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INFLUENCE OF COMPETING IONS ON THE EFFICIENCY OF DEFLUORINATION ON IRON-CONTAINING ADSORBENT

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Abstract

Groundwater sources in certain regions of Ukraine are characterized by elevated concentrations of fluoride, which may reach up to 14 or even 18 mg/dm^3. The intake of excessive amounts of fluoride ions through drinking water can seriously harm human health. Adsorption technology is a promising method for water defluoridation due to its simplicity, efficiency, and cost-effectiveness. However, the use of adsorption for fluoride removal from water faces several challenges, one of which is the reduced removal efficiency in the presence of foreign (competing) ions. Therefore, the effect of foreign ions on fluoride removal was investigated using iron-based adsorbent samples. Foreign ions compete with fluoride ions for adsorption sites on the surface of the adsorbent material, thereby reducing the overall efficiency of fluoride removal. The results obtained indicate that all studied ions adversely affect the process efficiency to varying degrees. The phosphate ion exhibited the most significant negative impact, as it is specifically adsorbed onto high-valent metal oxides and hydroxides via inner-sphere complexation. Therefore, it can easily compete with fluoride ions, which are also specifically adsorbed. Nitrate and chloride ions are non-specifically adsorbed (via outer-sphere complexation) onto metal oxides and thus cannot effectively compete with fluoride ions at equal concentrations. Sulfate ions may be adsorbed both specifically and non-specifically, and therefore showed a greater competitive effect than chloride and nitrate, but less than phosphate. The concentration ratios of anions in natural and wastewater vary significantly and should be taken into account when assessing the degree of competition.

Keywords*: water purification, defluorination, iron-containing sorbents, competing ions.*

Fluorine is an element commonly found in the natural environment. It can be found in minerals, ores, the Earth's crust, the atmosphere, and living organisms. The presence of fluorides in natural waters used for domestic and drinking water supply is determined by the existence of soluble fluorine-containing compounds in soils and rocks.

Fluorine compounds are present in both surface and groundwater, into which they enter from soils and rocks as a result of the weathering of fluorine-containing minerals by groundwater and surface runoff. Atmospheric precipitation is also a source of fluoride. Human activity has a significant impact on the migration and enrichment of fluorine in groundwater. In recent years, the development of industrial production (such as aluminum, semiconductors, iron and steel, pesticides, and agricultural chemical fertilizers) has greatly increased fluoride pollution [1].

Relying on the natural self-purification of water bodies from fluoride is virtually unrealistic, as fluoride compounds are persistent constituents of industrial wastewater.

Fluorides have a high affinity for hard tissues due to their ability to chemically bind with calcium phosphates [2]. Since fluorine imparts exceptional chemical stability to its compounds, certain amounts are essential for the human body to ensure the optimal structure of bones and teeth.

In addition to its beneficial effects on the human body, there are also examples of fluorine's toxic effects. Skeletal fluorosis is one of the most severe manifestations of fluoride toxicity. Fluorine can cause dental deformation and discoloration, osteochondrosis, joint stiffness and immobility, and abnormal bone growth. High concentrations of fluorine extract magnesium from lymph and blood, mobilize calcium from bones, which often leads to its deposition in the kidneys, muscles, and lungs.

According to many authors, fluoride intoxication may result in damage to the gastrointestinal tract, kidneys, liver, endocrine and nervous systems, reproductive dysfunction, and reduced nonspecific resistance of the body [3].

According to the latest World Health Organization guidelines, the fluoride content in drinking water should range between 0.5-1.5 mg/dm³. Due to socio-economic and geographical factors, the maximum allowable concentrations of fluoride in drinking water vary slightly across countries: USA – 0.6-0.9 mg/dm³, India – 1.0-1.5 mg/dm³, Ukraine – 0.7-1.5 mg/dm³ [1].

The use of groundwater for drinking water supply in more than 20 developed countries is impossible without removing excess fluoride. The issue of defluoridation of groundwater used for drinking purposes is also relevant for Ukraine, as fluoride concentrations in its underground sources average 2.5-5.0 mg/dm³, and in some regions, such as Poltava oblast, even higher values are recorded (up to 12 mg/dm³) [1].

The fluoride level in drinking water can be controlled through various water treatment processes such as adsorption, coagulation, electrocoagulation-flotation, chemical precipitation, and ion exchange. These processes can remove excess fluoride from water or, in the case of water fluoridation, add controlled amounts of fluoride to achieve optimal dental health benefits. Among the wide range of technologies, adsorption has attracted considerable attention as a promising strategy for fluoride removal. Adsorption technology has become a favorable approach to defluoridation due to its simplicity, efficiency, and cost-effectiveness.

Over the past decade, various types of defluoridation adsorbents have been developed, including those derived from natural minerals, industrial wastes, and biomass, as well as metal oxides, hydroxides, and carbon-based materials.

Recently, iron-based adsorbents have gained increasing attention. The advantages of iron-containing adsorbents include their high adsorption rate, large adsorption capacity, and low cost [4].

The aim of this study was to investigate the effect of competing ions on the efficiency of fluoride ion adsorption using iron-containing adsorbents A03 and A06. Foreign ions may contend with fluoride ions for adsorption sites on the surface of the adsorbent material, thereby reducing overall fluoride removal efficiency. The degree of competition in the adsorption process depends on the concentration and chemical characteristics of the competing ions.

Natural water contains anions such as chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and phosphate (PO_4^{3-}). These ions can compete for adsorption sites and form stable complexes with F^-. Additionally, bicarbonate and carbonate may form complexes with the adsorbent surface itself. This interaction reduces the number of active adsorption sites available for fluoride adsorption [5].

For the sorption experiments, the adsorbent samples were weighed using an analytical balance. A NaF solution was prepared by dissolving a calculated amount of solid salt in distilled water. When pH adjustment was required, it was achieved using 0.1 M HCl and 0.1 M KOH solutions. Potassium salts of nitrate, chloride, carbonate, sulfate, phosphate, and bicarbonate were used as competing ions. Various concentrations of these ions were studied: 10 mg/dm^3, 20 mg/dm^3, and 30 mg/dm^3. The experiments were conducted using a sorbent dose of 2 g/dm^3 for A03 and 6 g/dm^3 for A06. The NaF solution concentration was fixed at 10^{-3} M. The pH of the solution was adjusted to 4 for A03 and 6 for A06.

The adsorbent samples were transferred into plastic sorption containers, followed by the addition of 50 cm^3 of sodium fluoride solution and a calculated amount of solid salt containing the competing ion. The containers were then placed on a laboratory shaker, where the sorption process was carried out until equilibrium was established. Upon completion of the sorption process, the adsorbent was separated from the solution, and the residual fluoride ion concentration in the filtrate was determined.

In a 100 cm^3 beaker, 50 cm^3 of the test solution was added along with 10 cm^3 of an ionic strength adjustment buffer. The beaker was placed on a magnetic stirrer, and the electrodes were immersed. After 2-3 minutes, the current fluoride concentration was recorded.

The sorption capacity (mg/g) was calculated using the following formula:

$$\mathrm{a} = \frac{(C_0 - C_e) \times 0{,}05}{m_s},$$

where C_0 is the initial concentration of fluoride ions (mg/dm^3), C_e is the equilibrium concentration after sorption (mg/dm^3), 0.05 is the volume of the added solution in dm^3, and m_s is the mass of the adsorbent sample in grams.

The study of the effect of competing ions on fluoride ion sorption using adsorbents A03 and A06 revealed that all investigated ions had some impact on the efficiency of the process, except for nitrate ions, which at low concentrations improved fluoride adsorption on the A03 adsorbent. The results of the effect of competing ions on fluoride ion sorption for adsorbents A03 and A06 are shown in Figures 1 and 2, respectively.

The sequences of influence strength on the sorption capacity of A03 for a given initial concentration of competing ions are as follows:

- 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 sequences of influence strength on the sorption capacity of A06 are as follows:

- 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 results are in good agreement with the findings of other researchers. For instance, in [6], the authors confirm that the effect of bicarbonate can be explained by the fact that conjugate bases of weak acids produce more hydroxide ions, which compete with F^- for adsorption sites. In [7], it is noted that the decrease in the fluoride adsorption capacity with increasing bicarbonate concentration is due to a rise in solution pH.

According to the authors of [8], the adsorption mechanisms of phosphate result in its strong affinity for metal oxides and high-valent hydroxides, enabling it to effectively compete with fluoride ions. However, several authors [5] point out that, considering the typical concentration range of natural phosphate in groundwater (from 0 to 5 mg/dm³), its impact on fluoride adsorption is unlikely to be a limiting factor for groundwater defluoridation.

Data from [7] indicate that HCO_3^-, CO_3^{2-}, and PO_4^{3-} significantly affect F^- removal because these ions undergo hydrolysis, leading to an increase in pH. As a result, more OH^- ions are available to compete with F^- for active adsorption sites, thereby reducing the overall adsorption capacity.

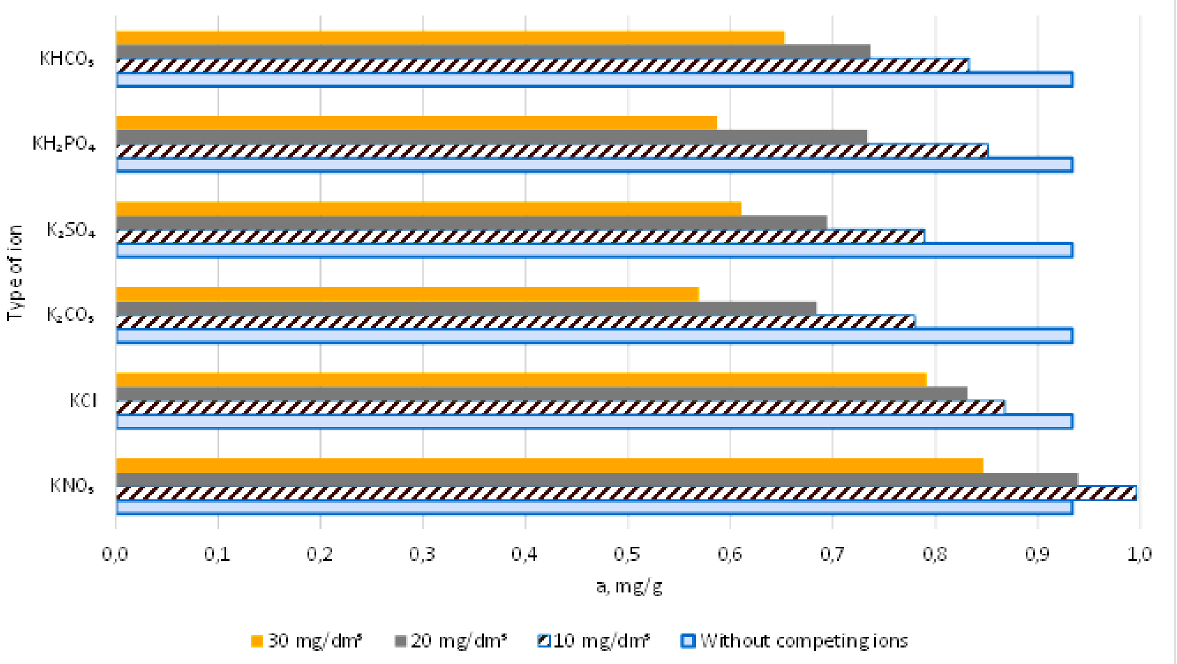

__Figure 1.__ The influence of competing ions on the sorption of fluoride ions on the sorbent A03

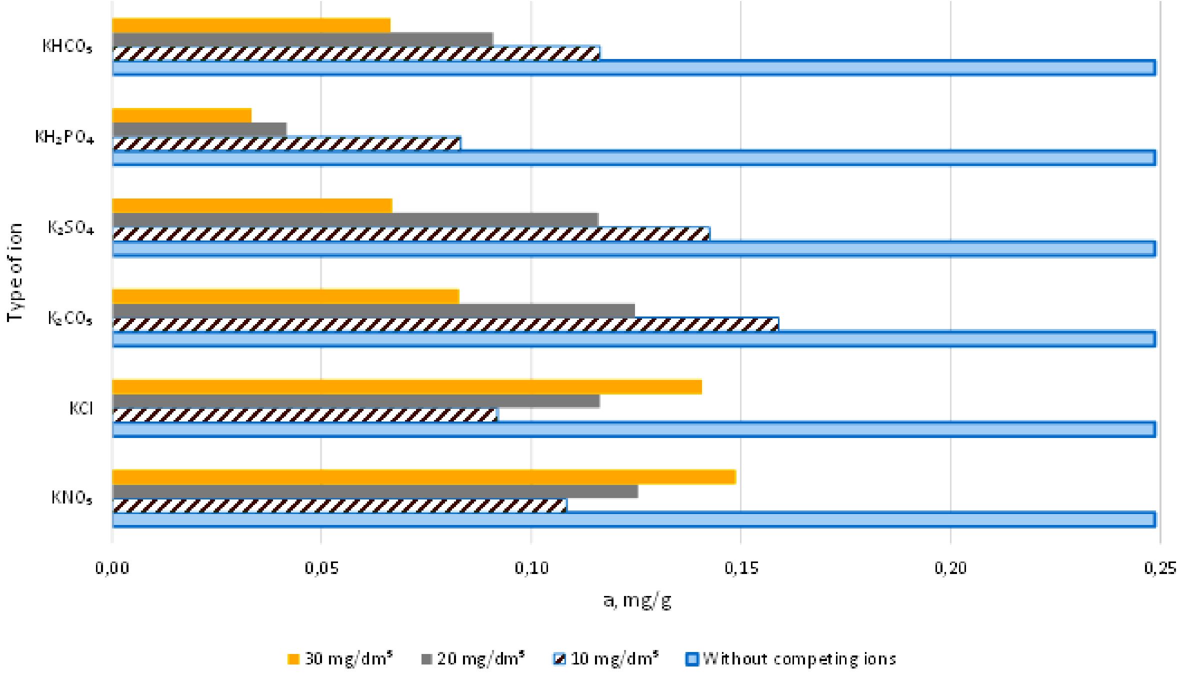

__Figure 2.__ The influence of competing ions on the sorption of fluoride ions on the sorbent A06

Thus, it was established that the presence of competing ions reduces the degree of fluoride ion removal from binary solutions. Phosphate is strongly and specifically adsorbed onto high-valent metal oxides and hydroxides through inner-sphere complexation. Therefore, it can readily compete with fluoride (F^-), which also exhibits specific adsorption behavior.

Nitrate and chloride ions, on the other hand, are non-specifically adsorbed (outer-sphere complexation) onto metal oxides and thus are poor competitors with fluoride ions at equal concentrations. Sulfate can undergo both specific and non-specific adsorption, making it a stronger competitor with fluoride than chloride and nitrate, but weaker than phosphate.

The observed order of anion competition is similar to that reported by other researchers [5]. The concentration ratios of anions in natural and wastewater vary significantly, and these ratios must be taken into account when evaluating the extent of competitive adsorption.

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ВПЛИВ СТОРОННІХ ІОНІВ НА ЕФЕКТИВНІСТЬ ДЕФТОРУВАННЯ НА ФЕРУМВМІСНИХ АДСОРБЕНТАХ

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Анотація

Джерела підземних вод у багатьох регіонах України характеризуються підвищеною концентрацією фтору, яка може сягати 14, а в окремих випадках –навіть 18 мг/дм^3. Надходження надмірної кількості іонів фтору з питною водою може серйозно зашкодити здоров'ю людини. Технологія адсорбції є перспективним методом дефторування води завдяки своїй простоті, ефективності та економічній ефективності. Однак використання адсорбції для видалення фтору з води стикається з кількома проблемами, однією з яких є зниження ефективності видалення у присутності сторонніх (конкуруючих) іонів. З урахуванням цього, було досліджено вплив сторонніх іонів на видалення фтору з використанням зразків адсорбентів на основі заліза. Сторонні іони конкурують з іонами фтору за центри адсорбції на поверхні адсорбуючого матеріалу, тим самим знижуючи загальну ефективність видалення фтору. Отримані результати свідчать про те, що всі досліджувані іони негативно впливають на ефективність процесу різною мірою. Фосфат-іон виявив найбільш значний негативний вплив, оскільки він специфічно адсорбується на високовалентних оксидах та гідроксидах металів шляхом комплексоутворення у внутрішній сфері. Тому він може значною мірою конкурувати з іонами фтору, які також специфічно адсорбуються. Іони нітратів та хлоридів неспецифічно адсорбуються (шляхом комплексоутворення у зовнішній сфері) на оксидах металів, і тому не можуть ефективно конкурувати з іонами фтору за рівних концентрацій. Іони сульфатів можуть адсорбуватися як специфічно, так і неспецифічно, і тому демонструють більший конкурентний ефект, ніж хлориди та нітрати, але менший, ніж фосфати. Співвідношення концентрацій аніонів у природних та стічних водах значно різняться і їх слід враховувати при дослідженні процесів сорбційного очищення води.

Ключові слова: очищення води, дефторування, ферумвмісні сорбенти, конкуруючі іоні.