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Structural, morphological, and adsorption properties of titanium dioxide doped with Fluorine

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This work is devoted to synthesizing titanium dioxide doped with Fluorine and investigating its structural, morphological, and adsorption properties. By sol-gel synthesis, samples of TiO_2 from 2, 4, and 8 *wt.* mass of Fluorine, labeled as 2F-TiO_2, 4F-TiO_2, and 8F-TiO_2, were created. To obtain these samples, NaF was injected into an aqueous solution of titanium aqua-complex $[Ti(OH_2)_6]^{3+}{\cdot}3Cl^-$ with a pH of ~ 0.5÷1.5. XRD, IR spectrometry, low-temperature N_2 adsorption-desorption isotherms, and pH of point of zero charges of as-synthesized samples were performed. A description of the structure-forming process is also given. The adsorption capacity of 2F-TiO_2, 4F-TiO_2, and 8F-TiO_2 samples toward strontium cations was investigated. The adsorption kinetics, equilibrium adsorption, and the effect of the solution's acidity on this process were measured. It was found that 8F-TiO_2 has the most potent adsorption properties toward strontium cations. The paper concludes that as the mass fraction of Fluorine atoms in TiO_2 increases, the number of acid adsorption centers $\equiv TiOH^{\delta+}$ increases. Compared to the basic sample of a-TiO_2, the number of adsorption centers in the 8F-TiO_2 sample increases by 3.5 times.

Keywords: adsorption, sol-gel synthesis, titanium dioxide, specific surface, pH_{pzc}, strontium.

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Introduction

The world scientific community is widely researching new methods and substances that can be used for the adsorption uptake of heavy metal ions and radionuclides from aqueous solutions. The relevance of adsorption research and the creation of new adsorbents is dictated not only by the problems of preserving the cleanliness of the environment but also by the need to develop regenerative technologies. For example, strontium (Sr^{2+}) plays a vital role in rocket fuel and modern 5G communication facilities [1]. Sr^{2+} is obtained mainly from solid strontium ores, but the price of Sr^{2+} products rises when depleted. It is worth noting that in salty lake brines and oilfield water, there are many resources containing strontium in dissolved form, that is, in the form of the Sr^{2+} cation [2]. Oilfield water, as a by-product of oil and gas production, is characterized by low mineralization (about $5 \sim 300\ g \cdot L^{-1}$) and a concentration of Sr^{2+} of about $> 100\ g{\cdot}L^{-1}$. As a new type of strontium resource, oilfield water is not yet exploited due to the heterogeneous composition of the matrix and the lack of cost-effective technologies for the extraction of Sr^{2+} [2]. Therefore, the search for effective adsorbents for strontium cations continues. As noted by the authors [7, 8, 9], the adsorption of strontium from aqueous solutions is highly relevant from ecology, industry, and economics, as well as from the point of view of fundamental research.

Effective in solving these scientific problems are adsorbents capable of uptake metal ions or radionuclides from aqueous solutions [10]. Adsorbents such as fumed silica [11], synthetic zeolites [12], MOFs, titanates, and adsorbents based on oxidized graphene are widely investigated by the scientific community [13-15]. Zirconium (IV) and titanium (IV) phosphates also show a high adsorption capacity toward heavy metal cations [1, 16, 17].

Titanium dioxide is the most promising adsorbent [19-24], according to such features as adsorption capacity, resistance to aggressive media, regenerating ability, and cost-effectiveness. The authors of publications [19-21] created effective adsorbents for binding Sr^{2+} cations or other heavy metal cations.

Chemical impregnation of oxygen-containing anions, PO_4^{3-}, CO_3^{2-}, or AsO_4^{3-} into the surface of the oxide material makes it possible to increase the adsorption capacity of mesoporous TiO_2 synthesized by the sol-gel method. The significantly higher electro-negativity of P (2.1), C (2.5) and As (2.0) in comparison with Ti (1.5) contributes to the fact that in the vicinity of the groups $=Ti(O_2POOH)$, $=Ti(O_2CO)$ or $= Ti(O_2AsOOH)$, impregnated in the structure of the surface layer, the number of active centers increases due to the inductive effect on the distribution of electron density in the bridges of Ti-O-Ti. Thus, when impregnation of 4 arsenate groups $=Ti(O_2AsOOH)$ in an area of 10 nm^2, the number of acid centers, $TiOH^{\delta+}$, increases from 36 to 90 units. The mesoporous TiO_2 modified in this way adsorbs 262.8 $mg \cdot g^{-1}$ of Sr^{2+} cations [20].

Recently, a solution of titanium-containing aqua complex $[Ti(OH_2)_6]^{3+} \cdot 3Cl^-$ [25] has been used as a precursor to obtaining adsorbents based on anatase modification of TiO_2 [25]. Its advantages are obtaining TiO_2 with a high specific surface area and reproducible physicochemical properties, compared with $TiCl_4$, $TiCl_3$, titanium alkoxides, or other precursors.

In this work, we aimed to investigate the structural and morphological properties of TiO_2 particles obtained by the sol-gel method using the titanium aqua-complex $[Ti(OH_2)_6]^{3+} \cdot 3Cl^-$ and the modifying component NaF as a precursor. This work also investigated the adsorption properties of titanium dioxide samples doped with Fluorine atoms toward Sr^{2+} cations.

The impregnation of anions F^+ into the structure of the surface layer of TiO_2 particles, due to the high electrical negative F (4.0), should increase the adsorption activity of the oxide material.

I. Methods of experimental research

1.1. Obtaining investigated samples

Samples of TiO_2 containing 2, 4, and 8 *wt.* %. F were synthesized to analyze the effect of impregnating Fluorine anions on titanium dioxide's structural, morphological, and adsorption properties. To obtain these samples in a solution of titanium aqua complex $[Ti(OH_2)_6]^{3+} \cdot 3Cl^-$ with pH ~ 0.5÷1.5, the appropriate amount of NaF was introduced. The mixtures were heated at 60°C for 60 minutes. Under these conditions, tiny particles of TiO_2 containing F atoms in their structure were formed in the volume of the reaction medium. The dispersion was deoxidized to pH ~ 6.0 ÷ 6.8 with a solution of NaOH. After that, the synthesized particles were removed with a vacuum filter, washed from Na^+ and Cl^- ions with distilled water, and dried at a temperature of 150°C. Investigated samples with a content of 2, 4, and 8 *wt.* % of Fluorine are further indicated in the text as $2F\text{-}TiO_2$, $4F\text{-}TiO_2$, and $8F\text{-}TiO_2$, respectively, and the base sample without dopant was named $a\text{-}TiO_2$.

1.2. Study of the characteristics of titanium dioxide samples

1.2.1. X-beam diffractometry (XRD)

The phase composition of basic $a\text{-}TiO_2$ and Fluorine-doped samples was investigated using the STOE STADIP diffractometer in copper anode radiation. The rays were focused on according to the Breg-Brentano scheme. Rietveld analysis of recorded diffractograms was performed using SHELXL-97 software [26, 27].

1.2.2. Low-temperature N_2 adsorption/desorption

The study of the surface area of the samples and their pore size was performed using isotherms of low-temperature adsorption-desorption of N_2 molecules. For this purpose, the Quantachrome Autosorb (Nova 2200e) Surface Area and Pore Size Analyzer was used. The samples were calcined in a vacuum at a temperature of 180°C for 24 hours before measurement. The surface area of the samples was calculated using the BET (Brunauer-Emmett-Teller) theory. Pore size was estimated using density functional theory (DFT).

1.2.3. Infrared spectroscopy (IR)

IR spectroscopy was used for qualitative and quantitative analysis of samples, with the help of which it is possible to assess the structure and phase composition of the samples under study. The IR spectra of the investigated samples were obtained on the SPECORD M80 spectrophotometer. To record the spectrum, the sample weight (4 mg) was mixed with KBr in a ratio of 1:100 and ground in a vibrating mill for 10 minutes. A transparent plate of 20×5 mm^2 was formed by pressing the resulting mixture.

1.2.4. Determination of the Point of Zero Charge of TiO_2 doped with Fluorine (pH_{pzc})

Determination of the pH of the point of zero charge of the investigated samples was performed using the drift method of hydrogen index, as described in the papers [19-21].

1.3. Study of the adsorption capacity of TiO_2 samples doped with Fluorine

Adsorption studies were performed under batch conditions. The kinetics of adsorption, equilibrium adsorption, and the dependence of the adsorption value on pH were studied. The liquid-to-solid-phase ratio (L:S) was equal to 100. When analyzing the adsorption value's dependence on the solution's acidity, the L:S ratio was equal to 200. The strontium cations' initial and residual (equilibrium) concentration was determined by direct complexometric titration with Eriochrome black T indicators [28]. The amount of adsorption was calculated using the formula (1):

$$q_e = \frac{[(C_o - C_e)V]}{m} \tag{1}$$

Where q_e – adsorption values, mg/g; C_o та C_e – initial and residual (or equilibrium) concentration of adsorbate, mg/L; V- solution volume, L; m- mass of adsorbent, g.

The four most common kinetic models were applied

Table 1.

Phase composition and structural characteristics of the investigated samples

Sample	Anatase					Brookite			
	Content, %	a, Å	c, Å	Ti-O (axial), Å	Ti-O (plane), Å	Content, %	a, Å	b, Å	c, Å
a-TiO_2	100	3.7955	9.4982	1.9766	1.9390				
2F-TiO_2	93±2	3.7946	9.4802	1.9728	1.9384	5-7	9.124	5.417	5.238
4F-TiO_2	95±2	3.7971	9.4954	1.9760	1.9398	4-6	9.0771	5.3657	5.238
8F-TiO_2	100	3.7920	9.4849	1.9738	1.9372				

to the experimental results of non-equilibrium adsorption: Elovich, diffusion model, as well as models of adsorption kinetics based on pseudo-first and pseudo-second order equations [29].

The equilibrium adsorption of Sr^{2+} cations was analyzed using the theories of Langmuir and Freundlich; the corresponding equations are given below:

$$q_e = \frac{q_{max} K C_e}{1+ K_L C_e} \qquad (2)$$

Where q_e – the amount of adsorbate uptake at equilibrium, $mg \cdot g^{-1}$; q_{exp} – maximal adsorption value, which corresponds to filling the whole adsorption centers, $mg \cdot g^{-1}$; K_L – Langmuir equation's constant, ($L \cdot mg^{-1}$) is the value inverse to the concentration of C_e, at which adsorption is ½ A_∞; C_e – adsorbate equilibrium concentration, $mg \cdot L^{-1}$

$$q_e = K_f C_e^n \qquad (3),$$

where K_f – Freundlich constant, $\left(\frac{mg/g}{\left(\frac{mg}{L}\right)n}\right)$; n – intensity parameter of adsorption.

II. Results and discussion

2.1. Phase composition of the samples

X–beam diffractograms of the 2F-TiO_2, 4F-TiO_2, and 8F-TiO_2 samples, as well as a-TiO_2, are shown in Fig. 1. The phase composition of these samples and their structural characteristics are given in Table 1.

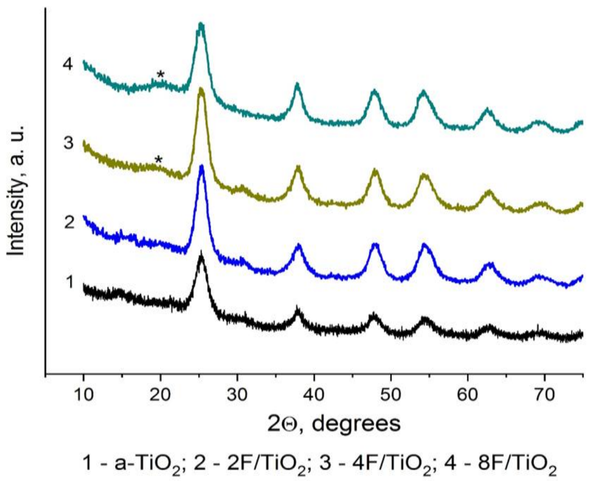


Fig. 1. X - diffractograms of investigated samples (1) a-TiO_2, (2) 2F-TiO_2, (3) 4F-TiO_2, and (4) 8F-TiO_2.

The base sample of a-TiO_2 is single-phase. The crystal structure of this phase is anatase (space group I41/amd). The presence of 2 and 4% F oxide material in the structure contributes to the fact that, in addition to anatase, (5-7) % and (4-6) % of brookite (Pbca spatial group), respectively, are formed in the samples.

The content of the anatase phase in the sample 8F-TiO_2 is 100%. It has been shown that there is no proportional increase or decrease in the parameters of the anatase cell with an increase in the content of F in titanium dioxide. This indicates that the groups TiF are localized mainly on the surface of oxide material particles.

The sizes of the coherent displacement domains (CDD) (in the first approximation, correspond to the size of the crystallite grains), determined by the reflex (101) of the tetragonal anatase lattice in the a-TiO_2 sample, are 4-5 nm and are smaller compared to the sizes of the domains (5-6 nm) in the doped samples.

2.2. Morphological state of samples

Low-temperature adsorption/desorption isotherms of N_2 molecules by basic and fluorine-containing samples of titanium dioxide are shown in Fig. 2. The parameters of their porous structure calculated according to these isotherms are shown in Table 2. The dependencies of the pore volume distribution by their size are shown in Fig. 3. We can see that the presence of Fluorine atoms in the structure of the oxide material significantly affects its morphological state. In the doped samples, compared to the base sample a-TiO_2, the specific surface area S is less developed, 125 $m^2 \cdot g^{-1}$, and is 1.9 times inferior in size to the specific surface area of a-TiO_2. There are no micropores in fluorine-containing samples, and the volume of V_{meso} mesopores in 2F-TiO_2 and 4F-TiO_2 samples is 0.136 $cm^3 \cdot g^{-1}$ and 0.148 $cm^3 \cdot g^{-1}$, respectively (less than the volume of mesopores of the base sample).

2.3. IR spectra of samples

IR spectra of fluorine-containing samples of titanium dioxide and base sample a-TiO_2 are shown in Fig. 4. In the spectrum of the base sample, the anatase phase is manifested by absorption bands of degenerate Eu oscillations of TiO_6 octahedra at 475 cm^{-1} and 604 cm^{-1}. Symmetrical oscillations of the atoms of the Au mode in the Ti-O-Ti anatase bridges belong to the bands 320-360 cm^{-1} and 745 cm^{-1} [30]. The bands at 490 cm^{-1} and 562 cm^{-1} in the spectra of the 2F-TiO_2 and 4F-TiO_2 samples are attributed to degenerate oscillations of the octahedra of the brookite phase. Although, according to X-ray diffractometry, the experimental sample 8F-TiO_2 is single-phase and has an anatase structure, however, in its

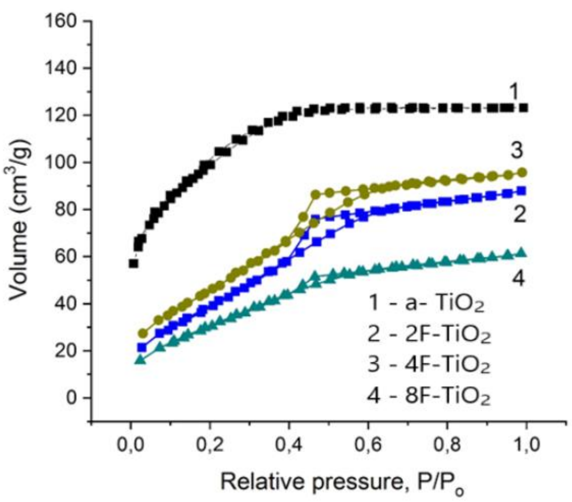


Fig. 2. Isotherms of low-temperature adsorption-desorption of nitrogen molecules by the studied samples of TiO_2.

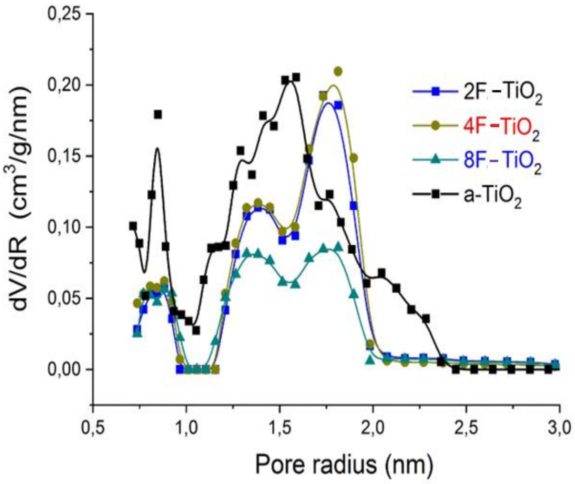


Fig. 3. Pore size distribution of the initial TiO_2 and fluorine-doped TiO_2 samples.

Table 2.

Morphological characteristics of initial and F-doped TiO_2 samples

Sample	S, м^2·г$^{-1}$	S$_{micro,}$ м^2·г$^{-1}$	S$_{meso,}$ м^2·г$^{-1}$	V, см^3·д$^{-1}$	V$_{micro,}$ см^3·г$^{-1}$	V$_{meso,}$ см^3·г$^{-1}$
α-TiO_2	239	100	139	0.152	0.054	0.098
2F-TiO_2	163	-	163	0.136	-	0.136
4F-TiO_2	186	-	186	0.148	-	0.148
8F-TiO_2	125	-	125	0.095	-	0.095

IR spectrum, in addition to the band of degenerate oscillations of anatase octahedra 475 cm^{-1}, a band of 427 cm^{-1} is recorded, which belongs to the degenerate oscillations of octahedra of the rutile phase [20]. The rutile phase in this sample is likely crystalline and imperfect since it contains only structural motifs of this phase, which cannot be manifested on diffractograms.

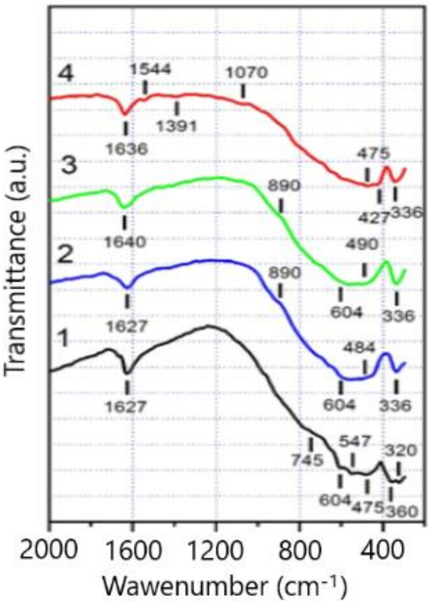


Fig. 4. IR – spectra of fluorine-containing samples of titanium dioxide and base sample a-TiO_2.

The band at 890 cm^{-1} in the spectra of samples containing 2% and 4% F atoms belongs to adsorbed CO_3^{2-} anions [19-21]. In the spectrum of the sample with 8% F in TiO_2, the bands at 1070 cm^{-1} and 1391 cm^{-1} are due to the formation of ≡TiOCOOH [31] groups on the surface of the crystalline disordered phase of rutile. Most likely, these groups occur at the formation stage of solid-phase embryos and cause the formation of structural motifs of rutile.

2.4. Structure-forming process

The aqua-complex titanium precursor $[Ti(OH_2)_6]^{3+}\cdot 3Cl^-$ has significant advantages compared to other titanium-containing precursors, primarily because it allows influencing the course of structure-forming processes, the growth rate of particles, the chemical state of their surface during the synthesis of TiO_2, and thus obtaining a product with predetermined and reproducible properties [25].

Chemical reactions involving this precursor are special, which ensure the formation of TiO_2 particles with a high degree of dispersion. Thus, when the precursor solution is heated at a temperature of 60°C, the titanium cation Ti (III) is oxidized:

$$Ti^{3+} \rightarrow Ti^{4+} + e \qquad (4),$$

Which causes the reduction of H_2O molecules in the aqua-complex for the production of hydroxyl anions OH^-:

$$2H_2O + O_2 + 4e \rightarrow 4OH^- \qquad (5).$$

In turn, OH^- anions attach to Ti^{4+} cations and form molecules $Ti\,(OH)_4{\cdot}2H_2O$. As a result of the condensation process, $TiO_2 \cdot 2H_2O$ particles are formed with the participation of these molecules. This process covers only a quarter of the Ti^{4+} cations.

Hydrolysis of rutile cations Ti^{4+} is carried out by oxidation of the NaOH reaction medium. Introducing the required amount of NaF into the precursor solution leads to adding anions F^+ to Ti^{3+} cations and producing fluorine-containing aqua-complexes $[TiF(OH_2)_5]^{2+}{\cdot}2Cl^-$. Oxidation of Ti^{2+} cations and subsequent hydrolysis leads to $TiF(OH)_3{\cdot}2H_2O$ molecules forming. With the participation of these molecules, as a result of the condensation process, fluorine-containing titanium dioxide F-TiO_2 is formed. The ionic radius of the F^+ anions is 1.36 Å and close to the ionic radius of the Oxygen anion (1.40 Å) [10]. Because of this, the anions F^+ easily occupy the positions of Oxygen in the structure of TiO_2. The large electrical negative of O (3,5) atoms causes an inductive effect on the redistribution of electron density in the ≡Ti-O-Ti≡ bridges to which the F atom is attached.

The shift in electron density from the Ti^+ atom to F leads to an elongation of the Ti-O bond in the Ti^+O_6 octahedron and a decrease in the value of this bond in the $Ti^{2+}O_6$ octahedron. The imbalance of the interatomic distances of Ti-O in the octahedra of TiO_6 contributes to the formation of the brookite phase since, in this crystalline modification, the distances from the Titanium atom to the Oxygen atoms in the octahedra are of different magnitudes.

In particular, Ti atoms bonding hydroxyl groups can be converted into acidic $\equiv TiOH^{\delta+}$ or the basis $\equiv TiOH^{\delta-}$ adsorption centers on the surface of particles of TiO_2 doped with Fluorine atoms. The activity of these centers and their number depend on the concentration of F atoms in the surface layer of TiO_2 particles and the distance from F atoms to Ti atoms that carry a hydroxyl group. Therefore, the addition of TiO_2 by F atoms should lead to an increase in the adsorption capacity for metal cations and anions of various natures.

2.5. Point of zero charge of the sample's surface

pH_{pzc} – is the value of the hydrogen pH of the electrolyte, at which the surface of the adsorbent acquires zero electric potential. The pH_{pzc} value is an essential characteristic of the adsorbent since it indicates the regions of pH values of the electrolyte in which the adsorbent behaves like a cationite or an anionite.

The pH value of the electrolyte pH of the base sample a-TiO_2, determined by the pH drift method, is 5.35. For fluorine-containing samples 2F-TiO_2, 4F-TiO_2, and 8F-TiO_2, this parameter equals 1.93, 3.02, and 3.54, respectively. As we can see, the entry of F atoms into the structure of TiO_2 shifts the point of zero charge of the surface to the acidic region. Changing the chemical state of TiO_2's surface expands the functionality of the adsorbent - it allows binding metal cations in acidic environments.

Figure 5 shows an analytical method for determining the point of zero charge on the pH scale for the doped samples.

2.6. Results of adsorption of strontium ions by the investigated samples of TiO_2

The results of adsorption studies of strontium ions by 2F-TiO_2, 4F-TiO_2, and 8F-TiO_2 are shown in Figures 6 (a-e), 7 (a-d), and 8. Figures 6-8 indicate the high adsorption ability of the samples toward strontium cations. At the same time, titanium dioxide with 8 wt. % F impregnated on the surface, 8F-TiO_2, has the most potent adsorption properties.

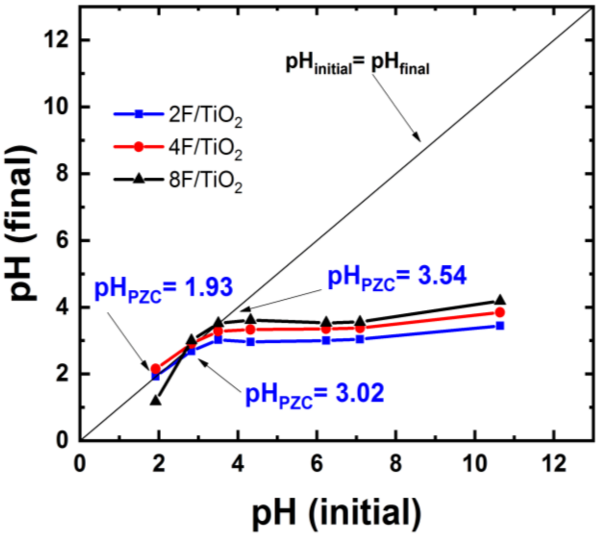


Fig. 5. pH of the point of zero charge of fluorine-doped TiO_2 samples.

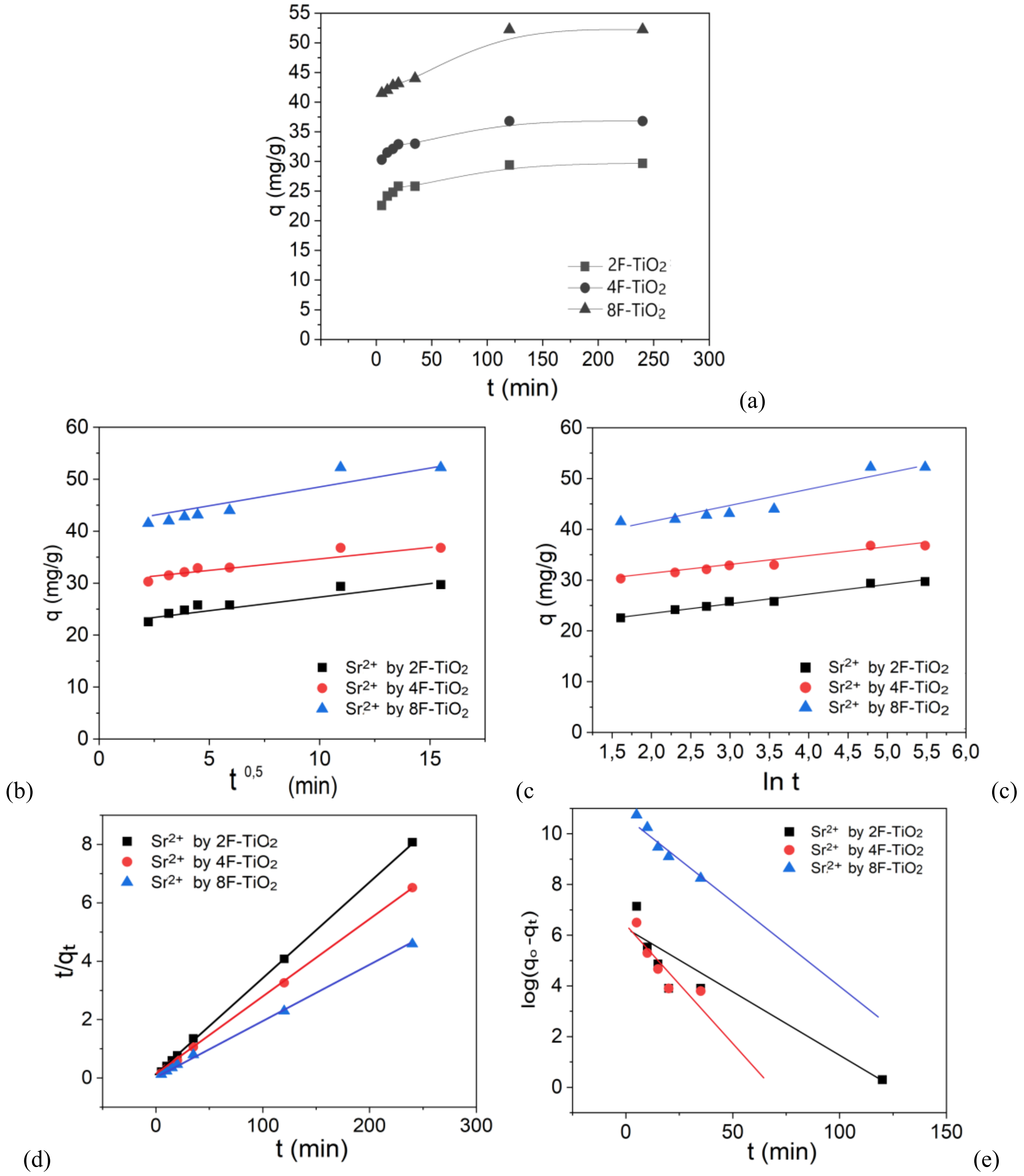
The dependence of the adsorption value of the Sr^{2+} cations on the duration of the interaction, i.e., kinetic dependence, indicates that the equilibrium in the system of "aqueous solution of adsorbate - the surface of TiO_2" is established 100 minutes after the start of the interaction. Adsorption kinetics describes the temporal evolution of adsorption values under non-equilibrium conditions. Therefore, there is an opinion among scientists [29, 32] that the kinetics of adsorption are mathematically more difficult to describe than equilibrium adsorption. However, with the help of kinetic models of adsorption, it is possible to establish certain patterns for specific cases.

In this work, the effect of strontium ion transport from the solution to the adsorbent surface was eliminated by rapid mechanical mixing so that it could be ignored. The most common kinetic models were applied to the experimental results of the kinetic dependence of strontium ion adsorption by TiO_2 doped with Fluorine: diffusion, Elovic model, and kinetic models based on pseudo-first and pseudo-second-order equations. The results are shown in Fig. 6 (a-e) and Table 3.

Applying the intraparticle diffusion model (Eq. 4) indicates that with an increase of impregnated Fluorine in the TiO_2 surface, the constant C (mg/g) also increases in the adsorption equation. This constant is associated with the influence of the boundary surface layer of the adsorbent on the adsorption process. As seen from Table 3, the constant C increases in the series 2F-TiO_2, 4F-TiO_2, and 8F-TiO_2, and its value equals 22.647, 30.09, and 39.25 mg/g.

$$q_t = D_{ipd}\, t^{1/2} + C \qquad (4)$$

Where, D_{ipd} – coefficient of intra-particle diffusion, mg/g $min^{0,5}$, C- the constant corresponds to the influence on the adsorption process of the boundary surface layer of the adsorbent (mg/g).



(a)

(b) (c (c)

(d) (e)

Fig.6. (a-e) Adsorption of strontium ions by TiO_2 dopped by Fluoride atoms: (a) Experimental adsorption kinetics; (b-e) Application of the diffusion and Elovich kinetic models, and kinetic models based on pseudo-first and pseudo-second order equations.

Table 3.

Application of kinetic models on experimental adsorption of Sr^{2+} by samples of Fluorine-Doped Titanium Dioxide.

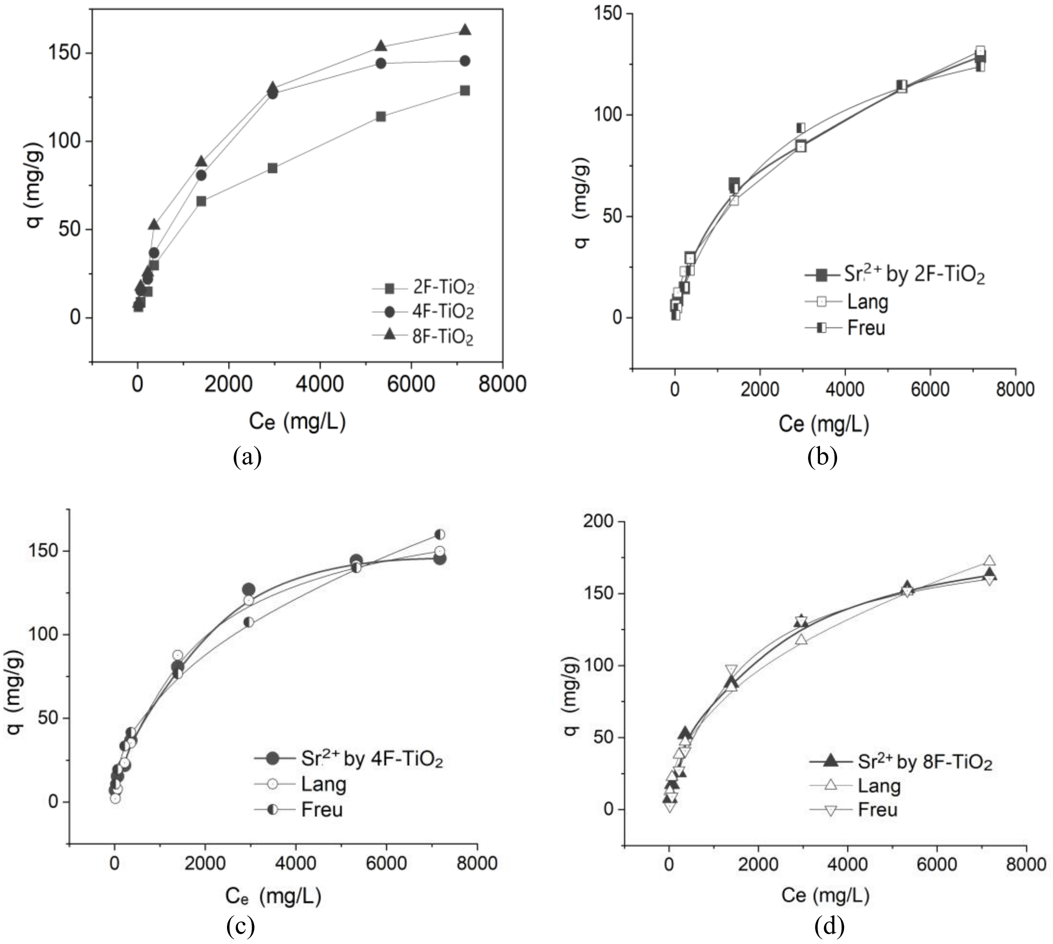
Kinetic model	Adsorption process	Parameters	R^2
Diffusion	Sr^{2+} by 8F-TiO_2	Step1 $Q=0{,}936\cdot t^{0{,}5}+39{,}25$	0.9213
	Sr^{2+} by 4F-TiO_2	Step1 $Q=0{,}494\cdot t^{0{,}5}+30{,}09$	0.9015
	Sr^{2+} by 2F-TiO_2	Step1 $Q=0{,}515\cdot t^{0{,}5}+22{,}647$	0.8948
Elovich	Sr^{2+} by 8F-TiO_2	$Q=3{,}26\cdot \ln t+34{,}48$	0.8989
	Sr^{2+} by 4F-TiO_2	$Q=1{,}803\cdot \ln t+27{,}3$	0.9616
	Sr^{2+} by 2F-TiO_2	$Q=1{,}895\cdot \ln t+19{,}69$	0.9714
Pseudo-first order equation	Sr^{2+} by 8F-TiO_2	$\log(qe-q_t) = -0{,}0828\cdot t+10{,}97$	0.9495
	Sr^{2+} by 4F-TiO_2	$\log(q_e-q_t) = -0{,}0837\cdot t+6{,}256$	0.7477
	Sr^{2+} by 2F-TiO_2	$\log(q_e-q_t) = -0{,}0492\cdot t+5{,}95$	0.8668
Pseudo-second order equation	Sr^{2+} by 8F-TiO_2	$t/q_t=0{,}0188\cdot t+0{,}067$	**0.9995**
	Sr^{2+} by 4F-TiO_2	$t/q_t=0{,}0269\cdot t+0{,}0615$	**0.9998**
	Sr^{2+} by 2F-TiO_2	$t/q_t=0{,}0334\cdot t+0{,}104$	**0.9998**

The coefficients of linear approximation also increase with an increase in the mass percentages of Fluorine on the surface, which agrees with the ideas about the course of the adsorption process. The speed of the process of adsorption of strontium ions by TiO_2 doped with Fluorine excludes the possibility of chemisorption. Therefore, there is a slight increase in R^2 of the Elovich model, with an increase in the percentage of Fluorine impregnated in TiO_2, which may only indicate an increase in the intensity of the interaction of Sr^{2+} with the surface of TiO_2.

However, the highest coefficient of linear approximation was obtained for all samples without exception using a kinetic model based on a pseudo-second-order equation [28, 29, 32]. The results are shown in Table 3.

Analyzing equilibrium adsorption can provide more complete conclusions about the adsorption mechanism. The analysis of the equilibrium adsorption of strontium cations by TiO_2 samples doped with Fluorine atoms is shown in Figures 7(a-d) and Table 4. The analysis was carried out using the equations of the adsorption theories of Langmuir and Freundlich. For this purpose, the "Solver add-in" software of Microsoft Excel was used [32].

The results of the investigation of equilibrium adsorption are shown in Figures 7 (a-d). Table 4 indicates that the Freundlich equation better describes the equilibrium adsorption of strontium ions by 2F-TiO_2. This is evidenced by a better correspondence of the adsorption value calculated according to this theory to the experimentally obtained one, a higher correlation coefficient $R^{2,}$ and a lower Pearson parameter χ^2. Freundlich's theory describes the adsorption process on a heterogeneous surface. Recall that in the structure of 2F-TiO_2, there is also a tiny proportion of brookite in addition to anatase. This determines the presence of several types of adsorption centers. The situation is unclear for samples with a higher percentage of fluorine on the surface (4F-TiO_2, 8F-TiO_2). The value of maximum adsorption calculated according to the Langmuir equation shows a better correspondence with the one determined experimentally. At the same time, the Freundlich equation gives an inflated result. R^2 values are also higher when applying Langmuir's theory than Freundlich's. At the same time, the higher the Pearson parameter. However, a detailed analysis of this parameter (which determines the discrepancy between experimental results and theoretically calculated ones) indicates that significant values of the Pearson parameter are observed only in the area of low adsorbate concentrations. Langmuir's theory in this region of concentrations gives underestimated results compared to the experiment due to the high adsorption activity of the surface of TiO_2 doped by 4% and 8% of Fluorine and its insignificant filling. Therefore, we believe that Langmuir's theory more reliably describes the process of adsorption of strontium ions by 4F-TiO_2 and 8F-TiO_2 samples.



(a) (b)

(c) (d)

Fig.7. (a) Experimental isotherms of adsorption of strontium ions TiO_2 doped by Fluoride atoms. Analysis of equilibrium adsorption of Sr^{2+} ions from aqueous solutions by investigated samples: (b) 2F-TiO_2; (c) 4F-TiO_2; (d) 8F-TiO_2.

Table 4.

Application of equilibrium adsorption theories to experimental data on adsorption of heavy metal cations by fluorine-doped TiO_2 samples.

Cation	Adsorbent	q_{exp}, mg/g	Adsorption Theory	q_{calc}, mg/g	Parameters	R^2	χ^2
Sr^{2+}	2F-TiO_2	128.8	Langmuir	123.84	K_L=0,00048 Q_{max}=160	0.9887	6.04
			Freundlich	131.57	K_f=1,592 n=0,5	0.9906	5.219
	4F-TiO_2	145.6	Langmuir	149.85	K_L=0,00068 Q_{max}=180,6	0.9918	20.11
			Freundlich	159.9	K_f=2,97 n=0,4489	0.9675	9.68
	8F-TiO_2	162.6	Langmuir	160.06	K_L=0,00077 Q_{max}=189	0.9876	23.66
			Freundlich	172.19	K_f=3,7 n=0,432	0.9819	9.7

The study of the effect of the acidity of the solution on the process of adsorption of strontium ions by the investigated samples is illustrated in Figure 8.

The adsorption values of Sr^{2+} ions increase with the transition of pH to the alkaline region, which coincides with the results of measurements of the point of zero charge of these adsorbents, as well as with the results of similar studies for other adsorbents based on titanium dioxide [21-24].

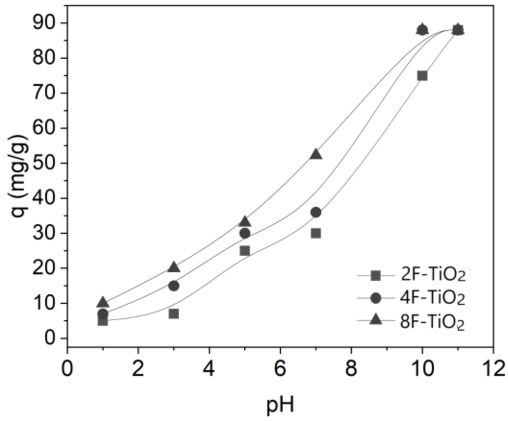


Fig.8. Dependence of the Sr^{2+} adsorption value on pH.

It can be said that this pattern of pH dependence is typical for most inorganic adsorbents. The results allow us to recommend using acid solutions to regenerate TiO_2 doped with Fluoride atoms. We conducted preliminary studies and found that investigated TiO_2 samples withstand at least five cycles of adsorption-desorption of strontium ions without loss of initial adsorption capacity.

The number of active adsorption centers on the surface area of the prototypes with an area of 10 nm^2 was calculated according to the formula (5):

$$N = \frac{q_{max}\cdot N_A}{S_{BET}\cdot 10^{17}} \qquad (5)$$

In the formula, q_{max} - is the experimentally determined maximum value of adsorption of Sr^{2+} cations in a neutral medium (mole·g^{-1}); S_{BET}- the specific surface area of the adsorbent (m^2· g^{-1}); N_A – Avogadro's number ($6.022\cdot 10^{23}$).

Results are shown in Table 5.

Table 5.

Number of active adsorption centers on the surface area of investigated samples with an area of 10 nm^2 for binding of Sr^{2+} cations in a neutral medium

Adsorbent	a-TiO_2	2F-TiO_2	4F-TiO_2	8F-TiO_2
Number of active adsorption centers	23	46	53	80

The data in the table shows that as the mass fraction of Fluorine atoms in TiO_2 increases, the number of acid adsorption centers $\equiv TiOH^{\delta+}$ also increases. Compared to the basic sample of a-TiO_2, the number of adsorption centers in the 8F-TiO_2 sample increases by 3.5 times.

The absence of micropores in the doped samples and the smaller specific surface area of these samples compared to the a-TiO_2 must be noted. The reason for this is a more active course of condensation processes during the synthesis of doped samples since the presence of both neutral ≡TiOH and acidic $\equiv TiOH^{\delta+}$ groups on the surface of the formed samples facilitates their fusion due to less energy expenditure on the formation of bridges ≡Ti – O – Ti≡:

$$\equiv TiOH + \equiv TiOH^{\delta+} \rightarrow \equiv Ti - O - Ti \equiv + H_2O \qquad (6)$$

Conclusions

The use of a solution of titanium aqua-complex $[Ti(OH_2)_6]^{3+}\cdot 3Cl^-$ and the modifying component NaF in sol-gel synthesis as a precursor ensures the formation of F-impregnated mesoporous titanium dioxide, which can effectively adsorb Sr^{2+} cations from the aqueous medium. As the F atoms increase in TiO_2 from 2% to 8% *wt*., the adsorption of Sr^{2+} cations increases and reaches 162.6 mg/g for 8F-TiO_2.

The reason is as follows: higher electronegativity of F – (4.0) atoms in comparison with Oxygen O (3.5) atoms causes an inductive effect on the redistribution of electron density in the bridges ≡Ti – O – Ti≡ and leads to the formation of a large number of acid centers $\equiv TiOH^{\delta+}$, on the surface of TiO_2.

This indicates that at the specified number of F atoms in TiO_2, virtually all hydroxylated atoms of those surfaces become acid centers. In the initial a-TiO_2, the number of acid centers on the specified surface area is only 19 units.

The formation in the process of synthesis of protoparticles containing neutral $\equiv TiOH$ and acid groupings $\equiv TiOH^{\delta+}$ on their surface activates condensation processes. It leads to the formation of titanium dioxide devoid of micropores and a smaller specific surface area compared to the base oxide material.

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Структурно-морфологічні та адсорбційні властивості діоксиду титану, допованого Фтором

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Дана робота присвячена синтезу та дослідженню структурно-морфологічних та адсорбційних властивостей діоксиду титану допованого Фтором. Методом золь-гель синтезу були синтезовані зразки TiO_2 із 2, 4 та 8 масовими відсотками Фтору, які позначені 2F-TiO_2, 4F-TiO_2 та 8F-TiO_2. Для одержання цих зразків у водний розчин титанового аквакомплексу $[Ti(OH_2)_6]^{3+}\cdot 3Cl^-$ із pH ~ 0.5÷1.5 вводили відповідну кількість NaF. Було проведено Х-променеву дифрактометрію, ІЧ-спектроскопію, вимірювання питомої площі поверхні та точки нульового заряду синтезованих адсорбентів. Також дано опис структуроутворюючого процесу. Досліджено адсорбційну здатність зразків 2F-TiO_2, 4F-TiO_2 та 8F-TiO_2 щодо катіонів стронцію. Проведено вимірювання кінетики адсорбції, рівноважної адсорбції а також впливу на даний процес кислотності розчину. Виявлено, що найбільшою адсорбційною здатністю щодо катіонів стронцію володіє адсорбент 8F-TiO_2. У роботі зроблено висновок, що в міру зростання масової долі атомів Фтору в TiO_2 чисельність кислотних адсорбційних центрів $\equiv TiOH^{\delta+}$ збільшується. В порівнянні з базовим зразком а-TiO_2 чисельність адсорбційних центрів у зразку 8F-TiO_2 зростає в 3.5 рази.

Ключові слова: адсорбція, золь-гель синтез, діоксид титану, питома поверхня, $pH_{\text{тнз}}$, стронцій.