STUDY OF SORPTION OF CU(II) IONS ON VERMICULITE-BASED SORBENT MODIFIED WITH DIETHANOLAMINE

Kholmurodova S., Muminova Sh., Kobulova M., Kholmurodova So., Alikulova I., Boboyeva M.,Turayeva S.-Termiz state university
Email:teachersaboxat@gmail.com

Abstract: The article covers vermiculite activated in strong acid, its pore formation, modification with hydrolyzed polyacrylonitrile. Also, experiments were carried out on the attachment of the obtained composite sorbent with monomers containing the amine group and the preparation of a highly selective sorbent for Cu(II) ion. The obtained results were tested by SEM and X-ray structural element analysis. Tests on absorption of benzene vapors by adsorption were carried out in the Mac-Ben-Bakr apparatus and appropriate adsorption and desorption isotherms were obtained, its surface area, monolayer capacity and pore sizes were given.

Keywords. Vermiculite, hydrochloric acid, copper, hydrolyzed polyacrylonitrile, diethanolamine, melamine, ethanolamine, adsorption.

Introduction. In today's era of rapidly increasing industrial production processes, there is an obligation to use natural resources and local resources wisely. It is important to treat wastewater generated during the production process and make it suitable for reuse[1]. Research is being conducted to create ion-exchange sorbents for the removal of heavy metals from wastewater and for the selective separation of metals from metal solutions[2-3].

Pollutants in water are classified into different types based on their physical and chemical properties. Thus, multiple sorbents may be required to remove them.

Kinetic studies have shown that a column packed with a mixture of ammonium and humic acid can purify 100 pore volumes to remove ammonium at an initial concentration of 10 mg/L and 500 pore volumes to remove humic acid at an initial concentration of 20 mg/L before wastewater concentration[4]. Against the backdrop of water scarcity, scientists have conducted research on the creation of new adsorbents for collecting atmospheric water. In order to increase the water-collecting capacity of the product, a new composite adsorbent MgCl2/vermiculite was synthesized. N_2 adsorption test, adsorption performance test, desorption performance test, cyclic adsorption test and adsorption characteristic curve fitting were conducted on this new type of composite adsorbent and positive results were obtained. The composite adsorbent

$MgCl_2$/vermiculite is an excellent adsorption material for water vapor compared to the traditional adsorbent[5]. Pesticides in agricultural surface water pose a significant threat to freshwater systems. The installation of filter systems or constructed wetlands in areas with preferential runoff is a possible measure to reduce pesticides. To develop such systems, combinations of filter materials suitable for the retention of both hydrophilic and hydrophobic organic pesticides were tested for pesticide removal in planted microcosms[6]. The problem of wastewater treatment from antibiotic residues is particularly relevant, since these drugs are used in many agricultural sectors. Antibiotics can enter water, animals and the human body, adversely affecting their health. Thus, vermiculite modified with 7% hydrochloric acid is a promising sorbent for cleaning water bodies from antibiotic residues[7].

Experimental part. Vermiculite in its natural state was expanded at a temperature of 800 ºC, that is, made porous. For this, 50 g of vermiculite was placed in a 100 ml porcelain container and placed in a kiln. Vermiculite is a natural sorbent mineral, its composition consists of several different oxides and layers.

The constitutional water present between the layers begins to escape during intense heating, this process begins after the temperature exceeds 150° C. As a result of the evaporation of non-hygroscopic water contained in vermiculite under the influence of temperature, the layers open up and take on an accordion-like appearance.

The expanded vermiculite was placed in a 250 ml glass bottle, 36% hydrochloric acid solution was poured over it, and left in a dark place for 48 hours. During this period, the process of chemical activation in vermiculite occurs. Active -OH- groups are formed in vermiculite, which is considered an almost chemically inert substance in its natural state.

The vermiculite mixture was filtered and treated with ammonia water to neutralize the acid residues. In the next step, it was decanted with boiling distilled water. The activated vermiculite was placed in a drying oven at 100 ºC and dried until all of its hygroscopic water was removed.

An organo-inorganic sorbent was obtained from hydrolyzed polyacrylonitrile, activated vermiculite, and diethanolamine. The reaction proceeded in an aqueous medium in the presence of an initiator.

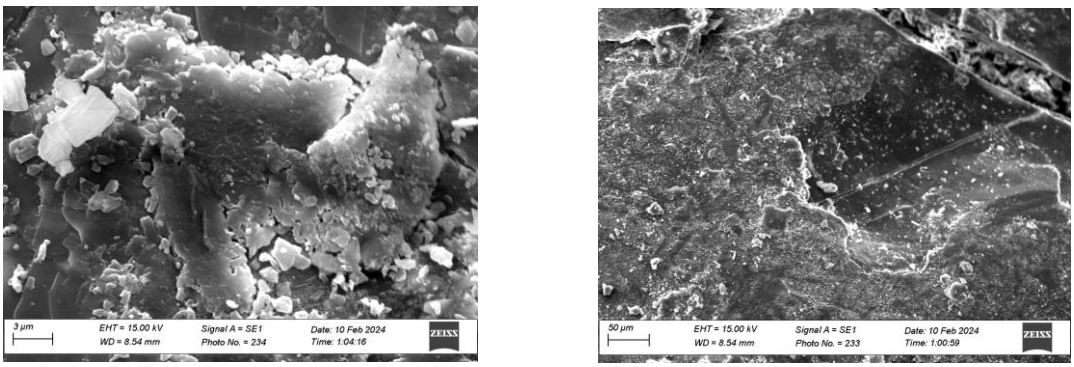
Various tests were conducted to check the sorbent properties of the obtained composite material. For this, a 0.1N solution of Cu (II) valent salt was prepared. 10 ml of saline solution and 30 mg of sorbent particles were placed in glass ampoules

The containers were left for 24 hours with the mouths closed and the concentration of Cu2+ ions remaining in the solution was determined. A standard solution without ion exchanger was also tested and determined based on the difference in concentrations using the following formula[8].

$$q_e = \frac{(C_0 - C_M) \cdot V}{m}$$

Here: qe - amount of ions absorbed by the ionizer, mg-ek/g
V0,I - solution volume, in l
C0i - initial concentration of the solution, mmol/l
C0i - equilibrium concentration mmol/l
m - mass of the ionite, g
According to the results calculated based on this formula, the static exchange capacity of the diethanolamine-modified, hydrolyzed polyacrylonitrile and vermiculite composite was calculated to be 7.8 mg.eq/g.

Results analysis:



a) b)

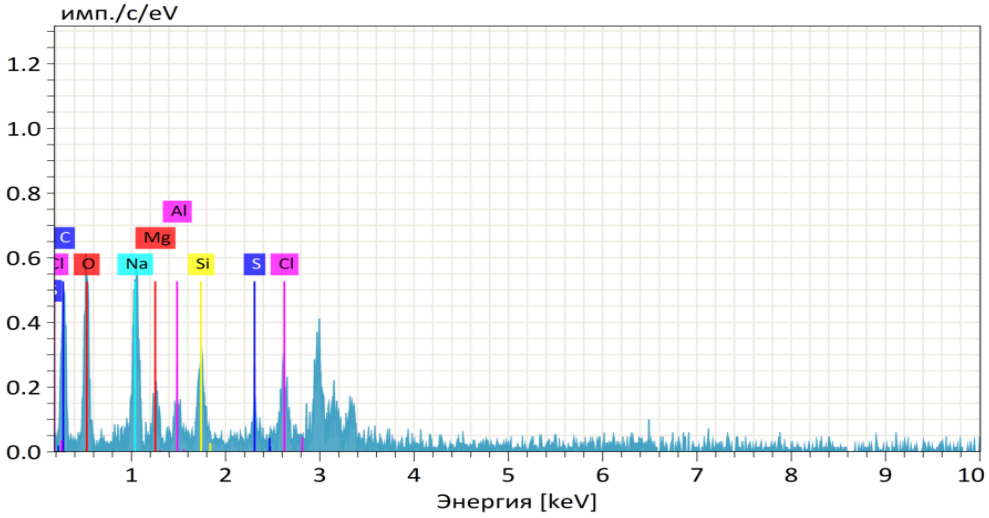
Figure 1. SEM images of the Wt/GIPAN/DEA composite: a) 3µm size and b) 50µm size

Based on the SEM images of the resulting sorbent, it is possible to observe the intact shape of the vermiculite layers on the surface of the material and other substances attached to it. There are no residues of unreacted starting materials on the surface of the sample, which reflects the presence of mesopores. The mass fractions of the elements in the sorbent are given in Table 1. According to the analysis, the highest mass fraction is 42.34% -C. This is due to the C content of the organic matter that modified the

vermiculite. The second highest indicator belongs to O, which is 32.84% of the mass fraction of the sample. The remaining elements are due to oxides in the vermiculite mineral.

Table 1. Elemental analysis results of the Wt/GIPAN/DEA composite (%)

element	C	O	Na	Si	Cl	Mg	Al	S
Atomic number	6	8	11	14	17	12	13	16
Mass fraction [%]	42.34	32.84	10.79	5.34	2.57	2.49	2.29	1.34
Sigma mass (%)	1.52	1.11	0.87	0.37	0.16	0.23	0.20	0.11



The metal ion-sorbed sample was regenerated using hydrochloric acid and nitric acid. In this case, the metal ions contained in the sorbent were transferred to the acidic solution. When the sample was washed in distilled water, cleaned of acid residue, and re-immersed in a salt solution, effective adsorption occurred[9].

Conclusion. The clay mineral vermiculite, which is a natural sorbent, was expanded and porous. A composite sorbent was obtained from the porous vermiculite with a binding agent of GIPAN and maleic anhydride. The sorbent was modified with diethanolamine.

The adsorption properties of the obtained sorbent were studied. Cu(II) was sorbed from a salt solution. The amount and conditions of sorption were studied. SEM images, elemental analyses and adsorption of the obtained organo-inorganic, composite

sorbent to water vapor were examined in a high vacuum in a Mac-Ben-Bakr device and adsorption isotherms were obtained.

Based on the analyses and calculations, it was determined that the obtained sorbent consists mainly of mesopores and micropores, and the surface area is relatively large. The fact that the sorbent is regenerative expands the possibilities of its exploitation. The desorption process in the presence of acids is almost complete. It was found that the difference between the results of the sorption process after desorption was small. It was concluded that the resulting sorbent is chemically harmless, has a large specific surface area, i.e., is lightweight, and is an excellent, selective ion exchanger for Cu(II) metal ions.

References:

1. Kholmurodova S. et al. Investigation of the Properties of Expanded Vermiculite Modified With Acrilonitrile // UniversumTechnical Sci. 2023. Vol. 109, № 4. DOI - 10.32743/UniTech.2023.109.4.15258

2. Syrmanova K.K. et al. Vermiculite absorption capacity increasing by acid activation // Orient. J. Chem. 2017. Vol. 33, № 1. P. 509–513.
DOI- 10.13005/ojc/330160

3. Eshchanov R.A. Vermikulit asosidagi ion almashinuvchi materiallarning xossalari. 2022. № January. DOI- 10.13140/RG.2.2.15947.31529

4. Zhang X. et al. Removal of Low Concentrations of Ammonium and Humic Acid from Simulated Groundwater by Vermiculite/Palygorskite Mixture // Water Environ. Res. 2012. Vol. 84, № 8.
DOI- 10.2175/106143012x13373550426751

5. Zhao H. et al. Synthesis of MgCl2/vermiculite and its water vapor adsorption-desorption performance // Int. J. Energy Res. 2021. Vol. 45, № 15.DOI- 10.1002/er.7188

6. Butkovskyi A. et al. Retention and distribution of pesticides in planted filter microcosms designed for treatment of agricultural surface runoff // Sci. Total Environ. 2021. Vol. 778.DOI- 10.1016/j.scitotenv.2021.146114

7. 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. DOI- 10.21285/2500-1582-2021-4-387-394

8. Kholmurodova S.A. Turayev X.X., Aliqulov R.V., Analysis of the sorption of Cu(II) ions on modified vermiculite-based sorbents.// NamSU Scientific Bulletin.-2024.-No. 9. -67-71 p.

9. Kholmurodova S., Turayev Kh., Alikulov R., Kholnazarov B., Eshmuradov Kh. Preparation of vermiculite and polypolyacrylonitrile composite and its modification with diethanolamine//Chemical problems. -.2024. -Vol. 23(1). -P. 1-17.