Uranium extraction with modified sorbents

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Abstract. Hydrometallurgical processing of uranium-containing raw materials generates a significant amount of liquid industry-related waste, namely waste solutions that require disposal. Sorption is known as one of the most effective methods for purifying liquid matters contaminated with radionuclides. Various modification options are being developed for the purpose of using natural sorbents and increasing their sorption capacity. The authors proposed the methods for modifying natural aluminosilicate and coal-mineral raw materials. Zeolite found at the Kusmurun deposit and shungite from the Koksu deposit were selected for the research. The methods are based on obtaining solid-phase extractants. It was proposed to modify natural sorbents with a mixture of tributyl phosphate and di2-ethylhexyl phosphoric acid in kerosene, as well as a mixture of phosphoric acid and polyacrylamide. It was demonstrated that the first method is preferable for zeolite, and the second one for shungite. The research addressed the sorption properties of modified sorbents in static and dynamic modes. Uranium sorption isotherms were plotted. The maximum sorption capacity and the Langmuir constant were calculated. The research allowed synthesizing an organopolymer based on shungite, glycicyl methacrylate, orthophosphoric, and hydroxyethyl diphosphoric acids. Its sorption properties were studied under dynamic conditions. Its sorption capacity was assessed in comparison with modified natural sorbents.

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Introduction

Recently, more and more attention has been paid to the ecological safety of the Republic taking into account the increased threat of radionuclide contamination, in particular with uranium, since the processing of uranium-containing raw materials generates a significant amount of liquid industry-related waste. The main waste disposal method is sorption, which requires the use of inexpensive sorbents [1].

Such sorbents may be obtained based on domestic natural raw materials. The significant disadvantages of natural sorbents include low sorption capacity, which can be increased by developing effective and inexpensive methods for their modification.

At the same time, the lack of inexpensive and easily feasible methods for obtaining modified sorbents that would work well in the uranium sorption processes represents a great obstacle to their use for environmental purposes.

Experimental part

Natural sorbents were modified with organic extractants and phosphoric acid in combination with polyacrylamide using the method for obtaining “solid-phase extractants”. Following the preliminary flotation, zeolite found at the Kusmurun deposit and shungite from the Koksu deposit were used as natural sorbents [2].

The experiments took place in the following way: 10 g of a natural sorbent (zeolite or shungite) was filled with a solution of the summed up extractants Di-2EHPA+TBP (di-2ethylhexylphosphoric acid and tributyl phosphate) in kerosene. The resulting compositions were kept for 72 hours, dried at room temperature for one day, and then dried in an oven at a temperature of 100°C.

The following conditions were applied for modification with phosphoric acid and polyacrylamide (PAA): a weighed portion of natural sorbent in the amount of 10 g was treated with a diluted (1:4) phosphoric acid solution, the sorbent was washed from excess acid in 12 h, dried, filled with a polyacrylamide solution (S: L=1:5) and kept in such a state for 12 hours. Then the polyacrylamide solution was poured off, and the sorbents were washed with distilled water and dried.

Organopolymer based on shungite was synthesized as described below. Glycidyl methacrylate (GMA) with the addition of orthophosphoric acid was loaded into a reaction vessel equipped with a thermometer and a mechanical stirrer. The mixture was heated to 100°C and stirred for 30 minutes. Then a solution of hydroxyethyl diphosphonic acid (HEDP) in 1,4-dioxane and the calculated amount of shungite were added followed by stirring for 30 minutes. Next, the mixture was kept in an oven in porcelain cups for 10 hours at 100°C, after which it was washed repeatedly with a solvent and dried to constant weight under vacuum. The resulting sample was treated with a 3% alkali solution and washed with distilled water until the washings were neutral, then it was converted to the H⁺ form using a 3% HCl solution.

The sorption capacity of the modified sorbents was tested under static conditions. Sorption at room temperature (~25°C) lasted for 4 hours. The initial uranium concentration in the product solution amounted to 8.9 mg/dm³, and S: L=1:5.

Besides, the dynamic sorption capacity of the modified sorbents and the synthesized organopolymer was determined, for which a uranium-containing solution was passed through the sorbent layer placed in the column. Samples of 10-15 ml each were collected and analyzed for uranium content during sorption.

Desorption took place in a static mode with the ratio S: L=1:10.

Analysis methods

The quantitative uranium content in the solutions before and after sorption was determined with the help of an Optima 8000DV inductively coupled plasma (ICP) atomic emission spectrometer.

Results and Discussion

There are many ways to modify natural materials in order to increase the efficiency and selectivity of radionuclide extraction. Many of them are based on the introduction of additional functional groups into the sorbent structure, which leads to the formation of new adsorption centers and increased sorption capacity and sorbent selectivity. Inorganic materials modified with amidoxime or iminodoxime groups, as well as heteropoly salts, serve this purpose [3, 4]. Sorbents with amidoxime groups on various carriers showed high efficiency in the radionuclide extraction, as well as good kinetic properties [5-8].

Organopolymer synthesis plays a special part in the modified sorbent generation. Thus, organo-zeolite was synthesized based on natural zeolite-containing tuffs and a water-soluble polymer of polyhexamethylene guanidine, as well as epichlorohydrin as a crosslinking agent, which simultaneously exhibits cation-exchange, anion-exchange and bactericidal properties [9].
sorbent is highly effective against oxygen-containing anions and uranium carbonate complexes.

It should be noted that all the described methods were developed using foreign raw materials, expensive modifying reagents, and many of them are difficult to implement.

Among the works presented by domestic scientists, the most interesting are the examples with modifying zeolite and shungite, previously activated with sulphuric acid, copper (II) and nickel hydroxide, which are presented in the article [10]. The authors discussed the features and general regularities of uranium sorption by modified sorbents. It was shown that the use of pre-activated and modified shungite and zeolite for the uranium sorption makes it possible to increase its extraction in comparison with the use of natural sorbents. However, the labor-intensive modification process is a deterrent for the widespread use of sorbents obtained by this method.

Thus, the described methods have a common disadvantage expressed in their complex implementation, high cost, and the use of not generally available reagents. In addition, the obtained organominerals are characterized by the unstable surface layer of the modifier and the need to create special conditions for optimal sorption. Therefore, the development of effective and inexpensive sorption materials using cheap local raw materials remains urgent in the current economic conditions [11].

The research included developing the modification methods and studying the properties of modified natural sorbents. Among the most promising with functional groups fixed on polymer matrices capable of forming complex compounds, there are sorbents based on natural minerals and extractants. Such “solid-phase extractants” are characterized by good sorption properties; therefore, we chose this method to develop modification methods. Determining the sorption degree followed the method described above. The uranium content in waste solutions is estimated at 5-15 mg/dm³. The uranium content in the product solutions used was 11.9 mg/dm³. The results are shown in Table 1.

Table 1 suggests that zeolite modified with a mixture of di-2ethylhexylphosphoric acid and tributyl phosphate in kerosene almost completely extracts uranium from product solutions under the described experimental conditions. The degree of uranium extraction by zeolite modified with a mixture of phosphoric acid and polyacrylamide is somewhat lower. Meanwhile, an inverse dependence is observed for shungite. In further studies, the first method was used to modify zeolite, and the second method was used for shungite.

The second stage of the research included doubling the modifier concentration, modifying natural sorbents according to the described methods, and tripled sorption-desorption. Desorption complied with the conditions described above. The results are shown in Table 2.

Table 2 Results of uranium sorption-desorption

<table>
<thead>
<tr>
<th>Stage</th>
<th>Process</th>
<th>Zeolite</th>
<th>Shungite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Uranium content, mg/dm³</td>
<td>Extraction degree, %</td>
<td>Desorption degree, %</td>
</tr>
<tr>
<td>I</td>
<td>Sorption</td>
<td>0.79</td>
<td>91.12</td>
</tr>
<tr>
<td></td>
<td>Desorption</td>
<td>9.504</td>
<td>40.2</td>
</tr>
<tr>
<td>II</td>
<td>Sorption</td>
<td>7.4</td>
<td>16.0</td>
</tr>
<tr>
<td></td>
<td>Desorption</td>
<td>0.39</td>
<td>10.4</td>
</tr>
<tr>
<td>III</td>
<td>Sorption</td>
<td>7.18</td>
<td>19.3</td>
</tr>
<tr>
<td></td>
<td>Desorption</td>
<td>0.3</td>
<td>7.8</td>
</tr>
</tbody>
</table>

Table 2 suggests that shungite can be used repeatedly with an increase in the modifier concentration. No such dependence was observed for zeolite.

Further, to modify the sorbents, a two-fold increased modifier concentration was used. The studies were based on model solutions with a uranium concentration of 70, 107.5, 142.8, and 212.6 mg/dm³ under static conditions at the ratio S:L =1:5 for 4 hours.

The balance ratio was used to calculate the sorption capacity of ion exchangers (SC, mg/g): 

\[ SC = (C_{init} - C_{fin}) V_{sol} / g, \]

where \( C_{init} \) and \( C_{fin} \) are the uranium concentrations in the initial solution and the solution after sorption, respectively, mg/l; \( V_{sol} \) is the solution volume, l; and \( g \) is the sorbent sample weight, g.

The study results are presented in Table 3. The obtained isotherms and their anamorphoses are shown in Figure 1. According to Figure 1 (a, b), the curves are convex and may be described by the Langmuir equation as follows:

\[ C_{equil} / SC = C_{equil} / SC_x + 1/(SC_x \times Const.), \]
Table 3 Results of uranium sorption from model solutions on modified natural sorbents with an increased concentration of modifying agents

<table>
<thead>
<tr>
<th>Initial uranium concentration in the solution, mg/dm³</th>
<th>Zeolite</th>
<th>Shungite</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>107.5</td>
<td>142.8</td>
</tr>
<tr>
<td>107.5</td>
<td>0.07</td>
<td>0.063</td>
</tr>
<tr>
<td>142.8</td>
<td>0.51</td>
<td>11.27</td>
</tr>
<tr>
<td>212.6</td>
<td>11.48</td>
<td>0.07</td>
</tr>
<tr>
<td>Uranium concentration in the solution after sorption, mg/dm³</td>
<td>0.07</td>
<td>0.02</td>
</tr>
<tr>
<td>Extraction degree, %</td>
<td>99.9</td>
<td>99.6</td>
</tr>
<tr>
<td>Sorption capacity, mg/g</td>
<td>0.349</td>
<td>0.713</td>
</tr>
</tbody>
</table>

Figure 1 Isotherms of uranium sorption by modified zeolites and shungite (a, b) and their anamorphoses in the Langmuir equation coordinates (c, d)

Figure 2 Output curves of uranium sorption on modified sorbents: 1 – shungite; 2 – zeolite; 3 – organopolymer

where SC is the sorption capacity, mg/g; SC_∞ is the maximum sorption capacity, mg/g; Const. is the Langmuir constant, ml/g; and C_{equil.} is the equilibrium concentration of metal in the solution after sorption, mg/l.

Isotherm anamorphoses of the uranium sorption by modified zeolite and shungite in the Langmuir coordinates are shown in Figure 1 (c, d) used to calculate the maximum sorption capacity for zeolite SC_∞ = 434.76 mg/g and for shungite SC_∞ = 225.99 mg/g, as well as the Langmuir constant Const. = 0.229 ml/g for zeolite and Const. = 0.187 ml/g for shungite.

At the next stage, sorption from product solutions with a concentration of 11.9 mg/dm³ took place under dynamic conditions according to the method described above.

Figure 3 Output curves of iron sorption on modified sorbents: 1 – shungite; 2 – zeolite; 3 – organopolymer
Figures 2 and 3 show the output curves representing the sorption of uranium and iron from the process solution on shungite modified with phosphoric acid with polyacrylamide, zeolite modified with a mixture of organic solvents and a shungite-based organopolymer. The flow rate of the solution on the modified zeolite and organopolymer is 30 ml/h, and 10 ml/h on the modified shungite. The studies performed allowed determining the total dynamic exchange capacity (TDEC, Table 5). As it follows from the table, the TDEC of the organopolymer for uranium and iron is lower in comparison with modified zeolite and shungite.

Table 5 Results obtained from the sorption of uranium and iron by modified sorbents and organopolymer under dynamic conditions

<table>
<thead>
<tr>
<th>TDEC (total dynamic exchange capacity), mg/g</th>
<th>Shungite</th>
<th>Zeolite</th>
<th>Organopolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>U Fe</td>
<td>1.068</td>
<td>1.07</td>
<td>0.77</td>
</tr>
<tr>
<td>Fe U</td>
<td>17.2</td>
<td>17.26</td>
<td>11.3</td>
</tr>
</tbody>
</table>

Conclusions

The research included proposed and tested methods for modifying natural sorbents, which make it possible to actively extract uranium. Mixtures of di-2ethylhexylphosphoric acid and tributyl phosphate in kerosene, as well as phosphoric acid and polyacrylamide, were used as modifiers. The methods are based on obtaining “solid-phase extractants” characterized by functional groups fixed on polymer matrices capable of forming complex compounds, which is regarded as the most promising method. Sorption in static and dynamic modes was studied in the framework of the research. It was shown that with an increase in the modifier concentration, shungite can be used repeatedly. No such dependence was observed for zeolite.

Uranium sorption isotherms were plotted. The maximum sorption capacity and the Langmuir constant were calculated.

The research allowed synthesizing an organopolymer based on shungite, glycicyl methacrylate, orthophosphoric, and hydroxyethyl diphostoric acids. Its sorption properties were studied under dynamic conditions. Its sorption capacity was assessed in comparison with modified natural sorbents.

Conflicts of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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Извлечение урана модифицированными сорбентами

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Аннотация. При гидрометаллургической переработке урансодержащего сырья образуется значительное количество жидкого техногенного отхода – сбросных растворов, требующих утилизации. Одним из наиболее эффективных приемов очистки, загрязненных радионуклидами жидким объектом является сорбция. С целью использования природных сорбентов и увеличения их сорбиционной емкости разрабатываются варианты модификации. Авторами предложены способы модификации природного алюмосиликатного и угольно-минерального сырья. Для исследований выбраны цеолит месторождения Космурм и шунгит месторождения Коксу. В основу способов положен метод получения твердофазных экстрагентов. Предложено модифицировать природные сорбенты смесью трибутилфосфата и ди2-этилгексилфосфорной кислоты в керосине, а также смесью фосфорной кислоты и полиакриламида. Показано, что для цеолита предпочтительней первый способ, а для шунгита – второй. Изучены сорбиционные свойства сорбентов в статическом и динамическом режимах. Построены изотермы сорбции урана. Расчитаны максимальная сорбиционная емкость и константа Ленгмиора. Синтезирован органополимер на основе шунгита, глицидилметаакрилата, ортофосфорной и оксиэтилдифосфорной кислот. Изучены его сорбиционные свойства в сравнении с модифицированными природными сорбентами.

Ключевые слова: природные сорбенты, модификация, сорбция урана, органоминерал.

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