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DEVELOPMENT OF IRON-CONTAINING ADSORBENTS FOR FLUORIDE ION REMOVAL

Ingestion of too much fluoride ions through drinking water can seriously harm human health. Adsorption is one of the most effective approaches that have been proposed for removing fluoride ions from the aquatic environment. Analysis of modern publications shows that the search for new effective sorbents obtained by resource-saving technologies is an urgent scientific and practical problem. It is proposed to use sediments from groundwater deironing stations as sorbents. These sludges are formed in significant quantities and create significant environmental problems. Therefore, the object of the study is samples of agglomerated iron-containing adsorbents.

Two samples of sorbents with different iron contents were studied. The influence of various parameters on the efficiency of fluoride ion adsorption was analyzed: contact time, initial fluoride concentration and adsorbent dose, pH value of the initial solution, and the presence of competing ions.

The experimental data fit well with the pseudo-second-order kinetic model (coefficient of determination $R^2 = 0.8581$ for sample A03 and $R^2 = 0.9947$ for A06). The best correlation of the experimental data with the Langmuir model is the coefficient of determination $R^2 = 0.965$ for A03 and for A06 $R^2 = 0.970$. It was found that the maximum efficiency was achieved at pH 4. With an increase in the initial fluoride concentration, the sorption capacity increases, and the removal efficiency first increases and then decreases.

For the sorbent A03, the optimal dose is 5 g/dm^3, and for A06 – 6 g/dm^3. The study of the influence of foreign ions on the sorption of fluoride ions on the sorbent showed that all the studied ions to some extent worsen the defluoridation efficiency.

The use of the proposed sorbent will allow solving the following environmental issues: replenishing the list of cheap Ukrainian sorbents for fluoride removal and utilization of sludge from iron removal stations.

Keywords: *fluoride ion removal, iron, granular adsorbents, water treatment sludge, kinetic models, isotherms.*

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1. Introduction

Fluoride is a common element found in many minerals and rocks, and its widespread distribution and high concentration in groundwater pose serious risks. It is crucial for human health, as it is necessary for the formation of strong bones and tooth enamel when consumed in the right amounts. However, consuming too much fluoride can be harmful to humans and can potentially lead to diseases such as skeletal fluorosis, joint deformity, and dental caries. Water with a high fluoride content poses a serious threat to public health. Fluoride can cause heart failure by binding to free calcium in the body [1]. With the rapid development of industry, a large amount of wastewater containing fluoride is generated. Fluoride pollution has been recognized as a major problem worldwide [2]. The World Health Organization (WHO) states that the optimal range of fluoride concentration in drinking water is 0.5 ~ 1.5 mg/dm^3 [3].

Excess fluoride ions in natural water bodies are harmful to ecosystems because they accumulate in soils, plants and animal organisms. This can cause plant growth disorders, the death of aquatic organisms and a decrease in biodiversity.

Water pollution with fluoride occurs through the dissolution of minerals containing fluorides, such as fluorite (CaF_2), ($Ca_5(PO_4)_3F$), cryolite (Na_3AlF_6) [2] or through anthropogenic sources, especially the semiconductor industry, electroplating, glass, steel, cement, etc. [4].

Therefore, it is important to investigate methods for purifying water from fluoride ions to ensure its safety for human health and protect the environment from its harmful effects.

To date, many methods have been developed for the removal of fluoride from water, such as ion exchange, membrane processes, electrodialysis, precipitation and coagulation [5]. However, the disadvantages of most of these methods are high maintenance and operation costs, secondary pollution (toxic sludge is formed) and multi-stage. Among the various available methods, adsorption is probably the best due to its flexibility, cost-effectiveness, environmental friendliness, simple equipment design and ease of operation. Various adsorbents have been reported for fluoride removal, including activated alumina, carbon materials, activated clay, rare earth oxides, titanium-rich bauxites, zeolites and biomaterials.

In the natural environment, fluoride is strongly adsorbed on the surface of many aluminum-iron-containing minerals [6]. Therefore, aluminum oxide and iron hydroxide are natural sorbents for fluoride removal. At present, a large number of studies have been carried out in the world on the application of wastewater defluorination technology, and significant progress has been made in the field of defluorination. Up to now, the commonly used fluoride removal methods include precipitation, adsorption, electrochemical technology, membrane separation technology, etc. Among them, the principle and operation of the precipitation method are simple [7]. However, due to the addition of chemical agents, the cost increases, and the fluoride ion content in the water after fluoride removal exceeds the pollutant emission standards for the inorganic chemical industry. The electrochemical method has a high fluoride removal rate, but there are problems with high equipment installation and maintenance costs [8]. Membrane filtration allows achieving high quality wastewater treatment for fluoride removal, but the disadvantages are membrane fouling, high energy consumption and high cost [9].

The adsorption method is characterized by a wide range of different types of adsorbents, good selection performance, high speed and a small amount of polluting products [10], but the environment and its factors (pH, coexisting ions, temperature, adsorbent pore size, etc.) will significantly affect the results of fluoride removal.

The authors of [11] used spent coffee grounds and iron sludge to remove fluoride from water. Studies have shown that for a 62.92% reduction of fluoride at an initial concentration of 3 mg/dm^3, the optimal dose of iron sludge is 30 g/dm^3 with a contact time of 30 minutes. When using coffee grounds, the best conditions were a dose of 60 g/dm^3 with a mixing time of 60 min or 50 g/dm^3 with a mixing time of 90 min. The results obtained indicate that the dose of the sorbent has a greater effect on the efficiency of reducing the fluoride concentration than the contact time. The study found statistically significant differences between the average fluoride concentrations for coffee grounds and iron sludge, which indicates their potential as effective adsorbents for water purification from fluoride. The main advantage of these materials is their availability and environmental friendliness, as they are secondary products, which helps to reduce water treatment costs and minimize waste. However, iron sludge has a higher efficiency at a lower dose and shorter contact time compared to coffee grounds, which makes it more suitable for practical use. Coffee grounds require higher doses and longer contact times, which may limit its competitiveness compared to other sorbents.

The authors of [12] synthesized $LaFeO_3$ nanoparticles by the hydrothermal method. Studies have shown that different initial fluoride concentrations (from 15 to 40 mg/dm^3) and contact time (from 15 to 120 min) affect the efficiency of fluoride removal by nanoparticles at pH 5. The optimal conditions for fluoride adsorption were: fluorine concentration – 20 mg/dm^3, pH 5, $LaFeO_3$ dose – 0.9 g/dm^3, temperature – 308 K and contact time – 60 min. The main advantage of this sorbent is the ability to work in a wide pH range, which allows it to be adapted to different environments. In addition, the adsorption model, which corresponds to the Freundlich isotherm and pseudo-second-order kinetics, indicates reliable fluoride adsorption even at relatively high initial concentrations. However, the adsorption capacity of the monolayer of 2.575 mg/g is somewhat limited compared to other current sorbents. This may require higher doses to achieve the required level of purification in heavily polluted waters, which may reduce the economic attractiveness of this material.

Thus, the development of an effective adsorbent with high adsorption capacity and low production cost for defluorination remains a challenge and requires further study.

The main disadvantage of using many sorbents is their lack of availability and high cost. Therefore, the search and creation of new, cheaper, but effective sorption materials are an urgent task.

Of great practical interest is the use of water treatment waste, for example, iron removal sludge, as raw materials for the production of sorbents. Such waste is formed in large volumes during the purification of natural waters from iron. Every year, about 4 thousand tons of iron oxide sludge accumulates at facilities for the treatment of washing water from iron removal stations, which requires disposal [13]. About a third of the mass of this waste consists of iron-containing compounds, mainly oxides, hydroxides, salts of divalent and trivalent iron [14]. Therefore, research into the use of such waste as sorption materials is promising. Currently, such waste is not used at all. Disposal by landfill is not rational, due to a secondary environmental problem. A lot of sludge is formed, and new areas are needed that need to be recultivated. The dry sludge is characterized by increased dustiness and when overdried there is a risk of air pollution and dusting of large areas. Therefore, the processing of iron sludge into cheap sorbents will help solve two environmental issues: expanding the range of domestic sorbents and recycling sludge from iron removal stations.

The aim of research is to develop an effective and cheap sorbent for purifying water of various origins from fluoride ions. To achieve the goal, the following tasks have been set:

- to investigate the possibility of using a cheap sorbent based on iron-containing water treatment sludge for defluoridation of natural and wastewater;
- to experimentally investigate various adsorption parameters, such as contact time, initial fluoride concentration and adsorbent dose, pH value of the initial solution.

2. Materials and Methods

2.1. Characteristics of adsorbents

The object of research is the purification of water of various origins from fluoride ions by adsorption.

Two samples of agglomerated adsorbents with different iron contents were studied: A03 and A06. These adsorbents were obtained from iron-containing sludges of various water treatment plants. Adsorbent A03 was obtained from sludge of groundwater deironing, which consists mainly of iron hydroxide. Adsorbent A06 was obtained from sludge of a water treatment plant for acidic mine waters. This material is synthesized by microbial oxidation of divalent iron and is ferric oxyhydroxysulfate ($Fe_8O_8(OH)_x(SO_4)_y$). To obtain agglomerates, the initial sludge was dried, a binder was added, a plastic mass was formed in the form of disks, gradually heated to a temperature of 130°C, kept for an hour, cooled, crushed in a jaw crusher and dispersed on sieves. The composition of the obtained agglomerates is given in Table 1. The characteristics of the sorbents are given in Table 2.

Table 1

Composition of the studied adsorbent samples

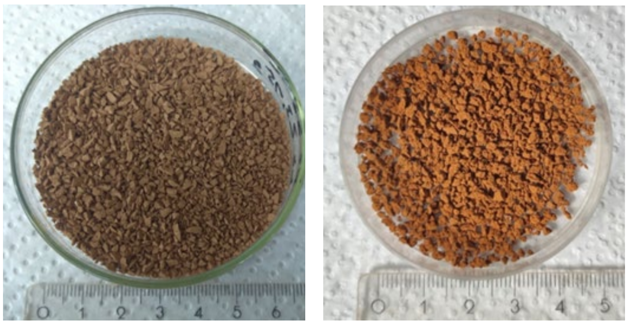
Components	A03, %	A06, %
Al_2O_3	0.51	0.02
As	0.001	0.009
Ba	0.055	< 0.001
CaO	21.3	0.14
Cl	0.04	0.01
Co	< 0.001	< 0.001
Cr_2O_3	0.002	< 0.001
Cu	< 0.001	< 0.001
Fe	26.56	48.41
K_2O	0.06	0.007
MgO	0.54	0.01
Mn	0.455	< 0.001
Na_2O	0.059	0.008
Ni	< 0.001	< 0.001
P	0.738	0.05
Pb	< 0.001	< 0.001
S	0.075	> 5.0
SiO_2	10.25	0.12
Sn	< 0.001	< 0.001
Sr	0.044	0.002
TiO_2	0.02	< 0.01
V	< 0.001	< 0.001
Zn	0.003	< 0.001
Zr	< 0.001	< 0.001

Table 2

Characteristics of the studied adsorbent samples

Parameter	Dimension	A03	A06
Bulk density	g/dm^3	0.52	0.54
Grain density (true)	g/dm^3	2.94	2.89
Porosity	%	82.4	81.3
Grain size	mm	0.5–2	0.5–2
Mechanical resistance	%	95	96
Specific surface area	m^2/g	36.3	58.0
Preferred pore diameter	nm	4.6	0.6
Moisture	%	7.2	5.1

Fig. 1 shows the appearance of the adsorbents.



a *b*

Fig. 1. Appearance of adsorbent samples: *a* – A03; *b* – A06

2.2. Adsorption studies

When conducting adsorption studies, model solutions of fluoride ions (NaF) in distilled water were used, which were prepared by dissolving the calculated amount of solid salt. Sorption of fluoride ions was studied under static conditions at room temperature. The sorbent sample was weighed in a beaker, added to 50 cm^3 of a solution with a known *F*-content in plastic sorption containers with a volume of 100 cm^3 and placed for shaking on a shaker with a water bath ELPAN Water bath shaker 357 (Poland). Rotation frequency – 150 rpm. After the sorption process was completed, the sorbent was separated from the solution and the residual fluoride ion content in the filtrate was determined on an AI-125 ionometer (Ukraine) using a fluoride selective electrode. 50 cm^3 of the solution under study was taken into a 100 cm^3 chemical beaker, 10 cm^3 of the solution was added to maintain a constant ionic strength. After that, the beaker was placed on a magnetic stirrer, and the ionometer electrodes were immersed in the solution. After 2–3 min, the fluoride ion concentration was recorded.

The amount of adsorbed fluoride was calculated as the average value of three parallel experiments.

The removal efficiency (q, %) and sorption capacity (a, mg F^-/g) were calculated using formulas (1) and (2)

$$q=\frac{C_0-C_e}{C_0}\cdot 100\%, \tag{1}$$

where C_0 – the initial concentration of fluoride ions, mg/dm^3; C_e – the equilibrium concentration of fluoride ions after adsorption, mg/dm^3

$$a=\frac{\left(C_0-C_e\right)\cdot V}{m}, \tag{2}$$

where C_0 – the initial concentration of fluoride ions, mg/dm^3; C_e – the equilibrium concentration of fluoride ions after adsorption, mg/dm^3; V – the volume of fluoride solution, dm^3; m – the adsorbent mass, g.

The Langmuir adsorption model quantitatively describes the formation of a monolayer of adsorbate on the surface of the sorbent and assumes the equality of energy of the entire surface of the sorbent. Based on the above assumptions, the Langmuir adsorption model is described by the equation

$$a_e=\frac{a_m\cdot K_L\cdot C_e}{1+K_L\cdot C_e}, \tag{3}$$

where a_e – the equilibrium adsorption, mg/g; a_m – the maximum adsorption capacity of the monolayer, mg/g; K_L – the Langmuir isotherm constant, dm^3/mg; C_e – the equilibrium concentration of the adsorbate, mg/dm^3.

To describe adsorption on a heterogeneous surface, the Freundlich model was used. According to this model, adsorption centers had different values of the interaction energy with the adsorbate. That is, adsorption centers with higher energy were saturated first. Equation of the Freundlich adsorption model

$$a_e=K_F+C_e^n, \tag{4}$$

where a_e – the equilibrium adsorption, mg/g; K_F – the Freundlich isotherm constant, mg/g; C_e – the equilibrium concentration of the adsorbate, mg/dm^3; n – the adsorption intensity parameter characterizing the interaction between the adsorbent and the adsorbate.

The Tiomkin adsorption model, taking into account the interaction between the adsorbent and the adsorbate, assumes a linear inversely proportional relationship between the heat of adsorption of adsorbate molecules and the degree of filling of the adsorbent surface. The equation of the Tiomkin adsorption model has the form

$$a_e=B\cdot\ln(K_T\cdot C_e), \tag{5}$$

where a_e – the equilibrium adsorption, mg/g; B – the heat constant of adsorption, J/mol; $B=RT/b$, R – the universal gas constant, 8.314 J/(mol·K); T – the temperature, K; b – the Tiomkin constant; K_T – the equilibrium constant of the adsorption interaction, dm^3/g; C_e – the equilibrium concentration of the adsorbate, mg/dm^3.

2.3. Kinetic studies

Studies of the kinetics of sorption by sorbent samples were performed similarly to the adsorption studies described in section 2.2. With the difference that the sorption containers were shaken for different periods of time. The residual concentration of fluoride ions was determined in each sample. The duration of sorption was increased to a constant value of the residual concentration of fluorides, which indicated that equilibrium had been achieved.

Modeling of kinetic processes is necessary to understand the mechanism of interaction between the sorbent and the sorbate. Analysis of experimental kinetic curves using pseudo-first and pseudo-second order models allows not only to quantitatively describe the rate of sorption, but also to determine its nature. Thus, if the pseudo-first order model better describes the process, this may indicate the predominance of physical adsorption mechanisms, such as weak van der Waals interactions. While the pseudo-second-order model fits more often indicate chemical sorption, involving ion exchange or the formation of chemical bonds between the sorbent and the sorbate.

The mathematical description of the pseudo-first-order model is as follows

$$\log\left(a_e-a_t\right)=\log a_e-\frac{k_1}{2.303}\cdot t, \tag{6}$$

where a_e – the equilibrium amount of the sorbed substance, mg/g; a_t – the amount of the substance sorbed at time t, mg/g; k_1 – the first-order sorption rate constant, min^{-1}; t – time, min.

The pseudo-second-order model is described by the equation

$$\frac{t}{a_t} = \frac{1}{k_2 \cdot a_e^2} + \frac{t}{a_e}, \tag{7}$$

where a_t – the amount of the substance sorbed at time t, mg/g; a_e – the equilibrium amount of the sorbed substance, mg/g; k_2 – the second-order sorption rate constant, g/(mg min); t – time, min.

The simulation makes it possible to calculate kinetic parameters such as rate constants and the equilibrium amount of the sorbed substance. These data allow to compare the effectiveness of different sorbents depending on the sorption conditions.

2.4. Study of the effect of the initial concentration of fluoride ions

To assess the effect of the initial concentration of fluoride ions on the efficiency of removal from aqueous solutions, a series of sorption experiments was conducted with different initial concentrations of NaF: 5, 10, 15 and 20 mg/dm^3.

In all experiments, the dose of sorbents was 6 g/dm^3. The pH value of the initial solutions was adjusted to 4. The experiments were carried out at a temperature of 20°C for 3 hours for A03, and 1.5 hours for A06. After the contact time, the solutions were filtered, and the residual content of fluoride ions was determined according to the method given in 2.2.

2.5. Study of the pH effect of the initial solution

To study the effect of the pH value on the sorption efficiency of fluoride ions, a series of experiments were conducted with varying the pH of the medium from 4 to 8 with a step of pH unit. In each experiment, an aqueous solution of NaF with an initial concentration of 10^{-3} mol/dm^3 was used.

The sorbent dose was 6 g/dm^3. The volume of NaF solution added to each sample was the same and was 50 cm^3. Before the start of sorption, the pH value in the solutions was set and adjusted using 0.1 M HCl and NaOH solutions. The experiments were carried out at a temperature of 20°C for 3 hours for A03, and 1.5 hours for A06. Upon completion of the experiment, the sorbent was separated from the solution by filtration and the residual concentration of fluoride ions was determined according to the method given in 2.2.

2.6. Effect of sorbent dose

To determine the effect of sorbent dose on the efficiency of fluoride ion removal from aqueous solution, a series of experiments were conducted with varying sorbent doses from 2 to 10 g/dm^3. The initial concentration of fluoride ions (NaF) in the solution was 15 mg/dm^3. The pH value of the initial solution was adjusted to 4. The experiments were carried out for 3 hours on a laboratory shaker.

Upon completion of the experiment, the sorbent was separated from the solution by filtration, and the residual concentration of fluoride ions was determined according to the method given in 2.2.

2.7. Influence of foreign ions

The influence of foreign ions on the adsorption value was studied.

The study was carried out using doses of sorbent A03 – 2 g/dm^3, A06 – 6 g/dm^3. The concentration of the NaF solution was 10^{-3} M, and the pH of the initial solution for A03 was 4, and for A06 – 6. Nitrate, chloride, carbonate, sulfate, phosphate, potassium bicarbonate was used as foreign ions. Different concentrations of these ions were investigated: 10 mg/dm^3, 20 mg/dm^3, 30 mg/dm^3.

3. Results and Discussion

3.1. Adsorption kinetics and modeling. Experiments on adsorption kinetics

The pseudo-first-order kinetic model is simple and widely used [15]. It assumes that sorption is irreversible and occurs only at localized sites without interactions between adsorbed ions. Moreover, the adsorption energy is independent of the surface coverage, and the maximum adsorption corresponds to a saturated monolayer of adsorbate on the adsorbent surface. The adsorbate concentration is assumed to be constant, and the uptake by the adsorbent is governed by a first-order rate equation. Pseudo-first-order reactions are second-order reactions that behave like first-order reactions. This type of reaction occurs when one reactant is present in a large excess concentration relative to the other reactants; thus, it appears to be at a constant concentration compared to the concentrations of the other substances [16].

In pseudo-second-order, the reaction rate depends on the amount of solvent adsorbed on the adsorbent surface and the equilibrium amount of adsorption. The pseudo-second-order kinetic model is based on similar assumptions. As for the pseudo-first-order model, the only difference is that the absorption of ions on the adsorbent is governed by a second-order rate equation. The adsorption rate is proportional to the square of the number of unoccupied surface areas; moreover, the number of occupied areas is proportional to the concentration of the adsorbate. The pseudo-second-order model (also known as the Lagergren model) has been widely used in recent years for the adsorption of pollutants from aqueous solutions [15]. The kinetic dependence of the removal of fluoride ions on adsorbent samples is shown in Fig. 2, 3.

The obtained data were analyzed for compliance with the pseudo-first order (3) and pseudo-second order (4) kinetic models.

The results of data processing for sorbent A03 are presented in Fig. 4, 5, and for A06 in Fig. 6, 7. The calculated values of the model parameters are given in Table 3.

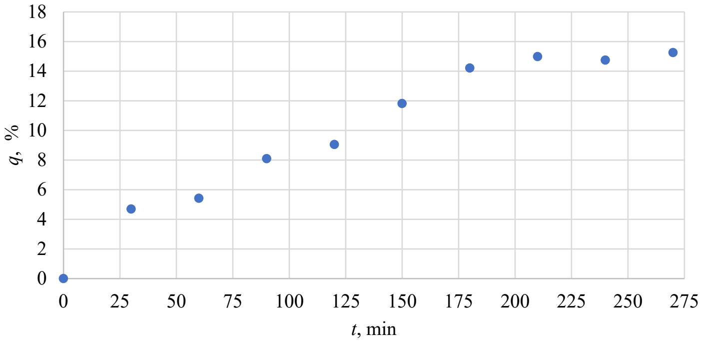


Fig. 2. Kinetic dependence of fluoride ion removal on adsorbent A03

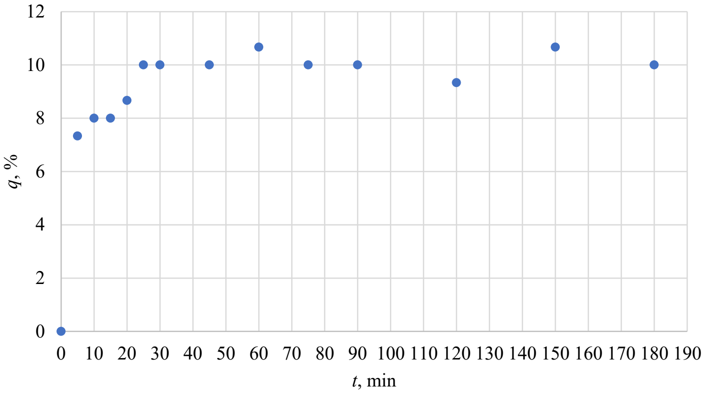


Fig. 3. Kinetic dependence of fluoride ion removal on sorbent A06

Comparison of the R^2 coefficients of both models showed that the pseudo-second-order model best describes the experimental data. This indicates that the sorption proceeds according to the mechanism of chemical adsorption, which includes the exchange or binding of the sorbate with the active centers of the sorbent.

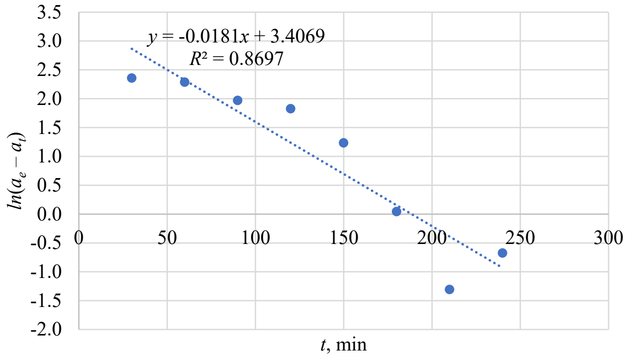


Fig. 4. Result of processing the kinetic curve according to the pseudo-first order model for sorbent A03

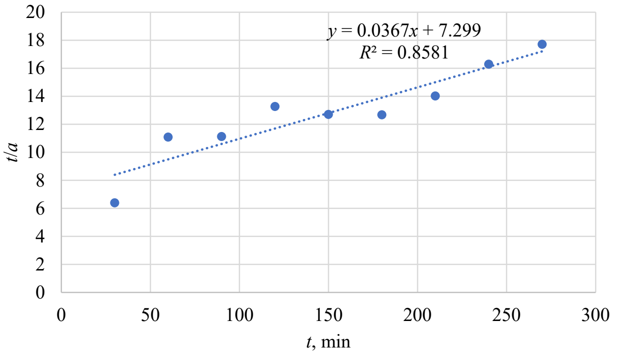


Fig. 5. Result of processing the kinetic curve using the pseudo-second-order model for sorbent A03

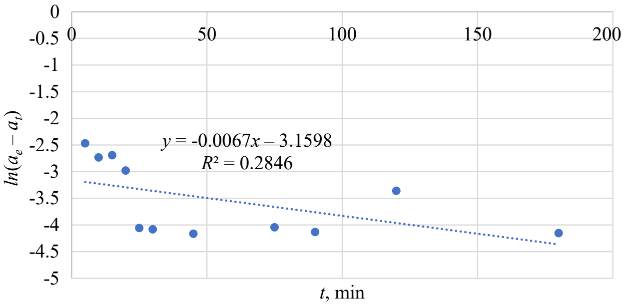


Fig. 6. Result of processing the kinetic curve using the pseudo-first-order model for sorbent A06

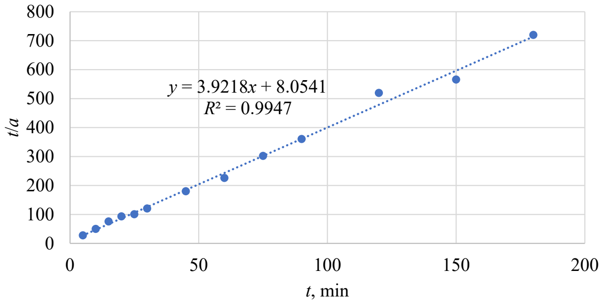


Fig. 7. Result of processing the kinetic curve using the pseudo-second-order model for sorbent A06

Table 3

Comparison of calculation results using the pseudo-first and pseudo-second-order models

Model	Equation	Model parameters	Sorbents	
			A03	A06
Pseudo-first-order model	$\log(a_e - a_t) = \log a_e - \frac{k_1}{2.303} \cdot t$	k_1, min^{-1}	0.0417	–
		a_m, mg/g	30.17	–
		R^2	0.8697	0.2846
Pseudo-second-order model	$\frac{t}{a_t} = \frac{1}{k_2 \cdot a_e^2} + \frac{t}{a_e}$	k_2, g/(mg·min)	0.00018	8.0541
		a_m, mg/g	27.25	0.1242
		R^2	0.8581	0.9947

3.2. Results of isothermal experiments and processing of isotherms

Adsorption isotherms are used to understand the mechanism of the adsorption process and to quantitatively assess the distribution of the adsorbate between the liquid phase and the solid adsorbent under conditions of equilibrium and constant temperature [17].

To construct the isotherm for the sorbent A03 and A06, solutions of NaF concentrations in the range of 10^{-3}–10^{-4} M were used. The dose of the sorbent A03 is 2 g/dm^3, pH – 4. The temperature at which the sorption was carried out was 13°C. For sorbent A06, the dose was 6 g/dm^3, and the pH was 6. The obtained isotherms are presented in Fig. 8, 9.

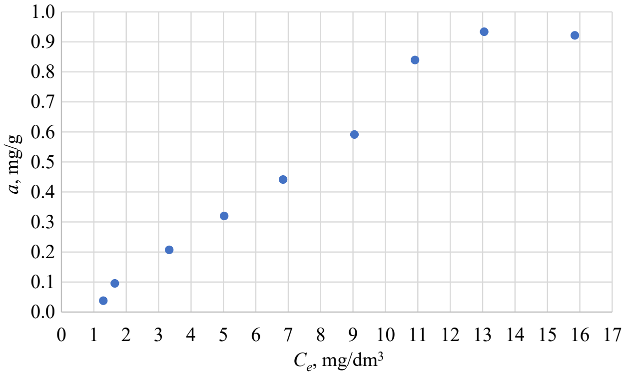


Fig. 8. Isotherm of fluoride ion sorption on sorbent A03

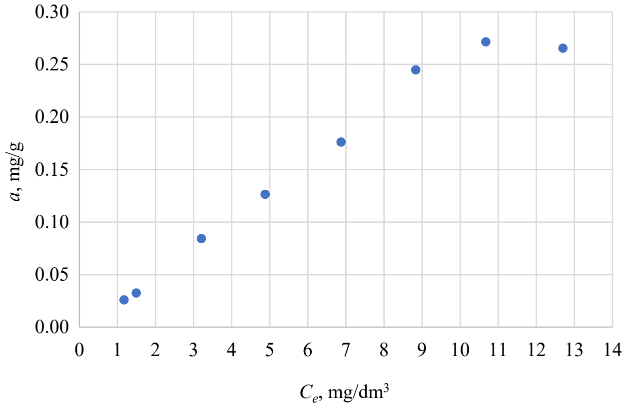


Fig. 9. Isotherm of fluoride ion sorption on sorbent A06

The adsorption isotherms obtained under experimental conditions were processed using the OriginPro software. The results of calculations using the Langmuir, Freundlich, and Tiomkin models for adsorbents A03 and A06 are presented in Fig. 10, 11, respectively. The calculated parameters of the models are given in Table 4.

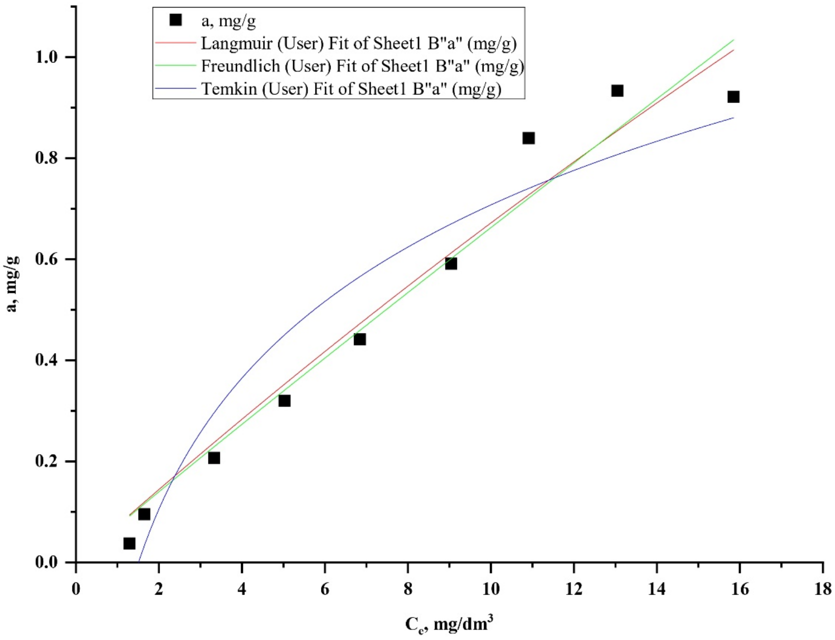


Fig. 10. Results of calculations using the Langmuir, Freundlich, and Tiomkin models for sorbent A03

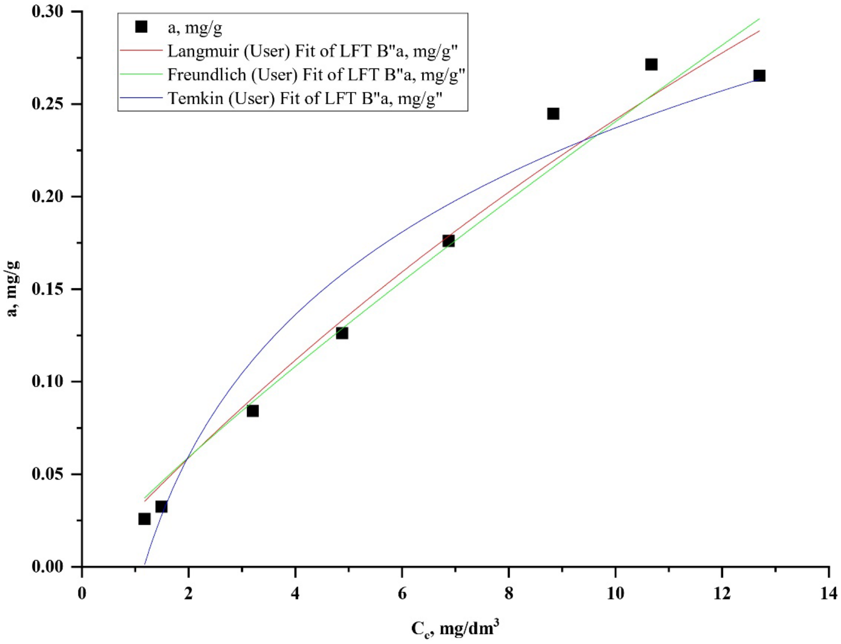


Fig. 11. Results of calculations using the Langmuir, Freundlich, and Tiomkin models for sorbent A06

Table 4

Parameters of fluoride ion sorption isotherms on iron-containing adsorbents

Model	Equation	Model parameters	Sorbents	
			A03	A06
Langmuir	$a_e = \frac{a_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e}$	R^2	0.965	0.970
		a_m, mg/g	7.84	1.0814
		K_L, dm^3/mg	0.00937	0.02879
Freundlich	$a_e = K_F + C_e^n$	R^2	0.9622	0.9601
		B	0.07154	0.03237
		N	1.034	1.148
Tiomkin	$a_e = B \cdot \ln(K_T \cdot C_e)$	R^2	0.912	0.9352
		B, J/mol	0.3742	0.1101
		K_T, dm^3/g	0.6627	0.8614

The best correlation of experimental data with the Langmuir model is the coefficient of determination $R^2 = 0.965$ for A03 and for A06 $R^2 = 0.970$. Adsorption on the studied sorbents is monolayer on a homogeneous surface.

3.3. The influence of the initial concentration of the solution on the sorption of fluoride ions

The results of the study for sorbents A03 and A06 are presented in Fig. 12, 13. As can be seen, with an increase in the initial concentration, the sorption capacity increases, and the removal efficiency first increases and then decreases. An increase in the initial concentration of *F* led to a corresponding increase in the adsorption capacity [18].

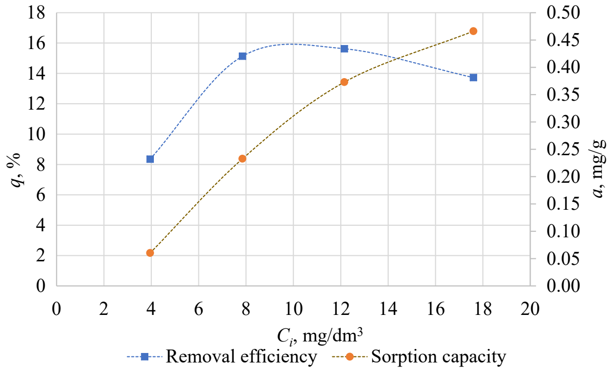


Fig. 12. Effect of initial concentration on the adsorption of fluoride ions on sorbent A03

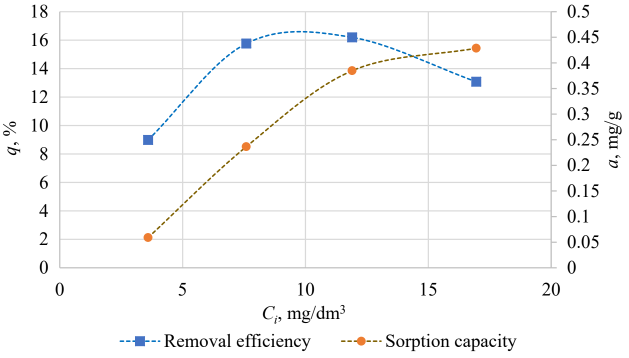


Fig. 13. Effect of initial concentration on the adsorption of fluoride ions on sorbent A06

3.4. Effect of pH of the initial solution on the sorption of fluoride ions

Determination of the pH value is a fundamental step, since it controls the entire process of chemical defluorination [18, 19]. pH affects the solid/liquid interface, changing surface charges and functional groups, modifying surface properties and active centers of adsorbents. Moreover, most adsorbents used for F^- removal are used only in narrow pH ranges [20].

The results of the study of the effect of pH of the initial solution for sorbents are presented in Fig. 14, 15. As can be seen from the graph, with increasing pH, the sorption capacity and removal efficiency decrease. For A03 by 5%, and for A06 by almost 10%. For sample A03, the efficiency is higher at pH 4. And for A06 at pH 5. The value of pH < 4 was not considered due to the presence of weakly ionized HF. When pH was increased to 8, a decrease in F^- adsorption was observed, which is associated with competition between OH^- and F^- for adsorption sites. At higher pH, the negative charge of the solution leads to repulsion between negatively charged adsorbents and F^- ions. Competition with OH^- ions further reduces adsorption. Therefore, when choosing an adsorbent for fluoride removal, it is necessary to consider the pH of the source water, and optimization of pH during purification is crucial for maximum efficiency. The authors of [19] showed the effect of pH (in the range from 2 to 11) on the adsorption of F^- on crystalline titanium dioxide (TiO_2) powder. The maximum F^- absorption was observed at acidic pH (pH 2) with an adsorption capacity of approximately 0.2 mg/g. The adsorption capacity decreased to 0.16 mg/g at pH 7, to 0.14 mg/g at pH 9 and was only 0.02 mg/g at pH 11. The decrease in the F^- content in the alkaline solution was attributed to the competition between hydroxyl groups and F^- ions for active sites on the adsorbent. On the other hand, positively charged surface sites in the acidic solution increased the F^- absorption. In our experiments, for pH values close to natural waters, the sorption capacity was higher and amounted to 0.5 mg/g.

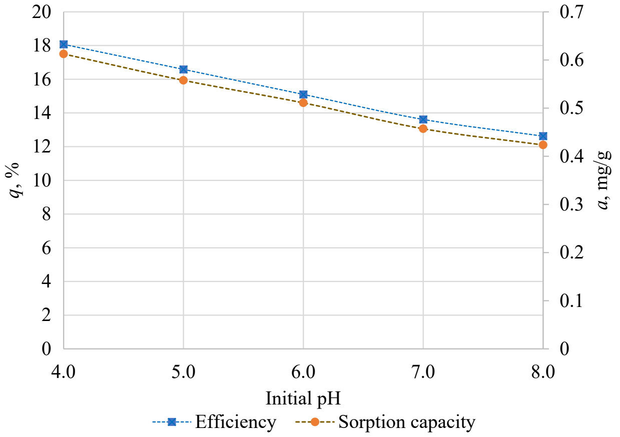


Fig. 14. Effect of initial pH on fluoride ion adsorption on sorbent A03

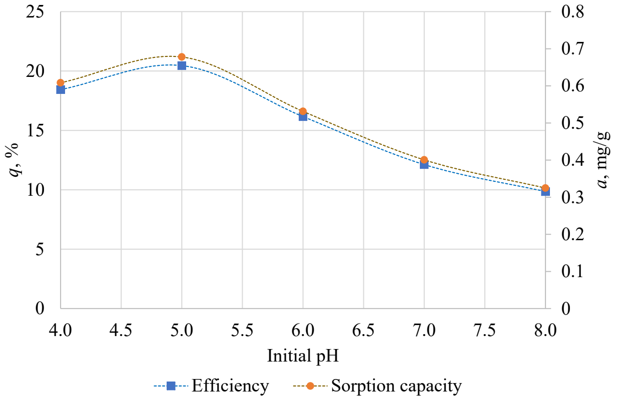


Fig. 15. Effect of initial pH on fluoride ion adsorption on sorbent A06

3.5. Effect of sorbent dose

One of the key parameters affecting the efficiency of the sorption process is the dose of sorbent introduced into the system. Changing the amount of sorbent allows to adjust the available number of active centers on its surface, which, in turn, affects the degree of fluoride ion removal from the solution. The optimal concentration of adsorbent material for fluoride removal depends on several factors, including the nature of the adsorbent, the initial fluoride concentration in water, and the desired level of fluoride removal. Increased doses of adsorbent can increase the number of active adsorption sites and expand the available surface area for fluoride adsorption. However, a very high concentration of the adsorbent can lead to the overflow of the adsorption centers, which will lead to a decrease in efficiency due to limited mass transfer. In addition, the economic aspect plays a decisive role, since the cost of the adsorbed material can impose restrictions on determining the optimal dose.

According to the literature [21], a stable trend is revealed. Regardless of the specific type of adsorbent, an increase in the amount of adsorbent leads to a greater availability of active participants for the binding of fluoride ions. However, there is a critical limit beyond which a further increase in the mass of the sorbent leads to a decrease in capacity. Beyond this point, the initial adsorbent does not contribute to an increase in the efficiency of use per unit mass, and the adsorption capacity begins to decrease. This decrease is explained by a decrease in the residual concentration of fluorides, which leads to a deterioration in the efficiency of the sorbent.

To establish the optimal dose of sorbent A03 and A06, a graph of the dependence of the efficiency of fluoride ion removal and sorption capacity on the dose of the sorbent was constructed. The intersection point of the graph and will be the optimal dose of the sorbent.

The obtained dependences are presented in Fig. 16 and 17 for A03 and A06, respectively.

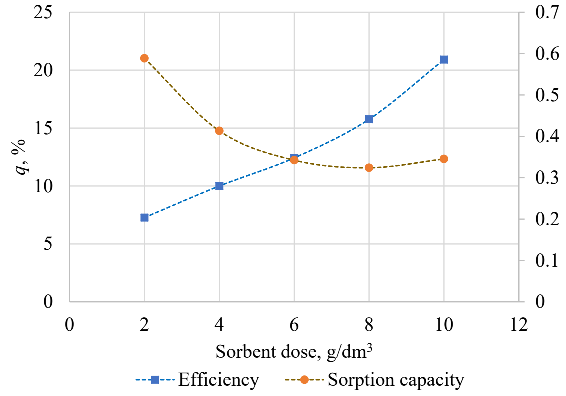


Fig. 16. Effect of the dose of sorbent A03 on the sorption of fluoride ions

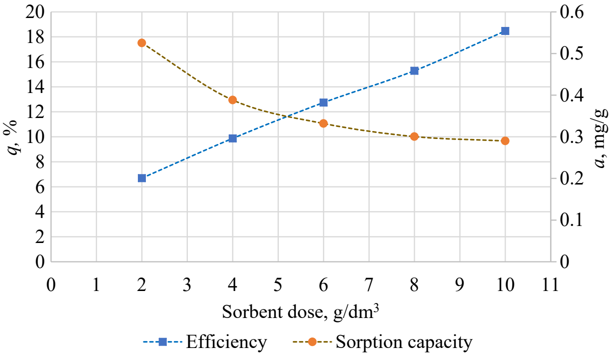


Fig. 17. Effect of the dose of sorbent A06 on the sorption of fluoride ions

According to Fig. 16, 17, for the sorbent A03 the optimal dose is 6 g/dm^3, and for A06 – 5 g/dm^3. Increasing the amount of adsorbent provides a sufficient number of surface-active centers for the adsorption of fluoride ions in aqueous solution. When the amount of adsorbent is high, the residual concentration of fluorine in aqueous solution is low.

3.6. Effect of foreign ions on the sorption of fluoride ions

Foreign ions can compete with fluoride ions for adsorption sites on the surface of the adsorbed material, reducing the overall efficiency of fluoride removal. The degree of competition in the adsorption process depends on the concentration and chemical characteristics of the ions. Natural water contains anions such as chlorides, nitrates, sulfates, bicarbonates, carbonates and phosphates, as well as metal cations. These ions can compete for adsorption sites and form stable complexes with F^-. In addition, other ions, such as bicarbonate and carbonate, can form complexes with the surface of the adsorbent material. This interaction reduces the number of active adsorption sites available for fluoride adsorption [22]. Therefore, the effect of such ions depends on the concentration and type of chemicals, as well as on the nature of the adsorbent material.

The study of the effect of foreign ions on the sorption of fluoride ions on the sorbent A03 and A06 showed that all the studied ions to some extent affect the efficiency of the process, except for nitrate ions, which in small concentrations improved the adsorption of fluoride ions on the sorbent A03. The results of the effect of foreign ions on the sorption of fluoride ions for sorbents A03 and A06 are shown in Fig. 18, 19, respectively. It is noticeable that the phosphate ion on the sorbent A06 (Fig. 19) had the greatest negative effect, which indicates that the active center of the sorbent can preferentially absorb it instead of fluorine. This is confirmed by the work of other researchers, for example, [13], where the sorption properties of similar sorbents were studied specifically in relation to phosphate ions. High removal levels were obtained. Therefore, the decrease in fluoride sorption in the presence of phosphates is natural and predictable.

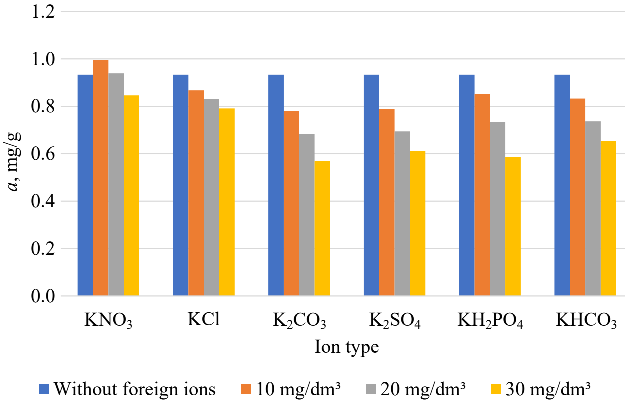


Fig. 18. Effect of foreign ions on the sorption of fluoride ions on sorbent A03

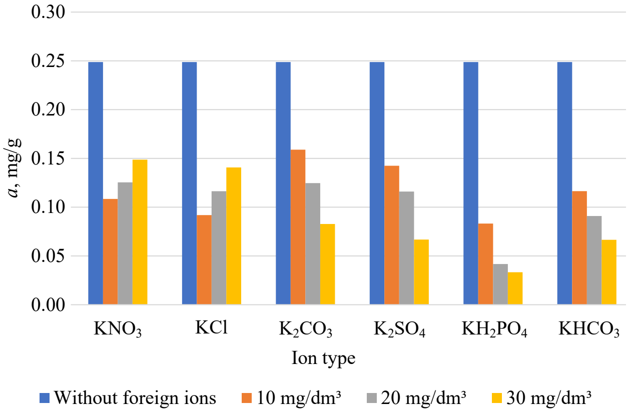


Fig. 19. Effect of foreign ions on the sorption of fluoride ions on sorbent A06

The series of the influence force on the sorption capacity of A03 for a given initial concentration of competing ions:

10 mg/dm^3: $CO_3^{2-} > SO_4^{2-} > HCO_3^- > H_2PO_4^- > Cl^- > NO_3^-$;
20 mg/dm^3: $CO_3^{2-} > SO_4^{2-} > H_2PO_4^- > HCO_3^- > Cl^- > NO_3^-$;
30 mg/dm^3: $CO_3^{2-} > H_2PO_4^- > SO_4^{2-} > HCO_3^- > Cl^- > NO_3^-$.

Similarly, the series of the influence force on the sorption capacity of A06:

10 mg/dm^3: $H_2PO_4^- > Cl^- > NO_3^- > HCO_3^- > SO_4^{2-} > CO_3^{2-}$;
20 mg/dm^3: $H_2PO_4^- > HCO_3^- > SO_4^{2-} > Cl^- > CO_3^{2-} > NO^{3-}$;
30 mg/dm^3: $H_2PO_4^- > HCO_3^- > SO_4^{2-} > CO_3^{2-} > Cl^- > NO^{3-}$.

The obtained data are well correlate with the results of other researchers. Thus, the authors of [23] confirm that the effect of bicarbonate can be explained by the fact that conjugate bases of weak acids produce more hydroxyl ions, which compete with F^- for the adsorption site. In [24] it is noted that the decrease in the adsorption capacity of F^- with increasing bicarbonate concentration occurs due to an increase in pH in the solution.

It is known that phosphate is strongly adsorbed on high-valent metal oxides and hydroxides by specific adsorption (complexation in the inner sphere) [20]. Therefore, it is able to easily compete with F, which is also specifically adsorbed [25]. Nitrate and chloride are nonspecifically adsorbed (complexation in the outer sphere) on metal oxides and therefore are not able to compete well with fluoride ion at equal concentrations. Sulfate, on the other hand, can be adsorbed specifically and nonspecifically, and therefore it competed with fluoride better than chloride and nitrate, but weaker than phosphate [26].

The nature of the order of anion competition is similar to that reported by others [27, 28]. The ratio of anion concentrations in natural water and wastewater is very different and therefore such ratios must be taken into account when assessing the degree of competition.

The presented study has some limitations. First of all, it is the use of model solutions to determine the efficiency of fluoride ion removal. Because natural and wastewater contain many different ions and substances that will affect the course of the adsorption process. In addition, the study of adsorption under static conditions provides a lot of valuable information on the influence of basic process parameters, equilibrium and kinetic dependencies on the adsorption of fluoride ions, but for the practical implementation of the proposed adsorbents, studies under dynamic conditions are necessary. This mode is more similar to the practical application of adsorbents and provides the necessary data for the design of adsorption filters. Such experiments can be a future development of this research. In addition, it is advisable to investigate the regeneration of the proposed sorbents and their modification to improve their sorption properties.

4. Conclusions

The sorption removal of fluoride ions on iron-containing granular sorbents was investigated. The influence of various parameters on the efficiency of fluoride ion adsorption was analyzed: contact time, initial fluoride concentration and adsorbent dose, pH value of the initial solution, presence of competing ions.

The obtained experimental data correspond well to the pseudo-second-order kinetic model (coefficient of determination $R^2=0.8581$ for sample A03 and $R^2=0.9947$ for A06). The best correlation of the experimental data was obtained with the Langmuir model – coefficient of determination $R^2=0.965$ for A03 and for A06 $R^2=0.970$. It was found that the maximum efficiency was achieved at pH 4. With an increase in the initial fluoride concentration, the sorption capacity increases, and the removal efficiency first increases and then decreases. For sorbent A03, the optimal dose is 5 g/dm^3, and for A06 – 6 g/dm^3. The study of the influence of foreign ions on the sorption of fluoride ions on the sorbent showed that all the studied ions to some extent worsen the efficiency of defluoridation.

The studied sorbents were obtained from waste – water treatment sludge. These sludges are formed in significant quantities and create significant environmental problems. Although the capacity and efficiency of iron-containing sorbents are inferior to known industrial samples, they have prospects for use in defluoridation of natural and wastewater.

Conflict of interest

The authors declare that they have no conflict of interest regarding this research, including financial, personal, authorship or other, which could affect the research and its results presented in this article.

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Data availability

Data will be provided upon reasonable request.

Use of artificial intelligence

The authors used artificial intelligence technologies within the permissible framework to provide their own verified data, which is described in the research methodology section.

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