresponds to the following formula recognized and proposed by chemical science and industry; only the amount of their share may differ slightly[13].

$$(Mg,Fe^{++},Al)_3(Al,Si)_4O_{10}(OH)_{2*}4(H_2O)$$
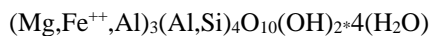
The composition of the Tebinbulok vermiculite of the following: SiO_2 38-41.10%, Fe_2O_3 and FeO 5.4-9.92%, MgO 20-23.5%, CaO 0.7-1.5 %, MnO 0.1-0.3 %, K_2O 5.2-7.9 %, SO_3 0.24-1.5 %, Na_2O 0.8-1.83 %, TiO_2 1.09 %, Al_2O_3 12, 64-17.5, $pH(H_2O)$ 6.8-7%. The main goal of this work is to develop a method for obtaining an organic-inorganic polymer vermiculite composite by modifying the vermiculite from the Tebinbulok mine in Uzbekistan with hydrolyzed polyacrylonitrile (GIPAN) grade 0.7 (GIPAN) and expanding it with melamine and to study its application.

2. Experimental Part
2.1. Materials
Vermiculite from the Tebinbulok mine in Uzbekistan was used as a local raw material for obtaining this sorbent. In the organic modification of vermculite, local mining vermiculite conforming to GOST 12865-67, hydrolyzed 0.7-grade polyacrylonitrile (10% ready aqueous solution) conforming to GOST TU 6-01-166 in technical condition was used. Also, in order to increase the surface-active groups of the obtained sorbent, 99.7% of melamine, grade 1, in powder form was used (GOST 7579-76). All chemical substances were purchased from "Merit Chemicals" company as "chemically pure" and "technical pure".

2.2. Methods
2.2.1. IR and Roman Analysis
The composition of the sorbent was investigated using IR-spectral analysis with Shimadzu IR Tracer-100 (SHIMADZU (Japan) and Japan's HORIBA device, determined in the range from 0 to 3500 cm^{-1}).

2.2.2. SEM-EDX- Analysis
The surface morphological and structural properties of the obtained sorbents were determined using element-dispersion analysis and a scanning electron microscope -JSM-IT200 (JEOL, Japan).

2.2.3. TGA and DTA Thermal Analysis
Thermogravimetric studies of changes in the physico-chemical properties of the obtained sorbents under the influence of temperature were studied in the DTG-60, SHIMADZU device (Japan) in an argon atmosphere with a porcelain crucible at a heating rate of 10°C/min.

2.2.4. Quantachrome Analysis
Calculations of the surface area of the obtained sorbent, absorption of cooled nitrogen and adsorption also, desorption isotherms of release in the gaseous state with increasing temperature (Quantachrome® ASiQwin™- Automated Gas Sorption Data, Acquisition and Reduction© 1994-2017, Quantachrome Instruments version 5.21) were performed on the Quantachrome device studied and analyzed.

2.2.5. Analysis of Surface Area Sizes in the Mc-Ben-Bakra Device
Adsorption and desorption isotherms of the obtained sorbent were obtained using the water vapor pressure in the Mc-Benn-Bakra balance device, and mathematical calculations were carried out to determine the specific surface area by the BET (Brunauer-Emmett-Teller) method.

2.2.6. Obtaining Organic-Inorganic Sorbent
The vermiculite, which was crushed and passed through a 0.5 mm sieve, was washed several times in distilled water and burned (porous) in a Digital Muffle Furnace FHX-05 furnace at a temperature of 650 °C. As a result of the evaporation of constitutional water contained in vermiculite, its volume expands up to 20-30 times. 300 ml of 35% hydrochloric acid of technical grade was poured over the porous vermiculite. The container was hermetically sealed with a glass lid and left for 60 hours in a dark place. The activated vermiculite was filtered and neutralized with ammonia water. It was decanted in water at a temperature of 95°C in order to wash off the salts and hydrochloric acid residue that formed as a result of neutralization. The cleaned vermiculite was filtered again and placed in a drying oven at a temperature of 75ºC for 24 hours. The cleaned and dried vermiculite was weighed on a scale and placed in a heat-resistant glass container. Hydrolyzed polyacrylonitrile (GIPAN) was dissolved and added to an equal amount of distilled water. The dish was placed on a magnetic stirrer connected to a reflux condenser. The device temperature was adjusted to 65º C and the rotation speed to 450 rpm. A cylinder-shaped 7x40 mm magnetic rod covered with polytetrafluoroethylene (PTFE) was placed in the vessel for magnetic mixing. At 20 minutes of mixing, a very small amount of initiator and melamine, measured on an analytical

balance, was added to the mixture. The speed of magnetic mixing was slightly reduced, i.e. 200 rpm. Dropped Polymerization of the composite was quickly noticed in the container. The polymer turned into a resinous state and sank to the bottom of the container. The vessel was removed from the magnetic stirrer, and the resulting resin was poured into a glass plate and placed in a drying oven at a temperature of 95ºC for 24 hours. Our dried composite is an orange-brown, hard, porous substance with low density.

2.2.7. Determination of Water Solubility of the Obtained Substance

1 g of substance was weighed on an analytical balance and placed in a clean container. The container was filled with 30 ml of distilled water and left for 24 hours. This test is one of the first and main requirements for sorbents and is a water resistance test. After one day, the composite was removed from the water and dried again at 95ºC. It was observed that the color of the water did not change, and the composite was slightly swollen. The organic-inorganic composite, which was dried and freed from hygroscopic water, was measured again on an analytical balance. The result showed that there was no change in its mass; that is, the obtained material was not dissolved in water.

2.2.8. Studying the Static Exchange Capacity of a Solution Containing a Metal ion with an ions Exchanger

Investigations were also carried out on the ability of the synthesized organic-inorganic composite sorbent to bind metals from solutions containing metal ions. To determine the static exchange capacity of the sorbent, 10 ml of a 0.1 N solution of $CuSO_4$ *$5H_2O$ and 30 mg of the sorbent weighed on an analytical balance were placed in a small glass container. After 24 hours, the concentrations of the solution in the glass container and the 0.1N solution were compared. Complexes were formed and checked in the device specialized for the determination of concentrations by ultraviolet light of the Japanese company SHIMADZU.

For verification, the ammonia: distilled water: solution mixture is based on the formation of a similar complex of ammonia by mixing in a mass ratio of 1:1:2 ml. The optical density of the studied solution was used to determine their concentrations. In order to determine the exact concentrations of Zn (II) and Ag(I) metal ions, complexometric titration was performed. Based on the obtained results, the amount of sorption was determined using the following formula:

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

Here: q_e is the amount of ion absorbed by the ionizer, mg-eq/g
$V_{0,i}$ – solution volume, in l
C_{0i} -Initial concentration of -solution, mmol/l
C_{0i}-equilibrium concentration mmol/l
m-ionite mass, g

Based on the above formula, the amount of Cu(II), Zn(II) and Ag(I) ions absorbed into the sorbent was found. The amount of ions absorbed into the obtained sorbent is q_e=9.5 mg-ek/g in the solution containing Cu (II) ion, q_e=6.01 mg-ek/g in the solution containing Zn(II) ion, and q_e=5.07 mg in the solution containing Ag(I) ion. - ek/g. the results are recorded. The SAS value of the substance obtained using this method was determined, and the results are recorded in Table 1.

2.2.9. Acidic Regeneration of ion Exchange Agent

The main feature that increases the value of the sorbent is its reusability. An acid regeneration test was performed on a sample showing ion exchange properties obtained by organic modification of vermiculite. The orange sorbent turned green due to the sorption of Cu(II) ions on its surface. For regeneration, it was lowered into a 2 N solution of hydrochloric acid. The metal ions contained in the sorbent went into a complete solution in the form of CuCl2 salt. The sorbent returned to its original color. It was washed repeatedly in distilled water and dried. The dried sorbent was again placed in a solution containing Cu(II) ions and left for 24 hours. The amount of sorption was measured again using the above method. It was found that the sorption level of the sorbent decreased by a small amount. For example, in the sorption of Cu(II) ions, the static exchange capacity of the ion exchanger decreased by 6 units and became equal to 8.9 mg-ek/g after regeneration.

3. The Process of Sorption in a Solution Containing a Metal Ion

The dynamic exchange capacity (DAS) of the new sorbent sample was also studied. For this, ion exchange sorbent particles the size of wheat grains were placed in a column with a diameter of 10 mm and a length of 15 cm. 0.1 N solutions of salts containing Zn(II), Cu(II) and Ag(I) ions were passed through the column. The solutions were slowly passed through the column at a speed of 1 ml/min.

Table 1. Study of sorption of V-HPM organic-inorganic polymer composite

Sorbents	Salts in which the sorption process is studied	Volume 0,1 N Saline solutions, ml	Weight sorbent, gr	Absorption time (hours)	Amount of sorption mg-eq/g	Amount of sorption after regeneration mg-eq/g
VK-GIPANMA	$CuSO_4$	10	0.03	24	9.5	8.9
VK-GIPANMA	$ZnSO_4$	10	0.03	24	6.01	4.7
VK-GIPANMA	$AgNO_3$	10	0.03	24	5.07	5.5

The results were recorded in Table 2. Different samples were taken using the same method, and the mass ratios were changed in the experiments conducted to obtain a new ion exchange sorbent by organic modification of vermiculite. The SAS and DAS values of these samples were studied using the above methods.

Table 2 below shows the mass ratios of the vermiculite: GIPAN: melamine composition material obtained in the study. The highest indicator was determined when starting materials were taken in a mass ratio of 2:4:0.5.

4. Results and Discussion
4.1. Roman Analysis

In order to study the structure of organic-inorganic sorbent (V-HPM) obtained by organic modification of vermiculite with hydrolyzed polyacrylonitrile and melamine,

Roman spectroscopy analysis was conducted. Analyzes were determined on a Japanese HORIBA device in the field range from 0 to 3500 cm^{-1}. Absorption lines in Roman spectroscopic analysis of V-HPM organic-inorganic sorbent obtained by organic modification of vermiculite are as follows. In the vibration field, 1483.13 cm-1 was recorded in the analysis curve. These vibration fields may belong to functional groups with asymmetric valence bonds –C-N=O. In the 1151.26 cm^{-1} valence vibration regions, spectrum peaks related to –C-N bonds are visible. In these areas, it can be said that it is due to the cyan functional group in hydrolyzed polyacrylonitrile. In the 857.16 cm^{-1} area, the spectra corresponding to the deformation vibration bonds related to the –C-H bonds are reflected. 321.90 cm^{-1} reflected in higher spectra; 390.22 cm^{-1}; 447.75 cm^{-1}; The bands that give high-intensity peaks in the 529.25 cm^{-1} area mainly belong to the metal compounds contained in vermiculite.

Table 2. The composition of the mass ratios of the starting materials of the V-HPM sorbent and their mobility properties

Vermiculite, GIPAN and melamine	Reaction product,%	Static exchange capacity in 0.1 N solution, mg-eq/g			Dynamic exchange capacity in 0.1 N solution, g/dm³		
		CuSO₄	ZnSO₄	AgCl	CuSO₄	ZnSO₄	AgCl
4:2:05	58%	5.1	4.1	5.3	0,608	0,304	0,201
1:1:0.5	75%	6.1	3.5	4.5	0,594	0,302	0,205
2:4:0.5	**95%**	**9.5**	**6.1**	**5.07**	**0,410**	**0,505**	**0,285**
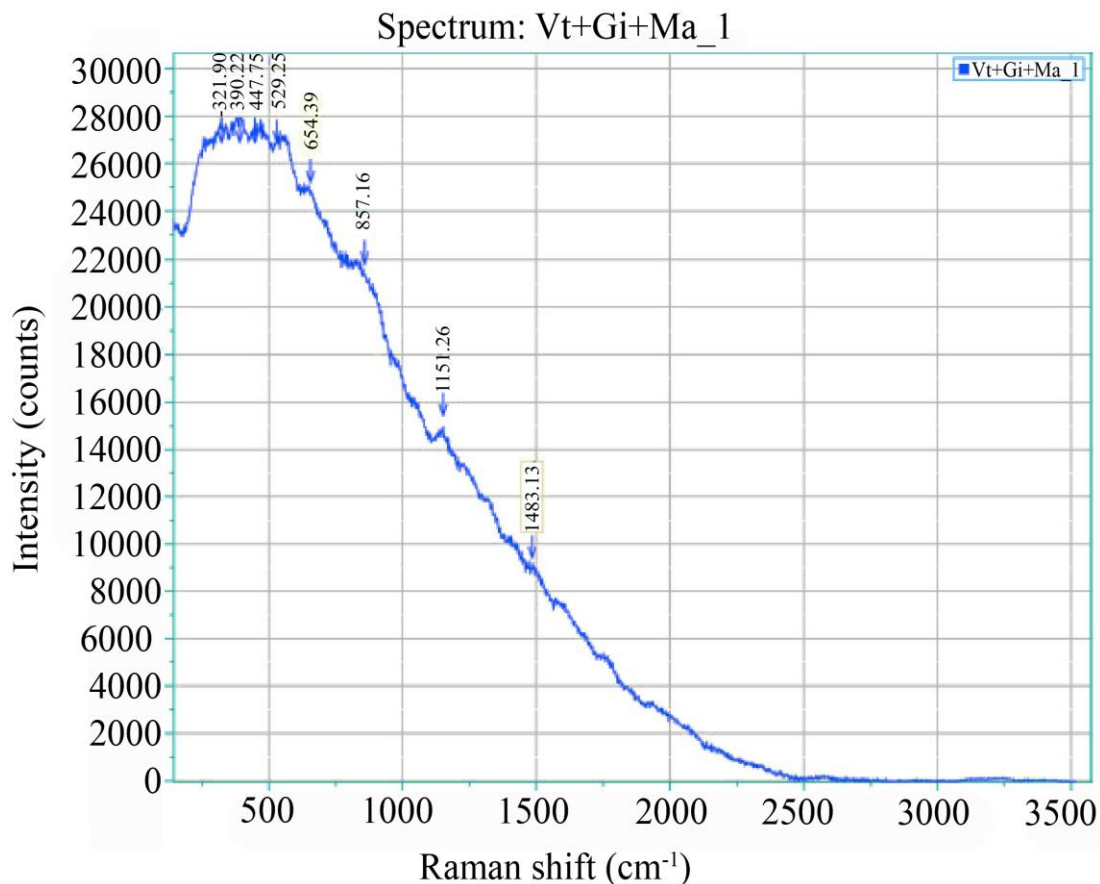
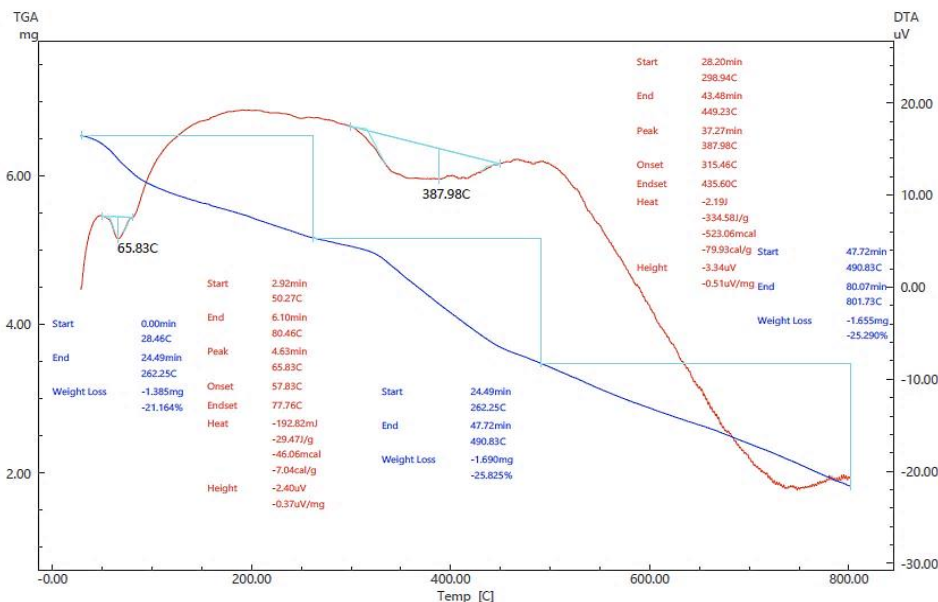Fig. 1 Novel spectroscopy analysis of V-HPM sorbent

Fig. 2 Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of V-HPM organic-inorganic ionite

4.2. TGA and DTA Thermal Analysis

Thermogravimetric (TGA) and Differential Thermal (DTA) analyzes of organically modified vermiculite with melamine and hydrolyzed polyacrylonitrile were conducted. The analyses were carried out on the DTG-60 device produced by the Tashkent Scientific Research Institute of Chemical Technology (Japan "SHIMADZU"). The analysis was carried out in an inert gas-argon atmosphere (80ml/min), and the temperature was increased by 10ºC/min. The device was set to a temperature of 800 ºC to record the analysis results. For the sample, the sorbent with a mass of 6.544 mg was placed in the device in a porcelain container. Analyzes were performed on the sample under the influence of temperature.

4.3. Thermogravimetric Analysis (TGA)

The dervitogram of the obtained sorbent is presented in Figure 2. According to the results, the thermogravimetric analysis curve (TGA-blue curves) shows changes in 3 intensive intervals. The sample underwent mass loss in three stages. The first mass loss started in the first minutes of thermal exposure at a temperature of 28.46ºC and ended at 262.25ºC at 24.44 minutes. At this stage, the sample lost 4% or 1.385 mg of mass in 21.1 minutes. In this case, some of the substances formed as a result of decomposition of maleic anhydride and Hypan, added for the purpose of sintering during polymerization, leave the sample[15].

The second mass loss started at 262.25 ºC at 24.49 minutes and lasted until 47.72 minutes. In the second stage of mass loss, which lasted up to 490.83 ºC, the mass of the sample decreased by 25.825%, i.e. 1.690 mg. During this mass loss, the hydrolyzed polyacrylonitrile and melamine in the sample completely decompose. The mass loss of the third stage of the sample began at the end of the second stage and

lasted until 80.07 minutes. In the third stage, at 801.73 ºC, we can see a mass loss of 25.290% (1.655mg). At this stage, it is estimated that some metal oxides, such as iron oxide contained in vermiculite, will break down. In the thermal analysis up to 800 C, 55.115% of the mass of the 3 V-HPM composite ionite sample is lost. The remaining 44.885% of the mass is vermiculite due to high temperature-resistant oxides.

### 4.4. Thermogravimetric Analysis (DTA)

DTA analysis (red curve) showed that the absorption of heat, i.e. the endothermic process, took place in two stages. The first stage started at 2.92 minutes of heating and absorbed a temperature of 50.27 ºC. Heat absorption is complete in 6.1 min when heating reaches 80.46 C. Energy absorption peaked at 4.63 minutes. This happened when the temperature reached 65.83 C. In this case, 192.82 mJ (45.06 cal), i.e. 29.47 J/g (7.04 cal/g) of heat, was absorbed compared to the mass of the sample. In this case, 2.40 mV of energy was spent, which is equal to 0.37 mV/mg compared to the sample mass. The second endothermic effect started at 28.10 minutes (298.94ºC) and ended at 43.48 minutes (449.23C) of heating.

The peak point occurred at 37.27 minutes of heating, i.e. when the temperature reached 387.98ºC. At the peak, heat absorption started at 315.46ºC and reached the highest level at 435.60 ºC. In the second endothermic stage, 2.191 J (523.6 cal) of heat was absorbed, which was equal to 334.58 J/g (79.93 cal/g) in relation to the sample mass. In the second endothermic effect, the energy consumption was equal to 3.34 mV, in which 0.51 mV/mg of energy was absorbed in relation to the sample mass. Analyzes of the sorbent sample taken above based on thermal exposure were presented [14]. Based on the analysis, the decomposition of the substance mass in three stages and the endothermic effect in two stages were

observed. In the research work, vermiculite was thermally treated during expansion before modification. Since it was treated at a temperature higher than 650 ℃, it can be concluded that very little decomposition occurred in the vermiculite part of the sample in this analysis. Decompositions in the mass of substances and thermal effects in this process occur in the organic component of the organic-inorganic sorbent.

4.5. SEM-EDX- Analysis

10μm, 50μm, and 100μm images of the morphological surface of the vermiculite composite sorbent modified with melamine and hydrolyzed polyacrylonitrile were taken using a scanning electron microscope (Figure 3). With these images, the amounts of each element in the sample were compared and analyzed using elemental analysis. (Figures 4 and 5) and percentages of elements are shown in Table 3.


| (a) | (b) | (c) |
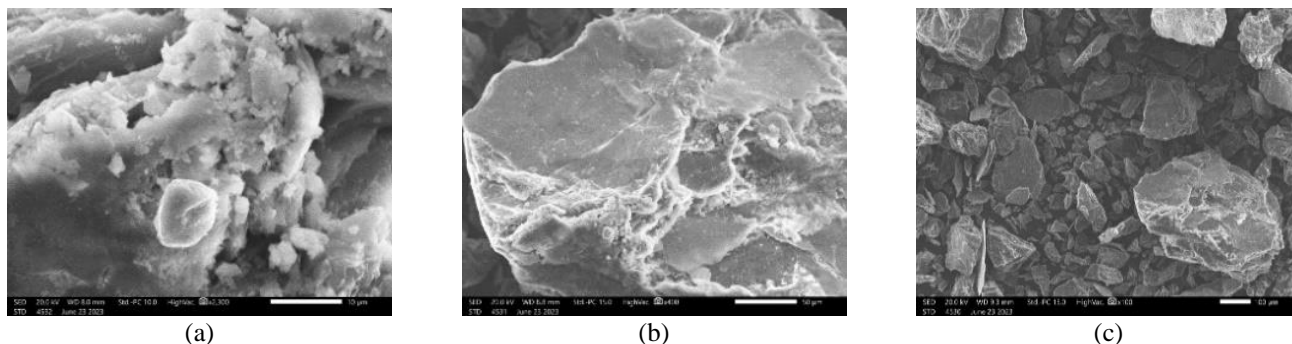
Fig. 3 SEM analysis of V-HPM composite, organic-inorganic ionite: a) 10μm (a); (b) 50 μm (b) and (b) 100 μm (c) magnified image

(a)   **(b)**
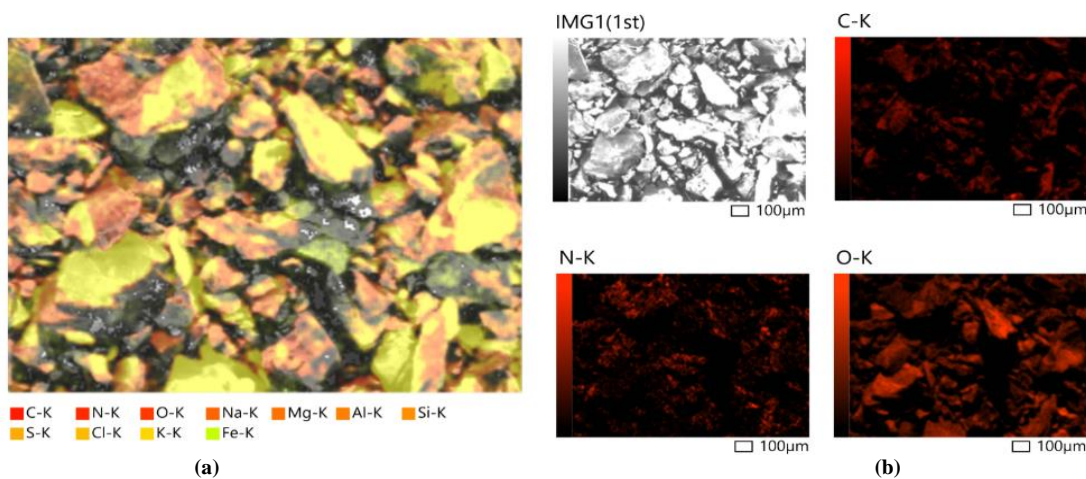
Fig. 4 Color images of the elements contained in the VK-GPMA sorbent in the 100 μm analysis: in the general state (a) and C; N; According to the elements of O (b)

(a)   **(b)**
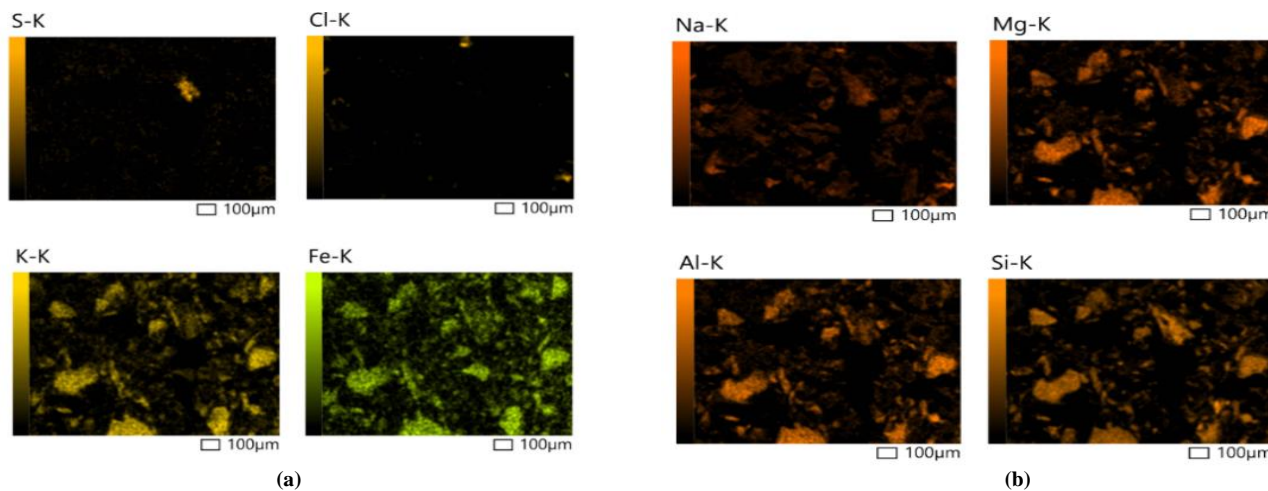
Fig. 5 Color images of elements contained in V-HPM sorbent in 100 μm analysis: (a) S; Cl; K; Fe elements and (b) Na; Mg; Al; Si elements
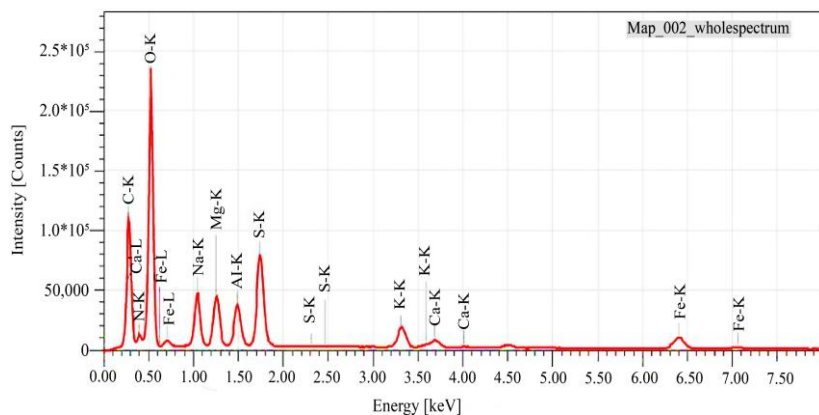
Element	Line	Mass%	Atom%
C	K	26.33±0.02	34.74±0.03
N	K	9.21±0.02	10.42±0.03
O	K	44.13±0.04	43.71±0.04
Na	K	4.44±0.01	3.06±0.01
Mg	K	2.90±0.01	1.89±0.00
Al	K	2.19±0.01	1.29±0.00
Si	K	5.01±0.01	2.83±0.00
S	K	0.20±0.00	0.10±0.00
Cl	K	0.88±0.00	0.39±0.00
K	K	2.00±0.01	0.81±0.00
Fe	K	2.72±0.01	0.77±0.00
Total		100.00	100.00

Fig. 6- X-ray spectroscopic analysis of elements contained in V-HPM sorbent
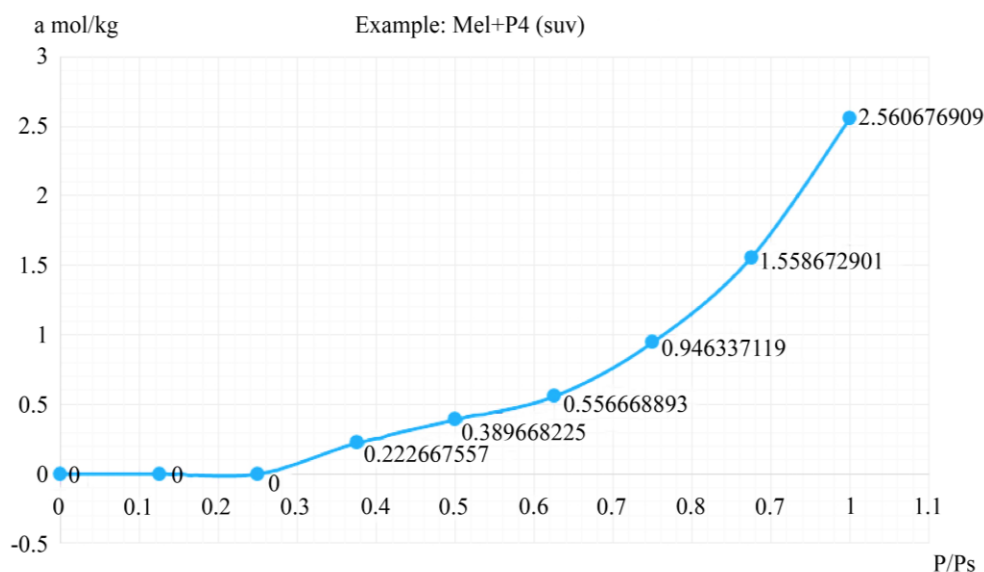

Fig. 7 Adsorption isotherm of V-HPM sorbent using water vapor pressure

Table 3. Surface area values calculated on the basis of water vapor adsorption of V-HPM sorbent

a_m (single floor capacity)	S comparative surface	Microporous W_0	Saturation volume Vs	Mesoporous W_{me}	Pore radius
0.122 mol/kg	7.90 m²/g	0.014855	0.04608	0.03	116.6Å 11.66 nm

4.6. X-ray Spectroscopy Analysis

On the basis of the elemental analysis of the obtained substance, the intensity values based on the return of the spectra of the elements in the sample were found based on the energy absorption in the X-ray spectroscopic analysis. Based on the curve given in the graph, it was seen that the peak of the highest intensity spectrum belongs to the O element and the next higher spectra are given by carbon. The fact that oxygen occupies 44.13% of the mass of the sample can be said to be the reason for the high spectrum. It can be said that the resulting substance gave an intense peak due to the presence of oxygen present in organic matter and vermiculite oxides. The carbon spectrum is due to organic substances in the substance, and N is due to the cyan and amide group in GIPAN

and nitrogen in the amine group in melamine. Silicon and other metals are reflected due to metals in the form of oxides in vermiculite. The presence of very few sulfur spectra in this graph is characteristic of local vermiculite.

4.7. Analysis of Mc-Ben-Bakra

4.7.1. Analysis of Adsorption Isotherms and Pore Sizes using Water Vapor
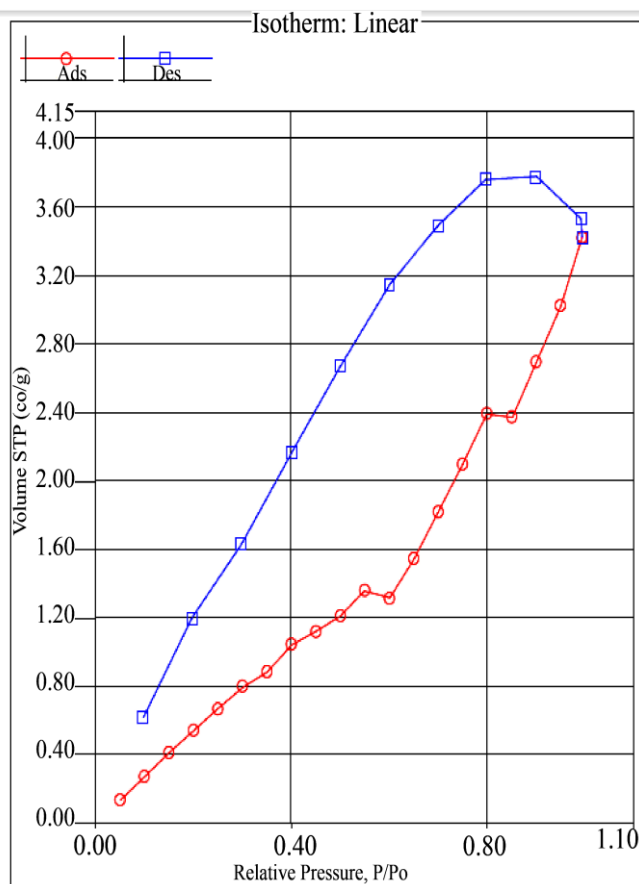
Adsorption and desorption isotherms of V-HPM composite ionite were obtained using the Mc-Benn-Bakra balance device using water vapor pressure, and mathematical calculations were carried out to determine the specific surface area using the BET (Brunauer-Emmett-Teller) method.The device is equipped with a highly sensitive quartz spiral. Its

sensitivity is $1.78 \cdot 10^{-3}$ kg/m. The Mc-Benn-Bakra device is equipped with a glass column, quartz spirals and containers (special cups) for adsorbents. During research work, the adsorption column (tube) with adsorbent samples is kept at 20 °C with a temperature accuracy of 0.1 °C in a water thermostat [16]. The main working parts of the device structure and working system are as follows: - quartz spring adsorption columns (supplied with cups, which were measured on an analytical scale with an accuracy of 1 g from the studied adsorbent samples in the cups), - for vacuum pump (VN-461M brand),-diffusion pump (it creates a vacuum until the residual pressure in the system is $1.33 \cdot 10^{-3}$ Pa.) it is provided with a screw, the pressure in the system was controlled with a thermovacuum meter (VIT - 2 brand). -U-shaped manometers, - a trap (functioning to trap various gases and water vapors in the system with liquid nitrogen), - ampoules for adsorbates and taps for separating the device parts. 1-10-5 mm.s.s. creates a vacuum until the pressure difference in the U-shaped monometers was measured using a V-630 type cathometer. The accuracy of the catheter is 0.05 mm. The samples prepared for the study were crushed to a powder state in an agate mortar, after mixing thoroughly, they were taken out in the amount of 1 g on a scale and placed in a cup.

The pressure in the system was stabilized by vacuum for 6-8 hours. In the experiments and calculations conducted using the BET method, it was found that the surface of the new substance obtained by organic modification of vermiculite mainly consists of mesopores and micropores.

4.8. Quantachrome Analysis

Adsorption and desorption isotherms of the sample were obtained using the nitrogen adsorption method, which is a more improved method of determining the surface-porosity dimensions of the obtained substance. This method is based on the analysis of conditions where nitrogen is absorbed into the surface of the substance in a cooled state and desorbed as a result of a gradual increase in temperature. Cold and liquid N_2 adsorption and heat desorption isotherms of the V-HPM sorbent obtained as a result of the study were obtained. The analysis was performed on the "Autosorb iQ 0 Station 2" device of the "QUANTACHROME instruments" company. The outgassing time was 1.2 hours, and the total analysis time was 3 hours. The bath temperature is 77.75K, and the final outlet temperature is 150 °C. The analysis was carried out using the standard method, with a density of 0.808 g/cc and a temperature of 77,350 K.
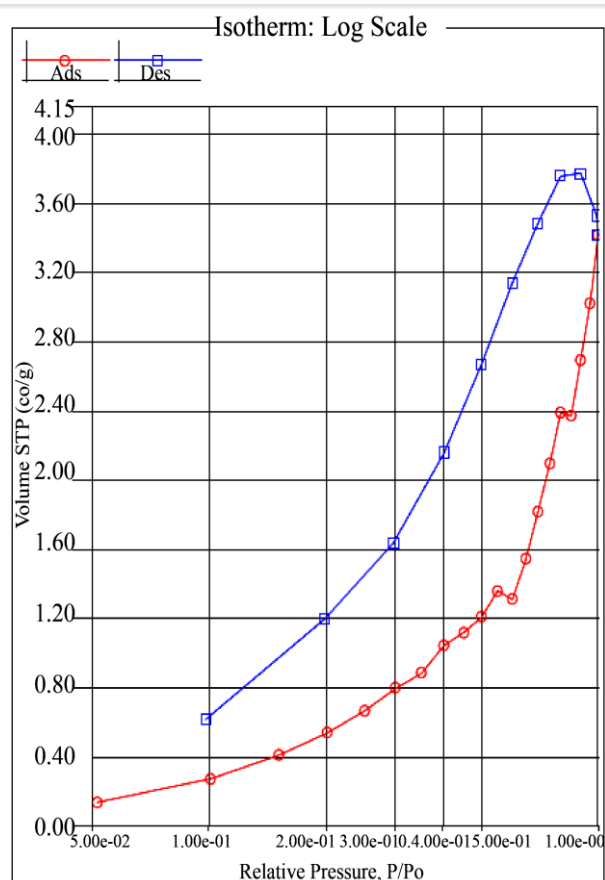
(a)   **(b)**

a) Linear isotherm; b) Log scale (log scale) isotherm); (The red lines in the graphs in the picture represent the adsorption curves, and the blue lines represent the desorption curves)
Fig. 8 Adsorption and desorption isotherms of V-HPM sorbent to N_2

Table 4. Relative pressure and volume values of the sorbent

Relative Pressure	Volume @ STP [cc/g]	Relative Pressure	Volume @ STP [cc/g]	Relative Pressure	Volume @ STP [cc/g]
5.16799e-02	0.1370	5.50982e-01	1.3587	9.92913e-01	3.5308
1.00990e-01	0.2724	6.01443e-01	1.3135	9.00464e-01	3.7735
1.51164e-01	0.4125	6.50801e-01	1.5467	7.97391e-01	3.7603
2.01187e-01	0.5415	7.00763e-01	1.8188	7.00479e-01	3.4872
2.51259e-01	0.6671	7.50597e-01	2.0962	6.00978e-01	3.1429
3.01181e-01	0.8004	8.00579e-01	2.3910	5.01139e-01	2.6683
3.51306e-01	0.8858	8.51252e-01	2.3736	4.01208e-01	2.1596
4.01130e-01	1.0453	9.00444e-01	2.6954	2.98189e-01	1.6328
4.51249e-01	1.1196	9.50552e-01	3.0225	1.97954e-01	1.1970
5.01282e-01	1.2121	9.95263e-01	3.4186	9.83227e-01	0.6145

Calculations of surface area and porosity of V-HPM sorbent based on nitrogen adsorption and desorption using the DFT method.
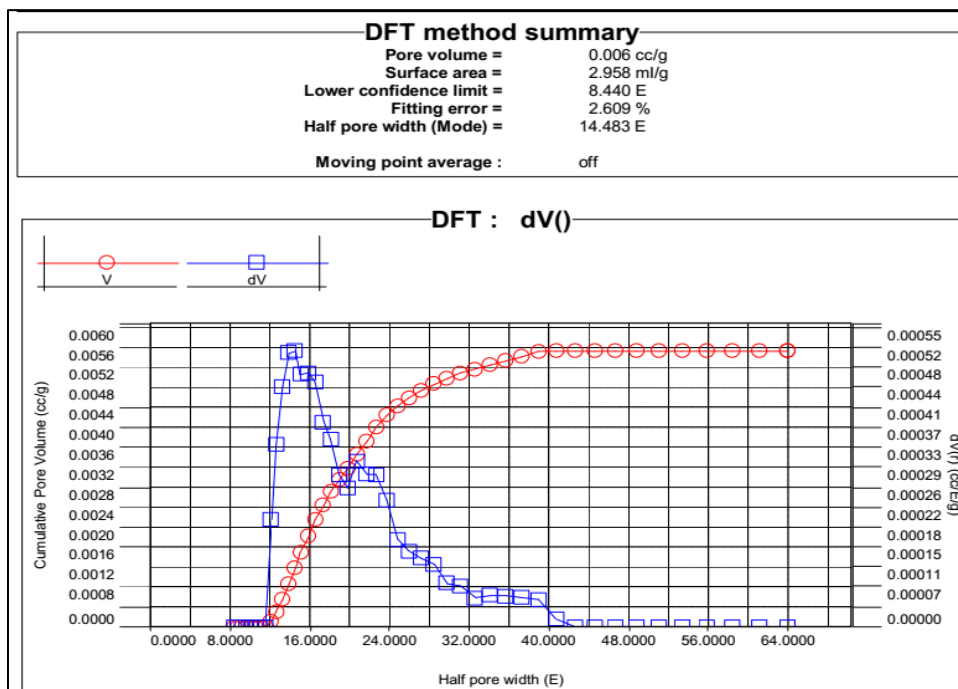

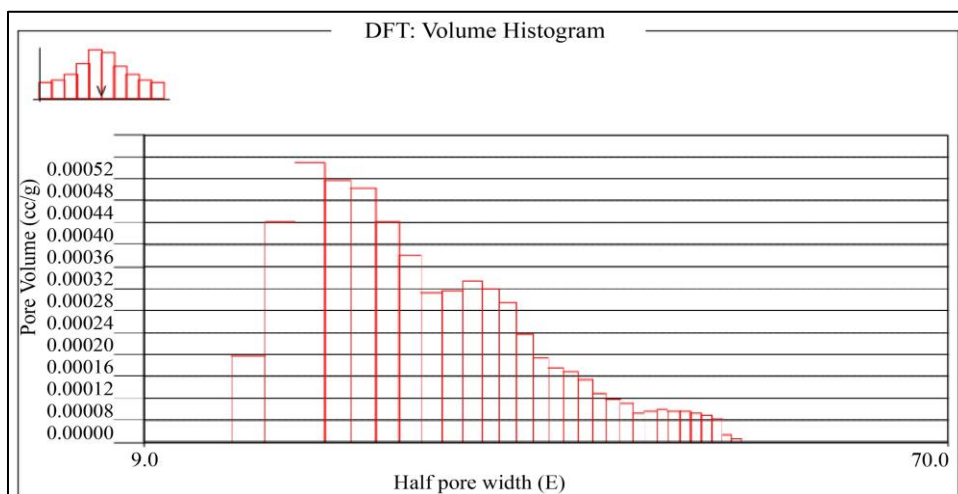**Fig. 9 Isotherm of half-pore volume and absorbing pore volume of V-HPM sorbent**

Fig. 10 Histogram of dependence of half-pore width and pore volume of V-HPM sorbent using the DFT method

Table 5. Indicators of V-HPM sorbent obtained based on the DFT method

DFT method Pore Size Distribution				
Half pore width [E]	**Cumulative Pore Volume [cc/g]**	**Cumulative Surface Area [ml/g]**	**dV(r) [cc/E/g]**	**dS(r) [ml/E/g]**
8.4397	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
8.8282	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
9.2345	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
9.6595	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
10.1041	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
10.5692	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
11.0557	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
11.5646	0.0000e+00	0.0000e+00	0.0000e+00	0.0000e+00
12.0969	1.0517e-04	8.6937e-02	1.9757e-04	1.6332e-01
12.6537	2.9233e-04	2.3485e-01	3.3614e-04	2.6565e-01
13.2361	5.5050e-04	4.2990e-01	4.4327e-04	3.3489e-01
13.8453	8.5879e-04	6.5257e-01	5.0604e-04	3.6550e-01
14.4826	1.1836e-03	8.7687e-01	5.0975e-04	3.5198e-01
15.1492	1.4945e-03	1.0821e+00	4.6630e-04	3.0781e-01
15.8465	1.8207e-03	1.2879e+00	4.6785e-04	2.9524e-01
16.57585	2.1503e-03	1.4867e+00	4.5184e-04	2.7259e-01
17.3388	2.4381e-03	1.6527e+00	3.7724e-04	2.1757e-01
18.1369	2.7142e-03	1.8050e+00	3.4599e-04	1.9077e-01

Calculations of surface area using BET method based on nitrogen adsorption and desorption of V-HPM sorbent.
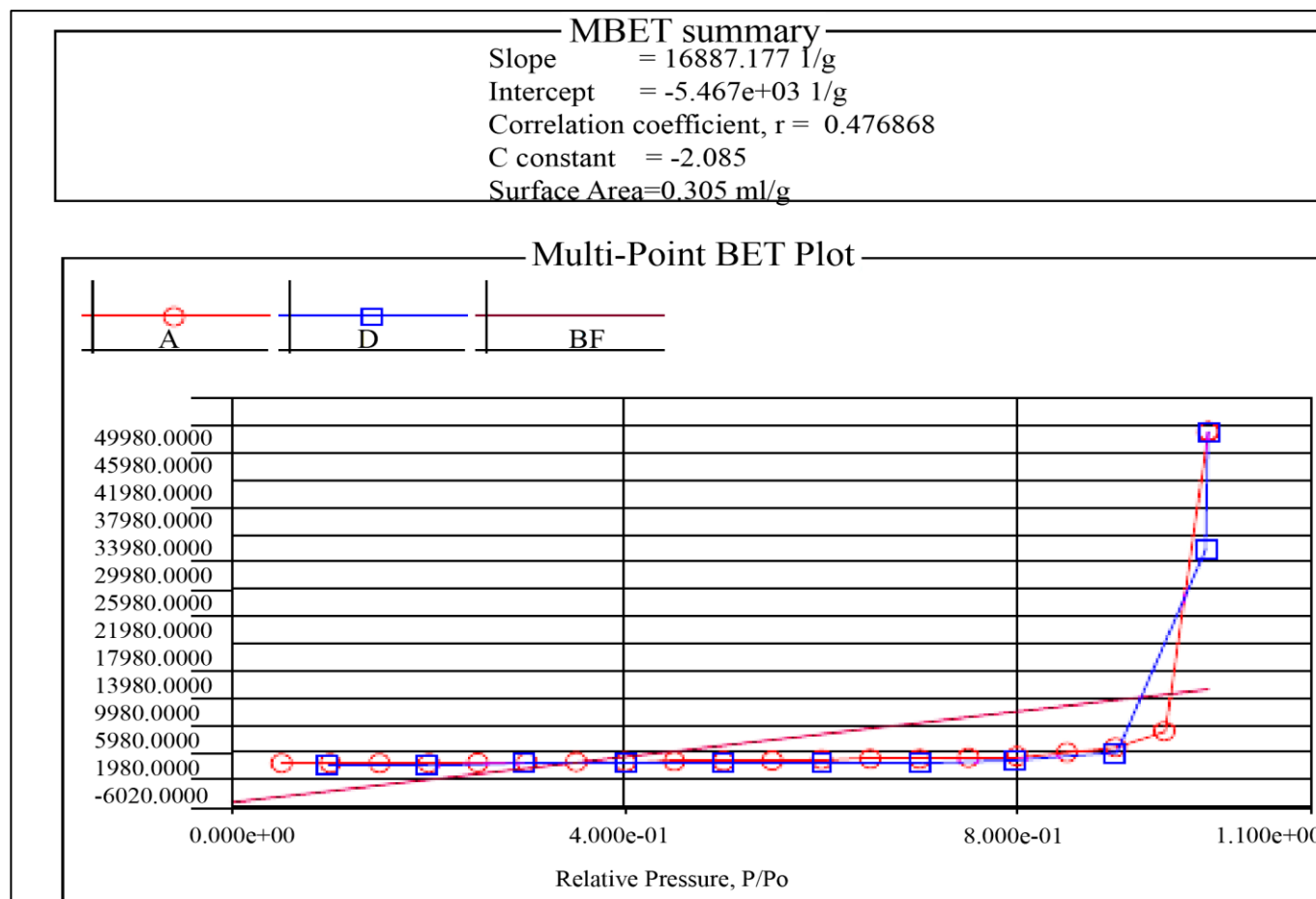

Fig. 11 Surface determination isotherm of V-HPM sorbent using the BET method
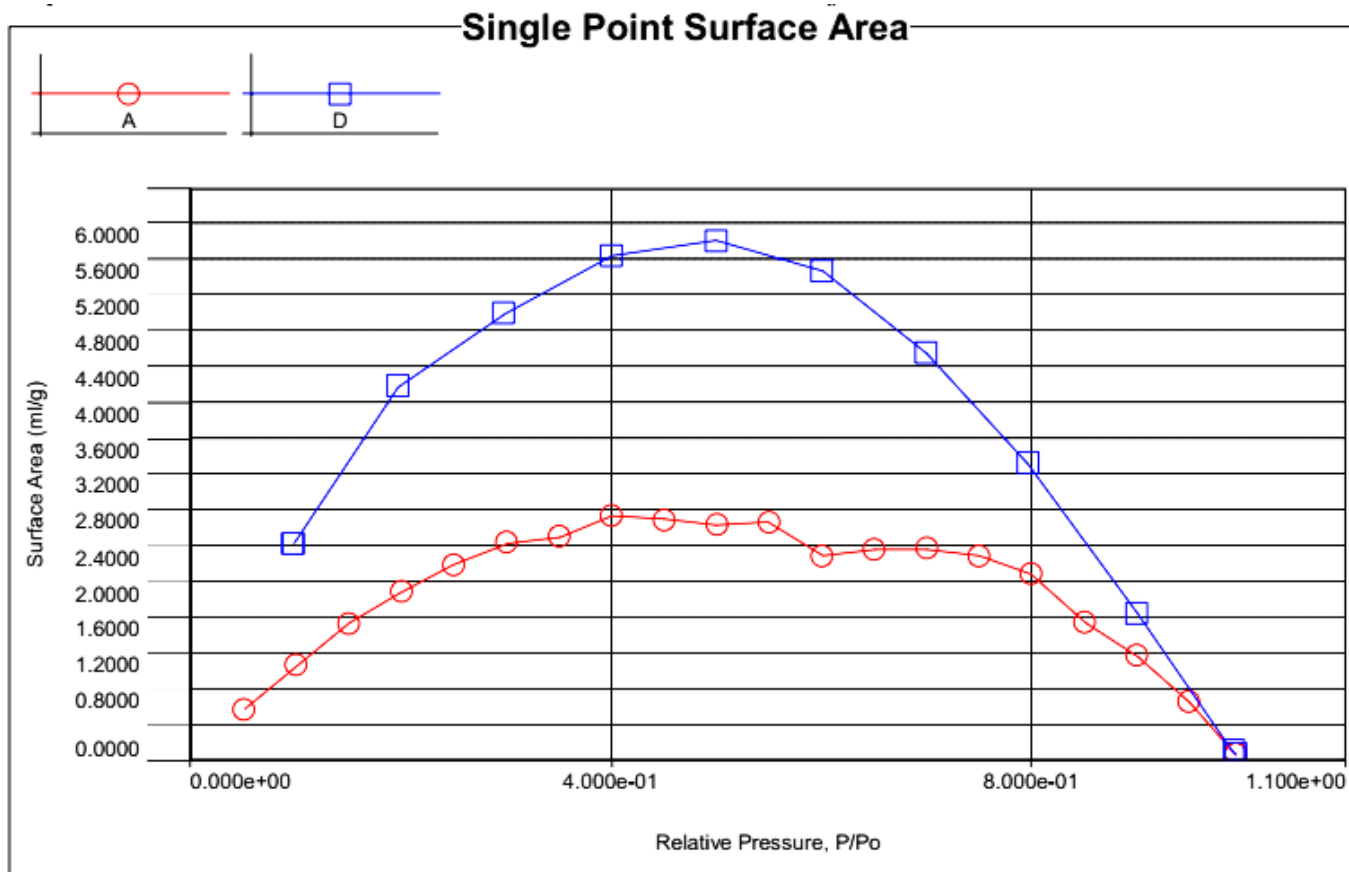
Fig. 12 Point isotherm of surface determination of V-HPM sorbent using the DFT method

The red lines in the graphs in the Figure 12 represent adsorption, and the blue lines show desorption curves.

Table. 6 Indicators of V-HPM sorbent obtained on the basis of BET method

Multi-Point BET					
Relative Pressure [P/Po]	Volume @ STP [cc/g]	1/[W((Po/P)-1] [1/g]	Relative Pressure [P/Po]	Volume @ STP [cc/g]	1/[W((Po/P)-1] [1/g]
5.16799e-02	0.1370	3.1838e+02	4.01130e-01	1.0453	5.1268e+02
1.00990e-01	0.2724	3.2995e+02	4.51249e-01	1.1196	5.8764e+02
1.51164e-01	0.4125	3.4540e+02	5.01282e-01	1.2121	6.6348e+02
2.01187e-01	0.5415	3.7217e+02	5.50982e-01	1.3587	7.2263e+02
2.51259e-01	0.6671	4.0251e+02	6.01443e-01	1.3135	9.1925e+02
3.01181e-01	0.8004	4.3082e+02	6.50801e-01	1.5467	9.6410e+02
3.51306e-01	0.8858	4.8919e+02	7.00763e-01	1.8188	1.0302e+03

5. Conclusion

As a result of the research, an organic-inorganic composite sorbent was obtained by organic modification of vermiculite with hydrolyzed polyacrylonitrile and melamine. The methods and properties of the sorbent synthesis were performed using the following experiments and studied through physico-chemical analysis.

- Vermiculite was cleaned, fired in an oven to create porosity and expansion, and activated in hydrochloric acid. Porous and activated vermiculite was modified using

hydrolyzed polyacrylonitrile and melamine. Reaction conditions and optimal temperatures of the synthesized composite were studied. The static exchange capacity of the sorbent was calculated in accordance with the requirements of GOST 20255.1-8. Sorption was carried out against Cu(II), Zn(II) and Ag(I) ions. The highest, i.e. 95%, occurred when the mass ratio of starting materials was 2:4:0.5. The SAS and DAS values found by calculating the solution differences were tabulated. The conditions for studying the sorption of solutions and the values of the ion machine and the solution are given.

- Vermiculite-based organo-inorganic sorbent modified with melamine and hydrolyzed polyacrylonitrile and their structure and physical-chemical properties Roman spectroscopic and their structure and physical-chemical properties Roman spectroscopic and the analysis of tolerance to thermal effects and other properties was carried out. DTA and TGA analyses of the sorbent were obtained. Three mass losses occurred due to thermal exposure to the sample up to 800 °C.
- Using a scanning electron microscope (SEM), 10µm, 50µm, and 100µm images of surface morphology were studied. In the scanner images magnified by 100 µm, the proportions of the elements on the surface of the composite were separated based on the corresponding colours, and the images and analyses of the distribution of the individual elements on the surface of the sample were presented.
- In the process of SEM scanning of the elements contained in the V-HPM sorbent, a graphic analysis of the element spectra based on the analysis of the surface area of the sorbent was performed.
- In the Mc-Ben-Bakra device of the V-HPM sorbent, adsorption isotherms and porosity dimensions were determined using water vapour. The analysis was carried out at a temperature of 200 °C. Analysis of isotherms by determining the sorbent mesoporous level, monolayer capacity, saturation volume, specific surface area, micropore, and pore radii were calculated, and the values were displayed based on tables. Adsorption and desorption isotherms were obtained on the V-HPM sample in the presence of nitrogen gas on the ASIQWIN device. Based on these isotherms, the specific surface area and porosity dimensions of the sorbent were calculated and checked.

Acknowledgment

Authors' Contribution Statement
Kholmurodova S.A: Writing – Original Draft. Turaev Kh.Kh: Reviewing and editing the paper. Alikulov R.V and Toshkulov A.Kh: Reviewing and editing paper. Kulbosheva Kh.Kh: Software, Validation. Toshev M.E: Writing – Original Draft, Conceptualization, Investigation, Visualisation.

References
[1] Sabohat Kholmurodova et al., "Investigation of the Properties of Expanded Vermiculite Modified with Acrilonitrile," *Universum Technical Science*, vol. 109, no. 4, pp. 1-5, 2023. [CrossRef] [Publisher Link]
[2] Yannan Zhang, Valeria Palomba, and Andrea Frazzica, "Development and Characterization of LiCl Supported Composite Sorbents for Adsorption Desalination," *Applied Thermal Engineering*, vol. 203, no. 4, 2022. [CrossRef] [Google Scholar] [Publisher Link]
[3] Majid Karim Nejhad, Devrim Aydin, and Marzieh Rezaei, "Experimental Investigation of a Solar-Charged Sorption Thermal Battery," *Proceedings of the Institution of Mechanical Engineers, Part E: Journal of Process Mechanical Engineering*, vol. 237, no. 3, pp. 896-906, 2022. [CrossRef] [Google Scholar] [Publisher Link]
[4] Khandamov Davron Abdikadirovich, Djumaniyazova Malokhat Rihsiyevna, and Tursunova Dilnozakhon Isroiljon Qizi, "Minerals that Make Up the Montmorillonite Group," *Asian Journal of Chemical Sciences*, vol. 11, no. 2, pp. 28-32, 2022. [CrossRef] [Google Scholar] [Publisher Link]
[5] Beikut Balgysheva et al. "Modified Vermiculite of the Mugodzhary Deposit and Its Sorption Properties," *Journal of Chemical Technology & Metallurgy*, vol. 57, no. 3, pp. 533-544, 2022. [Google Scholar] [Publisher Link]
[6] E.A. Krasavtseva et al., "Method for Treating Wastewater From Nitrogen Group in the Murmansk Region," *International Conference on Environmental Technologies and Engineering for Sustainable Development*, Tashkent, Uzbekistan, vol. 1112, pp. 1-5, 2022. [CrossRef] [Google Scholar] [Publisher Link]
[7] Yu Baikin et al., "Study of the Natural Mineral Sorbents' Absorption Properties of the Ural Region (Russia)," *International Scientific and Practical Conference: Development of the Agro-Industrial Complex in the Context of Robotization and Digitalization of Production in Russia and Abroad*, Yekaterinburg, Russia, vol. 949, pp. 1-6, 2022. [CrossRef] [Google Scholar] [Publisher Link]
[8] Andaç Batur Çolak et al., "Discharging Performance Prediction of Experimentally Tested Sorption Heat Storage Materials with Machine Learning Method," *Journal of Energy Storage*, vol. 56, no. C, 2022. [CrossRef] [Google Scholar] [Publisher Link]
[9] Elizaveta Mikhedova, and Uzorina Maria, "Ecological Aspects of Using Sorbents to Improve Bioremediation Efficiency of Oil-Contaminated Soils," *Fuentes Magazine*, *the Energy Explosion*, vol. 19, no. 1, pp. 65-73, 2021. [CrossRef] [Google Scholar] [Publisher Link]
[10] Pavel Topka et al. "Remediation of Brownfields Contaminated by Organic Compounds and Heavy Metals: A Bench-Scale Test of a Sulfur/Vermiculite Sorbent for Mercury Vapor Removal," *Environmental Science and Pollution Research*, vol. 27, no. 33, pp. 42182-42188, 2020. [CrossRef] [Google Scholar] [Publisher Link]
[11] Alexandra D. Grekova, Larisa G. Gordeeva, and Yuri I. Aristov, "Composite "LiCl/Vermiculite" as Advanced Water Sorbent for Thermal Energy Storage," *Applied Thermal Engineering*, vol. 124, pp. 1401-1408, 2017. [CrossRef] [Google Scholar] [Publisher Link]
[12] Duc Cuong Nguyen et al., "Highly Hydrophobic Polydimethylsiloxane-Coated Expanded Vermiculite Sorbents for Selective Oil Removal From Water," *Nanomaterials*, vol. 11, no. 2, pp. 1-13, 2021. [CrossRef] [Google Scholar] [Publisher Link]

[13] Dilnoza Shavkatova et al., "Preparing a New Type of Concrete Based on Sulfur-Melamine Modifier," *Baghdad Science Journal*, vol. 21, no. 3, pp. 1006-1020, 2024. [CrossRef] [Google Scholar] [Publisher Link]

[14] Nomozov Abror Karim Ugli et al., "Salsola Oppositifolia Acid Extract as a Green Corrosion Inhibitor for Carbon Steel," *Indian Journal of Chemical Technology,* vol. 30, no. 6, pp. 872-877, 2023. [CrossRef] [Google Scholar] [Publisher Link]

[15] Yulchieva Marguba Gafurjanovna et al., "Studying Synthesis of A Chelate-Forming Sorbent Based on Urea-Formaldehyde and Diphenylcarbazone," *Indian Journal of Chemistry*, vol. 63, pp. 579-585, 2024. [CrossRef] [Google Scholar] [Publisher Link]

[16] Gulnora A. Umirova et al., "Crystal Structure and Hirshfeld Surface Analysis of 8-Azaniumylquinolinium Tetrachloridozincate(II)," *Crystallographica Section E: Crystallographic Communications*, vol. 79, pp. 856-860, 2023. [CrossRef] [Google Scholar] [Publisher Link]

[17] Sh S. Nazirov et al., "Spectrophotometric Determination of Copper(II) Ion with 7-Bromo-2-Nitroso-1-Oxinaphthalene-3,6-Disulphocid," *Indian Journal of Chemistry*, vol. 63, no. 5, pp. 500-505, 2024. [CrossRef] [Google Scholar] [Publisher Link]

[18] Mokhichekhra Shaymardanova et al., "Studying of the Process of Obtaining Monocalcium Phosphate based on Extraction Phosphoric Acid from Phosphorites of Central Kyzylkum," *Baghdad Science Journal*, vol. 22, no. 1, 2024. [CrossRef] [Google Scholar] [Publisher Link]