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Adsorptive Purification of Aqueous Solution from Fluoride Ions by Carbonaceous Materials

Fluoride is a widely available element and is the 13th on the list of most common elements in nature. Fluorides are present in all environmental components: water, soil, air and living organisms. It finds its way into water as a result of rocks weathering and leaching, as well as precipitation along with gas and dust pollution of anthropogenic origin. In more and more areas of Poland exceedances are observed, relative to the maximum permitted levels established for fluoride concentration. The level of environmental pollution by fluoride ions increases along with the development of industrial activity of humans and the widespread use of fluorine compounds in agriculture and dental prophylaxis. Currently fluorine compounds are recognized as one of the most dangerous pollutants, contributing to environmental contamination. Fluoride ions can be removed from aqueous mediums using membrane techniques, adsorption, chemical precipitation, coagulation, electrocoagulation or ion exchange. Using adsorption processes is a very good method for water purification from fluoride ions due to its high effectiveness and simple application. The aim of this paper was to research fluoride ion adsorption statics and kinetics for two commercially available carbon materials: activated carbon (W1) and charcoal (W2). Adsorption tests were conducted in static conditions. Concentrations of fluoride ions in the samples were analyzed using the ion chromatography method. The adsorption kinetic occurred according to the pseudo-second-order kinetic model. Process equilibrium was achieved after 40 minutes of contact between the adsorbent and the adsorbive when using W1 and after an hour when using W2. Equilibrium adsorption was described using Freundlich's equations. Freundlich isotherms were characterized by large correlation coefficients ($R^2 > 0.92$). Adsorption capacities of both materials strongly depended on the pH solution. The highest adsorption capacities for both activated carbon (0.199 mg/g) and charcoal (0.169 mg/g) was observed where the initial pH = 2 and the 20 mg/L fluoride concentration. The efficiency of fluoride ions removal from aqueous solutions depended on the process conditions, the initial fluoride concentration, pH, companion ions presence, for example OH^- . The greatest adsorption efficiency (51.9% for a 5 mg/L initial concentration) was exhibited by charcoal.

Keywords: water treatment, adsorption, fluoride ions, carbonaceous sorption materials

Introduction

Growing industrialization, uncontrolled exploitation and use of natural resources in recent decades have led to significant environment pollution. In a time of economic growth, the aquatic environment is also affected by pollution arising from the urbanization process and industrialization. The purity of water can be threatened by the use of chemicals in agriculture, infiltration of wastewater and

effluents from landfill sites, open-pit and subterranean mining, as well as exhaust fumes and spills of petroleum compounds begin the result of the development of the automotive industry and expansion of public transport networks and the petrol stations. Water pollution, as well as a shortage of water are hazardous to the health, and quality of life for humans.

The chemical composition of water is the basis for determining its suitability for use residentially, and for industrial or agricultural purposes. In the area of Poland, underground water often contains increased levels of inorganic ions [1, 2], including fluoride ions [3]. Excessive levels of these ions have been identified in Police, Konin, Skawina, Kalisz, Malbork, in the area around Gdańsk and Tczew, as well as in the municipality of Dąbrowa and Dobrzeń Wielki in the Opole Voivodship [4-7]. Increased concentration levels of fluoride in water are particularly dangerous as they are highly toxic.

According to the Regulation of the Minister of Health of 13 November 2015 on the quality of water intended for human consumption [8] regulating the basic chemical requirements, which should be respected for drinking water, the maximum concentration level for fluoride is 1.5 mg/L. The defined concentration is compliant with the guidelines given by the World Health Organization [9, 10].

On the other hand, according to the Regulation of the Minister of Environment of 21 December 2015 establishing the criteria for and the way of classifying the state of uniform parts of groundwater [11], fluorides are a physicochemical element, for which the maximum value cannot be exceeded, when determining the quality class of groundwater at the measuring point, what testifies to its exceptional harmfulness.

Particular regulations along with the fluoride concentrations limit values have been provided in Table 1.

Table 1. **Maximum concentrations of fluoride in water**

Kind of water	Concentration mgF ⁻ /L					Legal basis
Surface water	Surface water quality classes					[12]
	I	II	III	IV	V	
	≤ 1.5		no established limits			
Groundwater	Groundwater quality classes					[11]
	I	II	III	IV	V	
	0.5	1	1.5	2	> 2	
Wastewater	25					[13]
Water for human consumption	1.5					[8]

Increased fluoride concentration levels in surface water usually indicates that they are contaminated with industrial wastewater [14]. Increased concentration of this ion in groundwater can also indicate leaching this element from a substrate

which is rich in fluorine mineral (CaF_2 , Na_3AlF_6 , MgF_2 , $\text{Ca}_5(\text{PO}_4)_3\text{F}$), as well as, to a lesser degree, can result from infiltration of precipitation. Moreover, significant amounts of fluorine are entering the groundwater as a result of gaseous and dust air pollution and also due to the penetration of wastewater from steel, chemical, glass, and agriculture industries. The greatest local enrichment of water with fluorine occurs in volcanic zones [15].

In the aqueous solutions fluorine occurs in the form of fluoride ions, containing fluorine in the form of anion at the first degree of oxidation. However, special forms, in which fluorine occurs (Fig. 1) are dependent on the solutions pH [16]. In solutions with a very low pH the dominant forms are undissociated HF molecules, whereas with increasing pH of the solution their contribution lowers towards the dissociated form of fluoride ions (F^-).

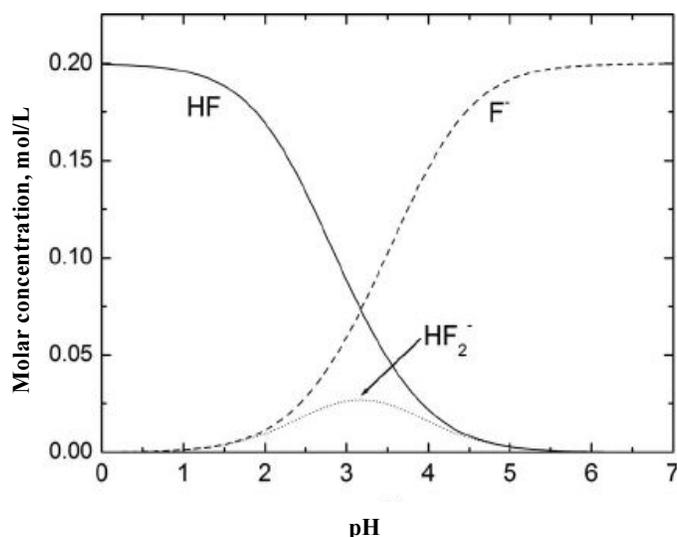


Fig. 1. Speciation diagram of fluorides in an aqueous solution with a 0.2 mol/L concentration as a pH function [16]

Fluorine compounds entering the human body play a significant role, both their surplus, as well as the deficiency of this element, has a negative impact on living organisms. In trace amounts it is necessary for the correct functioning of plants and animals. Insufficient amount of this element in organism threatens with tooth decay. Hydroxyapatite crystals, the fundamental component of dentin and tooth enamel, have the ability to exchange hydroxyl ions for fluoride ions, which subsequently causes inhibition of the demineralization process of dental tissues. The presence of fluorides is also linked with limiting the growth of cariogenic bacteria, which minimalizes the risk of tooth decay. In the prevention of tooth decay it is recommended that fluorine concentration should be maintained at about 1 mg/L.

On a list of the most common symptoms indicating that fluorine concentrations have been exceeded are skeletal changes, osteoporosis, arthritis as well as bone

cancer. An excessively high concentration of this element in an organism can also lead to the weakening of the immune and nervous system, and in children cause permanent fatigue, reduced intelligence levels, lethargy and depression [15]. Long-term delivery of excessive doses of fluorine to the organism manifests itself in disease known as fluorosis, which is characterized by the friability and fragility of teeth leading to tooth loss.

At present, fluorine along with heavy metals is recognized as one of the most hazardous contaminants causing environmental pollution. For this reason, monitoring concentrations levels and effective removal of this element is very important, mainly in water intended for human consumption.

From the numerous biological and chemical methods of removing fluoride ions from water, particular attention should be given to the adsorption process characterized by easy application and high effectiveness. As an adsorbent a wide range of materials can be applied, e.g. activated aluminum oxide [17], calcium [18], iron [19], iron oxide [20] or metal hydroxide [21] based adsorbents, naturally derived adsorbents (coal, lignite, fine coke, montmorillonite) [22, 23], modified biosorbents (chitosan [24], seaweed [25]), and even agricultural waste [26] and industrial waste [27]. High efficiency in the process of purifying water from fluoride ions is exhibited by carbon based adsorbents such as carbon nanotubes and carbon fibers, graphite and activated carbon [28, 29]. Application of activated carbon for the adsorptive fluoride ions removal from water has been the subject of numerous tests. The causes of increased interest in recent years regarding activated carbon can be assigned to relatively low production cost, wide range of raw material base and favorable physicochemical properties such as: highly developed specific surface area, high mechanical strength and chemical resistance, high ion-exchange properties and simplicity of surface modification to achieve the desired properties.

Another carbonaceous material used to remove contaminants from aqueous solutions is charcoal. It is a carbon product constantly obtained as a result of pyrolysis of wood or the process of dry distillation of wood, including forest waste, which is attributed significant adsorption potential [30, 31].

The aim of the tests presented in the paper is the assessment of the adsorption efficiency of fluoride ions by various origins carbon adsorbents.

1. Methodology

Adsorption test was conducted on two commercial carbon materials: activated carbon (W1) and charcoal (W2). These materials are characterized by different origins, graining and method of preparation. Granular activated carbon with a grain size of 0.6÷2.4 mm was derived from coal by way of the combined gas and steam method. Activated charcoal with a grain size of 0.3÷0.5 mm was derived by pyrolysis of wood at a temperature of 450°C. The adsorbents' properties defined by their manufacturers are presented in Table 2.

Table 2. Properties of the carbon adsorbent materials

Property	W1	W2
Specific surface area BET (min.), m ² /g	1000	900
Moisture, max, %	5.0	0.7
Ash content, max, %	12	8
Bulk density, g/dm ³	420	400÷500
Granulation, mm	0.6÷2.4	0.3÷0.5
pH	8.0	8.7

The stock fluoride solution of 100 mgF⁻/L was prepared by using sodium fluoride. Sodium fluoride is one of the most widely available fluorine compounds, and simultaneously it is an inorganic compound, which is highly soluble in aqueous mediums. Test solutions of 5, 10 and 20 mgF⁻/L were prepared from the stock solution. The mass of adsorbent as 5 g was added for every 100 mL of the prepared solution. Samples were shaken in a laboratory shaker at a speed of 160 rpm in order to achieve adsorption equilibrium. At the end of contact time, the test solutions were filtered through a syringe filter with a pore diameter of 0.45 µm, and then 0.2 µm and were analyzed by using an ion chromatography (Metrohm 850 Professional IC ion chromatograph). All tests were conducted at room temperature. The samples were analyzed in three repetitions, and the presented results are the average of parallel conducted tests. The conditions of chromatographic analysis conducting are shown in Table 3.

The effect of the pH solutions on the adsorption process was studied using ion fluoride solutions of wide range of concentrations (5, 7, 10, 15, 20 mgF⁻/L) and pH (2, 4, 6, 8, 10), which were controlled using 0.1 M HCl or NaOH.

The adsorption level of fluoride ions was expressed using the adsorption efficiency, which was calculated using the following formula:

$$S = \frac{(c_0 - c_k)}{C_0} \cdot 100$$

where S is the adsorption efficiency, %; C₀ is the initial fluoride concentration, mg/L; C_k is the fluoride concentration after the adsorption process, mg/L.

Table 3. Ion chromatographic conditions

Column	Metrosep A Supp 5
Column dimensions	150 mm x 4 mm
Eluent	3.2 M Na ₂ CO ₃ + 1.0 M NaHCO ₃
Detection	Suppressed conductivity detection
Permissible pH range	3÷12
Injection volume	100 mm ³
Pressure	~7.0 MPa (max 15.0 MPa)
Temperature	25°C
Analysis time	25 min

In the description of the adsorption process in equilibrium conditions the Freundlich isotherm equation was used (1). In the linear form (2) the constants of this equation were determined [32]:

$$q_e = K_F \cdot C_e^{\frac{1}{n}} \quad (1)$$

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \quad (2)$$

where q_e is equilibrium adsorption capacity, mg/g; K_F is the Freundlich isotherm constant defined as the minimum of adsorption capacity; n is the Freundlich isotherm constant, determining the adsorption intensity, C_e is the fluoride ion concentration at equilibrium, mg/L.

2. Results and discussion

The contact time of the fluoride ions with the adsorbent surface area affects the efficiency of the process up until equilibrium is achieved (Fig. 2). Adsorption efficiency on the surface of the W1 achieved a maximum value after forty minutes of contact with the adsorbative. In turn, adsorption on W2 achieved maximum efficiency after an hour of contact between the contaminant and the surface of the adsorbent. A longer contact time between the adsorbent surface and the adsorbative did not result in an increase of fluoride ions adsorption. This indicated that, at defined time points, the amount of the substance being desorbed from the adsorbent remained in a dynamic equilibrium state with the amount of substance being adsorbed.

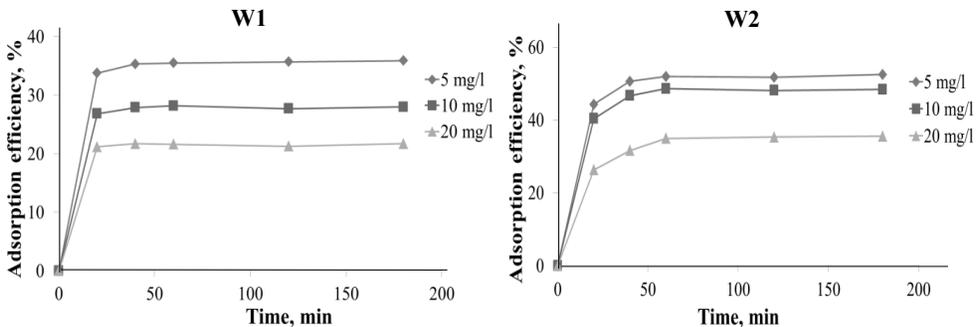


Fig. 2. Influence of the contact time between the adsorbent - adsorbative on the efficiency of fluoride ions adsorption

The presented data can be described using pseudo-second-order kinetic equations (3), which after linearization obtain the form (4):

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

where t is the adsorbent-adsorbive time contact, min; q_t is adsorption capacity in time t , mg/g.

Graphical courses of straight lines drawn on the basis of the presented equations were shown in Figure 3.

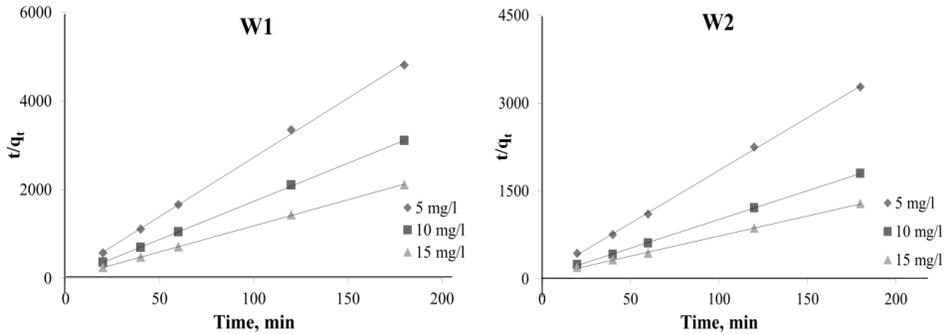


Fig. 3. Linearized pseudo-second-order kinetic model fluoride of ions uptake by W1 and W2 adsorbents

Rate constants of pseudo-second-order adsorption k_2 (g/mg·min) describing the kinetic of both adsorbents were calculated using directional coefficients of obtained linear equations (4).

The high correlation coefficients ($R^2 > 0.9991$) indicate that the kinetics of adsorption proceeded in accordance with the pseudo-second order model. Comparing the adsorption kinetics coefficients it can be seen that the W1 was characterized by much higher rate of adsorption than W2 carbon. Analyzing the rate constants of process describing the adsorption on the W1 carbon, it can be noted that increase in the fluoride ions concentration contributes to the growth of the reaction rate. In the case of W2 carbon these tendencies are reversed.

The reaction kinetics based on the pseudo-first-order kinetic model has been also investigated. However, correlation coefficients describing the fit to the model indicated very low values ($R^2 < 0.16$ in the case of W1). In the case of W2, received R^2 values were also lower than those obtained by using the pseudo-second order model.

Rate constants of pseudo-second-order reaction corresponding to the initial concentrations, together with correlation coefficients R^2 are compiled in Table 4.

Analyzing the effect of the initial fluoride ion concentrations on the efficiency of their adsorption on the carbons surfaces, it can be noticed that W1 carbon reacts to an increase of the adsorbive in the solution to a small degree. Increasing the fluoride ion concentration from 5 to 20 mg/L resulted in a drop in the removal efficiency on W1 carbon by 12.6%. In the case of W2 the difference equaled 16.9%. Maximum adsorption efficiencies were achieved in solution with the lowest concentration (5 mg/L). They were 33.8 and 51.9% respectively for W1 and W2 carbon (Fig. 4).

Table 4. Rate constants of the pseudo-second-order equations describing fluoride ion adsorption on W1 and W2 carbons

Type of carbon	Initial concentration mg/L	Pseudo-second-order kinetic model	
		$k_2, \frac{\text{mg}}{\text{g} \cdot \text{min}}$	R^2
W1	5	12.71	0.9991
	10	18.37	0.9999
	20	24.49	0.9998
W2	5	6.15	0.9994
	10	3.25	0.9998
	20	1.07	0.9993

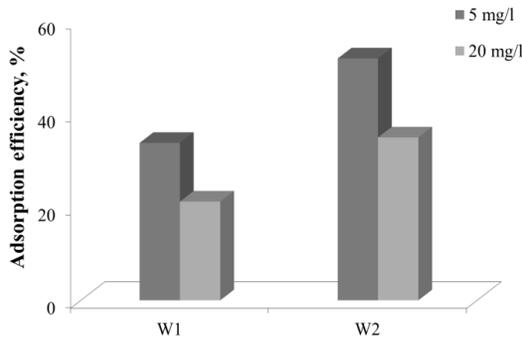


Fig. 4. Adsorption efficiency of fluoride ions by carbonaceous materials W1 and W2

Isotherm adsorption tests were conducted in solution of various pH levels (Fig. 6). Freundlich equation was used in order to interpret the isotherm adsorption of fluoride ions. On the basis of obtained Freundlich isotherm equations for solutions of different pH, n and K_F constants were determined (Tab. 5). pH values after the adsorption process were also examined (Fig. 5).

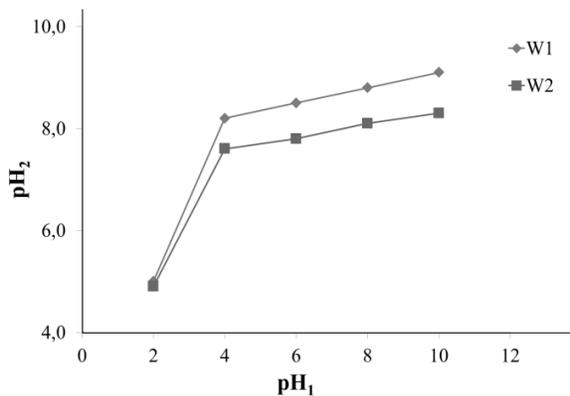


Fig. 5. Dependence between the pH before and after the adsorption process, pH₁ - initial pH, pH₂ - final pH

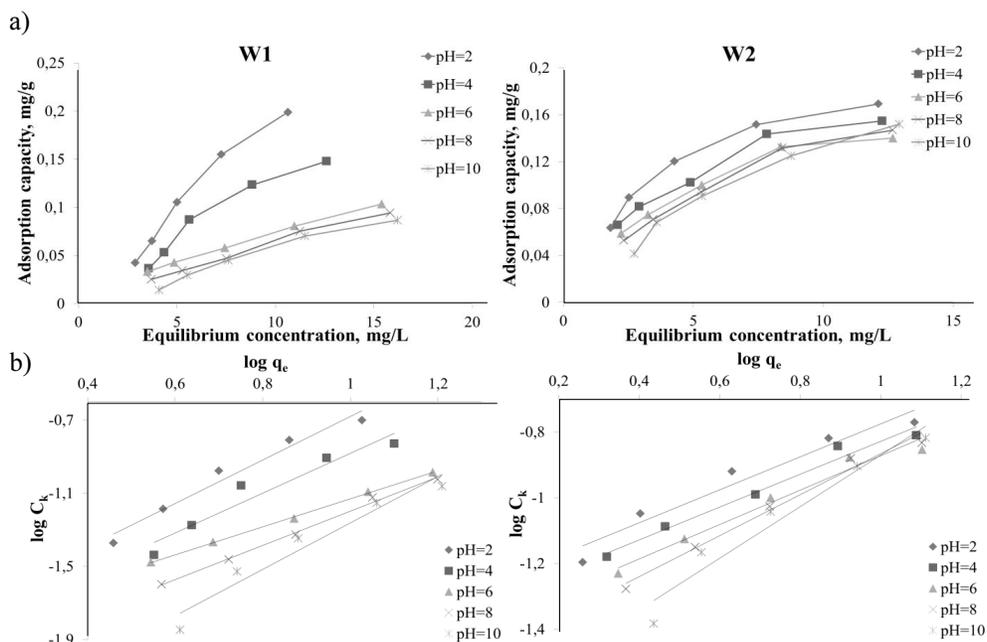


Fig. 6. Freundlich isotherms in exponential (a) and linear form (b)

Since the tests were conducted on activated carbons which were not ashed (pH water extract W1 - 8.0, and W2 - 8.7) the solutions pH after the adsorption process varied between 4.9 and 8.3 for W1 carbon, and 5.0 and 9.1 for W2. Most probably the ingredients of the ash from the carbons (and not the adsorption process) had a decisive effect on the pH of the solutions after adsorption. So, due to leaching of ash, in fact the tests conducted were narrowed pH scope. In these conditions, fluoride occurred foremost in the form of F^- ion.

Freundlich isotherms in exponential and linear form are presented in Figure 6. Analyzing the graph, it can be seen that adsorption capacities of both carbonaceous materials are strongly dependent on the pH of the solution, in which the adsorption process took place. General dependency is followed on the graphs, that along with lowering of the pH, adsorption capacity increases. These interdependence is consistent with literature reports describing the adsorption processes of fluoride ions removal by using activated carbon [33-35]. According to the speciation diagram, describing the contribution of individual fluorides forms in aqueous solutions of various pH, it was concluded that undissociated fluoride forms as weak hydrofluoric acid particles are dominated in a low pH. However, since after the adsorption process the pH values were changed, the decisive influence on the achieved results (greater adsorption in solution with lower pH) has the disassociation of functional groups on the activated carbons surface area, as well as the competitiveness, e.g. with OH^- ions.

Comparing activated carbons, different effects of the pH on the adsorption process were observed. W1 carbon more efficiently adsorbed fluoride ions from solu-

tions with an initial pH of 2 than W2 carbon. Among the solutions with a higher pH, adsorption F^- takes place more efficiently on W2 carbon.

Freundlich equation with high correlation coefficients ($R^2 > 0.92$) describes the laboratory test results. K_F coefficient indicating the adsorption capacities of applied adsorbents assumes larger values for W2 carbon than for W1 and it increases with decrease of pH in the solution (Tab. 5).

Table 5. Freundlich isotherms constants

pH	Correlation coefficient R^2	Freundlich isotherm constant $1/n$	Freundlich isotherm constant $K_F (\text{mg/g}) \cdot (\text{l/mg})^{\frac{1}{n}}$
W1			
2	0.9660	1.1891	0.0135
4	0.9299	1.0888	0.0107
6	0.9992	0.7699	0.0126
8	0.9949	0.9367	0.0073
10	0.9439	1.2713	0.0003
W2			
2	0.9440	0.5025	0.0528
4	0.9757	0.4997	0.0470
6	0.9707	0.5230	0.0402
8	0.9824	0.6236	0.0324
10	0.9451	0.7851	0.0221

Conclusions

The obtained fluoride ion adsorption results for carbonaceous materials indicate that adsorption is dependent on the applied adsorbent as well as on the pH of the solution. The adsorption degree is dictated by the chemical structure of the carbonaceous materials surface, and not by the specific surface area. Despite the specific surface area of W2 carbon being lower than that of W1 in alkaline solutions, larger adsorption capacities were achieved for W2 (charcoal). In the case of acidic solutions ($\text{pH}_1 = 2$, $\text{pH}_2 = 5$) adsorption was higher in W1 carbon. The highest adsorption capacities for both activated carbon (0.199 mg/g), as well as charcoal (0.169 mg/g) were observed in $\text{pH}_1 = 2$ while the initial solution concentrations were 20 mg/L. In turn, the highest fluoride ions adsorption efficiency was exhibited by charcoal (51.9% for concentration $C_0 = 5$ mg/L).

Adsorption processes proceeded according to the Freundlich adsorption model. Freundlich isotherms were characterized by high coefficient correlations, where the values oscillated between 0.9299÷0.9992 for adsorbent W1 and 0.9440÷0.9824 for adsorbent W2.

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