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THE TITANIUM SILICATE INFLUENCE ON THE Zn(II) AND Sr(II) MIGRATION IN THE AQUATIC ENVIRONMENT

The aim of the present work is titanium silicate influence on the zinc and strontium migration in the aquatic environment. The adsorption capacity of titanium silicate toward zinc and strontium ions was investigated. With the aid of a fluorescent X-ray analyzer and energy dispersive spectroscopy the composition of the sorbent formed was determined as well as zinc and strontium presence on the surface of the sorbent after the sorption process. It was shown, that adsorption of zinc and strontium by titanium silicate strongly depends on time of interaction and solution acidity and increases with increasing of both parameters. It was established, that for the initial concentration of zinc and strontium at the level of 0.005M the presence of ions that cause the natural mineralization of water does not affect their adsorption extraction.

Keywords: adsorption, strontium, zinc, titanium silicate, radionuclides migration, XRF-analysis.

1. Introduction

Natural waters from artesian wells often contain a certain amount of stable isotopes of strontium. Therefore, the adsorption of strontium cations by different types of adsorbents is actual to all regions of Ukraine and the Transcarpathia region as well. As the investigations in radioecology include the development of environmentally predictive models, the experience of extracting stable isotopes of strontium removing from natural waters of a certain mineral composition will be used to predict the possibility of removing its radioactive analog ⁹⁰Sr, which could enter any ecosystem as a result of accidents or terrorist attacks. Zinc is a waste of forest chemical production and a common polluter of the rivers of Transcarpathia. Zinc is found in the water and sediments of the River Uzh where it flows with rain or meltwater [1]. Radioactive zinc isotopes could be corrosive radionuclides as well. ⁹⁰Sr is a fission radionuclide [1, 2], which can be found in the NPP waste of 438 operating nuclear reactors in the world; liquid radioactive waste includes also ^{134,137}Cs, ^{154,155}Eu, ²²⁶Ra, ⁶⁰Co et al.

Many investigations are devoted to the migration of radionuclides in the environment. In publication [2] the migration of ^{134,137}Cs and ^{154,155}Eu were measured in the vertical profiles of the soils of 5-km nearest ChNPP zone. The uranium isotopes distribution was investigated in underground water and Cooling Pond [2 - 5]. It was shown, that migration of uranium ions increases with increasing pH higher than 9 - 10, and with increasing the amount of co-existing ions K⁺, Na⁺, Ca²⁺, CO₃²⁻, NO₃⁻, NO₂. The cycling charac-

ter of seasonal changes of ¹³⁷Cs activity concentration in water was analysed in publications [2, 7]. It was shown, that the cycling character of seasonal changes of ¹³⁷Cs activity is linked to hydrochemical, temperature, and oxygen regimes of the Cooling Pond.

The maximum permissible concentrations of some heavy metals in water are quite low, for example, 1.3 mg/L, 0.005 mg/L, 0.05 mg/L, and 0.05mg/L are the upper limits for Zn²⁺, Cd²⁺, Pb²⁺ and Cr⁶⁺ in drinking water (US Environmental Protection Agency) [6]. This is due to the fact, that the excess of heavy metals in water causes a number of dangerous diseases of the central nervous system, kidneys, liver, and even causes cancer. Therefore, the control of the content of heavy metals and radionuclides in the water environment is important, as well as clearing water from heavy metals and radionuclides waste. In this case, the presence of substances with adsorption properties in the cycle of migration radionuclides is able to reduce their content in environmental objects, impedes migration of pollutants, and significantly improves the quality of water [7].

Many synthetic and natural adsorbents are offered for the purification of aqueous solutions from contamination of zinc and strontium: zeolites [7], phosphates of polyvalent metals, adsorbents based on titanium compounds, carbon nanotubes with nitrogen or oxygen groups on the surface, or kaolinite nanotubes [8 - 12]. Among different adsorbents, the titanium compounds occupy an important place. Their unique properties ensure their widespread use for a variety of scientific purposes [8 - 10, 12, 13].

Some scientific publications are devoted to investigations of adsorption of strontium and other heavy metals by adsorbents based on titanium compounds [8, 10, 14, 15]. Among such compounds titanium silicate occupies a significant place. The synthesis of titanium silicate uses the waste of titanium production industries [15, 16], which is an advantage since titanium silicate has a dual environmental benefit. Titanium silicate exhibited high adsorption activity toward strontium ions [15, 16] from distilled water and different solutions such as 0.1M HCl, and Ringer-Locke's solution. However, the influence of co-existing ions K^+ , Na^+ , Ca^{2+} , CO_3^{2-} of natural water on the adsorption of zinc and strontium by titanium silicate is still unclear.

The present work is devoted to adsorption of zinc and strontium by titanium silicate from distilled water (environmentally predictive simulation), as well as investigation of the possibility of zinc and strontium adsorption from natural water from River Uzh (Uzhgorod). The influence of duration of interaction, water acidity, and presence of co-existing ions, which formed a natural mineralization of water, on adsorption of corresponding ions onto titanium silicate was tested.

2. Experimental technique

Titanium silicate was synthesized in ISPE, NAS of Ukraine, with the technique described in [15]. For the synthesis of titanium silicates, a titanium sulphate solution was used. This solution was not subjected to additional purification and was taken from the technological sulphate line of production of the rutile white titanium pigment. The surface area was measured using low-temperature adsorption-desorption of nitrogen 'Quantachrom', USA. Its value was $193 \text{ m}^2/\text{g}$, pore volume $V = 0.61 \text{ cm}^3/\text{g}$, pore radius $r = 73 \text{ \AA}$. This sample has a highly developed surface and has a certain amount of macropore. Chemical composition of the adsorbent was confirmed using XRF (Bruker AXS, Karlsruhe, Germany) and EDS (EVO 18 research) analysis (KINR, Kyiv, Ukraine). This adsorbent has a biporous structure, according to [15]. This fact is very useful, because zinc cation's adsorption is higher in micropores [10].

The stable isotopes of zinc and strontium were used in the form of $SrCl_2$ and $ZnSO_4$. Initial and residual concentration of Zn^{2+} and Sr^{2+} were determined using direct complexometric titration [15], and by XRF of the surface of titanium silicate as well.

The solution of Zn^{2+} and Sr^{2+} was prepared by dissolving of corresponding compound in distilled water or river water from River Uzh. The amount of zinc or strontium was the same and in the final solution the concentration of heavy metal was found to be

0.005 mol/L (325 mg/L of Zn^{2+} and 440 mg/L of Sr^{2+}). The samples of river water were taken in the time interval of 19.10.2019 - 12.12.2019 from the Uzh River within the city ($48^{\circ}37'00 \text{ N } 22^{\circ}18'00 \text{ E}$) according to the recommendations described in [1]. Water samples were filtered off from solid contaminants and sand.

The rivers of Ukrainian Carpathian have the water of pronounced hydro carbonate calcium composition and relatively small mineralization (150 - 250 mg/L) [17]. So, investigating of adsorption up-taking zinc and strontium from river water was provided with simultaneous presence co-existing ions (HCO_3^-), Ca^{2+} , Mg^{2+} et al. Such ions, as was shown in [5] increase radionuclides migration in the water environment, i.e. decreases their adsorption.

The effect of solution acidity on adsorption processes was investigated using a certain amount of HNO_3 or NH_4OH . The solution's acidity (pH) was controlled by pH-meter "Belarus' 2003". The adsorption values and residual concentrations were calculated by equations (1), (2) [10]:

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

$$C_{res} = \frac{C_o - C_e}{V}, \quad (2)$$

where are A_e – the amount of uptaken adsorbate, mg/g; C_o and C_e – initial and residual concentrations of adsorbate, mg; C_{res} – residual concentration, mg/L; V – the volume of solution, L; m – mass of adsorbent, g.

3. Results and discussion

The more common ion charge for zinc and strontium is (+2). Zinc has a relatively small ionic radius compared with strontium, which has a relatively large one. However, zinc in a neutral water medium is able to exist in the chemical form of $Zn(OH)^+$. Therefore, for adsorption of zinc and strontium can be suitable adsorbents with the large pores, i.e. meso- or macropores adsorbents. The investigating of adsorption of zinc and strontium from distilled water shows, that titanium silicate is an efficient adsorbent toward corresponding ions (Fig. 1 and Table 1). The results, which were obtained in present work, are in good agreement with results of strontium adsorption, which were described in publications [15, 16].

If we take into account adsorption value in (mmol/g) we observe that adsorption values of Zn^{2+} and Sr^{2+} by titanium silicate are the same (in the range of arithmetic mean) (see Table 1). It means, that the mechanism of adsorption of corresponding heavy

metals is the same for both ions. The difference in adsorption of zinc compared with strontium in 0 - 20 min of time of interaction is due to the less ionic

radius of Zn^{2+} compared with Sr^{2+} or due to the presence of a part of zinc ions in the chemical form of $ZnOH^+$ under $pH = 7$ [18, 19].

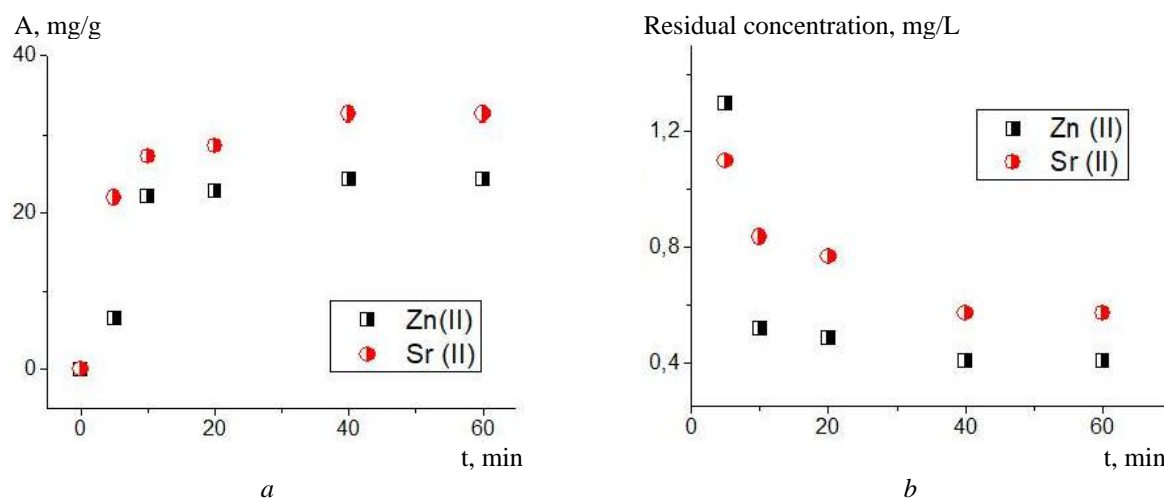


Fig. 1. Dependence of adsorption value (mg/g) of zinc and strontium cations on time of interaction (a). Dependence of residual concentration of ions in aqueous solution after their partially up-taking (mg/L) from time interactions (b). (See color Figure on the journal website.)

Table 1. Dependence of adsorption of zinc and strontium cations on time of interaction from distilled water medium, $N_{Zn,Sr} = 0.005M$, $pH = 7$, $S : L = 100$

T, min	A(Zn), mg/g	A(Sr), mg/g	A(Zn), mmol/g	A(Sr), mmol/g
5	6.5*	22	0.1	0.25
10	22.1	27.28	0.34	0.31
20	22.76	28.6	0.3502	0.325
40	24.38	32.56	0.375	0.37
60	24.38	32.56	0.3751	0.37

* Arithmetic mean. An error of arithmetic mean was not higher than 7 % for all investigations [20].

With the aid of a fluorescent X-ray analyzer and energy dispersive spectroscopy (EDS) the composition of the sorbent formed was determined, as well as zinc, and strontium presence on the surface of the

sorbent after the sorption process. Results, shown in Fig. 2 (Tables 2 and 3), confirm the intensive adsorption of zinc and strontium by titanium silicate.

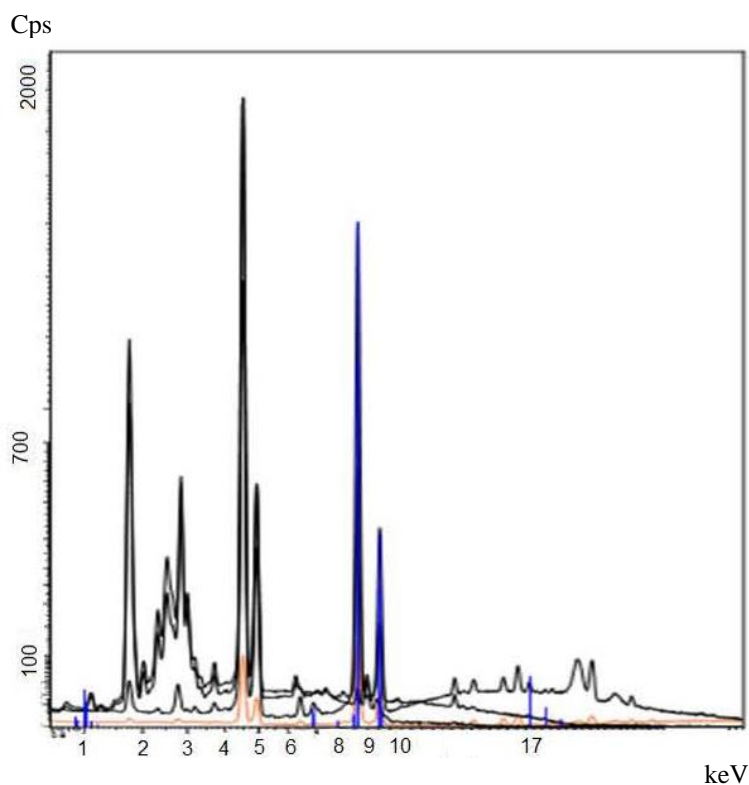
Table 2. XRF analysis data of titanium silicate with zinc on the surface

Element/Compound	Content in the compound, %	Line energy, keV
SiO₂	43.2	1.74
P ₂ O ₅	0.869	2.0137
SO ₃	1.88	2.307
Cl	0.499	2.62
TiO₂	47	4.511
CaO	0.220	3.69
ZnO	6.03	8.6

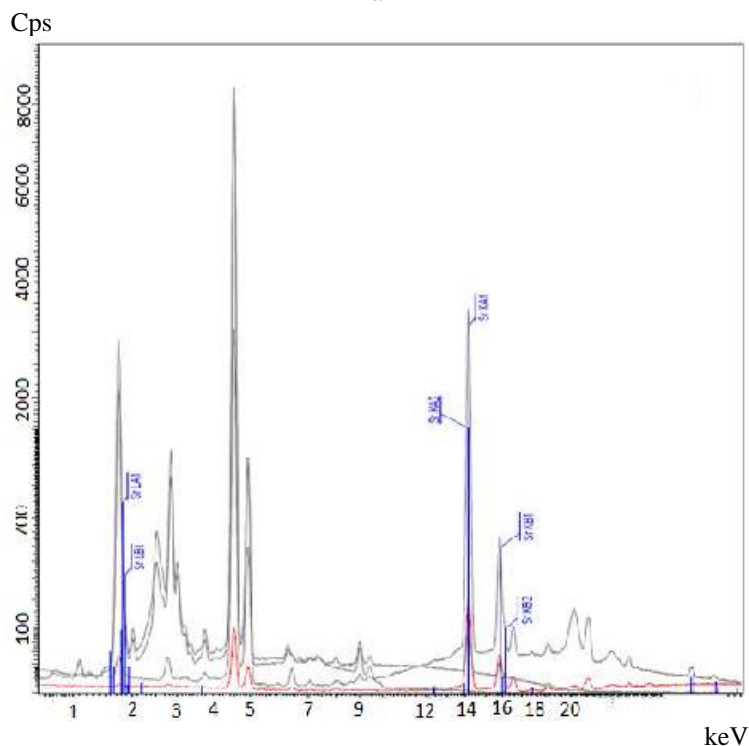
Table 3. XRF analysis data of titanium silicate with strontium on the surface

Element/Compound	Content in the compound, %	Line energy, keV
SiO₂	33.6	1.74
P ₂ O ₅	1.12	2.0137
SO ₃	0.927	2.307
Cl	0.591	2.62
TiO₂	42.3	4.511
CaO	0.714	3.69
SrO	1.41	14.166

Note. The bold font identifies the macroelements of titanium silicate and heavy metals adsorbed on its surface.



a



b

Fig. 2. XRF spectrum of titanium silicate with zinc (*a*) and strontium (*b*) on its surface (adsorption from distilled water). Peaks of zinc and strontium are in color. (See color Figure on the journal website.)

The presence of a certain amount of SO_3 in the sample (see Table 2) can be a consequence of incomplete dissociation of zinc sulfate molecules or repeated interactions of dissociated molecules. The chemical composition of the adsorbent was confirmed by EDS

spectroscopy as well, as the presence of zinc and strontium on its surface. Scanning electron microscopic (SEM) image of titanium silicate shows a high porosity, and a developed surface of the adsorbent (Fig. 3).

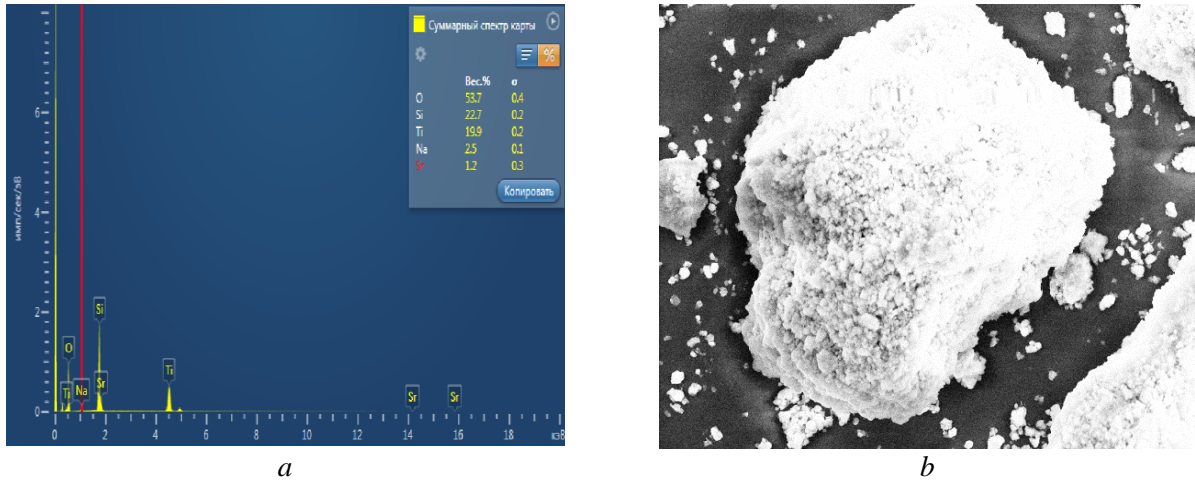


Fig. 3. EDS spectrum of titanium silicate with strontium adsorbed on its surface (a). SEM image of the morphology of the titanium silicate (b). (See color Figure on the journal website.)

The adsorption value of Zn²⁺ ions from river water remained unchanged. The hardness of the water, caused mainly by calcium and magnesium, decreased by 80 %. The adsorption of strontium from river water slightly decreases. The results are shown in Table 4.

Table 4. Maximal adsorption values of zinc and strontium (N_{Zn,Sr} = 0.005M, which corresponds to concentration of heavy metals of 325 mg/L for Zn²⁺ and 440 mg/L for Sr²⁺) and percent of up-taking of heavy metal from distilled and natural water (rw)

Adsorption values	Zn ²⁺	Sr ²⁺	Zn ²⁺ (rw)	Sr ²⁺ (rw)
A, mmol/g	0.375	0.37	0.36	0.31
A, mg/g	24.38	32.56	23.4	27.28
Residual concentration, mg/L	81.2	114.4	91	167.2
φ % of up-taking of Zn ²⁺ and Sr ²⁺	75 %	74 %	72 %	62 %

The influence of solution acidity on adsorption of zinc and strontium by titanium silicate from distilled water and natural water from River Uzh is shown in Fig. 4. Values of adsorption are given in Table 5.

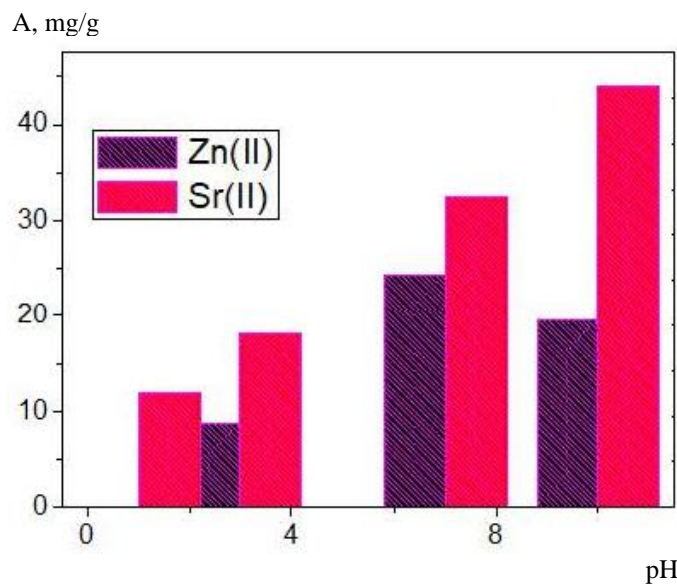


Fig. 4. The influence of solution acidity on adsorption of zinc and strontium by titanium silicate. (See color Figure on the journal website.)

Table 5. Dependence of adsorption up-taking of strontium and zinc from solution's acidity; $N_{Zn,Sr} = 0.005M$; L : S = 200

pH	A(Zn), mg/g	A(Sr), mg/g	A(Zn _(rw)), mg/g	A(Sr _(rw)), mg/g
1	0	12 ± 1.04	0	0
3	8.7 ± 0.98	18.2 ± 1.2	0	0
7	24.38 ± 1.56	32.56 ± 1.3	23.4 ± 1.5	27.28 ± 1.9
10	19.5 ± 1.07	44 ± 0.98	20.7 ± 2.09	28.48 ± 2.2

It was shown that the investigated elements are better adsorbed in alkali medium than in acidic ones. The zinc and strontium are not adsorbed in acid medium from river water. However, titanium silicate could be very useful in clearing water from heavy metals and radionuclides waste in neutral and alkali medium.

4. Conclusions

1. The adsorption up-taking of zinc and strontium by titanium silicate from distilled water and natural water from River Uzh was investigated.

2. It was shown that adsorption of zinc and strontium by titanium silicate strongly depends on

time of interaction and on solution acidity and increases with increasing of both parameters.

3. It was established, that for the initial concentration of zinc and strontium at the level of 0.005M the presence of ions that cause the natural mineralization of water does not affect their adsorption extraction. Titanium silicate effectively adsorbs zinc ions, thus preventing them from migrating into the environment. Also, this adsorbent significantly reduces the overall mineralization of water. Co-existing ions of natural water weakly increase strontium migration in the water environment, i.e. decrease its adsorption by titanium silicate.

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ВПЛИВ СИЛІКАТУ ТИТАНУ НА МІГРАЦІЮ Zn(II) та Sr(II) У ВОДНОМУ СЕРЕДОВИЩІ

Досліджено вплив силікату титану на міграцію цинку і стронцію в довкіллі. Аналіз адсорбованих елементів на поверхні силікату титану проведено з використанням XRF та EDS спектроскопії. Показано, що адсорбція цинку та стронцію силікатом титану сильно залежить від тривалості взаємодії та кислотності розчину і зростає при зростанні обох параметрів. Установлено, що при концентрації цинку і стронцію на рівні 0,005М присутність іонів, які зумовлюють природну мінералізацію води, не впливає на адсорбційне вилучення важких металів силікатом титану. При дослідженнях адсорбції з природних вод даний адсорбент знижує загальну твердість води.

Ключові слова: адсорбція, стронцій, цинк, силікат титану, міграція радіонуклідів, XRF-аналіз.

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