H. Vasylyeva¹, I. Mironyuk², I. Mykytyn², N. Danyliyk²

Adsorption of Barium and Zinc Ions by Mesoporous TiO₂ with Chemosorbed Carbonate Groups

¹Uzhgorod National University, Uzhgorod, Ukrain, hv.vasylyeva@hotmail.com
²Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, Ukrain, mry555@gmail.com

In the present paper the mesoporous TiO₂ with chemosorbed carbonate groups was investigated as an adsorbent for the removal of Zn²⁺ and Ba²⁺ cations from aqueous solutions.

The dependence of the adsorption values of Zn²⁺ and Ba²⁺ on the agitation time, solution’s acidity, and modification of surface of TiO₂ was determined. The process of Zn²⁺ and Ba²⁺ adsorption fit well by Lagergren’s pseudo-second-order kinetic model. The equilibrium adsorption was investigated in the concentration of heavy metal’s ranges 27.46 mg/L - 7809 mg/L. The experimental data was approximated by Langmuir and Dubinin-Radushkevich equations, and was found to be 15.82 - 9.399 kJ/mol, which corresponds to the mechanism of physical adsorption. The application of Langmuir theory to experimental adsorption data gives high R², close to unit. Separation factor Rᵢ indicates, that adsorption Zn²⁺ and Ba²⁺ onto modified TiO₂ is very favorable.

The mechanism of adsorption of bivalent cations by the modified sample is approximately the same. The difference in the adsorption of Zn²⁺ compared with Ba²⁺ is that cations of Zn²⁺ (with small size) can diffuse into the micro pores of modified TiO₂. The adsorption of Zn²⁺ is not so strongly influenced by the presence of Ba²⁺, as in the adsorption of Ba²⁺ the presence of Zn²⁺ in the solution. This fact can be used for the separation of the Zn²⁺ - Ba²⁺ pair.

Modified mesoporous TiO₂ is very efficient adsorbent toward Zn²⁺ and Ba²⁺ cations from their individual solutions as well as from their mixture, and able to compete with the best world analogues.

Key words: mesoporous TiO₂, adsorption, zinc, barium.


Introduction

The relevance of adsorption removal of Ba²⁺ from water solutions is caused by many factors. Barium is a heavy metal cation and has negative impact on human body.¹³⁹-¹⁴¹ Ba isotopes are formed during nuclear fission reaction of ²³⁵U and are always present in waste of NPP. The need for water purification from barium cations arises in extracting natural gas using hydraulic fracturing (HF) technologies [1, 2]. Zinc is emitted into environment as industrial waste in metallurgy, mining, pharmaceutical, textile and ceramic production [3, 4]. Extraordinary relevance of zinc adsorption studies is caused by the use of ⁶⁵Zn in positron emission tomography. After irradiation of copper target and the formation of ⁶⁵Zn there is a need for separating ⁶⁵Zn from target’s atoms [4-6]. For this purpose an ion exchange resins are used. But the search of new sorbents that possess radiation resistance and high adsorption capacity is still in progress.

For adsorption of Ba²⁺ and Zn²⁺ from water solutions a large number of adsorbents is offered: chitosan, lignocellulose-derived bio sorbents, α-cellulose, mixed silica-alumina oxide, activated fly ash, Na-bentonite, natural zeolite, activated carbon; sorbents based on Fe₃O₄, Al₂O₃, SiO₂ as well as TiO₂ [1-15].

In this work, the mesoporous TiO₂ with chemosorbed carbonate groups was studied to assess its potential for removal of Zn²⁺ and Ba²⁺ cations from aqueous solutions.

Adsorption kinetics, equilibrium and dependence from pH studies were performed to understand the adsorption mechanism. The energy of adsorption E, kJ/mol and separation factor Rᵢ were calculated using Dubinin-Radushkevych and Langmuir equations, as well as adsorption values of Ba²⁺ and Zn²⁺ cations from their mixture.
I. Experimental technique. Synthesis of adsorbents

Synthesis of adsorbents was carried out by the method of liquid phase hydrolysis of aqua complex of TiCl₄. The titanium precursor [Ti(OH₂)₆]³⁺·3Cl⁻ was obtained according to the procedure described in [16]. Sodium carbonate was chosen as a modifying agent.

The synthesis and study of surface characteristics of the mesoporous TiO₂ is describe in detail in the publication I. Mironyuk at all. 2019 [17]. According to results described in [17], adding a modifying agent for percentage provide obtaining TiO₂ nanoparticles with chemosorbed carbonate groups of 2, 4 and 8 percent. The optimum amount of the modifying reagent is 4% (4С-TiO₂). The highest coefficients of Sr²⁺ adsorption were obtained for this sample [17].

The pilot investigation of adsorption of Zn²⁺ by TiO₂ samples with 2, 4, and 8 wt. % modifying reagent were resulted in that the 4С-TiO₂ sample shows the highest adsorption capacity (fig. 1) toward zinc cations. So, 4С-TiO₂ was chosen as an adsorbent for effective removal of Ba²⁺ and Zn²⁺ cations in this study.

The surface area of the modified and unmodified samples was measured by the method of low-temperature adsorption-desorption of nitrogen and calculated by the BET equation. It was found that 4C-TiO₂ 379.9 m²·g⁻¹ is compared with unmodified TiO₂ 239.4 m²·g⁻¹. Mesoporous diameter value was calculated using density functional theory (DFT). Their value is 2.4 - 4.4 nm. Pore volume of 4C-TiO₂ is 0.280 cm³·g⁻¹ that is 2.84 times higher than for unmodified TiO₂. The values of the acidity of the solution at which the point of zero charge was observed are equal pH_pzc = 5.35 for TiO₂ and pH_pzc = 3.36 for 4C-TiO₂.

Modifying the surface with carbonate groups increases pores volume and surface area of mesoporous almost in three times, as well as the total surface area of the adsorbent. Modifying the surface also increases the number of active adsorption centers ≡ТіОНδ⁺, which can attach the cations [17]. The modified 4C-TiO₂ has the largest number of such centers as well as the highest percentage of active centers, compared with other investigated samples. In [17] was shown, that the main mechanism of adsorption of Sr²⁺ associated with the presence of ≡ТіОНδ⁺ - groups on the surface of 4C-TiO₂.

The surface area of the modified and unmodified samples was measured by the method of low-temperature adsorption-desorption of nitrogen and calculated by the BET equation. It was found that 4C-TiO₂ 379.9 m²·g⁻¹ is compared with unmodified TiO₂ 239.4 m²·g⁻¹. Mesoporous diameter value was calculated using density functional theory (DFT). Their value is 2.4 - 4.4 nm. Pore volume of 4C-TiO₂ is 0.280 cm³·g⁻¹ that is 2.84 times higher than for unmodified TiO₂. The values of the acidity of the solution at which the point of zero charge was observed are equal pH_pzc = 5.35 for TiO₂ and pH_pzc = 3.36 for 4C-TiO₂.

Fig. 1. Effect of contact time on the adsorption of Zn²⁺ onto unmodified and modified TiO₂ (a); (b) Isotherms of adsorption of Zn²⁺ cations onto unmodified and modified TiO₂ (pH = 7, ratio of solid / liquid phase 100).

Table 1

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>239.4</td>
<td>100.5</td>
<td>138.9</td>
<td>58</td>
<td>0.152</td>
<td>0.054</td>
<td>0.098</td>
<td>64.5</td>
</tr>
<tr>
<td>4C-TiO₂</td>
<td>379.9</td>
<td>7.26</td>
<td>372.6</td>
<td>98</td>
<td>0.280</td>
<td>0.001</td>
<td>0.279</td>
<td>99.6</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>By Holdshmidt</td>
<td>By Poling</td>
<td>By Shanon CN** 6</td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>1.37</td>
<td>9.39</td>
<td>18.0</td>
<td>0.83</td>
</tr>
<tr>
<td>Barium</td>
<td>2.24</td>
<td>5.21</td>
<td>10.0</td>
<td>1.29</td>
</tr>
</tbody>
</table>

** By Shanon for coordination number 6 [18].

Therefore, modified mesoporous TiO$_2$ is a very promising adsorbent toward Zn$^{2+}$ and Ba$^{2+}$ cations.

Results of adsorption of heavy metals cations onto modified TiO$_2$ has been compared with ones onto unmodified TiO$_2$.

II. Butch adsorption studies

Adsorption investigations are provided in butch mode with solid / liquid phase ratio equal to 100. The effect of solution pH, contact time, initial (equilibrium) ion concentrations on adsorption of metal ions were studied. For each experiment, 0.05g of adsorbent is mixed with 5mL of a corresponding cation and slowly shaken. The initial and residual concentration of heavy metals cations was determined using complexonometric titration with Eriochrom Black T as indicator. Studying the negative effect of simultaneous presence of Ba$^{2+}$ and Zn$^{2+}$ in their mixture was provided from the solution, which consist of equal volume of 0.01M BaCl$_2$ and 0.01M ZnCl$_2$. The combination of complexonometric titration and precipitation of Ba$^{2+}$ into the form of barium chromate were used [18, 19].

To investigate the influence of pH on adsorption of barium and zinc a certain amount of the solutions of 1M, 0.1M, 0.01M HNO$_3$ as well as 1% і 10% NH$_4$OH were used. The value of solution’s acidity was controlled by pH meter “Belarus” – 2003”.

The adsorption values were measured using equations (1, 2):\
\[
A_e = \frac{(C_0 - C_e) \times V}{m}, \quad (1)
\]
\[
\% \text{ removal} = \frac{C_0 - C_e}{C_0} \times 100, \quad (2)
\]
were $C_0$ (mg/L) - $C_e$ (mg/L) initial and residual (equilibrium) concentration of adsobate in solution, respectively; $V$ (L) - solution volume, m (g) – dried mass of used adsorbent.

To determine the mechanism of adsorption of barium and zinc cations a nonlinear approximation of Langmuir equations (3)
\[
A_e = \frac{A_{max} K_L C_e}{1 + K_L C_e}, \quad (3)
\]
as recommended by H.N.Tran, S.-J. You at all. [13] and linear approximation of Dubinin-Radushkevych equation (5, 6) were used. The adsorption energy was measured using Dubinin-Radushkevych equations (4) and (5):
\[
A_e = A_{max} \times \exp(-\beta \varepsilon^2) = A_{max} \times \left[-\beta \times \left(RT \ln \left(1 + \frac{1}{C_e}ight)\right)\right], \quad (4)
\]
\[
E = \frac{1}{(2\beta)^{1/2}} \quad (5)
\]

According H.N.Tran, S.-J. You at all. 2017 and ref. [20], calculation of the parameter of Langmuir equation $K_L$ allows to estimate the factor $R_L$ for adsorption process of Ba$^{2+}$ and Zn$^{2+}$ cations using equation (6)
\[
R_L = 1/(1 + K_L C_0), \quad (6)
\]

III. Result and discussion

3.1.Effect of contact time on the adsorption of Zn$^{2+}$ and Ba$^{2+}$ by modified and unmodified TiO$_2$

To determine a suitable contact time between the studied sorbent and the metal solutions, the fraction removed from Ba$^{2+}$ and Zn$^{2+}$ ions is determined and plotted as a function of time from 5 to 150 min if other parameters are constant. Fig. 2 shows the obtained results.

Adsorption kinetic data in the initial contact time period play an important role in drawing valid conclusions. Four simplified kinetic models: pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich (or Roginski-Zeldovych) kinetic models were applied to experimental data.

The results on fig. 3 and in table 3 shows that that adsorption of Ba$^{2+}$ by 4С−ТіО$_2$ occurs rapidly: the equilibrium established in the first thirty minutes of interaction. For Zn$^{2+}$ a state of equilibrium is reaching only after 120 min.

The adsorption value of Ba$^{2+}$ cations (for initial concentration of BaCl$_2$ 0.005M) by 4С−ТіО$_2$ equal 63.39 mg/g which is higher than 15.6 mg/g for unmodified samples. The adsorption value of Zn$^{2+}$ onto the sample 4С−ТіО$_2$ equal 28.5 mg/g, and 9.425 mg/g onto the unmodified TiO$_2$.

The Lagergren’s pseudo-second-order kinetic model the best described the process of adsorption of cations.

The initial rate of adsorption of barium cations from individual solutions is higher than that for zinc cations. This is evidenced by the form of the experimental kinetics plots of the Ba$^{2+}$ and Zn$^{2+}$. This conclusion was confirmed by the calculated constants of the kinetic models: intra-particle diffusion and Elovich (table. 3).
3.2. Investigation of equilibrium adsorption.

The Langmuir adsorption theory is used to describe the equilibrium between adsorbate and adsorbent system, supposing that adsorption is limited to one molecular layer and locate on adsorption centers. The adsorption capacity is calculated by Langmuir equation (3). From the other hand, the Dubinin-Radushkevich equation (4) was proposed as the empirical adaptation of the Polanyi adsorption potential theory [21]. The Dubinin-Radushkevich equation (4) generally applies well to adsorption system involving only Van der Waals forces in micro pores of adsorbent [21]. In our work were used both of this theory. Results in table 4, 5 and on fig. 5 and 6.

The best correspondence between the experimental adsorption values and theoretically calculated using Dubinin-Radushkevych equation, as well as the highest R² (0.92) was obtained for adsorption of barium by 4C-TiO₂. The energy of adsorption of Ba²⁺ by 4C-TiO₂ calculated using Dubinin-Radushkeyvych equation is 9.399 kJ/mol, which corresponds to the mechanism of physical adsorption.

### Table 3

<table>
<thead>
<tr>
<th>Model</th>
<th>adsorbent</th>
<th>Ba (II) Rate constants of Correspond equation</th>
<th>R²</th>
<th>Zn (II) Rate constants of Correspond equation</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first</td>
<td>4C·TiO₂</td>
<td>-0.008 min⁻¹</td>
<td>0.7843</td>
<td>-0.009 min⁻¹</td>
<td>0.9603</td>
</tr>
<tr>
<td></td>
<td>TiO₂</td>
<td>-0.0148 min⁻¹</td>
<td>0.8565</td>
<td>-0.015 min⁻¹</td>
<td>0.9835</td>
</tr>
<tr>
<td>Pseudo-second</td>
<td>4C·TiO₂</td>
<td>0.015 g·mg⁻¹ min⁻¹</td>
<td>0.9990</td>
<td>0.0337 g·mg⁻¹ min⁻¹</td>
<td>0.9846</td>
</tr>
<tr>
<td></td>
<td>TiO₂</td>
<td>0.063 g·mg⁻¹ min⁻¹</td>
<td>0.9997</td>
<td>0.098 g·mg⁻¹ min⁻¹</td>
<td>0.9803</td>
</tr>
<tr>
<td>Elovich</td>
<td>4C·TiO₂</td>
<td>β = 0.1695 mg·g⁻¹ min⁻¹</td>
<td>0.9233</td>
<td>β = 0.2906 mg·g⁻¹ min⁻¹ and 9.62</td>
<td>0.8248</td>
</tr>
<tr>
<td></td>
<td>TiO₂</td>
<td>β = 1.075 mg·g⁻¹ min⁻¹</td>
<td>0.8052</td>
<td>β = 0.74 mg·g⁻¹ min⁻¹ and 9.62</td>
<td>0.8383</td>
</tr>
<tr>
<td>Diffusion</td>
<td>4C·TiO₂</td>
<td>K_ped = 0.3 mg·g⁻¹ min⁻¹²⁺</td>
<td>0.5443</td>
<td>K_ped = 1.38 mg·g⁻¹ min⁻¹²⁺</td>
<td>0.9240</td>
</tr>
<tr>
<td></td>
<td>TiO₂</td>
<td>K_ped = 2.04 mg·g⁻¹ min⁻¹²⁺</td>
<td>0.7439</td>
<td>K_ped = 0.53 mg·g⁻¹ min⁻¹²⁺</td>
<td>0.9000</td>
</tr>
</tbody>
</table>

Fig. 3. Application of kinetic models: a – pseudo-first-order; b – pseudo-second-order; c – intraparticle diffusion; d – Elovich to experimental data of adsorption of Ba²⁺ and Zn²⁺ by 4C-TiO₂ and unmodified TiO₂.
The equilibrium adsorption of Ba\(^{2+}\) and Zn\(^{2+}\) fits well to Langmuir adsorption theory. The nonlinear approximation was applied to optimization the parameter of Langmuir equation \(K_L\) and \(A_{\text{max}}\); means decrease the bias between \(A_e\) values determined from the experiment and those estimated from the model [20, 22-24].

The results shown on fig. 6 (a, b).

In brief description, the experimental results of equilibrium adsorption are better approximated by the Langmuir model compared with the Dubinin-Radushkevich model. Calculated values of maximal adsorption are in good agreement with the experimental ones.

The factor \(R_L\) for both cations is smaller than unit.

### Table 4

Parameters of Dubinin-Radushkevich equation and adsorption energy for adsorption Zn\(^{2+}\) and Ba\(^{2+}\) by TiO\(_2\) and 4C-TiO\(_2\).

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>(A_{\text{exp}},) mg/g</th>
<th>(A_{\text{calc}},) mg/g</th>
<th>(\beta)</th>
<th>(E = 1/\sqrt{2}\text{slope}) kJ/mol</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(II) TiO(_2)</td>
<td>40.937</td>
<td>1540</td>
<td>-0.004</td>
<td>11.1856</td>
<td>0.7699</td>
</tr>
<tr>
<td>Zn(II) 4C-TiO(_2)</td>
<td>130</td>
<td>50.40</td>
<td>-0.002</td>
<td>15.8227</td>
<td>0.7644</td>
</tr>
<tr>
<td>Ba(II) TiO(_2)</td>
<td>104</td>
<td>57.397</td>
<td>-0.0048</td>
<td>10.207</td>
<td>0.6466</td>
</tr>
<tr>
<td>Ba(II) 4C-TiO(_2)</td>
<td>302</td>
<td>232.75</td>
<td>-0.0056</td>
<td>9.399</td>
<td>0.9214</td>
</tr>
</tbody>
</table>

### Table 5

Parameters of Langmuir equation of adsorption isotherms of Ba\(^{2+}\) and Zn\(^{2+}\) cation by the sample of TiO\(_2\) and 4C-TiO\(_2\) and factor \(R_L\).

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>(A_{\text{exp}},) mg/g</th>
<th>(A_{\text{max}},) mg/g</th>
<th>(K_L)</th>
<th>(R_L)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(II) TiO(_2)</td>
<td>40.94</td>
<td>42.5</td>
<td>0.002651</td>
<td>0.94-0.06</td>
<td>0.999</td>
</tr>
<tr>
<td>Zn(II) 4C-TiO(_2)</td>
<td>130</td>
<td>169.23</td>
<td>0.000611</td>
<td>0.88-0.22</td>
<td>0.990</td>
</tr>
<tr>
<td>Ba(II) TiO(_2)</td>
<td>104</td>
<td>161.55</td>
<td>0.000228</td>
<td>0.99-0.36</td>
<td>0.812</td>
</tr>
<tr>
<td>Ba(II) 4C-TiO(_2)</td>
<td>302</td>
<td>324</td>
<td>0.001399</td>
<td>0.95-0.08</td>
<td>0.999</td>
</tr>
</tbody>
</table>

**Fig. 4.** Isotherms of adsorption of Zn\(^{2+}\) and Ba\(^{2+}\) by TiO\(_2\) and 4C-TiO\(_2\); pH=7; solid / liquid phase ratio equal 100.

**Fig. 5.** Isotherms of adsorption of Zn\(^{2+}\) and Ba\(^{2+}\) by TiO\(_2\) and 4C-TiO\(_2\). Linear approximation by Dubinin-Radushkevich model.

**Fig. 6.** Langmuir Isotherm of adsorption of Ba\(^{2+}\) by (a) 4C-TiO\(_2\) and (b) TiO\(_2\) (nonlinear approximation [20]).
(R_k < 1). This, according to H.N.Tran, S.-J. You at all. 2017 [20], shows that the process of adsorption of Ba^{2+} and Zn^{2+} is favorable for investigated adsorbents.

3.3. pH dependence of adsorption of Ba^{2+} and Zn^{2+} by modified and unmodified TiO_2

It was found that the pH solution has a great influence on the adsorption process [20, 25-28]. The effect of solution pH on the sorption removal of Ba^{2+} and Zn^{2+} ions by modified and unmodified TiO_2 is shown on fig. 7.

As it has already mentioned, the point of zero charge of the surface of the synthesis samples is pH_{PZC} = 5.35 for TiO_2 and pH_{PZC} = 3.36 for 4C-TiO_2. Minimum of the adsorption values were observed in the range of pH near of point of zero charge (fig.7). The sample 4C-TiO_2 exhibits a higher adsorption capacity in the acidic medium than the unmodified TiO_2, which at the pH < 5.35 practically does not adsorb metal cations. Carbonate groups shift the point of a zero charge pH_{PZC} from 5.35 to 3.36; the functionality of the sorbent expands, and provides an effective adsorption of metals in the acid solutions.

Fig. 7. pH dependence of adsorption of Ba^{2+} and Zn^{2+} onto modified and unmodified TiO_2. Initial concentration of cations 0.005 M.

Adsorption of the studied cations occurs through

![Figure 7](image)

**Table 6**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Element</th>
<th>A, mg/g</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na_2Ti_3O_7-T3 nanofibers</td>
<td>Ba^{2+}</td>
<td>160</td>
<td>[6]</td>
</tr>
<tr>
<td>α_2Ti_3O_5-3(H)</td>
<td>Ba^{2+}</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>Titanate nanoflowers</td>
<td>Zn^{2+}</td>
<td>98.1</td>
<td></td>
</tr>
<tr>
<td>Titanate nanotubes TNT</td>
<td>Zn^{2+}</td>
<td>44.67</td>
<td></td>
</tr>
<tr>
<td>Titanate nanotubes TNW</td>
<td>Zn^{2+}</td>
<td>27.66</td>
<td></td>
</tr>
<tr>
<td>TiO_2-AM</td>
<td>Zn^{2+}</td>
<td>27.66</td>
<td></td>
</tr>
<tr>
<td>Nano γ-Fe_2O_3</td>
<td>Zn^{2+}</td>
<td>84.95</td>
<td></td>
</tr>
<tr>
<td>TiO_2</td>
<td>Zn^{2+}</td>
<td>40.94</td>
<td>Present work</td>
</tr>
<tr>
<td>4C-TiO_2</td>
<td>Ba^{2+}</td>
<td>104.36</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zn^{2+}</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ba^{2+}</td>
<td>275</td>
<td></td>
</tr>
</tbody>
</table>
surface reactions between the hydroxide surface and the dissolved metal cations. On the surface of 4C-TiO$_2$ in the range of pH value 1-7 this reaction could be described as:

\[ 2 \text{TiO}_2 \cdot \text{Zn}^2+ + 2\text{Zn}^2+ + 2\text{OH}^- \rightarrow 2\text{Zn}^2+(\text{TiO}_2 \cdot \text{Zn}^2+) + 2\text{H}_2\text{O} \] (pH = 1-7)

In alkali medium Zn exist in the form ZnOH$^+$ [25], and interaction realize by the reaction below:

\[ \text{TiO}_2 \cdot \text{Zn}^2+ \leftrightarrow \text{TiO}_2 \cdot \text{ZnOH}^+ \ (\text{pH} > 7) \]

The mechanism of adsorption of bivalent cations (Sr$^{2+}$ [17], Ba$^{2+}$ and Zn$^{2+}$) by the modified sample is approximately the same. The difference in the adsorption of Zn$^{2+}$ is that Zn$^{2+}$ can diffuse into the micro pores due to its small size. Therefore, the plots of A (mg/g) of Zn$^{2+}$ vs t (min)/ln t fig. 2, 2(d) have a gradual form.

### 3.4. Adsorption of barium and zinc from their mixture by modified TiO$_2$

As can be seen on figure 8 (a), 4C-TiO$_2$ adsorbed 80% of whole barium and 60% of whole zinc from individual solutions. With the simultaneous presence of Ba$^{2+}$ and Zn$^{2+}$ in the solution, their adsorption decreases to 50% for Zn$^{2+}$ and 45% for Ba$^{2+}$.

The adsorption of Zn$^{2+}$ is not so strongly influenced by the presence of Ba$^{2+}$, as in the adsorption of Ba$^{2+}$ the presence of Zn$^{2+}$ in the solution. This fact can be used for the separation of the Zn$^{2+}$ - Ba$^{2+}$ pair. On the other hand, even with the presence of a competing ion in the solution, the modified TiO$_2$ intensively adsorb cations of investigated heavy metals, especially Zn$^{2+}$ cations. To our opinion, this is due to the fact that, ion radius of Zn$^{2+}$ is much smaller than that for Ba$^{2+}$ and some of Zn$^{2+}$ cations is adsorbing in the microporous of the modified sample.

Sample 4C-TiO$_2$ is very efficient adsorbent toward Zn$^{2+}$ and Ba$^{2+}$ cations from their individual solutions as well as from their mixture. 4C-TiO$_2$ able to compete with the best world analogues [1-15, 20-28] (Table 6.).

### Conclusion

The mesoporous TiO$_2$ with chemosorbed carbonate groups was investigated as an adsorbent for the removal of Zn$^{2+}$ and Ba$^{2+}$ cations from aqueous solutions. In electrolytic mediums, modified adsorbent shows higher adsorption capacity toward Zn$^{2+}$ and Ba$^{2+}$ cations, compared to unmodified adsorbent.

Increasing of adsorption of barium and zinc cations onto modified TiO$_2$ are in good agreement with increasing of surface area and pore volume/diameter. The developed mesoporous structure, large surface area and the ionogenic nature of chemosorbed groups provides its high selectivity for the adsorption of Zn$^{2+}$ and Ba$^{2+}$ cations. In solutions with concentrations BaCl$_2$ and/or ZnCl$_2$ from 0.01 mol L$^{-1}$ to 0.1 mol L$^{-1}$ the adsorption of heavy metal cations by modified adsorbent in 2-2.7 times higher than adsorption by an unmodified adsorbent. The experimental data of adsorption kinetic of Zn$^{2+}$ and Ba$^{2+}$ cations fits well with the pseudo-second order kinetic model.

The equilibrium adsorption of Zn$^{2+}$ and Ba$^{2+}$ cations was investigated in the range of concentrations 27.46 - 7809 mg/L. The equilibrium adsorption is fitting well by Langmuir adsorption theory. Supposing, that adsorption centers of 4C-TiO$_2$ are the positive ≡TiOH$^+$ groups in mesoporous.

The application of Dubinin-Radushkevich theory shows, that the best correspondence between the experimental adsorption values and theoretically calculated using Dubinin-Raduskevych equation was obtained for adsorption of barium by 4C-TiO$_2$. The energy of adsorption of Ba$^{2+}$ by 4C-TiO$_2$ is 9.399 kJ/mol, which corresponds to the mechanism of physical adsorption.

Since carbonate groups shift the point of a zero charge pH$pzc$ from 5.35 to 3.36, Modified 4C-TiO$_2$ provides an effective adsorption of metals in the acid solutions.

The mechanism of adsorption of bivalent cations (Sr$^{2+}$ [17], Ba$^{2+}$ and Zn$^{2+}$) by the modified sample is approximately the same. The difference in the adsorption of Zn$^{2+}$ is that cations of Zn$^{2+}$ can diffuse into the micro pores due to its small size. Sample 4C-TiO$_2$ is very efficient adsorbent toward Zn$^{2+}$ and Ba$^{2+}$ cations from their individual solutions as well as from their mixture. 4C-TiO$_2$ able to compete with the best world analogues.

### Acknowledgements

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

---

**Vasylyeva H.V.** - Associated Professor;  
**Mironyuk I.F.** - Professor, head of Department of Chemistry;  
**Mykytyn I.M.** - Associated Professor of Department of Chemistry;  
**Danyliyk N.** - magister of Department of Chemistry.

---


[3] Evelina Muuri. The sorption and diffusion of $^{137}$Ba in granitic rocks. (Master’s thesis University of Helsinki Faculty of Science Department of Chemistry Laboratory of Radiochemistry, 2015).

Adsorption of Barium and Zinc Ions by Mesoporous TiO$_2$...


Адсорбція йонів барію та цинку мезопористим TiO₂ з хемосорбованими карбонатними групами

Г. Васильєва¹, І. Миронюк², І. Микитин², Н. Данилюк¹

Адсорбція їонів барію та цинку мезопористим TiO₂ з хемосорбованими карбонатними групами

¹Ужгородський національний університет, Ужгород, Україна. h.v.vasylyeva@hotmail.com
²Прикарпатський національний університет ім. Василя Стефаника, Івано-Франківськ, Україна. myrif555@gmail.com

У даній роботі запропоновано мезопористий TiO₂ з хемосорбованими карбонатними групами у якості адсорбенту для вилучення катіонів цинку і барію із водних розчинів. Досліджено залежність величин адсорбції від тривалості взаємодії, кислотності розчину, рівноважної концентрації катіонів Zn²⁺ і Ba²⁺ а також модифікації поверхні TiO₂. До одержаних результатів застосовано чотири найбільш поширених кінетичних моделей: Лагергрена псевдо-першого та псевдо-другого порядків, модель внутрішньочастинкової дифузії та модель хемосорбції Еловича. Показано, що експериментальні величини адсорбції Zn²⁺ і Ba²⁺ апроксимуються кінетичною моделлю Лагергрена псевдо-другого порядку з великою степінню достовірності (R²=0.99).

Досліджено рівноважну адсорбцію у інтервалі концентрації важких металів 27.46 мг/л - 7809 мг/л. До одержаних експериментальних даних застосовано теорії адсорбції Ленгмюра і Дубініна-Радушенковича. З використанням рівняння Дубітіна-Радушенковича розраховано енергію адсорбції цинку і барію модифікованим і немодифікованим TiO₂, значення якої лежать у межах 15.82 - 9.399 кДж/моль, що відповідає механізмові фізичної адсорбції. Експериментальні результати адсорбції катіонів барію і цинку добре описуються теорією Ленгмюра (R²=0.99).

Механізм адсорбції двовалентних катіонів приблизно однаковий. Висловлено припущення, що різниця у адсорбції їонів цинку порівняно з їонами барію полягає у тому, що катіони Zn²⁺, маючи невеликий їонний радіус, здатні дифундувати у мікроорієнтаційного TiO₂, тоді як катіони Ba²⁺ адсорбуються у мезопорах. При одночасній присутності катіонів барію і цинку у розчині у першу чергу поглинається цинк. На його адсорбцію не так сильно впливає присутність Ba²⁺, як на адсорбцію барію – присутність катіонів цинку. Цей факт може бути корисним при необхідності сорбційного розділення пари Zn²⁺ - Ba²⁺.

Мезопористий TiO₂ з хемосорбованими карбонатними групами є дуже ефективним адсорбентом щодо катіонів Zn²⁺ і Ba²⁺. Він здатний адсорбувати катіони Zn²⁺ і Ba²⁺, як із індивідуальних розчинів, так і з сумішей. Досліджений адсорбент є кращим у цьому плані, ніж більшість світових аналогів.

Ключові слова: мезопористий TiO₂, адсорбція, цинк, барій.