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Removal of Cr (III) and Cr (VI) ions by adsorbent based on Titanium Dioxide

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In this paper, the adsorption of trivalent chromium cations by a sample of sodium-modified TiO_2 was studied. XRF analysis of the TiO_2 surface was performed. The dependence of the adsorption value on the duration of the interaction in the system of the adsorbent–solution of chromium compound was investigated. The influence of the acidity of the solution and the equilibrium concentration of chromium ions on the adsorption value was also determined. It is shown that the adsorption kinetics of trivalent chromium ions is best described by the pseudo-second-order equation and the diffusion kinetic model. Freundlich's adsorption theory best describes equilibrium adsorption. Mass spectrometry proved the enhanced adsorption of trivalent chromium ions from a mixture with hexavalent chromium. This statement was evidenced by Raman spectroscopy of the surface of Na-TiO_2. The maximum adsorption of Cr (III) ions is 62 mg/g. Separation factor of trivalent chromium and hexavalent chromium is $SF_{Cr^{3+}/Cr^{6+}} = 7.279$.

Keywords: chromium (III), chromium (VI), Raman spectroscopy, XRF-analysis, adsorption.

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Introduction

Chromium is a very interesting element. It has several stable isotopes ^{50}Cr, ^{52}Cr, ^{53}Cr, and ^{54}Cr. Chromium can be found in oxidation states from 0 to +6, although its most common oxidation states are +3 and +6. Also, this element can be in an aqueous solution as a cation (in acid solutions) or be in an anionic state (in neutral or basic pH). Finally, trivalent chromium is an essential trace element for the proper functioning of the animal and human body, while hexavalent chromium is ranked among the top sixteen toxic pollutants that have very harmful consequences on human health and aquatic life. Cr(VI) contamination of soil and aquatic systems is a significant problem worldwide [1]. Trivalent chromium is of great importance for science and technology development. For example, according to the authors [2], Cr^{3+} is necessary for the production of optically active crystals. Oxides of chromium, are widely used as coating materials in magnetic recording devices. It was found that the properties of these devices depend strongly on the stoichiometry of the chromium oxides [3]. This element is an important anti-corrosion additive to alloys and, as we have already noted, Cr^{3+} is an important trace element in our body. However, the literature pays much more attention to the adsorption of hexavalent chromium, due to its high toxicity. Many works are devoted to methods of purification of aqueous solutions from hexavalent chromium ions. For example, for up-take hexavalent chromium from aqueous solutions, different authors proposed to use chemically modified chitosan [4] or Chitosan-SiO_2-TiO_2 nanocomposite [5], carbon nanotubes, inorganic layered double hydroxides [6], amorphous and mesoporous silica nanoparticles [7], zeolites, adsorbents based on activated carbon, oxidized graphene [8] and titanium dioxide [9] etc. Several scientific papers are devoted to the removal of hexavalent chromium by reducing it to a trivalent state using inorganic adsorbents or biomaterials [10, 11]. Also, the authors of the work [12] propose to remove hexavalent chromium by chemical precipitation, as the authors note, by the method of "selective crystallization", in the form of insoluble compounds. Much less work is devoted to the adsorption of trivalent chromium. A particularly interesting scientific task, in our opinion, is the separation of ions of trivalent chromium and hexavalent chromium from aqueous solutions.

During the investigation of the possibility of separating ions of trivalent chromium and hexavalent chromium, it is advisable to determine the residual amount of chromium by mass spectrometry, which makes it possible to study a large number of atoms, ions, or fragments of molecules at the same time in one experiment.

For this work, we have chosen the method of mass spectrometry with ionization of the analyte by electron shock with an electron energy of 70 eV. Although this method of mass spectrometry is not the most modern, it allows us to determine the chemical forms of elements in mixtures by ionized fragments of their molecules.

Many modern scientific works are devoted to the use of chromatographic or adsorption separation of ions or fragments of analyte molecules along with mass spectrometry [13]. Therefore, in the study of the selective adsorption of Cr^{3+} ions, the inverse problem can be solved, namely, the possibility of using selective adsorption of cations from a mixture to simplify its mass-spectrometric analysis.

As an adsorbent, we chose sodium-modified titanium dioxide (Na-TiO_2). It is a well-known adsorbent [14, 15], which has a high adsorption capacity toward metal cations, such as Sr^{2+}, Ba^{2+}, Zn^{2+}, and Y^{3+}. Na-TiO_2 is chemically and radiation-resistant. The advantage of this material is also good reproducibility of results and an established adsorption mechanism that allows predicting its behavior.

The purpose of our work is to investigate the adsorption of Cr^{3+} and hexavalent chromium (Cr^{6+}) by the adsorbent Na-TiO_2 and to establish the possibility of selective adsorption of Cr^{3+} cations from a mixture with (Cr^{6+}) ions.

I. Experimental techniques

1.1. Materials and methods.

$CrCl_3 \cdot 6H_2O$ (dark green crystals hexahydrate), and K_2CrO_4, $AgNO_3$, $BaCl_2$, Na-ed, H_2SO_4, diphenylcarbazide (DPC), $NiSO_4$ and indicator reagent Murexide ($NH_4C_8H_4N_5O_6$, or $C_8H_5N_5O_6 \cdot NH_3$), also called ammonium purpurate or MX were analytical grade and were used without further purification. Sodium-modified titanium dioxide was chosen as an adsorbent. The main textural characteristics of this adsorbent are presented in Table 1.

In the vicinity of the centers of ≡TiOHa, = Ti $(OHa)_2$, both basic (≡$TiOH^{\delta-}$) and acid (≡$TiOH^{\delta+}$) Brønsted centers are additionally formed on the surface of the Na-TiO_2. Therefore, the surface of the sodium-modified TiO_2, along with high adsorption of cations, is capable of adsorption of a small number of anions.

1.2. Adsorption studies

Adsorption studies were performed under batch conditions. To assess the adsorption capacity of sodium-modified TiO_2 toward trivalent chromium cations and hexavalent chromium anoins, individual solutions of $CrCl_3 \cdot 6H_2O$ and K_2CrO_4 salts were used, respectively.

The weight of the adsorbent was 50 mg, the volume of the corresponding salt solution was 5 ml. The duration of the interaction, the equilibrium concentration of the adsorbate, and the acidity of the solution were varied. Initial and equilibrium concentrations of metal cations or anions were measured. The adsorption value was calculated using the formula (1).

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

were 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.

1.3. Methods of determining the initial and residual concentration of Cr (III) and Cr (VI) in the water solutions of $CrCl_3$ and K_2CrO_4 respectively.

1.3.1. Method of determining the initial and residual concentration of Cr (III).

Complexonometry is a titrimetric method of analysis based on reactions of the formation of soluble, very strong complexes of polydentate ligands-complexes with cations of alkaline earth and heavy metals [16]. Complexometry can determine both complex ions and ligand ions or molecules. To determine the initial and residual amount of trivalent chromium ions in solution, the method of reverse complexometry was used.

An excess of 0.05M sodium edetate was added to the chromium solution and boiled for 15 minutes. In this case, the solution turns purple, which is due to the formation of chromium complexonate. Then 10 mL of ammonium buffer mixture is injected and the excess sodium edeteate is titrated with 0.05M $NiSO_4$ with the indicator murexide until a yellow color appears. At the same time, 1 ml of 0.05M sodium edeteate corresponds to 0.0026 g of chromium.

1.3.2. Spectrophotometric determination of hexavalent chromium in water using 1.5-diphenylcarbazide.

According to the method [9] 1.5 - diphenylcarbazide must be dissolved in acetone, a small amount of sulfuric acid and a spectrophotometer are also required for determination. The concentration of chromate anions in the supernatant was determined spectrophotometrically (540 nm, 5 cm, ULAB 102-UV) after a reaction with 1.5-diphenylcarbazide in an acidic solution [9].

Table 1.

Textural characteristics of sodium-modified titanium dioxide, according to [14, 15]

Sample	S_{BET} m^2/g	S micro, m^2/g	S meso, m^2/g	S meso/ S_{BET}, %	V, cm^3/g	V_{micro}, cm^3/g	V_{meso}, cm^3/g	V_{meso}/ V
Na-TiO_2	239	100	139	58	0.152	0.054	0.098	64

1.3.3. Precipitation of hexavalent chromium with barium chloride.

The precipitation of the strongly colored silver chromate indicates the endpoint in the titration of chloride with silver nitrate in the Mohr method [14]. Considering the Mohr method, the amount of chromate anions can be determined using a titration of freshly formed silver chromate by $BaCl_2$. The reactivity of the chromate anion with silver is lower than with halides.

$$AgNO_{3(aq)} + Cl^{-}_{(aq)} + CrO^{2-}_{4(aq)} \rightarrow AgCl_{(s)} + CrO^{2-}_{4(aq)} + NO^{-}_{3(aq)} \quad (2)$$

Silver chromate forms and precipitates only when all chloride (or halogen) is left. At the same time, the Barium chromate precipitation is strongly insoluble in water.

$$Ba^{2+} + 2Cl^{-} + Ag_2CrO_4 \rightarrow BaCrO_4\,(s) + 2AgCl\,(s) \quad (3)$$

In this case, the endpoint will be indicated by the disappearance of the bright red-brown precipitate of silver chromate. This reaction was used to perform a large number of routine studies. However, we also used spectrophotometry to investigate the residual concentration of chromate anion in solution.

1.4. XRF –analysis.

X-ray fluorescence (XRF) analysis of samples before and after adsorption was performed using a fluorescence X-beam analyzer (Bruker AXS, Karlsruhe, Germany). The content of chromium cations adsorbed by the surface of Na-TiO_2 was determined by a peak of 5.415 keV (Cr) [13]. To perform an effective X-fluorescence analysis of the surface of the studied adsorbents, the adsorbent was washed with distilled water after the adsorption process and dried to an air-dry state.

1.5. Measurement of trivalent chromium ions using mass-spectrometry.

The possibility of selective adsorption of trivalent chromium cations in the simultaneous presence of hexavalent chromium anions was investigated from a freshly prepared model solution of a mixture of $CrCl_3 \cdot 6H_2O$ and K_2CrO_4, (ratio 1:10) with a concentration of 0.001M.

The experimental setup and methodology are described in detail in [17-19]. An MX-7304A monopole mass spectrometer, which belongs to the class of dynamic mass analyzers, was used as an analytical instrument.

The range of recorded masses was 0 - 140 Da with a resolution not worse than $\Delta M = 1$ Da. Electron sources for mass spectrum measurement operated in the mode of fixed electron energy in the range of 10 - 70 eV and stabilization of electron current in the range of 0.05 - 0.5 mA. The ions were formed as a result of the interaction of molecules with electrons and were separated by mass and recorded by an automated system with a digital indication of mass number and intensity. The concentration of molecules in the zone of interaction with the electron beam was in the range of 5×10^{10} - 10^{11} cm^{-3}.

The mass spectra at the energy of ionizing electrons of 70 eV were measured carefully, repeatedly, and the formula determined the time for measuring the set of masses:

$$T_{full} = t_1 \cdot n \cdot C, \quad (4)$$

where t_1 - is the measurement time of one fragment, n - is the number of fragments and C - is the number of cycles, which was determined depending on the value of the useful signal.

Data registration and processing were carried out automatically. Particular attention was paid to the mass scale, for this purpose the control mass spectra of inert gases of argon, krypton, and xenon were measured, according to the main and isotopic peaks of which calibration was carried out. This mass spectrometry device is capable of analyzing only ions that are positively charged.

1.6. Analysis of experimental adsorption data using kinetic models and adsorption theories.

The analysis of experimental data on adsorption kinetics was carried out using kinetic models: Lagergren models based on pseudo-first- and pseudo-second-order equations; Elovitch chemisorption and Weber-Morris intraparticle diffusion models [20, 21].

The application of these models to the results of the adsorption of trivalent chromium ions was aimed at determining the main regularities of the direction of this process. For example, when applying the Elovitch model to the experimental results of adsorption kinetics, the experimental dependence is represented in the form of a plot of the dependence of the adsorption value q_t on the logarithm of the duration of the interaction (ln t). The plot of the dependence of q_t on ln t should be a straight line, the slope of which is equal to $(1/\beta)$ and the intercept with the OY axis is equal to $(1/\beta)\ln(\alpha \cdot \beta)$, from where the initial adsorption rate and the desorption constant of a certain adsorbate can be found.

These models are more or less flexible mathematical formulas that can adequately simulate the characteristic behavior of the physical kinetics of processes of various kinds that occur during adsorption (surface chemical reaction, intra-particle diffusion, formation of surface hydrogen bonds, ion exchange, etc.).

In previous works, it was determined that the adsorption of metal cations by the adsorbent Na-TiO_2 is

Table 2.

Kinetic models are used in this paper for the analysis of experimental data

Kinetic models	Linear equation	Model's plot
Elovich	$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t$ (5)	$q_t \; f(\ln t)$
Intra- particle diffusion	$q_t = D_{ipd}\, t^{1/2} + C$ (6)	$q_t \; f(t^{1/2})$
Pseudo-first-order equation	$\ln(q_e - q_t) = \ln q_t - k1t$ (7)	$\ln(q_e - q_t) \; f(t)$
Pseudo-second-order equation	$t/q_t = [1/k2q_e^2] + t/q_e$ (8)	$t/q_t \; f(t)$

localized on the adsorption sites. For example, the adsorption of Y^{3+} cations is unsatisfactorily described by the Dubinin-Radushkevich theory of non-localized adsorption [15]. At the same time, the theories of Langmuir and Frendlich give a good result of application to the experimental results of the adsorption o0f heavy metal cations by Na-TiO_2. The basic equation of Langmuir's theory is given below:

$$q_e = \frac{q_\infty K C_e}{1+KC_e}, \qquad (9)$$

q_∞ is the maximal adsorption, which corresponds to the filling of all adsorption centers, mg/g; K_L – Langmuir's constant, L/mg; C_e - is the equilibrium concentration of adsorbate in solution, mg/L.

The equation of the Freundlich (Herbert Max Finlay Freundlich) is an empirical relationship between the amount of adsorbed substance (q_e) and its equilibrium concentration in solution (C_e) at a constant temperature.

The equation is true at low concentrations of C_e during adsorption on a heterogeneous surface.

$$q_e = K_f C_e^n, \qquad (10)$$

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

In this work, Temkin's theory was also applied along with the theories of Langmuir and Freundlich [22]. Temkin's theory is also a theory of localized adsorption, but unlike Langmuir's theory, it takes into account the interaction of adsorbate molecules with each other. Temkin's theory also makes it possible to calculate the heat of adsorption.

The equations of this theory (11) or (12) are given below.

$$q_e = \frac{RT}{b_T} \ln\left(K_t C_e\right). \qquad (11)$$

Another representation of the equation is as follows:

$$q_e = BlnAC_e \qquad (12)$$

where is b_T –Temkin constant (J·mol^{-1}) which is related to the heat of sorption, and K_t – is Temkin isotherm constant.

The analysis of the experimental adsorption isotherm using the described theories was carried out by the method of nonlinear approximation using the Solver add-in of Microsoft Excel. Parameters of the corresponding theories (for example, the Langmuir constant and the value of the maximum adsorption when using the Langmuir theory) were chosen as the parameters that need to be optimized in nonlinear approximation. The correlation coefficient and Pearson's parameter were calculated using formulas (13) and (14):

$$R^2 = 1 - \frac{\sum(q_{e,exp},-q_{e,calc})^2}{\sum(q_{e,exp}-q_{e,mean})^2}, \qquad (13)$$

$$\chi^2 = \sum \frac{(q_{e,exp}-q_{e,calc})^2}{q_{e,calc}}. \qquad (14)$$

1.7. Raman spectrometry of the Na-TiO_2 before and after adsorption.

Raman spectroscopy of adsorbent samples was performed using XploRA PLUS equipment with a direct Optical microscope. The wavelengths of excitation lasers were 532 nm. Raman spectrometer was loaded at the Center for Collective Use of Scientific Equipment “Laboratory of Experimental and Applied Physics” of Uzhhorod National University.

II. Results and discussion

2.1. XRF-analysis of Na-TiO_2 surface.

As it was discovered, the adsorbent Na-TiO_2 absorbs trivalent chromium ions from an aqueous solution more intensively than hexavalent chromium ions. Intensive adsorption of Cr^{3+} ions was proved by determining the residual concentration of the corresponding ions in solution after the adsorption process, as well as by XRF analysis of the Na-TiO_2 surface. The results of XRF analysis of the adsorbent surface before and after adsorption are shown in Figures 1(a, b) and in Tables 3 and 4.

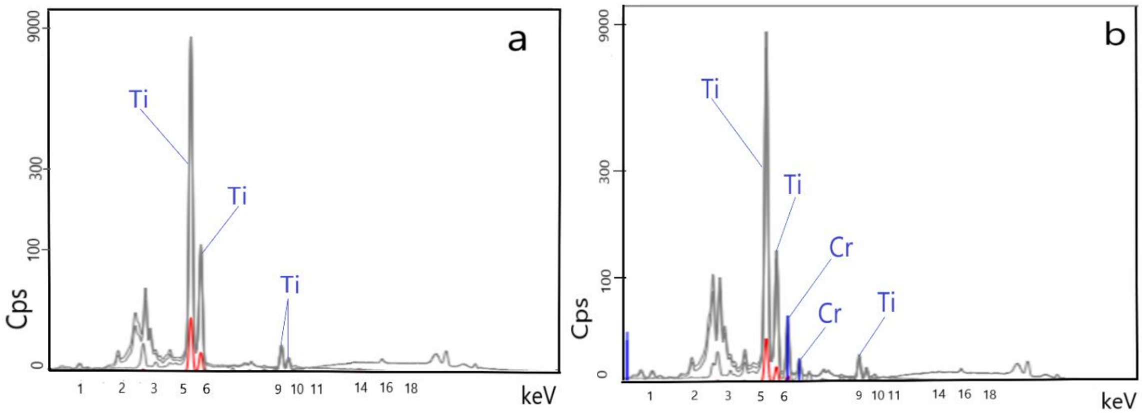


Fig. 1. XRF spectra of pure Na-TiO_2 (a) and Na-TiO_2 with adsorbed Cr (III) on its surface.

Table 3.

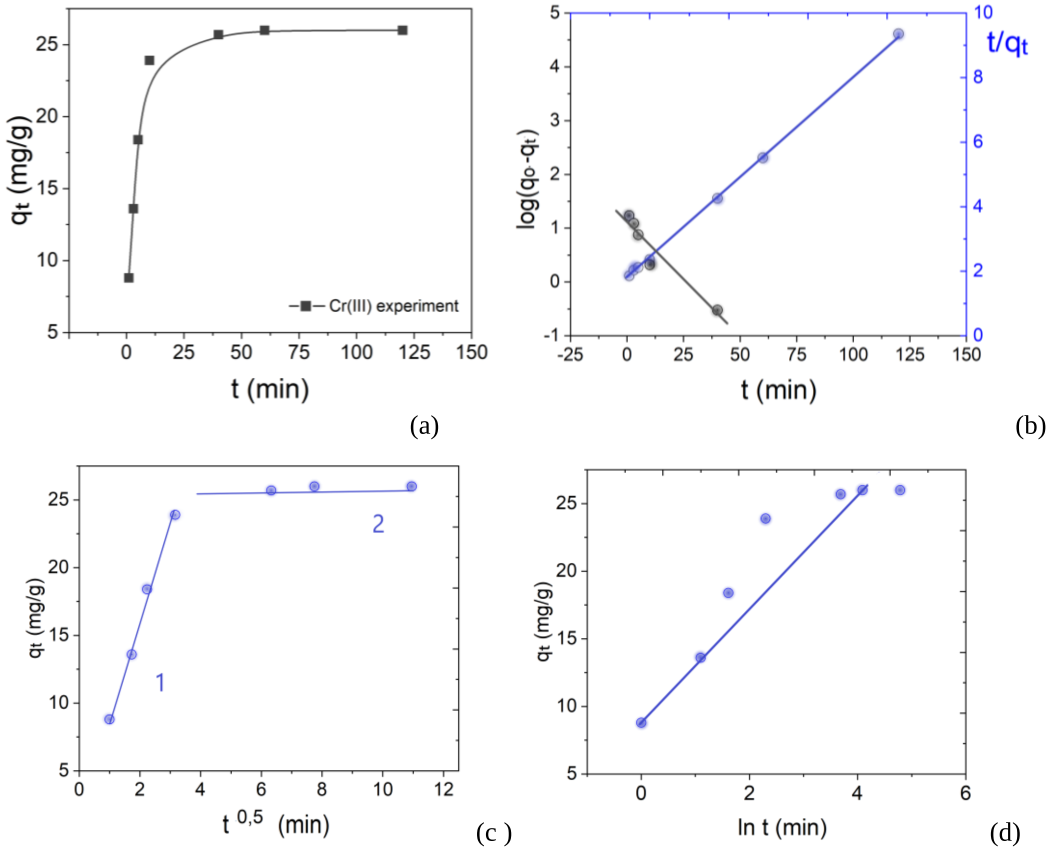
XRF-analysis of Na-TiO$_2$ surface

Formula	Z	Concentration	Line 1	Line energy
TiO$_2$	22	76.7	Ti KA1/EQ20	4.511
Na$_2$O	11	20.4	Na KA1/EQ20	1.041
Cl	17	1.62	Cl KA1/EQ20	2.6225
P$_2$O$_5$	15	0.873	P KA1/EQ20	2.0137
CaO	20	0.854	Ca KA1/EQ20	3.6918
SO$_3$	16	0.703	S KA1/EQ20	2.3079
K$_2$O	19	0,514	K KA1/EQ20	3,3139

Table 4.

XRF-analysis of Na-TiO$_2$ surface after Cr (III) adsorption

Formula	Z	Concentration	Line 1	Line energy
TiO$_2$	22	74.7	Ti KA1/EQ20	4.511
Na$_2$O	11	19.2	Na KA1/EQ20	1.041
Cr$_2$O$_3$	**24**	**2.55**	Cr KA1/EQ20	5.4149
Cl	17	1.62	Cl KA1/EQ20	2.6225
SiO$_2$	14	1.15	Si KA1/EQ20	1.74
Al$_2$O$_3$	13	0.875	Al KA1/EQ20	1.4868
P$_2$O$_5$	15	0.873	P KA1/EQ20	2.0137
CaO	20	0.854	Ca KA1/EQ20	3.6918
SO$_3$	16	0.703	S KA1/EQ20	2.3079
K$_2$O	19	0.514	K KA1/EQ20	3.3139
Fe$_2$O$_3$	26	0.157	Fe KA1/EQ20	6.4041



(a) (b)

(c) (d)

Fig. 2. Kinetics of adsorption of Cr^{3+} cations from aqueous solution by Na-TiO$_2$ adsorbent (a) experimental dependence of the value of adsorption of chromium cations on the duration of interaction; (b) application of pseudo-first-order and pseudo-second-order kinetic models to experimentally measured adsorption values; (c) application of the Weber-Morris kinetic model of intra-particle diffusion; (d) application of the Elovitch kinetic model of chemisorption to the experimental results of adsorption of Cr^{3+} cations.

Table 5.

Analysis of experimental adsorption kinetics using kinetic models

Kinetic models	Parameters	R^2
Elovich	$\alpha = 1.17$; $\beta = 0.3942$	0.9020
Pseudo-first	-0.0297	0.9269
Pseudo-second	0.079	0.9994
Intra-particle diffusion Step1	$D_{ipd} = 4.52$; $C = (-3.9)$	0.9774
Step 2	$D_{ipd} = 0.064$; $C = 11.49$	0.9992

2.2. Adsorption kinetics.

The kinetic dependencies of the adsorption of trivalent chromium cations by the adsorbent Na-TiO_2 are shown in Figures 2 (a-d).

As shown in Figures 2 (a-d) and Table 5. The process of adsorption of trivalent chromium ions Na-TiO_2 is best described by the pseudo-second-order model, as well as the Weber-Morris diffusion model.

It can be assumed that adsorption occurs mainly by a physical mechanism [20, 21]. Constant D_{ipd} (mg/g·min$^{1/2}$) is the rate constant of the intra-particle diffusion model and C (mg/g) is a constant associated with the thickness of the boundary layer, where a higher value of C corresponds to a greater effect on the limiting boundary layer.

As can be seen from Table 5, the diffusion constant is quite high in the first stage of adsorption. The double electric layer of the surface of Na-TiO_2 does not limit adsorption in any way ($C < 0$). In the second stage of diffusion, the value of the diffusion constant decreases, and the double surface layer begins to play a significant role in the process. At the same time, the coefficient of linear approximation is extremely close to 1 (0.9992).

The application of the kinetic model of Elovitch makes it possible to estimate the initial adsorption rate $\alpha = 1.17$ and the desorption constant, which is equal to $\beta = 0.3942$ for this experiment (Table 5).

2.3. Adsorption isotherms and pH dependence of Cr^{3+} adsorption by Na-TiO_2.

Equilibrium adsorption of Cr^{3+} cations was studied under batch conditions with an interaction duration of at least 1 hour. The experimental adsorption isotherm is shown in Figure 3.

The figure also shows the curves of the nonlinear approximation of experimental adsorption results by the theories of Langmuir, Frendlich, and Temkin. The parameters of the corresponding theories are given in Table 6.

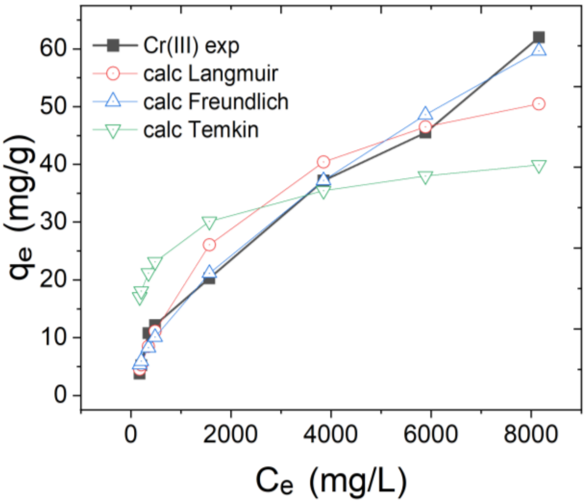


Fig. 3. Isotherm of adsorption of Cr^{3+} cations by Na-TiO_2 adsorbent.

As for the previous results of adsorption of metal cations by this adsorbent [14, 15], Freundlich's theory better describes the experimental results of adsorption. The highest value of R^2 (0.9906) and the lowest value of the Pearson parameter χ^2 (2.095) can be as evidence. These results indicate that the surface of this TiO_2 is not homogeneous according to Langmuir's terminology, that is, on the surface of Na-TiO_2, along with the ≡Ti-OH groups, there are groups ≡TiONa and =Ti(ONa)$_2$, which are also involved in adsorption. Application of Temkin's adsorption theory to the experimental results of adsorption of chromium ions by Na-TiO_2 gives the lowest coefficient R^2 (0.6172) and the highest parameter χ^2 (46.69). It can be concluded that the interaction of adsorbate ions with each other does not occur.

The dependence of adsorption of Cr^{3+} cations on the acidity of the solution is shown in Figure 4. The adsorption of Cr^{3+} by Na-TiO_2 decreases across the

Table 6.

Parameters of Langmuir Freundlich and Temkin equations for adsorption of Cr^{3+} ions sodium-modified TiO_2

Adsorption Theory	Langmuir		Freundlich		Temkin	
Adsorption experiment	Parameter of the corresponding equation and calculated values					
Q_{max} experimental = 62 mg/g	K_L	0.00043	K_f	0.206	A	0.1
	q_∞	64.99	n	0.629	B	5.959
	Q_{max} calc	50.49	Q_{max} calc	59.66	Q_{max} calc	39.92
	R^2	0.9417	R^2	0.9906	R^2	0.6172
	χ^2	5.047	χ^2	2.095	χ^2	46.69

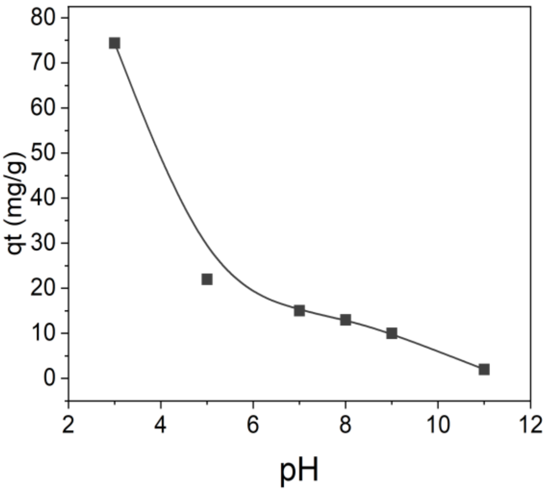


Fig. 4. pH – dependence of adsorption of chromium (III) cations from aqueous solution by Na-TiO_2.

changing from an acidic environment to a neutral one. In an alkaline environment, chromium can form insoluble hydroxide $Cr(OH)_3$, therefore adsorption values decrease to almost zero when the pH increases. A similar form of dependence of the adsorption value of trivalent chromium ions on pH is described, for example, in the literature [7].

According to the paper [23], the schematic state of chromium (III) ions in an aqueous solution depending on pH is represented by transformations (15):

$$Cr^{3+}(H_2O)_6 \leftrightarrow Cr(OH)\,(H_2O)_5{}^{2} \leftrightarrow Cr(OH)_2(H_2O)_4 \qquad (15)$$

Low pH Hydrolysis High pH

2.4. Adsorption of hexavalent chromium from aqueous solution of potassium chromate.

Anhydrous chromium (III) chloride adopts the YCl_3 structure [24], with Cr^{3+} occupying one-third of the octahedral interstices in alternating layers of a pseudo-cubic close-packed lattice of Cl^- ions. Therefore, the high adsorption of trivalent chromium cations by this adsorbent was predictable.

The adsorbent Na-TiO_2 also contains adsorption centers on its surface capable of absorbing anions. However, the adsorption of anions by this adsorbent is not as intense as the adsorption of trivalent chromium cations. The data presented in the literature confirms our results [9]. The reasons may be as follows: firstly, a low number of surface adsorption centers capable of exchanging the OH^- group for an anion, and secondly, a large size of the chromate anion, which may affected. The structure 3D form of chromate anions is shown in Figure 5.

The results of studies of adsorption of chromate anions from aqueous solution of K_2CrO_4 by Na-TiO_2 are shown in Figure 6.

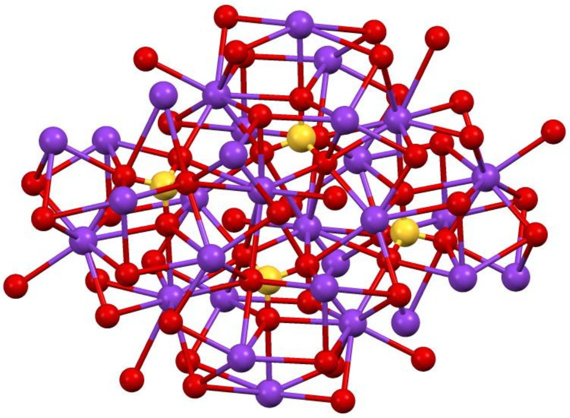


Fig. 5. The structure 3D form of chromate-anions adapted from the internet source [25].

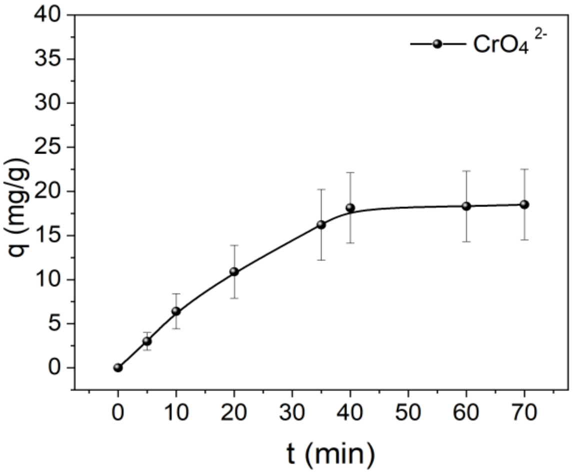


Fig. 6. Dependence of adsorption of hexavalent chromium ions (chromate anions) on the duration of interactions with Na-TiO_2 surface.

According to the work [14], the adsorption of cations and anions by this adsorbent occurs with the involvement of different adsorption centers, which means that it occurs independently. With an interaction duration of more than 40 minutes, the adsorption of chromate anions increases. This conclusion is made from a decrease in the concentration of chromate anions in the solution after adsorption. However, as some authors point out, hexavalent chromium is capable of reducing to a trivalent state on the surface of TiO_2. The amount of hexavalent chromium can be reduced not only as a result of adsorption but also due to other processes, such as photocatalytic reduction. Therefore, these results require more research.

2.5. Mas-spectrometry investigation of selective adsorption of Cr^{3+} by Na-TiO_2 from aqueous solution of $KCrO_4$ (pH = 4 - 6).

The mass spectra of $CrCl_3$ and K_2CrO_4 solutions as well as data on dependence of the chromium state on the solution's pH are shown in Table 7 and Fig. 7.

Figure 7 shows the mass spectra of $CrCl_3$ and K_2CrO_4 solutions (salt concentration ratio 1:10), i.e. an aliquot of 10 ml was taken from a freshly prepared mixture of 100 ml of 0.01M K_2CrO_4 and 100 ml of 0.001M $CrCl_3$ before and after adsorption in the mass range of 10 - 55 Da. A common characteristic of the presented mass spectra is the presence of peaks of different intensities. Thus, in the range of 10 - 35 Da, the most intense peaks correspond to m/z = 14, 16, 18, 28, 32, which can belong to ions and radicals: N·, O·, OH·, H_2O^+, N_2^+, O_2^+. The mass range of 39 - 41 corresponds to isotopes of potassium. This is logical since a solution of potassium chromate was studied. However, the ratio of peaks does not correspond

Table 7.

The dependence of the chromium isotopes state on the solution's pH, according to [26-28]

Main Cr species	Cr species (m- to z ratio)			
pH	1-3	3-6	6-9	9-11
^{50}Cr 4.34%	Cr^{3+} (16.67) Cr^{2+} (25)	$CrOH^{2+}$ (33.5)	CrO^{+} (66)	
^{52}Cr 83.8%	Cr^{3+} (17.33) Cr^{2+} (26)	Cr^{2+}. $CrOH^{2+}$ (34.5) $HCrO_4^-$	Cr^{2+}. $CrOH^{2+}$ $HCrO_4^-$ CrO_4^{2-}	CrO^{+} $HCrO_2$aq CrO_4^{2-}
^{53}Cr 9.5%	Cr^{3+} (17.66) Cr^{2+} (26.5)	$CrOH^{2+}$ (35)	CrO^{+} (69)	
^{54}Cr 2.37%	Cr^{3+} (18) Cr^{2+} (27)	$CrOH^{2+}$ (35.5)	CrO^{+} (70)	
^{39}K 93.3%	39			
^{40}K 0.012%	40	1.248 10^{9} y…β+. β-. e capture		
^{41}K 6,73%	41			

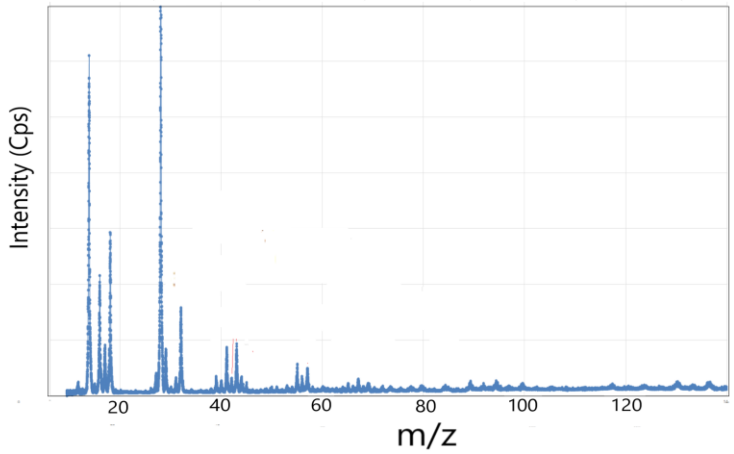


Fig.7. Initial mas-spectrum of water solution of mixture of chromium compounds $CrCl_3$ and K_2CrO_4.

to the natural ratio of potassium isotopes (Table 7). At the same time, the peaks are not intense enough for the cation, which is a macronutrient in the mixture. The reasons may be as follows: first, the potassium may not have completely dissociated in the solution. That is, there may be a $KCrO_4^-$ ion in the solution, which is difficult to analyze since this mass spectrometer captures only cations. The second reason may be the peculiarity of this mass spectrometer, the recording efficiency of which decreases with an increase in the atomic mass of the analyte. This can be seen in Fig. 7. Peaks that may belong to chromium isotopes are quite clearly distinguished: ^{50}Cr, ^{51}Cr, ^{52}Cr, ^{53}Cr, and ^{54}Cr, in the range of 50 - 55 Da (Fig. 8,(a) and (b)). However, we can only draw qualitative conclusions about these peaks.

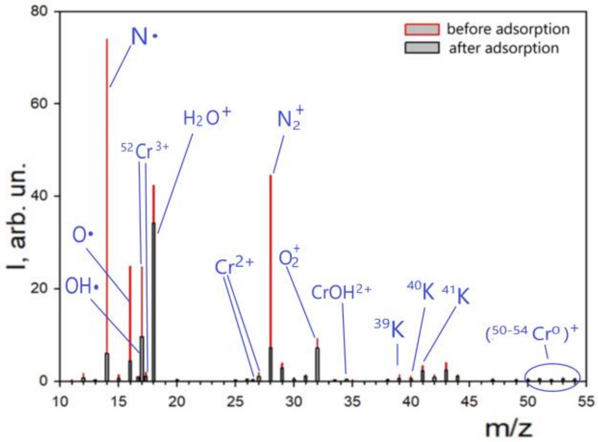
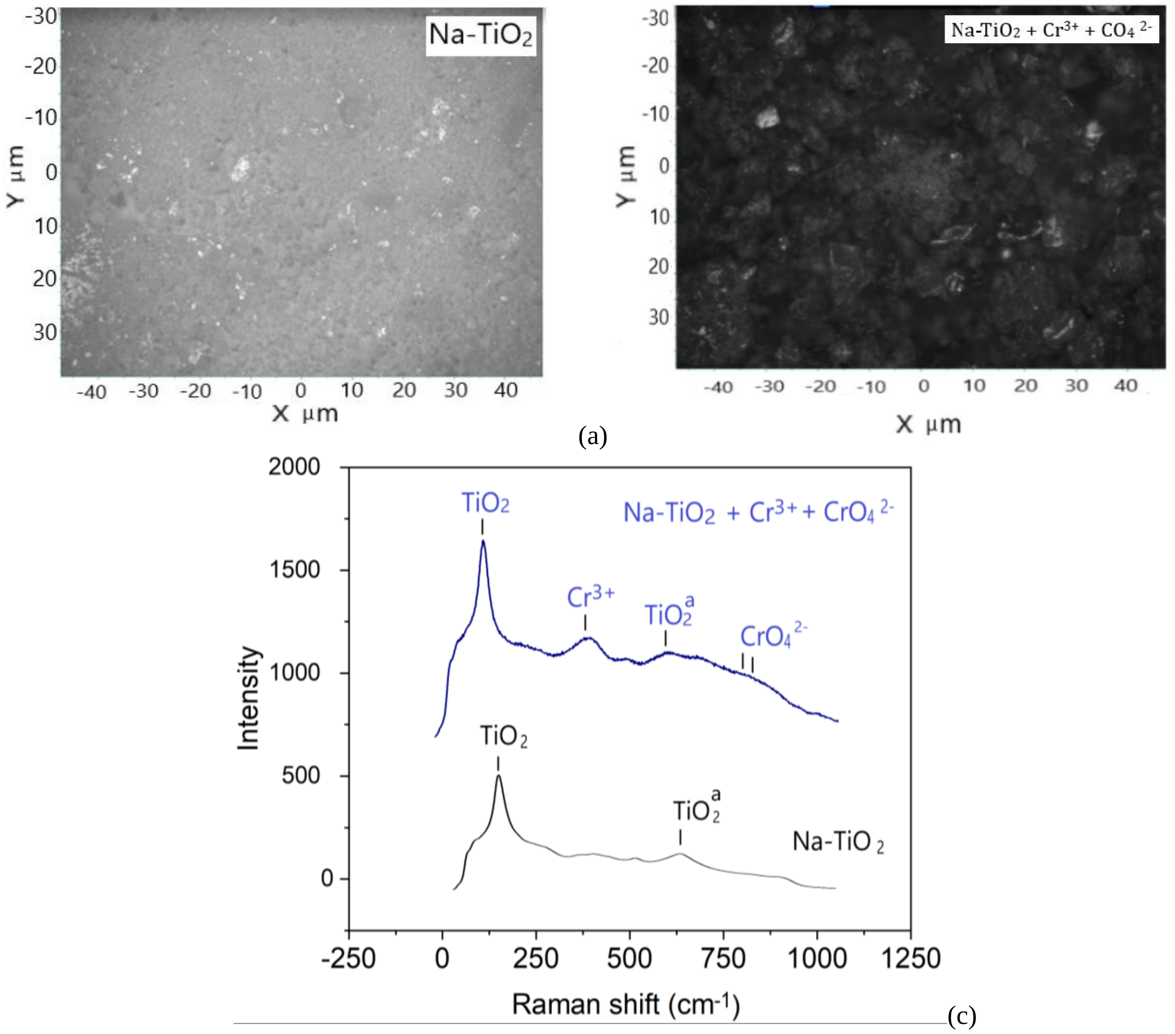


Fig. 8. Mass spectrum of aqueous solution of mixture $CrCl_3$ and K_2CrO_4 before and after adsorption.

Elements that are in the form of cations in solution, did not reduct to charge +1, during the ionization by electrons with an energy of 70 eV. Trivalent chromium remains in the charge power of +3 and is therefore defined in the vicinity of masses 16 - 17, but not 50 - 54. Therefore, a peak with a mass of 17 can refer to trivalent chromium cations as well as (theoretically) to a dissociated water molecule (OH·). The peak in the vicinity of masses 17 decreases greatly after adsorption, indicating the removal of trivalent chromium cations from the mixture with potassium chromate. The residual intensity is due to (OH·) - radicals that are formed during the ionization of water molecules. It is well-known that solvent molecules also ionize and fragment during mass



(a) (b) (c)

Fig 9. (a) Raman photo of initial Na-TiO_2; (b) Raman photo of Na-TiO_2 after interaction with mixture of $CrCl_3$ and K_2CrO_4 (30 min); (c) Raman spectra of initial Na-TiO_2 and Na-TiO_2 after adsorption of Cr^{3+} and little amount of Cr^{6+} from mixture of $CrCl_3$ and K_2CrO_4 (TiO_2^a – anatase modification of TiO_2) [29-31].

spectrometry and can be visualized on spectra. Divalent chromium peaks are not very intense but are observed on the spectrum. We can also notice a slight decrease in these peaks after adsorption. A peak with a mass of 28 may belong to nitrogen from the atmosphere or a nitrogen molecule formed by the ionization of nitric acid residues.

It can also be assumed that some N_2 molecules evaporate from the solution as a result of stirring during adsorption.

Raman images of the adsorbent before and after the adsorption of chromium ions from a mixture of $CrCl_3$ and K_2CrO_4 are shown in Figure 9 (a) and (b).

As can be seen from Figures 9 (a) and (b), the Na-TiO_2 changes its color after adsorption of trivalent chromium. This is due to the intense adsorption of Cr^{3+} cations. Changes in the Raman spectrum of Na-TiO_2 after adsorption in the vicinity of 750 - 900 cm^{-1} indicate the presence of a small amount of adsorbed CrO_4^{2-} anions [29-31].

A comparison of Na-TiO_2 with world analogs of adsorbents for Cr^{3+} and Cr^{6+} adsorption is given in Table 8.

This technique needs to be improved, but it can be concluded that the Na-TiO_2 adsorbent can selectively adsorb trivalent chromium ions from a mixture with hexavalent chromium ions from aqueous solutions. Separation factor (SF) was calculated by formula, according to [37] q_e Cr^{6+}=0.1638 mmol/g; q_e Cr^{3+} = 1.1923 mmol/g:

$$SF_{Cr^{3+}/Cr^{6+}} = \frac{q_{Cr3+}}{q_{Cr6+}} = \frac{1,1923}{0,1638} = 7.279.$$

Also, the studied material can effectively remove trivalent chromium ions and markedly reduce the presence of hexavalent chromium in aqueous solutions.

Conclusions

The adsorption of chromium from aqueous solutions of $CrCl_3$ and K_2CrO_4, as well as from their mixture, was studied. It is shown that the maximum adsorption of Cr^{3+} cations is 62 mg/g. The kinetics of adsorption of Cr^{3+} ions is best described by the diffusion model, as well as by the pseudo-second-order kinetic model.

Freundlich's theory best describes the equilibrium adsorption of chromium cations by the adsorbent Na-TiO_2.

Table 8.

Adsorption of chromium cations by various adsorbents according to the literature

Adsorbent	Adsorption value of Cr III mg/g	Adsorption value of Cr VI mg/g	Conditions	References
CsC@SiO_2@TiO_2		182.43	pH 3.0, contact time of 120 min, adsorbent dose of 50 mg, Cr (VI) concentration of 100 mg L^{-1}	[5]
grafting chitosan (CTS)		205	pH 4.0; the adsorption time was 80 min	[4]
NH_2-ASN		32.6	4 mL of 100mg/L Cr(VI) solution (pH = 2.0) + 8mg of NH_2–ASN, and NH_2–MSN. Adsorption duration~120min.	[7]
NH_2-MSN		39.8	4 mL of 100mg/L Cr(VI) solution (pH = 2.0) + 8mg of NH_2–ASN, and NH_2–MSN. Adsorption duration~120min.	[7]
Graphene Oxide – Calcium-Zinc Nanocomposite (GO@CZ)	285.7		pH=7, the pseudo-second-order kinetic model and Langmuir adsorption theory was best fitted to adsorption data	[8]
Coconut fiber	19.21	9.6		[23]
TiO_2		8.9	Mass of the adsorbent 25 mg and 50 ml of a solution of Cr VI and then shaken for 24 h at 25°C.	[9]
$CoFe_2O_4$@TiO_2		20.9	Mass of the adsorbent 25 mg and 50 ml of a solution of Cr VI and then shaken for 24 h at 25°C.	[9]
CdS quantum dots/nano-TiO_2 incorporated wood		482	Adsorption and photocatalytic reductions, (q_{max} calc by Langmuir theory)	[32]
Pine	12.4	1.23		[33]
Pine/TiO_2	2.83	27	Adsorbed Cr VI reduced to Cr III onto TiO_2	[33]
Fe-BDC		100	C_0 = 50 mg/L; contact time: 60 min; adsorbent dose: 50 mg; T = 25 ◦C; pH = 5.5	[34]
(Fe/Co)-BDC		588	C_0 = 50 mg/L; contact time: 60 min; adsorbent dose: 50 mg; T = 20 ◦C; pH = 5.3	[34]
3D porous $CoFe_2O_4$@SiO_2 -NH_2		126	C_0 = 150 mg/L; contact time: 600 min; adsorbent dose: 1 g/L; T = 25 ◦C; pH = 2.0	[35]
Fe_3O_4 -GO		280.6	C_0 = 600 mg/L; T = 25 ◦C; adsorbent dose: 125 mg/L; pH = 6.0	[36]
Amberlite IRA-458		52	Time 2 h., pH=2-7, Dose of adsorbent 0,2 g/L	[1]
Commercial activated carbon		28	Time 4 h., pH=1-6, Dose of adsorbent 0,1 g/L, T=22℃	[1]
Na-TiO_2	62	19	pH=6-7, T=20℃, t =40 min	Present work

The application of Temkin adsorption theory to the experimental results of adsorption of chromium ions by sodium-modified TiO_2 gives the lowest coefficient R^2 (0.6172) and the highest parameter χ^2 (46.69). It can be concluded that the interaction of adsorbate ions with each other during the adsorption process does not occur.

Also, the studied material can reduce the presence of hexavalent chromium in aqueous solutions, the mechanism of this process still needs to be explained. Mass spectrometry and Raman studies have shown that the Na-TiO_2 adsorbent can selectively adsorb trivalent chromium ions mixed with hexavalent chromium ions from aqueous solutions.

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Вилучення йонів Cr (III) та Cr (VI) адсорбентом на основі діоксиду титану

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У роботі проведено дослідження адсорбції катіонів тривалентного хрому зразком натрованого TiO_2. Проведено XRF-аналіз поверхні TiO_2. Досліджено залежність величини адсорбції від тривалості взаємодії системи адсорбент – розчин хрому. Також визначено вплив кислотності розчину та рівноважної концентрації йонів хрому на величину адсорбції. Показано, що кінетика адсорбції йонів тривалентного хрому найкраще описується рівнянням псевдо-другого порядку та дифузійною кінетичною моделлю. Рівноважну адсорбцію найкраще описує теорія Френдліха. Методом мас-спектрометрії доведено підсилену адсорбцію йонів тривалентного хрому із суміші із шестивалентним хромом. Дане твердження було доведено Раманівською спектроскопією поверхні Na-TiO_2. Максимальна адсорбція йонів тривалентного хрому складає 62 мг/г. Фактор сепарації хрому тривалентного і хрому шестивалентного $SF_{Cr^{3+}/Cr^{6+}} = 7.279$.

Ключові слова: йони Cr (III) та Cr (VI), Раманівська спектроскопія, XRF-аналіз, адсорбція.