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

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In the present paper the mesoporous TiO₂ with chemosorbed carbonate groups was investigated as an adsorbent for the removal of Zn^{2+} and Ba^{2+} cations from aqueous solutions.

The dependence of the adsorption values of Zn^{2+} and Ba^{2+} on the agitation time, solution's acidity, and modification of surface of TiO₂ was determined. The process of Zn^{2+} and Ba^{2+} 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-Radushcevich adsorption theories. The energy of adsorption Zn^{2+} and Ba^{2+} onto modified TiO₂ and unmodified TiO₂ was calculated using 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 R^2, close to unit. Separation factor R_L indicates, that adsorption Zn^{2+} and Ba^{2+} 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 Zn^{2+} compared with Ba^{2+} is that cations of Zn^{2+} (with small size) can diffuse into the micro pores of modified TiO₂. 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.

Modified mesoporous TiO₂ is very efficient adsorbent toward Zn^{2+} and Ba^{2+} 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 Ba^{2+} 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 [235]U 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 [63]Zn in positron emission tomography. After irradiation of copper target and the formation of [63]Zn, there is a need for separating [63]Zn 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 Ba^{2+} and Zn^{2+} 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 Fe_2O_3, Al_2O_3, SiO_2 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 Zn^{2+} and Ba^{2+} 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 R_L were calculated using Dubinin-Radushkevych and Langmuir equations, as well as adsorption values of Ba^{2+} and Zn^{2+} 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 TiCl$_4$. The titanium precursor [Ti (OH$_2$)$_6$]$^{3+}$·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 TiO$_2$ 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 TiO$_2$ nanoparticles with chemosorbed carbonate groups of 2, 4 and 8 percent. The optimum amount of the modifying reagent is 4% (4C-TiO$_2$). The highest coefficients of Sr^{2+} adsorption were obtained for this sample [17].

The pilot investigation of adsorption of Zn^{2+} by TiO$_2$ samples with 2, 4, and 8 wt. % modifying reagent were resulted in that the 4C-TiO$_2$ sample shows the highest adsorption capacity (fig. 1) toward zinc cations. So, 4C-TiO$_2$ was chosen as an adsorbent for effective removal of Ba^{2+} and Zn^{2+} 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-TiO$_2$ 379.9 m^2·g^{-1} is compared with unmodified TiO$_2$ 239.4 m^2·g^{-1}. Mesoporous diameter value was calculated using density functional theory (DFT). Their value is 2.4 -4.4 nm. Pore volume of 4C-TiO$_2$ is 0.280 cm^3·g^{-1} that is 2.84 times higher than for unmodified TiO$_2$ (Table 1.). The values of the acidity of the solution at which the point of zero charge was observed are equal pH$_{PZC}$ =5.35 for TiO$_2$ and pH$_{PZC}$ =3.36 for 4C-TiO$_2$

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 ≡TiOH$^{\delta+}$, which can attach the cations [17]. The modified 4C-TiO$_2$ 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 Sr^{2+} associated with the presence of ≡TiOH$^{\delta+}$ - groups on the surface of 4C-TiO$_2$.

| a | b |
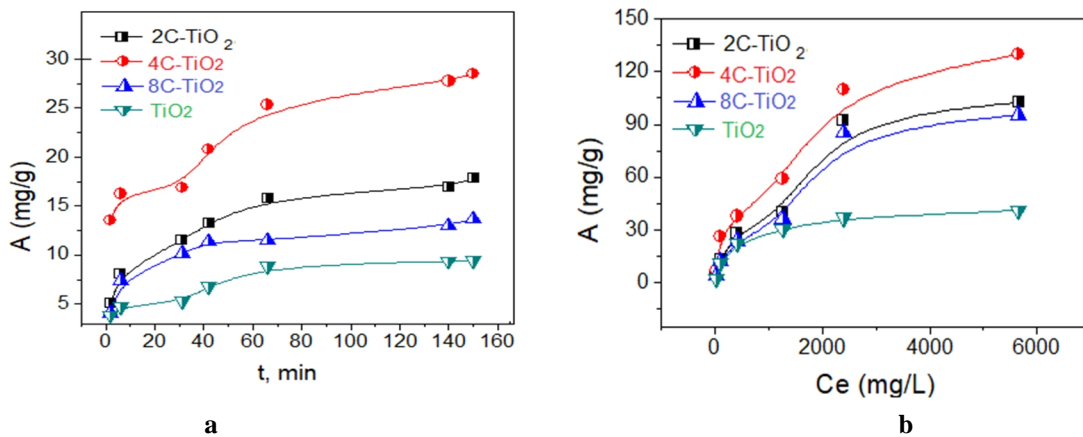
Fig. 1. Effect of contact time on the adsorption of Zn^{2+} onto unmodified and modified TiO$_2$ (a); (b) Isotherms of adsorption of Zn^{2+} cations onto unmodified and modified TiO$_2$ (pH = 7, ratio of solid / liquid phase 100).

Table 1

Morphology of investigated adsorbents according to I. Mironyuk at all. 2019 [17]

Adsorbent	S, m^2·g^{-1}	S$_{micro}$ m^2·g^{-1}	S$_{meso}$ m^2·g^{-1}	S$_{meso}$/S, %	V cm^3·g^{-1}	V$_{micro}$ cm^3·g^{-1}	V$_{meso}$ cm^3·g^{-1}	V$_{meso}$/V, %
TiO$_2$	239.4	100.5	138.9	58	0.152	0.054	0.098	64.5
4C-TiO$_2$	379.9	7.26	372.6	98	0.280	0.001	0.279	99.6

Table 2

Atomic radii and ionization energy of barium and zinc [18]

Element	Atomic radius*, [11]	1st Ionization Energy, eV	2nd Ionization Energy, eV	Ion radius, Zn^{2+} and Ba^{2+}		
				By Holdshmidt	By Poling	By Shanon CN** 6
Zinc	1.37	9.39	18.0	0.83	0.74	0.88
Barium	2.24	5.21	10.0	1.29	1.35	1.49

** 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 solution of 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% i 10% NH_4OH were used. The value of solution's acidity was controlled by pH meter "Belarus' – 2003".

The adsorption values were measured using equations (1, 2):

$$Ae = \frac{(C_0 - C_e) \times V}{m}, \quad (1)$$

$$\%removal \ \frac{(C_0 - C_e) \times 100}{C_0}, \quad (2)$$

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)

$$A_e = \frac{AmaxKLC_e}{1 + KLC_e}, \quad (3)$$

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):

$$A_e = A_{max} \times exp(-\beta \varepsilon^2) = A_{max} \times \left[-\beta \times \left(RT \ln \left(1 + \frac{1}{C_e} \right)^2 \right) \right], \quad (4)$$

$$E = \frac{1}{(2\beta)^{\frac{1}{2}}} \quad (5)$$

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)

$$R_L = 1/(1 + K_L C_o), \quad (6)$$

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.
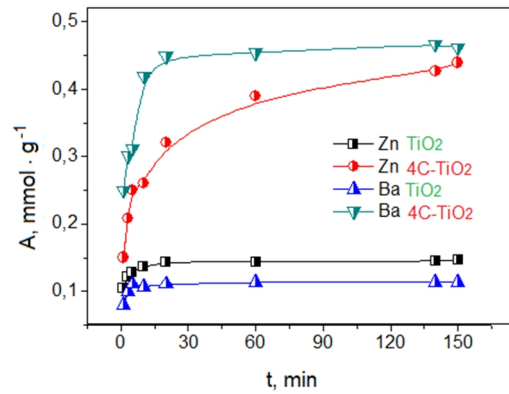
Fig. 2. Efect of contact time on the adsorption of Zn^{2+} and Ba^{2+} by TiO_2 and $4C\text{-}TiO_2$; initial metal concentration 0.005M; pH = 7; solid/liquid phase ratio equal 100.

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 $4C\text{-}TiO_2$ 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 $4C\text{-}TiO_2$ 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 $4C\text{-}TiO_2$ 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).
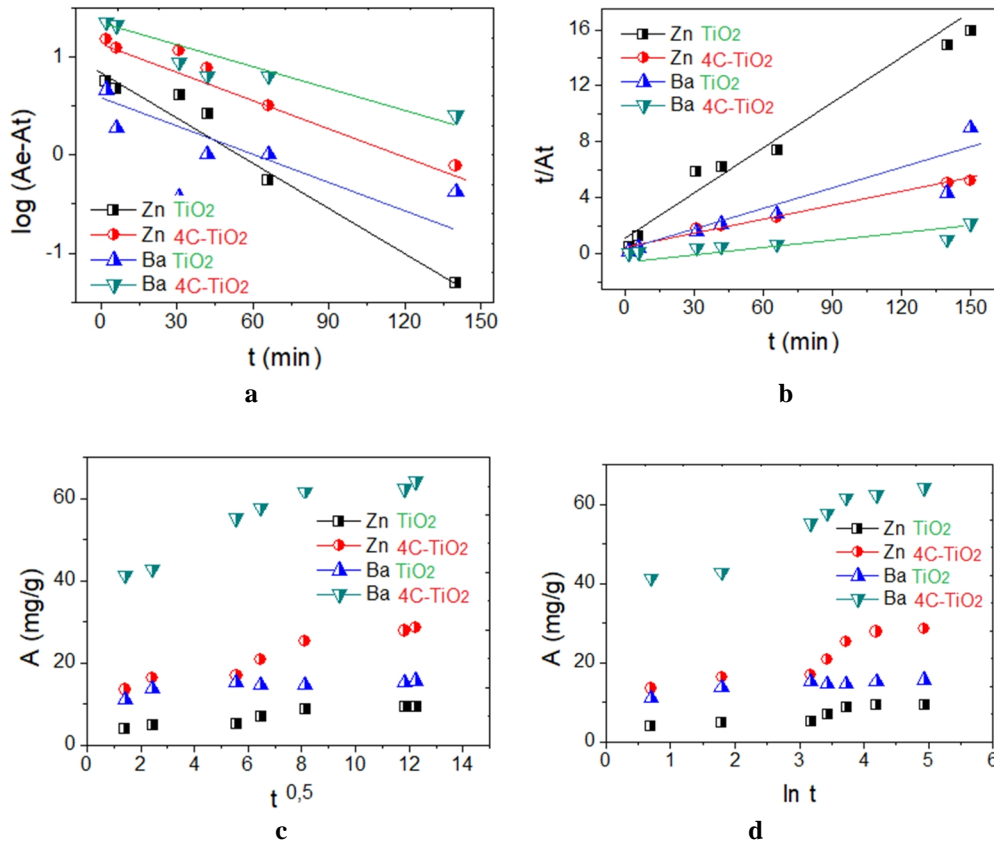
Fig. 3. Application of kinetic models: a – pseudo-first-order; b –pseudo-second-order; c – intraparticle diffusion; d – Elovich to experimental data of adsorption of Ba^{2+} and Zn^{2+} by 4C-TiO$_2$ and unmodified TiO$_2$.

Table 3

Parameters of equations of kinetic models

Model	adsorbent	Ba (II) Rate constants of Correspond equation	R^2	Zn (II) Rate constants of Correspond equation	R^2
Pseudo-first	4C- TiO$_2$	-0.008 min^{-1}	0.7843	-0.009 min^{-1}	0.9603
	TiO$_2$	-0.0148 min^{-1}	0.8565	-0.015 min^{-1}	0.9535
Pseudo-second	4C- TiO$_2$	0.015g·mg^{-1}min^{-1}	0.9990	0.0337g·mg^{-1}min^{-1}	0.9846
	TiO$_2$	0.063 g·mg^{-1}min^{-1}	0.9997	0.098 g·mg^{-1}min^{-1}	0.9803
Elovich	4C- TiO$_2$	$\beta = 0.1695$ mg·g^{-1}min^{-1}	0.9233	$\beta = 0.2906$ mg·g^{-1}min^{-1} 9,62	0.8248
	TiO$_2$	$\beta = 1.075$ mg·g^{-1}min^{-1}	0.8052	$\beta = 0.74$ mg·g^{-1}min^{-1} 2,3	0.8383
Difusion	4C- TiO$_2$	$K_{ipd} = 0.3$ mg·g^{-1} min^{0,5}	0.5443	$K_{ipd} = 1.38$ mg·g^{-1} min^{0,5}	0.9240
	TiO$_2$	$K_{ipd} = 2.04$ mg·g^{-1} min^{0,5}	0.7439	$K_{ipd} = 0.53$ mg·g^{-1} min^{0,5}	0.9000

### 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-Radushkevich equation, as well as the highest R^2 (0.92) was obtained for adsorption of barium by 4C-TiO$_2$. The energy of adsorption of Ba^{2+} by 4C-TiO$_2$ calculated using Dubinin-Radushkevych equation is 9.399 kJ/mol, which corresponds to the mechanism of physical adsorption.

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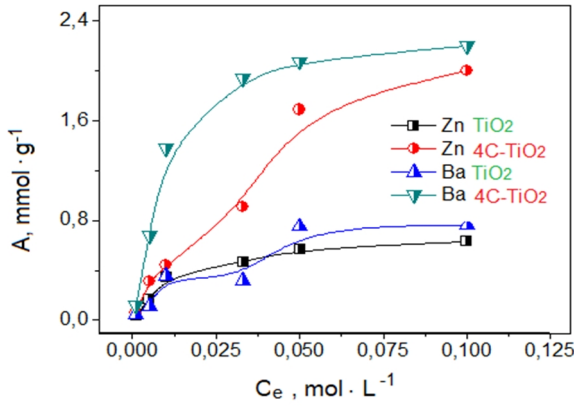
Fig. 4. Isotherms of adsorption of Zn^{2+} and Ba^{2+} by TiO_2 and 4C- TiO_2; pH=7; solid / liquid phase ratio equal 100.
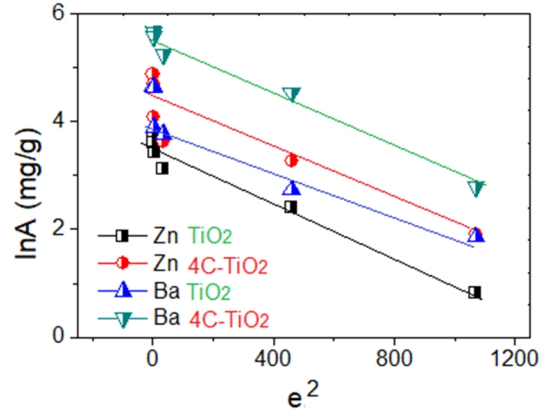
Fig. 5. Isotherms of adsorption of Zn^{2+} and Ba^{2+} by TiO_2 and 4C- TiO_2. Linear approximation by Dubinin-Radushkevich model.

Table 4

Parameters of Dubinin-Radushkevych equation and adsorption energy for adsorption Zn^{2+} and Ba^{2+} by TiO_2 and 4C- TiO_2

| Adsorbent	A_{exp}, mg/g	A_{calc} mg/g	β	E =$1/\sqrt{2slope}$ kJ/mol	R^2
Zn(II)TiO$_2$	40.937	1540	-0.004	11.1856	0.7699
Zn(II) 4C- TiO$_2$	130	50.40	-0.002	15.8227	0.7644
Ba(II)TiO$_2$	104	57.397	-0.0048	10.207	0.6466
Ba(II) 4C- TiO$_2$	302	232.75	-0.0056	9.399	0.9214

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

Adsorbent	A_{exp}, mg/g	A_{max}, mg/g	K_L	R_L	R^2
Zn(II)TiO$_2$	40.94	42.5	0.002651	0.94-0.06	0.999
Zn(II) 4C- TiO$_2$	130	169.23	0.000611	0.88-0.22	0.990
Ba(II)TiO$_2$	104	161.55	0.000228	0.99-0.36	0.812
Ba(II) 4C- TiO$_2$	302	324	0.001399	0.95-0.08	0.999
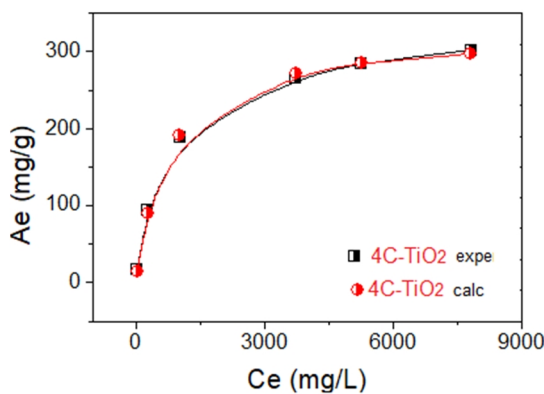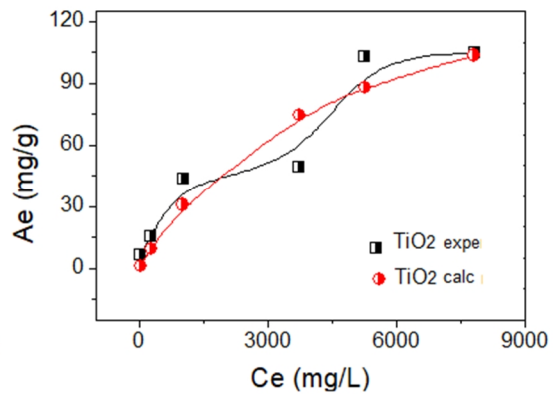
a **b**

Fig.6. Langmuir Isotherm of adsorption of Ba^{2+} by (a) 4C-TiO_2, and (b) TiO_2 (nonlinear approximation [20]).

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_{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-Radushkevych 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

($R_L < 1$). 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 $4C\text{-}TiO_2$. Minimum of the adsorption values were observed in the range of pH near of point of zero charge (fig.7). The sample $4C\text{-}TiO_2$ 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.
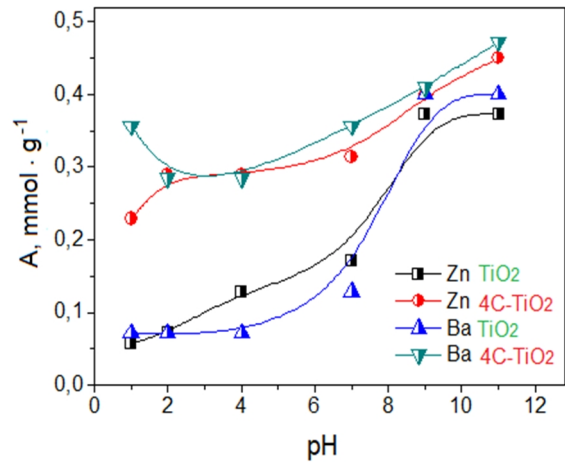
Fig. 7. pH dependence of adsorption of Ba^{2+} and Zn^{2+} onto modified and unmodified TiO_2. Initial concentration of cations 0.005 M.

Adsorption of the studied cations occurs through

a

b
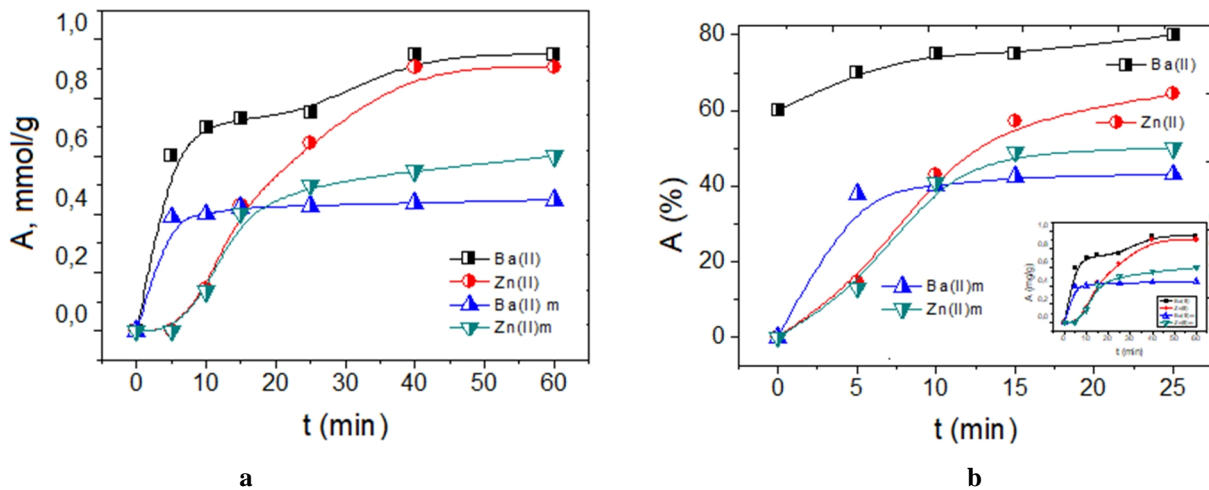
Fig. 8. Adsorption of barium and zinc by $4C\text{-}TiO_2$ from their mixture: (a) adsorption values in mmol/g; (b) in percent; $N_{Ba,Zn} = 0.01M$; pH=7; adsorption values of Ba^{2+} and Zn^{2+} from the mixture is indicate on the (fig.8) by index 'm'.

Table 6

Adsorption capacity values of different types of adsorbents toward Ba^{2+} i Zn^{2+} [6]

Adsorbent	Element	A, mg/g	Source
Na₂Ti₃O₇-T3 nanofibers	Ba^{2+}	160	[6]
α₂ Ti₃O – 3(H)	Ba^{2+}	130	
Titanate nanoflovers	Zn^{2+}	98.1	
Titanate nanotubes TNT	Zn^{2+}	44.67	
Titanate nanotubes TNW	Zn^{2+}	27.66	
TiO₂-AM	Zn^{2+}	27.66	
Nano γ-Fe₂O₃	Zn^{2+}	84.95	
TiO₂	Zn^{2+}	40.94	Present work
	Ba^{2+}	104.36	
4C-TiO₂	Zn^{2+}	130	
	Ba^{2+}	275	

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:

$$2 \equiv TiO- + Zn^{2+} \leftrightarrow (TiO-) \, 2 \, Zn^{2+} \, (pH = 1-7)$$

In alkali medium Zn exist in the form ZnOH$^+$ [25], and interaction realize by the reaction below:
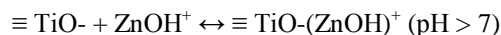
$$\equiv TiO- + ZnOH^+ \leftrightarrow \equiv TiO-(ZnOH)^+ \, (pH > 7)$$

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 $\equiv TiOH^{\delta+}$ groups in mesoporous.

The application of Dubinin-Radushkevich theory shows, that the best correspondence between the experimental adsorption values and theoretically calculated using Dubinin-Radushkevych 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.

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Адсорбція йонів барію та цинку мезопористим TiO₂ з хемосорбованими карбонатними групами

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У даній роботі запропоновано мезопористий TiO₂ з хемосорбованими карбонатними групами у якості адсорбенту для вилучення катіонів цинку і барію із водних розчинів. Досліджено залежність величини адсорбції від тривалості взаємодії, кислотності розчину, рівноважної концентрації катіонів Zn^{2+} і Ba^{2+} а також модифікації поверхні TiO₂. До одержаних результатів застосовано чотири найбільш поширені кінетичні моделі: Лагергрена псевдо-першого та псевдо-другого порядку, модель внутрішньочастинкової дифузії та модель хемосорбції Еловича. Показано, що експериментальні величини адсорбції Zn^{2+} і Ba^{2+} апроксимуються кінетичною моделлю Лагергрена псевдо-другого порядку з великою степінню достовірності (R^2= 0.99).

Досліджено рівноважну адсорбцію у інтервалі концентрацій важких металів 27.46 мг/л - 7809 мг/л.

До одержаних експериментальних даних застосовано теорії адсорбції Ленгмюра і Дубініна-Радушкевича. З використанням рівняння Дубініна-Радушкевича 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 (R^2 =0,99).

Механізм адсорбції двовалентних катіонів приблизно однаковий. Висловлено припущення, що різниця у адсорбції йонів цинку порівняно з йонами барію полягає у тому, що катіони Zn^{2+}, маючи невеликий йонний радіус, здатні дифундувати у мікропори модифікованого TiO₂ , тоді як катіони Ba^{2+} 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 Ba^{2+} , як на адсорбцію барію – присутність катіонів цинку. Цей факт може бути корисним при необхідності сорбційного розділення пари Zn^{2+} - Ba^{2+}.

Мезопористий TiO₂ з хемосорбованими карбонатними групами є дуже ефективним адсорбентом щодо катіонів Zn^{2+} і Ba^{2+}. Він здатний адсорбувати катіони Zn^{2+} і Ba^{2+} 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.