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INVESTIGATION OF THE PROCESS OF FLUORIDE IONS ADSORPTION BY NATURAL SORBENTS

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Abstract. A detailed analysis of literature sources on the content of fluorides in the environment, methods of conditioning and defluoridation of water was held. The mechanism of interaction of fluorides with zeolite in the process of adsorption treatment of wastewaters and domestic waters was clarified. It was first established that in the process of adsorption there is the formation of magnesium fluoride compounds due to the binding of cations extracted from the zeolite by the mechanism of ion exchange. The mechanism of chemisorption of fluoride ions by the formation of insoluble CaF_2 was also proved. According to the results of experimental research, a technological scheme has been developed, which provides the preliminary treatment of fluoride ions in the form of complexes with aluminium. In order to prevent the permeation of aluminium fluoride into the treated water, a stage of adsorption water purification was proposed. Calculations of the amount of reagent necessary to ensure the required degree of purification of water from fluoride ions were done. The statistical parameters of the process and the significance of the obtained results were calculated. The coefficient of determination of experimental data was 0.87…0.99, the standard deviation was 0.017…0.026.

Keywords: adsorption, fluorides, sorbents, wastewaters, reagent treatment.

1. Introduction

Despite numerous surface water sources for water supply, some settlements are forced to use groundwater, the quality of which according to the main standardized indicators meets sanitary requirements except for the presence of high concentrations of fluoride (Mahmoudi et al., 2019; He et al., 2019). According to medical studies, the use of water with a fluoride concentration of more than 1.5 mg/l by the population causes dental fluorosis, which manifests itself in darkening and destruction of enamel, as well as bone fluorosis and a number of chronic diseases associated with metabolic disorders, cardiovascular, digestive and nervous systems. Therefore, a necessary condition for the use of such water is its defluoridation with subsequent maintenance of optimal residual concentrations of fluorine at the level of MPC (0.7–1.2 mg/l) (Maity et al., 2018; Kang et al., 2017). Various methods are used to remove fluoride compounds. Modern membrane technologies retain at the molecular and ionic levels such contaminants as ions of calcium, magnesium, iron, fluorides and others. However, in some industries, there are special requirements for water quality, which is sometimes impossible to meet using reverse osmosis or nanofiltration (Maity et al.). The difficulty is that the membranes retain different ions in proportion to the selectivity of the membranes. The most available method for removing fluoride ion contaminants is adsorption and ion exchange. Carbon sorbents (He i et al., 2019; Borgohain et al., 2020), zeolites (Maity et al., 2018; Saha, 1993), nanocomposites based on chitosan (Kang et al., 2017), etc. are used to extract fluorides from drinking water.

Since in Ukraine there are areas with high fluoride content in water – Sosnivka, Toporov (Ukraine, Lviv region), etc., there is a practical need to conduct research to intensify methods of water defluoridation to

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choose not only technically feasible but also cost-effective method of groundwater defluoridation with a high concentration of fluoride (Sabadash, 2019).

Most technologies are not widely used in our country due to the lack of quality materials, significant reagent costs, complexity of equipment operation and the multi-stage process) (Hyvlud et al., 2019; Srivastav et al., 2013). Existing defluoridation methods are ineffective and do not provide the required quality of drinking water.

There are also no data on the utilization and disposal of fluoride-containing waste (Tor, 2006; Bazrafshan et al., 2016). One of the ways to prevent environmental pollution by wastewater containing fluorides is the need to develop and implement effective and at the same time inexpensive in the implementation and operation treatment technologies, which include the adsorption method of wastewater treatment from fluoride ions using natural sorbents (Çengeloğlu et al., 2002; Sabadash et al., 2017; Sabadash, 2013).

Problem statement. To investigate the sorption capacity of zeolite in relation to fluorides, to improve the technology of groundwater defluoridation at high fluoride content and environmentally safe disposal of fluoride-containing sludge. To identify the influence of the main technological characteristics and parameters of the process of reagent defluoridation of water on the efficiency of fluoride removal.

2. Experimental researches

Sorbent characteristics

To purify water from these components, we used a natural mineral sorbent – clinoptilolite of the Sokyrnytsky deposit from the Transcarpathian region.

To determine the adsorption capacity of zeolite relative to fluoride ions, in glass flasks, we measured 200 cm^3 of sodium fluoride solution prepared in distilled water of different initial concentrations (C_{in} = 0.01–0.2 g/dm^3) and added the same samples of zeolite (~1 g). The flasks were sealed and left with periodic stirring for 48 h at 20 °C. The sorbent was separated from the solution, which was analyzed for sodium and fluoride ions by potentiometric method according to known methods (Sabadash et al., 2017; Sabadash, 2013).

3. Results and their interpretation

Experimental study of the adsorption of fluoride ions by zeolite – clinoptilolite of the Sokyrnytsky deposit was carried out under static conditions from sodium fluoride solutions.

The experimentally obtained isotherm of adsorption of sodium fluoride on zeolite is presented in Fig. 1.

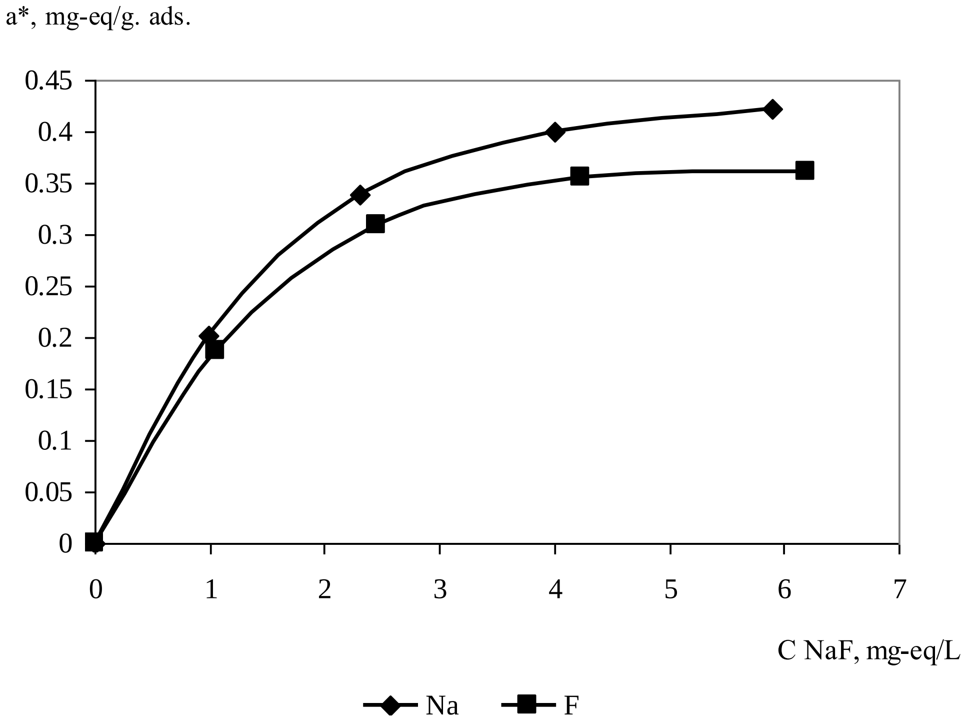

Fig. 1. Isotherms of NaF adsorption on clinoptilolite of Sokyrnytsky deposit

Experimental data shown in Fig. 1 indicate a significant adsorption of sodium – up to 0.01 g/g ads. due to the replacement of sodium by exchangeable cations of zeolite. The deviation of theoretical and experimental data was not more than 0.12 %, which indicates a satisfactory convergence of the results with the calculated data.

$$[\mathrm{Zeolite}]^{n-}\text{-}\frac{n}{2}(\mathrm{Ca}^{2+}+\mathrm{Mg}^{2+})+n\mathrm{Na}^{+}\rightarrow \\ \rightarrow[\mathrm{Zeolite}]^{n-}\text{-}n\mathrm{Na}^{+}+\frac{n}{2}(\mathrm{Ca}^{2+}+\mathrm{Mg}^{2+}) \quad (1)$$

$$\mathrm{Ca}^{2+}+2\mathrm{F}^{-}\rightarrow \mathrm{CaF}_2\downarrow \\ \mathrm{Mg}^{2+}+2\mathrm{F}^{-}\rightarrow \mathrm{MgF}_2 \quad (2)$$

The sorption capacity of zeolite relative to fluoride ions is slightly lower. This may be due to the fact that as a result of ion exchange of sodium for exchange cations of zeolite in the solution gets less calcium and magnesium ions from the crystal lattice. With calcium and magnesium fluorides form stable insoluble compounds of ion fluoride compared to sodium, which is probably due to the fact that some fluorides are sparingly soluble in water: magnesium fluoride at 18 °C – 76 mg/l, calcium fluoride – 15 mg/l.

Therefore, it can be assumed that all magnesium and calcium are deposited in the volume of the sorbent and on its surface. In case of formation of potassium fluorides, part of the fluoride will be in solution. Also in the solution may be crystals of insoluble fluorides (He et al., 2019; Sabadash, 2019).

Therefore, the process of fluoride adsorption follows the mechanisms of ion exchange and chemisorption.

According to the results of the experiments, linearized isotherms of fluoride ion adsorption under static conditions were constructed and presented in Fig. 2.

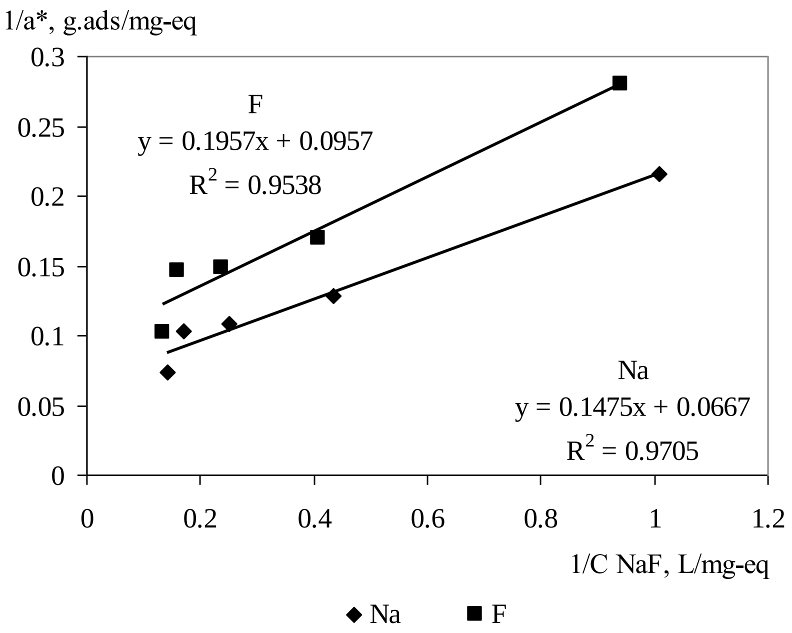

Fig. 2. Interpretation of the results of laboratory tests of the Langmuir isotherm for NaF adsorption by natural zeolite

From Fig. 2 we determined the constant of the Langmuir equation K = 0.49. The value of the adsorption capacity, calculated by the Langmuir formula, is $a\infty$=10,45 mg-eqv/g ads .

As can be seen from Fig. 2, the experimental results are approximated by a linear dependence with a coefficient of determination of 0.9538…9.9705, which indicates the adequacy of the theoretical model.

For the studied adsorption system "F^- - zeolite" the general equation of the Langmuir isotherm will be:

$$a^{*}=10.45*\frac{0.49C}{1+0.49C} \quad (3)$$

For sodium, the general equation of the Langmuir isotherm will be:

$$a^{*}=15*\frac{0.44C}{1+0.44C} \quad (4)$$

The linearization of the adsorption isotherm in accordance with the Freundlich equation is graphically shown in Fig. 3.

As can be seen from Fig. 3, the experimental results are approximated by a linear dependence with a coefficient of determination of 0.9028…9.9371, which indicates the adequacy of the theoretical model.

The equation of the Freundlich isotherm for fluoride will be:

$$a^{*}_{F^-}=0.2\cdot C^{0.3801} \quad (5)$$

The equation of the Freundlich isotherm for sodium will be:

$$a^{*}_{Na^+}=0.21\cdot C^{0.4765} \quad (6)$$

The adsorption of sodium fluoride by natural zeolite is better described by the Langmuir isotherm.

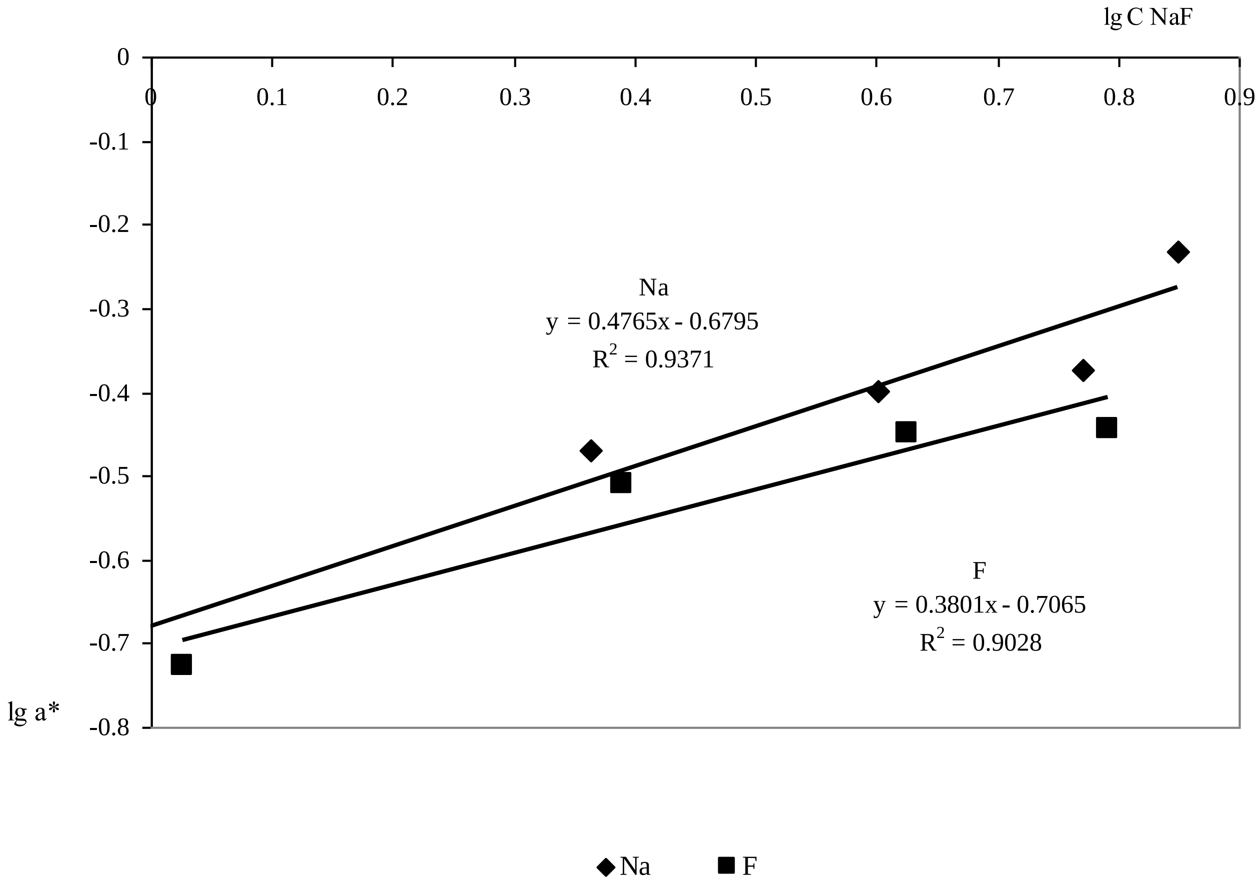

Fig. 3. Interpretation of the results of laboratory tests of the Freundlich isotherm for adsorption of NaF by natural zeolite

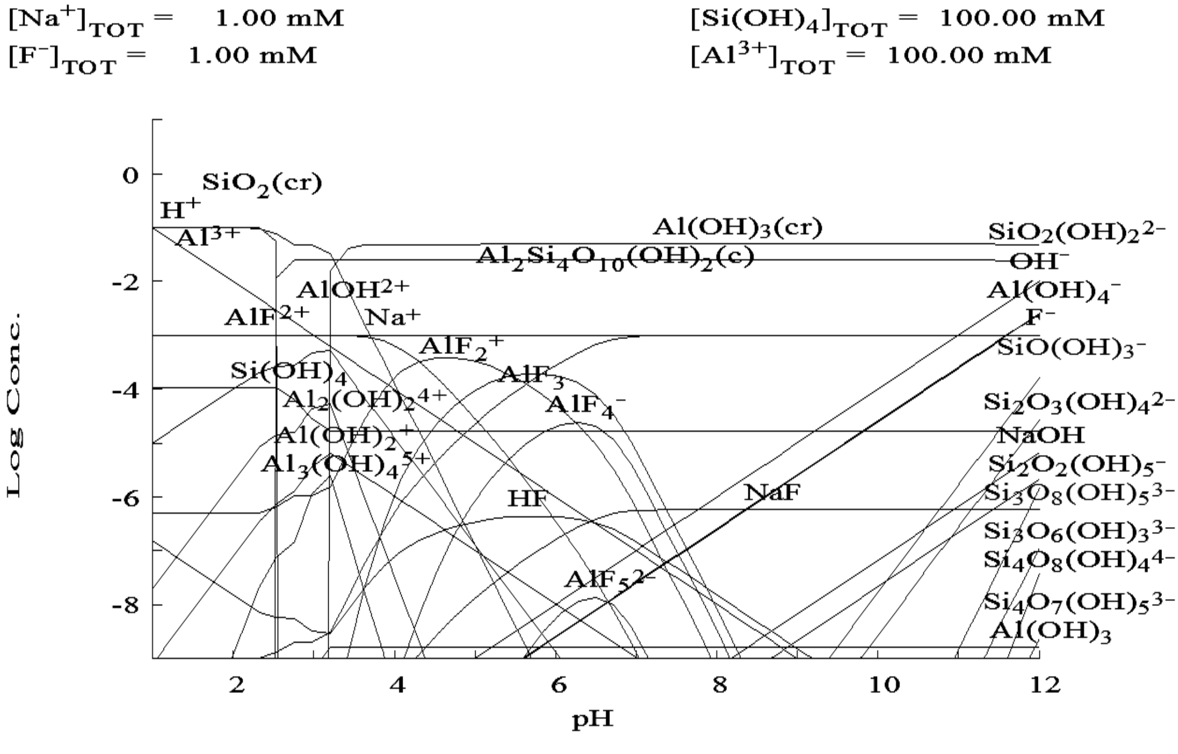

Fig. 4. Approximate composition of the products of the interaction of sodium fluoride with aluminosilicate depending on pH (Sabadash, 2019)

The mechanism of interaction of clinoptilolite is based on the fact that fluoride with aluminum forms complex compounds of different composition depending on the pH of the medium. Within the insoluble compounds its aluminum fluoride. The distribution of concentrations of the products of the interaction of sodium fluoride with aluminosilicate was constructed for the experimental conditions. To obtain the calculated dependences, it was taken into account that the studied zeolite contains Al_2O_3 and SiO_2 in a ratio of 1: 6. HCl and NaOH solutions were used as a medium to adjust pH.

Taking into account the presence of hydrolysis products of aluminum salts on the surface of clinoptilolite grains, the removal of fluoride can occur due to ion exchange and chemisorption to form complex compounds. As can be seen from Fig. 4 (ploted in such programs as MEDUSA (Make Equilibrium Diagram Using Sophisticated Algorithms) and HYDRA (Hydrochemical Equilibrium Constant Database) (Sabadash, 2019), the formation of aluminofluoride compounds is most likely at pH of 3.5…8. Due to the fact that the process of fluoride adsorption was accompanied by a decrease in pH by about 1.5 units (Fig. 5), we can assume the ion exchange mechanism of fluoride extraction.

Zeolite in this case manifests itself as an ampholyte, as it can exchange not only cations but also anions for hydroxyl groups contained in the zeolite framework (Srivastav et al., 2013).

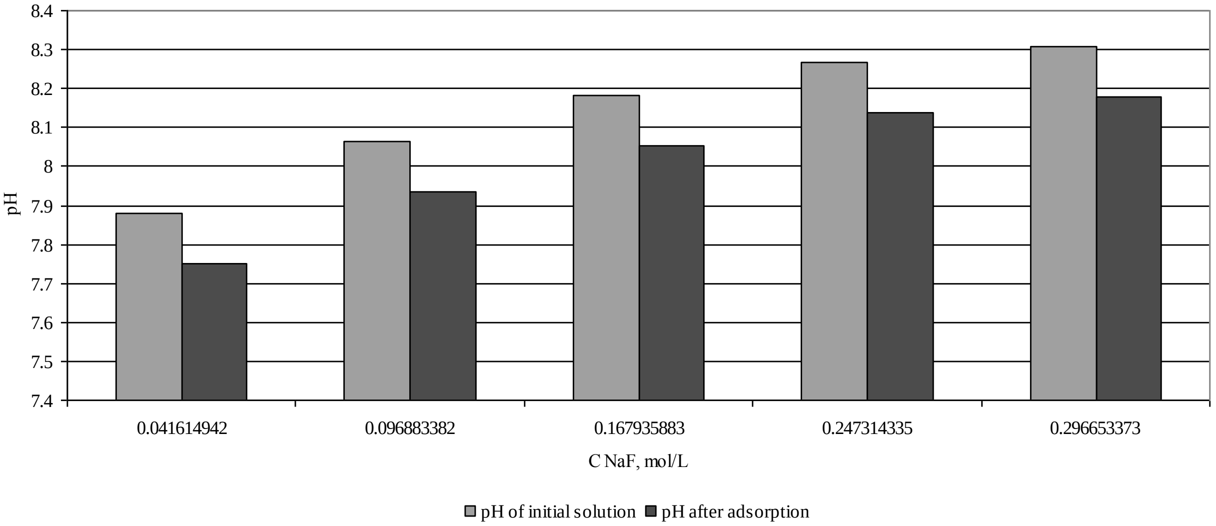

Fig. 5. Change in pH of NaF test samples as a result of adsorption interaction

Analyzing the results of experimental research, we can conclude that the experimental data correlate with numerical calculations of the mathematical model of adsorption statics. Thus, the adsorption of sodium fluoride by zeolite has the following Langmuir expression for monomolecular adsorption. This may be true for chemisorption. Therefore, the adsorption process is described by two mechanisms: ion exchange of sodium for calcium and magnesium, ion exchange of fluorides for hydroxyl groups and chemisorption of fluoride ion due to the formation of insoluble calcium, magnesium and aluminum fluoride.

In the case of high concentrations of fluoride, it is impractical to use sorption methods. Aluminum-based reagents can be used for this purpose.

Sorption of fluoride by zeolites from the formation of aluminofluoride complexes can be described by the following equation (Sabadash, 2019):

$$Al^{3+} + 2F^{-} \rightarrow AlF_2^{+} ;$$

$$2Al(OH)_3 + AlF_2^{+} \rightarrow 3Al(OH)_2F \qquad (7)$$

Thus, at high fluoride concentrations, sorption and reagent methods using $Al_2(SO_4)_3$ or other aluminum-containing reagents can be used to intensify the fluoride ion-extraction process.

According to the test results, the following graphical dependences were constructed, which allow us to calculate the required amount of reagent for the extraction of the fluoride anion. In Fig. 6 and 7, methods for calculating the optimal dose of aluminum-containing reagent for the extraction of fluoride ion $DAl^{3+}opt$ are presented.

The peak on the differential curve and the minimum on the linear curve, which are analogues of the titration curves, will show the optimal ratio of the molar concentration of aluminum-containing reagent to the molar fraction (concentration) of fluorides in the working solution.

As can be seen from Fig. 6 and Fig. 7, there are enough fluoride ions in the solution left – C_F-min = = 0.43 mol/l, so other methods must be used for further purification.

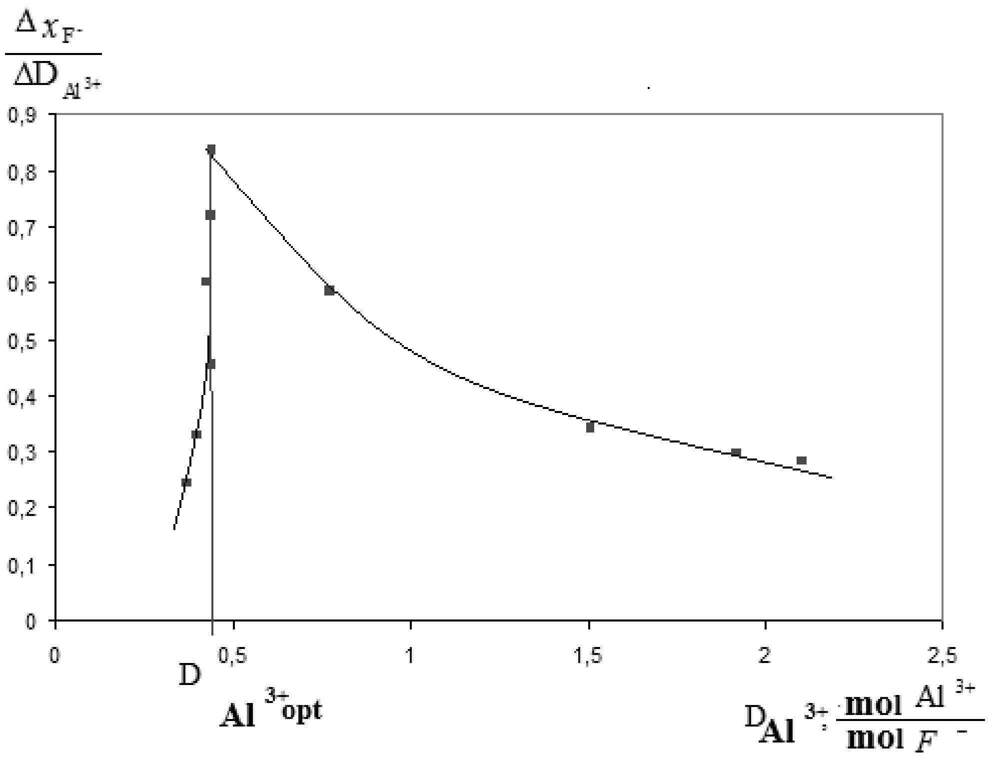

Fig. 6. Differential curve of extraction of fluorides by the aluminum-containing reagent

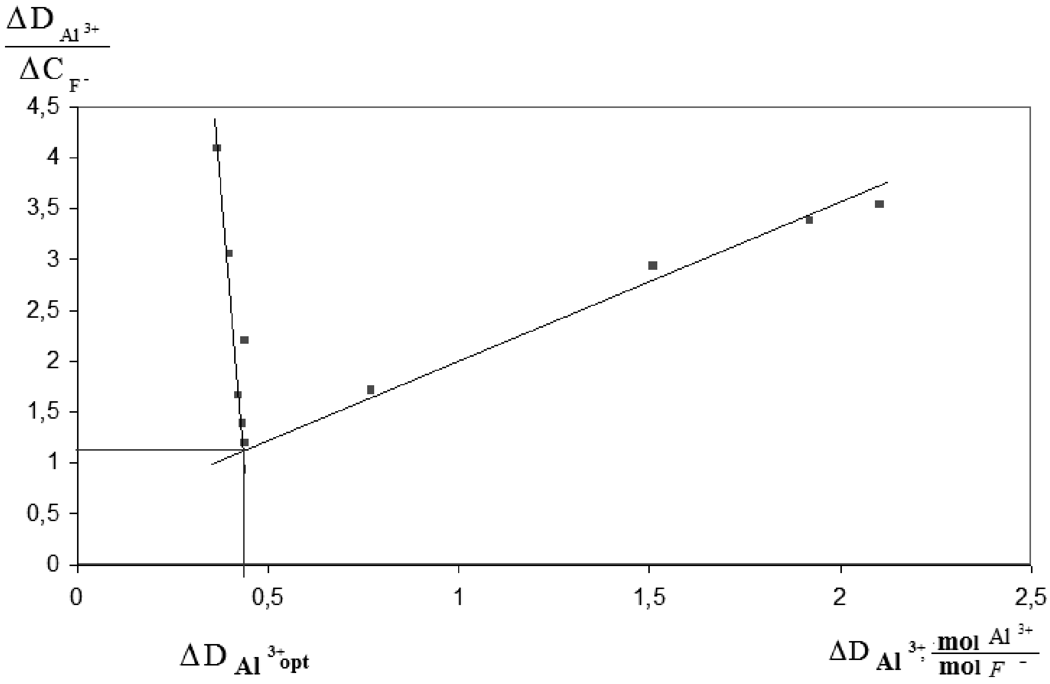

Fig. 7. Linear method for determining the optimal dose of aluminum-containing reagent for the extraction of fluorides

4. Conclusions

Analyzing the results of experimental studies presented in this section, we can conclude that the experimental data correlate with numerical calculations for model wastewaters. Thus, the absorption of sodium fluoride by zeolite is described by the Langmuir equation for monomolecular adsorption of the following type: $a^{*}=10.45*0.49C/(1+0.49)$. It was established that fluorides were also absorbed by the mechanism of chemisorption. Therefore, the adsorption process is described by two mechanisms: ion exchange of sodium for calcium and magnesium and chemisorption of fluoride ion due to the formation of insoluble calcium fluoride. Statistical evaluation of the obtained results showed a satisfactory significance of the results. Methods for determining the optimal dose of aluminum-containing reagent for the extraction of fluorides are presented. The differential curve of extraction of fluorides by the aluminum-containing reagent was constructed experimentally. The coefficient of determination R^2 ranged from 0.6767…0.9998.

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