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FLUORIDE IN DRINKING WATER: THE PROBLEM AND ITS POSSIBLE SOLUTIONS

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Abstract. Removal of fluoride ions from model solutions of Tallinn drinking water was tested using Aqua Juraperle (calcium carbonate) and activated alumina as filtration media. The experiments with Aqua Juraperle demonstrated that this filter medium does not maintain fluoride ions. Other water constituents, except iron, were not influenced by the filtration either. The total iron content was reduced by 50%. Filtration through activated alumina reduced the fluoride concentration in water. The sorption capacity of alumina was 4.5 g/kg and volumetric capacity 3.95 g/L. Different coagulants and their doses were tested to remove fluoride with coagulation as well. The coagulant consumption for fluoride removal was 80 mg $Al_2(SO_4)_3$ per 1 mg F^-. The use of lime milk as a coagulant for water defluoridation is not expedient.

Key words: drinking water, fluoride content and removal, filter media, activated alumina, Aqua Juraperle, coagulation.

INTRODUCTION

The content of fluoride in drinking water and tooth paste attracts public attention nowadays. On the one hand, fluoride is added to many drinking waters in small quantities to prevent dental caries. On the other hand, fluoride is a carcinogen, a bone seeker and is linked to hip fractures and brittle bones [1]. Recalling the basics of inorganic chemistry we should keep in mind that among the four best known halogens (chlorine, bromine, iodine, and fluorine) namely fluorine is the most chemically active, being a very strong oxidant. All salts of fluorine are toxic, but some of them more, some less. Sodium fluoride, for example, a common additive to tooth pastes nowadays, a very toxic compound, far more toxic than calcium fluoride salts, is used also as a wood preservative and pesticide.

Research of several investigators during the last 5–6 years has proved that life-long impact and accumulation of fluorides causes not only human skeletal and teeth damage, but also changes in the DNA-structure, paralysis of volition, cancer, etc. IG Farben supplied the German Army with fluorine gas already during World War I. During World War II both sides of the front made plans how to paralyse the volition of war prisoners and population of occupied territories with drinking water fluoridation [2]. Because of the toxicity of fluoride and danger of overdosing, fluoridation of drinking water has been stopped in many countries. Some examples are as follows (the years when fluoridation started and stopped shown in brackets): German Federal Republic (1952–71), Sweden (1952–71), the Netherlands (1953–76), Czechoslovakia (1958–88/90), German Democratic Republic (1959–90), Soviet Union (1960–90), Finland (1959–93), Japan (1952–72), etc. [3]. This means that about 53 million people in Europe were liberated from fluoride consumption with everyday drinking water [3].

For fluoride consumption by humans 3 mg F/day is a figure that should never be exceeded, and, of course, sodium fluoride in tooth pastes should be replaced with calcium fluorides, which are much less toxic.

Dean et al. [4] conducted a study in the 1940s to determine the optimum fluoride concentration in drinking water that would decrease dental decay without producing a significant amount of fluorosis. Another study indicated almost twice as many Mongoloid births in Illinois and other areas where the fluoride content in the drinking water is high compared with areas where the fluoride content is low [5].

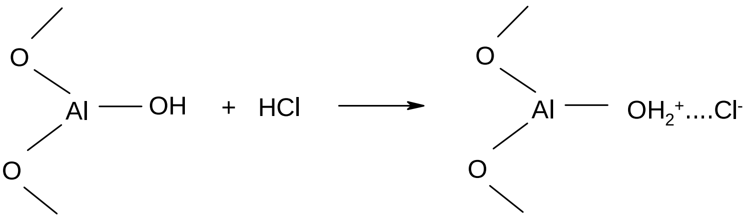
What could be an optimum concentration of fluoride in drinking water? Estonian and EU requirements set a limit at 1.5 mg/L [6]. A study in the USA showed that the optimum fluoride concentration in temperate climates is 1.0–1.2 mg/L [7].

The concentration of fluoride in groundwater in different regions of Estonia varies from 0 to 6 mg/L [8], which means that the guidelines are exceeded quite frequently. Therefore, fluoride removal has to be conducted in many Estonian towns and settlements. What are the possible technologies for fluoride removal? As filtration is widely used in water treatment, it should be possible to find out a suitable filter medium that is able to sorb fluoride from water.

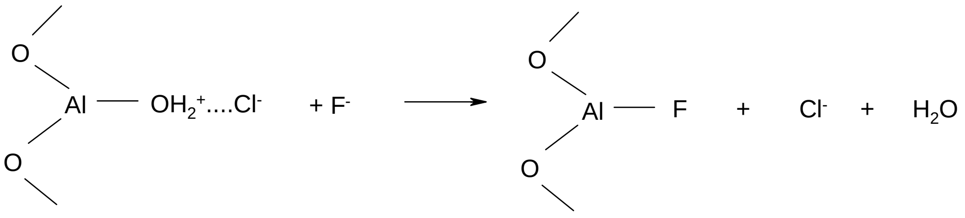
Strong anion-exchange resins are not usually considered for fluoride removal because of their low capacity and relatively high cost. Ion-exchange process can be effective only if the fluoride concentration is less than 10 mg/L [9]. As the sorption of fluoride is accompanied by the sorption of other anions, the sorption capacity does not exceed 0.3–0.5 mg F^-/L [10].

As fluoride ion forms insoluble compounds with calcium ions, the application of filter media based on calcite and limestone is one of the advanced trends in water treatment. Such materials were quite effective for fluoride removal from wastewaters of metallurgic and electronic industries [11, 12]. Activated alumina has also been successfully applied as a defluoridation medium. There are several advantages of using alumina in down-flow columns: it is somewhat specific for F^- and has a relatively high exchange capacity for this ion. This capacity is not affected by the SO_4^{2-} or Cl^- contents of water and the material has a relatively low cost [13, 14]. Activated alumina acts as anionite, charged with chloride ions when regenerated with hydrochloric acid or with OH^- ions when regenerated with sodium hydroxide. According to Liponkoski [14] the mechanism of activated alumina performance is as follows:

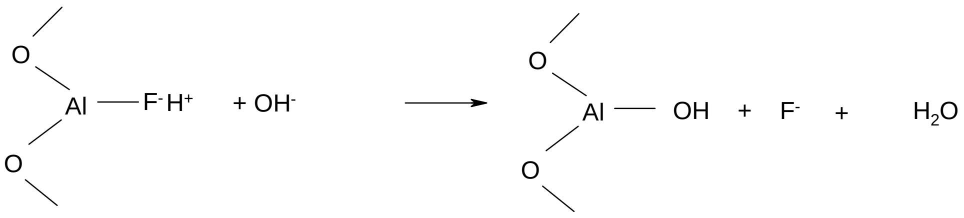
– during the flushing with a hydrochloric acid the formation of a complex ligand takes place at the initial stage of the process:



– at the next stage the complex participates in the fluoride bounding acting as the anion exchanger:



There is a possibility of regeneration of alumina after the saturation with fluoride ions by sodium hydroxide:



The sorption capacity of the material may be theoretically restored up to 100% [9]. Multiple reuse of the regeneration solution (1% NaOH) is possible and the duration of the regeneration cycle does not exceed 1 h [10].

Another method that enables to remove fluoride from water is precipitation with such coagulants as aluminium sulphate and/or polyaluminium chloride $Al_n(OH)_mCl_{3n-m}$. The aluminium fluoride formed in this process settles with the aluminium hydroxide flocks. The coagulant doses required are significantly higher ($Al_2(SO_4)_3$ consumption varies from 35 to 135 mg/mg F^-) than those usually used in water treatment [14].

The sorption of fluoride from water is influenced by such factors as pH, acidity, alkalinity, etc. Therefore, the aim of the present study was to establish how high degree of fluoride removal can be achieved for Estonian groundwater. Two filter media – Aqua Juraperle (material based on calcium carbonate) and activated alumina – were studied in order to determine their sorption capacity. Different coagulants and their doses were used to remove fluoride with coagulation. Changes in various water quality parameters were followed during the experiments.

EXPERIMENTAL

Filtration experiments were carried out with Tallinn drinking water as a model solution. The main parameters of this water are given in Table 1. As the drinking water had quite a low fluoride content, some sodium fluoride was added before the experiments to bring the initial fluoride concentration up to 6.00 ± 0.59 mg/L.

Table 1. The main parameters of the water studied

Parameter	Mean ± SD	Parameter	Mean ± SD
pH	7.38 ± 0.33	Cl^-, mg/L	21.7 ± 16.9
Alkalinity, mg-eq/L	2.49 ± 0.29	SO_4^{2-}, mg/L	61.3 ± 14.0
Acidity, mg-eq/L	0.41 ± 0.13	NO_3^-, mg/L	1.01 ± 0.63
Hardness, mg-eq/L	6.03 ± 0.64	F^-, mg/L	6.00 ± 0.59
Fe_{tot}, mg/L	1.12 ± 0.36	Silicates, mg SiO_2/L	1.15 ± 0.36

The experiments of filtration were performed using the laboratory equipment described in our previous study [15]. A filtration column was filled with filter media, such as Aqua Juraperle or activated alumina. The operating conditions of the process are given in Table 2. Activation of alumina was carried out with 0.1 N hydrochloric acid and regeneration with 0.1 N NaOH according to Liponkoski [14].

Table 2. Operation conditions

Parameter	Aqua Juraperle	Alumina
Effective size, mm	0.5–1.6	2.0–2.5
Bed depth, m	0.53	0.65
Bed mass, g	151	97
Flow rate, mL/min	38	38
Filtration rate, m/h	11.2	10.2
pH	6.93 ± 0.14	7.56 ± 0.19
Temperature, °C	19.4 ± 2.0	20.7 ± 1.1

Laboratory coagulation tests were carried out using mixing equipment Flocculator (Kemira Kemivesi). Different coagulant doses were added to the samples (with the volume of 800 mL). The samples were mixed during 30 s at a speed of 30 rpm and then settled during 20 min. Aluminium sulphate liquid (ALS) coagulant produced by AS Kemivesi ($Al_2(SO_4)_3$ content 27.4%), aluminium sulphate solution with a concentration of 20 g/L, and a milk of lime (280 g CaO/L) were used as coagulants in these experiments.

The changes in water quality parameters during the experiments were followed. Water hardness, alkalinity, acidity, pH, and SiO_2 content were measured according to [16]. The concentration of chloride, nitrate, sulphate, and fluoride in the water was determined with ion chromatography [17].

RESULTS AND DISCUSSION

The experiments with Aqua Juraperle demonstrated that this filter medium does not maintain fluoride ions. The other water parameters, except iron, were not influenced by the filtration either. The total iron content was reduced by 50%. Thus, Aqua Juraperle does not suit for water defluoridation.

Filtration through activated alumina reduced the fluoride concentration in water up to zero during the first minutes of filtration. The saturation of the surface layer of the filter medium caused in this case a stepwise increase in the fluoride concentration at the outlet of the filter (see Fig. 1). The sorption capacity of alumina was 4.5 g/kg and the volumetric capacity was 3.95 g/L. Such sorption capacity is somewhat lower than the value reported by Liponkoski [14]. The difference is probably due to the granulometric composition of the filter medium. The filtration through alumina did not influence all other water parameters, which indicates the selectivity of this medium towards fluoride ions.

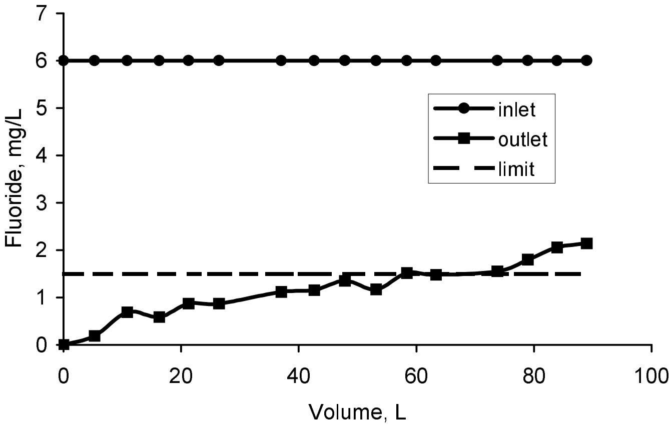


Fig. 1. Changes in the concentration of fluoride ion versus volume of water during filtration through alumina.

When the filter medium was saturated with fluoride ions (the outlet concentration of fluoride ions exceeded the Estonian Standard requirements of 1.5 mg/L after passing 60 L of solution), the medium was regenerated with sodium hydroxide and hydrochloric acid [14], and the filtration cycle was repeated. Unfortunately, after such regeneration the sorption capacity of alumina was not restored and it was not any more able to remove fluoride ions from the water. This does not coincide with the results reported by Liponkoski [14] and Ivleva et al. [10]. The reason may be formation of a ferric oxide film on the surface of alumina grains during the filtration of water with a high concentration of iron. This film was not removed during the activating of alumina with 0.1 N HCl. In the next experimental series, in order to remove the ferric oxide from the surface of filter medium, alumina was flushed with 5% HCl until no brown precipitate of ferric oxide was visible. Such an approach enabled restoration of the sorption capacity of alumina.

The results of the precipitation of fluorides from water samples with $Al_2(SO_4)_3$ and ALS are presented in Fig. 2, which demonstrates that the removal of fluoride takes place identically for both coagulants. The decrease in fluoride concentration in water is dependent on the coagulant dose. According to the results of the present study, 280 mg/L of the coagulant is necessary to reduce the content of fluoride in water from 5 to the required 1.5 mg/L. Thus, the coagulant consumption for fluoride removal is 80 mg $Al_2(SO_4)_3$ per 1 mg F^-. The results of our study are in good conformity with the results presented earlier [14, 18].

There is an opinion that fluoride ions form hardly precipitating complex compounds with iron. Therefore, coagulation with $Al_2(SO_4)_3$ was carried out with model solutions containing from 0.4 to 6.0 mg/L of total iron. It was ascertained that the increase in the iron content in water in such range did not affect fluoride removal with $Al_2(SO_4)_3$ coagulation.

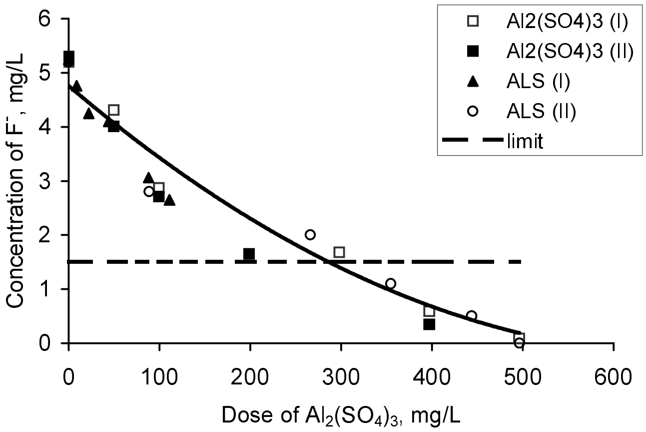


Fig. 2. Concentration of fluoride in water versus aluminium sulphate dose (I, 0.4 mg Fe/L; II, 6.0 mg Fe/L).

Fluoride forms insoluble compounds not only with aluminium, but also with calcium salts. Therefore, the use of lime milk as a very cheap coagulant was studied as well. No significant decrease in the fluoride concentration in water was observed in our experiments, when a very large range of coagulant concentrations (from 350 to 3500 mg CaO/L) was applied. Thus, the use of lime milk as well as filter media based on calcium carbonate for water defluoridation is not expedient.

CONCLUSIONS

A feasibility study on the use of two filter media – Aqua Juraperle and alumina – for the removal of fluoride ions from water demonstrated that the former was not suitable for defluoridation as it did not remove fluoride from water. The sorption capacity of alumina was 4.5 g/kg. The regeneration of alumina succeeded only after preliminary removal of the ferric oxide layer from the surface of the filter medium. Fluoride may be removed from water by coagulation with coagulants based on aluminium sulphate. The coagulant consumption for fluoride removal was 80 mg $Al_2(SO_4)_3$ per 1 mg F^-. The use of lime milk as a coagulant for water defluoridation is not expedient.

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FLUORIID JOOGIVEES: PROBLEEM JA SELLE VÕIMALIKKE LAHENDUSI

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Laboratoorsel filtrimisseadmel on uuritud fluoriidioonide eraldamist kahe materjali – Aqua Juraperle (kaltsiumkarbonaat) ja aktiveeritud alumiiniumoksiidi abil. Katsed näitasid, et Aqua Juraperle ei eralda veest fluoriidioone. Ka vee teiste komponentide, välja arvatud raua, sisaldus jäi muutumata. Üldraua sisaldus vähenes filtrimisel läbi Aqua Juraperle 50% võrra. Filtrimine läbi aktiveeritud alumiiniumoksiidi vähendas katse esimestel minutitel fluoriidi sisaldust vees nullini. Seejärel hakkas materjali aktiivsete ioonivahetustsentrite küllastumise tõttu fluoriidi sisaldus filtrist väljuvas vees pikkamööda kasvama. Selgus, et aktiveeritud alumiiniumoksiidi tasakaaluline sorptsioonivõime fluoriidi suhtes on 4,5 g/kg ja dünaamiline sorptsioonivõime 3,95 g/l. Materjali regenereerimise ajal selgus, et protsess õnnestus ainult siis, kui enne regenereerimist eraldati raudoksiidi kiht, mis oli veest graanulite pinnale sadenenud. Niipea, kui see kiht oli 5% soolhappega välja pestud, taastus materjali sorptsioonivõime täielikult.

Fluoriidioone saab eraldada veest ka koagulatsiooni abil. Väga hea efekti andis selline koagulant nagu alumiiniumsulfaat. Selle vajalik doos oli 80 mg 1 mg fluoriidi kohta. Lubjapiima kasutamine, vastupidi, ei andnud positiivset efekti. See fakt annab võimaluse väita, et kaltsiumi sisaldavad ained ei sobi fluoriidi eemaldamiseks veest.