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Removal of Fluoride Ions from Aqueous Medium by Adsorption on Activated Carbon

Usuwanie jonów fluorkowych ze środowiska wodnego w procesie adsorpcji na węglach aktywnych

Environmental pollution with fluoride ions has been observed to increase with the growth of industrial activity of man and with the expansion of fluorine compounds in agriculture and dental prophylaxis. Hazards involved in the excess of fluorine, especially in the aquatic environment, is generated also in the processes of leaching and erosion of fluorine compounds from minerals which occur naturally in the soil. In a growing number of areas of Poland, especially in groundwater, the highest permissible concentrations of fluoride ions are exceeded; this is especially hazardous because of their high toxicity. The use of activated carbons in the adsorption of fluorides from aqueous solutions was described in many reports of studies on the elimination of such pollutants. Some of the physical and chemical properties of activated carbons are especially desirable in adsorption processes; they include: a well-developed specific surface, high mechanical strength and chemical resistance, ion exchange properties, susceptibility to surface modification enabling improvement of the materials in terms of selectivity to the specific pollutant.

The objective of this paper was to investigate the statics and kinetics of fluoride adsorption on the commercially available activated carbons F-100 and WG-12. The study included the surface characterization of the activated carbons tested. The impact of the parameters of the activated carbons tested as well as process parameters (such as the porous structure of carbon, chemical structure of the surface, pH of the adsorption process, initial concentration of the pollutant) on the efficiency of the fluoride removal from aqueous solutions was also investigated. The fluoride content in samples of model solutions was analyzed by the potentiometric method using a fluoride ion selective electrode. The adsorption kinetics was conformable with the pseudo-second order model. The process equilibrium was reached after 1 h and 2 h for F-100 and WG-12, respectively.

It was found that adsorption efficiencies for both activated carbons are strongly related to the pH of the model solution, as well as to the initial concentration of the fluorides in the model solution. Ion exchange, which strongly depends on the pH of the model solution, was one of the mechanisms controlling the course of the adsorption process. Fluoride adsorption on activated carbons was described using Freundlich isotherms. High correlation coefficients (> 0.96) were obtained for the isotherms, which seems to indicate that the course of the process was conformable with the Freundlich model assumptions.

Keywords: adsorption, fluoride ions, water purification, activated carbons

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Introduction

Intense industrialization and assorted industrial activities of man have a significant impact on the condition of the environment, contributing to the pollution of waters, soils, and the air. Among hazardous materials, fluorine and its compounds are classified as substances which are highly hazardous to the environment. Hazards involved in the presence of excess fluorine in the environment depend both on natural environmental conditions and on anthropogenic factors.

Natural sources of fluorine include mineral deposits with high fluorine contents which occur in soils, as well as volcanic dust and gases, marine aerosols. The element is found at considerable levels in post-volcanic soils, in the seas and oceans. The highest percentage of fluorine is found in igneous rocks and in clay deposits. Groundwater intakes are enriched by natural minerals, including fluorite (CaF_2), cryolite (Na_3AlF_6), sellaite (MgF_2) and fluoroapatite $Ca_5(PO_4)_3F$ owing to leaching and erosion processes in fluorine compounds which, in the aquatic environment, are in the form of fluoride ions where fluorine has an oxidation state of -1. Fluorine is also present in organisms, for instance as a component of certain enzymes. Its content in the human body is ab. 3 mg/kg b.w. [1].

Pollution by fluorine compounds of anthropogenic origin results mainly from emissions from glass-works, aluminum works, cement plants, brickyards and ceramic factories, as well as the manufacture of phosphorus-based fertilizers. Other sources of fluorine pollution include the chemical industry, specifically, manufacturers of hydrogen fluoride and its salts, the metallurgic industry using fluorine compounds as fluxing agents, as well as glass- and enamel makers, where fluorine compounds are used for the opacification of glass and enamel, and in glass etching. Fluorine compounds are also used in the production and in the use of insecticides and fungicides, thus contributing to environmental pollution [2, 3].

Pursuant to the Regulation of the Minister of Health of 13 November 2015 relating to the quality of water intended for human consumption [4], which regulates the essential chemical requirements applicable to potable water, the highest permissible fluoride concentration in potable water is 1.5 mg/dm^3. This is conformable with the values specified by the World Health Organization (WHO) [5, 6]. In the Regulation of the Minister of the Environment of 19 January 2016 relating to the criteria and methods of assessment of the quality of groundwater [7], the highest permissible fluoride concentration is in the range 0.5÷2 mg/dm^3 for class I-IV waters and may exceed 2 mg/dm^3 for the lowest quality potable water (class V). According to that Regulation, fluorides are a physico-chemical component for which the limit value at the measurement point may not be exceeded in the classification of the quality of underground water; this indicates that fluorides are particularly detrimental.

Water pollution by fluoride ions is a global problem. Too high levels of fluorides in waters were found in such countries as India, Argentina, China, Ghana, Pakistan and Egypt [8-13]. The permissible level of fluoride ions in groundwater

was exceeded in 19 out of the 29 states of the Republic of India [14]. This is attributed to the evapotransipiration process taking place in areas with prevalent low-pH soils [15]. Another source of fluorides in water intakes in India is the leaching of fluorine from granite rocks in which the element is high, ranging from 325 to 3200 mg/kg in certain parts of India [16].

In Poland, the highest permissible fluoride concentrations are exceeded in a growing number of areas. As early as in the 1980's, unusually high fluoride concentrations (above 5 mgF$^-$/dm^3) were recorded in underground waters in Gdańsk [17]. More recently, elevated fluorine levels were found in Ciechocinek, Cieplice, Lądek-Zdrój, Świeradów, Malbork and in some areas of the Opole province, including Nysa and Strzelce Opolskie and the communes of Dąbrowa and Dobrzeń Wielki [3, 18, 19]. Excessive fluoride concentrations in water are especially hazardous because of high toxicity of these ions. Chronic poisoning with fluorine results in fluorosis affecting the osseous system which, in the case of dentition, manifests itself as dental discoloration. The main symptoms of skeletal fluorosis include pain in the joints, limbs, the spine, deformed or damaged components of the osseous system. Other symptoms of too high intakes of fluorine are: apathy, drowsiness, vision and memory problems [20]. According to many reports indicating the high toxicity of fluorine, great care is required when fluorine is used in the diet, in dental formulations or medications [21, 22].

A number of methods are known for the removal of fluorine ions from the aquatic environment. The most widely known and often-used methods for the elimination of fluorine ions from water include: membrane processes, ion exchange, coagulation, chemical precipitation, electrocoagulation, and adsorption [23]. The use of activated carbons for the removal of fluorine ions from water by adsorption was described in many reports. The reason why activated carbons are often used as adsorbents is that they have physico-chemical properties which are highly desired in adsorption processes: a very well-developed surface area, rather high mechanical strength and chemical resistance, good ion exchange properties, and susceptibility to surface modification to obtain desirable properties. The knowledge of such properties and their interactions may be valuable in the selecting and application of the most appropriate activated carbon for a given adsorption process; in this case, for the removal of fluoride ions from aqueous solutions. Fluoride ion adsorption on activated carbons is possible because they are porous, the structure of their adsorption surface favors the process, and desirable chemical interactions take place between the adsorbate and the adsorbent [24].

1. Methodology

The adsorption studies were conducted using two commercially available activated carbons: F-100 (Chemviron) and WG-12 (Gryfskand), having different physico-chemical properties. General parameters which characterize the adsorption materials, as specified by their manufacturers, are provided in Table 1.

Table 1. **The physical and chemical properties of activated carbons**

Property	F-100	WG-12
Bulk density, g/dm^3	500	410
Water absorptivity, cm^3/g	0.60	0.82
Methylene blue number MBN	28	35
Iodine number IN	850	1100
Grain-size uniformity coefficient d_{60}/d_{10}	1.80	1.20
pH of water extract	6.8	10.10
Ash content, %	7.44	11.00

Before the tests, the activated carbons were subjected to a preparatory proce-dure: they were treated with a HNO_3 solution to remove ash and washed several times with plenty of deionized water before being dried to constant weight at 105°C. Physical and chemical tests were carried out on the two activated carbons to determine the impact of the characteristics of the test materials on their ability to adsorb fluoride ions. BET surface area, BET (S_{BET}), was determined from low-temperature nitrogen adsorption isotherms at –196°C (77 K). The measurements were performed using the ASAP 2010 sorptomat from Micromeritics Instrument Corp. The experimental nitrogen adsorption isotherms were used also for determi-nation of the parameters of the porous structure of the carbons, including pore volumes and pore-volume distribution.

Acidic and basic functional groups were determined on the surface of the acti-vated carbons using the Boehm titration method. Surface basicity was found as the adsorption of hydrogen ions (H_3O^+) during the titration of carbon suspension in a 0.1 M hydrochloric acid solution using a 0.05 M sodium hydroxide solution. Acidity was found by the adsorption of hydroxyl ions (OH^-) in the titration of carbon suspension in a 0.1 M sodium hydroxide solution using a 0.05 M hydro-chloric acid solution as titrant.

Additionally, the samples were subjected to elemental analysis by combustion in high-temperature conditions, determining their percentage of carbon, hydrogen and nitrogen contents (Vario Macro, Elementar Analysensysteme GmbH).

After obtaining their characteristics, the activated carbon samples were subjected to adsorption tests to examine their adsorption abilities relative to fluoride ions in aqueous solutions. All the measurements were carried out using 100 cm^3 samples of model unary solutions obtained from sodium fluoride with 1 g of activated carbon. The fluoride stock solution at a concentration of 100 mgF^-/dm^3 was obtained from sodium fluoride. The compound is one of the most readily available inorganic fluorine compounds and is readily soluble in water. The stock solution was used for making model solutions at the following concentrations: 0.5; 1.0; 2.0; 3.0; 4.0; 5.0 and 10,0 mgF^-/dm^3.

The resulting test samples were shaken in a laboratory shaker at 160 rpm until the adsorption equilibrium was obtained. After the lapse of that time, the test

samples were filtered to separate the carbon grains from the filtrate. The final concentration of fluoride ions in the test solutions was determined by the potentiometric method using pH/ionometer (SevenExcellence[TM], Mettler Toledo) equipped with the fluoride ion selective electrode (perfectION[TM], Mettler Toledo).

The kinetic study of adsorption was performed by measuring the fluoride ion adsorption after shaking a mixture of the solution with the activated carbon for 0.5, 1, 2, 3, 4 and 5 h. All the tests were carried out at 20°C.

The impact of the solution pH on the adsorption process was investigated using fluoride ion solutions at concentrations in the range from 0.5 to 10.0 mgF$^-$/dm^3 at the pH values of 3, 6 and 10. The pH values were obtained using HNO_3 or $NaOH$ solutions.

The adsorption of fluoride ions was expressed as adsorption efficiency, calculated from the formula:

$$S = \frac{(c_0 - c_k)}{c_0} \cdot 100 \tag{1}$$

where:
S - adsorption efficiency, %,
C_0 - initial fluoride concentration, mg/dm^3,
C_k - fluoride concentration after adsorption, mg/dm^3.

The adsorption process at equilibrium conditions was described by means of the Freundlich adsorption isotherm model (2). Its linear form (3) was used for calculating the constants of the equation [25]:

$$q_e = K_F \cdot C_e^{\frac{1}{n}} \tag{2}$$

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \tag{3}$$

where:
q_e - adsorption capacity at equilibrium conditions, mg/g,
K_F - Freundlich isotherm constant, determined as the minimum adsorption capacity, $(mg/g) \cdot (l/mg)^{\frac{1}{n}}$,
n - Freundlich isotherm constant, determining adsorption intensity,
C_e - fluoride ion concentration in equilibrium condition, mg/dm^3.

The adsorption kinetics was described using the pseudo-first order (4) and pseudo-second order (5) kinetic equations which, after transformation into their linear forms, are as follows (4.1, 5.1):

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{4} \qquad\qquad \frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \quad (4.1) \qquad\qquad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (5.1)$$

where:

t - adsorbent-adsorptive contact time, min,

q_t - adsorption capacity at time, t, per mass unit of adsorbent, mg/g,

k_1 - pseudo-first order adsorption rate constant, min^{-1},

k_2 - pseudo-second order adsorption rate constant, g/mg min.

2. Results and discussion

The experimental part consisted of two steps: characterization of the test samples of activated carbons (mainly in respect of their surface chemistry), followed by determination of the adsorption abilities of the activated carbons in relation to fluoride ions.

2.1. Characterization activated carbons

When examining the surface of the test adsorbents, it was found that acidic groups on the surface prevailed on the activated carbon WG-12: the content of acidic functional groups was 1.018 mmol/g, that of the basic functional groups was 0.105 mmol/g. A reverse relationships was observed for the surface of the activated carbon F-100, where basic groups were dominant (0.624 mmol/g), and the content of acidic groups was 0.355 mmol/g.

The high surface acidity of WG-12 may contribute to the high adsorption of anions, including the analyzed fluoride ions, especially in the acidic process conditions. The activated carbon WG-12 also has a much larger specific surface area, compared with F-100, and a larger volume of the capillaries below 1.5 nm which, given the small size of the adsorbed F-ions, may have a positive impact on the course of the process.

Detailed parameters characterizing the analyzed sorption materials were collected in Tables 2 and 3.

Table 2. **Physico-chemical parameters of activated carbons F-100 and WG-12**

Property		F-100	WG-12
BET surface area, m^2/g		674	1098
Content of oxygen functional groups mmol/g (±0.01)	acidic	0.355	1.018
	basic	0.624	0.105
C content, %		87.76	82.80
H content, %		0.818	1.169
N content, %		0.813	0.786

Table 3. **Pore size distribution and capillary volumes of activated carbons F-100 and WG-12**

Activated carbon	Pore size, nm					$\Sigma \frac{\Delta V}{cm^3/g}$
	< 1.5	1.5÷10	10÷100	100÷2000	2000÷8000	
	Capillary volume ΔV, cm³/g					
F-100	0.2872	0.1428	0.0634	0.0868	0.1201	0.7003
WG-12	0.4213	0.1049	0.0648	0.2731	0.1478	1.0114

2.2. Adsorption abilities studies

In order to determine the conditions of fluoride ion adsorption on the test materials, the time it took for the process to reach an equilibrium condition was measured. The measurements were carried out for the initial concentration of the model solutions of 5 mg/dm³. The dependence of adsorption efficiency on the time of contact between the activated carbons and the model solution is shown in Figure 1.
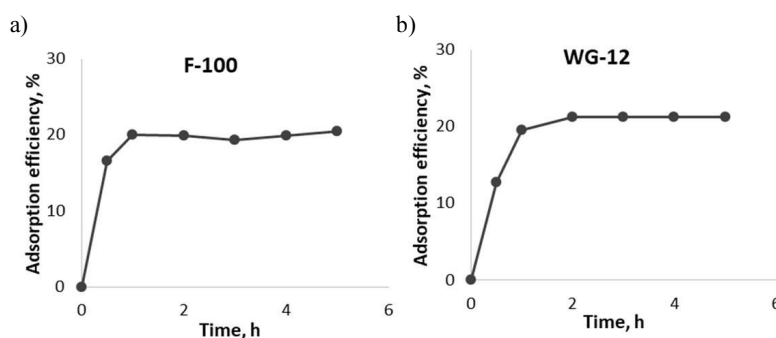

Fig. 1. Impact of adsorbent-adsorptive contact time on fluoride ions adsorption efficiency on activated carbons: a) F-100, b) WG-12

The efficiency of adsorption on the activated carbon F-100 was maximum (20%) after continuing the process for just 1 h. For WG-12, the adsorbent-adsorptive contact time that was required for the obtaining of the maximum adsorption efficiency (21.2%) was 2 h. Continuing the adsorption of fluoride ions for a longer time did not result in higher adsorption efficiencies in either case. This indicates that an adsorption equilibrium was established after the lapse of 2 h on both of the activated carbon samples. Straight lines, obtained by plotting the pseudo-second order kinetic equations (5.1), are shown in Figure 2.

Adsorption rate constants (k_2, g/mg·min), describing its kinetics for the tested activated carbons (Table 4) were calculated from the slopes of the straight-line dependences (5.1). For each of the two adsorbents, the adsorption process kinetics was conformable with the pseudo-second order model, as indicated by the high correlation coefficients ($R^2 > 0.9991$), determining the goodness of fit between the experimental data and the analyzed model. A comparison of the coefficients

of adsorption kinetics indicates that the adsorption rate was much higher for the activated carbon WG-12, compared with F-100.
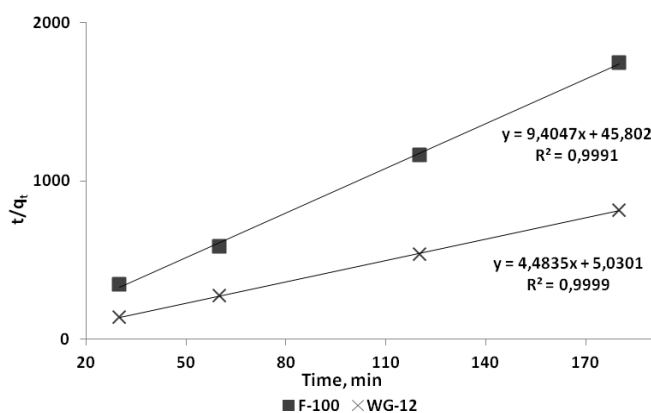

Fig. 2. **Linear form of kinetic model of pseudo-second order adsorption of fluoride ions on activated carbons F-100 and WG-12**

Table 4. **Rate constants of pseudo-secondary order equations, describing fluoride ion adsorption on activated carbons F-100 and WG-12**

Activated carbon	Pseudo-secondary model	
	$k_2, \dfrac{g}{mg \cdot min}$	R^2
F-100	1.93	0.9991
WG-12	4.00	0,9999

The reaction kinetics was also analyzed on the basis of the pseudo-first order kinetic model. It was found that correlation coefficients, describing the goodness of fit to the model, were characterized by much lower values ($R^2 < 0.83$), compared with the pseudo-second order model.

The relationship between adsorption efficiency for the activated carbons and initial concentration of fluoride ions at different pH conditions of the process was shown in Figure 3. The adsorption efficiency depends on the initial concentration of fluoride ions in the model solution and on its pH.

When investigating the adsorption abilities of the activated carbon F-100, it was found that increasing the concentration of F^- ions in the solution from 0.5 to 10 mg/dm³ contributed to their reduced removal efficiency. The highest adsorption efficiency was observed for the process running at a pH of 6.

At very low pH of the solution, the dominant form of fluorine is the non-dissociated HF molecules; their content decreases and the dissociated form F^- increases with increasing pH values (starting from above 3.5). This seems to indicate that, because of the increasing amount of the dissociated forms F^-, which are preferred in the adsorption process, their adsorption in the solution was high for a pH of 6.

At a pH of 10, the solution has a high content of OH$^-$ ions; they compete with the negatively charged F$^-$ ions for a place on the active sites on the surface of the carbon material. Among all of the analyzed data, the highest fluoride ion adsorption efficiency (54%) was recorded for the process running on WG-12 at a pH of 3. The test results seem to indicate that, in the adsorption process running on WG-12, the non-dissociated HF molecules are more preferred. As the basicity of the reaction medium increases and the content of the non-dissociated HF forms is lower as the result, adsorption efficiencies are observed to decrease to 12.8 for a pH of 10. It is probable that high adsorption efficiencies in that case are connected with the dissociation of basic groups on the surface of WG-12.
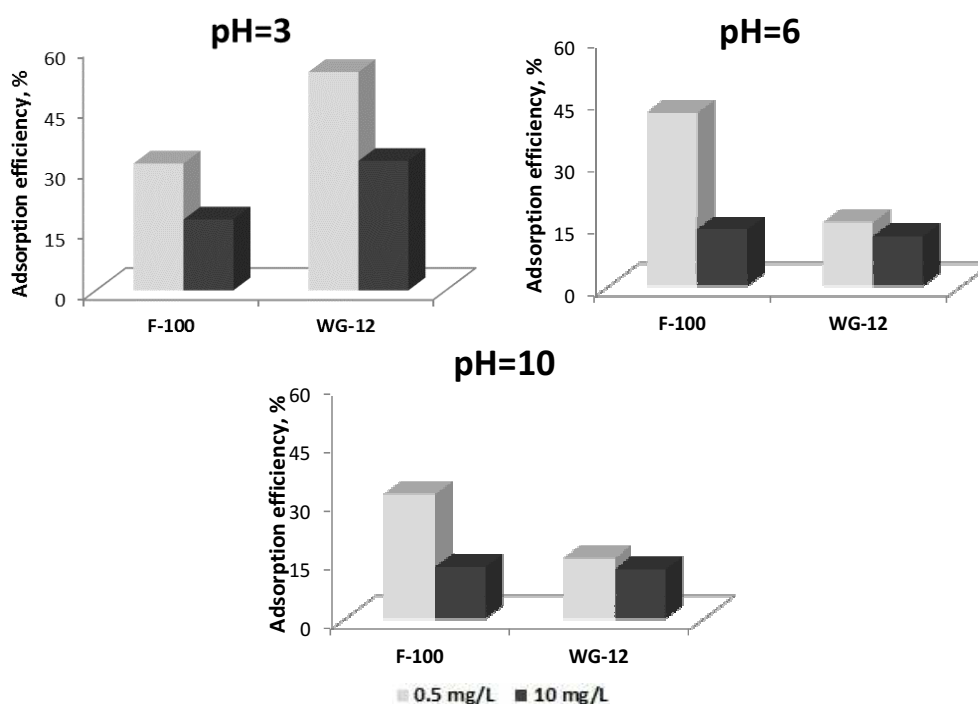

Fig. 3. Adsorption efficiency for fluoride ions on activated carbons F-100 and WG-12 vs. pH of solution

For a pH value of 3, adsorption efficiencies were observed to gradually decrease with increasing initial concentrations of the anions in the process of their removal; this may be attributable to the fact that active sites on the carbon surface are occupied. As the concentration of the adsorbate in the solution increases, the quantity of free active sites decreases, as shown by the decreasing adsorption efficiency.

Figure 4 shows the straight-line Freundlich isotherms characterizing adsorption on the adsorption materials.

The Freundlich equation with a high correlation coefficient ($R^2 > 0.96$) describes the experimental results. The K_F coefficient, which reflects the adsorbents' capacities for the fluoride ions is the highest in the case of WG-12, which adsorbs

the fluorides at pH = 3 (Table 5). The parameters are conformable with the adsorption efficiencies which characterize the tested activated carbons.
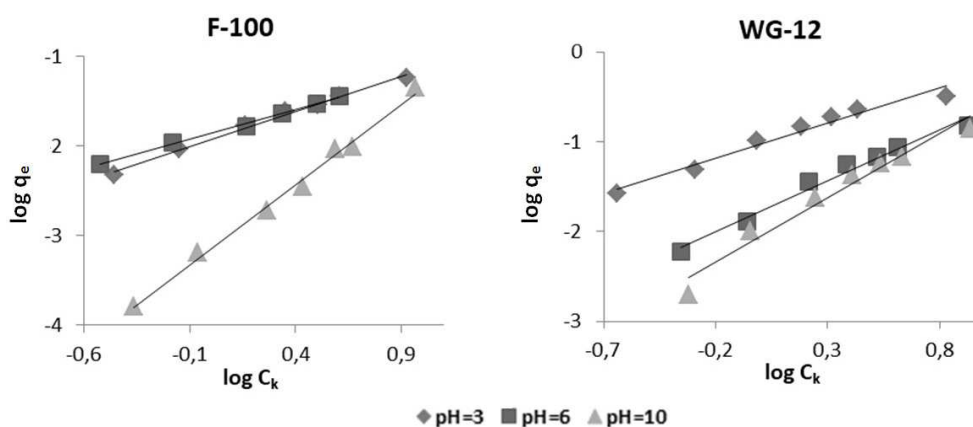

Fig. 4. Freundlich isotherms in linear form

Table 5. **Freundlich isotherm constants**

pH	Correlation coefficient R^2	Isotherm constant $1/n$	Isotherm constant, K_F $(mg/g) \cdot (l/mg)^{\frac{1}{n}}$
F-100			
3	0.9930	0.7788	0.0372
6	0.9929	0.6965	0.0436
10	0.9934	1.8031	0.0022
WG-12			
3	0.9648	0.7761	0.0943
6	0.9815	1.1314	0.0170
10	0.9607	1.4305	0.0089

Conclusions

The surface of activated carbons has a unique, heterogeneous nature. It has both a complex porous structure which determines its adsorption ability, and a complicated, diverse chemical structure which determines what compounds can be adsorbed.

The analysis of the course of the adsorption process covers both of the above: nature and concentration of surface chemical groups, specific surface, pore-size distribution, concentration and pH of model solution, as well as the physical and chemical characteristics of the adsorbate.

The activated carbon WG-12 had an acidic surface, favoring fluoride ion adsorption, mainly in the acidic environment having a low content of hydroxyl ions which compete with the F^- ions. In spite of the high specific surface and a desirable pore-volume distribution for WG-12, the activated carbon F-100 showed higher adsorption efficiencies at pH values of 6 and 10. On the other hand, the number of basic groups, which are capable of ion exchange, was much higher in F-100. Apparently, that process was dominant in the elimination of fluoride ions from the solutions with a pH of 6 and 10. The two activated carbons had different acidic-to-basic group ratios. The values were 9.7:1 for WG-12 and merely 1:1.7 for F-100. The presence of a high number of acidic groups hinders adsorption because of repulsion of functional groups single sign charges and of the adsorbed fluoride ions. This indicates that the activated carbon F-100 is a more optimal material, adsorbing the F^- ions in a wide spectrum of pH values.

High values of the Freundlich isotherm correlation coefficients were obtained. This was assumed to indicate that the fluoride ion adsorption on the examined activated carbons followed the Freundlich adsorption model. The Freundlich isotherms were characterized by high correlation coefficients: their values were in the range 0.9929÷0.9934 for the F-100 and in the range 0.9607÷0.9815 for WG-12.

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Streszczenie

Zanieczyszczenie środowiska jonami fluorkowymi wzrasta wraz z rozwojem przemysłowej działalności człowieka i coraz powszechniejszym stosowaniem związków fluoru w rolnictwie oraz profilaktyce stomatologicznej. Zagrożenie wynikające ze zbyt dużych zawartości fluoru, zwłaszcza w środowisku wodnym, ma swoje źródło również w procesach wypłukiwania i wymywania związków fluoru z naturalnie występujących w glebie minerałów. W Polsce odnotowuje się coraz więcej obszarów, gdzie, głównie w wodach podziemnych, występują lokalne przekroczenia najwyższych dopuszczalnych stężeń jonów fluorkowych, co jest szczególnie niebezpieczne z uwagi na ich wysoką toksyczność. Zastosowanie węgli aktywnych w procesach adsorpcji fluorków z roztworów wodnych jest obiektem wielu prac badawczych dotyczących sposobów usuwania tych zanieczyszczeń. Węgle aktywne przejawiają korzystne właściwości fizykochemiczne istotne w procesach adsorpcyjnych, takie jak rozwinięta powierzchnia właściwa, wysoka wytrzymałość mechaniczna i chemiczna, właściwości jonowymienne, podatność na modyfikację powierzchni umożliwiającą uzyskanie większej selektywności tych materiałów względem określonego rodzaju usuwanego zanieczyszczenia.

Celem pracy jest zbadanie statyki i kinetyki procesu adsorpcji fluorków na komercyjnie dostępnych węglach aktywnych F-100 i WG-12. W toku przeprowadzonych badań dokonano również charakterystyki powierzchni analizowanych węgli aktywnych. Oceniono wpływ parametrów badanych węgli aktywnych i parametrów procesowych (takich jak struktura

porowata węgla, chemiczna budowa powierzchni, pH procesu adsorpcji, stężenie początkowe substancji zanieczyszczającej) na skuteczność usuwania fluorków z roztworów wodnych. Zawartość fluorków w próbkach roztworów modelowych analizowano metodą potencjometryczną z użyciem jonoselektywnej elektrody fluorkowej. Kinetyka adsorpcji przebiegała zgodnie z modelem pseudodrugiego rzędu, a równowaga procesu ustaliła się po czasie 1 h w przypadku węgla F-100 oraz 2 h dla węgla WG-12.

Stwierdzono, iż skuteczności adsorpcji obu węgli są silnie związane z wartością pH roztworu, z którego zachodził proces, jak również ze stężeniem początkowym fluorków w roztworze modelowym. Jednym z mechanizmów regulujących przebieg procesu adsorpcji był mechanizm wymiany jonowej, silnie uzależniony od odczynu roztworu modelowego. Adsorpcja fluorków na węglach aktywnych została opisana za pomocą izoterm Freundlicha. Opierając się na uzyskanych wysokich współczynnikach korelacji wykreślonych izoterm (> 0,96), można przypuszczać, iż proces przebiegał zgodnie z założeniami modelu Freundlicha.

Słowa kluczowe: adsorpcja, jony fluorkowe, oczyszczanie wody, węgle aktywne