PHYSICS AND CHEMISTRY OF SOLID STATE
V. 24, No. 1 (2023) pp. 114-125

Section: Chemistry

DOI: 10.15330/pcss.24.1.114-125

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ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 24, № 1 (2023) С.114-125

Хімічні науки

PACS: 64, 82.20 Hf

ISSN 1729-4428

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Adsorption of Sr(II) cations onto titanium dioxide, doped with Boron atoms

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The adsorption of Sr(II) cations by Boron-doped TiO_2 was investigated. The adsorbent samples were obtained by liquid-phase sol-gel method using the aqua complex precursor $[Ti(OH_2)_6]^{3+}3Cl^-$ and modifying reagent hydrogen borate H_3BO_3. It was found, that single-phase rutile titanium dioxide or two-phase anatase-rutile oxide materials were formed under the different initial ratios of components.

Boron atoms are combined with Oxygen atoms into triangular structural cell BO_3 in the rutile sample 0.5B-TiO_2 and are localized in the surface layer of the nanoparticle material as a grouping $=O_2BOH$. The introduction of Boron atoms into the structure of the rutile adsorbent causes an increase in its adsorption capacity for the binding of Sr(II) cations in the aqueous electrolyte medium. The maximal adsorption values for Sr(II) cations by the rutile adsorbent in a neutral electrolyte environment reach 102.3 mg g^{-1}, while it is equal to 68.8 mg g^{-1} for the unmodified anatase adsorbent a-TiO_2.

The number of acid adsorption centers $\equiv TiOH^{\delta+}$ on the surface of the rutile adsorbent 0.5B-TiO_2 is ~ 50 units on a surface area of 10 nm^2, which is twice the number of centers on the surface of the anatase adsorbent a- TiO_2. The ionic strength of the acid centers of the $\equiv TiOH^{\delta+}$ $pK_{\alpha 1}$ and the base centers of the $\equiv TiOH^{\delta-}$ $pK_{\alpha 2}$ of the rutile sample is the largest in comparison with the centers of other investigated adsorbents and, accordingly, are equal to 0.6 and 12.3.

Anatase-rutile adsorbents 1.0B-TiO_2 and 1.5B-TiO_2 contain, respectively, 70% and 57% of the anatase phase. They are significantly inferior in adsorption ability toward cations of Sr(II) compared with the rutile adsorbent 0.5B-TiO_2. This is because Boron atoms are mainly localized in the anatase phase and with oxygen atoms form tetrahedral groups of BO_4^-. Tetrahedral coordination of Boron atoms with respect to Oxygen atoms in the structure of anatase reduces the induction effect of Boron atoms on the redistribution of electron density in the B-O-Ti bridges and does not lead to the formation of additional acid adsorption centers on the surface of the anatase.

Keywords: Titanium dioxide, Boron, Adsorption, Strontium.

Received 30 August 2022; Accepted 24 January 2023.

Introduction

Adsorption technologies are widely used to solve environmental problems at present time. In particular, the synthetic adsorbents – activated carbon, zeolites, metal oxide-adsorbents Fe_3O_4, ZnO, TiO_2, titanium or zirconium phosphates, ion exchange resins, etc., are often used for the removal of heavy metal cations Pb (II), Cd (II), Ba (II), Hg (II), Sr (II) as well as some anions AsO_4^{3-}, SeO_4^{2-}, F^- from the aquatic environment [1-5]. The disadvantage of known adsorbents is low adsorption capacity, instability to aggressive media, or complexity of synthesis. In this regard adsorbents based on TiO_2 have unique properties: resistance to acid medium, simplicity of synthesis, and high adsorption capacity toward heavy metal cations. The adsorption binding of metal cations by TiO_2-based adsorbents is carried out by hydroxylated Ti atoms of only a certain type on the surface of TiO_2.

The surface of the anatase modification of TiO_2 with an area of 10 nm^2 may contain 120-140 $\equiv$TiOH – groups, but only ~ 30 titanium groups are $\equiv TiOH^{\delta+}$ acidic centers, which take part in the metal cations adsorption. Most titanium groups, 70-76 (%) percent of the whole amount, demonstrate a neutral nature and are not involved in adsorption.

The authors of publications [6-9] impregnated $=TiO_2CO$, $=TiO_2POOH$ or $=TiO_2AsOOH$ grouping in the amount of 3 to 13 units per 10 nm^2 on the surface of the anatase TiO_2 to increase the number of acid adsorption centers in 2-2.8 times. Exactly the high electronegativity of atoms C (2.5), P (2.1), and As (2.0) in these groupings, compared to the electronegativity of Ti atoms (1.5), causes the formation of additional acidic centers of $\equiv TiOH^{\delta+}$ capable of binding metal cations around these atoms.

According to our publication [10], sol-gel synthesis of nanoparticle TiO_2 using aqua complex precursor $[Ti(OH_2)_6]^{3+}3Cl^-$ and modifying reagent of borate acid H_3BO_3 (which is also known as hydrogen borate or boric acid) leads to the formation of Boron-containing TiO_2 of different phase composition. In particular, the Boron-containing sample of 0.5B-TiO_2 is a rutile material with a particle shape in the form of villi. Samples with a higher content of Boron atoms 1.0B-TiO_2 and 1.5B-TiO_2, in addition to rutile, contain 70% and 57% of the mass of anatase, respectively.

Since the electronegativity of atoms B is 2.0 and exceeds the electronegativity of Ti atoms, we can assume a high adsorption capacity of Boron-containing samples of TiO_2 toward metal cations.

In this work, we aim for the following tasks:

- find out the ionic strength of acid $\equiv TiOH^{\delta+}$ and the base $\equiv TiOH^{\delta-}$ adsorption centers of the surface of modified TiO_2 samples;
- investigate the adsorption of Sr(II) cations by Boron-containing TiO_2;
- determine the average number of acid $\equiv TiOH^{\delta+}$ and the main $\equiv TiOH^{\delta-}$ adsorption centers on a surface area of 10 nm^2 of base and modified samples.

I. Experimental techniques

1.1. Synthesis of titanium dioxide samples

Experimental samples of Boron-containing TiO_2 were obtained by the liquid-phase sol-gel method using as a precursor solution of titanium aqua complex $[Ti(OH_2)_6]^{3+}3Cl^-$ and modifying agent – borate acid H_3BO_3.

The synthesis of investigated samples was carried out at different ratios of components. The conditions for the synthesis of investigated samples and the mechanism of influence of the modifying agent on the course of structure-forming processes are described in detail in the publication [10].

1.2. Investigations of the characteristics of titanium dioxide samples

In this work, special emphasis was placed on the study of the surface characteristics of TiO_2 samples, which can affect the course of adsorption processes.

TEM and IR analyses were conducted; textural characteristics such as surface area and pore size distribution were determined, as well as the pH of the point of zero charges (pH_{pzc}).

Images of bare a-TiO_2 and Boron-doped TiO_2 were obtained using the LSM 2100F transmission electron microscope (TEM). The accelerating voltage during the operation of the transmission electron microscope was 200 kV or more, which made it possible to record images on a nanometer scale. Light field rendering mode was also used.

The phase composition of the bare a-TiO_2 and modified samples 0.5B-TiO_2, 1.0B-TiO_2, 1.5B-TiO_2, the parameters of the lattice and the dimensions of primary crystallites were investigated using the STOE STADIP diffractometer in the radiation of copper anode. The focus of the rays was carried out according to the Bragg-Brentano scheme. Rietveld's analysis of recorded diffractograms was performed using SHELXL-97 software [11, 12].

The study of the surface area of the samples and their pore size distribution was carried out with the help of isotherms of low-temperature N_2 adsorption-desorption. Quantachrome Autosorb (Nova 2200e) equipment was used for this purpose. Before measurement, the samples were calcined in a vacuum at 180°C for 24 hours. The surface area of the samples was calculated according to the theory of BET (Brunauer-Emmett-Teller). Pore size was estimated using density functional theory (DFT). It should be noted, that when calculating the surface area of adsorbents, the theories of BET and DFT give results that are well consistent with each other. However, since the calculation of surface area using the Brunauer-Emmett-Teller theory is generally accepted, we also used this particular theory.

IR spectroscopy was used, for qualitative and quantitative analysis of samples, with which it is possible to assess the structure of the complex, ions in compounds, phase composition, as well as the different coordination states of Boron atoms in the structure of anatase and rutile. The IR spectra of the samples were obtained on the Double-beam spectrophotometer SPECORD M80 device. To record the spectrum, the sample weight (4 mg) was mixed with KBr at a ratio of 1:100, and crushed in a vibration mill for 10 minutes. The resulting mixture formed a transparent plate size of 20×5 mm^2 by pressing.

The pH of the point of zero charges of the surface was determined to assess the surface ability of synthesized adsorbents to attach cations or anions. As a rule, pH_{pzc} is the value of a negative decimal logarithm of the activity of the potential-defining ion of the surface of a solid, that comes into contact with the electrolytic medium. Determination of the pH of the point of zero-charge of the surface a-TiO_2 and samples of TiO_2 doped by the Boron atoms was carried out by the method of drift of the hydrogen indicator of the medium.

1.3. Adsorption research and calculation of the number of adsorption centers of TiO_2 samples

Adsorption studies were carried out in batch conditions. To the 0.05 g of the adsorbent was added 5 ml of the studied aqueous solution of $SrCl_2$. The ratio of liquid: solid phase (L:S) was, respectively, 100. Initially, the dependence of the adsorption of strontium ions on the duration of interaction, the so-called kinetics of adsorption, was investigated. Thus, the duration of the interaction was determined, in which adsorption equilibrium was established in the reaction mixture. In addition, a possible mechanism for the course of adsorption processes was determined using the four most common kinetic models of adsorption.

Adsorption isotherms were measured at a certain time of equilibrium. For this purpose, the initial concentration of strontium ions in the solution was increased. The initial and residual (equilibrium) concentration of strontium ions was determined by direct complexonometric titration with the indicator Eriochrom Black T.

In studies of anion adsorption, the equilibrium concentration of adsorbate was defined by Mohr's method, which uses the titration by the standard solution of silver nitrate with potassium chromate as an indicator. The value of adsorption was calculated according to the formula (1):

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

For the analytical description of the equilibrium adsorption of the cations Sr (II) by the TiO_2 samples, the Langmuir (2) and Freundlich (3) equations were used [13, 16]:

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

Where, q_e – the amount of adsorbate uptake at equilibrium, $mg \cdot g^{-1}$; A_∞ – 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.

The number of acid adsorption centers N, on the surface of the adsorbent area of 10 nm^2, was calculated according to equation (4):

$$N = \frac{q_{max} \cdot N_A}{S_{BET} \cdot 10^{17}} \qquad (4)$$

Here q_{max} – experimentally defined maximal adsorption of Sr (II) cations, ($mole \cdot g^{-1}$); S_{BET}- the specific surface area of the adsorbent, ($m^2 \cdot g^{-1}$); N_A – Avogadro constant ($6.022 \cdot 10^{23}$).

Studies of the effect of the acidity of the solution on the adsorption values were performed by adding to the reaction mixture 5 ml of HNO_3 solution or ammonium buffer solution to achieve the required pH value. Accordingly, the L:S ratio increased to 200. The acidity of the solution was controlled using a pH meter with a chlorine-silver electrode.

II. Results and discussion

2.1. The phase composition of the investigated samples

The phase composition of the bare a-TiO_2 and modified samples 0.5B- TiO_2, 1.0B- TiO_2, and 1.5B- TiO_2 the lattice parameters and the dimensions of the primary crystallites of these phases are given in Table 1.

The bare a-TiO_2 contains a single phase – anatase (spatial group I_{41}(amd)). The presence of Boron atoms in the sample of 0.5B-TiO_2 leads to the formation of a single-phase material – rutile (spatial group P_{42} (mnm) [17]. However, increasing the content of Boron atoms leads to the formation of two-phase samples 1.0B-TiO_2 and 1.5B-TiO_2. These Boron-containing samples consist of anatase and rutile modifications of TiO_2 in quantities of 30 wt., % and 70 wt., % (57 wt., % and 43 wt., %) masses, respectively.

The textural characteristics of the bare a-TiO_2 and Boron-containing samples calculated by the method of low-temperature adsorption-desorption of N_2 molecules (Fig.1) are given in Table 2. They show that according to the specific surface of S_{BET} and the volume of pores V_p, the rutile sample 0.5B-TiO_2 is inferior to the base anatase sample a-TiO_2 and anatase-rutile samples 1.0B-TiO_2 and 1.5B-TiO_2. Thus, S_{BET} and the volume of pores V_p anatase-rutile sample 1.0B-TiO_2 is more than twice as high as these characteristics for 0.5B-TiO_2 rutile. However, the comparison of the rutile sample 0.5B-TiO_2 with the Boron-containing samples of TiO_2 described in the literature [18-20] indicates that the surface area of the sample 0.5B-TiO_2 remains higher than that described for Boron-containing world-wide analogs.

Sol-gel synthesis of investigated samples is special in the aspect of obtaining TiO_2 materials with very small mesopores with a radius of 1.0-3.0 nm and micropores with a radius up to 1.0 nm. (Fig. 1 (b)).

The micropores and mesopores in the samples are the gaps between the primordial particles and their associate or aggregates. The radii of the mesopore of the 0.5B-TiO_2 rutile sample are in the range of 1.0-2.0 nm values. They are smaller in size compared to the radii of other adsorbents. This is because the particles of this sample have the form of villi (Fig. 2 (a)).

Their diameter is 0.8-1.2 nm, and the length is 16-24 nm. The main features are that the villi are folded into "sheaves" in the associates, and this causes the formation of especially small mesoporous. The appearance of such particles is shown in Fig. 2.

2.2. Amphoteric properties of TiO_2

Titanium dioxide belongs to amphoteric oxides of metals, which have both acidic and basic properties. The amphoteric properties of titanium dioxide are manifested in the fact that its surface titanium groups change their chemical state, depending on the pH of the medium:

$$\equiv TiOH_2^+ \leftrightarrow \equiv TiOH^{\delta-} + H^+ \qquad (5)$$

$$\equiv TiOH^{\delta+} \leftrightarrow \equiv TiO^- + H^+ \qquad (6)$$

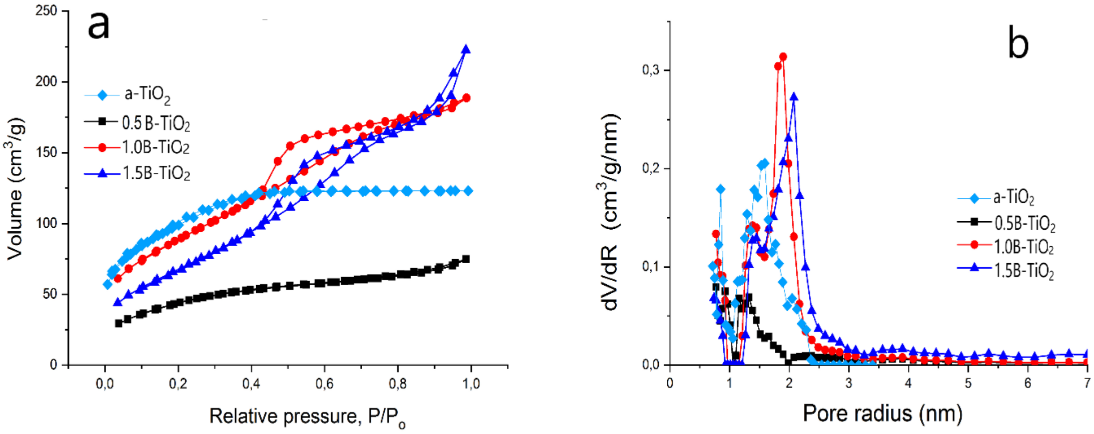


Fig.1. Isotherms of low-temperature N_2 adsorption/desorption of bare a-TiO_2 and Boron-containing TiO_2 samples (a); (b) the pores size distribution in the investigated samples studied by the magnitude of their effective radii.

Table 1.

Textural characteristics of investigated samples and parameters of the lattice of anatase and rutile modification of TiO_2.

Sample	Anatase						Rutile					
	Con-tent, %	a, A	c, A	Ti-O (axial), Å	Ti-O (plane), Å	Particle size, nm	Con-tent, %	a, nm	c, nm	Ti-O (axial), Å	Ti-O (plane), Å	Par–ticle size, nm
a-TiO_2	100	3.784	9.513	1.9787	1.9337	2.9±1.4	–	–	–	–	–	–
0.5B/TiO_2	–	–	–	–	–	–	100	4.610	2.955	1.9924	1.9466	5.1
1.0B/TiO_2	70±4	3.796	9.496	1.9752	1.9395	3.5	30±3	4.637	2.946	2.0040	1.9480	6.1
1.5B/TiO_2	57±2	3.787	9.499	1.9758	1.9351	3.9	43±2	4.602	2.958	1.9889	1.9463	5.7

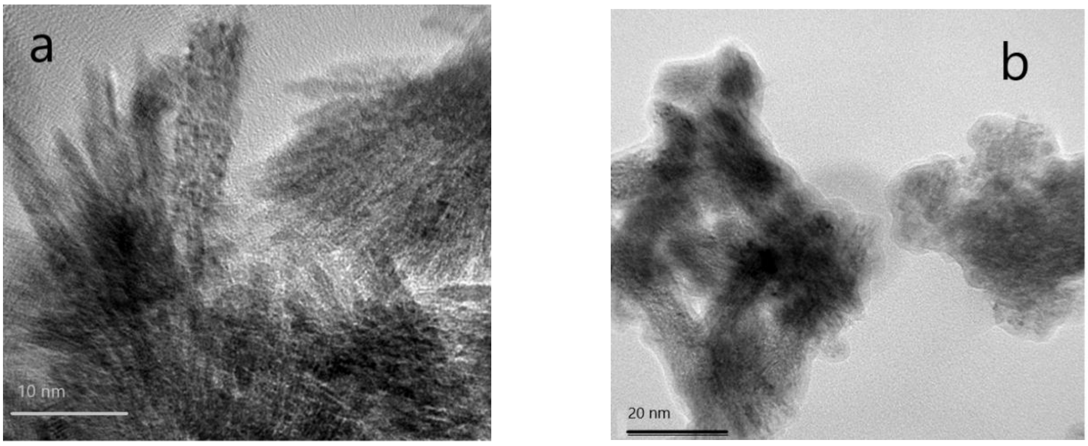


Fig. 2. TEM-image of nanoparticles of the rutile sample 0.5B-TIO_2 (a); and anatase-rutile sample 1.0 B-TiO_2 (b).

Table 2.

Textural characteristics (specific surface area, pore volume).

Sample	**S_{BET} (m^2g^{-1})**	**S_{micro} (m^2g^{-1})**	**S_{meso}, (m^2g^{-1})**	**V_p, (cm^3g^{-1})**	**V_{micro} (cm^3g^{-1})**	**V_{meso} (cm^3g^{-1})**
a-TiO_2	239.4	100.5	138.9	0.1519	0.054	0.098
0.5B-TiO_2	151.6	81.73	69.87	0.1158	0.04175	0.07405
1.0B-TiO_2	316.1	14.25	301.85	0.2918	0.00661	0.28519
1.5B-TiO_2	254.1	-	254.1	0.3442	-	0.3442

Titanium surface groups attach the proton H^+ in an acidic environment (scheme 5), and in the alkaline medium, they give it away (Scheme 6). The surface of TiO_2 must contain a proton acceptor, which ensures the transition of the proton from the acid to the base, to reach ionic equilibrium in solution. Therefore, on the surface of the TiO_2 particles, there are both: the base $\equiv TiOH^{\delta-}$ and acid $\equiv TiOH^{\delta+}$ grouping. The establishing of the protolithic equilibrium of the TiO_2 surface can be written in the form of a scheme (7):

$$\equiv TiOH_2^+ + \equiv TiOH^{\delta-} \leftrightarrow \equiv TiO^- + H^+ \qquad (7)$$

The constant of protolithic equilibrium K_n of the surface of TiO_2 is calculated according to the equation:

$$K_n = \frac{[\equiv TiO^{\delta+}][\equiv TiO^-]}{[\equiv TiOH_2^+][\equiv TiO^{\delta-}]} \qquad (8)$$

The values of the constants of acid groups $K_{\alpha 1}$ and the base groups $K_{\alpha 2}$ can be determined accordingly, from the following equations:

$$K_{\alpha 1} = [H^+]\frac{[\equiv TiO^-]}{[\equiv TiOH_2^+]} \qquad (9)$$

$$K_{\alpha 2} = [H^+]\frac{[\equiv TiOH^{\delta-}]}{[\equiv TiOH^{\delta+}]} \qquad (10)$$

The negative decimal logarithm of the value $K_{\alpha 1}$ ($-\lg K_{\alpha 1} = pK_{\alpha 1}$) characterizes the ion strength of Brønsted's acid centers $\equiv TiOH^{\delta+}$, and the negative decimal logarithm value $K_{\alpha 2}$ ($-\lg K_{\alpha 2} = pK_{\alpha 2}$) that of base centers of Brønsted $\equiv TiOH^{\delta-}$.

The acid-base model of the solid surface was proposed by S. Morrison [21]. According to his model for assessing acidity, pK_α is selected – a scale that is limited by the limit values of the dissociation constants of water molecules:

$$-1{,}76 < pK_\alpha < 15{,}76 \qquad (11)$$

The area of the Brønsted centers includes OH- groups of different acidic strengths, as well as water molecules with different stages of protonation, coordinating with the main and acid centers of Lewis following the pK value of water-acid (-1.76) and the pK of the water-base (15.76). The acid centers of Brønsted are to the left of the neutrality point ($pK_\alpha = 7.0$). Their acidity increases from right to left with a decrease in the donor capacity of the orbitals of the metal atom and the displacement of electron density from the atom H to the orbital of the atom O. The bases of Brønsted are situated to the right of the point of neutrality ($pK_\alpha = 7.0$). Their basicity increases with a decrease in the donor capacity of the metal atom. There is a shift in electron density from the metal atom to the orbital of the Oxygen atom, which enhances the connection of O-H in the hydroxyl group and increases the basicity of the Brønsted center ($pK\alpha > 7.0$).

The ion strength of the acid and basic titanium groups, respectively, $pK_{\alpha 1}$ and $pK_{\alpha 2}$ of the TiO_2 surface, we calculated by hydrogen indicator – the pH of point of zero charges (pH_{pzc}) of the oxide material and the pH of its suspension. pH_{pzc} is a pH value in which a solid immersed in an electrolyte has a zero electrical charge on the surface.

According to [21] the average value of the ionic strength of the adsorption centers of the surface $pK_{\alpha\ mean}$ is calculated by the equation (12):

$$pK_{\alpha\ mean} = \frac{1}{2}\,(K_{\alpha 1} + K_{\alpha 2}) \qquad (12)$$

Moreover, the value $pK_{\alpha\ mean}$ identicals the value of pH_{pzc}:

$$pK_{\alpha mean} = pH_{pzc} \qquad (13)$$

Taking into account the Henderson–Hasselbalch equation [13, 14, 21] (14):

$$\frac{[\equiv TiO^-]}{[\equiv TiOH_2^+]} = 10^{(pH - pH_{pzc})} \qquad (14)$$

it is easy to conclude that the ionic force $pK_{\alpha 1}$ of acid centers can be calculated by the equation (15):

$$pK_\alpha = pH + |(pH - pH_{pzc})| \qquad (15)$$

In the last two equations, pH is a hydrogen index of 1% suspension of oxide material.

The hydrogen indicator of electrolyte in which the surface of the adsorbent acquires a zero electrical charge (pH_{pzc}) is an important parameter since it indicates the areas of pH values within which the adsorbent behaves like cationic or anionic.

The data given in Table 3 show that the pH_{pzc} of the sample 0.5B-TiO_2 is 6.0 and exceeds the values pH_{pzc} of other samples. At the same time, as the number of Boron atoms increases in TiO_2, the point of zero charges on the pH scale shifts towards an acidic environment.

Table 3.

Properties of bare a-TiO_2 and surface modified TiO_2 samples.

Sample Name	Analytical data			
	pH_{susp}	pH_{pzc}	$pK_{\alpha 1}$	$pK_{\alpha 2}$
a-TiO_2	4.4	5.35	3.4	10.6
0.5B-TiO_2	3.2	6.0	0.4	12.3
1.0B-TiO_2	3.1	3.2	3.0	9.4
1.5B-TiO_2	3.1	2.2	4.0	8.4

For samples 0.5B-TiO_2, the ionic strength $pK_{\alpha 1}$ of the acid centers $\equiv TiOH^{\delta+}$ is 0.4 and significantly exceeds the ionic strength of these centers in the basic sample a-TiO_2 (3.4) and modified samples 1.0B-TiO_2 (3.0) and 1.5B-TiO_2 (4.0). At the same time, the ionic strength of the base centers $pK_{\alpha 2}$ of the 0.5B-TiO_2- sample is equal to 12.3 and also exceeds the ionic strength of the base centers of other samples.

The analytical data given in Table 3 may indicate the expected high adsorption capability of the 0.5B-TiO_2 sample for the adsorption of the metal cations in an environment with a pH > 6.0. The same sample can effectively adsorb Cl-, Br-, I- anions in an acidic environment with a pH of < 6.0.

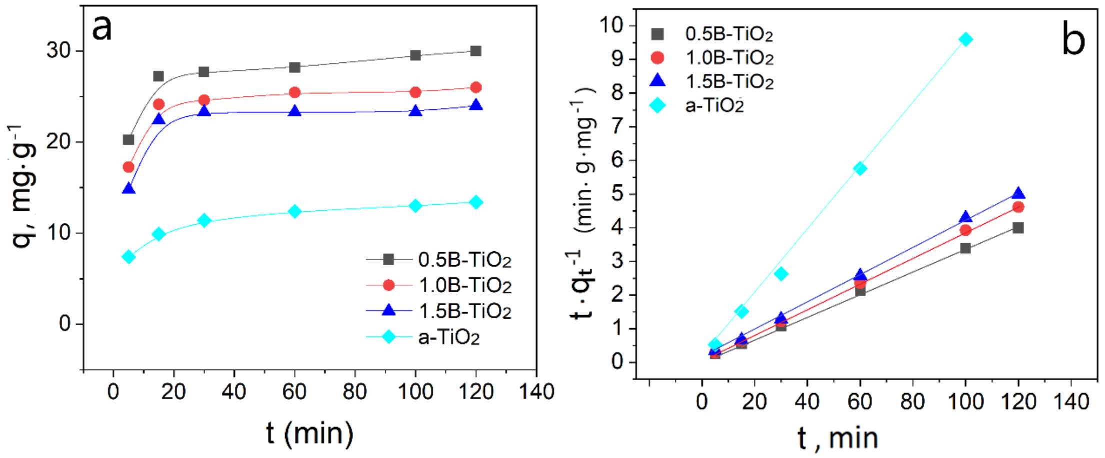


Fig. 4. Dependence of the value of adsorption of strontium ions on the duration of interaction (a); (b) application of the Lagergren model based on the pseudo-second-order equation.

Table 4.

Analytical equations of kinetic models.

Kinetic model	**Linear equation**
Diffusion	$q_t = K_1 t^{1/2} + K_o$
Elovich	$q_t = \frac{1}{\beta}\ \text{lnt} + \frac{1}{\beta} \ln(\alpha\cdot\beta)$
Pseudo-first-order	$\text{Lg}\ (q_p - q_t) = \ln q_p - \frac{K_2}{2.303} t$
Pseudo-second-order	$\frac{t}{q_t} = \frac{1}{K_3 {q_p}^2} + \frac{t}{q_p}$

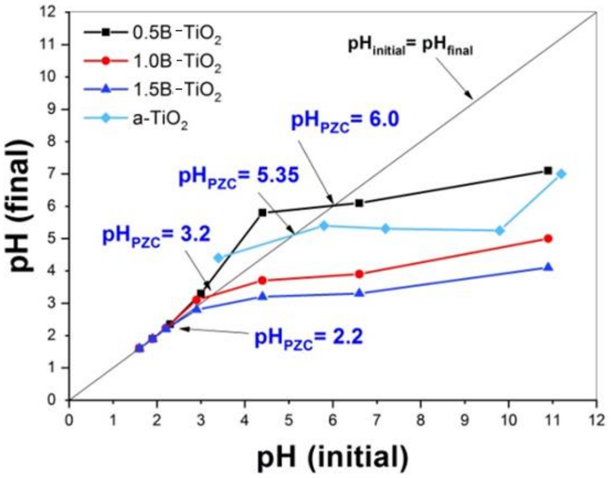


Fig. 3. "Drift" hydrogen suspension indicator during the determination of the pH_{pzc} of investigated TiO_2 samples.

2.3. Adsorption studies. Kinetics of Sr (II) ions adsorption

Kinetic dependences of Sr(II) adsorption from 0.005M solution of $SrCl_2$ by the investigated TiO_2 samples are shown in Fig. 4. They show that 75% of cations are adsorbed within 30 minutes of contact of the electrolyte with the adsorbent, but the equilibrium state in this process occurs only after 2-2.5 hours.

Four well-known kinetic models: a model of Weber-Morice, Elovich's, and Lagergren's model of pseudo-first and pseudo-second-order [13-16] (Table 4) were used to describe the adsorption of Sr (II) by investigating TiO_2.

In this equations: q_o and q_t - adsorption capacity at equilibrium and at time t, respectively, mg g^{-1}; K_1 (mg/g min^{0,5}), K_0, k_2(min^{-1}), k_3 (g·mg^{-1} min^{-1}), α (mg/g min) – rate coefficients of pseudo - first order, pseudo-second order, intra-particle diffusion, and in Elovich kinetic models equations, respectively; β (mg/g)- desorption constant in Elovich equation [16].

The correspondence of the equation of the kinetic model of adsorption with experimental results was estimated by the correlation coefficient R^2 [16]. The results of the approximation of experimental dependences to the theoretical calculations are given in Table 5. They show that the most adequate kinetics of cation adsorption by Boron-doped TiO_2 is described by the Lagergren pseudo-second-order equation. The R^2 for equations is high and equal to 0.9997-0.9994.

2.4. Equilibrium adsorption of strontium ions by TiO_2 samples

Figure 5 (a-d) shows the isotherms of adsorption of cations Sr(II) by TiO_2 samples. They show that the adsorption capacity of modified adsorbents 0.5B-TiO_2; 1.0B-TiO_2 and 1.5B-TiO_2 are higher than the corresponding value for unmodified adsorbent a-TiO_2.

The single-phase rutile adsorbent 0.5B-TiO_2 shows the most effectivity among all Boron-doped samples.

The equations of the Sr (II) adsorption isotherms most reliably describe the adsorption process in the approximation of Langmuir's theory. This is indicated by the high values of the correlation coefficient R^2 (0.9953-0.9905) and the low values of the parameter χ^2 (1.899-12.02). The results are in good agreement with the calculations of kinetic models, according to which, the highest coefficients of linear approximation are obtained for the pseudo-second-order equation (Table 5).

This significantly increases the reliability of calculations of the number of acid and base adsorption centers on the TiO_2 surface area of 10 nm^2. The number of acids and base adsorption centers on the TiO_2 surface area of the 10 nm^2 was calculated by the adsorption values of the Sr(II) cations in a neutral medium (with a pH = 7.0).

At the medium pH equal pH_{pzc} of the corresponding adsorbent, when surface charge equals zero, the number of acid centers is equal to the number of base ones. As the pH of the environment increases concerning the pH_{pzc}, the number of the base centers $\equiv TiOH^{\delta-}$ is sharply decreasing, and the number of acid centers $\equiv TiOH^{\delta+}$ remains unchanged. Conversely, with a decreasing the pH of the

Table 5.

Values of parameters and coefficients in equations of kinetic models applied to describe the adsorption of Sr (II) cations.

Equation parameter		**0.5B-TiO_2**	**1.0B-TiO_2**	**1.5B-TiO_2**	**a-TiO_2**
Pseudo-first-order					
K_2		-0.0111	-0.0108	-0.0086	0.0042
R^2		0.8603	0.7006	0.4664	0.9312
Pseudo-second-order					
K_3		0.0329	0.0381	0.0414	0.0098
R^2		0.9994	0.9997	0.9994	0.9968
Elovich					
α		205.2	155.2	60.1	0.271
β		0.376	0.4217	0.414	0.104
R^2		0.8446	0.7759	0.7123	0.6442
Intra particle diffusion model					
K_1 step1		2.29	2.27	2.63	0.5588
K_0		16.21	13.24	10.02	8.01
R^2		0.8041	0.8005	0.8338	0.9725
κ_1 step2		0.394	0.218	0.0937	-
K_0		25.5	23.51	22.67	-
R^2		0.9642	0.8581	0.4301	-

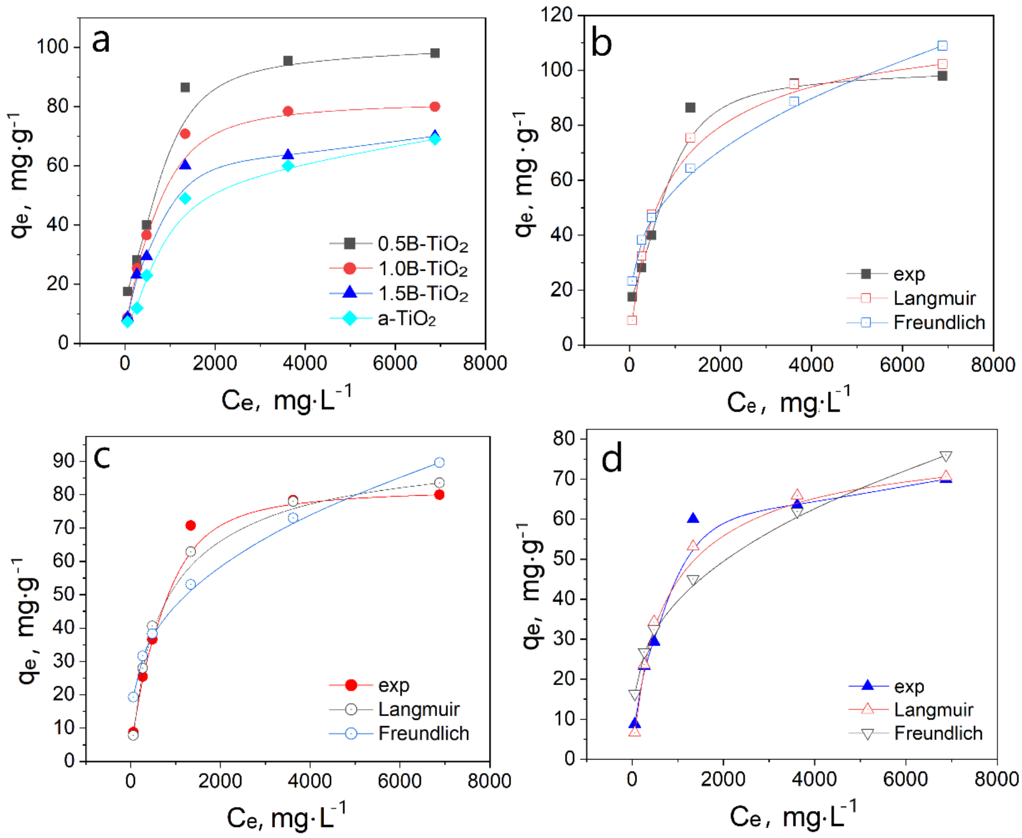


Fig.5. (a) Adsorption isotherms of Sr(II) by investigated samples of TiO_2. Nonlinear approximation of experimental equilibrium results by Langmuir and Freundlich adsorption theories for (b) 0.5B-TiO_2; (c) 1.0B-TiO_2; (d) 1.5B-TiO_2.

Table 6.

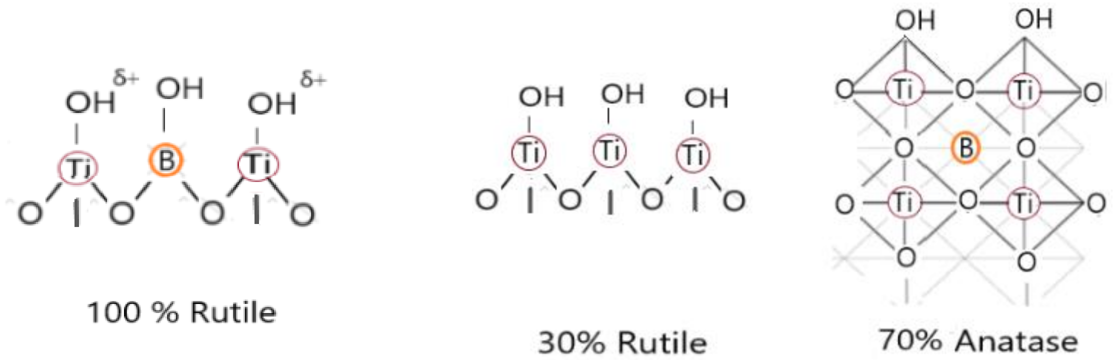
Parameters of Langmuir and Freundlich equations for adsorption of Sr(II) ions by Boron-doped TiO_2.

Adsorption theory	**Parameters of equation**	**Adsorbent**			
		0.5B-TiO_2	**1.0B-TiO_2**	**1.5B-TiO_2**	**a-TiO_2**
Langmuir	K_L	0.001549	0.00169	0.00169	0.00012
	A_{max}	111.92	90.77	76.68	151.66
	Q_{max} calc	102.3	83.58	70.6	68.84
	Q_{max} exp	98	80	70	70.8
	R^2	0.9905	0.9953	0.9944	0.9428
	χ^2	12.02	1.899	2.408	42.38
Freundlich	K_f	6.42	5.34	4.52	0.358
	n	0.32	0.319	0.319	0.5946
	Q_{max} calc	108.9	89.66	75.99	67.58
	Q_{max} exp	98	80	70	70.8
	R^2	0.9730	0.9724	0.9770	0.9574
	χ^2	14.11	14.32	9.74	21.26

Table 7.

The number of acid and base adsorption centers on the TiO_2 surface area of 10 nm^2.

Adsorbent	**The number of adsorption centers on the surface area of 10 nm^2**			**Percentage of $\equiv TiOH^{\delta+}$, %**
	$=O_2BOH$	$\equiv TiOH^{\delta+}$	$\equiv TiOH^{\delta-}$	
a-TiO_2	-	19.8	-	15.2
0.5B-TiO_2	1.6	49.8	46.9	38.3
1.0B-TiO_2	-	17.3	4.4	13.3
1.5B-TiO_2	-	18.9	2.3	14.5



Model 1. Model 2.

Fig. 6. Boron-containing grouping on the surface of particles of the rutile sample 0.5B-TiO_2 (Model 1), and the surface of anatase-rutile particles 1.0B-TiO_2 (Model 2).

environment concerning pH_{pzc} the number of acid centers $\equiv TiOH^{\delta+}$ decreases sharply, and the number of the base centers $\equiv TiOH^{\delta-}$ - does not change. The data, which are given in Table 7, show, that the number of acid centers $\equiv TiOH^{\delta+}$ on the surface area of 10 nm^2 of the rutile sample 0.5B-TiO_2 is 49.8 units and it is the largest compared to other samples.

The number of base centers $\equiv TiOH^{\delta-}$ in this sample is equal to 46.9 units. It is smaller compared to the number of $\equiv TiOH^{\delta+}$. This is due to a greater hydrogen index of the medium compared to the pH_{pzc} of this sample. The number of acid centers of anatase-rutile samples 1.0B-TiO_2 and 1.5B-TiO_2 respectively are equal to 17.3 and 18.9 units on the surface area of 10 nm^2. The specified number of acid centers is close to the number of these centers in the bare a-TiO_2 sample.

Therefore, the higher adsorption capacity of the rutile sample 0.5B-TiO_2 toward Sr(II) cations than bare a-TiO_2 is due to its crystalline structure and the presence of incorporated Boron atoms in this structure.

Boron atoms in the rutile sample 0.5B-TiO_2 form a grouping $=O_2BOH$, which are impregnated in the surface layer of titanium dioxide particles. In these groups, atom B is surrounded by three oxygen atoms, two of which are involved in a chemical bond with Ti atoms. Since the electronegativity of atoms B is 2.0 and exceeds the electronegativity of Ti atoms (1.5), therefore, inductive redistribution of the electron density causes the formation of additional acid centers $\equiv TiOH^{\delta+}$ in the vicinity of the impregnated Boron-containing group (see Model 1).

In the IR spectrum of sample 0.5B-TiO_2 (Fig. 7, spectrum 2), fluctuations in groups of BO_3 are weak in intensity in bands of 1400; 1110, and 974 cm^{-1}. The first two bands belong to the degenerate asymmetric oscillations of BO_3^- groupings, and the third band we attribute to the asymmetric deformation oscillation of B-OH [22, 23].

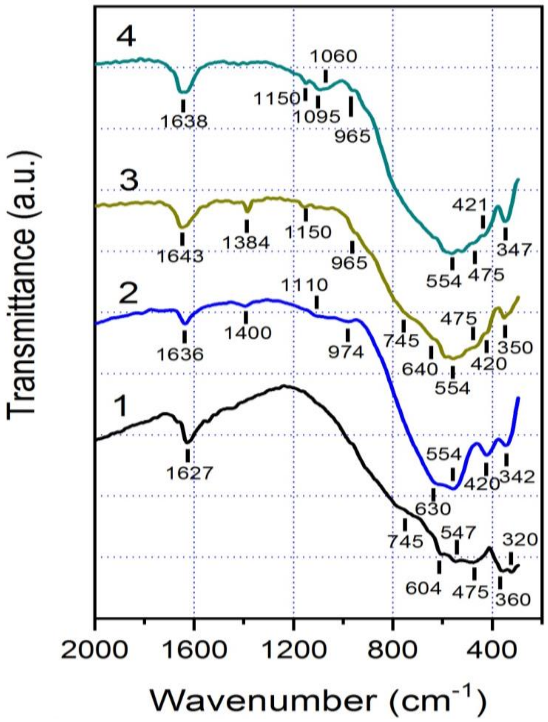


Fig. 7. IR spectra of the basic sample a-TiO_2 (1) and 0.5B-TiO_2 (2), 1.0B-TiO_2 (3), 1.5B-TiO_2 (4).

Titan borate monodentate molecules are creating $Ti(OH)_3OB(OH)_2 \cdot 2H_2O$ during the synthesis of the sample 0.5B-TiO_2 in the reaction mixture of titanium aqua complex precursor $[Ti(OH_2)_6]^{3+} \cdot 3Cl^-$ and borate acid $B(OH)_3$. These molecules in the polycondensation process act as a promoter for the formation of rutile, since the length of the Ti-O bond in them, is commensurate with the average length of Ti-O in the octahedra of TiO_6 rutile.

Molecules with a bidentate mononuclear structure $Ti(OH)_2O_2BOH \cdot 2H_2O$ occur, causing the formation of the anatase phase, due to the high chemical potential of the reaction mixture, in the process of synthesis of the samples 1.0B-TiO_2 and 1.5B-TiO_2. The distance of Ti-O in this molecule is commensurate with the average length of the Ti-O bond in the octahedra of the anatase phase. In addition to anatase, these samples contain respectively 30 and 43% percent of rutile. B atoms are in tetrahedral coordination related to Oxygen atoms in anatase TiO_2. The IR spectra of the anatase phase of the anion BO_4^- belong to bands 1150 and 965 cm^{-1} (Fig. 8, spectrums 3 and 4) [22-25].

Anions BO_4^- mainly localized in the volume of the anatase phase (model 2). Tetrahedral coordination of Boron atoms relate to Oxygen atoms reduces the induction effect of Boron atoms on the redistribution of electron density in B-O-Ti bridges and does not lead to the formation of additional acid adsorption centers on the surface of the oxide material.

The number of acid centers $\equiv TiOH^{\delta+}$ on a surface area of 10 nm^2 in samples 1.0B-TiO_2 and 1.5B-TiO_2 is 17.3 and 18.9 units, respectively (Table 7). This number of acid centers roughly corresponds to the number of centers of unmodified a-TiO_2. These data indicate the absence of Boron atoms in the structure of rutile of two-phase samples.

It should be noted, that the increase in the number of acid centers $\equiv TiOH^{\delta+}$ in the rutile sample 0.5B-TiO_2 is more than two times due to the impregnation of only 1.6 units of groups $=O_2BOH$ on a surface area of 10 nm^2. An increase in the number of acid centers on the surface of the investigated adsorbent can be ensured by preventing the formation of titanium-borate molecules with a bidentate structure during synthesis.

2.5. Mechanism of Sr (II) cations bonding

For adsorption of one Sr(II) cation, one or two adsorption centers may be involved in electrolyte environments with $pH > pH_{pzc}$ (16):

$$2{\equiv}TiO^- + Sr^{2+} \leftrightarrow ({\equiv}TiO^-)_2\, Sr^{2+} \qquad (16)$$

$$\equiv TiO^- + H_2O + Sr^{2+} \leftrightarrow \equiv TiO^-\,(SrOH)^+ + H^+ \qquad (17)$$

Adsorption of cations according to the scheme (16) is observed in an acidic and slightly acidic electrolyte medium (pH = 2 ÷ 6). The connection of cations is carried out according to the scheme (17) in a neutral electrolyte medium (pH ~ 7) [6-8, 13, 21].

The presence of OH^- anions ensures the high efficiency of binding of Sr(II) cations in an alkaline environment (pH ~ 8-12):

$$\equiv TiO^- + Sr^+ + OH^- \leftrightarrow \equiv TiO^-\,(SrOH)^+ \qquad (18)$$

Graphical dependences of adsorption of cations Sr(II) from the pH of the medium by investigated samples of TiO_2 are shown in Fig. 8. Fig.8 shows, that there is a tendency of differences in Sr (II) adsorption. In an alkaline environment with a pH of ~ 10-11 adsorption of cations Sr (II) increases, compared with adsorption in a slightly acidic environment, by 1.5-2.0 times.

Adsorption of cations should not be carried out in an environment with $pH < pH_{pzc}$. However, the adsorption value of the Sr(II) cations is 85 $mg{\cdot}g^{-1}$ by the 0.5B-TiO_2, and is equal to the value of adsorption in an environment with a pH of ~ 6.0 is close to corresponding values which are obtained at a pH of ~ 2.0.

This anomaly can be explained by the fact that the adsorption of anions recharges the surface of the adsorbent. The negative charge of anions is not compensated by a completely positive charge of adsorption centers. Therefore, favorable conditions are created for the adsorption of Sr(II) cations. The binding of Sr(II) cations in an acidic environment from $SrCl_2$ solution occurs according to the scheme (19):

$$2{\equiv}TiOH_2^- + 2Cl^- + Sr^{2+} \leftrightarrow 2{\equiv}Ti^+\, 2Cl^-\, Sr^{2+} + H_2O \qquad (19)$$

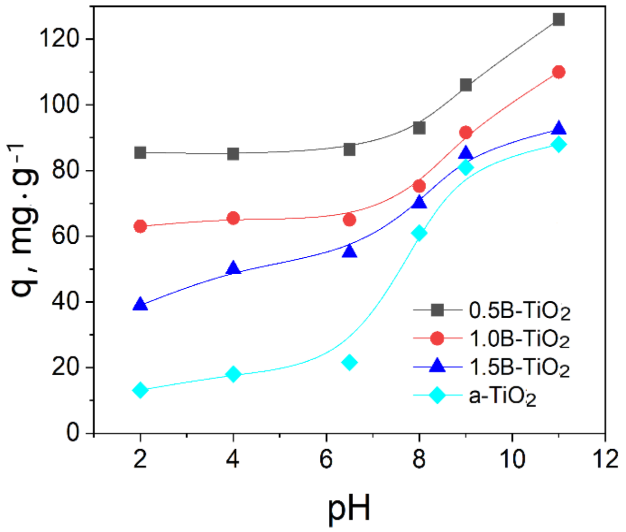


Fig. 8. Adsorption of Sr (II) cations by TiO_2 samples in the medium with different pH.

2.6. Regeneration of the adsorbents

The possibility of the adsorbent regeneration was performed according to the scheme of adsorption-desorption of Sr (II) cations- drying the adsorbent and repeated adsorption. Adsorption of cations was performed from a 0.01M solution of strontium chloride at pH = 8. Removal of adsorbed strontium cations was performed using 0.01M HNO_3 as eluent. Regenerated adsorbents were washed with distilled water, dried, weighed, and again used for adsorption of Sr(II) cations under the same conditions. The value of adsorption of Sr (II) cations remained unchanged, during the seven adsorption-desorption cycles.

In addition, the adsorption value after regeneration was 39.8÷7.2 $mg{\cdot}g^{-1}$ for adsorbent 0.5B-TiO_2 at a confidence level of 95%. The test results indicate the suitability of Boron-dopped titanium dioxide in the acid medium and its ability for regeneration [26].

Conclusions

Synthesis of Boron-containing TiO_2 by liquid-phase sol-gel method using aqua complex precursor $[Ti(OH_2)_6]^{3+}\cdot 3Cl^-$ and borate acid H_3BO_3, as a modifying reagent, according to the corresponding ratio of components, leads to the formation of a single-phase rutile titanium dioxide or a two-phase anatase-rutile oxide material.

In the rutile sample 0.5B-TiO_2, Boron atoms are combined with Oxygen atoms into the triangular structural cell of BO_3 and are localized in the surface layer of the nanoparticle material as a grouping $=O_2BOH$.

The impregnation of Boron atoms into the structure of the rutile adsorbent causes an increase in its adsorption capacity toward Sr(II) cations. The maximal adsorption of Sr(II) cations by the rutile adsorbent reaches 102.3 $mg{\cdot}g^{-1}$, compared to the bare a-TiO_2 – 68.8 $mg{\cdot}g^{-1}$ in a neutral electrolyte environment.

In particular, the number of acid adsorption centers $\equiv TiOH^{\delta+}$ on the surface of the rutile adsorbent 0.5B-TiO_2 is ~ 50 units on a surface area of 10 nm^2, which is twice higher than the number of centers on the surface of the base anatase adsorbent a-TiO_2.

The ionic strength of the acid centers of the $\equiv TiOH^{\delta+}$ $pK_{\alpha 1}$ and the main centers of the $\equiv TiOH^{\delta-}$ - $pK_{\alpha 2}$ of the rutile sample is the highest in comparison with the centers of other investigated adsorbents and, accordingly, is equal to 0.6 and 12.3.

Two-phase adsorbents 1.0B-TiO_2 and 1.5B-TiO_2 contain, respectively, 70 and 57% of the anatase phase. They are significantly inferior in adsorption ability toward cations Sr(II) compared with the rutile adsorbent 0.5B-TiO_2. This is because Boron atoms are localized mainly in the anatase phase and form tetrahedral groups of BO_4^- with oxygen atoms.

Tetrahedral coordination of Boron atoms concerning Oxygen atoms in the structure of anatase reduces the induction effect of B atoms on the redistribution of electron density in B-O-Ti bridges and does not lead to the formation of additional acid adsorption centers on the surface of the anatase.

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Адсорбція катіонів Sr(II) діоксидом титану, допованим атомами Бору

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Досліджувалась адсорбція катіонів Sr(II) борвмісними зразками TiO_2, одержаними рідкофазним золь-гель методом з використанням аквакомплексного прекурсора $[Ti(OH_2)_6]^{3+}\,3Cl^-$ і модифікуючого реагента боратної кислоти H_3BO_3. З'ясовано, що за відповідних співвідношень компонентів утворюється однофазний рутильний діоксид титану або двохфазний анатаз-рутильний оксидний матеріал. В рутильному дослідному зразку 0.5B-TiO_2 атоми Бору поєднуються з атомами Оксигену в трикутні структурні мотиви BO_3 і локалізуються у поверхневому шарі наночастинкового матеріалу як групування = O_2BOH. Інкорпорація атомів Бору у структуру рутильного адсорбенту спричинює зростання його адсорбційної спроможності щодо зв'язування катіонів Sr(II) у водному електролітному середовищі. Максимальна адсорбція катіонів Sr(II) в нейтральному електролітному середовищі рутильного адсорбента сягає 102.3 мг·г$^{-1}$, у той час, як для немодифікованого анатазного адсорбента a-TiO_2 вона рівна 68.8 мг·г$^{-1}$.

Чисельність кислотних адсорбційних центрів $\equiv TiOH^{\delta+}$ на поверхні рутильного адсорбента 0.5B-TiO_2 становить ~ 50 одиниць на ділянці поверхні площею 10 нм^2, що в два рази перевищує чисельність центрів на поверхні базового анатазного адсорбента a-TiO_2. Йонна сила кислотних центрів $\equiv TiOH^{\delta+}$ $pK_{\alpha 1}$ та основних центрів $\equiv TiOH^{\delta-}$ $pK_{\alpha 2}$ рутильного зразка є найбільшою в порівнянні з центрами інших досліджуваних адсорбентів і, відповідно, рівна 0.6 та 12.3.

Анатаз-рутильні адсорбенти 1.0B-TiO_2 та 1.5B-TiO_2 містять відповідно 70 та 57 мас.% анатазної фази. Вони суттєво поступаються за адсорбційною спроможністю зв'язувати катіони Sr(II) рутильному адсорбенту 0.5B-TiO_2. Це зумовлено тим, що атоми Бору в основному локалізуються в анатазній фазі і з атомами Оксигену утворюють тетраедричні групування BO_4^-. Тетраедрична координація атомів Бору по відношенню до атомів Оксигену в структурі анатазу знижує індукційний вплив атомів Бору на перерозподіл електронної густини в містках B-O-Ti і не приводить до утворення додаткових кислотних адсорбційних центрів на поверхні анатазу.

Ключові слова: Діоксид титану, Бор, Адсорбція, Стронцій.