INVESTIGATION OF THE PROCESS OF AMMONIUM ION ADSORPTION BY NATURAL AND SYNTHETIC SORBENTS BY METHODS OF MULTIDIMENSIONAL CLUSTER ANALYSIS

Vira Sabadash, Yaroslav Gumnitsky, Oksana Liuta

Lviv Polytechnic National University,
12, S. Bandery Str., Lviv, 79013, Ukraine
virasabadash@gmail.com, oksana.lyuta@gmail.com

Abstract. The results of the research of the adsorption capacity of a number of sorbents of natural and synthetic origin for ammonium ions have been clustered. The natural zeolite of the Sokyrnytsia deposit, a synthetic sorbent based on the fly ash of Dobrotvir state district heat power plant, Al_2O_3, SiO_2, as well as some types of soil: sandy soil, black soil, and clay were used in the research. Equations describing the regularities of adsorption processes depending on the type of sorbent were obtained. According to the obtained dendrograms, two main clusters of sorbents were identified. The statistical parameters of the process and the significance of the obtained results were calculated. The coefficient of determination of the experimental data was 0.67–0.99, the standard deviation was 0.017–0.026.

Key words: adsorption, ammonium, sorbents, wastewater, cluster analysis

1. Introduction

Today, there is a problem of wastewater treatment from ammonium ions, because due to the high degree of volatility, these compounds pollute the environment. Therefore, while choosing a method of treatment of industrial wastewater, you need to pay attention to the possibility of releasing ammonia through desorption into the gas phase [1, 2]. The efficiency of ion absorption depends on many factors, in particular on external and internal diffusion transfer. The ion exchange occurs when the concentration of sorbed cation is equal to or less than the concentration of exchange cations. As the concentration increases, the process of adsorption intensifies [3, 4]. It is known that zeolites are able to adsorb ions not only by the mechanism of physical adsorption but also due to ion exchange and show themselves as cation exchangers. In the literature, mechanisms of adsorption, the isotherms of adsorption of various substances on clinoptilolite are described [5]. However, it is necessary to determine the mechanism of interaction of ammonium ions with clinoptilolite and to estimate the adsorption capacity of zeolite relative to ammonium ions. Data on the adsorption of ammonium ions on natural zeolites are given in the literature. The results on the sorption of ammonium from model solutions of ammonium chloride under static conditions are presented.

Data on the study of the sorption capacity of zeolite for NH_4^+ ions were obtained. The mechanism of ionic adsorption of ammonium by zeolite was indicated, which leads to the replacement of compensating Ca^{2+} and Na+ ions, as well as H+ ions retained in the Si-OH-Al chain by ammonium ions [5, 6]. It was found that the amount of adsorbed ammonium is 8.7 times greater than the amount of Ca^{2+} and Na^+ ions released due to ion exchange. At low concentrations (0–0.5 g/l), the amount of adsorbed ammonium is equivalent to the sum of sodium and calcium ions leached from the framework during the adsorption of ammonium. According to the literature, in addition to the ion exchange of ammonium ions for calcium and sodium, NH_4^+ is adsorbed accompanied by protonation of the zeolite framework, which leads to the rupture of chains between oxygen and aluminum and leads to the destruction of the zeolite surface. This fact is explained by the presence of fine and colloidal particles in the test solution. When the surface is destroyed, new adsorption centers located in

the lower layers of the adsorbent are released. However, it is important to determine the nature of the interaction of ammonium with the zeolite framework, because it is known that the sorption capacity of zeolites depends on their content of aluminum. The results of the study of the statics of adsorption of NH_4^+ ions from ammonium chloride solutions in the concentration range 0–1 g/l on clinoptilolite and Al_2O_3 showed that at a specific surface area of clinoptilolite of 59 m^2/g against alumina 6.169 m^2/g the sorption capacity of the zeolite is only twice as high as the sorption capacity of Al_2O_3. It is established that during the adsorption of ammonium ions on alumina there is a change in the hydrogen index of the investigated solution, which is explained by the amphoteric properties of the sorbent [7].

2. Experimental researches

2.1. Sorbent characteristics

To study the surface morphology of the sorbents we used X-ray phase analysis, microprobe X-ray spectral analysis with a Nova-200-NanoSEM scanning electron microscope. Quantitative oxide and chemical composition of sorption materials and soils was performed using an ARL - 9800 - XP X-ray spectrometer.

2.2. Adsorbent

Model systems were used to determine the adsorption capacity of each type of sorbent for ammonium under static conditions. 50 cm^3 of ammonium nitrate solution and the corresponding sorbent (0.5 g), prepared in distilled water at different initial concentrations (C = 0.05–5 g/dm^3) were placed into glass flasks. The flasks were sealed and left with periodic mixing for 48 h at a temperature of + 20 °C. The sorbent was separated from the solution and analyzed for NH_4^+ ion content using a SPECORD-75-IR spectrophotometer and a CFC-2 photocolorimeter [4].

2.3. Adsorbate

A model solution of NH_4NO_3 was obtained by dissolving fixanals. The resulting 0.1N solution was diluted to obtain the desired concentration. The initial concentration of the solution was 2.030 g/l. The concentration of ammonium ions in solutions was determined by photometry or atomic absorption spectroscopy [8, 9].

2.4. Methodology of statistical calculations

For statistical interpretation of the results of ammonium ion adsorption studies, the coefficients of the Langmuir and Freundlich models, which were

constructed according to the results of experimental studies, were determined. Additionally, cluster analysis of the results was performed in order to identify the classification features of the efficiency of sorbents. As a result, a matrix was obtained that included data on the sorption capacity of a particular sorbent – 8 variables representing the categories × 8 variables representing the sorption capacity at a certain point of time. Cluster analysis (STATISTICA 7.0) was used to detect spatial and temporal differences in the sorption capacity of the studied materials. To do this, all data were normalized (the ratio of the current and mean values to the standard deviation). Objects were clustered using the Ward method. We used hierarchical cluster analysis and clustering of K-means. These methods were used to classify hydrological objects into separate hydrochemical groups based on their similarities. Experimental data were imported into the package STATISTICA 7.0 [10].

The clustering algorithm was to determine correspondence of the set of objects to the sets of cluster numbers. The results of clustering were formed into a dendrogram. The square of the Euclidean distance for the studied objects was calculated by the formula:

$$\text{Distance}(Q_i, Q_j) = \sum_{j=1}^{n} (X_{1j} - X_{2j})^2 \qquad (1)$$

where Q_i is the i-th sorbent; X_{ij} means the sorption capacity j for the i-th sorbent

The squares of the Euclidean distances used to determine the ratio of clusters were calculated by the Ward method.

The correlation method in the STATISTICA 7.0 package was used to calculate the reliability of the results.

3. Results and their interpretation

Sorbent characteristics

The adsorption capacity of sorbents depends on their chemical and structural-mechanical properties [10, 11]. The surface morphology was investigated according to claim 2. The results of X-ray phase analysis are presented in Table 1.

The static regularities of a number of systems which are given in Table 2 were investigated. These adsorption isotherm equations were obtained experimentally for homogeneous adsorption systems, including adsorbent and adsorbate. Studies of the adsorption of ammonium ions on silica gel and alumina were aimed at establishing the mechanisms of adsorption on zeolite, since SiO_2 and Al_2O_3 are components of zeolite, but not as independent compounds, but as part of the aluminosilicate framework.

Sorbent characteristics

Zeolite	The total area of the pores S, m^2/g	The average radius of the pores r, nm	Density ρ, kg/m^3	Porosity ε, %
Clinoptilolite of the Sokyrnytsya deposit	14.08	27	1534	28.2
Fly ash	14.8	14.19	1700	24
Al_2O_3 (chromatographic)	6.169	6.9	3990	22
SiO_2 (silica gel)	8	3.7	700	35
Sand	1	1.7	2600	30
Black soil	5	27.2	2100	20
Peat	9	44	1900	34
Clay	6.11	11	2720	22

According to Table 2, the adsorption isotherms of ammonium by natural zeolite, synthetic zeolite based on removal ash, silica gel, and peat are better described by the Langmuir's equation. The Freundlich isotherm is more suitable for describing the adsorption of ammonium on Al_2O_3, black soil, sand, and clay. Soils, of course, should not be used as sorbents due to their low sorption capacity and economic importance, but the results can be applied in agronomy.

During the analysis of the array of experimental data by the method of multidimensional cluster data analysis [1], we identified two clusters. The first cluster corresponded to the results of sorption of ammonium ions by zeolite, Al_2O_3, and SiO_2. The following sorbents were isolated in the second cluster: synthetic zeolite, synthesized by hydrothermal method, sandy soil, black soil, peat, and clay.

Due to the fact that the construction of clusters was carried out on the basis of the sorption capacity of the respective materials, the first cluster characterizes highly efficient sorbents. The second cluster comprises two groups: Group I – synthetic sorbent based on fly ash of Dobrotvir state district heat power plant and Group II – the main soils of the Lviv region. The clustering of the array of experimental data is presented in Fig. 1.

Equations of adsorption isotherms for one-component investigated liquid systems

| System, units of mass of adsorbent	Langmuir's equation	R^2	Freundlich equation	R^2
Zeolite	$$a* = 0.07*\frac{65.28C}{1+65.28C}$$	0.9963	$$a^* = 0.29C^{1.49}$$	0.9436
fly ash	$$a* = 0.11\cdot\frac{1.3\cdot C}{1+1.3\cdot C}$$	0.9998	$$a^* = 7.17\cdot C^{0.38}$$	0.9934
Al_2O_3	$$a* = 0.011\cdot\frac{83487\cdot C}{1+83487\cdot C}$$	0.9396	$$a^* = 2.012\cdot C^{0.98}$$	0.9808
SiO_2	$$a* = 0.018\cdot\frac{18516\cdot C}{1+18516\cdot C}$$	0.9839	$$a^* = 2.013\cdot C^{0.91}$$	0.9718
Sand	$$a* = 0.0276113\cdot\frac{6584.9091\cdot C}{1+6584.9091\cdot C}$$	0.82	$$a^* = 2.47\cdot C^{0.72}$$	0.9531
Black soil	$$a* = 0.017231\cdot\frac{19345\cdot C}{1+19345\cdot C}$$	0.6767	$$a^* = 2.41\cdot C^{0.69}$$	0.9511
Peat	$$a* = 0.0052863\cdot\frac{2101888.9\cdot C}{1+2101888.9\cdot C}$$	0.937	$$a^* = 2.13\cdot C^{0.8}$$	0.8769
Clay	$$a* = 0.0227894\cdot\frac{5850.6667\cdot C}{1+5850.6667\cdot C}$$	0.8306	$$a^* = 2.13\cdot C^{0.44}$$	0.9664
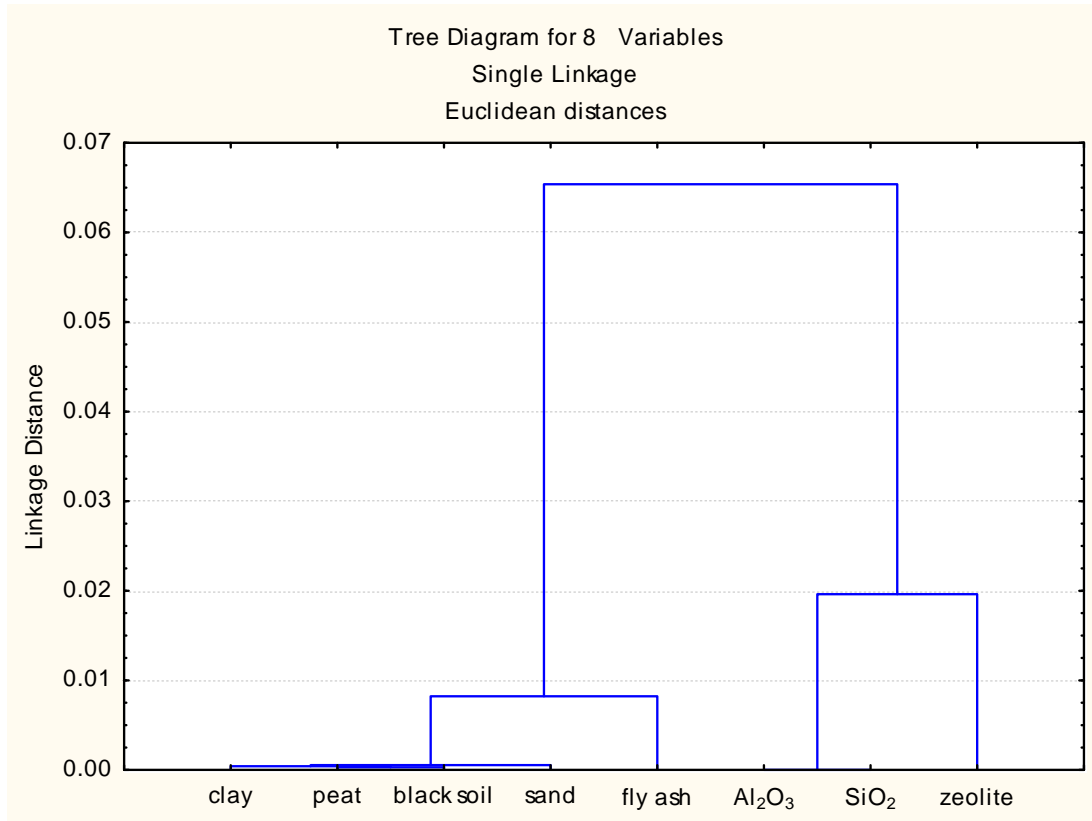
Fig. 1. Cluster analysis of the sorption capacity of various substances in relation to ammonium ions

Due to the fact that the sorption capacity of the studied materials is very different, we evaluated the significance of the results (Table 3).

Table 3

Evaluation of the significance of clustering results for natural and synthetic sorbents

Means and Standard Deviations (Spreadsheet3)		
	Mean	**Std.Dev.**
zeolite	0.043286	0.026325
SiO$_2$	0.039431	0.020853
Al$_2$O$_3$	0.039431	0.020853
fly ash	0.015649	0.020473
sand	0.015070	0.017977
black soil	0.015202	0.018171
peat	0.015265	0.018281
clay	0.015358	0.018436

The results of statistical analysis of experimental data presented in Table 2 showed high significance and reliability of the results.

The obtained results of cluster analysis of data on the adsorption of ammonium ions were processed using the iterative algorithm k – means. Two clusters were obtained, the results of calculations are given in Table 4 and in Fig. 2.

Table 4

Euclidean distances between clusters

Euclidean Distances between Clusters (Spreadsheet3) Distances below diagonal Squared distances above diagonal		
	No. 1	**No. 2**
No. 1	0.000000	0.000764
No. 2	0.027638	0.000000

The results of the variational analysis of the data shown in Fig. 2 and in Table 4 are presented in Table 5.

The results of statistical evaluation of the results of clustering of adsorption isotherms of adsorption ions by natural and synthetic sorbents showed a satisfactory convergence of experimental results and the obtained theoretical calculations.
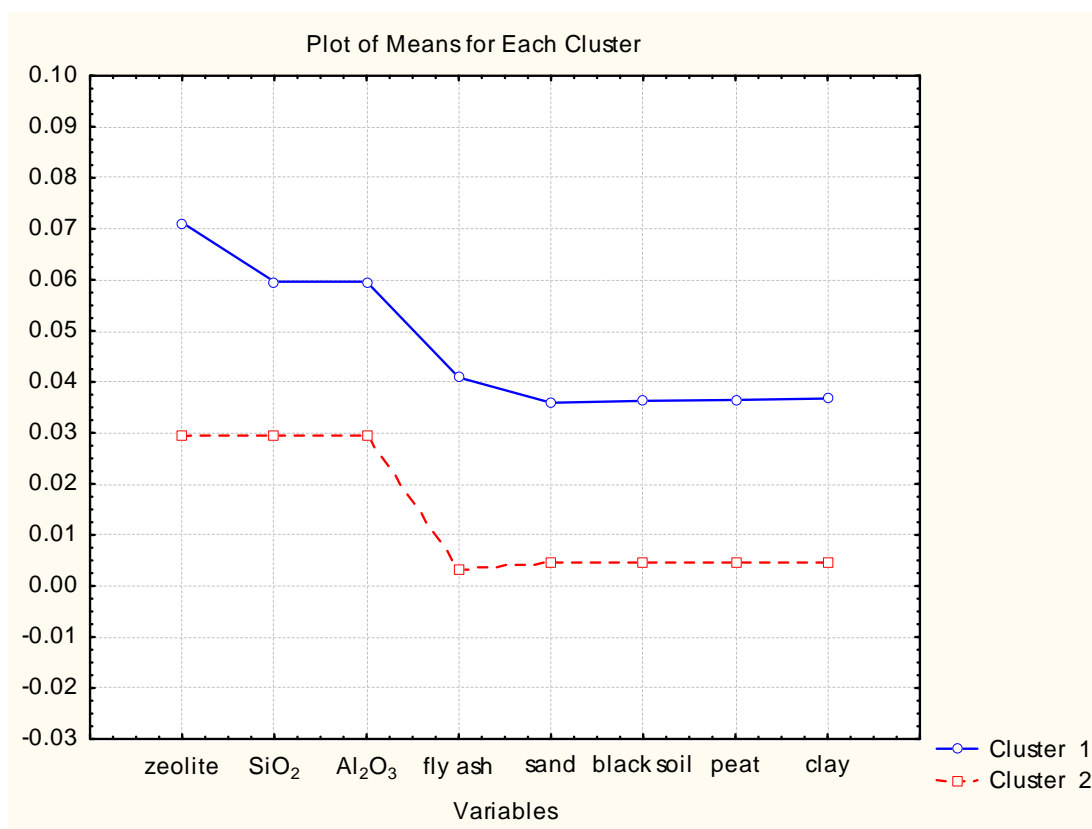
Fig. 2. Cluster analysis of the sorption capacity of various substances in relation to ammonium ions

Table 5

**Statistical evaluation of ammonium ion adsorption
by natural zeolite by multidimensional cluster analysis**

Name	Analysis of Variance					
	Between SS	df	Within SS	df	F	signif.p
zeolite	0.002340	1	0.001125	4	8.31744	0.044832
SiO$_2$	0.001226	1	0.000948	4	5.17344	0.085301
Al$_2$O$_3$	0.001226	1	0.000948	4	5.17344	0.085301
fly ash	0.001908	1	0.000187	4	40.73544	0.003092
sand	0.001302	1	0.000314	4	16.59101	0.015183
black soil	0.001332	1	0.000319	4	16.72257	0.014983
peat	0.002340	1	0.001125	4	8.31744	0.044832

Conclusions

The paper presents the results of the mathematical processing of the adsorption capacity of the most spread sorbents and typical soils in the Lviv region concerning ammonium ions. Analytical dependencies for the calculation of adsorption processes according to the Langmuir's and Freundlich equations were obtained.

The regularities of adsorption of ammonium ions by a number of sorbents of synthetic and natural origin were studied by the methods of multidimensional cluster analysis. As a result of the clustering of experimental data, the dendrogram reflecting the basic laws of the affinity of sorbents for adsorbate was constructed. The first cluster included sorbents with a high specific surface area and a higher aluminum content. In the second cluster, sorbents with a smaller specific surface area were grouped. And, accordingly, with a lower affinity for ammonium.

Statistical evaluation of the obtained results showed a satisfactory significance of the results, the standard deviation ranged from $0.017977…0.26325$. The coefficient of determination R^2 ranged from $0.6767…0.9998$. Thus, the isotherm of ammonium adsorption by black soil cannot be described by the Langmuir equation $R^2 = 0.6767$, but obeys the Freundlich equation $R^2 = 0.9511$. Studies on the adsorption of ammonium ions by soils have shown that soils have insignificant barrier function to ammonium and the potential to accumulate ammonium fertilizers. For industrial use, it is advisable to use sorbents such as synthetic and natural zeolites, Al_2O_3 and silicagel.

References

[1]   Arkhipova H., Mudrak O., Zavertana D.: Visnyk NAU., 2010, 1.

[2]   Gomonay V., Golub N., Gomonay P.: Book of Proceedings of the International Regional Seminar "Environment Protection: Modern Studies in Ecology and Microbiology" 1997, 2.

[3]   Han, R., Zou L., Zhao X., Xua Ya., Xua F., Lia, Y., Wanga, Yu. : Chem. Engineering J.., 2009, 149. https://doi.org/10.1016/j.cej.2008.10.015

[4]   Kuliyeva, T. Z., Lebedeva N. N., Orbuh V. I., Sultanov Ch. A.: Fizika., 2009, 3.

[5]   Nethaji S., Sivasamy A., Mandal A.: Int. J. Environ. Sci. Technol., 2013, 10, 231. https://doi.org/10.1007/s13762-012-0112-0

[6]   Matłok M., Petrus R., Warchoł J.: Ind. Eng. Chem. Res., 2015, 54, 6975. https://doi.org/10.1021/acs.iecr.5b00880

[7]   Sabadash V., Hyvlyud A., Gumnitsky Ya.: Chem. Chem. Technol., 2016, 2.

[8]   Hyvlyud A., Sabadash V., Gumnitsky Ya., Ripak N. Chem. Chem. Technol., 2019, 2, 95. https://doi.org/10.23939/chcht13.01.095

[9]   Lur'e Yu. Yu.: Spravochnyk po analytycheskoy khymyy. Moskva, 1989.

[10] Spravochnik khymyka. 1971, 2.

[11] Petrukhyn O. M.: Praktykum po fyzyko-khymycheskym metodam analyza. Khymyya, Moskva, 1987.