

УДК 538.9, 54-1

PACS 64, 82.20 Hf

DOI 10.24144/2415-8038.2018.43.28-33

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KINETIC OF SORPTION OF Sr²⁺ IONS FROM AQUEOUS SOLUTIONS BY SYNTHETIC INORGANIC SORBENTS

Purpose: All chemical processes including adsorption occur in complicated mechanism and are reversible. After some time equilibrium has introduced. These complex mechanisms can be divided into a number of simple stages, which can be described by relatively simple mathematical equations. In this study the adsorption of Sr²⁺ ions from aqueous solutions by synthetic inorganic sorbents Titanium Phosphate (PhTi) and Zirconium Silicate (ZrSi) was investigated. To simulate the adsorption kinetic, two commonly used models Elovich and Diffusion kinetic models were applied. In addition to Elovich kinetic model experimental data of sorption must have a linear dependence in coordinates A_t vs $\ln t$, investigating adsorption processes is chemisorption, and limiting step of adsorption is surface chemical reaction. In addition to Diffusion kinetic model, for example, intra particle diffusion - the limiting step of adsorption is the diffusion stage of Sr²⁺ from solution to the surface of sorbent. Diffusion in micro porous carries the character of activated diffusion, which usually described by Weber and Morris. The experimental data is the plot in coordinate A_t vs $t^{1/2}$.

Methods: Titanium Phosphate (PhTi) and Zirconium Silicate (ZrSi) synthesized in Institute of Sorption and Endoecology Problems NAS of Ukraine, Kyiv. Porous radius and volume, as well as surface area were investigated in the same institute using low temperature adsorption-desorption of Nitrogen and BET adsorption equation. To study the effect of pH and agitation time on adsorption of Sr²⁺ ions, batch studies performed and unadsorbed ions of Sr²⁺ analyzed using complexometric titration.

Results: For all the systems, which examined, the Elovich kinetic model provided better correlation of the experimental data. For ZrSi the stage of diffusion deep into the sorbent is also an important stage. This is due to the fact, that Zirconium Silicate is a micro porous material with a narrow distribution of pore radii. It was observed that maximum adsorption coefficients take place at pH ~ 11.

Conclusions: It was shown, that adsorption of Sr²⁺ ions strongly depend on time of interaction between solution and surface of sorbents; as well as solution's acidity. The sorption coefficients of Sr²⁺ by Titanium Phosphate are higher than by Zirconium Silicate. To simulate the adsorption kinetics, two commonly used models Elovich and Diffusion were applied. For all the systems, the Elovich kinetic model provided better correlation. It was observed that maximum adsorption coefficients take place at pH ~ 11. The pH of the solution may change the surface charge of the adsorbent and increase the probability of surface complex formation of -OH-Sr⁺ or -OH-Sr-OH compounds.

Keywords: strontium, titanium phosphate, zirconium silicate, kinetic model.

The adsorption of Strontium (Sr²⁺) ions from aqueous solutions is of considerable practical importance in many areas. Many types of sorbents can be used for this purpose.

In this study the adsorption of Sr²⁺ ions from aqueous solutions by synthetic inorganic

sorbents Titanium Phosphate (PhTi) and Zirconium Silicate (ZrSi) was investigated. For the practical use of the sorbents, it is necessary to know the kinetics of the sorption process (dependence the course of the sorption process on time). The possibility of

representing the experimental data of the dependence of value of adsorption on time within some kinetic model allows better understanding the sorption mechanism and predicting the results.

All chemical processes including sorption occur in complicated mechanism and are reversible. After some time equilibrium has introduced. However, these complex mechanisms can be divided into a number of simple stages, which can be described by relatively simple mathematical equations.

To simulate the adsorption kinetic, two commonly used models Elovich and Diffusion kinetic models were applied for Sr^{2+} - PhTi and Sr^{2+} - ZrSi interactions. The main equations of two these models are given in table 1.

Table 1. Simplified equations of Elovich and Diffusion kinetic models.

Kinetic models	Linear equation of kinetic model
Elovich	$A_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t$ (1)
Diffusion (Intra-particle diffusion)	$A_t = k_{\text{dif}} t^{1/2} + C$ (2) $A_t = k_{\text{dif}} \sqrt{t}$

A_t – adsorption coefficient [$\text{mg}\cdot\text{g}^{-1}$] or [$\text{mmol}\cdot\text{g}^{-1}$] at contact time t [min]; A_e – equilibrium adsorption coefficient, [$\text{mg}\cdot\text{g}^{-1}$] or [$\text{mmol}\cdot\text{g}^{-1}$]; k_{dif} , α , β – constants of Elovich and Diffusion kinetic models.

In addition to Elovich kinetic model experimental data of sorption must have a linear dependence in coordinates A_t vs $\ln t$. In that case the under investigating sorption processes is chemical sorption process.

In addition to Diffusion kinetic model, for example, intra particle diffusion -the limiting step of sorption is the diffusion stage of Sr^{2+} from solution to the surface of sorbent. Diffusion in micro porous carries the character of activated diffusion, which usually is described by Weber and Morris [4-6]. The experimental data is the plot in coordinate A_t vs $t^{1/2}$.

Experimental technique

Experimental studies of strontium removal from aqueous solutions carried out

using stable isotopes of Sr in the form of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$.

Titanium Phosphate (PhTi) and Zirconium Silicate (ZrSi) were synthesized in Institute of Sorption and Endoecology Problems NAS of Ukraine, Kiyv. Porous radius and volume, as well as surface area were investigated in the same institute using low temperature (77 K) adsorption-desorption of Nitrogen [1, 2] and BET adsorption theory.

To study the effect of pH and agitation time on adsorption of Sr^{2+} ions, we were performed batch studies at the room temperature of 18°C. The mass of sorbent was 50 mg, volume of solution – 5 ml. We performed intermittent shaking. We withdrew the mixture at specified interval of time and unabsorbed supernatant liquid was analyzed for the residual dye concentration using complexometric titration. The initial concentration of Sr^{2+} ions in aqueous solutions were $0,005 \text{ mol}\cdot\text{l}^{-1}$ (2,2 mg of element in 5 ml of solution). Amount of adsorbed Sr^{2+} was calculated using the concentration in solutions before and after adsorption process.

The initial pH's of the solutions were controlled by adding a 4 ml 10% HNO_3 or 5ml 10% NH_4OH , using pH – meter pH-150M «Bilorus' 2003».

All the adsorption tests were performed at least twice. The sorption coefficients were measured using equation from literature [1]. The correlation coefficients (R^2), arithmetic mean and error of arithmetic mean were calculated using EXCEL and internet sources [10, 11].

Results and discussion

The effect of contact time on adsorption of Sr^{2+} ions onto Titanium Phosphate and Zirconium Silicate as well as the pH dependence of sorption coefficients were measured. The obtained results are shown in figures 1-3, 5, and tables 2, 3.

For all the systems, which were examined, the Elovich kinetic model provided better correlation of the experimental data. For ZrSi the stage of diffusion deep into the sorbent is also an important stage. This is due to the fact, that zirconium silicate is a micro

porous material with a narrow distribution of pore radii (see in fig.4).

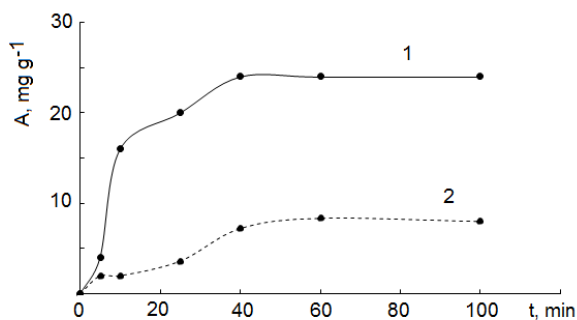
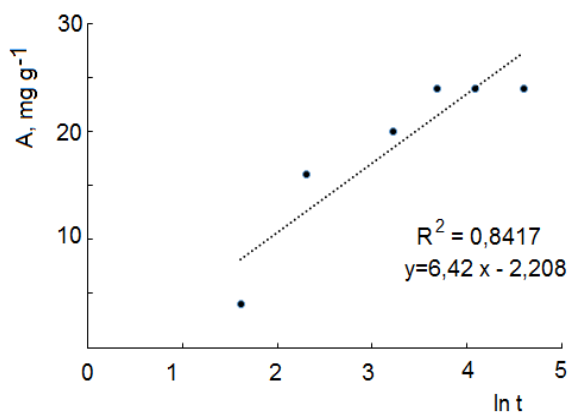


Fig. 1. The effect of contact time on adsorption of Sr^{2+} ions onto: (1) Titanium Phosphate, (2) Zirconium Silicate.

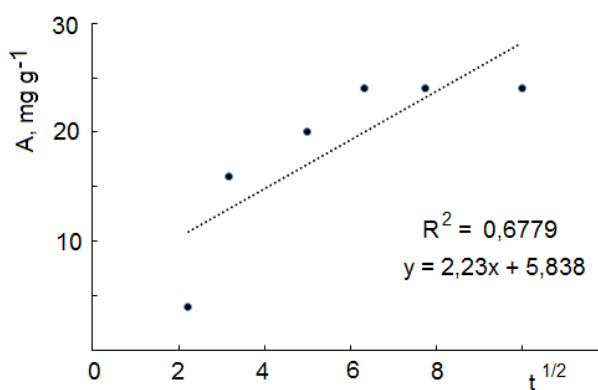
It was observe that maximum adsorption coefficients take place at $\text{pH} \sim 11$. The pH of the solution may change the surface charge of the adsorbent and increase

the probability of surface complex formation of $-\text{OH}-\text{Sr}^+$ or $-\text{OH}-\text{Sr}-\text{OH}$ compounds. While the both adsorbents Titanium Phosphate and Zirconium Silicate has $-\text{OH}$ functional groups on their surface.

For the neutral and alkaline medium, the sorption coefficients of Sr^{2+} onto both sorbents have not changed. This means, that with this value of the solution's acidity, sorption equilibrium already has been establish. In the acidic medium, the equilibrium of sorption of Sr^{2+} ions is set slower and therefore in the range of 45 – 90 minute the coefficients of sorption of Sr^{2+} ion are still increasing. For Titanium Phosphate, the coefficients of Sr^{2+} 's adsorption in the range of 45 – 90 minute, on the contrary, decreases; and the pH dependence acquires the standard form.

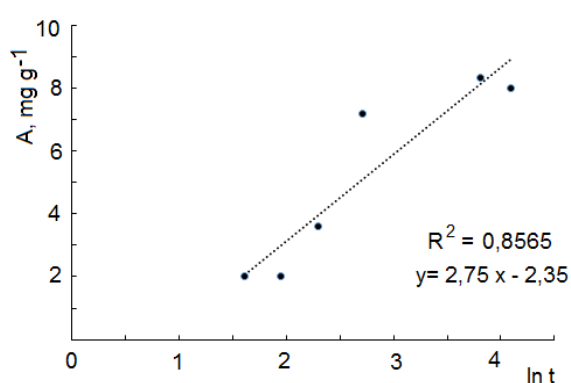


(1)

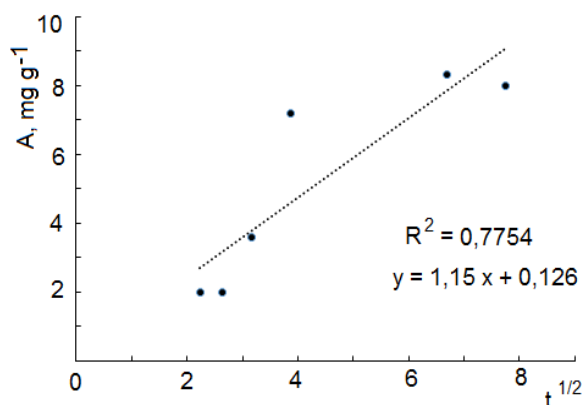


(2)

Fig.2. Plot of: (1) Elovich equation, (2) Diffusion model equation for sorption of Sr^{2+} ions on to Titanium Phosphate.



(1)



(2)

Fig.3. Plot of: (1) Elovich equation, (2) Diffusion model equation for sorption of Sr^{2+} ions on to Zirconium Silicate.

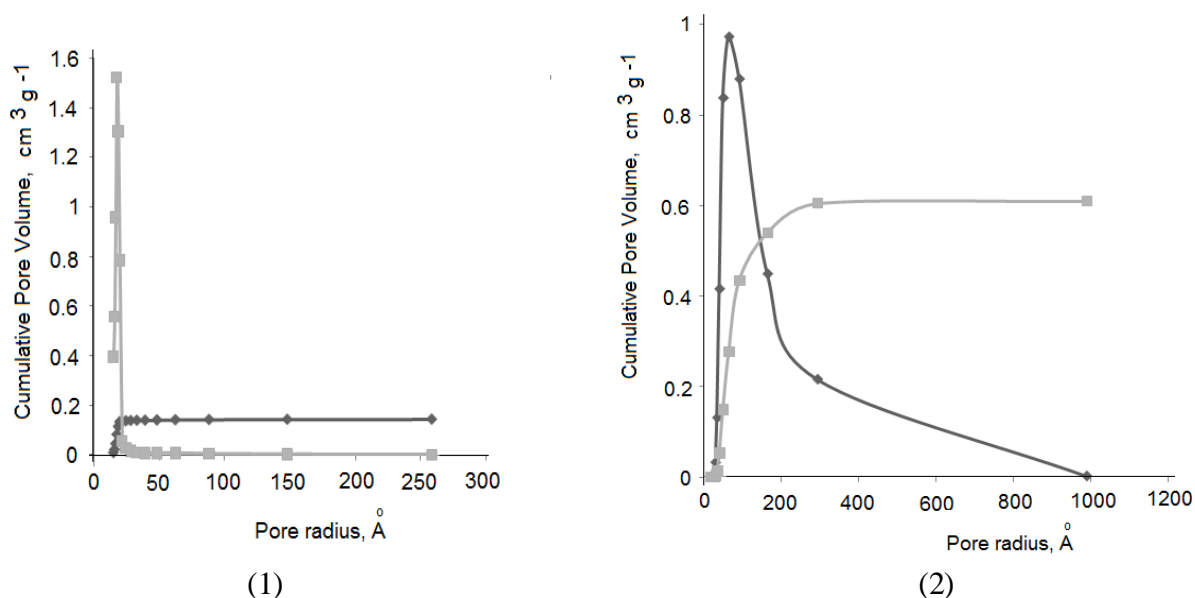


Fig.4. Pore radius and volume (1) for ZrSi; (2) for PhTi

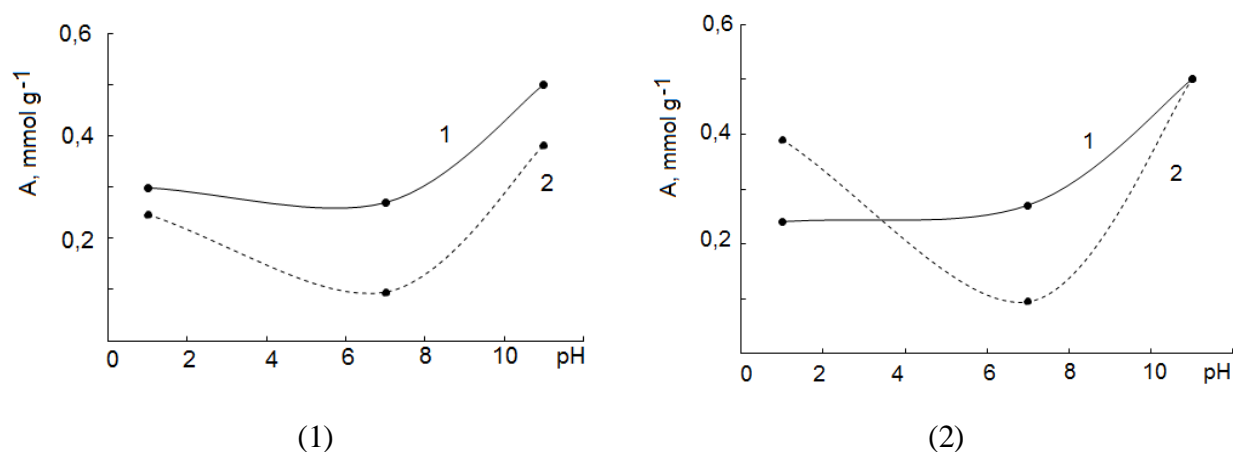


Fig.5. pH dependence of sorption of Sr^{2+} ions: 1- PhT; 2- ZrSi (1) contact time is 45 min; (2) contact time is 90 min.

Table 2. Apply the Elovich and Diffusion kinetic models to experimental adsorption data for Sr^{2+} ions from aqueous solutions at pH=7.

sorbent	Elovich kinetic model	R^2	Diffusion kinetic model	R^2
PhTi	$A = 6,4 \ln t + 2,21$	0,84	$A = 2,23 \sqrt{t} + 5,84$	0,68
ZrSi	$A = 2,75 \ln t - 2,35$	0,86	$A = 1,15 \sqrt{t} + 0,13$	0,78

Table 3. pH dependence of sorption coefficients (A , mmol/g) of Sr^{2+} ions by titanium phosphate and zirconium silicate (45 min sorption)

sorbent	pH = 1	pH = 7	pH = 11
titanium phosphate	$0,299 \pm 0,019$	$0,27 \pm 0,015$	$0,5 \pm 0,025$
zirconium silicate	$0,246 \pm 0,018$	$0,095 \pm 0,008$	$0,5 \pm 0,020$

Conclusion

1. In this study, the kinetic of removal of Sr²⁺ ions from aqueous solutions onto PhTi and ZrSi was investigate in the batch mode. It was shown, that sorption of Sr²⁺ ions strongly depend on time of interaction between solution and surface of sorbents; as well as solution's acidity. The sorption coefficients of Sr²⁺ by Titanium Phosphate are higher than by Zirconium Silicate.
2. To simulate the adsorption kinetics, two commonly used models Elovich and

Diffusion were apply. For all the systems, which were examined, the Elovich kinetic model provided better correlation of the experimental data.

3. It was observe that maximum adsorption coefficients take place at pH ~ 11. The pH of the solution may change the surface charge of the adsorbent and increase the probability of surface complex formation of –OH-Sr⁺ or –OH-Sr-OH compounds.

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Стаття надійшла до редакції 09.04.2018.

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КИНЕТИКА СОРБЦИИ ИОНОВ Sr^{2+} ИЗ ВОДНЫХ РАСТВОРОВ СИНТЕТИЧЕСКИМИ НЕОРГАНИЧЕСКИМИ СОРБЕНТАМИ

В этом исследовании исследовали кинетику удаления ионов Sr^{2+} из водных растворов на фосфат титана и силикат циркония в периодическом режиме. Сорбция ионов Sr^{2+} сильно зависит от времени взаимодействия раствора и поверхности сорбентов; а также кислотности раствора. Для моделирования кинетики адсорбции применялись две широко используемые модели Elovich и Diffusion. Для всех рассматриваемых систем кинетическая модель Эловина обеспечивала лучшую корреляцию экспериментальных данных.

Ключевые слова: стронций, фосфат титана, силикат циркония, модель кинетики.

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КИНЕТИКА СОРБЦІЇ ІОНІВ Sr^{2+} З ВОДНИХ РОЗЧИНІВ СИНТЕТИЧНИМИ НЕОРГАНІЧНИМИ СОРБЕНТАМИ

Досліджено кінетику видалення іонів Sr^{2+} з водних розчинів на фосфат титану і силикат цирконію в періодичному режимі. Сорбція іонів Sr^{2+} сильно залежить від часу взаємодії розчину і поверхні сорбентів; а також кислотності розчину. Для моделювання кінетики адсорбції застосовувалися дві широко відомі кінетичні моделі Еловича (Elovich) і внутрішньо частинкової дифузії (Intra particle Diffusion). Для всіх розглянутих систем кінетична модель Еловича забезпечувала кращу кореляцію експериментальних даних.

Ключові слова: стронцій, фосфат титану, силикат цирконію, модель кінетики.

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