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STUDY OF THE PROCESS OF ADSORPTION OF PETROLEUM PRODUCTS METHODS OF MULTIVARIATE CLUSTER ANALYSIS

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Abstract. The article is devoted to studying the process of adsorption of oil products using multivariate cluster analysis methods. The study solves the problem of environmental pollution with petroleum substances and the search for effective cleaning methods. The work aims to study the prospects of using synthetic zeolites to effectively purify industrial wastewater from oil products. The scientific novelty of the study is the study of the potential of synthetic zeolites as adsorbents to ensure an efficient and environmentally friendly process of cleaning industrial wastewater from petroleum products. The adsorption research methodology included selecting and preparing eight types of adsorbents, determining temperature and concentration range, measuring adsorption capacity, data processing and analysis of results. In the experimental study, the photometric method was used, one of the most accurate and widely used methods for measuring the adsorption of petroleum products. The study results indicate some materials potential for the effective adsorption of petroleum products. The study provides grounds for recommendations regarding the optimal conditions for the adsorption process and the selection of materials for further research and development. The application of multivariate cluster analysis in the study of the adsorption process of oil products opens up new opportunities for solving environmental pollution problems and developing effective technologies for cleaning the environment. The outcomes of this study are anticipated to significantly benefit industries dealing with petroleum product separation and pollution control. By offering a more comprehensive understanding of the adsorption process, this research opens avenues for developing tailored adsorption strategies for specific applications.

Keywords: adsorption, greenhouse oil products, adsorbent, synthetic zeolites.

1. Introduction

Cleaning superficial water from oil and hydrocarbons carry out by help mechanical, physical and chemical and biochemical methods cleaning. Despite their use, these methods have many significant drawbacks (Hyvlud et al., 2019).

Chemical methods of water purification involve the introduction of chemical reagents, but this can lead to the formation of toxic substances. Mechanical methods, in turn, only remove oil on the surface without removing emulsified and soluble oil, so they are not very effective. Flotation treatment, although used, leads to additional water pollution due to the introduction of reagents (Wang et al., 2021).

Biological oxidation can be effective, but only under certain conditions, such as low oil concentrations and a specific pH and temperature range. Sorptive treatment of water from oil is effective but quite expensive, as it requires the use of expensive sorbents (Bai et al., 2022).

In order to solve this urgent problem, developing highly effective and relatively inexpensive methods of cleaning surfaces and wastewater from

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oil is necessary. Adsorption methods are simple, affordable and effective methods of purification, so they are promising for use in this field.

Researchers (Mohammadi et al., 2020) showed interest in the use of carbonate-containing bentonite clays, which are widespread, in particular, waste rock dumps in the area of sulfur mining by the quarry method. Montmorillonites, kaolinites and vermiculites, which are the components of the studied clay, have increased selectivity towards non-polar substances, which contributes to the effective purification of water from petroleum products.

One of the promising ways to create new types of sorbents with specified properties is the introduction of compounds of various natures into the structure of natural aluminosilicates. This can lead to agglomerates that are easily collected from the surface of the water, providing effective cleaning (Melaibari et al., 2023).

Therefore, the use of adsorption methods based on natural aluminosilicates is a promising approach to solving the problem of water purification from petroleum products. Research in this direction can contribute to the provision of more effective and environmentally friendly technology for cleaning water bodies and the environment as a whole (Wang et al., 2021).

Of all the unique water purification methods, adsorption methods are more straightforward, more affordable and more effective. The production of highly effective sorbents can be carried out without necessarily using pure clay minerals, the reserves of which may be limited. Instead, widely distributed carbonate-bearing bentonite clays, such as waste rock dumps in the area of open-pit sulfur mining (for example, the Yaziv deposit in the Yavoriv district of Lviv region), can be successfully used. This will make it possible to reduce the cost of sorbents and solve the problem of waste disposal (Wiśniewska, 2023).

The use of fly ash-based synthetic zeolites for water purification from petroleum products is one of the promising directions in the field of water purification. This is a technologically and ecologically convenient method that can contribute to solving the problem of water pollution by oil substances.

Synthetic zeolites are microporous materials with unique structures that can interact with different types of molecules. The use of fly ash as a basis for the synthesis of zeolites makes it possible to effectively use this waste material and turn it into a valuable product for water purification.

One of the critical advantages of synthetic zeolites is their high surface area and microporous structure, which provides high adsorption capacity. This allows them to effectively remove oil products from water by adsorbing molecules on the zeolite surface (Fawaz et al., 2021).

The use of fly ash-based synthetic zeolites for water purification from petroleum products has several advantages:

Recovery of secondary resources: The use of fly ash for the synthesis of zeolites makes it possible to turn waste material into a valuable product, which contributes to the ecological efficiency of the process.

High adsorption capacity: Synthetic zeolites have a large surface area and the ability to retain petroleum products in their pores, which makes them effective adsorbents for water purification.

Selectivity: Synthetic zeolites can be engineered for selectivity for petroleum products, allowing them to remove only the desired contaminants while retaining the beneficial substances in the water.

Wide range of applications: Synthetic zeolites can be used to purify water from various types of petroleum products, including oil, fuel oil, gasoline, diesel fuel and others.

Although the use of fly ash-based synthetic zeolites for the treatment of petroleum products water has many advantages, they also have their limitations. For example, it can be an expensive technology for the production of synthetic zeolites and the need to use special equipment for their application (Wang & Chen, 2021).

Prospects for researching the process of oil product adsorption using multivariate cluster analysis methods are promising and have the potential to open up new opportunities in the field of remediation of polluted environments and improving the efficiency of oil refining processes (Mouandhoime & Brouillette, 2021). Multivariate cluster analysis is a method that allows you to process and analyze large volumes of data from many variables at the same time, providing a deeper understanding of the relationships between various parameters.

Here are some of the prospects for researching the process of oil product adsorption using multivariate cluster analysis methods:

Optimization of adsorption materials: Using multivariate cluster analysis allows identifying the most effective adsorbents for specific types of petroleum products and wastewater. This method can help reduce the loss of adsorbents and provide better pollution control (Samanta et al., 2022).

The application of multivariate cluster analysis allows the identification of optimal conditions, such as temperature, contact time, pH, and other parameters, which maximize the efficiency of the oil product adsorption process.

The application of the multivariate cluster analysis makes it possible to establish specific features of various petroleum products and their interaction with adsorbents. This approach allows for predicting their behaviour in different environments and provides more accurate planning and remediation strategies (Roulia et al 2022).

Development of effective remediation technologies: The use of multivariate cluster analysis helps develop more effective technologies for treating wastewater from petroleum products. This approach can help to reduce pollution and improve the quality of the environment (Hayawin et al 2023). Cost and time reduction: Implementing multivariate cluster analysis can help reduce research and development costs and shorten the time required to implement new technologies (Fawaz et al., 2021).

In general, the study of the process of adsorption of petroleum products by the methods of multivariate cluster analysis has great potential to improve the efficiency of adsorption processes and solve environmental pollution problems due to petroleum products. Implementation of the results of such research can help preserve the environment and ensure sustainable development (Sabadash et al., 2020).

2. Experimental studies

2.1. Theoretical part

Various methods and equipment were used for the study of oil products. The surface morphology of the sorbents was studied using X-ray phase analysis and microprobe X-ray spectral analysis using a Nova200NanoSEM scanning electron microscope.

An ARL-9800-XP X-ray spectrometer was used to determine sorption materials and soils' quantitative oxide and chemical composition.

The adsorption capacity of each type of sorbent for oil products was determined under static conditions using model systems. 50 cm³ of a solution containing petroleum products (diesel fuel) and a suitable sorbent (approximately 1 gram) dissolved in distilled water at different initial concentrations (C=5–2000 mg/l) were placed in glass flasks. The flasks were hermetically closed and left with periodic stirring for 48 hours at a temperature of 20±1 °C. After that, the sorbent was separated from the solution, and its content of oil products was analyzed using an infrared analyzer IKAN-1.

These methods made it possible to obtain detailed information about the morphology, composition, and adsorption capacity of various sorbents, which is important for the study of the properties of petroleum products and the development of effective methods for cleaning the environment.

2.2. Materials and methods

Determination of the adsorption capacity of zeolites for petroleum products. The method of determining petroleum products in wastewater using the IKAN-1 IR analyzer includes the following steps:

Sample preparation: Samples of model wastewater must be prepared prior to further analysis. This method includes filtration to remove solid sorbent particles and using chemical solvents to clean the samples further.

Calibration of the IKAN-1 IR analyzer: The analyzer must be calibrated before starting the analysis. This involves measuring standard solutions with various known concentrations of petroleum products to construct a calibration curve.

Collection of IR absorption spectra: After calibration, place the prepared samples on the sample holder of the IKAN-1 analyzer and conduct the analysis using infrared radiation. The analyzer will record IR absorption spectra for each sample.

Data processing: The resulting IR absorption spectra, including data analysis software, are processed. The concentrations of petroleum products in the wastewater samples were determined by comparing the obtained spectra with the calibration curve.

This technique provides a quick and effective way to determine petroleum products in wastewater using the IKAN-1 IR analyzer, which allows for obtaining accurate data on pollution and monitoring the effectiveness of remediation processes (Fawaz et al., 2021).

Methodology of statistical calculations. The following methods were used for statistical interpretation of the results of oil product adsorption studies :

The determination of coefficients of determination of Langmuir and Freundlich models is based on the results of experimental studies, where the adsorption behavior of various sorbents in relation to petroleum products was studied. Using the Langmuir and Freundlich models, determination coefficients were determined, indicating the adequacy of these models in describing adsorption processes.

Cluster analysis of results: It was used to identify classification features of sorbent efficiency. This analysis investigated the sorption capacity of specific sorbents, and the data were presented as a matrix of 8 categories and eight variables. The values of the variables in the categories reflected the sorption capacity at a certain point in time, which made it possible to identify patterns and the distribution of sorbents according to their characteristics.

Object clustering: Ward's technique, hierarchical cluster analysis, and K-means clustering were used. These methods helped group sorbents into clusters according to their similarity or difference in adsorption properties, which simplified further analysis and comparison of sorbent efficiency.

Calculation of the squared Euclidean distance: Was used to determine the correspondence between objects and cluster numbers. This approach helped to establish how far or close the objects are from each other in the space of the characteristics of the sorbents.

Correlation method: It was used to calculate the reliability of the results in the STATISTICA 7.0 package. This method made it possible to evaluate statistical relationships between various properties of sorbents and adsorption characteristics, which emphasizes the importance and reliability of the obtained data.

3. Results and Discussion

The adsorption capacity of sorbents largely depends on their chemical and structural-mechanical properties (Mouandhoime, Brouillette, 2021; Samanta et al., 2022). In this study, the surface morphology of the sorbents was analyzed by point 2. The results of the X-ray phase analysis are presented in Table 1.

The data in Table 1 reflect the main characteristics of sorbents, such as total pore area, average pore radius, density and porosity. They play an essential role in determining the ability of the sorbent to bind substances on its surface. For example, sorbents with a large pore area and high porosity can store a more significant amount of adsorbed substances, so they can be effective in cleaning the environment. The data from Table 1 are essential for further analysis and selection of optimal sorbents for specific applications.

Studies of static regularities of many systems were conducted, the results of which are presented in Table 2. Equations of adsorption isotherms were obtained experimentally for homogeneous adsorption systems, which included an adsorbent and an adsorbate. Particular emphasis was placed on the study of the adsorption of petroleum products on silica gel and aluminium oxide to establish the mechanisms of adsorption and the study of adsorption on zeolite. It is noted that SiO_2 and Al_2O_3 are components of zeolite, but they do not exist as independent compounds but are part of the aluminosilicate framework.

Table 1

Characteristics of the sorbent

Sorbent	The total pore area of the sorbent S, m^2/g	The average pore radius of the sorbent r, nm	Density of sorbent ρ, kg/m^3	Porosity of the sorbent ε, %
The zeolite of the Sokyrnytsky deposit	14.091	27	1533	28.32
Ash takeaway	14.822	14.191	1702	25.01
Al_2O_3	6.178	6.92	3992	23.12
SiO_2	8.1	3.72	703	36.101
Sand	1.1	–	2602	31.11
Black soil	5.1	–	2103	21.01
Peat	–	–	1903	35.21
Clay	–	–	2722	23.09

Table 2

Equation of adsorption isotherms for one-component liquid systems under study

Sorbent	Langmuir isotherm equation	R^2	Freundlich isotherm equation	R^2
Zeolite	$a^* = 0.06 * \frac{55.2 \cdot C}{1 + 55.2 \cdot C}$	0.944	$a^* = 0.281C^{1.4}$	0.944
Ash takeaway	$a^* = 0.02 \cdot \frac{1.2 \cdot C}{1 + 1.2 \cdot C}$	0.994	$a^* = 1.27 \cdot C^{0.28}$	0.995
Al_2O_3	$a^* = 0.011 \cdot \frac{987 \cdot C}{1 + 987 \cdot C}$	0.994	$a^* = 2.1 \cdot C^{0.8}$	0.988
SiO_2	$a^* = 0.011 \cdot \frac{485 \cdot C}{1 + 485 \cdot C}$	0.939	$a^* = 2.01 \cdot C^{0.81}$	0.978
Sand	$a^* = 0.03 \cdot \frac{984.91 \cdot C}{1 + 984.91 \cdot C}$	0.872	$a^* = 2.4 \cdot C^{0.22}$	0.952
Black soil	$a^* = 0.018 \cdot \frac{195 \cdot C}{1 + 195 \cdot C}$	0.447	$a^* = 2.42 \cdot C^{0.69}$	0.951
Peat	$a^* = 0.005 \cdot \frac{888.9 \cdot C}{1 + 889 \cdot C}$	0.937	$a^* = 2.3 \cdot C^{0.9}$	0.994
Clay	$a^* = 0.023 \cdot \frac{590 \cdot C}{1 + 590 \cdot C}$	0.834	$a^* = 2.15 \cdot C^{0.4}$	0.944

Two clusters were identified during the analysis of the array of experimental data using the method of multivariate cluster data analysis (Hyvlud et al., 2019). The first cluster included the results of sorption of oil products by zeolite, Al_2O_3 and SiO_2. The sorbents were located in the second cluster: synthetic zeolite obtained by the hydrothermal method, sandy soil, black soil, peat and clay.

The construction of these clusters was carried out based on the sorption capacity of the corresponding materials. Thus, the first cluster is characterized by highly effective sorbents capable of effectively binding petroleum products. The second cluster consists of two groups: the first group includes a synthetic sorbent based on the fly ash of the Dobrotvirsk DRES, and the second group – the primary soils of the Lviv region.

A representation of the clustering of the experimental data is presented in Fig. 1.

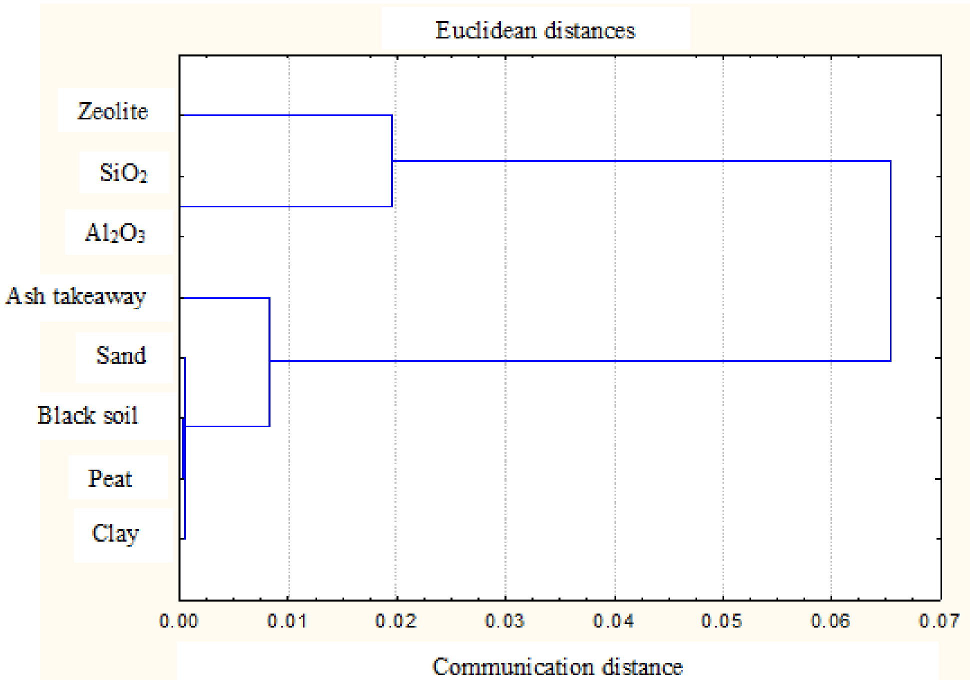

Fig. 1. Clustering of the array of experimental data on the adsorption of petroleum products by various sorbents

Table 3

Statistical evaluation of the adsorption of petroleum products by the method of multivariate cluster analysis

Statistical parameter	Zeolite	SiO_2	Al_2O_3	Ash removal	Sand	Black soil	Peat	Clay
MEAN cases 1–6	0.053	0.039	0.039	0.016	0.015	0.015	0.015	0.015
MEDIAN cases 1–6	0.053	0.053	0.053	0.005	0.007	0.007	0.007	0.007
SD cases 1–6	0.026	0.021	0.021	0.020	0.018	0.018	0.018	0.018
VALID_N cases 1–6	6	6	6	6	6	6	6	6
SUM cases 1–6	0.260	0.237	0.237	0.095	0.090	0.091	0.092	0.092
MIN cases 1–6	0.009	0.009	0.009	0.000	0.001	0.001	0.001	0.001
MAX cases 1–6	0.081	0.062	0.062	0.050	0.058	0.058	0.058	0.059
_25th % cases 1–6	0.021	0.021	0.021	0.002	0.002	0.002	0.002	0.002
_75th % cases 1–6	0.062	0.058	0.058	0.032	0.025	0.025	0.025	0.025

This table presents a statistical assessment of the adsorption of petroleum products by various materials using the method of multivariate cluster analysis. Various statistical parameters are given based on six experimental measurements for each material (zeolite, SiO_2, Al_2O_3, ash takeaway, sand, black soil, peat, clay).

Description of statistical parameters:

MEAN case 1–6: Arithmetic mean value of oil product adsorption for 6 experimental measurements.

MEDIAN case 1–6: Median value of oil product adsorption for 6 experimental measurements.

SD case 1–6: Standard deviation of oil product adsorption for 6 experimental measurements.

VALID_N case 1–6: Number of valid observations (measurements) for oil product adsorption (6 measurements in this case).

SUM case 1–6: Sum of oil product adsorption for 6 experimental measurements.

MIN case 1–6: The minimum value of oil product adsorption among 6 experimental measurements.

MAX case 1–6: The maximum value of oil product adsorption among 6 experimental measurements.

_25th % case 1–6: 25th percentile of adsorption of oil products, i.e. the value that exceeds 25% of the data.

_75th % case 1–6: The 75th percentile of oil product adsorption, i.e., the value that exceeds 75% of the data.

These statistical parameters make it possible to understand the distribution of oil product adsorption for each material, to determine typical values and the difference in the adsorption capacity of different materials. The results of these studies help select optimal materials for cleaning and decontaminating oil-containing environments, depending on their characteristics and the requirements of a specific application.

4. Conclusions

Based on the results of studies conducted using the method of multivariate cluster analysis, the following conclusions can be drawn:

The adsorption capacity of different materials for petroleum products varies significantly. Zeolite, SiO_2, and Al_2O_3 proved to be highly effective sorbents capable of effectively binding petroleum products, which makes them potentially interesting for use in environmental cleanup processes. On the other hand, fly ash, sand, chernozem, peat and clay showed a lower adsorption capacity, which indicates the need to improve their properties for more efficient use.

Cluster analysis made it possible to group materials according to their similarity in the adsorption of oil products. Separating two clusters indicates that materials from one cluster have similar adsorption characteristics, while materials from another cluster have different characteristics. This approach makes it possible to identify groups of materials with potentially high adsorption capacity and single out those that require further improvement.

The obtained statistical parameters (mean value, median, standard deviation, minimum and maximum value, percentile) indicate the stability and reliability of research results. High values of the coefficients of determination R^2 for the Langmuir and Freundlich isotherm equations confirm the adequacy of the models in the description of adsorption processes.

The obtained data can help determine the optimal materials for further applications in cleaning and decontamination of oil-containing environments.

Considering each material's properties and effectiveness, we can choose the most effective and economically feasible sorbents for specific pollution removal tasks.

The study of the adsorption of oil products with various materials lays the foundation for further research and development of new materials with improved adsorption characteristics, which will contribute to developing effective environmental cleaning technologies.

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