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Article

Fluoride Adsorption from Water Using Activated Carbon Modified with Nitric Acid and Hydrogen Peroxide

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Abstract: Adsorption on activated carbon is one of the most commonly used methods for removing excess amounts of fluoride from water. This research has tested the parameters of fluoride adsorption on four commercial activated carbons modified with nitric acid and hydrogen peroxide. The adsorption properties included the initial fluoride concentrations (2–40 mg/L), pH (4–9), dosage of activated carbon (2–20 g/L), contact time (15–360 min) and temperature (25–45 °C). The research results showed a decrease in the proportion of adsorbed fluoride by increasing its initial concentration, while an increase in temperature had a positive effect on the proportion of removed fluoride. The highest fluoride adsorption capacity of 1 mg/g belonged to HN-H_2O_2 active carbon at a temperature of 45 °C. The maximum adsorption capacities were recorded at pH 4 for all adsorbents oxidized with H_2O_2 (0.041–0.168 mg/g) and at pH 6 for all adsorbents oxidized with HNO_3 (0.065–0.134 mg/g). An increase in the temperature to 45 °C resulted in the maximum increase in the adsorption capacity for all adsorbents, and the adsorbent HN-HNO_3 (0.158 mg/g) had the highest adsorption capacity. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms were used to determine the adsorption mechanism. The experimental data showed the best match with the Freundlich model at all temperatures, while the pseudo-second-order kinetic model described the adsorption rate the best.

Keywords: adsorption; fluoride; activated carbon; isotherms; kinetic models

1. Introduction

The fluoride contamination of drinking water is a global health problem, as more than 260 million people worldwide consume water with fluoride concentrations exceeding 1.5 mg/L. According to the recommendation of the World Health Organization, this is the maximum permissible level of fluoride in drinking water [1–3]. In groundwater, the concentration of fluoride is primarily determined by the geological composition of the aquifer, but there is an increasing influence of various industries, which significantly increase its concentration through the discharge of wastewater and gasses [4]. Most of the health consequences from the intake of water with an excessive fluoride concentration, which most often manifest as dental and skeletal fluorosis, have been recorded in underdeveloped countries where drinking water from which fluoride has not been previously removed is mainly consumed [5,6]. However, even developed countries do not avoid the problem of elevated fluoride concentrations entirely, because of the developed industries and their impact on the environment [7].

There are numerous methods used to reduce elevated fluoride concentrations in water, such as ion exchange, membrane processes, electrocoagulation, coagulation and precipitation and adsorption [8–10]. High concentrations of fluoride can be adsorbed on different materials such as activated alumina, bone carbon, oxides and hydroxides, bauxite, red mud, biomass, zeolite, activated carbon and similar porous materials [11,12].

Activated carbon is an adsorbent which is used very often in water treatment processes due to its developed microporous structure and the exceptional number of different functional groups on its surface, a low production cost and high availability. The use of cheap

and easily available adsorbents with high carbon content for the preparation of activated carbon has recently been increased. Economical and efficient adsorbents that are potentially good for removing pollutants from water and wastewater are being developed [13,14]. An important advantage of activated carbon is its large surface area, well-developed internal pore structure and the surface area of chemical functional groups located on its external and internal surfaces. These characteristics make AC adsorption an attractive approach to removing contaminants from water [15].

Surface modification methods such as chemical, physical and microwave treatments and impregnation can change the activated carbon into a more polar material and change the pore size distribution [15–18]. Among them, chemical surface modification methods are widely used.

In their research, numerous authors report the positive influence of oxidizing agents, such as HNO_3, NH_3, H_2O_2 and $HClO_4$, H_2SO_4, $H_2S_2O_4$, $(CH_3CO)_2O$, $KMnO_4$, $(NH_4)_2S_2O_8$, H_3PO_4 and $NaOH$, on the increase in the adsorption capacity of activated carbon. There are changes in the structure and functional groups on the surface of activated carbon, whereby the structure of the oxidized surface of activated carbon depends on the type of oxidizing agent as well as the oxidation conditions [17,19–24].

Although activated carbons are the most used adsorbents worldwide with high capacities, they are generally characterized by low selectivity for fluoride ions due to physical adsorption. In most studies, prior to the examination of fluoride removal efficiency, activated carbons are modified by oxidation and subsequent impregnation with high-valent ions such as zirconium, titanium, iron, calcium, etc. Chemical activants may promote crosslinking, forming a rigid, less volatile matrix with a smaller volume contraction at high temperatures. An advantage of chemical activation is the lower temperature required. Chemical activation gives higher global yields since char burn-off is not required [25–28].

The treatment of activated carbon with hydrogen peroxide increases the enrichment efficiency relative to non-oxidized activated carbon [29]. Oxidation with nitric acid produces a slight decrease in the porosity and the surface area of activated carbon, although drastic changes in the chemical nature of the surface take place [30,31].

On the basis of the above-mentioned research, in this work, commercially available activated carbons modified with nitric acid and hydrogen peroxide were used. The objectives of this study were to evaluate the best conditions for fluoride adsorption onto the modified commercial activated carbons and to determine the adsorption mechanisms using adsorption isotherms and kinetic models. Based on the results of the research, possible positive effects on increasing the adsorption capacity of the tested adsorbents were analyzed.

The adsorption properties of the activated carbons before modification were reported in previously published original research [32]. In the aforementioned article, the chemical and physical properties of the four analyzed commercial activated carbons were presented.

By modifying activated carbons with hydrogen peroxide and nitric acid, an attempt was made to prove the connection between the positive effect of the oxidation of the activated carbon's surface and its adsorption properties. Previous research by numerous authors highlighted the positive effect of oxidation on the adsorption capacity of activated carbons including hydrogen peroxide and nitric acid, which is why they were chosen for this research. The adsorption process was characterized in the literature and in practice as economical. With this in mind, cheap and readily available commercial activated carbons were used in this experiment. In this way, we wanted to test the conditions under which the removal of fluoride from the water would be the most effective.

On the other hand, there were limitations in the application of these commercial activated carbons, which were unavailability in the market and standard properties that could not be changed easily and perhaps could be improved.

2. Materials and Methods

2.1. Preparation of Adsorbents

The adsorbents used in this research were four commercially available activated carbons: Norit ROW 0.8 Supra (Norit Nederland BV, Amersfoort, The Netherlands), Norit GAC 1240 (Norit Nederland BV), Cullar D (Culligan International Company, Rosemont, IL, USA) and Hydraffin 30 N (Donau Carbon GmbH & Co., Frankfurt, Germany). The agents used for oxidation were 65% nitric acid (Carlo Erba Reagents, Cornaredo, Italy) and 30% hydrogen peroxide (Carlo Erba Reagents, Cornaredo, Italy). The oxidation process began by mixing a sample of activated carbon and an oxidizing agent in a ratio of 1:10, after which the mixture was left at room temperature for 24 h with occasional stirring. The mixture was then filtered using a membrane filter paper with a pore size of 0.45 μm and washed several times with deionized water until the pH was neutral. Filtered and washed activated carbon samples were dried in a dryer at 105 °C, cooled in a desiccator and stored in a suitable package without access to air. The abbreviations of all tested samples are listed in Table 1.

Table 1. Abbreviations of adsorbents.

Activated Carbon	Activated Carbon Oxidized with HNO_3	Activated Carbon Oxidized with H_2O_2
Norit ROW 0.8 SUPRA	NR-HNO_3	NR-H_2O_2
Norit GAC 1240	NG-HNO_3	NG-H_2O_2
Cullar D	CD-HNO_3	CD-H_2O_2
Hydraffin 30 N	HN-HNO_3	HN-H_2O_2

2.2. Fluoride Adsorption Experiments

A standard fluoride solution with a concentration of 100 mg/L was prepared by dissolving 0.221 g of anhydrous sodium fluoride (Sigma-Aldrich, Saint Louis, MO, USA) in 1 L of deionized water. Model solutions with mass concentrations of 2, 5, 10, 20, 30 and 40 mg/L were prepared by diluting the standard solution. Before adsorption, the pH value of the solutions was adjusted using 0.1 M NaOH and 0.1 M HCl solutions (Kefo, Sisak, Croatia). The pH adjustment was monitored using a Seven Easy pH meter (Mettler Toledo, Greifensee, Switzerland). The adsorptive influence of the initial fluoride concentration was tested at the temperatures of 25, 35 and 45 °C for 120 min at pH 7 and an activated carbon concentration of 10 mg/L. The influence of pH 4–9 on adsorption was tested at the temperatures of 25, 35 and 45 °C for 120 min, where the concentration of the fluoride solution was 5 mg/L and the concentration of the adsorbent was 10 g/L. The influence of activated carbon concentrations (2, 4, 6, 8, 10 and 20 g/L) was tested for a 5 mg/L fluoride solution for 120 min at pH 7, at the temperatures of 25, 35 and 45 °C.

Adsorption was carried out on a laboratory scale using 100 mL conical flasks with 100 mL of the test solution at three different temperatures (25 °C, 35 °C and 45 °C) in a temperature-controlled shaker (Kottermann Labortechnik, Uetze, Germany) at 120 rpm. After the adsorption, the aqueous solutions were filtered through 0.45 μm cellulose acetate membrane filters and the fluoride concentration was determined using the potentiometric method. To determine the initial and final concentration of fluoride in aqueous solutions, a fluoride ion-selective electrode (Hach, Loveland, CO, USA) and total ionic strength adjustment buffer (TISAB), for increasing the ionic strength and ensuring that other ions did not interfere with the fluoride ions during the measurements, were used. The measurement was performed in three repetitions, and the results show the mean value.

The equilibrium adsorption capacity q_e (mg/g) of each used activated carbon was determined according to the following equation [33]:

$$q_e = \frac{(c_0 - c_e)}{m} \times V$$

where c_0 and c_e were the initial and the equilibrium fluoride concentrations in aqueous solutions (mg/L), respectively, V was the solution volume (L) and m (g) was the adsorbent mass.

2.3. Adsorption Isotherm and Kinetic Analysis

The description of the adsorption process at different temperatures is shown using adsorption isotherms: Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (Table 2). The experimental data obtained in this work were processed with mathematical models that described the equilibrium states of adsorption processes at the temperatures 25 °C, 35 °C and 45 °C. Adsorption isotherms for all activated carbon samples were determined by the adsorption of fluoride on activated carbon using standard solutions with concentrations of 2, 5, 10, 20, 30 and 40 mg/L at pH 7 for 120 min.

Table 2. The equations of isothermal and kinetic parameters [34–37].

Isotherm	Langmuir	Freundlich	Temkin	Dubinin–Radushkevich
Equation	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$q_e = K_F C_e^{1/n}$	$q_e = \left(\frac{RT}{b}\right) ln(A_T C_e)$	$q_e = q_m \exp\left(-K_{DR}\varepsilon^2\right)$

q_e = equilibrium adsorption capacity (mg/g); q_m = maximum adsorption capacity (mg/g); K_L = Langmuir isotherm constant (L/mg); C_e = equilibrium concentration of adsorbate (mg/L); n = Freundlich adsorption intensity; K_F = Freundlich isotherm constant (mg/g)(mg/L)$^{1/n}$; R = universal gas constant (J/molK); T = temperature (K); A_T = Temkin equilibrium binding constant (L/g); K_{DR}—Dubinin–Raduschkevich constant (mol^2/kJ^2); ε—Polanyi potential

Kinetic model	Pseudo-first-order	Pseudo-second-order	Intraparticle diffusion	Elovich
Equation	$\frac{dq_t}{dt} = k_1(q_{m1} - q_t)$	$\frac{dq_t}{dt} = k_2(q_{m2} - q_t)^2$	$q_t = k_{id}t^{1/2} + C$	$\frac{dq_t}{d_t} = \alpha \, exp(-\beta q_t)$

q_{m1}—equilibrium adsorption capacity (mg/g); q_t—adsorption capacity in time t (mg/g); t—time (min); k_1—pseudo-first-order adsorption rate constant (min^{-1}); q_{m2}—equilibrium adsorption capacity (mg/g); k_2—pseudo-second-order adsorption rate constant (g/mg min); k_{id}—interparticle diffusion rate constant (mg/g min$^{1/2}$); C—thickness of the boundary layer; α—initial adsorption rate (mg/g min); β—desorption constant (g/mg)

Four kinetic models were used to determine the behavior of fluoride ions during adsorption onto oxidized activated carbons: pseudo-first-order, pseudo-second-order, intraparticle diffusion and the Elovich model (Table 2). In order to ensure the quality of the obtained results, each experiment was performed in duplicate and only the average values were reported. Kinetic models were tested for correlations with three different adsorption temperatures (25 °C, 35 °C and 45 °C) with an initial fluoride concentration in the model solution of 5 mg/L, an adsorbent mass concentration of 10 g/L and pH 7 ± 0.3. Adsorption was carried out in a thermostatic shaker with 120 shakes per minute for a time period of 15, 30, 60, 120, 240 and 360 min.

3. Results and Discussion

3.1. Effect of Initial Fluoride Concentration

The efficiency of fluoride adsorption on oxidized activated carbons depends on the initial fluoride concentration and temperature as shown in Figure 1a–d. The influence of the initial concentration of fluoride (2, 5, 10, 20, 30 and 40 mg/L) on the adsorption capacity (q_e) was determined at pH 7 and at three different temperatures (25, 35 and 45 °C) for 120 min using an adsorbent dosage of 10 g/L. The adsorption capacity of all adsorbents increased by increasing the initial concentration of fluoride as well as by increasing the adsorption temperature. The highest adsorption capacities were achieved at 45 °C at the maximum concentration of fluoride in the solution (40 mg/L). At a temperature of 25 °C, activated carbon oxidized with HNO_3 had a higher adsorption capacity than the activated carbon oxidized with H_2O_2. At the adsorption temperature of 35 °C, the difference in the adsorption capacity between the mentioned adsorbents decreased. A further increase in the temperature favored an increase in the adsorption capacity of all adsorbents. HN-H_2O_2 active carbon had the highest adsorption capacity (1 mg/g) at 45 °C.
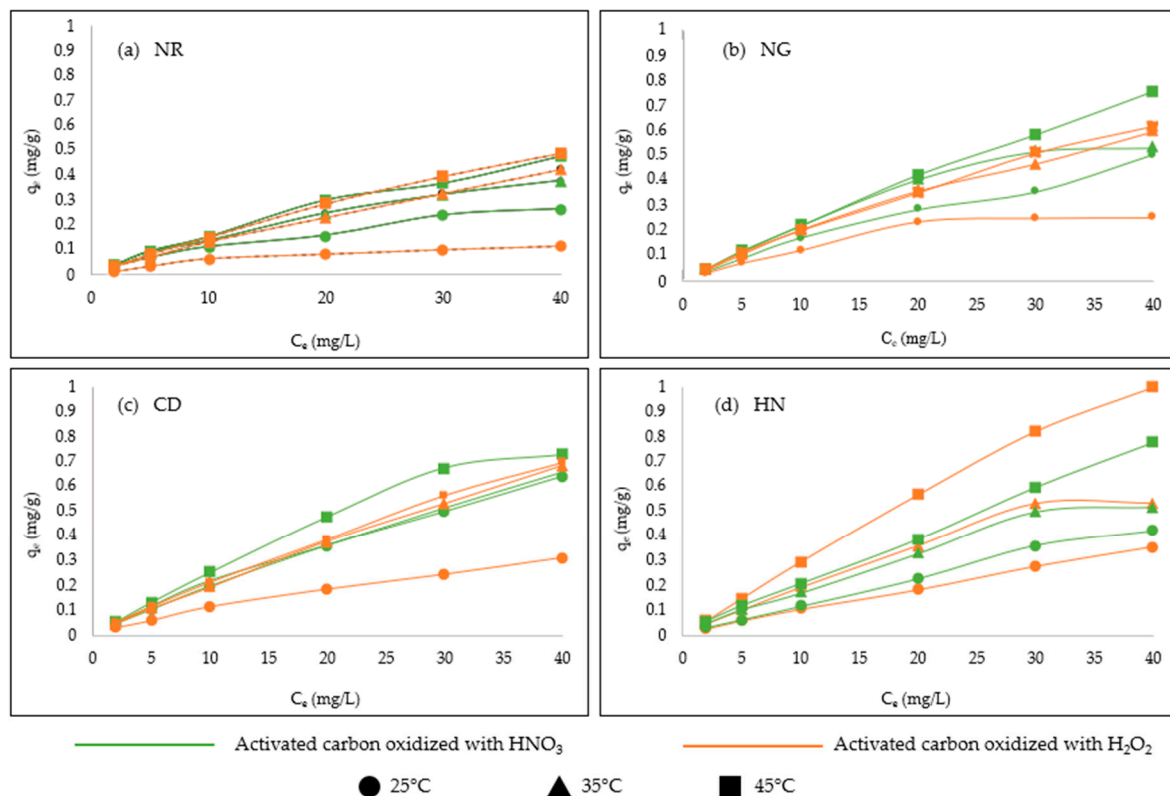
Figure 1. Effect of initial fluoride concentration and temperature on fluoride adsorption capacities (mg/g) of (**a**) NR-HNO$_3$ and NR-H$_2$O$_2$, (**b**) NG-HNO$_3$ and NG-H$_2$O$_2$, (**c**) CD-HNO$_3$ and CD-H$_2$O$_2$ and (**d**) HN-HNO$_3$ and HN-H$_2$O$_2$.

The reason for the decrease in the proportion of fluorides removed by increasing their initial concentration Sivasankar et al. [37] attributed to the high intermolecular competition to occupy sites on the adsorbent surface of a lower energy value. Other authors, who also deal with the problem of water defluoridation by adsorption, believe that the cause of the mentioned phenomenon is the increased number of free fluoride ions created by increasing their share, which compete with each other for the unchanged number of free adsorption sites; thereby, the surface becomes saturated very quickly and the share of fluorides removed in total decreases [38–40].

3.2. Effect of Adsorbent Dosage

The influence of different adsorbent concentrations on adsorption was determined: 2, 4, 6, 8, 10 and 20 g/L. Adsorption was carried out for 120 min at an initial fluoride concentration of 5 mg/L, pH 7 and the temperatures of 25 °C, 35 °C and 45 °C. As can be seen in Figure 2a–d, the amount of adsorbed fluorides in all activated carbon samples at all adsorption temperatures (25 °C, 35 °C and 45 °C) decreases with an increasing mass concentration of the adsorbent, while the adsorption effect increases with an increasing temperature. Adsorbents oxidized with HNO$_3$ have a higher adsorption capacity at all adsorption temperatures, except for HN-H$_2$O$_2$, whose values are higher at 45 °C. Increasing the temperature reduces the difference in the adsorption effect depending on the type of oxidation of the samples. Several authors have pointed out that increasing the concentration of the adsorbent increases the number of its adsorption sites that remain unsaturated during the adsorption process. This leads to a drop in the capacity of the adsorbent (q$_e$). There is also the possibility that the agglomeration of adsorbent particles due to an increase in the concentration leads to a decrease in the size of its active surface, which results in an increase in the length of the diffusion path, and thus in a decrease in the adsorption effect [34,41,42].
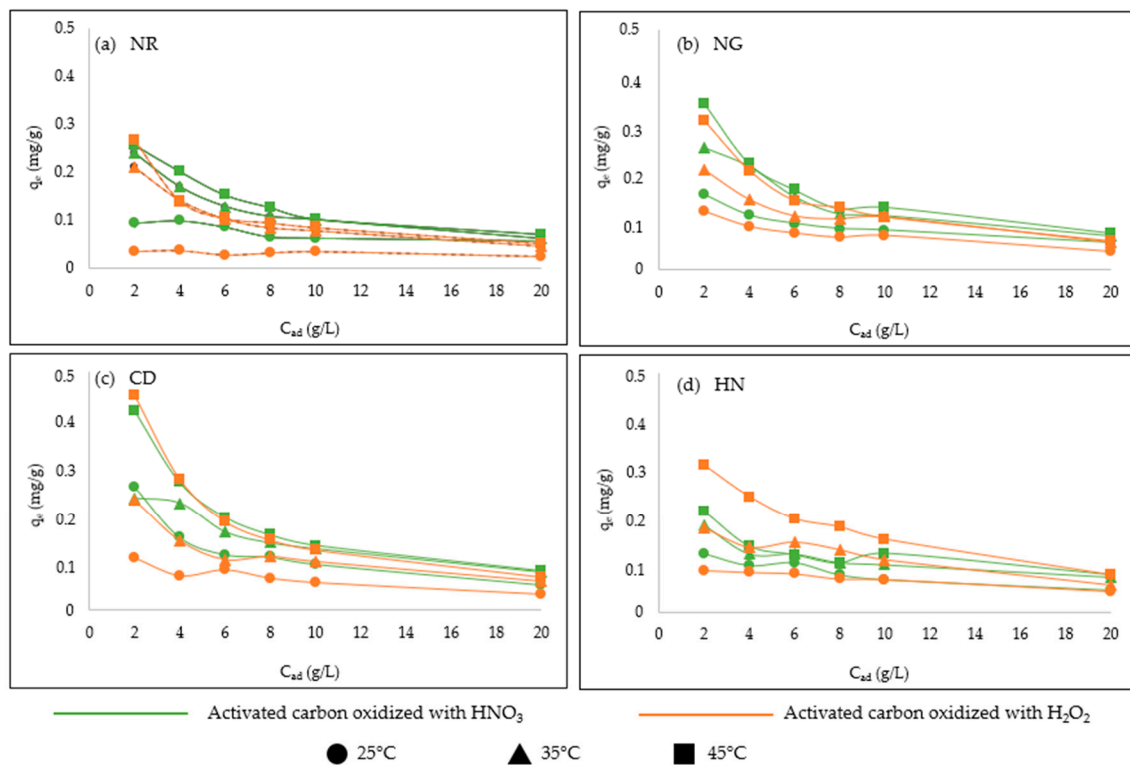
Figure 2. Effect of adsorbent dose and temperature on fluoride adsorption capacities (mg/g) of (**a**) NR-HNO_3 and NR-H_2O_2, (**b**) NG-HNO_3 and NG-H_2O_2, (**c**) CD-HNO_3 and CD-H_2O_2 and (**d**) HN-HNO_3 and HN-H_2O_2.

3.3. Effect of Contact Time

The test of the adsorption efficiency over time was performed with an initial fluoride concentration of 5 mg/L, an adsorbent concentration of 10 mg/L and at pH 7. Adsorption took place at 25, 35 and 45 °C with 120 shakes per minute for the following time intervals: 15, 30, 60, 120, 240 and 360 min. The results of testing the influence of the contact time between the adsorbent and fluoride in the solution on the adsorption effect are shown in Figure 3a–d. Observing the obtained values, it can be concluded that the adsorption of fluoride on all adsorbents increases gradually over time, whereby the intensity of binding up to 120 min is higher compared to the entire adsorption time of 360 min. The type of oxidizing agent has the greatest role in the increased adsorption effect at 25 °C, which is slightly less at 35 °C, while at the adsorption temperature of 45 °C the difference is not very pronounced. At 25 °C, activated carbon oxidized with HNO_3 has a better capacity with a maximum value of 0.102–0.123 mg/g compared to that oxidized with H_2O_2 (0.056–0.099 mg/g). The maximum adsorption capacity was achieved at a temperature of 45 °C for all adsorbents, and the highest adsorption capacity belonged to the adsorbent HN-HNO_3 (0.158 mg/g).

The tendency to establish an equilibrium state begins after 120 min of adsorption for all four adsorbents. Namely, during a certain time, which in all cases of tested adsorption processes on all previously mentioned adsorbents amounted to about 120 min, a more intense adsorption occurs compared to the rest of the time, when the adsorption equilibrium is established between the ions attached to the adsorbent and those which are still present in the solution. The two-phase binding of fluoride to the adsorbent can be explained by the way in which the vacancies on the adsorbent are filled. The time after which the rate of adsorption significantly slows down indicates the end of adsorption due to the assumption that the fluoride ions have filled the monolayer on the adsorbent or that multilayer adsorption has occurred through the diffusion of fluoride ions into the interior of the adsorbent through the film [43].
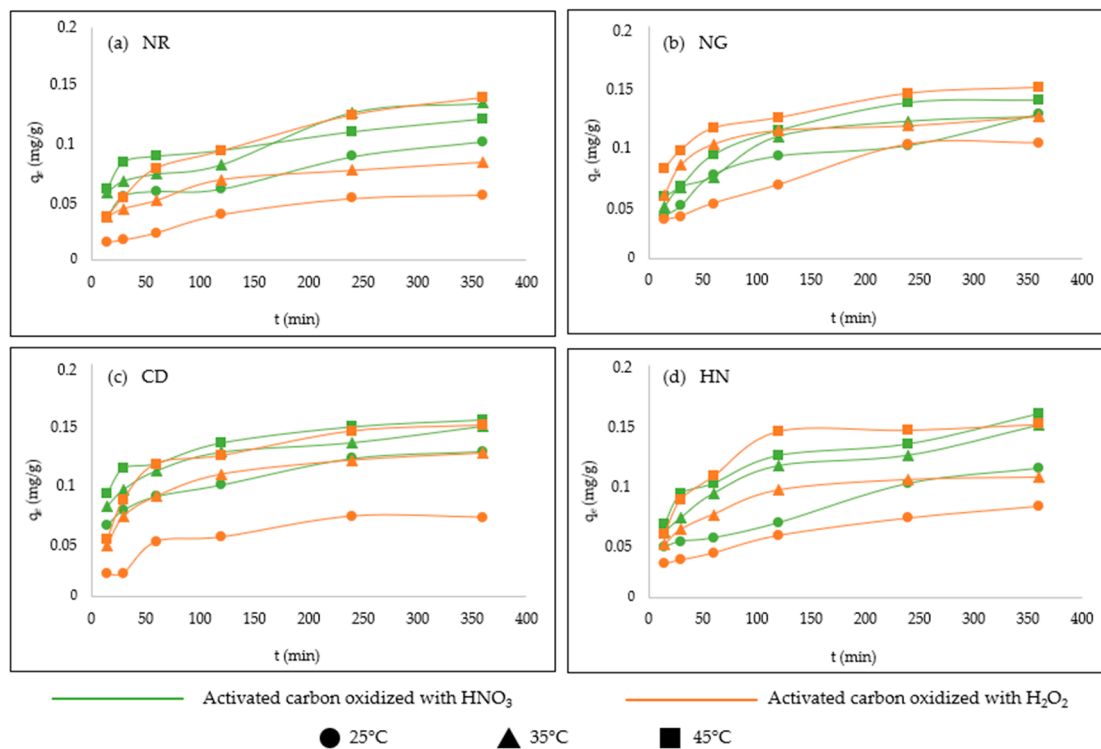
Figure 3. Effect of contact time and temperature on fluoride adsorption capacities (mg/g) of (**a**) NR-HNO$_3$ and NR-H$_2$O$_2$, (**b**) NG-HNO$_3$ and NG-H$_2$O$_2$, (**c**) CD-HNO$_3$ and CD-H$_2$O$_2$ and (**d**) HN-HNO$_3$ and HN-H$_2$O$_2$.

3.4. Effect of pH

The influence of pH on the adsorption of fluoride on activated carbon was tested in the value range from four to nine. Adsorption was carried out at the temperatures of 25, 35 and 45 °C for 120 min. The fluoride concentration was 5 mg/L, and the adsorbent concentration was 10 g/L. The effect of the initial pH value of the aqueous solution on the capacity of the adsorbents is shown in Figure 4a–d. Maximum adsorption capacities were recorded at pH 4 for all adsorbents oxidized with H$_2$O$_2$ (0.041–0.168 mg/g) and at pH 6 for all the adsorbents oxidized with HNO$_3$ (0.065–0.134 mg/g). At higher pH values than when the maximum efficiency was achieved, there was a decrease in the affinity towards fluoride ions at all tested adsorption temperatures (25 °C, 35 °C and 45 °C). In order to understand the effect of pH on the adsorption mechanism, numerous authors have explained a series of reactions that may occur in the system during fluoride binding to the adsorbent. At a low pH, the dissociation of the hydrogen fluoride molecule occurs, and this is precisely the limiting factor for the binding of fluoride ions to activated carbon in systems with a lower than optimal pH. This results in a very small proportion of the free fluoride ions, while on the other hand, the proportion of H$^+$ is large. When the adsorption system is at the optimal pH, i.e., when there is a sufficient amount of the free fluoride ions in the solution with a non-dominant concentration of other ions (H$^+$ and OH$^-$), the functional groups on the surface of the activated carbon are protonated and can attract fluoride ions of the opposite charge. At high pH values, there is a high concentration of OH$^-$ ions of the same charge as fluoride ions in the adsorption system, which is why they have the possibility to compete with them for a free place on the adsorbent, although in some cases fluoride ions "win" over hydroxide ions, which makes it possible to remove fluoride from solutions even at high pH values, but in a much smaller proportion [44,45].
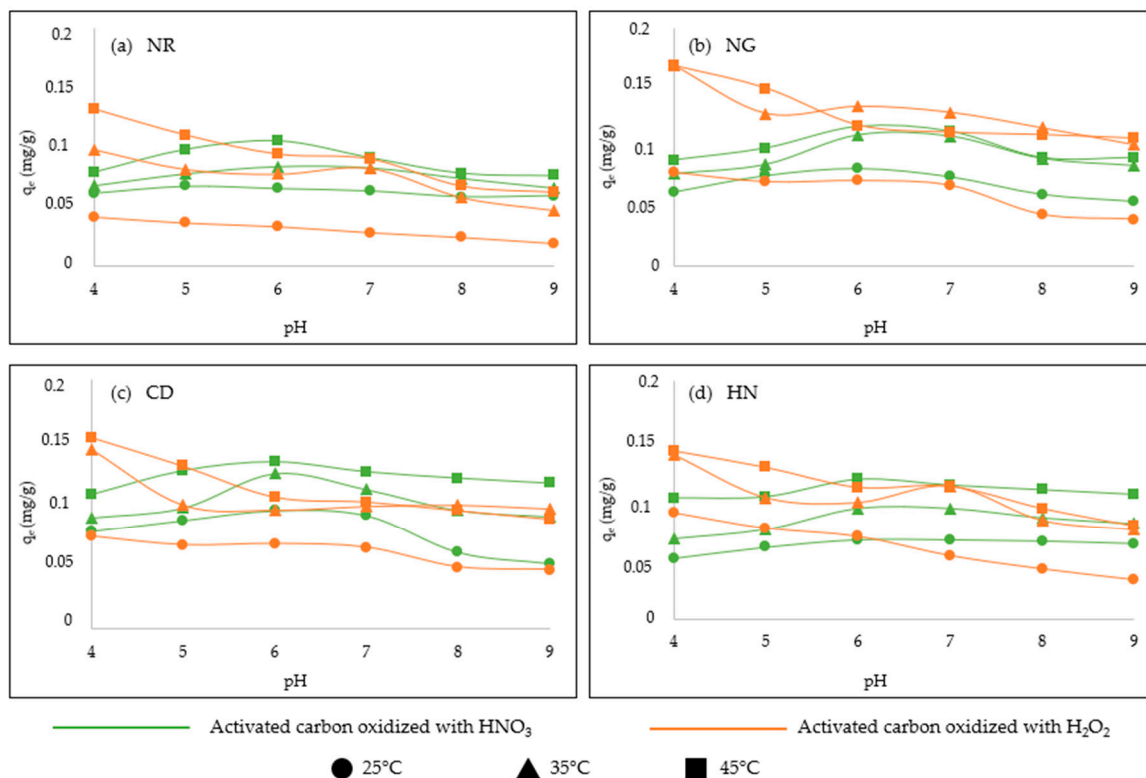
Figure 4. Effect of pH and temperature on fluoride adsorption capacities (mg/g) of (**a**) NR-HNO$_3$ and NR-H$_2$O$_2$, (**b**) NG-HNO$_3$ and NG-H$_2$O$_2$, (**c**) CD-HNO$_3$ and CD-H$_2$O$_2$ and (**d**) HN-HNO$_3$ and HN-H$_2$O$_2$.

3.5. Adsorption Isotherms

The values of the linear correlation coefficients of the obtained data (R^2) for all samples suggest that the Freundlich isotherm has the best agreement with the experimental data and represents a suitable model for describing the equilibrium state of the adsorption process (Table 3). The constant n is a parameter that is significant for describing the adsorption process in the equilibrium state defined by the Freundlich isotherm. It represents the adsorption intensity, and its value should be above one, usually in the range of one to ten, for the adsorption process to give satisfying results. Smaller values of the constant n suggest a lower strength of adsorption, which points to a greater heterogeneity of the adsorbent surface [46]. For all adsorbents, at all three adsorption temperatures, the values of n are above one, which indicates the success of the adsorption process. The oxidation of activated carbon with HNO$_3$ generally gives higher values of n at all temperatures compared to activated carbon oxidized with H$_2$O$_2$. An increase in the adsorption temperature leads to a decrease in the strength of adsorption, which is reflected in a decrease in the value of the constant n for all adsorbents. A decrease in the Freundlich constant n with an increasing temperature was also observed by Ayoob and Gupta [47], examining the effectiveness of cement as an adsorbent for the removal of fluoride from water at 17 °C. Similar results were obtained by Bhaumik et al. [48] using eggshell powder as an adsorbent when, for the range of adsorption temperatures from 30 °C to 60 °C, the values of the constant n were from 1.18 to 1.06.

Table 3. Isotherm models for adsorption of fluoride onto adsorbents.

		Isotherm											
		Langmuir			Freundlich			Temkin			Dubinin–Radushkevich		
		q_m (mg/g)	K_L (L/mg)	R^2	n	K_F (mg/g) $(L/mg)^{1/n}$	R^2	A_T (L/g)	B_T	R^2	q_m (mg/g)	K_{DR} (mol^2/kJ)	R^2
25 °C	NR-HNO$_3$	0.417	0.044	0.889	1.554	0.026	0.986	0.686	0.075	0.911	0.164	$1 \cdot 10^{-6}$	0.653
	NG-HNO$_3$	1.089	0.021	0.863	1.257	0.027	0.993	0.554	0.141	0.903	0.738	$2 \cdot 10^{-7}$	0.458
	CD-HNO$_3$	2.112	0.012	0.739	1.151	0.030	0.998	0.523	0.189	0.886	0.337	$1 \cdot 10^{-6}$	0.709
	HN-HNO$_3$	1.565	0.010	0.588	1.146	0.019	0.995	0.461	0.129	0.877	0.221	$2 \cdot 10^{-6}$	0.672
	NR-H$_2$O$_2$	0.153	0.067	0.852	1.492	0.012	0.904	0.779	0.034	0.864	0.087	$2 \cdot 10^{-6}$	0.849
	NG-H$_2$O$_2$	0.271	0.103	0.835	1.542	0.026	0.935	0.865	0.068	0.809	0.178	$1 \cdot 10^{-6}$	0.808
	CD-H$_2$O$_2$	0.578	0.028	0.931	1.327	0.021	0.997	0.569	0.088	0.922	0.178	$1 \cdot 10^{-6}$	0.718
	HN-H$_2$O$_2$	0.983	0.014	0.809	1.888	0.016	0.999	0.486	0.103	0.881	0.188	$2 \cdot 10^{-6}$	0.714
35 °C	NR-HNO$_3$	0.656	0.037	0.961	1.375	0.029	0.993	0.642	0.111	0.939	0.239	$1 \cdot 10^{-6}$	0.776
	NG-HNO$_3$	1.047	0.034	0.937	1.224	0.035	0.981	0.653	0.170	0.957	0.677	$2 \cdot 10^{-7}$	0.539
	CD-HNO$_3$	1.557	0.021	0.948	1.199	0.036	0.996	0.579	0.191	0.914	0.371	$1 \cdot 10^{-6}$	0.773
	HN-HNO$_3$	1.129	0.025	0.847	1.275	0.035	0.993	0.596	0.160	0.903	0.313	$1 \cdot 10^{-6}$	0.710
	NR-H$_2$O$_2$	1.010	0.018	0.866	1.232	0.023	0.999	0.526	0.122	0.897	0.229	$1 \cdot 10^{-6}$	0.706
	NG-H$_2$O$_2$	1.327	0.023	0.986	1.203	0.035	0.998	0.639	0.159	0.911	0.352	$1 \cdot 10^{-6}$	0.759
	CD-H$_2$O$_2$	1.197	0.016	0.861	1.178	0.032	0.999	0.534	0.201	0.891	0.362	$1 \cdot 10^{-6}$	0.719
	HN-H$_2$O$_2$	1.263	0.024	0.867	1.213	0.033	0.991	0.584	0.172	0.919	0.333	$1 \cdot 10^{-6}$	0.731
45 °C	NR-HNO$_3$	0.927	0.028	0.927	1.294	0.031	0.995	0.599	0.128	0.922	0.280	$1 \cdot 10^{-6}$	0.759
	NG-HNO$_3$	2.465	0.013	0.959	1.129	0.036	0.991	0.545	0.223	0.902	0.631	$3 \cdot 10^{-7}$	0.447
	CD-HNO$_3$	1.929	0.021	0.911	1.158	0.042	0.992	0.601	0.232	0.935	0.449	$1 \cdot 10^{-6}$	0.771
	HN-HNO$_3$	2.409	0.013	0.609	1.182	0.039	0.996	0.551	0.222	0.855	0.390	$1 \cdot 10^{-6}$	0.682
	NR-H$_2$O$_2$	1.367	0.015	0.970	1.167	0.025	0.999	0.522	0.147	0.914	0.276	$1 \cdot 10^{-6}$	0.745
	NG-H$_2$O$_2$	1.496	0.021	0.959	1.203	0.035	0.998	0.639	0.159	0.911	0.352	$1 \cdot 10^{-6}$	0.759
	CD-H$_2$O$_2$	1.950	0.013	0.902	1.148	0.036	0.999	0.556	0.206	0.898	0.378	$1 \cdot 10^{-6}$	0.721
	HN-H$_2$O$_2$	4.570	0.009	0.950	1.076	0.046	0.998	0.574	0.310	0.911	0.554	$1 \cdot 10^{-6}$	0.755

The agreement of the adsorption mechanisms with the Freundlich model is also evident from the size of the Freundlich constant K_F. The constant K_F refers to the relative adsorption capacity of the adsorbent, which indicates that adsorption takes place through physical forces and is not limited to the formation of a monomolecular layer on the surface of the adsorbent, but fluoride ions can still bind to the previously created layer. For all adsorbents, the K_F constant increases with an increasing temperature, and the values are higher for adsorbents oxidized with HNO$_3$ compared to those oxidized with H$_2$O$_2$. The Freundlich constants K_F and n are a measure of the adsorption capacity or the intensity of adsorption on the energetically heterogeneous surface of the adsorbent. It is also considered that the constant n represents a common measure of relative magnitude and energy diversity associated with a specific adsorption process [49]. Sepehr et al. [50] stated in their study on fluoride adsorption on pumice stone that the heterogeneity of the adsorbent surface increases with the increase in the constant n of the Freundlich adsorption isotherm, as well as that the agreement of experimental data with a certain isotherm model does not necessarily mean the development of the mechanism according to the applied model, but certainly indirectly points to the degree of heterogeneity of the adsorbent surface. If there are several of the same adsorption sites on the adsorbent, the mechanism of the adsorption process varies until all the sites with a higher affinity towards fluoride ions are filled, whereby sites with a lower affinity become dominant. Therefore, the proportion of adsorbed fluorides is the sum of all filled adsorption sites, where the sites with higher energy are occupied first. The adsorption energy decreases exponentially with the degree of filling of free adsorption sites, and is lowest at the end of the adsorption process. According to the mentioned authors, the value of the Freundlich constant (K_F), which refers to the

degree of retention of fluoride on the adsorbent, should be less than one, which is also in accordance with the experimental data obtained in this paper.

3.6. Kinetic Models

Determining the mechanisms of adsorption processes using different kinetic models is important in order to estimate the degree of adsorption within a certain time. The adsorption behavior on modified activated carbons was investigated using four kinetic models, the pseudo-first order, pseudo-second-order, interparticle diffusion and Elovich kinetic models, at 25 °C, 35 °C and 45 °C (Table 4). The results of the research of the adsorption mechanism on modified activated carbons using kinetic models showed the best match with the pseudo-second-order kinetic model ($R^2 = 0.964$–0.999). The values of the equilibrium adsorption capacity (q_m^2) for all adsorbents increase with an increasing temperature, as does the adsorption rate constant k_2. An increase in the constant k_2 results in a decrease in the rate at which fluorides are adsorbed onto activated carbon. The lower the rate at which fluoride ions are adsorbed onto activated carbon, the greater the amount of fluoride that will be adsorbed onto the adsorbent [51]. An increase in temperature has a positive effect on the increase in q_m^2 in all activated carbon samples. The modification of the surface with HNO_3 favors a greater intensity of the increase in the amount of adsorbed fluoride ions per the adsorbent mass (0.110–0.165 mg/g) compared to the modification with H_2O_2 (0.069–0.161 mg/g).

Table 4. Kinetic models for adsorption of fluoride onto adsorbents.

		Kinetic Model											
		Pseudo-First-Order			Pseudo-Second-Order			Intraparticle Diffusion			Elovich		
		q_{m1} (mg/g)	k_1 (g/mg min)	R^2	q_{m2} (mg/g)	k_2 (g/mg min)	R^2	k_i (mg/gmin$^{1/2}$)	C	R^2	α (mg/g min)	β (g/mg)	R^2
25 °C	NR-HNO$_3$	0.068	0.006	0.921	0.110	0.131	0.966	0.004	0.026	0.949	0.823	54.05	0.906
	NG-HNO$_3$	0.083	0.005	0.889	0.135	0.133	0.977	0.005	0.021	0.851	0.670	38.02	0.966
	CD-HNO$_3$	0.064	0.007	0.979	0.133	0.261	0.995	0.004	0.049	0.974	0.952	48.02	0.987
	HN-HNO$_3$	0.086	0.007	0.936	0.126	0.118	0.989	0.004	0.192	0.966	0.723	45.66	0.867
	NR-H$_2$O$_2$	0.059	0.012	0.978	0.069	0.158	0.982	0.003	0.002	0.963	0.614	69.44	0.942
	NG-H$_2$O$_2$	0.052	0.021	0.890	0.120	0.116	0.977	0.005	0.011	0.963	0.633	42.55	0.918
	CD-H$_2$O$_2$	0.047	0.007	0.888	0.077	0.211	0.983	0.003	0.010	0.881	0.667	62.11	0.938
	HN-H$_2$O$_2$	0.058	0.007	0.996	0.087	0.198	0.991	0.003	0.014	0.993	0.933	62.89	0.944
35 °C	NR-HNO$_3$	0.106	0.009	0.903	0.125	0.184	0.964	0.005	0.034	0.953	0.818	40.32	0.876
	NG-HNO$_3$	0.095	0.013	0.990	0.151	0.137	0.996	0.005	0.031	0.919	0.742	38.17	0.969
	CD-HNO$_3$	0.066	0.009	0.936	0.151	0.312	0.996	0.004	0.069	0.944	0.761	48.08	0.993
	HN-HNO$_3$	0.087	0.006	0.902	0.157	0.155	0.985	0.005	0.039	0.960	0.793	35.84	0.974
	NR-H$_2$O$_2$	0.051	0.009	0.977	0.091	0.321	0.995	0.004	0.003	0.964	0.890	64.52	0.982
	NG-H$_2$O$_2$	0.058	0.009	0.873	0.127	0.295	0.999	0.004	0.056	0.806	0.891	50.25	0.937
	CD-H$_2$O$_2$	0.077	0.011	0.981	0.132	0.246	0.999	0.005	0.040	0.884	0.826	40.65	0.981
	HN-H$_2$O$_2$	0.076	0.016	0.998	0.111	0.227	0.999	0.004	0.038	0.896	0.914	51.54	0.977
45 °C	NR-HNO$_3$	0.054	0.006	0.933	0.149	0.337	0.993	0.004	0.057	0.915	0.752	59.52	0.945
	NG-HNO$_3$	0.129	0.016	0.975	0.188	0.172	0.997	0.006	0.036	0.935	0.748	34.60	0.981
	CD-HNO$_3$	0.074	0.010	0.988	0.158	0.355	0.998	0.004	0.081	0.932	0.634	50.51	0.981
	HN-HNO$_3$	0.085	0.006	0.911	0.165	0.173	0.986	0.005	0.051	0.953	0.908	36.63	0.969
	NR-H$_2$O$_2$	0.112	0.008	0.989	0.160	0.399	0.992	0.007	0.002	0.979	0.164	30.84	0.989
	NG-H$_2$O$_2$	0.078	0.010	0.981	0.155	0.413	0.998	0.005	0.068	0.939	0.808	45.05	0.992
	CD-H$_2$O$_2$	0.095	0.013	0.965	0.159	0.299	0.999	0.006	0.049	0.835	0.817	33.56	0.949
	HN-H$_2$O$_2$	0.086	0.014	0.821	0.161	0.342	0.998	0.006	0.051	0.814	0.810	32.36	0.936

4. Conclusions

This study shows that activated carbon modified with nitric acid or hydrogen peroxide has a good adsorption capacity. The effects of modification on different types of activated carbon are specific. Common to all tested activated carbons is that their adsorption capacity increases with an increasing initial fluoride concentration, contact time and temperature, but decreases with an increasing activated carbon concentration.

The greatest improvement in adsorption properties was achieved by the oxidation of activated carbon with nitric acid (CD-HNO$_3$), which removed twice as much fluoride compared to the other adsorbents at 25 °C. Fluoride adsorption was found to be more suitable under acidic conditions with maximum adsorption capacities of 0.065–0.134 mg/g at pH 6 for adsorbents oxidized with HNO$_3$ and of 0.041–0.168 mg/g at pH 4 for adsorbents oxidized with H$_2$O$_2$. The adsorption of fluoride on modified activated carbons was more intense for the first 120 min, followed by a slow adsorption phase. With all activated carbons, the maximum adsorption capacity was achieved at a temperature of 45 °C, and the adsorbent HN-HNO$_3$ (0.158 mg/g) had the highest adsorption capacity. The adsorption capacity decreased with an increasing mass concentration of the adsorbent for all tested samples. The greatest increase in the proportion of removed fluorides with an increasing temperature was recorded at an adsorbent concentration of 2 g/L, while increasing the concentration above 10 g/L decreased the positive effect regardless of the type of activated carbon and modification. This refers to the formation of ever greater overlaps of active sites on the adsorbent by increasing its concentration, which reduces the total available active surface that can bind fluoride ions.

The analysis of different adsorption models like Langmuir, Freundlich, Temkin and Dubinin–Radushkevich showed the best match with a Freundlich isotherm model. It describes systems where adsorption takes place through physical forces. This suggests that fluoride adsorption is not limited to monolayer adsorption. Fluoride ions can still bind to the previously created layer. The K$_F$ constant increases by increasing the adsorption temperature, regardless of the type of activated carbon and modification, with the increase being most pronounced at 25 °C. It was also found that the rate of adsorption can be better described by the pseudo-second-order model (R^2 = 0.9464–0.999). The values of the constant related to the adsorption rate (k$_2$) point to a decrease in the rate at which fluorides bind to oxidized activated carbons, mostly to CD-HNO$_3$. Decreasing the rate of adsorption enables a greater proportion of fluoride to be bound to the adsorbent, so that the obtained relationship confirms the values of the experimental results. The modification of the activated carbon surface with HNO$_3$ favors a greater intensity of the increase in the amount of adsorbed fluoride ions per the adsorbent mass (0.110–0.165 mg/g) compared to modification with H$_2$O$_2$ (0.069–0.161 mg/g).

The application of adsorption and the modification of adsorbents is extremely useful for the purification of water with elevated fluoride levels. The results of this research are only a part of the immense possibilities offered by the application of activated carbon as a potential adsorbent for fluoride removal. Improvements are always possible, which is why the potential of varying the type of oxidizing agents and their concentration during the oxidation of activated carbon could be highlighted. Therefore, experimental research comparing the adsorption efficiency on activated carbons with different degrees of oxidation could help to elucidate the influence of surface chemistry on adsorption mechanisms. This would not only enrich existing research, but also emphasize its implications in the field of the optimization of adsorption materials.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

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