H.V. Vasylyeva 1, I.F. Mironyuk 2, I.M. Mykytyn 2

**ADSORPTION OF Co^{2+} AND RADIOACTIVE 60Co BY MESOPOROUS TiO2**

1 Uzhgorod National University
14 University Str., Uzhgorod, 88000, Ukraine, E-mail: h.v.vasylyeva@hotmail.com
2 Vasyl Stefanyk Precarpathian National University
57 Shevchenka Str., Ivano-Frankivs'k, 76000, Ukraine, E-mail: myrif555@gmail.com

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 Co^{2+} 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 TiCl4.

The dependence of adsorption value on agitation time, solutions acidity, and equilibrium concentration of Co^{2+} 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 complexonometric 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 Co^{2+} 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 ($\varepsilon$) (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. The results obtained are well describing by the Langmuir model, the adsorption energy of Co^{2+} 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 Co^{2+} (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 Co^{2+} 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 Co^{2+} 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
Adsorption of Co\textsuperscript{2+} and radioactive 60\textsuperscript{Co} by mesoporous TiO\textsubscript{2}

mercaptopbutyric acid (Fe\textsubscript{3}O\textsubscript{4}-MBA), meso-2,3-dimercaptosuccinic acid (Fe\textsubscript{3}O\textsubscript{4}-DMSA) or ethylenediaminetetraacetic acid (Fe\textsubscript{3}O\textsubscript{4}-EDTA); metal-organic framework-based adsorbents (MOF), nano-silica or aluminium silicate are proposed for adsorption removal of Co\textsuperscript{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 Ti, 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 60Co in the environment determines the search for new adsorption materials with high adsorption capacity, high recovery, and chemical, thermal, and radiation resistance.

TiO\textsubscript{2} is known as efficient adsorbent toward bivalent heavy metal cations Ba\textsuperscript{2+}, Pb\textsuperscript{2+}, Hg\textsuperscript{2+}, and radionuclides such as strontium [9–12]. Among all the TiO\textsubscript{2} synthesis methods, method of liquid phase hydrolysis of aqua complex of TiCl\textsubscript{4} [9–14] occupies an important place. Features of TiO\textsubscript{2} synthesis allows to change its surface to obtain the required properties. Mesoporous TiO\textsubscript{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\textsubscript{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\textsubscript{2} synthesized by reaction of liquid-phase hydrolysis of aqua complex of TiCl\textsubscript{4} for the adsorption of Co\textsuperscript{2+} and 60Co from aqueous solutions.

EXPERIMENTAL TECHNIQUES.
SYNTHESIS OF MESOPOROUS TiO\textsubscript{2}

Synthesis of adsorbents was carried out by the method of liquid phase hydrolysis of TiCl\textsubscript{4} aqua complex Conditions of mesoporous TiO\textsubscript{2} synthesis are described in detail in publications [11–14]. The guidance of mesoporous TiO\textsubscript{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\textsubscript{2} surface by arsenate or carbonate groups increases the volume/surface area of mesoporous TiO\textsubscript{2}, and increases the adsorption capacity of samples toward the heavy metal cations with large ionic radius, such as Sr\textsuperscript{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\textsubscript{meso}/S = 58 %; V\textsubscript{meso}/V = 64 % [12]) may be promising for the adsorption of Co\textsuperscript{2+} with relatively small ionic radius. Therefore, TiO\textsubscript{2} synthesized without the addition of modifying reagents was selected as adsorbent.

Mesoporous TiO\textsubscript{2} was synthesized in anatase modification with cell parameters: a = 3.78 Å; c = 9.5 Å, and crystallite size 4.7 nm. The specific surface area, pore volume, pore size distribution were estimated from N\textsubscript{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 m\textsuperscript{2}·g\textsuperscript{-1}, and surface area of micropores is 100.5 m\textsuperscript{2}·g\textsuperscript{-1}; that of mesopores is 138.9 m\textsuperscript{2}·g\textsuperscript{-1}. Pore radii calculated using DFT method are 1 to 2.5 nm. The point of zero charge of mesoporous TiO\textsubscript{2} pH\textsubscript{pzc} = 5/35 [11, 12].

ANALYSIS OF Co\textsuperscript{2+} AND 60Co

The dependence of adsorption value from agitation time, solutions acidity and equilibrium concentration of Co\textsuperscript{2+} were investigated in butch mode with liquid : solid phase ratio equal to 100 (m\textsubscript{ads} = 0.05 g, V\textsubscript{sol} = 5 ml). The investigations of adsorption value dependence on agitation time and initial concentration of Co\textsuperscript{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\textsubscript{3} or NH\textsubscript{4}OH and was controlled by a pH meter “Bilorus’ 2003”. The initial and residual concentration of Co\textsuperscript{2+} was determined using direct complexonometric titration with xylenol orange [15].

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

\[
\text{A}_{e} = \frac{|C_{0} - C_{e}|V}{m} \tag{1}
\]

where \(C_{0}\) (mg/L) and \(C_{e}\) (mg/L) initial and residual concentration of cations respectively;
The volume of solution, \( m (g) \) – mass of adsorbent; \( A_e \) – adsorption value (mg/g);

\[
R_L = \frac{1}{(1 + K_L C_0)}
\]

(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):

\[
A_e = \frac{A_\infty K C_e}{1 + K C_e}
\]

(3)

where \( A_\infty \) – 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 \( A_\infty \) and \( K \):

\[
\frac{1}{A_e} = \frac{1}{A_\infty K} \times \frac{1}{C_e}
\]

(4)

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

\[
A_e = A_{\text{max}} \times \exp(-\beta \varepsilon^2) =
A_{\text{max}} \times \left[ -\beta \times \left( RT \ln \left( 1 + \frac{1}{C_e} \right)^2 \right) \right]
\]

(5)

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

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

\[
E = \frac{1}{(2\beta)^2}
\]

(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]:

\[
R^2 = 1 - \frac{\sum (q_{e,\text{exp}} - q_{e,\text{calc}})^2}{\sum (q_{e,\text{exp}} - q_{e,\text{mean}})^2}
\]

(7)

\( A_{\text{exp}} \) (mg/g) is the amount of adsorbate uptake at equilibrium, \( A_{\text{cal}} \) (mg/g) is the amount of adsorbate uptake achieved from the model using the ‘Solver add-in’, and \( A_{\text{mean}} \) (mg/g) is the mean of the \( A_{\text{exp}} \) 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 (\( \alpha \)) Be compound was used as a source of neutrons (\( \varphi = 1.3 \times 10^6 \) n/cm\(^2\)·s; \( E_n = 1–10 \) 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 (\( \alpha \)) 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 \(^{60}\)CoCoCl\(_2\) was 0.005 M; only the mass of the adsorbent was doubled (\( m = 0.1 \) g) for the convenience of gamma-spectrometry and XRF analysis.

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

\[
DF(\%) = \frac{A_i - A_f}{A_i} \times 100
\]

(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             | $K_1 = 0.0237$ min$^{-1}$  | 0.8949|
| Lagergren’s pseudo-second-order            | $K_2 = 0.0428$ g/mg min$^{-1}$ | 0.9982|
| Diffusion model (intraparticle diffusion)  | $K_{ipd} = 0.560$ mg/g$^{-1}$min$^{-0.5}$ (calc. $A_{max} = 16.99$ mg/g) | 0.7878|
| Elovich                                    | $k_e = 1.8$ mg/g min$^{-1}$ (calc. $A_{max} = 14.4$ 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 {≡Ті–OH} groups. High correlation coefficient of the pseudo-second order equation means that bivalent Co^{2+} can interact with two {≡Ті–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[{≡Ті–OH}] groups:

$$\text{Co}^{2+} + 2[≡\text{Ті–OH}] \rightarrow 2[≡\text{Ті–O}^-] \text{Co}^{2+}.$$  

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 $C_e/A_e(C_e)$ 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 of Co$^{2+}$ and radioactive $^{60}$Co by mesoporous TiO$_2$

Adsorption isotherm of Co$^{2+}$ by mesoporous TiO$_2$ in Dubinin-Radushkevich coordinates (ln $A_f(\varepsilon^2)$) is shown in Fig. 7.

The constant $\beta$, which can be determined from the dependence $A_f(\varepsilon^2)$, 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 $8.104\pm0.361$ kJ/mol. However, for each value of Polanyi’s potential ($\varepsilon$) (which corresponds to certain equilibrium concentration $C_e$, mg/L) adsorption energy is different. It smoothly 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)](image)

![Fig. 4. Langmuir isotherm of adsorption of Co$^{2+}$ by mesoporous TiO$_2$; (a) linear approximation; (b) nonlinear approximation using “Solver add in” option)](image)

### 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       | $49\pm4.478$ (±9.05 %)                    | $R_L = 0.968-0.174$ |
In the case of physical adsorption of heavy metal by inorganic adsorbents, the value of adsorption energy is equal to $E \leq 8 \text{ kJ·mol}^{-1}$ [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 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 |
|-------------|-------------|-----------------------------|-------------|
| 38          | 25          |                            | 8.104       |
| 75          | 9.26        |                            | 8.22        |
| 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 $E \leq 8 \text{ kJ·mol}^{-1}$ [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 $A_{\text{max}}$, mg/g | $\beta$, mol$^2$·J$^{-2}$ | $E_{\text{ads}}$, kJ·mol$^{-1}$ | $R^2$ |
|------------------------------------------|---------------------------|-------------------------------|-------|
| 90.017                                   | 0.00765                   | 8.104±0.361                   | 0.9337|

### DEPENDENCE OF ADSORPTION OF Co$^{2+}$ BY MESOPOROUS TiO$_2$ ON pH

Co$^{2+}$ exists in the form of [Co$^{3+}$] in the range of pH = 1–7 [25–29]. When solutions acidity is increasing (pH = 9–13) [Co$^{2+}$] transforms into [HCo$^{2+}$], CoO$_2$, CoO$_2$$_2$, Co(OH)$_2$. Dependence of adsorption of Co$^{2+}$ cations by mesoporous TiO$_2$ on pH was investigated in the range of pH = 1–7.

The point of zero charge of mesoporous TiO$_2$ pH$_{ZPC} = 5.35$. Near this value of pH the adsorption of Co$^{2+}$ begins and increases with increasing pH from 2.82 (pH = 4) to 20.5 mg/g (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].
Adsorption of $\text{Co}^{2+}$ and radioactive $^{60}\text{Co}$ by mesoporous $\text{TiO}_2$

The unmodified $\text{TiO}_2$ is favorable for adsorption cations with small ionic radius, like $\text{Co}^{2+}$. We can compare with other adsorbents: chitosan (7.65 mg/g) [9]; cellulose/HO$_7$Sb$_3$ (25 mg/g) [1]; synthetic aluminum silicate modified by magnesia (9 mg/g) [27]; Zr-ATMP 0.91 meq/g $\sim$ 54 mg/g [6].

![Graph of pH vs Adsorption]

**Fig. 6.** Effect of pH on adsorption of $\text{Co}^{2+}$ by mesoporous $\text{TiO}_2$. The initial concentration is 0.01 M $\text{CoCl}_2$

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

**Table 5.** Dependence of adsorption of $\text{Co}^{2+}$ cations by mesoporous $\text{TiO}_2$ on pH. Initial concentration is 0.01 M $\text{CoCl}_2$

| element | Atomic radius, \(\text{Å}\) | Ion radius, \(\text{Å}\) [26] | By Holdshmidt | By Poling | By Shannon (for coordination number 6) |
|---------|-----------------|-----------------|---------------|-----------|--------------------------------------|
| $\text{Co}^{2+}$ | 1.25 | 0.82 | 0.72 | 0.78 |
| $A$, mg/g | | | | | 29.5 (0.5 mmol/g) present work |
| $C_1 = 0.01 \text{M CoCl}_2$ | | | | | |
| $\text{Sr}^{2+}$ | 2.15 | 1.10 | 1.13 | 1.32 |
| $A$, mg/g | | | | | 25.69 (0.292 mmol/g) data from [12] |
| $C_1 = 0.01 \text{M SrCl}_2$ | | | | | |

**Table 6.** Comparative studies of adsorption affinity of mesoporous $\text{TiO}_2$ toward $\text{Co}^{2+}$ and $\text{Sr}^{2+}$ cations

**ADSORPTION OF $^{60}\text{Co}$**

Adsorption of $^{60}\text{Co}$ by mesoporous $\text{TiO}_2$ was investigated in batch mode under and neutral pH from low-level radioactivity solution with dissolved $^{60}\text{Co}$ compound. $^{60}\text{Co}$ emits two $\gamma$-lines with energy 1.17 and 1.33 MeV [19]. The activity of aqueous radioactive solutions of $^{60}\text{Co}$ was determined by a gamma-counter using a NaI(Tl) 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 $\text{TiO}_2$ could be useful as an adsorbent for water purification from $\text{Co}^{2+}$ and in decontaminating of radioactive waste containing $^{60}\text{Co}$.

**CONCLUSIONS**

Adsorption of $\text{Co}^{2+}$ by mesoporous $\text{TiO}_2$ 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 $\text{Co}^{2+}$ by mesoporous $\text{TiO}_2$ 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.

ACKNOWLEDGEMENTS

This work was financially supported by the Ministry of Education and Science of Ukraine (Project number MESU 0117U002408).

Адсорбція катіонів Co$^{2+}$ і радіоактивного $^{60}$Co мезопористим TiO$_2$

Г.В. Васильєва, І.Ф. Миронюк, І.М. Микитин

Ужгородський національний університет
вул. Університетська, 14, Ужгород, 88000, Україна, h.v.vaslyeva@hotmail.com

Прикарпатський національний університет ім. В. Стефаника
вул. Т. Шевченка, 57, Івано-Франківськ, 76000, Україна, myrif555@gmail.com

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

Метою даної роботи – дослідити адсорбцію Co$^{2+}$ і $^{60}$Co із водних розчинів мезопористим TiO$_2$.

Методика експерименту детально описує адсорбційні дослідження. Як агент адсорбент був вибраний мезопористий TiO$_2$ зі співвідношенням мікро- і мезопор $S_{meso}/S = 58 \%$; $V_{meso}/V = 64 \%$. Синтез дослідженої адсорбенти здійснювався за методикою рідкофазного гідролізу титанового аквакомплекса. Як попередній тетрахлорид титану TiCl$_4$.

Залежність адсорбції іонів кобальту від тривалості взаємодії адсорбента з поверхнею адсорбента, кислотності розчину, рівноважної концентрації іонів кобальту була досліджена у статичних умовах. Присутність кобальту на поверхні мезопористого TiO$_2$ була доведена методом рентгенофлуоресцентної спектроскопії.

Похвально та рівноважну концентрацію іонів кобальту визначали методом комплексометричного титрування. Як індикатор використовували ксиленоловий полардановий.

Чотири найбільш поширених кінетичних моделі: Лагергра, псевдо-першого та псевдо-другого порядку, внутрішньофазових дифузії та модель Еловича була застосована 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 рівнянь Дубініна-Радушкевича.

Одержані результати показують, що експериментальні залежності величини адсорбції від часу взаємодії добре апроксимуються кінетичною моделлю Лагергра 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/л) добре узгоджується із розрахунками за теорією Ленгмюра (63.81 мг/л). Енергія адсорбції, розрахована за рівнянням Дубініна-Радушкевича становить 8.104±0.361 кДж/моль, що відповідає фізичному механізму адсорбції. Однак, для кожного окремо взятого потенціалу Польні (якому відповідає певна рівноважна концентрація адсорбату, мг/л) енергія адсорбції змінюється при зростанні рівноважної концентрації Co$^{2+}$ у розчині. Це свідчить про залежність енергії адсорбції йонів
Adsorption of Co\textsuperscript{2+} and radioactive \textsuperscript{60}Co by mesoporous TiO\textsubscript{2}

Адсорбция катионов Co\textsuperscript{2+} и радиоактивного \textsuperscript{60}Co мезопористым TiO\textsubscript{2}

А.В. Васильева, И.Ф. Миронюк, И.Н. Микитин

Ужгородский национальный университет
ул. Университетская, 14, Ужгород, 88000, Украина, h.v.vasylieva@hotmail.com
Прикарпатский национальный университет им. В. Стефаника
ул. Т. Шевченко, 57, Ивано-Франковск, 76000, Украина, myryf555@gmail.com

Вступление к работе раскрывает актуальность данного направления исследований. \textsuperscript{60}Co с периодом полураспада 5.3 года является одним из антропогенных радионуклидов, которые диагностируются в жидких отходах водных установок. Необходимость контроля \textsuperscript{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\textsuperscript{2+} и \textsuperscript{60}Co из водных растворов мезопористым TiO\textsubscript{2}.

Методика эксперимента детально описывает адсорбционные исследования. В качестве адсорбента был выбран мезопористый TiO\textsubscript{2} с соотношением микро- и мезопор S\textsubscript{meso}/S = 58 %, V\textsubscript{meso}/V = 64 %. Синтез исследованного адсорбента осуществляли по методике жидкокристаллического гидролиза титанового оксикомплекса. В качестве прекурсора был выбран тетраклорид титана TiCl\textsubscript{4}. Зависимость адсорбции ионов кобальта от времени взаимодействия адсорбента с поверхностью адсорбента, кислотности раствора, равновесной концентрации ионов кобальта была исследована в статических условиях. Присутствие адсорбированных Co\textsuperscript{2+} на поверхности мезопористого TiO\textsubscript{2} подтверждено методом рентгеновской спектроскопии. Начальной и равновесной концентрации ионов кобальта определяли методом комплексонометрического титрования. В качестве индикатора был использован этилендиаминтетраэтаминовый оранжевый.

Четыре наиболее известные кинетические модели: Лагергrena псевдо-первого и псевдо-второго порядка, модель диффузии встроенная часть адсорбента (модель Бейбера-Морриса) и модель хемосорбции Евловым были использованы для анализа экспериментальных данных кинетики адсорбции ионов кобальта мезопористым TiO\textsubscript{2}. Для описания равновесных изотерм адсорбции были использованы теории адсорбции Лэнгмюра и Дубинина-Радушевского.

Полученные результаты свидетельствуют о том, что экспериментальные зависимости коэффициентов адсорбции от времени взаимодействия хорошо аппроксимируются кинетической моделью Лагергrena псевдо-второго порядка. Используя модель хемосорбции Евлова также даёт высокий коэффициент корреляции (R\textsuperscript{2} > 0.9).

Результаты равновесной адсорбции могут быть описаны теорией Лэнгмюра с высокой степенью достоверности. Экспериментальные значения максимальной адсорбции ионов кобальта мезопористым TiO\textsubscript{2} (49.4 мг/л) хорошо согласуются с величинами, теоретически определенными по теории Лэнгмюра (63.81 мг/л). Энергия адсорбции, определенная по уравнению Дубинина-Радушевского, равна 8.104±0.361 кДж/моль, что соответствует физическому механизму адсорбции. Однако, для каждого отдельно взятого потенциала Польца (которому соответствует определенная равновесная концентрация адсорбата, мг/л) энергия адсорбции разная. Ее значение плавно уменьшается при возрастании равновесной концентрации Co\textsuperscript{2+} в растворе. Это свидетельствует о зависимости энергии адсорбции ионов кобальта мезопористым TiO\textsubscript{2} от степени заполнения поверхности, а значит и о том, что адсорбционные центры.
данных образцов 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 Co²⁺ мезопористым TiO₂ сильно зависит от кислотности раствора.

Чтобы смоделировать условия эксперимента, близкие к реальным, была исследована адсорбция ⁶⁰Co мезопористым TiO₂. Показано, что исследованный адсорбент извлекает большое количество радиоактивного кобальта.

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

**REFERENCES**

1. Abdel-Galila E.A., Moloukhiaa H., Abdel-Khalik M., Mahrousaa S.S. Synthesis and physico-chemical characterization of cellulose/HO-Sb₃ nanocomposite as adsorbent for the removal of some radionuclides from aqueous solutions. *Appl. Radiat. Isot.* 2018. **140**: 363.

2. Xiang-Hong Fang, Fang Fang, Chun-Hai Lu, Lei Zeng Removal of Cs⁺, Sr²⁺, and Co²⁺ ions from the mixture of organics and suspended solids aqueous solutions by zeolites. *Nuclear Engineering and Technology*. 2017. **49**(3): 556.

3. Ray Ph.Z., Shipley H.I. Inorganic nano adsorbents for the removal of heavy metals and arsenic: a reiew. *RSC Adv.* 2015. **5**(38): 29985.

4. Saad A. Al-Jlil Equilibrium study of adsorption of cobalt ions from wastewater using saudi roasted date pits. *Research Journal of Environmental Toxicology*. 2010. **4**(1): 1.

5. Anastopoulos J., Mittal A., Usman M., Mittal J. A review on halloysite-based adsorbents to remove pollutants in water and wastewater. *J. Mol. Liq.* 2018. **269**: 855.

6. Shan B., Chudasma U. Kinetics, thermodynamics and metal separation studies of transition (Co²⁺ , Ni²⁺, Cu²⁺, Zn²⁺) and heavy metal ions (Cd²⁺, Hg²⁺, Pb²⁺) using novel hybrid ion exchanger – Zirconium amino triis methylene phosphonic acid. *Sep. Sci. Technol.* 2018. **54**(10): 1560.

7. Li J., Wang X., Zhao G., Chen Ch., Chai Z., Alsaedi A., Hayat T., Wang X. Metal-organic framework-based materials: superior adsorbents for the capture of toxic and radioactive metal ions. *Chem. Soc. Rev.* 2018. **47**(7): 2322.

8. Al-Shahrani H., Alakhras F., Al-Abbad E., AL-Mazaideh G., Hosseini-Bandegharaei A. Ouerfelli N. Sorption of cobalt (II) ions from aqueous solutions using chemically modified chitosan. *Global NEST Journal*. 2018. **20**(3): 620.

9. Mansoor A., Khosravi F., Dehghan R. Application of hydrothermal and non-hydrothermal TiO₂ nanoporous materials as new adsorbents for removal of heavy metal ions from aqueous system. *J. Ultrafine Grained Nanostructured Materials*. 2016. **49**(1): 36.

10. Graca B., Zakrzewska D., Szymczyhna B. Sorption of Cr, Pb, Cu, Zn, Cd, Ni and Co to nano-TiO₂ in seawater. *Water Sci. Technol*. 2017. **77**(1–2): 145.

11. Mironyuk I., Tatarchuk T., Vasylyeva H., Gun’ko V.M., Mykytyn I. Effects of chemosorbed arsenate groups on the mesoporous titania morphology and enhanced adsorption properties towards Sr(II) cations. *J. Mol. Liq.* 2019. **282**: 587.

12. Mironyuk I., Tatarchuk T., Naushad M., Vasylyeva H., Mykytyn I. Highly efficient adsorption of strontium ions by carbonated mesoporous TiO₂. *J. Mol. Liq.* 2019. **285**: 742.

13. Mironyuk I.F., Chelyadyin V.L. Obtaining methods of titanium dioxide (review). *Phys. Chem. Solid State*. 2010. **11**(4): 815. [in Ukrainian].

14. Mironyuk I.F., Chelyadyin V.L., Kotsyubynsky V.O., Myronyuk L.I. Structure and Morphology of TiO₂ obtaining by Liquid-Phase TiCl₄ hydrolysis. *Phys. Chem. Solid State*. 2011. **12**(2): 416.

15. "Complexometric Titrations." Sigma-Aldrich- Analytical Chromatography. Web. http://www.sigmaaldrich.com/analyticalchromatography/titration/complexometric-titration.html

16. Tran H.N., You S.-J., Hosseini-Bandegharaei A., Chao H.-P. Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: a critical review. *Water Res*. 2017. **120**: 88.

17. Lagergren S., Sven K. About the theory of so-called adsorption of soluble substances. *Vetenskapsakademiens Handlingar*. 1898. **24**(4): 1.
Adsorption of Co$^{2+}$ and radioactive $^{60}$Co by mesoporous TiO$_2$

18. Nguyen C., Do D.D. The Dubinin-Radushkevich equation and the underlying microscopic adsorption description. *Carbon*. 2001. **39**: 1327.

19. https://www.oecd-nea.org/janis

20. Figueiraa P., Lourençob M.A.O., Pereirac E, Gomesa J.R.B., Ferreirab P., Lopesa C.B. Periodic mesoporous organosilica with low thiol density – a safer material to trap Hg(II) from water. *J. Environ. Chem. Eng.* 2017. **5**(5): 5043.

21. Tomul F., Arslan Y., Başoğlu F.T., Babuçcuoğlu Y., Tran H.N. Efficient removal of anti-inflammatory from solution by Fe-containing activated carbon: Adsorption kinetics, isotherms, and thermodynamics. *J. Environ. Manag.* 2019. **238**: 296.

22. Wanga Q., Lia J.Sh., Poona Ch.S. Recycling of incinerated sewage sludge ash as an adsorbent for heavy metals removal from aqueous solutions. *J. Environ. Manag.* 2019. **247**: 509.

23. Tran H.N., Leeb Ch.K., Nguyen T.V., Chaoa H.P. Saccharide-derived microporous spherical biochar prepared from hydrothermal carbonization and different pyrolysis temperatures: synthesis, characterization, and application in water treatment. *Environ. Technol*. 2017. **39**(21):2747.

24. Itodo A.U., Itodo H.U. Sorption Energies Estimation Using Dubinin-Radushkevich and Temkin Adsorption Isotherms. *Life Science Journal*. 2010. **7**(4): 31.

25. Atlas of Eh-pH diagrams Intercomparison of thermodynamic data bases Geological Survey of Japan Open File Report No. 419.

26. Mackay K.M., Mackay R.A., Henderson W. *Introduction to modern inorganic chemistry*. 5th edition. (Blackie Academic and professional, and imprint of Chapman and Hall, 2-6 Boundary Row, London SE1 8NH, UK, 1996).

27. Mansy M.S., Hassan R.S., Selim Y.T., Kenawy S.H. Evaluation of synthetic aluminum silicate modified by magnesia for the removal of $^{137}$Cs, $^{60}$Co and $^{152-154}$Eu from low level radioactive waste. *Appl. Radiat. Isot.* 2017. **130**: 198.

28. Yankovskaya V.S., Dovhyi I.I., Bezinh N.A., Milyutin V.V., Nekrasova N.A., Kapranov S.V., Shulgin V.F. Sorption of cobalt by extraction chromatographic resin on the base of di-(tert-butylbenzo)-18-crown-6. *J. Radioanal. Nucl. Chem.* 2018. **318**(2): 1085.

29. Baldermann A., Criebacher C.A., Baldermann C., Purgstaller B., Letofsky-Papst I. Removal of barium, cobalt, strontium, and zinc from solution by natural and synthetic allophane adsorbents. *J. Geosci.* 2018. **8**: 309.

30. http://www.calculator.net/standard-deviation-calculator.html

*Received 12.08.2019, accepted 20.11.2019*