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Removal of Fluorides from Aqueous Solutions Using Exhausted Coffee Grounds and Iron Sludge

Irma Siaurusevičiūtė [1] and Ramunė Albrektienė [2,*]

[1] Faculty of Chemistry and Geosciences, Vilnius University, Naugarduko str. 24, 03225 Vilnius, Lithuania; irma.siauruseviciute@chgf.stud.vu.lt

[2] Department of Chemistry and Bioengineering, Vilnius Gediminas Technical University, Sauletekio ave. 11, 10223 Vilnius, Lithuania

* Correspondence: ramune.albrektiene@vilniustech.lt

Abstract: Many countries are confronted with a striking problem of morbidity of fluorosis that appears because of an increased concentration of fluorides in drinking water. The objective of this study is to explore opportunities for removal of fluoride from aqueous solutions using cheap and easily accessible adsorbents, such as exhaustive coffee grounds and iron sludge and to establish the efficiency of fluoride removal. Twelve doses (1, 2, 3, 4, 5, 6, 10, 20, 30, 40, 50 and 60 g/L) of adsorbents were used and five durations of the sorption process (30, 60, 90, 120 and 150 min). The results showed that the most optimum dose of iron sludge for 3 mg/L of fluoride removal was 30 g/L and the contact time was 30 min, the efficiency of fluoride removal achieved 62.92%; the most optimum dose of exhausted coffee grounds was 60 g/L with the most optimum contact time of 60 min; at a dose of 50 g/L with contact time of 90 min, the efficiency of fluoride removal achieved 56.67%. Findings demonstrate that adsorbents have potential applicability in fluoride removal up to the permissible norms.

Keywords: fluorides; drinking water; sorption; exhausted coffee grounds; iron sludge

1. Introduction

Fluoride is one of the earth's most abundant elements and exists in almost all ground-waters around the world. High concentrations of fluoride in drinking water raise concerns about its effect on human health. Fluoride ions are abundant in mineral and water sources as they can appear in the food chain while drinking water or consuming vegetable food [1]. Depending on its concentration in drinking water, fluoride ions can be useful or harmful for human health. At concentrations of 0.4–1 mg/L, fluoride is useful for children to prevent tooth decay. In return, overuse of fluoride can lead to tooth or skeletal fluorosis [1–3]. Increased concentrations of fluoride ions in drinking water can cause various diseases, such as rachitis, neurological disorders, tendon and ligament ossification and dental diseases [4]. Very high concentrations can cause disorders of kidneys, thyroid, liver and testicles [5]. With prolonged exposure [6] at higher fluoride concentrations, dental fluorosis progresses to skeletal fluorosis (Table 1). Fluoride is thus considered beneficial in drinking water at levels of about 0.7 mg/L but harmful once it exceeds 1.5 mg/L, which is the World Health Organization limit being followed in most nations [7,8].

Table 1. Effect of prolonged use of drinking water on human health, related to fluoride content [6].

Fluoride Concentration, mg/L	Health Outcome
<0.5	Dental caries
0.5–1.5	Optimum dental health
1.5–4.0	Dental fluorosis
4.0–10	Dental and skeletal fluorosis
>10.0	Crippling fluorosis

It is estimated that more than 200 million people worldwide rely on drinking water with fluoride concentrations greater than 1.5 mg/L, the guideline value for fluoride set by the World Health Organization (WHO) [9,10]. In China, the spread area with water-drinking endemic fluorosis covers about 2.2 million km^2, 1.4 million people have suffered from skeletal fluorosis caused by drinking higher-fluoride water [11]. More than 8 million people are subjected to high fluoride groundwater in the Ethiopian rift valley [12,13]. Endemic fluorosis occurs distinctly in the East African Rift System [14]. As well, Malawi, Iran and India suffer from concentrations of fluoride in water that are too high [15–18].

The chief natural source of fluoride in soil is the parent rock itself [19]. Fluorite, the only principal mineral of fluorine in nature, occurs mostly as an accessory mineral in granitic rocks [20]. The fluoride occurs mainly as sellaite (MgF_2), fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite [$3Ca_3(PO_4)_2 Ca(F,Cl_2)$]. As fluorspar, it is found in sedimentary rocks and as cryolite—in igneous rocks. These fluoride minerals are nearly insoluble in water. Hence, fluorides will be present in groundwater only when conditions favour their dissolution or high fluoride containing effluents are discharged to the water bodies from industries [7]. Use of phosphate fertilizers in agricultural and industrial activities contributes to fluorine appearance in groundwater as well [21]. Considerable quantities of fluorides are observed in calcium-free groundwater where fluorine-containing mineral substances are often used [22].

Worldwide, abundant and various methods for fluoride removal from water are applied. The key methods for fluoride removal from drinking water include: coagulation and precipitation methods [23], electro-coagulation [24], reverse osmosis and nanofiltration [7,25], dialysis and electro-dialysis [26], freeze concentration [27], ion-exchange method [28] and adsorption technique [7,23]. A wide variety of adsorbents are usable for fluoride removal, including alumina and aluminum based adsorbents (alumina plus manganese dioxide, alumina plus manganese oxide, alumina plus calcium minerals, bauxite, red mud, lateritic ores, lanthanum and cerium modified mesoporous alumina, fungus hyphae-supported alumina [7,29–33], clays and soils (clay, fired clays, coated clays, related low-cost materials, soils) [7,34], calcium, carbon (graphite, alumina-impregnated graphitic carbon, carbon nanotubes, alumina-impregnated carbon nanotubes, nano-magnetically modified activated carbon prepared by oak shell) [1,7], zeolites [35], synthetic resins, layered double hydroxides (LDHs) [7], hybrid adsorbent lanthanum–carbon [36], lanthanum-loaded magnetic cationic hydrogel composite [4] and 3D rice-like lanthanum-doped La@MgAl nanocomposites [37]. In Table 2, an availability of common adsorbents for aqueous fluoride removal is presented.

**Table 2.** Availability of common adsorbents for aqueous fluoride removal [38].

Material	Comments	Availability
Metal oxides and hydroxides	Exhibit relatively low efficiency without physico-chemical modification	low
Biosorbents	Exhibit relatively low efficiency without physico-chemical modification	very high
Geomaterials	Exhibit relatively low efficiency without physico-chemical modification	high
Carbonaceous Materials	Typically require expensive physico-chemical activation	low
Bone char	Produced by carbonizing animal bones	high
Industrial by-Products	Typically require expensive physico-chemical activation	low
Metallic iron (Fe^0)	Under natural conditions a ubiquitous (hydr)oxide layer is also present	high

Recently, various sorts of coffee have been used as adsorbents. Coffee is usable for removal of dyes [39], cadmium [40] and chromium [41]. Despite a small area of the surface, as compared to activated carbon, the waste of coffee grounds is saturated with valuable

organic components that stimulate higher sorptive ability [42]. Bio-sorbent, as exhausted coffee grounds, is also recyclable and capable of removing the lead and fluoride from the domestic and industrial waste-water sources, with an overall removal efficiency of about 90% [43].

Iron oxides, oxyhydroxides and hydroxides (all are called 'iron oxides') play an important role in a variety of industrial applications [44]. Iron oxides have been widely used as adsorbents for removal of various contaminants from water, wastewater and liquid hazardous waste [45–47]. The iron oxide minerals used as adsorbents of arsenic in water are goethite (a-FeOOH), hematite (Fe_2O_3), siderite ($FeCO_3$), limonite, ferrihydrite and magnetite (Fe_3O_4) [48]. Those iron oxide, green rusts can be chemically synthesized by the precipitation of Fe(III) or Fe(II) salts through the hydrolysis and oxidation processes [49].

Lithuania's water supply, which is rich by underground water resources, utilises only groundwater for its residents. However, the iron concentration in 87% of groundwater resources exceeds the permissible hygiene rates [50]. Although iron does not have a significant impact on human health, iron compounds should be removed from the groundwater because when soluble Fe(II), compounds interact with oxygen, and when insoluble, Fe(III) compounds, which fall into sediments, are formed. As a result, the water's turbidity increases, it takes on an unpleasant metallic taste and iron compounds give the water a brownish colour [51]. Due to these aesthetic issues, the World Health Organization recommends that the maximum permissible iron concentration in drinking water should not exceed 300 µg/L [8]. In drinking water treatment plants, these ions and compounds are efficiently removed by aeration and filtration through granular media filters [52,53]. The Antaviliai Water Supply Plant is the largest drinking water treatment plant in Lithuania and removes iron and manganese from the water. The facilities apply non-reagent technologies for water aeration and one-stage open filtration with a quartz sand filter. This technology does not produce water damage waste. The backwash water is precipitated, filtrated and then restored back to the water preparation stream, where it is filtered again and then supplied. Iron sludge is dehumidified using a chamber draining press, then stored and transported for recycling [54]. Iron sludge forms when soluble Fe(II) ions are oxidized to insoluble Fe(II) ions during aeration. The oxygen is oxidizing divalent iron ions to $Fe(OH)_3$ according to the equation [55]:

$$4Fe^{2+} + O_2 + 8HCO_3^- + 2H_2O \rightarrow 4Fe(OH)_3\downarrow + 8CO_2\uparrow \tag{1}$$
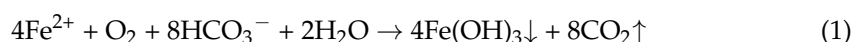
Iron hydroxide $Fe(OH)_3$ is a major constituent of iron sludge. Iron oxides are obtained by heat treatment of iron hydroxide [56]:

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O \tag{2}$$
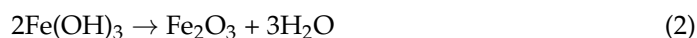
The hematite (Fe_2O_3) can be used as an adsorbent of arsenic in water [48]. The other researchers have found that the high iron concentration in drinking water sludge has the potential to be beneficially reused in sewer networks for sulphide control [57]. Yoo and colleagues reused iron sludge as an iron source for a Fenton reaction [58]. The adsorptive properties have been investigated by the use of iron sludge for the removal of organic compounds [54] and for removal of lead from water [59]. The study of Nde-Tchoupe and colleagues has demonstrated that Fe(0) filters are not suitable for fluoride removal [60]. Other studies confirmed the ion-selective nature of the Fe^0/H_2O system and demonstrated the relatively low efficiency of the same for fluoride removal [61]. However, in both studies, very high concentrations of fluoride—20 and 22.5 mg/L were used [60,61].

The goal of this research is to explore opportunities of small concentrations of fluoride removal from aqueous solutions using cheap and easily accessible adsorbents, such as exhaustive coffee grounds and iron sludge, to establish the efficiency of fluoride removal at different doses of sorbent and different contact times of the sorption process. The link between two sorbents (iron sludge and exhaustive coffee grounds) and two independent

factors (the sorbent dose A and the contact time B) is analysed using the two-factor ANOVA model [62].

2. Materials and Methods

2.1. Materials

The test water was distilled water contaminated by fluoride with the concentration of 3 mg/L. The concentration of fluoride in water has been chosen upon taking into account the chemical composition of the groundwater bores of Klaipėda watering-place—3 mg/L. Stock solutions of fluoride (1000 ± 2 mg/L, NaF) were used for water samples. Six flasks of 1 L with 3 mg/L of fluoride of test water were used for the tests.

The suppressed iron sludge was taken from the JSC (Joint-Stock Company) Vilniaus Vandenys Antaviliai drinking water treatment plant. This plant removes iron and manganese from the water. The facilities apply non-reagent technology for water aeration and one-stage open filtration with a quartz sand filter. Drinking water is saturated with oxygen from the air only. With this technology, it is not necessary to use extra chemical reagents. This technology does not produce water damage waste. The backwash water is precipitated, filtrated and then restored back to the water preparation stream, where it is filtered again and then supplied. Iron and manganese hydroxide sludge is dehumidified using a chamber draining press, then stored and transported for recycling [53]. The iron sludge composition data are presented in Table 3.

Table 3. The composition of the iron sludge [63].

Element	Quantity %
Iron (Fe)	33.9
Calcium (Ca)	4.5
Siliceous (Si)	2.7
Phosphorus (F)	2.2
Aluminium (Al)	0.4
Manganese (Mn)	0.25
Microelements (Zn, Ba, S, and ect.)	1.05

The iron sludge was transported from the water treatment plant. It was humid and contained 55% water. To evaporate this water, the iron sludge and coffee grounds were dried in a dryer at 105 °C for 3 h. The sludge was then crushed and sieved to obtain a homogenous powder.

2.2. Fluoride Removal Procedure

According to an analysis of the scientific literature and from practical knowledge, six doses (1 g/L, 2 g/L, 3 g/L, 4 g/L, 5 g/L and 6 g/L) of iron sludge powder and the corresponding doses of coffee grounds selected for the first stage of research, another six doses (10 g/L, 20 g/L, 30 g/L, 40 g/L, 50 g/L and 60 g/L) of iron sludge powder and the corresponding doses of coffee grounds were selected for the second one. The laboratory experiment was performed by mixing 1 L of the water, which should be discarded after some contact time. The test water was mixed with sorbents in a stirrer at 200 rpm. The water samples were taken in the quantities of 20 mL after different contact times: 30, 60, 90, 120 and 150 min. After adsorption, the solution was filtered through a membrane filter (47 mm diameter, pore size 0.45 μm). After filtration, tests of water quality were performed.

2.3. Analytical Methods

The concentration of fluoride was determined according to ISO 10359-1:1992 "Water quality—Determination of fluoride—Part 1: Electrochemical probe method for potable and lightly polluted water".

2.4. Statistical Methods

According to the "Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption" [64], the result is acceptable, when trueness and precision of method is less than 10%. Trueness (Table 4) is a measure of systematic error, i.e., the difference between the mean value of the large number (10 measurements) of repeated measurements and the true value. Stock solutions of fluoride are 1.5 mg/L, according to the "Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption" parametric value of fluoride is 1.5 mg/L [64]. Precision is a measure of random error and is usually expressed as the standard deviation (within and between batches) of the spread of results from the mean. Acceptable precision is twice the relative standard deviation.

Table 4. Trueness and precision of method.

Element	Trueness	Precision
Average value, mg/L	1.54	1.54
Assigned value, mg/L	1.5	1.5
Standard deviation, mg/L	0.01	1.01
Relative standard deviation, %	0.67	0.67
Acceptable trueness, %	2.47	1.34

The obtained result of the analysis is the arithmetical average of concentrations of three samples, when distribution does not exceed 10%, if tests with higher concentrations were repeated.

For analysing the research data, the analysis of variance (ANOVA) was used. ANOVA answers the question whether statistically significant differences between average values of the samples exist; however, it does not specify the average values of what samples show statistically significant differences. We applied dispersive analysis of two factors for comparing the average values of the variable under research. In the research, we use two independent variables: factor A (the sorbent dose) and factor B (the contact time). For establishing the statistically significant average values of samples, we applied the Tukey criterion. For verification of equality of average values, the confidence interval, when $\alpha = 0.05$, was used [62].

3. Results and Discussion

Figure 1 presents the results of the research when iron sludge is used. In all the samples, the fluoride concentration is 3 mg/L. How the fluoride concentration varies in samples when the sorbent dose and the contact time are changed was explored. Figure 1a shows how fluoride concentration varies depending on the contact time, when the iron sludge doses are 1, 2, 3, 4, 5 and 6 g/L and Figure 1b shows how the fluoride concentration varies depending on the contact time when the iron sludge doses are 10, 20, 30, 40, 50 and 60 g/L. In order for concentrations of fluoride in drinking water to correspond to the permissible norm of the World Health Organization, there are three main operating parameters of filtration: (1) nature of adsorbents, (2) extent of contaminants and (3) the hydraulics need to be investigated. In our research, we examine only one of the parameters—nature of sorbent. But in order to observe the changes in concentration of fluoride and compare whether it decreases enough as a reference point, we used the limit of permissible norm (1.5 mg/L) of the World Health Organization in Figures 1 and 2.
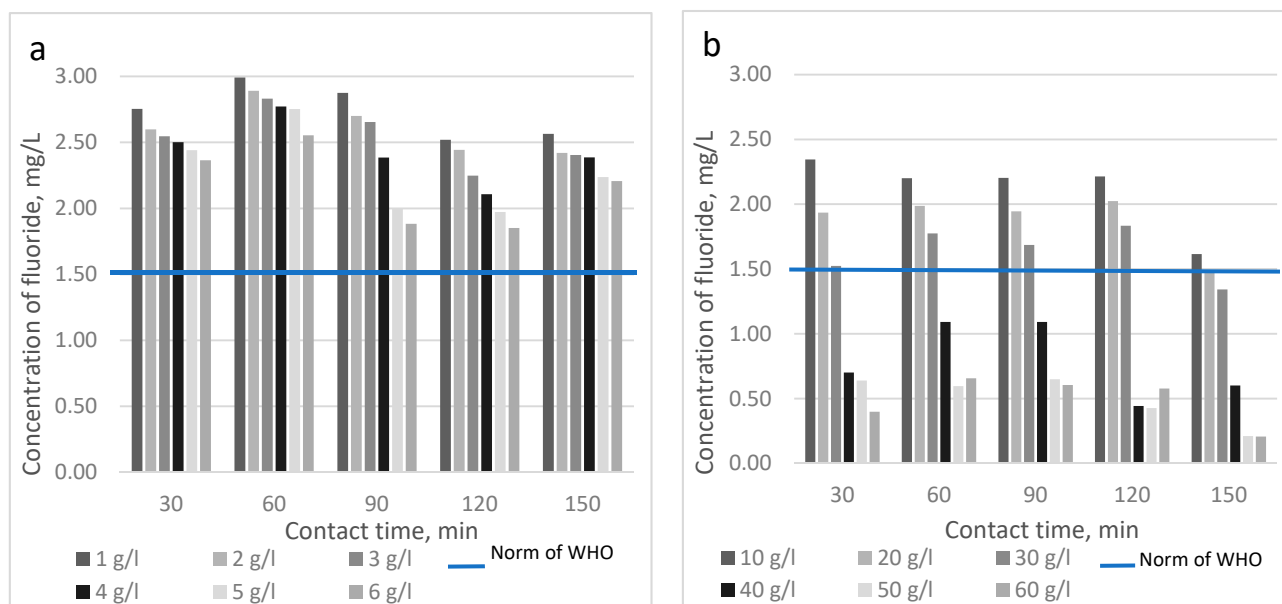
Figure 1. Dependence of fluoride concentration (initial concentration 3 mg/L) on sorption contact time at (**a**) doses 1, 2, 3, 4, 5 and 6 g/L of iron sludge; (**b**) doses 10, 20, 30, 40, 50 and 60 g/L of iron sludge.
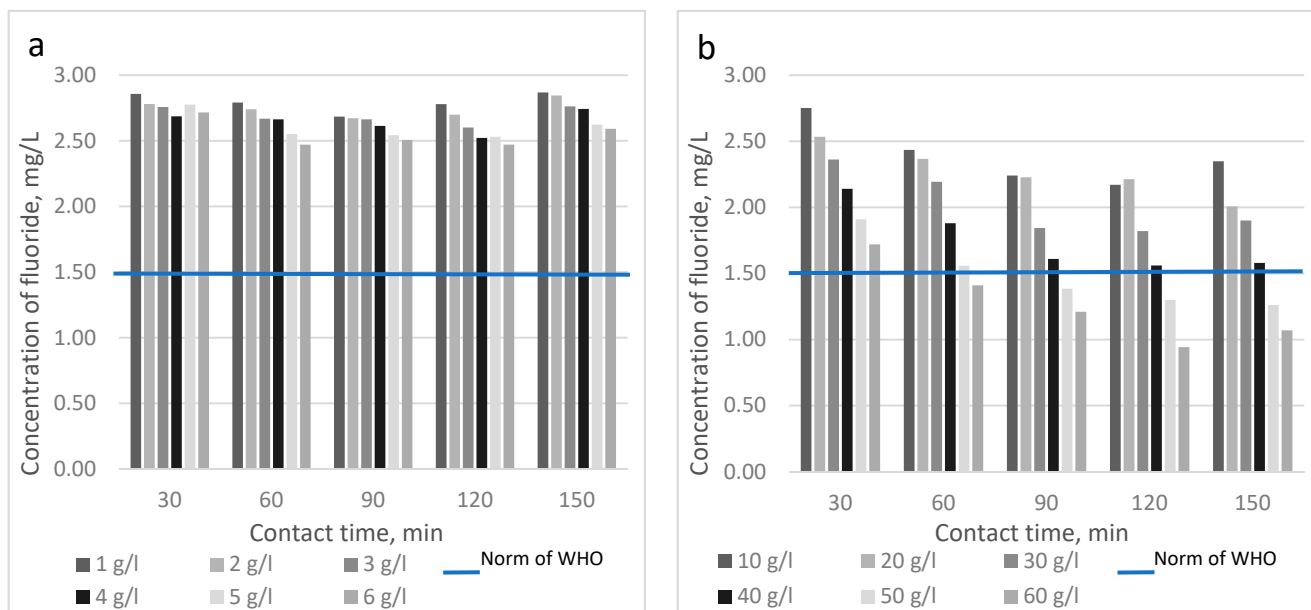

Figure 2. Dependence of fluoride concentration (initial concentration 3 mg/L) on sorption contact time at (**a**) doses 1, 2, 3, 4, 5 and 6 g/L of exhausted coffee grounds; (**b**) doses 10, 20, 30, 40, 50 and 60 g/L of exhausted coffee grounds.

The results of the research presented in Figure 1a show that when doses of iron sludge are from 1 to 6 g/L and the mixing time is 30 min, the fluoride concentration does not fall to the permissible norm of 1.5 mg/L. When a dose of 1 g/L is used, the fluoride concentration falls to 2.75 mg/L (8.2%); when the mixing time is the same and the dose of iron sludge is 6 g/L, the fluoride concentration falls to 2.36 mg/L (21.17%). After 60 min from the start of mixing, the fluoride concentration falls to 2.99 mg/L (4.18%), if the dose of iron sludge is 1 g/L, and if the mixing time remains the same and the dose is 6 g/L, the concentration falls to 2.55 mg/L (37.23%). After 90 min from the start of mixing, the fluoride concentration falls from 2.88 to 1.88 mg/L (0.27–14.87%). Upon further mixing, in water where the dose of sorbent was 1 g/L, the fluoride concentration is 2.52 mg/L (16.00%) after 120 min and 2.57 mg/L (14.50%) after 150 min. If the dose of iron sludge is

6 g/L the fluoride concentration in water falls down mostly after 120 min of mixing—to 1.85 mg/L (38.30%); after 150 min—it falls down to 2.21 mg/L (26.43%). However, if all the doses of iron sludge are used and they are held in the solutions for 30 to 150 min, the fluoride concentration does not fall to the permissible norm of 1.5 mg/L, so higher doses of iron sludge are used in further research works.

In Figure 1b, it may be observed that if 10, 20 and 30 g/L sorbent doses are used, the fluoride concentration falls to 2.35, 1.93 and 1.52 mg/L (21.83, 49.20 and 62.91%), and if the mixing time remains the same, when the dose of iron sludge is 40, 50 and 60 g/L, the fluoride concentration falls to 0.70, 0.64 and 0.40 mg/L (78.67, 78.67 and 86.70%), i.e., does not exceed the permissible level of 1.5 mg/L. After 60 min from the start of mixing, if 10, 20 and 30 g/L doses of iron sludge are used, the fluoride concentration falls to 2.20, 1.99 and 1.77 mg/L (26.67, 33.77 and 10.87%). If 40, 50 and 60 g/L doses of iron sludge are used, the fluoride concentration falls to 1.09, 0.60 and 0.66 mg/L (63.63, 80.13 and 78.10%) and does not exceed the permissible norms again. A similar trend took place after 90 and 120 min of mixing: when 10, 20 and 30 g/L doses of sorbent were used, the fluoride concentration exceeds the permissible norms; however, when 40, 50 and 60 g/L doses of iron sludge were used, the fluoride concentration does not exceed the permissible norms. Only after 150 min, if all the doses of iron sludge (except of 10 g/L) were used, the fluoride concentration falls from 1.48 to 0.21 mg/L (from 50.72 to 93.10%) and no longer exceeds the permissible norms.

Figure 2 presents the results of the research when exhausted coffee grounds are used. In all the samples, the fluoride concentration is 3 mg/L. It was explored whether the fluoride concentration in the samples changes when the sorbent dose and the contact time are changed. Figure 2a shows how the fluoride concentration varies depending on the contact time, when the used doses of coffee grounds are 1, 2, 3, 4, 5 and 6 g/L and Figure 2b shows how the fluoride concentration varies depending on the contact time, when the used doses of coffee grounds are 10, 20, 30, 40, 50 and 60 g/L.

We can see from the results presented in Figure 2a that using doses of exhausted coffee grounds from 1 to 6 g/L and mixing the sorbent in the solution for 30 to 150 min, the fluoride concentration falls to the minimum extent, i.e., from 2.47 to 2.87 mg/L (from 17.63 to 4.37%) and exceeds the permissible norms. So, we can see a trend that higher doses of sorbent cause a gradual reduction of the fluoride concentration; however, the said reduction is not sufficient to comply with the permissible norms. The highest efficiency of fluoride removal to 2.47 mg/L (17.63%) is achieved when the dose of exhausted coffee grounds is 6 g/L and the mixing time is 60 or 120 min; however, for time saving, the shorter time (60 min) is preferable.

Because the attempts to remove fluorides to the permissible norms upon using low doses of sorbents have been unsuccessful, higher doses of exhausted coffee grounds (10, 20, 30, 40, 50 and 60 g/L) were used in further research works. If the exhausted coffee grounds were mixed for 30 min and all the doses of them were used, the fluoride concentration exceeded the permissible norms; however, a higher dose of the sorbent caused increasing efficiency of reduction of the fluoride concentration. The fluoride concentration fell from 2.75 to 1.72 mg/L (from 8.27 to 42.67%). A similar trend is observed on mixing for 60, 90, 120 and 150 min. On mixing for 60 min and using doses of 10, 20, 30 and 40 g/L, fluoride concentration is falls; however, it exceeds the permissible norms. When the dose of 50 g/L is used, the fluoride concentration falls to 1.56 mg/L, i.e., very close to the permissible norm; however, when the dose of exhausted coffee grounds is 60 g/L, the fluoride concentration is 1.41 mg/L, i.e., does not exceed the permissible norms. On mixing the solutions for 90, 120 and 150 min and using the doses of 10, 20, 30 and 40 g/L, the fluoride concentration falls from 2.24 to 1.56 (from 25.30 to 48.07%); however, it exceeds the permissible norms. When the solutions are mixed for 90, 120 and 150 min and doses of 50 and 60 g/L are used, the fluoride concentration falls from 1.38 to 0.94 (from 54.00 to 68.59%) and no longer exceeds the permissible norms.

In this research, the experimental data are analysed starting from squaring the data averages and subsequently summarising the squares in order to explore whether the average values of dependent interval variables in different samples of the research data differ. In the beginning, the research data, in which differences are predetermined by the values of the first factor, are being analysed, then the research data, in which differences are predetermined by the values of the second factor, are being analysed. One more purpose of two-factor dispersive analysis is to explore an interaction of two independent factors. It is sufficiently resistant to temperate violations of assumptions, therefore the square model is applicable to describe the influence of the process indicators on the fluoride sorption process upon using iron sludge and exhausted coffee grounds.

The statistical value of the averages was found upon applying post hoc criteria, using the Tukey criterion and the omega squared coefficient (ω^2) that is an estimate of how much variance in the response variables is accounted for by the explanatory variable.

After two-factor ANOVA analysis for iron sludge sorption, we can see that the ratio between the sum of squares of the "sorbent dose" (A) and the sum of squares of errors is 373 times bigger than one—this shows that not all the averages are the same. The statistical criterion "sorbent dose" obtained for iron sludge during the analysis (F_A) is bigger than Fisher distribution $\acute{\alpha} = 0.05$ ($F_{\acute{\alpha}}$), i.e., 118,166 > 2.37. So, the average values in distributed data samples of the factor "sorbent dose" (A) differ significantly. Consequently, factor A provides its influence. It is evident that fluoride sorption is influenced by doses of iron sludge (at a significance of 5%).

After finding that not all the averages of samples are the same, we get to know what averages of samples statistically differ. This is done by applying the Tukey criterion. While comparing the values of the Tukey criterion for factor A obtained in Table 5 to the statistically critical value ($Q_{0.05}$), we can see that all the values $Q_{0.05} < T_A$, i.e., 129.37, 291.46, 226.01, 162.09, 655.73, 655.73 and 493.63 > 3.63. So, there are statistically significant differences between the averages of factor A according to the chosen level of significance $\acute{\alpha} = 0.05$.

Table 5. Post hoc criteria obtained during ANOVA analysis.

Dose of Sorbent, g/L A	1–3	4–6	10–30	40–60	1–3	4–6	10–30	40–60	$Q_{0.05}$
	Tukey's criterion of exhausted coffee grounds				Tukey's criterion of exhausted iron sludge				
1–3	-	61.19	219.35	634.50	-	129.37	2.91.46	226.01	>3.63
4–6	219.35	-	158.16	465.86	291.46	-	162.09	655.73	>3.63
10–30	527.06	465.86	-	307.71	785.10	655.73	-	493.63	>3.63
40–60	634.50	465.86	307.71	-	226.01	655.73	493.63	-	>3.63

Contact Time, min B	30	60	90	120	150	30	60	90	120	150	
30	-	71.51	119.94	138.57	107.18	-	67.45	2.21	60.04	88.38	>3.86
60	71.51	-	48.42	18.63	35.66	67.45	-	69.66	57.82	155.83	>3.86
90	119.94	48.42	-	18.63	12.76	2.21	69.66	-	57.82	86.17	>3.86
120	138.57	18.63	18.63	-	31.39	60.04	57.82	57.82	-	28.34	>3.86
150	107.18	35.66	12.76	12.76	-	88.38	155.83	86.17	28.34	-	>3.86

The ratio between the sum of squares of the factor "contact time" (B) and the sum of squares of errors is 15 times bigger than one—this shows that not all the averages are the same. The sum of squares of errors for the factor "contact time" (B) is 24 times bigger than for the factor "sorbent dose" (A). The statistical criterion "contact time" (F_B) is bigger than Fisher distribution $\acute{\alpha} = 0.05$ ($F_{\acute{\alpha}}$), i.e., 6.13 > 2.60. So, the average values of the variables of the distributed research data for the value of factor B differ; however, this difference is lower than for the factor "sorbent dose". For this reason, we assume that contact time of iron sludge provides less influence on sorption of fluorides at the significance of 5%.

Thus, we assume that averages of variables for the factor "contact time" (B) statistically differ. While comparing the Tukey criterion for factor B (T$_B$) with the statistically critical value, we can also see that all the values 67.45, 2.21, 60.05, 8.38, 69.66, 57.82, 155.83, 57.82, 86.17 and 28.34 > 3.86, and there are statistically significant differences between the averages of factor B.

For iron sludge, an interaction between the factor "sorbent dose" (A) and the factor "contact time" (B) exists because their coefficient of interaction of statistical criteria F$_{AB}$ is bigger than the Fisher criterion, i.e., 12,582 > 1.75. While comparing to omega squared (ω^2), it was found that the influence of factor B is less significant at $\omega^2 = 0.03$, and the influence of factor A provides the most influence on sorption of iron sludge because $\omega^2 = 0.68$. The interaction of factors A and B is not significant where $\omega^2 = 0.29$. The sorbent dose value is about 23 times more important than the contact time and about two times more important than the interaction of both factors. The same trend was shown by the results of the research: a reduction of fluoride concentration was more influenced by the dose of the added iron sludge than by the mixing time.

ANOVA analysis of the influence of two factors on the sorption of exhausted coffee grounds shows that the ratio between the sum of squares of the "sorbent dose" (A) and the sum of squares of errors is 165 times larger than one—this shows that not all the averages are the same. The statistical criterion "sorbent dose" for exhausted coffee grounds obtained during the analysis (F$_A$) is bigger than Fisher distribution $\acute{\alpha} = 0.05$ (F$_{\acute{\alpha}}$), i.e., 55,531 > 2.37. So, the average values in distributed data samples of the factor "sorbent dose" (A) differ significantly. Consequently, factor A provides its influence. It is evident that fluoride sorption is more influenced by doses of exhausted coffee grounds (5% significance).

When it was established that the averages of all samples are not the same, averages of samples that were statistically different were revealed. For this purpose, we used the Tukey criterion. While comparing the values of the Tukey criterion for factor A provided in Table 6 (T$_A$) with the statistically critical value (Q$_{0.05}$), we can see with all the values that Q0.05 < T$_A$, i.e., 3.63 < 61.19, 219.35, 634.50, 158.16, 465.86 and 307.71. Consequently, differences between the averages of the factor "sorbent dose" (A) are statistically significant according to the chosen level of significance $\acute{\alpha} = 0.05$.

Table 6. Results of ANOVA analysis.

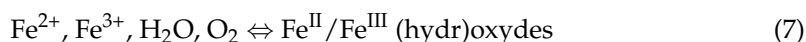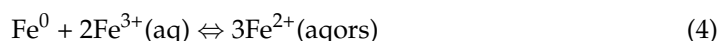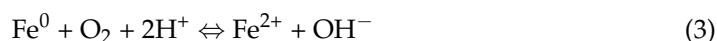|	Sum of Squares	Degrees of Freedom (Df)	Dispersion Estimates	Statistics (F)	Fisher Distribution $\acute{\alpha} = 0.05$	ω^2	Notes
			Sorption of iron sludge				
A	596.41	3	198.80	118166	>2.37	0.68	Makes an impact
B	24.54	4	6.13	3646	>2.60	0.03	Makes an impact
AB	254.01	12	21.17	12582	>1.75	0.29	There is an interaction
			Sorption of exhausted coffee grounds				
A	231.49	3	77.16	55531	>2.37	0.70	Makes an impact
B	16.62	4	4.15	2990	>2.60	0.05	Makes an impact
AB	80.10	12	6.67	4803	>1.75	0.24	There is an interaction

The sum of squares of errors for the factor "sorbent dose" (A) is about 14 times bigger than for the factor "contact time" (B). The ratio between the sum of squares and the sum of squares of errors for factor B is 11 times bigger than one—this shows that not all the averages are the same. The statistical criterion "contact time" (F$_B$) is bigger than the Fisher distribution $\acute{\alpha} = 0.05$ (F$_{\acute{\alpha}}$), i.e., 2990 > 2.60. So, the values of the averages of variables in the distributed research data for the factor "contact time" (B) differ. It can be seen from the performed analysis that the contact time at the significance of 5% differs inconsiderably, i.e., the influence of the mixing time on the sorption is too low. Consequently, we assume

that the averages of variables for the factor "contact time" (B) statistically differ. While comparing the values of the Tukey criterion for factor (B) (T_B) with the statistically critical value, it was also found that 3.63 < 71.51, 119.94, 138.57, 107.18, 48.42, 18.63, 35.66, 18.63, 12.76 and 31.39. Consequently, there are statistically significant differences between the averages of the factor "contact time" (B).

An interaction between the factor "sorbent dose" (A) and the factor "contact time" (B) for exhausted coffee grounds exists, because their coefficient of interaction of statistical criteria F_{AB} is bigger than the Fisher criterion, 4803 > 1.75. While comparing the values of the omega squared (ω^2), it is observed that the influence of the factor "contact time" (B) is of low significance ($\omega^2 = 0.05$), and the influence of the factor "sorbent dose" (A) on reduction of fluoride concentration is significant, because $\omega^2 = 0.70$. The interaction between AB factors is inconsiderable, because $\omega^2 = 0.24$. The sorbent dose value is about 14 times more important than the contact time and about three times more important than the interaction of both factors.

4. Discussion

Nde-Tchoupe and colleagues [60] and Heimann and colleagues [61] have used metallic iron (Fe^0) in their works on the removal of fluoride. Fe^0 is currently regarded as (a) a reductant for some species, (b) an adsorbent for other species, (c) a coagulant for various anionic species [65–67] and (d) a long-term supplier of Fe^{2+} for activation of oxidation processes [68]. The properties making Fe^0 suitable for environmental remediation include: (a) its ready availability and (b) its environmental friendliness implying the generation of non-toxic hydroxides and oxides [69]. In fact, Fe^0 is oxidized by water to form Fe^{II} species (Equation (5)) that are further transformed to Fe^{III} species and mixed Fe^{II}/Fe^{III} species including hydroxides and oxides (Equation (7)) [70–74]. The Fe^0/H_2O system contains (a) oxidizing agents (e.g., Fe^{III} species), (b) reducing agents (e.g., H_2, Fe^{II}, Fe_3O_4) and (c) adsorbing agents (e.g., hydroxides and oxides) acting in synergy. Fe^0 can also be specifically used to generate Fe^{II}/Fe^{III} [75,76], H_2 [76], or hydroxides and oxides [75]. In our study we are using iron sludge, where a major constituent is iron hydroxide $Fe(OH)_3$. The relationship between metallic iron Fe^0 and iron hydroxide $Fe(OH)_3$ is given in the reaction equations:

$$Fe^0 + O_2 + 2H^+ \Leftrightarrow Fe^{2+} + OH^- \tag{3}$$

$$Fe^0 + 2Fe^{3+}(aq) \Leftrightarrow 3Fe^{2+}(aqors) \tag{4}$$

$$Fe^0 + 2H^+ \Leftrightarrow Fe^{2+} + H_2 \tag{5}$$

$$4Fe^{2+} + O_2 + 8HCO_3^- + 2H_2O \rightarrow 4Fe(OH)_3\downarrow + 8CO_2\uparrow \tag{6}$$

$$Fe^{2+}, Fe^{3+}, H_2O, O_2 \Leftrightarrow Fe^{II}/Fe^{III} \text{ (hydr)oxydes} \tag{7}$$

The study of Nde-Tchoupe and colleagues has demonstrated that Fe^0 filters are not suitable for fluoride removal [60]. Other studies confirmed the ion-selective nature of the Fe^0/H_2O system and demonstrated the relatively low efficiency of the same for fluoride removal [61]. In Figure 1b, it may be observed that the following trend is visible: with a longer contact time as well as higher doses of sorbent, the fluoride concentration is falling gradually; in addition, at higher doses of sorbent, the efficiency of the removal is growing. When the doses of iron sludge are 40, 50 and 60 g/L and they are held in the solutions for 30 to 150 min, the efficiency is sufficient and achieves from 63.63% to 93.10%. It may be seen from the results of the research that the most optimum dose of iron sludge is 30 g/L and the contact time is 30 min, when the fluoride concentration falls down to 62.91% and does not exceed the permissible norms. These results of the research show that the reduction of the fluoride concentration is more affected by the dose of the sorbent than by the contact time. The competition of natural ligands as fluoride may contain further anions; Cl^-, SO_4^{2-}, PO_4^{3-}, HCO_3^- and NO_3^- might reduce removal efficiency of fluoride in Fe^0/H_2O systems. Heimann and colleagues observed that (a) the addition of 0.82 mM Cl^- completely inhibited removal of fluoride, (b) the addition of 0.82 mM HCO_3^-

significantly impaired removal of fluoride and (c) the best fluoride removal efficiency was observed in tap water. The main inhibition processes being: (a) the competition with fluoride for adsorption sites and (b) the relative solubility of Fe/L complexes (L = Cl^-, H_2O, HCO_3^-). Heimann and colleagues used tap water for their research, which had a composition of: $Cl^- = 9.7$ mg/L, $NO_3^- = 7.7$ mg/L, $SO_4^{2-} = 30.0$ mg/L, $HCO_3^- = 88.5$ mg/L and $F^- = 22.5$ mg/L [61]. Our test water was distilled water contaminated by fluoride with the concentration of 3 mg/L. In the study of other authors, results demonstrated the relative low capacity of iron corrosion products generated during the pre-corrosion time for water defluorination. It was observed that efficiency of fluoride removal is 30%, a two times lower efficiency compared with our results. The authors predicate that significant amounts of Fe(0) materials would be needed to achieve acceptable residual levels of fluoride [63]. In research, very high concentrations of fluoride—20 mg/L—were used. Therefore, there may be four reasons why fluoride removal is more efficient in our study compared to other authors: (a) in our study water did not contain anions that inhibited fluoride removal, (b) the fluoride concentration in our study was 6.7–7.4 times lower, (c) we used high enough doses of iron sludge (40, 50 and 60 g/L) to remove fluoride and (d) there were different conditions for fluoride removal.

Exhausted coffee grounds are capable of removing the fluoride from the water sources with a removal efficiency from 88.8 till 95.1% [43]. In our study, we can see a trend: the fluoride concentration is more influenced by the dose of the exhausted coffee grounds than by the time of mixing. In this case, the optimum conditions are the dose of 60 g/L and the mixing time of 60 min or the dose of 50 g/L and the mixing time of 90 min, when the fluoride concentration falls to 56.67%. The difference in the lower fluoride removal efficiency in our study may be due to the fact that we did not change the pH of the solution, and the researchers, Naga Dabu and colleagues, obtained the most efficient fluoride removal at very low pH = 4 [43].

In order to obtain a flow rate of 5 L/s of treated water, a scrubber dispenser of iron sludge with a capacity of 800 kg and a mixer with a water volume of 18 m³ were selected with a sorbent dose of 40 g/L and a contact time of 30 min. When cleaning water with used exhausted coffee grounds, a dispenser of 1620 kg of used coffee grounds and a mixer with a volume of 27 m³ of water are required, with a sorbent dose of 60 g/L and a contact time of 60 min. After 1 h 30 min, the fluoride removal process is repeated.

5. Conclusions

After the research, it was found that the optimum dose of iron sludge for fluoride removal, with an initial concentration of 3 mg/L, should be 30 g/L and the contact time should be 30 min; in such a case, the fluoride concentration decreases by 62.92% and does not exceed the permissible norms. If exhausted coffee grounds are used as a sorbent in the research, it was found that the most optimum conditions are a dose of 60 g/L and a mixing time of 60 min, or a dose of 50 g/L and a mixing time of 90 min, when the fluoride concentration decreases by 56.67%. The adsorbents have potential applicability in fluoride removal to the permissible norms. The said results show that the sorbent dose provides a stronger influence of reduction of fluoride concentration than the mixing time. The same results are also shown by two-factor ANOVA analysis. On its base, it was found that statistically significant differences exist between averages of samples of research data for the explored sorbents (exhausted coffee grounds and iron sludge). The influence of the factor "sorbent dose" (A) is stronger and the influence of the factor "contact time" (B) is low. The interaction between the sorbent dose and the contact time is low for both sorbents.

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