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Introduction shows the important of this scientific direction. ⁶⁰Co with half-life of 5.3 years is one of the few anthropogenic, gamma-emitting radionuclides, that can be detected in aquatic environments affected by liquid effluent discharged from nuclear facilities. The need for control of the content of ⁶⁰Co in the environment, determines the search for new adsorption materials with high adsorption capacity and chemical, thermal, and radiation resistance.

The aim of present work is to investigate the adsorption of Co²⁺ and ⁶⁰Co by mesoporous TiO₂ from aqueous solutions.

Experimental techniques describes the adsorption studies in detail. The mesoporous TiO₂ with the initial pore size ratio ($S_{meso}/S = 58\%$; $V_{meso}/V = 64\%$) was selected as adsorbent. Synthesis of adsorbents was carried out by the method of liquid phase hydrolysis of aqua complex of TiCl₄.

The dependence of adsorption value on agitation time, solutions acidity, and equilibrium concentration of Co²⁺ was investigated in batch mode. The presence of cobalt on the surface of mesoporous TiO₂ was confirmed using XRF-analysis. The initial and residual concentration of cobalt was controlled by complexometric titration with xylenol orange as indicator.

Four simplified kinetic models: pseudo-first order and pseudo-second order equations, firstly applied by Lagergren, intraparticle diffusion and Elovich (Roginsky-Zeldovich) kinetic models were applied to experimental data. Langmuir and Dubinin-Radushkevich adsorption theory applied for experimental equilibrium data of adsorption of cobalt cations by mesoporous TiO₂. The adsorption energy was measured using Dubinin-Radushkevich equation.

The results obtained have shown that the experimental data on the adsorption kinetics of Co²⁺ by mesoporous TiO₂ fit well by Lagergren pseudo-second kinetic model. Applying of Elovich kinetic model gives also high correlation's coefficients, close to unit ($R^2 > 0.9$).

The equilibrium adsorption data are well approximated by Langmuir adsorption theory. Maximal adsorption value obtained experimentally (49 ± 4 mg/g) is in good agreement with calculated by Langmuir adsorption theory (63.81 mg/g).

The adsorption energy calculated using Dubinin-Radushkevich equation is 8.104 ± 0.361 kJ/mol, which correspond to physical adsorption mechanism. However, for each values of Polanyi's potential (ϵ) (which correspond to certain equilibrium concentration C_e , mg/L) adsorption energy is different. It smooth decreases with increasing concentration of adsorbate in the solution. Although the experimental results are well describing by the Langmuir model, the adsorption energy of Co²⁺ ions by mesoporous TiO₂ depends on the degree of surface filling, which means that the adsorption centers of this sample are not independent. At the low equilibrium concentration of Co²⁺ (38 mg/L), the adsorption energy is much higher than the corresponding value for adsorption by the physical mechanism. To our opinion, that is why applying of Elovich kinetic model to experimental data gives high R^2 .

The adsorption of Co²⁺ by mesoporous TiO₂ strongly depends on solutions acidity.

To simulate conditions close to real, the adsorption of ⁶⁰Co by mesoporous TiO₂ was investigated. The percentage of ⁶⁰Co, adsorbed onto TiO₂ is more than 90 %.

The main conclusion is that mesoporous TiO₂ could be useful as an adsorbent for water purification from Co²⁺ and in decontaminating of radioactive waste containing ⁶⁰Co.

Keywords: adsorption, titanium dioxide, cobalt, radioactive contaminations

INTRODUCTION

⁶⁰Co with half-life of 5.3 years is one of the few anthropogenic, gamma-emitting radionuclides, that can be detected in aquatic environments affected by liquid effluent discharged from nuclear facilities. ⁶⁰Co forms by slow neutron capture in ⁵⁹Co, and exist in the

materials of the internal structure of the reactor core [1]. In river environment, it can be measured up to 20 km down-stream of NPP. Although cobalt is an essential trace element, it is toxic when concentration levels are too high.

Biosorbents, zeolites, modified zeolites [2], Fe₃O₄ nanoparticles, and Fe₃O₄ modified by

mercaptobutyric acid ($\text{Fe}_3\text{O}_4\text{-MBA}$), meso-2,3-dimercaptosuccinic acid ($\text{Fe}_3\text{O}_4\text{-DMSA}$) or ethylenediaminetetraacetic acid ($\text{Fe}_3\text{O}_4\text{-EDTA}$); metal-organic framework-based adsorbents (MOF), nano-silica or aluminum silicate are proposed for adsorption removal of Co^{2+} [3–8]. These adsorbents have certain limitations. Most of adsorbents have low adsorption capacities and selectivity. Their surface needs to be modified by chemical treatment [2]. Modified iron oxide nanoparticles are offered to be used for removal of Tl, Cd, Co, Cu, Ag, Pb [3], but among listed metals, cobalt adsorption is the worst. In addition, iron oxides limitation includes poor regeneration, which increases the cost of nanomaterials [3]. The need in the control of the content of ^{60}Co in the environment determines the search for new adsorption materials with high adsorption capacity, high recovery, and chemical, thermal, and radiation resistance.

TiO_2 is known as efficient adsorbent toward bivalent heavy metal cations Ba^{2+} , Pb^{2+} , Hg^{2+} , and radionuclides such as strontium [9–12]. Among all the TiO_2 synthesis methods, method of liquid phase hydrolysis of aqua complex of TiCl_4 [9–14] occupies an important place. Features of TiO_2 synthesis allows to change its surface to obtain the required properties. Mesoporous TiO_2 has a high chemical stability, and saves its adsorption properties even after 10 cycles of regeneration [11]. It is resistant to acidic and alkali medium, it has developed surface area, and is nontoxic. Also, mesoporous TiO_2 has a high thermal stability [11, 12] and thus, its radiation stability can be predicted.

In the present investigations, we use a new mesoporous TiO_2 synthesized by reaction of liquid-phase hydrolysis of aqua complex of TiCl_4 for the adsorption of Co^{2+} and ^{60}Co from aqueous solutions.

EXPERIMENTAL TECHNIQUES. SYNTHESIS OF MESOPOROUS TiO_2

Synthesis of adsorbents was carried out by the method of liquid phase hydrolysis of TiCl_4 aqua complex. Conditions of mesoporous TiO_2 synthesis are described in detail in publications [11–14]. The guidance of mesoporous TiO_2 synthesis, which was used in present investigations, is given in publications [11, 12]. This sample relates to mesoporous materials by porous size distribution. However, on its surface there are a considerable number of pores with

diameters less than 2 nm [12] classified as micro pores by IUPAC. Modification of the TiO_2 surface by arsenate or carbonate groups increases the volume/surface area of mesoporous TiO_2 , and increases the adsorption capacity of samples toward the heavy metal cations with large ionic radius, such as Sr^{2+} [11, 12]. Mean while, the volume of micro pore remains unchanged or weak decreases after modification [12]. It has been suggested that the initial pore size ratio of the unmodified sample ($S_{\text{meso}}/S = 58\%$; $V_{\text{meso}}/V = 64\%$ [12]) may be promising for the adsorption of Co^{2+} with relatively small ionic radius. Therefore, TiO_2 synthesized without the addition of modifying reagents was selected as adsorbent.

Mesoporous TiO_2 was synthesized in anatase modification with cell parameters: $a = 3.78 \text{ \AA}$; $c = 9.5 \text{ \AA}$, and crystallite size 4.7 nm. The specific surface area, pore volume, pore size distribution were estimated from N_2 adsorption/desorption isotherms using a BET-surface area analyzer (Quantachrome Autosorb Nova 2200e) at 77 K. The total surface area of this sample is $239.4 \text{ m}^2 \cdot \text{g}^{-1}$, and surface area of micropores is $100.5 \text{ m}^2 \cdot \text{g}^{-1}$; that of mesopores is $138.9 \text{ m}^2 \cdot \text{g}^{-1}$. Pore radii calculated using DFT method are 1 to 2.5 nm. The point of zero charge of mesoporous TiO_2 $\text{pH}_{\text{pzc}} = 5/35$ [11, 12].

ANALYSIS OF Co^{2+} AND ^{60}Co

The dependence of adsorption value from agitation time, solutions acidity and equilibrium concentration of Co^{2+} were investigated in batch mode with liquid : solid phase ratio equal to 100 ($m_{\text{ads}} = 0.05 \text{ g}$, $V_{\text{sol}} = 5 \text{ ml}$). The investigations of adsorption value dependence on agitation time and initial concentration of Co^{2+} were provided in neutral medium in the concentration ranges of 38–5497 mg/L. The effect of solution acidity on adsorption processes was investigated using certain amount of HNO_3 or NH_4OH and was controlled by a pH meter “Bilorus’ 2003”. The initial and residual concentration of Co^{2+} was determined using direct complexometric titration with xylenol orange [15].

The adsorption value and separation factor were measured by equations (1) and (2):

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

where C_o (mg/L) and C_e (mg/L) initial and residual concentration of cations respectively;

V (L) – volume of solution, m (g) – mass of adsorbent; A_e – adsorption value (mg/g);

$$R_L = 1/(1 + K_L C_o) \quad (2)$$

where K_L – constant of Langmuir equation [16].

For quality control of the adsorption experiments, replicate assays at least two times were carried out in different days under the same experimental conditions. The kinetic study of each experiment started with the addition of the mesoporous TiO_2 to the solution with dissolved cobalt compound. The solution was filtered after 5, 10, 20 *etc.* minute, then immediately analyzed for Co^{2+} .

Four simplified kinetic models: pseudo-first order and pseudo-second order equations, firstly applied by Lagergren [16, 17], intraparticle diffusion and Elovich (Roginsky-Zeldovich) kinetic models were applied to experimental data.

Langmuir and Dubinin-Radushkevich adsorption theory were applied to experimental equilibrium data. For describing isotherms of adsorption, equations were used, named Langmuir equation (3), or a linear form (4):

$$A_e = \frac{A_\infty K C_e}{1 + K C_e} \quad (3)$$

where A_∞ – maximal adsorption value, which corresponds of filling the whole adsorption centers (mg/g); K – Langmuir equation constant (L/mg); C_e – equilibrium concentration (mg/L). Linear form of Langmuir equation (4) is often used for measuring values of A_∞ and K

$$\frac{1}{A_e} = \frac{1}{A_\infty K} \times \frac{1}{C_e} \quad (4)$$

The adsorption energy was measured using Dubinin-Radushkevich equations (5) and (6) [16–19].

$$\begin{aligned} A_e &= A_{max} \times \exp(-\beta \varepsilon^2) = \\ &= A_{max} \times \left[-\beta \times \left(RT \ln \left(1 + \frac{1}{C_e} \right)^2 \right) \right] \end{aligned} \quad (5)$$

where A_e – adsorption value, $mmol \cdot g^{-1}$ under corresponding adsorptive concentration $C_e \text{ mol} \cdot L^{-1}$; A_{max} – maximal adsorption value, $mmol \cdot g^{-1}$; β – constant ($mol^2 \cdot J^{-2}$); ε – Polanyi's potential ($J \cdot mol^{-1}$); R – universal gas constant, $J \cdot mol^{-1} \cdot K^{-1}$, T – temperature (K).

The constant β is related to adsorption energy by equation (6)

$$E = \frac{1}{(2\beta)^2} \quad (6)$$

When the linear approximation was applied, the value of R^2 was calculated using Microsoft Office Excel or Origin Pro 8. In nonlinear approximation, the equation (7) was used to calculate R^2 according to literature [16]:

$$R^2 = 1 - \frac{\sum(q_{e,exp} - q_{e,calc})^2}{\sum(q_{e,exp} - q_{e,mean})^2} \quad (7)$$

A_{exp} (mg/g) is the amount of adsorbate uptake at equilibrium, A_{cal} (mg/g) is the amount of adsorbate uptake achieved from the model using the ‘Solver add-in’, and A_{mean} (mg/g) is the mean of the A_{exp} values [16].

To simulate conditions close to real, the radioactive isotopes of ^{60}Co were obtained using reaction: $^{59}Co(n, \gamma) \rightarrow ^{60}Co$.

For this purpose, 20 g of $CoCl_2$ was positioned near neutron source. Pu (α) Be compound was used as a source of neutrons ($\varphi = 1.3 \cdot 10^6 \text{ n/cm}^2 \cdot \text{s}$; $E_n = 1-10 \text{ MeV}$). The highest cross section for interaction between ^{59}Co and neutron, according to [19] is for neutrons with energies 100 eV. So, the neutrons from Pu (α) Be sources were slowed down by paraffin to the ranges of energies 100 eV – 1 MeV. The thickness of paraffin was calculated using Fermi age equation. The exposure time of the compound was at least 90 days [19]. The sample activity was detected by a scintillate spectrometer with NaI (Tl) crystal [1].

The adsorption conditions of ^{60}Co by mesoporous TiO_2 were the same as for stable Co^{2+} : solution acidity was neutral, duration of interaction was at least 60 min, initial concentration of (^{60}Co) $CoCl_2$ was 0.005 M; only the mass of the adsorbent was doubled ($m = 0.1 \text{ g}$) for the convenience of gamma-spectrometry and XRF analysis.

The decontamination factor (DF) was calculated by the following equation (8):

$$DF(\%) = \frac{A_i - A_f}{A_i} \times 100 \quad (8)$$

where (A_i) and (A_f) are the initial and final activities in (Bq/mL) of the radioactive solutions.

XRF ANALYSIS

The elemental chemical composition of the samples were done by XRF-analysis. The analysis was provided in the scan mode using an S2Ranger ©2010 Bruker AXS GmbH under next conditions: voltage 50 kV; tube current 1000 μA ; pressure 1000 mBar; filter 250 mm Cu. The peaks of cobalt were observed with the energy 6.93 keV. The quantity of Co^{2+} on sorbent surface is 0.146 % which equal to 1.46 mg of Co^{2+} per 1 g of adsorbent for initial concentration of Co^{2+} 50 mg/L.

RESULTS AND DISCUSSIONS.
KINETICS OF ADSORPTION OF Co^{2+} BY MESOPOROUS TiO_2

Contact time between adsorbent and solution of corresponding metal has an important role in understanding of adsorption processes. Kinetics of adsorption of Co^{2+} by mesoporous TiO_2 is shown in Fig. 1.

Adsorption of Co^{2+} from aqueous solution strongly depends on the time of interaction. Application of kinetic models to the results of adsorption of Co^{2+} by mesoporous TiO_2 is shown in Fig. 2 (a-d).

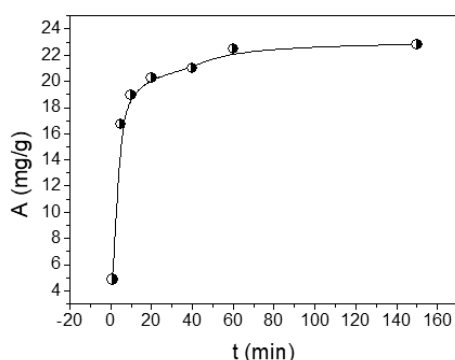


Fig. 1. Kinetics of adsorption of Co^{2+} by mesoporous TiO_2 . Initial concentration of CoCl_2 is 0.01 M; L:S = 100; pH = 7

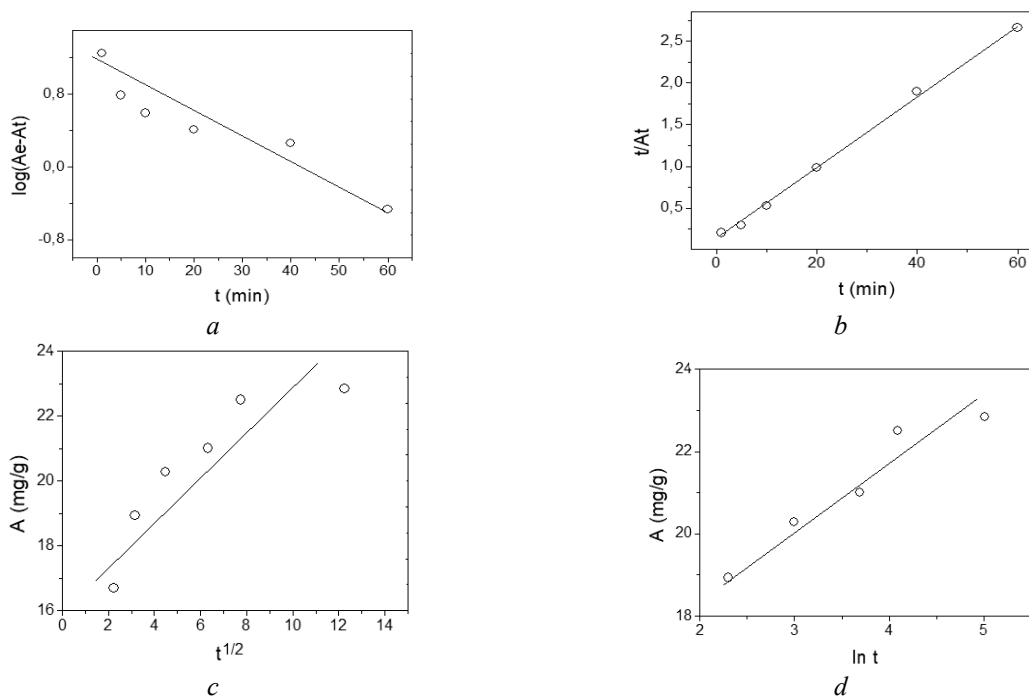
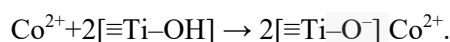


Fig. 2. Results of linear approximation of experimental data of adsorption of Co^{2+} by mesoporous TiO_2 : (a) Lagergren kinetic model based on pseudo-first order equation; (b) Lagergren kinetic model based on pseudo-second order equation; (c) diffusion kinetic model; (d) Elovich kinetic model. The kinetic models are widely used for mathematically describing the intrinsic kinetic adsorption constant

Table 1. Kinetic adsorption constant of Co^{2+} onto mesoporous TiO_2

Kinetic model	Constant of applying model	R^2
Lagergren's pseudo-first-order	$K_1 = 0.0237 \text{ min}^{-1}$	0.8949
Lagergren's pseudo-second-order	$K_2 = 0.0428 \text{ g/mg}^{-1}\text{min}^{-1}$	0.9982
Difussion model (intraparticle diffusion)	$K_{\text{ipd}} = 0.560 \text{ mg}\cdot\text{g}^{-1}\text{min}^{0.5}$ (calc. $A_{\text{max}} = 16.99 \text{ mg/g}$)	0.7878
Elovich	$k_e = 1.8 \text{ mg}\cdot\text{g}^{-1}\text{min}^{-1}$ (calc. $A_{\text{max}} = 14.4 \text{ mg/g}$)	0.9404

The equilibrium of Co^{2+} adsorption was achieved after 60 minutes of interaction between TiO_2 and solution of Co^{2+} . The Lagergren's pseudo-second order kinetic model provided better correlation than other kinetic models. As well known, a pseudo-second order reaction is a third order reaction in nature in which one of the reagents is in excess (in our case adsorbent). According to [11, 12], adsorption of bivalent cations by mesoporous TiO_2 occurs by interaction with surface $\{\equiv\text{Ti}-\text{OH}\}$ groups. High correlation coefficient of the pseudo-second order equation means that bivalent Co^{2+} can interact with two $\{\equiv\text{Ti}-\text{OH}\}$ groups. We suppose the physical mechanism of adsorption of Co^{2+} by mesoporous TiO_2 as the main mechanism, but the first step of this process may be surface complexation between Co^{2+} and $2[\equiv\text{Ti}-\text{OH}]$ groups:



That is why applying of Elovich kinetic model to present experimental data gives also high R^2 value ($R^2 = 0.94$).

INVESTIGATION OF EQUILIBRIUM ADSORPTION OF Co^{2+} BY MESOPOROUS TiO_2

Adsorption under equilibrium conditions provides fundamental data about the adsorption process. The parameters of equilibrium equations often give some insight into the sorption mechanism, the surface properties, and the capacity of the sorbent [16]. Adsorption equilibrium studies were provided in batch experiments and neutral conditions. Results are shown in Fig. 3.

Curve of isotherm adsorption of Co^{2+} by mesoporous TiO_2 has a form close to Langmuir isotherm. According to Langmuir, adsorption is limited to one molecular layer, and locates on adsorption centers, which are independent on

each other. Adsorption centers is bonding with one molecule of adsorptive [16].

In coordinates of $C/A_f(C_0)$ Langmuir isotherm has a linear form, slope and intercept of which correspond to parameters of Langmuir equation, and the square of linear approximation coefficient (R^2) indicates the degree of reliability of the calculated results. However, the Tran *et al.* [16] recommend applying a nonlinear approximation, which gives the values of the parameters of the Langmuir equation as close as possible to the true ones. Other authors [20–23] confirmed that the use of nonlinear approximation of experimental data of equilibrium adsorption gives values that are reliable relevant for modelling the isotherms of adsorption.

In present investigations linear and nonlinear approximation of Langmuir isotherm were applied. Nonlinear approximation is carried out using "Solver add in" option in Microsoft Office Excel [16].

Results are shown in Fig. 4, and in Table 2.

The experimental data of Co^{2+} adsorption by mesoporous TiO_2 are adequately described by Langmuir model. Value of A_{max} (mg/g) calculated using nonlinear approximation is closer to the experimental value of Co^{2+} adsorption by mesoporous TiO_2 (Table 2) than the same parameter calculated using linear approximation. R_L was measured using parameter of Langmuir equation K_L calculated by nonlinear approximation (0.00086 L/mg). Obtained value of separation factor is less than unit ($R_L < 1$, see Table 2), so adsorption of Co^{2+} onto mesoporous TiO_2 is favorable [16].

The Dubinin-Radushkevich equation (7) generally applies well to adsorption system involving only Van der Waals forces [16–19]. According to Dubinin-Radushkevich theory, adsorption process is nonlocal, polymolecular, and based on the postulate that the mechanism in micropores is pore filling rather than layer-by-layer surface coverage [17].

Adsorption isotherm of Co^{2+} by mesoporous TiO_2 in Dubinin-Radushkevich coordinates ($\ln A_e f(\varepsilon^2)$) is shown in Fig. 7.

The constant β , which can be determine from dependence $A_e f(\varepsilon^2)$, allows us to calculate the adsorption energy value by equation (8). Arithmetic mean of adsorption energy of Co^{2+} by mesoporous TiO_2 in concentration ranges of CoCl_2 0.001–0.1 mol/L (or 38–5497 mg/L) is 8.104 ± 0.361 kJ/mol. However, for each value of Polanyi's potential (ε) (which corresponds to

certain equilibrium concentration C_e , mg/L) adsorption energy is different. It smooth decreases with increasing of adsorbate concentration in the solution. Although the experimental results are well described by the Langmuir model, the adsorption energy of Co^{2+} ions by mesoporous TiO_2 depends on the degree of surface filling, what means that, according to Adamson [24], the adsorption centers of this sample are not independent.

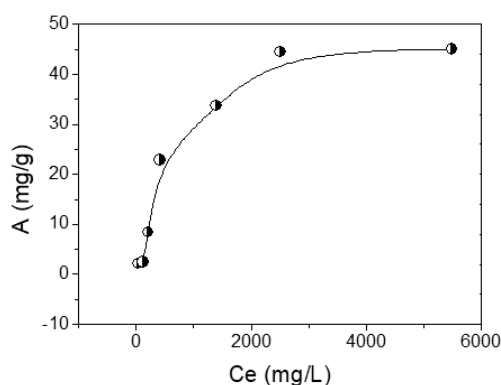


Fig. 3. Isotherm of adsorption of Co^{2+} by mesoporous TiO_2 (pH=7; S:L=100)

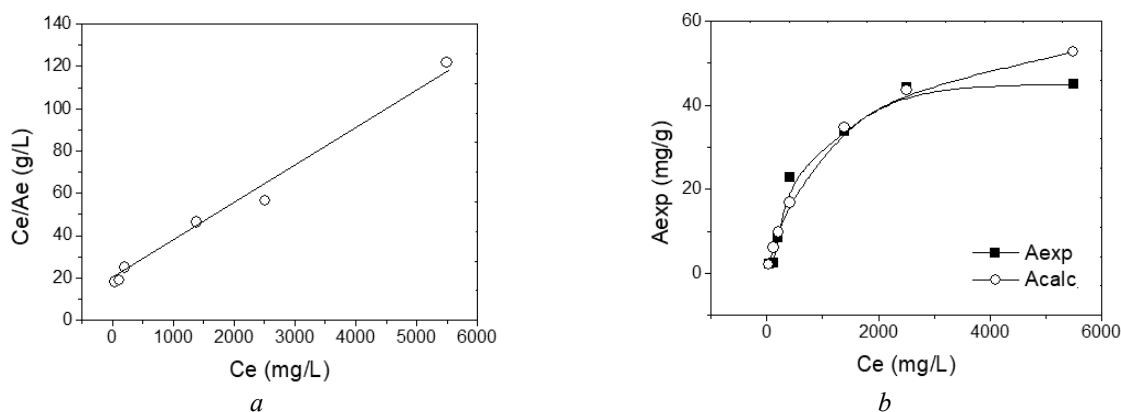


Fig. 4. Langmuir isotherm of adsorption of Co^{2+} by mesoporous TiO_2 ; (a) linear approximation; (b) nonlinear approximation using “Solver add in” option

Table 2. Parameters of Langmuir equation of adsorption of Co^{2+} by mesoporous TiO_2 and factor R_L

Langmuir isotherm	Maximal adsorption value A_{\max} , mg/g	K_L , L/mg	R^2
Linear fitting	16.67	0.0185	0.9891
Nonlinear fitting	63.8148	0.00086	0.9990
Experimental data	49 ± 4.478 ($\pm 9.05\%$)	$R_L = 0.968 - 0.174$	

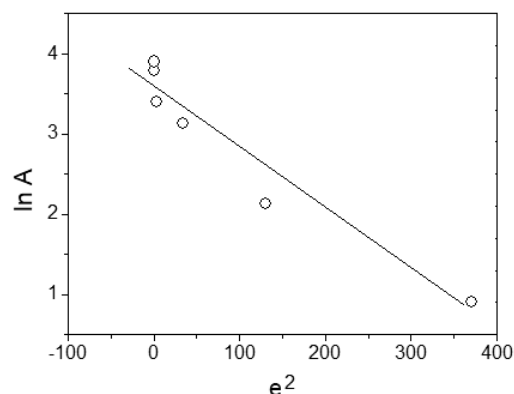


Fig. 5. Dubinin-Radushkevich isotherm of adsorption of Co^{2+} cations by mesoporous TiO_2

Table 3. The energy of adsorption of Co^{2+} by mesoporous TiO_2 , calculated using equation (8) and as $E = 1/\sqrt{-2\text{slope}}$, [16]

C_e , mg/L	E , kJ/mol	Arithmetic mean of E , kJ/mol	E , kJ/mol $E = 1/\sqrt{-2\text{slope}}$ [16]
38	25	8.104	8.22
75	9.26		
123	7.86		
210	6.06		
417	4.78		
1394	1.69		
2506	2.08		

In the case of physical adsorption of heavy metal by inorganic adsorbents, the value of adsorption energy is equal to $E \leq 8 \text{ kJ}\cdot\text{mol}^{-1}$ [16]. At the low equilibrium concentration C_e of Co^{2+} (38 mg/L), the adsorption energy is much higher than the corresponding value for adsorption by the physical mechanism (see Table 3).

The mesoporous TiO_2 shows a high affinity to cobalt cations at low concentrations of cobalt in solution, which determines a high decontamination factor for ^{60}Co and could be useful for purification of aqueous solutions from cobalt waste with high accuracy.

Table 4. Parameter of Dubinin-Radushkevich equation and average of adsorption energy of Co^{2+} by mesoporous TiO_2

Adsorption capacity A_{max} , mg/g	β $\text{mol}^2\cdot\text{J}^{-2}$	E_{ads} $\text{kJ}\cdot\text{mol}^{-1}$	R^2
90.017	0.00765	8.104 ± 0.361 $\pm 4.47\%$	0.9337

DEPENDENCE OF ADSORPTION OF Co^{2+} BY MESOPOROUS TiO_2 ON pH

Co^{2+} exists in the form of $[\text{Co}^{2+}]$ in the range of $\text{pH} = 1-7$ [25–29]. When solutions acidity is increasing ($\text{pH} = 9-13$) $[\text{Co}^{2+}]$ transforms into $[\text{HCo}^{2-}]$, $\text{CoO}_{2\text{s}}$, CoO_{aq} , $\text{Co}(\text{OH})_{2\text{aq}}$. Dependence of adsorption of Co^{2+} cations by mesoporous TiO_2 on pH was investigated in the range of $\text{pH} = 1-7$.

The point of zero charge of mesoporous TiO_2 $\text{pH}_{\text{pzc}} = 5.35$. Near this value of pH the adsorption of Co^{2+} begins and increases with increasing pH from 2.82 ($\text{pH} = 4$) to 20.5 mg/g ($\text{pH} = 7$) (see in Table 5, and Fig. 6).

These patterns of dependence of adsorption Co^{2+} on pH are in good agreement with those shown in literature [27, 29].

The unmodified TiO_2 is favorable for adsorption cations with small ionic radius, like Co^{2+} . We can compare with other adsorbents: chitosan (7.65 mg/g) [9]; cellulose/ HO_7Sb_3

(25 mg/g) [1]; synthetic aluminum silicate modified by magnesia (9 mg/g) [27]; Zr-ATMP 0.91 meq/g ~ 54 mg/g [6].

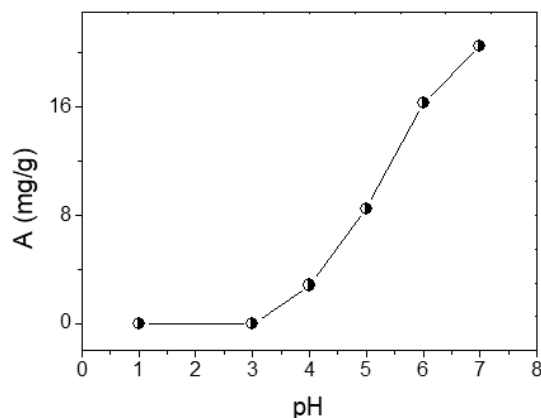


Fig. 6. Effect of pH on adsorption of Co^{2+} by mesoporous TiO_2 . The initial concentration is 0.01M CoCl_2

Table 5. Dependence of adsorption of Co^{2+} cations by mesoporous TiO_2 on pH. Initial concentration is 0.01 M CoCl_2

pH	1	3	4	5	6	7
A, mg/g	0	0	2.82	8.44	16.3	20.5

Table 6. Comparative studies of adsorption affinity of mesoporous TiO_2 toward Co^{2+} and Sr^{2+} cations

element	Atomic radius, Å	Ion radius, Å [26]		
		By Holdshmidt	By Poling	By Shanon (for coordination number 6)
Co^{2+}	1.25	0.82	0.72	0.78
A, mg/g $C_i = 0.01\text{M CoCl}_2$		29.5 (0.5 mmol/g) present work		
Sr^{2+}	2.15	1.10	1.13	1.32
A, mg/g $C_i = 0.01\text{M SrCl}_2$		25.69 (0.292 mmol/g) data from [12]		

ADSORPTION OF ^{60}Co

Adsorption of ^{60}Co by mesoporous TiO_2 was investigated in batch mode under and neutral pH from low-level radioactivity solution with dissolved ^{60}Co compound. ^{60}Co emits two γ -lines with energy 1.17 and 1.33 MeV [19]. The activity of aqueous radioactive solutions of ^{60}Co was determined by a gamma-counter using a NaI-(TI) scintillation spectrometer [1, 19, 27–29]. Arithmetic mean and deviation of arithmetic mean were calculated using source [30].

Decontamination factor measured using equation (8) is equal to 98 %. Investigated

mesoporous TiO_2 could be useful as an adsorbent for water purification from Co^{2+} and in decontaminating of radioactive waste containing ^{60}Co .

CONCLUSIONS

Adsorption of Co^{2+} by mesoporous TiO_2 was investigated in the batch mode. The influence of agitation time, equilibrium concentration and solutions acidity were determined. The elemental chemical composition of the samples were done by XRF analysis.

The experimental data of adsorption kinetic of Co^{2+} by mesoporous TiO_2 fitting well by

Lagergren pseudo-second kinetic model. The equilibrium adsorption data well approximation by Langmuir adsorption theory. Maximal adsorption value, obtained experimentally (49 ± 4 mg/g), is in good agreement with that calculated by Langmuir adsorption theory (63.81 mg/g).

Adsorption energy calculated using Dubinin-Radushkevich equation decreases with increasing of adsorbate concentration in the solution. Although the experimental results are well described by the Langmuir model, the adsorption

energy of Co^{2+} ions by mesoporous TiO_2 depends on the degree of surface filling.

Investigated mesoporous TiO_2 could be useful as adsorbent for water purification from Co^{2+} and in decontaminating of radioactive waste containing ^{60}Co .

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Адсорбція катіонів Co^{2+} і радіоактивного ^{60}Co мезопористим TiO_2

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У вступі до даної роботи розкрито актуальність подібного напрямку досліджень. ^{60}Co із періодом напіврозпаду 5.3 роки є одним із числа антропогенних радіонуклідів, гамма-випромінювачів, які можуть діагностуватися у рідких відходах ядерних установок. Необхідність контролю вмісту ^{60}Co у довкіллі обумовлює пошук нових адсорбційних матеріалів з високою адсорбційною ємністю, хімічною, термічною та радіаційною стійкістю.

Мета даної роботи – дослідити адсорбцію Co^{2+} і ^{60}Co із водних розчинів мезопористим TiO_2 .

Методика експерименту детально описує адсорбційні дослідження. Як адсорбент був вибраний мезопористий TiO_2 із співвідношенням мікро- і мезопор $S_{\text{meso}}/S = 58\%$; $V_{\text{meso}}/V = 64\%$. Синтез дослідженого адсорбента здійснювався за методикою рідкофазного гідролізу титанового аквакомплекса. Як прекурсор був вибраний тетрахлорид титану TiCl_4 . Залежність адсорбції іонів кобальту від тривалості взаємодії адсорбата з поверхнею адсорбента, кислотності розчину, рівноважної концентрації іонів кобальту була досліджена у статичних умовах. Присутність кобальту на поверхні мезопористого TiO_2 була доведена методом рентгено-флуоресцентної спектроскопії.

Початкову та рівноважну концентрацію іонів кобальту визначали методом комплексонометричного титрування. Як індикатор використовували ксиленоловий помаранчовий.

Чотири найбільш поширені кінетичні моделі: Лагергрена псевдо-першого та псевдо-другого порядку, внутрішньочастинкової дифузії та модель Еловича були застосовані до експериментальних результатів досліджень кінетики адсорбції іонів кобальту мезопористим TiO_2 . До рівноважних ізотерм адсорбції були застосовані теорії Ленгмюра і Дубініна-Радушкевича. Було розраховано енергію адсорбції з використанням рівняння Дубініна-Радушкевича.

Одержані результати показують, що експериментальні залежності величини адсорбції від часу взаємодії добре апроксимуються кінетичною моделлю Лагергрена псевдо-другого порядку. Застосування моделі Еловича (моделі хемосорбції) також дає високий коефіцієнт лінійного наближення ($R^2 > 0.9$).

Результати рівноважної адсорбції можуть бути описані теорією Ленгмюра з високим ступенем достовірності. Експериментальні значення максимальної адсорбції іонів кобальту мезопористим TiO_2 (49 ± 4 мг/г) добре узгоджуються із розрахованими за теорією Ленгмюра (63.81 мг/г). Енергія адсорбції, розрахована за рівнянням Дубініна-Радушкевича становить 8.104 ± 0.361 кДж/моль, що відповідає фізичному механізмові адсорбції. Однак, для кожного окремо взятого потенціалу Поляні (якому відповідає певна рівноважна концентрація адсорбата, мг/л) енергія адсорбції різна. Її величина плавно зменшується при зростанні рівноважної концентрації Co^{2+} у розчині. Це свідчить про залежність енергії адсорбції іонів

кобальту мезопористим TiO_2 від ступеня заповнення поверхні. З цього факту можна зробити висновок, що адсорбційні центри дослідженого мезопористого TiO_2 не є незалежні.

При низьких значеннях рівноважної концентрації катіонів кобальту (38 мг/л) величина енергії адсорбції вища, ніж така, що відповідає механізмові фізичної адсорбції. На нашу думку, це може бути причиною високих коефіцієнтів лінійного наближення при застосуванні моделі Еловича до даних експериментальних результатів. Адсорбція Co^{2+} мезопористим TiO_2 залежить від кислотності розчину.

Щоб змоделювати умови експерименту, близькі до реальних, було досліджено адсорбцію ^{60}Co мезопористим TiO_2 . Показано, що досліджений адсорбент вилучає понад 90% радіонукліду. Мезопористий TiO_2 є перспективним матеріалом для глибокої очистки водних розчинів від Co^{2+} і дезактивації радіоактивних відходів, які містять ^{60}Co .

Ключові слова: адсорбція, діоксид титану, кобальт, радіоактивні відходи

Адсорбция катионов Co^{2+} и радиоактивного ^{60}Co мезопористым TiO_2

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Вступление к работе раскрывает актуальность данного направления исследований. ^{60}Co с периодом полураспада 5.3 года является одним из антропогенных радионуклидов, гамма-эмиттеров, которые диагностируются в жидких отходах ядерных установок. Необходимость контроля ^{60}Co в окружающей среде определяет поиск новых адсорбентов, которые владеют высокой сорбционной емкостью, химической, термической и радиационной стойкостью.

Цель данной работы – исследовать адсорбцию Co^{2+} и ^{60}Co из водных растворов мезопористым TiO_2 .

Методика эксперимента детально описывает адсорбционные исследования. В качестве адсорбента был выбран мезопористый TiO_2 с соотношением микро- и мезопор $S_{\text{meso}}/S = 58\%$; $V_{\text{meso}}/V = 64\%$. Синтез исследованного адсорбента осуществляли по методике жидкофазного гидролиза титанового аквакомплекса. В качестве прекурсора был выбран тетрагидрат титана TiCl_4 . Зависимость адсорбции ионов кобальта от времени взаимодействия адсорбата с поверхностью адсорбента, кислотности раствора, равновесной концентрации ионов кобальта была исследована в статических условиях. Присутствие адсорбированного Co^{2+} на поверхности мезопористого TiO_2 подтверждено методом рентгено-флуоресцентной спектроскопии. Начальную и равновесную концентрацию ионов кобальта определяли методом комплексонометрического титрования. В качестве индикатора был использован ксиленоловый оранжевый.

Четыре наиболее известные кинетические модели: Лагергрена псевдо-первого и псевдо-второго порядка, модель диффузии внутрь частиц адсорбента (модель Веббера-Морриса) и модель хемосорбции Еловича были использованы для анализа экспериментальных данных кинетики адсорбции ионов кобальта мезопористым TiO_2 . Для описания равновесных изотерм адсорбции были использованы теории адсорбции Лэнгмюра и Дубинина-Радушкевича.

Полученные результаты свидетельствуют о том, что экспериментальные зависимости коэффициентов адсорбции от времени взаимодействия хорошо аппроксимируются кинетической моделью Лагергрена псевдо-второго порядка. Использование модели хемосорбции Еловича также дает высокий коэффициент корреляции ($R^2 > 0.9$).

Результаты равновесной адсорбции могут быть описаны теорией Лэнгмюра с высокой степенью достоверности. Экспериментальные значения максимальной адсорбции ионов кобальта мезопористым TiO_2 (49 ± 4 мг/г) хорошо согласуются с величинами, теоретически определенными по теории Лэнгмюра (63.81 мг/г). Энергия адсорбции, определенная по уравнению Дубинина-Радушкевича, равна 8.104 ± 0.361 кДж/моль, что соответствует физическому механизму адсорбции. Однако, для каждого отдельно взятого потенциала Поляни (которому соответствует определенная равновесная концентрация адсорбата, мг/л) энергия адсорбции разная. Ее значение плавно уменьшается при возрастании равновесной концентрации Co^{2+} в растворе. Это свидетельствует о зависимости энергии адсорбции ионов кобальта мезопористым TiO_2 от степени заполнения поверхности, а значит и о том, что адсорбционные центры

данного образца не являются независимыми. При низких значениях равновесной концентрации катионов кобальта в растворе (38 мг/л), значение энергии адсорбции выше, нежели таковое для физической адсорбции. Это, по нашему мнению, и есть причина высоких коэффициентов корреляции при аппроксимации моделью хемосорбции Еловича полученных результатов. Адсорбция Co^{2+} мезопористым TiO_2 сильно зависит от кислотности раствора.

Чтобы смоделировать условия эксперимента, близкие к реальным, была исследована адсорбция ^{60}Co мезопористым TiO_2 . Показано, что исследованный адсорбент извлекает больше 90 % радионуклида. Мезопористый TiO_2 – перспективный материал для очистки водных растворов от Co^{2+} и дезактивации радиоактивных отходов, содержащих ^{60}Co .

Ключевые слова: адсорбция, двуокись титана, кобальт, радиоактивные отходы

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