1. Introduction

Protection of the natural aquatic environment from pollution with dangerous inorganic toxicants, including arsenic compounds, is an important environmental challenge of our time. Arsenic belongs to the chemical elements that exhibit carcinogenic and mutagenic effects on living organisms. According to the directive documents of the World Health Organization and the countries of the European Union (EU), the permissible concentration of arsenic in drinking water should exceed 10 µg/dm³ [1]. According to Ukrainian regulatory documents, the content of arsenic in drinking water is also regulated at the level of 10 µg/dm³, in the wastewater – 20 µg/dm³ [2].

Pollution of water bodies with arsenic compounds is caused by both natural factors (the passing of geochemical leaching processes from arsenic rocks) and man-made (sewage from mining enterprises, nonferrous metallurgy, oil refineries, coal-fired power plants). A potential source of water pollution is the use of arsenic in the production of pigments, paints, ceramics and substances to prevent bio-growing.

In natural surface waters, the degree of arsenic oxidation depends on the concentration of dissolved oxygen in them, the redox potential and the pH of the aquatic environment. Among the inorganic forms of arsenic, arsenites (oxidation degree +3) and arsenates (oxidation degree +5) are most common. The former dominate in water bodies with anaerobic conditions, the latter in water, saturated with oxygen. In uncontaminated natural waters, the concentration of arsenic does not exceed 1–10 µg/dm³. However, in the water bodies of the regions exposed to the waste waters of metal-mining enterprises, its content reaches tens and hundreds of micrograms per 1 dm³. The groundwater of these regions is particularly polluted with arsenic compounds. This problem is very important for countries where groundwater is used as a source of drinking water supply for the population [2].

Various chemical and physico-chemical methods are used to purify water from metal ion pollution. However, the existing traditional water purification technologies do not always provide the normative quality of purified water.

Today, one of the most promising and effective methods for purifying large volumes of water from metal ions contained in very small concentrations compared with other compounds is sorption. It is their use in the purification of water allows to achieve a high degree of extraction of metal ions. Now there are a large number of synthetic sorption materials. However, along with high efficiency, they have a significant drawback – they require complex synthesis schemes and are relatively expensive. Therefore, the preparation of sorbents based on cheap natural layered silicates for water purification from inorganic toxicants is

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ECOLOGY AND ENVIRONMENTAL TECHNOLOGY

FROM ARSENIC COMPOUNDS

CONTAMINATED WATER PURIFICATION

SILICATE COMPOSITES FOR

OBTAINING OF IRON-CONTAINING

Ключеви слова: сорбція арсену, очищення води, оксигідроксиди заліза, глинисті мінерали, модифікування поверхні.
promising. The structural features of clay minerals make it possible to modify their surface with various compounds and to obtain new functional materials with unique properties.

One of the methods to increase the adsorption capacity of aluminosilicates with respect to metal ions is to treat their surface with metal oxides and hydroxides. It is known that composite sorbents based on clay minerals and iron oxides have an increased adsorption capacity compared to the original aluminosilicates and acquire anion-exchange properties, while maintaining the cation-exchange ability. In this regard, the relevance of the work is due to the need to develop highly efficient composite materials based on natural clay minerals for purifying water from As(V) compounds.

2. The object of research and its technological audit

The object of research is palygorskite – a natural clay mineral with a layered ribbon structure. At the heart of its structure is twinned infinite silicate ribbon of pyroxene type. Two oppositely returned to each other vertices of the tetrahedra of silicon-oxide elements are connected into ribbons with Mg2+, Al3+ and Fe3+ ions in octahedral coordination. Since ribbons of the tetrahedra are combined in staggered order among themselves, rigid internal «zeolite» channels with a size of 0.37 nm by 1.2 nm and a developed secondary porous structure appear. The structural formula of this mineral has the following form: Mg2(Mg2H2O)(OH)2[Si4O10]⋅4H2O [3].

It is known that sorption materials based on natural clays, including palygorskite, are widely used in water purification processes from ion-black earth compounds. However, a technological audit suggests that cleaning water from metal anions, for example, arsenic compounds, with natural clays, including palygorskite, are widely used in water purification sorption technologies [15, 16]. Complicates the separation of solid and liquid phases when they have a significant drawback – high dispersion, which negatively charged. In addition, a significant drawback of the use of highly dispersed clay minerals is the difficulty of separating the solid and liquid phases during sorption purification of water from metal ions in a static mode.

3. The aim and objectives of research

The aim of research is obtaining iron-containing silicate composites based on palygorskite to protect the environment.

Objectives of research:

1. To investigate the parameters of the synthesis of palygorskite-based iron-containing silicate composites and determine the structural sorption properties of the obtained composites.

2. To study the physico-chemical characteristics of the purification of aqueous solutions from metal ions on the example of arsenic(V) compounds using the obtained samples.

4. Research of existing solutions of the problem

A number of methods are used to extract arsenic compounds from polluted waters: oxidation of As(III) to As(V) with various reagents, coagulation and flocculation, filtration, methods of membrane separation and sorption methods [4, 5]. Sorption methods are among the most effective, due to the ability to achieve a high degree of purification at relatively low costs. The ideal method for removing small amounts of arsenic impurities from diluted polluted water is ion exchange [6]. To date, a large number of various sorbents have been developed for extracting arsenic compounds from polluted waters [7, 8]. At the same time, oxides of metals have high efficiency, in particular:

- titanium [9];
- zirconium [10];
- copper [11];
- iron [12].

When developing cheap sorption materials, particular attention is paid to various iron compounds (oxides, hydroxides and oxyhydroxides) [13, 14], which is caused by the high adsorption tendency of the latter to remove arsenic. However, along with their efficiency and cheapness, they have a significant drawback – high dispersion, which complicates the separation of solid and liquid phases when used in water purification sorption technologies [15, 16]. Therefore, it is advisable to ferment the iron-containing compounds on different substrates, which significantly improves the processability of sorption processes. As the substrate it is possible to use:

- ion exchange resins [17, 18];
- activated carbon [19];
- organic porous materials [20];
- diatomite [21];
- nanotubes based on boron nitride [22];
- polymeric materials [23].

Natural clay minerals are not very effective in purifying arsenic anion water. However, the existing technologies for modifying their surface make it possible to develop composite sorption materials based on them. Thus, iron oxides are applied to pillared clay [24], as a result, it is possible to obtain materials with increased porosity and sorption capacity. The use of surfactants and polycationic iron in the synthesis of silicate sorption materials also makes it possible to significantly improve the selectivity of montmorillonite for arsenic compounds [25]. And deposition of nano-sized iron on the surface of layered minerals results in a highly efficient reactive material [26].

Thus, the results of literary analysis allow to conclude that the preparation of sorption materials based on natural clay minerals and iron-containing compounds will allow the creation of effective, more technological and economically feasible schemes for purifying water from arsenic contamination.

5. Methods of research

The synthesis of iron(III) oxyhydroxide – ferrihydrite (Fh) was carried out according to a modified procedure [27]. To this end, in 200 cm3 of a 0.2 M solution of Fe(NO3)3⋅9H2O, with constant stirring, a certain volume of 1 M solution of KOH was added to a pH of 7–8. The precipitate was washed with distilled water, defened and the dark brown precipitate was separated by filtration under vacuum. The sample was dried at 80 °C, triturated in a porcelain mortar, sieved to obtain a fraction of ≤0.2 mm and stored in a container without air access.

The surface treatment of the natural form of palygorskite (PG) was done by iron-containing compounds using iron salts (III). To do this, a solution of Fe(NO3)3⋅9H2O was added with a weight of silicate in various mass ratios of Fe(g):clay mineral (g) – 0.01:1, 0.025:1, 0.05:1.
0.075:1, 0.1:1, 0.25:1, 0.5:1, 0.75:1 and 1:1. The suspension was stirred for 1 hour. And then 1 M KOH solution was added to a pH of 7–8 for the formation of silicate composites PG-Fh. The precipitate was washed several times with distilled water from excess salts and settled for a certain time. Then the suspension was filtered under vacuum. The obtained samples were dried at 80 °C in a drying cabinet, triturated and sieved to obtain a fraction of ≤0.2 mm and stored in a container without air access.

The infrared (IR) spectra of the natural palygorskite and its ferrihydrite-modified sample were obtained on a Spectrum Two FT-IR spectrometer (Perkin Elmer, USA) in the range of 4000–4500 cm⁻¹ at the configuration of total internal reflection (ATR-IR).

To determine the parameters of the porous structure of natural clay minerals and ferrous silicates, the method of low-temperature nitrogen adsorption-desorption was used (Quantachrome Nova 2200e Surface Area and Pore Size Analyzer, USA). Samples were evacuated at room temperature for 30 minutes and kept for 5 minutes after establishing equilibrium at each point of the isotherm. The specific surface area and total pore volume were determined by the Brunauer, Emmett and Teller method (BET), and the pore size distribution was determined by the Barrett-Joyner-Halenda method (BJH) [28].

Water purification from contamination with As(V) com- pounds using natural clay minerals and iron-containing composites was studied in a wide range of concentrations. For the preparation of aqueous solutions of As(V), a standard solution of H₃AsO₄ (concentration 1000 mg/dm³) was used. All samples were prepared in distilled water with the addition of 1 M NaCl solution to create ionic strength (I=0.01). The pH of the aqueous systems was adjusted with a 0.1 M NaOH solution and the ionomers were monitored.

Sorption of As (V) by natural palygorskite and composite materials based on it was carried out under static conditions at room temperature. The volume of the aqueous phase was 50 cm³, the sorbent sample was 0.1 g. To establish the adsorption equilibrium, the samples were continuously shaken for 1 hour. After that, the aqueous phase was separated by centrifugation and the equilibrium metal concentration in it was determined by inductively coupled plasma atomic adsorption spectrometry (Thermo Scientific iCAP 7400 ICP-OES, USA).

The value of the sorption a (mg/g) was calculated by the formula:

\[ a = \frac{C_0 - C_e}{m}V, \]

where \( C_0, C_e \) – initial and equilibrium metal concentration, mg/dm³; \( V \) – volume of solution, dm³; \( m \) – sorbent sample weight.

### 6. Research results

Fig. 1 shows the IR spectra of the iron-containing silicate composite (PG-Fh) and natural palygorskite (PG). In the IR spectrum of the clay mineral, the main characteristic absorption bands of palygorskite are observed, cm⁻¹: 990 – oscillations of the Si-O-Si group and 910 – oscillations of the Si-O group [29]. After the modification with iron compounds in the IR spectra, bands are clearly pronounced at 883 cm⁻¹ and 1619 cm⁻¹, which correspond to asymmetric and symmetric stretching vibrations of Fe-O and OH groups to ferrihydrite, which are sorbed on the surface of the mineral [30].

![Fig. 1. Infrared spectra of the natural (PG) and modified palygorskite (PG-Fh)](image)

Nitrogen adsorption-desorption isotherms (Fig. 2) for both modified and natural palygorskite have a waveform that is inherent in layered silicates, and belong to type II isotherms in accordance with the IUPAC classification [31].

In the range of values \( p/p_0>0.4 \), distinct hysteresis loops are observed, which indicates the presence of a well-developed meso- and macropore structure characteristic of such samples. Table 1 shows the parameters of the porous structure of the samples (specific surface \( S \), m²/g, total pore volume \( V_p \), cm³/g, micropore volume \( V_m \), cm³/g, and pore size distribution \( r_1, r_2 \), nm). So, after carrying out the process of modifying palygorskite with ferrihydrite, the value of the specific surface increases and amounts to 275 m²/g, and the pore volume increased from 1.9 nm to 2.25 nm.

### Table 1

| Sample | \( S \), m²/g | \( V_p \), cm³/g | \( V_m \), cm³/g | BJH dV (r) |
|---|---|---|---|---|
| PG | 213 | 0.512 | 0.084 | 1.90 | 6.26 |
| Fh-Pg | 275 | 0.327 | 0.089 | 2.25 | 6.2 |
The process of extracting arsenic from water is affected by the shape of its location. In natural waters, As is mainly found in the form of inorganic forms $\text{As}^{3+}$ and $\text{As}^{5+}$, the ratio between which is determined by the redox potential of the medium and its pH value. $\text{As}^{5+}$ is the dominant form of arsenic in water, under oxidative conditions, and $\text{As}^{3+}$ is thermodynamically stable in a reducing environment. It is known that $\text{As}^{5+}$ is in the form of arsenate acid $\text{H}_3\text{AsO}_4$ and its anions $\text{H}_2\text{AsO}_4^-$ and $\text{HAsO}_4^{2-}$. The distribution of forms of arsenic(V) in waters depending on pH is shown in Fig. 3. The data presented indicate that, in a wide range of pH values, the solution of the compound $\text{As}^{5+}$ is predominantly negatively charged [32].

![Fig. 3. The distribution of the forms of arsenic(V) in the aquatic environment, depending on pH](image)

When studying the optimal conditions for carrying out sorption experiments, the establishment of the time of sorption equilibrium is of paramount importance. Therefore, the kinetics of As(V) sorption processes was studied by natural palygorskite, ferrihydrite, and iron-containing material. Fig. 4 shows the kinetic dependencies obtained at pH 6.

![Fig. 4. Kinetic dependences of As(V) sorption on natural palygorskite (PG), ferrihydrite (Fh) and iron-containing material (PG-Fh)](image)

Presented in Fig. 4 experimental data indicate that the process of removal of arsenic by sorption materials proceeds fairly quickly. In the first few minutes, most of the arsenates are sorbed, and after 1 hour of contact, the amount of adsorption remains almost unchanged. Therefore, in further studies, the duration of the sorption process was 1 h.

To determine the optimal conditions for the production of iron-containing silicate composites, the effect of the mass ratio of ferrihydrite (in terms of iron) to palygorskite on arsenic sorption from water was studied. Fig. 5 is a diagram of the dependence of As(V) sorption on the content of Fe(III) on the surface of a clay mineral. The data obtained indicate that with an increase in the content of (oxy)hydroxides iron hydroxides (III) in the composition of the composite, the arsenic sorption first increases, and after reaching the maximum value does not change. This is due to the full coverage of the surface of palygorskite with ferrihydrite.

![Fig. 5. Diagram of the dependence of the sorption of As(V) on the content of Fe(III) on the surface of a clay mineral](image)

So, the optimal ratio of ferrihydrite: clay mineral, at which there is a maximum sorption capacity under the given conditions of the experiment, is 0.1:1.

It is known that the pH of the aquatic environment affects the process of extracting metal ions by sorption materials. Fig. 6 shows the dependence of the amount of As(V) sorption by a ferrous silicate material on the pH of an aqueous solution. For comparison, the dependences on natural palygorskite and ferrihydrite are given. The obtained experimental data indicate that for composite sorbent and ferrihydrite the pH value does not affect the process of As(V) sorption in the range of 3–8, which is due to the physicochemical features of the surface of the obtained sorbent. Thus, during the treatment of iron-containing compounds with palygorskite surface compounds, a composite of reactivity is formed due to OH groups to ferrihydrite, with which arsenates can be bound both by ion exchange and complex formation.

![Fig. 6. Effect of pH on As(V) sorption by natural palygorskite (PG), ferrihydrite (Fh), and iron-containing material (PG-Fh)](image)
observed. In an acidic environment, the sorption of arsenic is insignificant (up to 0.02 mg/g), and with increasing pH it increases, reaches its maximum at pH 6±0.5 (0.05 mg/g) and then decreases in a slightly alkaline medium. This is due both to the distribution of the forms of arsenates in the aquatic environment, and the chemistry of the surface of palygorskite.

Fig. 7 shows the sorption isotherms of As(V) by a iron-containing composite material and natural palygorskite. The obtained data indicate that, when modifying the surface of the palygorskite, the iron oxyhydroxides sorption capacity of the obtained samples with respect to As(V) increases significantly. The maximum sorption rate of arsenic for a iron-containing sorbent is 7.8 mg/g, and for a natural mineral it is 0.2 mg/g. This is due to an increase in the number of active sites and the surface of the iron-containing composite after modification.

To assess the adsorption capacity of sorbents by arsenic compounds, the coefficients of the Langmuir and Freundlich equations are calculated (Table 2).

The obtained data indicate that the sorption of arsenic by both natural palygorskite and iron-containing silicate is better described by the Langmuir equation – the correlation coefficient $R^2$ is 0.97–0.99.

7. SWOT analysis of research results

**Strengths.** The main advantage of using iron-containing silicate materials based on natural clay minerals for purifying water from arsenic contamination is their environmental friendliness, low cost, accessibility and processability. Similar sorption materials are obtained using complex synthesis schemes and expensive chemical reagents, which significantly increases their cost.

Weaknesses. The use of high purity iron salts (III) as reagents in the process of obtaining a composite sorbent increases its cost.

Opportunities. A promising direction for further research is the development of granulation technology for the iron-containing silicate sorbent using and studying the possibility of replacing iron compounds (III) with cheaper analogues.

Threats. The presence on the market of highly effective sorption materials based on expensive, but widely used ion exchange resins, activated carbon, inorganic synthetic metal oxides creates a fairly strong competitive environment.

8. Conclusions

1. By treating the surface of the palygorskite oxyhydroxides of iron (III), iron-containing silicate materials are obtained and their structural sorption and properties are studied. It is shown that after applying the ferrihydrite layer on surface of the clay mineral, the specific surface of the modified sample increases from 213 m²/g to 275 m²/g and the pore size from 1.9 nm to 2.25 nm. The presence of iron oxyhydroxide (III) on the surface of palygorskite is confirmed by IR spectroscopy.

2. The physicochemical features of the removal of arsenic compounds from water using obtained iron-containing silicates are investigated. It has been established that the sorption capacity of the sorption materials obtained significantly exceeds that for the natural palygorskite. So, for arsenates, the maximum sorption rate of arsenic compounds by composite sorbents is 7.8 mg/g, and at the natural palygorskite ~ 0.2 mg/g, respectively. It is shown that the pH of the aqueous medium does not affect the process of sorption by iron-containing silicate sorbents in a wide range.

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