Modified sorbents based on natural mineral and its mechanical properties

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Abstract: The use of modified sorbents based on natural minerals, widely distributed in Kazakhstan, is a promising direction. This direction is related to the development of domestic ion-exchange materials. The republic lacks its own production of synthetic sorbents. The environmental situation in the regions of uranium ore mining and processing is also important. Moreover, the application of synthetic sorbents is not always justified due to their high cost, while the use of natural sorbents is limited by their low sorption capacity. The development of modified ion-exchange materials based on a combination of these is a pressing issue for various industries. Research has been conducted on the choice of modification methods for natural sorbents and the evaluation of their sorption capacity after modification. The modification of natural minerals zeolite and shungite using the "solid-phase extractants" method was carried out in two stages. At the first stage, the modification was performed with organic extractants and compositions based on them, and at the second stage with phosphoric acid in combination with polyacrylamide. The natural sorbents used were zeolite from the Kusmuryn deposit and shungite from the Koksu deposit, following preliminary flotation. The mechanical strength of sorbents modified by different methods was compared with the original ion-exchange materials. Studies of the sorption process have shown that the best results for uranium sorption were obtained with modified sorbents: zeolite modified with a mixture of extractants Di-2-Ethylhexyl phosphoric acid (Di-2-EHPA), Tributyl phosphate (TBP), kerosene, and shungite modified with phosphoric acid in the presence of Polyacrylamide (PAA).

Keywords: Natural sorbents; Technogenic solutions; Sorption; Extraction rate

1. Introduction

Kazakhstan ranks second in the world in terms of proven natural uranium reserves and holds a leading position in uranium extraction. Currently, uranium mining in the republic is carried out by the most environmentally friendly and low-cost method of underground borehole leaching. However, waste from previous years accumulated at uranium mining enterprises, as well as large uranium-bearing hydrological provinces and many small deposits remain a dangerous source of contamination of natural waters with radionuclides. According to experts, the greatest environmental threat comes from liquid radioactive waste (LRW) and radionuclide-contaminated natural waters (Krupskaya et al., 2020). The heightened danger of this type of waste is due to its large volume and the potential for uncontrolled spread.

It should be noted that the issue of cleaning radioactive-contaminated wastewater and natural waters is critical for the further development of nuclear energy and industry, not only in Kazakhstan but worldwide. There are several methods for the disposal of LRW, with sorption being the most indemand, according to experts (Borai et al., 2008; Hassan et al., 2021; Nekrasova et al., 2023). The development of sorption processes received a significant boost with the advent of synthetic sorbents. Currently, the main synthetic ion-exchange resins used in the uranium extraction process are Purolite, Amberlite, Ambersep, and others. Despite the high results achieved in uranium sorption using synthetic ion-exchange resins, their widespread application for LRW disposal is hindered by their high cost. Moreover, an important problem is the absence of domestic production of synthetic sorbents in Kazakhstan. In this regard, natural ion-exchange materials, which are available in reserves measured in millions of tons, deserve special attention.

Natural sorbents are used in industry for gas purification from sulfur dioxide, in automotive exhaust systems, for separating gas mixtures such as nitrogen and oxygen, for wastewater treatment from cyanides, organic compounds, petroleum products, heavy and non-ferrous metals, for collecting industrial oils, spilled oil, and mercury. However, their low sorption capacity is a limiting factor for even broader applications (Elizondo et al., 2000; Misaelides, 2011; Osmanlioglu, 2006). The simplest method of modifying natural ion-exchange materials is by treating them with chemical reagents: acids, alkalis, and salts. In some cases, chemical treatment is combined with heat treatment. In more complex conditions, organic and inorganic compounds of non-ferrous and rare metals are used. Of particular interest are natural sorbents modified with phosphorus compounds, which exhibit increased sorption capacity (Abbasi & Streat, 1994; Chen et al., 2018).

Recently, research has focused on creating composites through chemisorptive modification of natural minerals with organic or inorganic compounds, including phosphorus compounds. In this way, sorbents are obtained that differ from the original mineral in the nature of the surface and porosity of the structure and combine the beneficial properties of the original mineral and synthetic sorbents. Such ion-exchange materials allow for deeper extraction of certain elements by forming complexes with them through functional groups anchored on the natural sorbent matrices (Bhattacharyya & Gupta, 2011; Gaillard et al., 2010; Hua et al., 2012). There is significant interest in the development of research in the field of "solid-phase extractants," which have demonstrated high efficiency in extracting components with low concentrations (Jiang et al., 2009).

It is important to note that all of the above-mentioned research has been conducted using foreign raw materials. Among the works of domestic scientists, the most noteworthy examples involve the modification of zeolite and shungite, pre-activated with sulfuric acid, copper (II) hydroxides, and nickel hydroxides, as presented in (Kenzhaliev B.K et al., 2019). The authors discuss the specific features and general patterns of uranium sorption using modified sorbents. It has been shown that the use of pre-activated and modified shungite and zeolite for uranium sorption increases extraction efficiency compared to natural sorbents. However, the labor-intensive process of modification remains a limiting factor for industrial use. Thus, the brief review presented demonstrates that, despite the variety of methods for modifying natural ion-exchange materials, only a few have found industrial application. The main disadvantages include complexity in execution and the use of scarce reagents. Therefore, the problem of developing modified sorbents based on natural minerals remains relevant.

2. Methods

In the first stage, 10 g of the natural mineral was treated with extractants and their compositions: Di-2-EHPA (di-2-ethylhexylphosphoric acid), TBP (tributyl phosphate) and kerosene. The resulting compositions were aged for 72 hours, dried at room temperature, and then in an oven at 100°C. In Figure 1 shows a diagram of the modification of natural shungite sorbent with preliminary flotation.

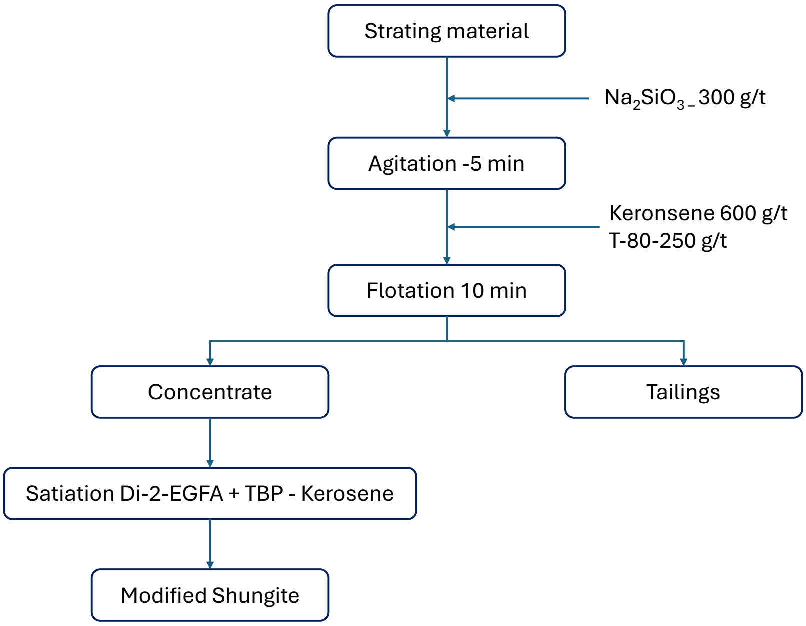

Figure 1. Scheme of flotation and modification of shungite

In the second stage, the natural sorbent was treated with a dilute phosphoric acid solution. After 12 hours, the sorbent was washed from the excess acid and dried. The resulting mixture was divided into two parts: one part was sent for uranium sorption, while the other was treated with a polyacrylamide solution and left for 12 hours. After that, the polyacrylamide solution was drained, the mixture was again divided into two parts, with one part washed with distilled water and dried, and the other dried without washing.

Test experiments on uranium sorption by modified ion-exchange materials were carried out from diluted productive solutions of a uranium mining enterprise. The experiments were conducted for 4 hours in a static mode at room temperature (~25°C). The initial concentration of uranium in the solution was 4 mg/L (T=1:25) and 26 mg/L (T=1:5). To determine the strength of the modified material (zeolite, shungite), a universal floor testing machine, Autograph AG-X 100 kN (Shimadzu GmbH, Japan), was used. Pressed briquettes were made using a PSU-10 hydraulic press, designed for static testing of standard construction material samples under compression (Fig. 2).

Figure 2. Universal Floor Testing Machine Autograph AG-X 100 kN

Samples were pressed at loads of 200 and 300 kg/dm³, using water and liquid glass as binders, to obtain cylindrical briquettes (r=8, h=16), which were carefully dried and compressed until the first crack appeared. The compression rate was 0.1 mm/s. The quantitative uranium content in the residual solutions after sorption was determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES) Optima 8000DV. The X-ray phase analysis of natural sorbents was performed on a D8 Advance diffractometer (Bruker AXS GmbH) with a cobalt anode, and X-ray fluorescence was analyzed using a Venus 200 wavelength dispersive spectrometer (PANalytical). Scanning electron microscopy (SEM) and X-ray spectral microanalysis (EDS) were performed using a JEOL JXA-8230 device. Infrared spectroscopy (IR) of modified natural sorbents was carried out using an FTIR spectrometer "Avatar 370."

3. Results and discussion

Test experiments on uranium sorption using modified ion exchangers, following the methodology described above. The study utilized modified natural sorbents, including shungite concentrate after preliminary flotation and zeolite, as well as uranium-containing process solutions. The efficiency of the method was evaluated through experimental tests by analyzing changes in uranium sorption on modified natural materials. The obtained results are presented in Tables 1 and 2.

Table 1. Uranium Sorption Results Using Natural Sorbents Modified with Organic Solvents

No	Organic solvents for modification	Zeolite		Shungite after flotation	
		Residual conc., mg/dm^3	Extraction rate., %	Residual conc., mg/dm^3	Extraction rate., %
1	Di-2-EGFA	0.0032	99.8	0.00002	99.9
2	Di-2-EGFA + TBP+kerosene	< 0.0002	99.9	0.007	99.8
3	TBP	2.08	50.5	1.8	57.0

As shown in Table 1, the maximum uranium extraction (99.8–99.9%) was achieved using zeolite and shungite samples modified with Di-2-EGFA, as well as compositions based on it Di-2-EGFA+ TBP + kerosene. Modification of natural sorbents with tributyl phosphate (TBP) does not result in complete uranium extraction (50.5–57.0%). Table 2 presents the results of experimental tests on uranium sorption using natural ion-exchange resins modified with phosphoric acid.

Table 2. Uranium sorption results using natural sorbents modified with phosphoric acid

No	Method modification	Zeolite		Shungite after flotation	
		Residual conc., mg/dm^3	Extraction rate., %	Residual conc., mg/dm^3	Extraction rate., %
1	H_3PO_4 (diluted) with flushing	2.762	34.24	0.091	98.0
2	H_3PO_4 + PAA	3.841	< 1.0	0.087	98.2
3	H_3PO_4 + PAA with flushing	3.298	<1.0	0.009	99.8

The data presented in Table 2 indicate that zeolite modified with phosphoric acid sorbs uranium at a rate of 34.24%, while modification with a mixture of phosphoric acid and polyacrylamide does not promote uranium sorption. Shungite, after flotation and modified with phosphoric acid and the mixture of phosphoric acid and polyacrylamide, showed maximum uranium extraction rates of 99.9%. One of the main properties of sorbents, especially those modified based on natural minerals, is mechanical strength. During the research, the mechanical strength of sorbents modified in various ways was determined in comparison to the original minerals. Studying the relationship between strain and compressive strength is crucial for developing new types of sorbents and improving their operational characteristics. This knowledge allows for the optimization of technological processes such as pressing, drying, or modifying sorbents, as well as predicting their behavior during real-world applications, such as filtration or the adsorption of contaminants.

The mechanical strength of a material is characterized by its ability to resist various external mechanical impacts and is described by the following strength limits: 1) compression; 2) tension; 3) bending; and 4) wear resistance. The compressive strength of natural sorbents was investigated (Table 3). The mechanical strength of a material is typically assessed through tests of standard samples made from the same material. To determine the effect of activators (H_3PO_4 + PAA, Di-2-EGFA + TBP + kerosene) on mechanical strength, six samples were produced in the form of pressed briquettes made from the previously modified natural sorbents (zeolite and shungite).

In the first case, all samples were pressed with a load of 200 kg/dm³, using water as a binder. Cylindrical briquettes (r=8, h=16) were obtained, which were then carefully dried and subjected to compression until the first crack appeared. The compression rate was 0.1 mm/sec. The obtained results are presented in Table 3, which shows that when zeolite and shungite are saturated with phosphoric acid in the presence of polyacrylamide, the strength increases, while using a mixture of extractants (Di-2-EGFA+TBP+kerosene) results in a decrease in strength. The results are presented in Table 3.

Table 3. Influence of Activators on the Mechanical Strength of Natural Sorbents (Binder – Water)

Sorbents	No	H_3PO_4+PAA		Di-2-EGFA + TBP+kerosene		Original	
		Strain	Strength, MPa	Strain	Strength, MPa	Strain	Strength, MPa
Zeolite	1	546.662	2.49572	92.4110	0.41688	266.870	1.24808
	2	834.624	3.81038	133.260	0.60838	573.476	2.68199
Shungite	1	2254.25	10.2915	275.103	1.24104	308.259	1.40732
	2	1892.14	8.43508	174.491	0.79662	365.273	1.66761

In the second case, the samples were pressed at 300 kg/dm³, using water glass as a binder, and the tests were conducted in the same way as in the previous case. The results of the research also showed that the use of liquid glass as a binder increases the mechanical strength of the modified sorbents (Table 4).

Table 4. Influence of activators on the mechanical strength of natural sorbents (binder - liquid glass)

Sorbents	No	H_3PO_4+PAA		Di-2-EGFA + TBP+kerosene		Original	
		Strain	Strength, MPa	Strain	Strength, MPa	Strain	Strength, MPa
Zeolite	1	6338.23	30.0048	2200.43	11.3663	2430.07	11.2283
	2	6443.26	30.5020	2143.67	9.90494	1303.88	6.02464
Shungite	1	7797.23	36.4655	966.485	4.41238	6274.54	28.9919
	2	7381.95	34.1087	838.995	3.78487	7035.62	32.9037

Based on the studies conducted, it has been shown that the ability to resist external mechanical influences (in our case, compression) when treating both zeolite and shungite with orthophosphoric acid and PAA increases significantly, and the mixture of extractants does not have a positive effect. When shungite is saturated with orthophosphoric acid together with polyacrylamide, the strength increases by 7-8 MPa, while the mixture of extractants (Di-2-EGFA + TBP + kerosene) significantly deteriorates the mechanical properties of shungite compared to the original material. Thus, during the research, methods for modifying natural sorbents have been proposed and tested, allowing for the effective extraction of uranium, the properties of the modified sorbents have been studied, and the mechanical strength of the modified sorbents has been determined.

4. Conclusion

The introduction of additional functional groups into the structure of the sorbent will lead to the formation of new adsorption centers, increasing the sorption capacity and selectivity of the sorbent. By correctly selecting the modification method, it is possible to preserve the rigid framework of the mineral while imparting new qualities and properties, making them selective towards uranium. During the research, methods for modifying natural minerals such as zeolite and shungite concentrate with organic reagents and their compositions were proposed and studied, with optimal options chosen based on the examination of the sorption properties of the modified sorbents. One of the key properties of sorbents, especially those modified from natural minerals, is mechanical strength. The results of testing modified sorbents for mechanical strength showed that the strength of zeolite and shungite increases when saturated with phosphoric acid in the presence of polyacrylamide, while the mixture of extractants (Di-2-EGFA+TBP+kerosene) leads to a decrease in strength.

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Declarations

Author contribution

Kenzhaliyev B. K: Conceptualization, Methodology, and Software. Surkova T. Y: Data curation and Writing - Original draft preparation. Dossymbayeva Z. D: Visualization and Investigation. Yessimova D.M.: Visualization and Investigation. Abdikerim B: Software and Validation.

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Conflict of interest

There are no competing interests for all authors.

Ethical Clearance

There are no human or animal subjects in this manuscript and informed consent is not applicable.

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