The object of research is granular composites based on zirconium-iron alginites and laponite. The task of research is to determine the influence of the Zr:Fe ratio on the structure of granular composites and efficiency of uranium (VI) removal from aqueous solutions. The influence of the zirconium and iron ratio on the parameters of the material’s pore structure has been established, particularly on the change in the content of micropores within the matrix. The specific surface area of the materials ranges from 86 to 112 m²/g. The sorption properties of the composites regarding uranium (VI) have been investigated. The impact of the charge of surface groups and the form of uranium (VI) presence in sulfate solutions on their sorption characteristics has been demonstrated. The maximum adsorption capacity reaches 265.1 μmol/g at pH 6. It is shown that an elevated electrolyte content positively affects the efficiency of uranium (VI) removal in neutral and alkaline medium. It has been established that structural changes in the materials occur due to the intensive interaction of iron ions and alginate molecules, resulting in the formation of a dense gel-like structure. The mechanism of uranium (VI) removal is associated with the formation of surface complexes in the presence of electrolytes. The synthesized granulated composites exhibit improved removal efficiency of uranium (VI) under conditions of high mineralization of solutions, making them attractive for potential use as sorbents. The obtained results can be utilized in the development of effective methods for purifying water environments from uranium (VI) in high mineralization conditions, which is a relevant issue in the field of nuclear energy and the removal of radioactive substances from water systems.

Keywords: granular composites, zirconium-iron alginites, uranium (vi) removal, sulfate solutions, laponite

1. Introduction

Effective control over the management of radioactive pollutants, in particular uranium (VI), in the environment is critical for preserving ecosystems and ensuring human safety. There are various strategies for the development of efficient and cost-effective methods for the removal and immobilization of uranium (VI) from aqueous solutions [1].

One of the main problems of uranium (VI) extraction is its complex behavior in aqueous solutions with the possibility of the formation of a wide range of polynuclear hydroxo-, carbonate, and other complexes depending on the chemical composition of the solution [2].

In recent years, a promising direction is the use of composite materials due to their unique properties and increased sorption capacity [3, 4].

The use of water-soluble polymers of natural origin makes it possible to obtain composites with various properties. Alginites of various metals should be noted among such polymers. The contact of sodium alginate solutions with solutions of polyvalent metals leads to the crosslinking of alginate molecules and the transformation of the sol into a gel. Such a sol-gel transition makes it possible to obtain granules of a given chemical composition. Moreover, the addition of various fillers, such as activated carbon, clay minerals, oxides makes it possible to obtain composite materials in granular form. Such materials are more effective in technologies for cleaning polluted waters due to the ease of separation of solid and liquid phases [5, 6].

Among the effective fillers, it is worth noting clay minerals, which usually have a developed specific surface and a high cation exchange capacity [7]. One of the promising clay minerals is laponite—a synthetic layered clay mineral that has a 2:1 structure and is characterized by nano-sized plates with the possibility of cation exchange. The combination of these materials makes it possible to use their individual advantages and create a composite system that could potentially have improved physicochemical properties [8].

Ionotropic strengthening of alginate with transition metal ions is a promising area of research. For this purpose,
compounds of iron and zirconium are the most promising in the field of obtaining sorption materials. Iron ions are known for their redox nature and strong affinity for uranium (VI) [9], while zirconium compounds also have high sorption properties, especially for anion extraction [10].

Thus, the study of the structure and sorption properties of granular composites based on zirconium-iron alginites and laponite is a relevant task.

2. Literature review and problem statement

Recent studies indicate a significant interest in the use of granular composites based on alginites for the removal of heavy metals, radionuclides, and dyes from aquatic environments [11].

Sufficiently high values of uranium sorption (up to 0.6 mmol/g) are demonstrated by granular composites based on calcium alginate modified with iron (III) phosphates and magnetite [12]; however, in the cited work mainly acidic solutions up to pH 4 were investigated. In addition, the synthesis of composites includes too many stages and reagents. The authors of paper [13] studied the sorption extraction of uranium (VI) by composites based on hydroxyethyl cellulose and sodium alginate with a sorption capacity of up to 1.32 mmol/g. At the same time, glutaraldehyde was used for the synthesis of composites, which can have a negative environmental effect.

Composites based on alginate and graphene oxide [14] also demonstrate high sorption properties for uranium extraction (up to 1.5 mmol/g). However, in the cited work, the effect of mineralization of solutions was demonstrated only by the content of sodium ions. At the same time, the extraction efficiency was investigated in the pH range of 4.0–4.5, which is too different from the acidity of natural polluted waters.

A sorption capacity of up to 1.1 mmol/g was achieved by the authors of [15] in the extraction of uranium (VI) by composites based on calcium alginate and metal-organic framework structure (UiO-66). However, the synthesis of such composites requires a large number of expensive reagents, which negatively affects the cost of adsorbents. In addition, sorption isotherms are presented for pH 4.

The authors of [16] synthesized composites based on magnetite, agarose, and calcium alginate, which demonstrate a sorption capacity of up to 0.44 mmol/g (pH 5). But the paper does not report the influence of electrolytes or the general mineralization of the solution on the efficiency of uranium (VI) removal.

At the same time, pure alginites of metals show lower values of sorption capacity for the extraction of uranium (VI). The authors of work [17] demonstrated the extraction of uranium on pure calcium alginate with a sorption capacity of up to 0.17 mmol/g (pH 5). However, the effect of mineralization of the solution or the effect of ionic strength on the efficiency of uranium (VI) sorption was not investigated.

Granular composites based on compounds of iron, zirconium, and alginites show high sorption properties for anions such as phosphates [18].

However, there are no papers on the study of uranium (VI) sorption by granular composites based on iron-zirconium alginites and laponite. This allows us to state that it is appropriate to conduct a study aimed at examining the structure and sorption properties of granular composite materials based on iron/zirconium alginites and laponite. In addition, the study of extraction of uranium (VI) from sulfate solutions and close to neutral (pH 6–7) solutions with increased mineralization is of great interest.

3. The aim and objectives of the study

The purpose of our research is the development of composites based on Zr/Fe-alginates and laponite with the evaluation of their structure, physical and chemical properties, and the determination of the features of uranium (VI) sorption on such materials. This will make it possible to evaluate the effectiveness of granular composites in solving the issues of water pollution with uranium (VI) in the places of its extraction and processing.

To achieve the goal, the following tasks were set:

– to synthesize granular composites based on laponite and alginate ionotropically strengthened with zirconium and iron ions and determine their porous structure characteristics;

– to investigate the effect of pH of the solution and the ratio of iron and zirconium ions in strengthening solutions on the sorption capacity of granular composites during the removal of uranium (VI);

– to investigate the effect of mineralization of the source solutions on the efficiency of uranium (VI) removal from them.

4. The study materials and methods

The object of research is composites based on zirconiumiron alginate and laponite.

The hypothesis of the study assumed that the use of iron and zirconium ions in different molar ratios can create conditions for the formation of granular composites with improved sorption properties in relation to uranium (VI). Considering the complexity of the proposed system and the number of components, the following simplifications were adopted: only one ratio of alginate and laponite in the composites was chosen, and the influence of individual types of anions on the efficiency of uranium (VI) extraction was not included in the study.

The procedure of forming granular composites due to ionotropic hardening was used for the synthesis of samples. Iron and zirconium ions interact with sodium alginate molecules forming insoluble compounds in the form of a hydrogel. In the study, Laponite RD (Laponite RD, Rockwood Additive Limited, 99 %, specific surface area of 370 m²/g with a cation exchange capacity (CEC) of 0.7 mmol/g) and sodium alginate (Sigma-Aldrich, Germany) were used. Ferric chloride hexahydrate (III) (FeCl₃·6H₂O) and zirconium oxychloride hydrate (ZrOCl₂·8H₂O) were used to prepare ionotropic strengthening solutions. Uranium (VI) solutions of different concentrations were prepared using uranyl sulfate trihydrate (UO₂SO₄·3H₂O) (Sigma-Aldrich, Germany). 0.1 M HCl and 0.1 M NaOH were used to adjust the pH of the initial solutions.

The structure of the samples was determined by low-temperature nitrogen adsorption using a NOVA-2200 station (Quantachrome, USA). Before measurements, the samples were degassed for 20 hours at a temperature of 110 °C (0.0134 Pa). The specific surface area (S_BET) of the samples was calculated using the Brunauer-Em-
mott-Teller (BET) method. Pore size distribution was determined using the Barrett-Joyner-Halenda (BJH) method. The t-Plot method was used to estimate the volume of micropores ($V_{t-m}$). The total pore volume ($V_\Sigma$) was calculated at the maximum volume of adsorbed nitrogen at a relative pressure of $p/p_0=0.99$. The content of micropores ($W_{micro}$, %) was calculated using the formula $W_{micro}=V_{t-m}/V_\Sigma \cdot 100$.

Determination of the pH of the point of zero charge (pH$_{pzc}$ of materials) was carried out according to a procedure from [19].

IR spectra were obtained using the broken total internal reflection spectroscopy method using an IRAffinity-1S QATR 10 spectrometer (Shimadzu, Japan) in the wavenumber range of 400–4000 cm$^{-1}$.

Adsorption properties of granular composites were determined by standard procedures. A weight of 0.25 g of the sample (hydrogel with a humidity of 95 %) was brought into contact with 50 cm$^3$ of a uranium (VI) solution of the appropriate concentration and pH. With the help of HCl or NaOH solutions of different concentrations, the pH of the initial solutions was adjusted. To study the dependence of the sorption capacity on the pH of the initial solution, an initial concentration of uranium (VI) of 100 μmol/dm$^3$ was used. The duration of contact between the solid and liquid phases was 240 minutes with continuous shaking on an orbital shaker. After reaching the adsorption equilibrium, the residual content of uranium (VI) was determined spectrophotometrically using the Arsenazo III reagent at a wavelength of 665 nm on a UNICO-UV 2100 spectrophotometer (United Products Instruments, USA).

5. Results of investigating the structure and sorption properties of granular composites

5.1. Synthesis of granular composites and study of their porous structure characteristics

For the synthesis of granular composites, a suspension of laponite (1.5 % by weight) and a solution of sodium alginate (1.5 % by weight) were mixed (1:1 % by weight). The resulting mixture was homogenized for 2 hours using a magnetic stirrer. The obtained suspension was added dropwise to solutions with different contents of zirconium and iron ions (0.1 M Zr$^{4+}$ or Fe$^{3+}$) with the molar ratio: Zr 25 % – Fe 75 %, Zr 50 % – Fe 50 % and Zr 75 % – Fe 25 %. When the suspension is in contact with the solution, the droplets are instantly transformed into hydrogel granules. The obtained granules were left in the solutions for 24 hours for the complete passage of the ionotropic hardening reactions. After exposure, the granules were washed several times with distilled water from the remains of iron or zirconium ions and other electrolytes. The synthesized composites were stored in distilled water before further use. Schematically, the synthesis of granular composites is shown in Fig. 1. The as-synthesized samples were designated as ZrxFey, where "x" and "y" denote the molar fraction of zirconium and iron in the hardening solutions.

Nitrogen adsorption at low temperatures is an important method for evaluating the porous structure of materials. In the case of the tested samples shown in Fig. 2, the complex character of nitrogen adsorption isotherms is observed. The branches of desorption do not intersect with the branches of adsorption in the region of medium and low pressure. This behavior is characteristic of microporous samples with bottle-like or slot-like pores, in which the desorption of nitrogen molecules is complicated. This may indicate the presence of narrow areas in the pore channels. According to the IUPAC classification, the obtained isotherms correspond to type IV. It can also be noted that the existing hysteresis loops can be attributed to the H4 type [20].

The application of adsorption models makes it possible to calculate the parameters of the porous structure of granular composites, which are given in Table 1.

The results of the analysis of nitrogen sorption isotherms using different models indicate the similarity of the structural properties of the studied samples. The specific surface area ($S_{BET}$) of the samples ranges from 86 to 112 m$^2$/g. The total pore volume ($V_p$) for samples of granular composites is 0.046–0.066 cm$^3$/g. The Zr100 sample has the largest micropore volume with a value of 0.034 cm$^3$/g. The calculated values of the content of micropores ($W_{micro}$) gradually decrease with an increase in the content of iron in the hardening solutions.

The application of IR spectroscopy makes it possible to determine different types of active centers on the surface of
the composite. As is known [21], the main active centers of the studied materials will be hydroxyl and carboxyl groups (Fig. 3).

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>S_{BET}, m²/g</th>
<th>S_{micro}, m²/g</th>
<th>V_{BET}, cm³/g</th>
<th>V_{micro}, cm³/g</th>
<th>W_{micro}, %</th>
<th>( \tau_{0}, ) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr100</td>
<td>105.5</td>
<td>75.5</td>
<td>0.056</td>
<td>0.034</td>
<td>61.2</td>
<td>1.066</td>
</tr>
<tr>
<td>Zr75Fe25</td>
<td>109.9</td>
<td>74.0</td>
<td>0.054</td>
<td>0.033</td>
<td>61.6</td>
<td>1.061</td>
</tr>
<tr>
<td>Zr50Fe50</td>
<td>100.3</td>
<td>62.2</td>
<td>0.057</td>
<td>0.027</td>
<td>47.7</td>
<td>1.136</td>
</tr>
<tr>
<td>Zr25Fe75</td>
<td>112.8</td>
<td>59.9</td>
<td>0.066</td>
<td>0.026</td>
<td>39.6</td>
<td>1.180</td>
</tr>
<tr>
<td>Fe100</td>
<td>86.7</td>
<td>62.3</td>
<td>0.046</td>
<td>0.016</td>
<td>35.7</td>
<td>1.186</td>
</tr>
</tbody>
</table>

Fig. 3. IR spectra of composite samples

In the region of high wavenumbers, a broad band at 3336 cm⁻¹ is observed, which indicates the presence of hydroxyl groups with adsorbed water molecules. The 2338 cm⁻¹ and 2325 cm⁻¹ bands belong to the valence vibrations of adsorbed water molecules. These bands also confirm the presence of water molecules in the structure of the composite. Absorptions at 1587 and 1470 cm⁻¹ correspond to presence of water molecules in the structure of adsorbed water molecules. These bands also confirm the presence of water molecules in the structure of the composite. Absorptions at 1587 and 1470 cm⁻¹ correspond to valence symmetric vibrations of the C=O bond in alginate molecules. The absorption band at 1022 cm⁻¹ corresponds to valence vibrations of Si–O–Si siloxane bonds in the structure of the tetrahedral layer of laponite. In the region of low wavenumbers, the bands at 656 cm⁻¹ and 632 cm⁻¹ may be responsible for the deformation fluctuations of metal-oxygen bonds (Fe–O or Zr–O) [22].

5. 2. Effect of solution pH and ratio of iron and zirconium ions on sorption efficiency

The pH value of the solution significantly affects the processes of sorption of heavy metals from aqueous solutions. For uranium (VI), the dependence of the sorption value on the pH of the solution is complex (Fig. 4, a). In an acidic environment, uranium (VI) exists in the form of a cation \( \text{U}^{4+} \) (Fig. 4, b). In such conditions, the surface groups of adsorbents have a positive charge, which significantly reduces the intensity of sorption processes with the formation of surface complexes of various compositions. As a result, low values of sorption are observed, for which the existing cation exchange centers on the basal surface of laponite particles are mainly responsible.

As the pH of the solution increases, the proportion of protonated groups \( =\text{S–OH}^+ \) decreases significantly. Cations \( \text{UO}_2^{2+} \) are either positively charged complexes \( \text{UO}_2^{2+} \text{(OH)}_2^- \) or \( \text{UO}_2^{2+} \text{(OH)}_2^+ \) which can interact with neutral \( =\text{S–OH}^- \) and deprotonated \( =\text{S–O}^- \) hydroxyl groups on the surface. In this way, surface complexes of various compositions are formed [23]. In the pH range of 6.5–9, a decrease in sorption is observed due to the formation of negatively charged carbonate and hydroxyl complexes of uranium (VI). For example, these are complexes \( \text{UO}_2^{2+} \text{(CO}_3\text{)}^2^- \) or \( \text{UO}_2^{2+} \text{(CO}_3\text{)}^3^- \) that do not adsorb on the negatively charged surface of samples with deprotonated groups \( (=\text{S–O}^-) \).

![Fig. 4](image-url)

The results of our research indicate a decrease in pH values of the point of zero charge (pHpzc). The determined pHpzc values for samples of granular composites are: Fe100 – 7.29, Zr25Fe75 – 7.14, Zr50Fe50 – 6.91, Zr75Fe25 – 6.93, Zr100 – 6.85. Such a change indicates changes in the characteristics of the surface charge and indicates that the inclusion of Fe and Zr ions increases the content of positively charged areas on the surface of the composite. Thus, the ability of such materials to extract anionic forms of uranium (VI) increases. The increased adsorption efficiency can be explained by the synergistic interaction between Fe and Zr ions, which contributes to the creation of a surface structure with an increased density of active centers (hydroxyl groups). Such centers provide stronger electrostatic attraction and interaction with anionic complexes of uranium (VI), which leads to increased adsorption capacity.

Sorption isotherms indicate a significant influence of the ratio of Zr:Fe in hardening solutions on the amount of uranium (VI) sorption (Fig. 5). An increase in the number of different types of active centers in the structure of composites leads to an increase in sorption values. Hydroxyl groups belonging to laponite particles \( (=\text{Si–OH}) \) on the side surface and carboxyl \( (=\text{COOH}) \) groups of alginates can be involved...
in sorption processes. In addition, \(-\text{Zr}–\text{OH}\) and \(-\text{Fe}–\text{OH}\) groups also take part in sorption processes. It is most likely that carboxyl groups contribute to the formation of surface complexes of uranium (VI) of different composition [24].

Freundlich \(a = K_f \cdot C_e^{1/n}\) and Langmuir \(a = \frac{K_L \cdot C_e}{1 + K_L \cdot C_e}\) models were used to process the obtained data. The coefficients of the specified adsorption equations are given in Table 2. The proposed sorption models describe the experimental data well, which is confirmed by the values of the correlation coefficient \((R^2)\) in the range of 0.96–1. However, the Langmuir model for most samples better describes the experimental data with higher values of the correlation coefficient.

The dependence of the values of the maximum sorption capacity \((a_\infty, \mu\text{mol}/\text{g})\) and affinity \((K_L)\) with an increase in the Zr:Fe ratio in hardening solutions is not monotonic, although there is a tendency to increase the value of these parameters (Table 2). The Freundlich model describes sorption isotherms less effectively. The values of the \(K_f\) constant, which is related to the interaction energy between the adsorbent and the adsorbate, vary between 18–42 dm\(^3\)/μmol.

5.3. The effect of mineralization of initial solutions on the efficiency of uranium (VI) removal from them

The selective removal of heavy metals from complex solutions with high electrolyte content is a serious challenge. Removal of uranium (VI) from tailings sites of the uranium mining and uranium processing industry in order to prevent groundwater and soil pollution remains an urgent problem. For this purpose, the sorption of uranium (VI) from a solution with a high level of mineralization was investigated. The composition of the solution is close to the actual composition of groundwater near the uranium ore enrichment waste tailings (Zhovti Vody, Ukraine). The chemical composition of such water is given in Table 3.

![Graph](image)

### Table 3

| Chemical composition of groundwater near the tailing dump (pH 7.4; g/dm\(^3\)) [25] |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| \(\text{Ca}^{2+}\) | \(\text{Mg}^{2+}\) | \(\text{Na}^+\) | \(\text{K}^+\) | \(\text{Cl}^-\) | \(\text{SO}_4^{2-}\) | \(\text{NO}_3^-\) | \(\text{CO}_3^{2-}\) | Total mineralization |
| 0.456            | 1.323           | 0.54            | 0.019           | 1.763           | 6.579           | 0.54            | 0.402           | 11.622          |

To study the efficiency of uranium (VI) removal under real water conditions with high mineralization of the aqueous solution, a Fe100 composite sample was selected. The results indicate a significant increase in the amount of sorption from mineralized waters by the Fe100 sample when the pH of the solution increases (Fig. 6, a). This behavior is characteristic of complex systems involving uranium (VI). The chemical composition of uranium (VI) solutions affects the possibility of formation of surface complexes of various compositions. In systems with high mineralization, carbonate, sulfate, and phosphate complexes show a higher affinity for surface hydroxyl groups [26].

A similar trend is observed on the sorption isotherms (Fig. 6, b), especially at high equilibrium concentrations of uranium. This indirectly indicates the formation and sorption of polynuclear surface complexes of uranium with the participation of anions \(\left(\text{CO}_3^{2-}\right)\) and cations (for example, \(\text{Mg}^{2+}\), \(\text{Ca}^{2+}\)).

![Graph](image)

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Freundlich model</th>
<th>Langmuir model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(K_f, \text{dm}^3/\mu\text{mol})</td>
<td>(n)</td>
</tr>
<tr>
<td>Fe100</td>
<td>25.8</td>
<td>2.92</td>
</tr>
<tr>
<td>Zr25Fe75</td>
<td>24.6</td>
<td>2.61</td>
</tr>
<tr>
<td>Zr50Fe50</td>
<td>20.1</td>
<td>2.92</td>
</tr>
<tr>
<td>Zr75Fe25</td>
<td>42.1</td>
<td>3.28</td>
</tr>
<tr>
<td>Zr100</td>
<td>18.8</td>
<td>3.49</td>
</tr>
</tbody>
</table>

The coefficients of the Langmuir and Freundlich equations for uranium (VI) sorption isotherms by granular composites (pH 6)

![Graph](image)
According to the diagram of the distribution of uranium forms in a solution with increased mineralization (Fig. 6, c), a significant content of sulfate complexes and only a small proportion of uranyl ions is observed in the pH range of 1–4.5. Polynuclear negatively charged uranium carbonate complexes predominate in the pH range of 4.5–9.0.

6. Discussion of results of investigating the structure of granular composites and the features of uranium (VI) sorption

The analysis of low-temperature nitrogen adsorption data allows us to state that the synthesized materials have a microporous structure with the presence of bottle-shaped pores. In addition, there is a decrease in the content of micropores in composites from 61 to 35 % with an increase in the content of iron in the strengthening solutions. The specific surface area of the samples varies between 86–112 m²/g, which is typical for similar materials discussed above. The formation of the pore structure of Zr/Fe-alginates occurs in different ways because alginate molecules have different affinity for iron and zirconium ions. This is especially evident in the change in the parameters of the pore structure of the materials (Table 1). The change in the content of micropores can be associated with a more intensive interaction of Fe³⁺ ions and alginate molecules, improvement of the diffusion process inside the granule and the formation of a denser gel structure, compared to Zr⁴⁺ ions, which are more prone to hydrolysis and the formation of polynuclear complexes. Probably, such zirconium complexes primarily react with hydroxyl and carboxyl groups of alginites on the surface of the granules, which leads to the formation of a dense structure and limits the further diffusion of ions inside the granule [27]. Thus, changing the ratio of zirconium and iron ions in the strengthening solutions makes it possible to regulate the porous structure of granular composites.

Our studies allow us to evaluate the synthesized granular composites from the point of view of their effectiveness in removing uranium (VI) from aquatic environments. The sorption properties of composites depend both on the charge of surface groups and on the forms of uranium (VI) in solutions. The resulting sorption curve depending on the pH of the solution has a classic form for uranium (VI) with an extremum in the pH range of 6–7. This dependence is explained by the complex behavior of uranium, which can exist in the form of a number of mono- and polynuclear complexes. The most likely will be hydroxo and carbonate complexes. The most likely will be hydroxo and carbonate complexes, such as UO₂(OH)₂, UO₂CO₃, (UO₂)₂CO₃(OH)₄⁻, and others (Fig. 4, b). They are able to adsorb on positively charged groups (carboxyl or hydroxyl) of composite samples. It should be noted that unlike analog materials, synthesized composites have an advantage. Extraction of uranium (VI) with maximum efficiency occurs precisely in neutral environments at pH 6–7 (Fig. 4, a). Analysis of the obtained data makes it possible to determine the most effective sample for uranium (VI) removal. In particular, the Zr25Fe75 sample (265.1 μmol/g) at pH 6 has the highest adsorption capacity (aₐ) for the removal of uranium (VI). The equilibrium constant (Kₑ) reflects the bond energy, therefore higher values (Kₑ=0.026 dm³/μmol) indicate a stronger interaction (affinity) between the adsorbate and the adsorbent. Accordingly, the Zr75Fe25 sample appears to be the most effective for uranium (VI) removal.

The cost of zirconium compounds still remains quite high compared to iron compounds. From a practical point of view, the sample based on Fe100 iron can serve as the most promising. This sample was chosen to study the effect of mineralization of solutions on the efficiency of uranium extraction (Fig. 6, a, b). In most cases, an increase in mineralization or ionic strength negatively affects the efficiency of extraction of heavy metals in both cationic and anionic forms. However, in some works, the preservation of sorption characteristics or even a slight increase is observed [28]. This behavior can be explained by the formation of surface polynuclear complexes of uranium with the participation of calcium ions, magnesium, and carbonate ions [28].

The increase in the sorption capacity of the sample up to 20 % during the removal of uranium from highly mineralized solutions together with the technological possibility of phase separation after purification indicates the promising nature of the proposed sorption materials.

Understanding the U(VI) sorption behavior of laponite/alginate composites and the effect of ionotropic hardening has the potential to provide valuable knowledge for the development of new composite materials for efficient U (VI) removal. This research can provide some contributions to devising sustainable and environmentally friendly strategies for the removal and immobilization of radioactive contaminants. Thanks to the use of zirconium and iron ions for ionotropic strengthening, sorption granular materials with increased affinity for uranium (VI) and improved sorption efficiency in mineralized solutions were obtained.

Our results make it possible to plan the synthesis in more detail and conduct research on granular composite materials of this type. In addition, for the application of granular adsorbents under dynamic conditions of polluted water treatment, data obtained under static conditions are necessary.

Spent granular composites can be disposed of using standard methods. Granular composites are a hydrogel with a high moisture content of up to 94–97 %. After drying, a small volume of solid matter remains in the form of iron-zirconium alginites and laponite with adsorbed uranium compounds. Waste of a similar composition can be immobilized by using ceramic technology or in special glasses with high chemical resistance.

At the same time, the current research has limitations in the form of conditions of use of synthesized composites. When the properties of the initial solutions (chemical composition or temperature) change, the efficiency of uranium (VI) extraction may change.

The lack of a detailed study of the effect of each of the electrolytes (anions and cations) on the efficiency of uranium (VI) extraction should be attributed to the shortcomings of the study. Future research should be conducted to address this shortcoming.

Our study may advance towards modifying the porous structure of granular composites in order to increase the specific surface area and, as a result, increase the efficiency of uranium (VI) extraction. An obstacle to solving such a problem can be the peculiarity of the structure formation of zirconium and iron alginites with a tendency to form a microporous structure, especially in the presence of laponite.

7. Conclusions

1. We have successfully synthesized granular composites based on laponite and alginate ionotropically strengthened
by zirconium and iron ions. The resulting granular materials have high mechanical and hydrolytic stability under various solutions. The characteristics of the porous structure of granular composites were established by the method of low-temperature nitrogen adsorption. It is shown that the synthesized materials have a microporous structure with the presence of bottle-shaped pores. The specific surface area of the samples ranges from 86 to 112 m²/g. It was established that the content of micropores in composites naturally decreases from 61 to 35 % with an increase in the content of iron in the hardening solutions. Such changes can be explained by the difference in the interaction processes of iron and zirconium ions with alginate molecules.

2. The study of the influence of pH of the solution indicates that for all synthesized composites the shape of the curves is similar with the maximum values of sorption in the pH range of 6–7.5 at the level of 125–175 μmol/g. It was established that the ratio of iron and zirconium ions in hardening solutions has a complex effect on the sorption capacity of granular composites during the removal of uranium (VI). The Zr25Fe75 sample (265.1 μmol/g) shows the highest sorption capacity.

3. The influence of general mineralization on the efficiency of uranium (VI) removal was studied. It was established that the increased content of electrolytes has a positive effect on the efficiency of uranium (VI) removal, especially in neutral and alkaline environments. Our results indicate the possibility of using synthesized granular composites to solve the problems of cleaning uranium (VI)-contaminated waters in the places of its extraction and processing.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

Funding

The study was conducted without financial support.

Data availability

All data are available in the main text of the manuscript.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the presented work.

References


