

Article

Titanium Silicates Precipitated on the Rice Husk Biochar as Adsorbents for the Extraction of Cesium and Strontium Radioisotope Ions

Igor Zhuravlev

Institute for Sorption and Problems of Endoecology NAS of Ukraine, Gen. Naumov str., 13, 03164 Kiev, Ukraine; igorzhuravlev1@gmail.com

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Abstract: The aim of the work was the development of cheap and effective adsorbents based on titanium silicates deposited on the products of thermochemical processing of rice husk to extract cesium and strontium radioisotopes from aqueous media. Synthesis of adsorbents was carried out using the cheapest and widely used titanium water-soluble reagent, titanium sulfate (an intermediate product of white rutile pigment production), as feedstock. After treatment with titanium sulfate and neutralization, hydrothermal treatment was carried out in various ways. The traditional method of processing in an autoclave was used, as well as the blowing at different temperatures by steam. The distribution coefficients and the adsorption capacity for cesium and strontium ions on these sorbents were studied. Along with the chemical composition of adsorbents obtained by those ways, the type and the temperature of hydrothermal treatment also affected the adsorption properties. It was found that the adsorbent obtained by hydrothermal treatment in an autoclave has the highest degree of cesium ions extraction ($K_d = 27,500$). The highest degree of strontium ions extraction ($K_d = 2,095,000$) has an adsorbent obtained by hydrothermal treatment with water vapor blowing.

Keywords: hydrated titanium silicates; cesium; strontium; ion-exchangers; rice husk biochar; radioisotope extraction

1. Introduction

Radionuclide contamination of the environment is a very serious problem from the moment the work in this area was started to the present day. The main risks are associated with harm to human health by penetrating radiation, which occurs when a radioactive nuclide is decomposed [1]. These hazards are relevant for the areas contaminated by the Chernobyl nuclear power plant accident and by Fukushima. The spectrum of radionuclide pollutants is quite wide. To extract them, various ion exchange materials are mostly often used. Organic ion exchange resins are unstable in strong radiation fields [2,3]. Therefore, recently inorganic ion-exchange materials are considered to be the most promising. Starting from the classical works of Amphlett [4] to this day, many inorganic ion exchangers have been synthesized and investigated [5–14]. Among inorganic ion exchangers for adsorption of radionuclides, it is necessary to note the titanium and zirconium phosphates and hydroxides. As powders, these materials have already been known for a long time [15–23]. Further research allowed synthesis of ion exchangers such as a granulated gels, which favorably differ from powders [24–26]. Recent studies have allowed increasing the porosity, the selectivity of adsorption and the exchange capacity of such gels to radionuclides and other cationic and anionic contaminants [27–32]. Adsorption of heavy radionuclide ions which have a complex-forming ability—uranium, plutonium, americium, lanthanides, cobalt, etc.—can be carried out onto the above-mentioned adsorbents, apatites, and onto the metal-substituted forms of silica gel [33–38]. For the selective and highly efficient

adsorption of cationic radionuclides which do not possess the complex-forming ability—cesium and strontium—the powder titanium silicate ion exchangers were investigated and prepared [39–43]. Adsorbents based on heavy metal (iron, copper, nickel, titanium) ferrocyanides also are known. They contain ion-exchangeable alkali metal cations in the structure. Such ion exchangers exhibit high selectivity at adsorption of cesium cations, and to strontium cations [44–46]. Iron ferrocyanide under the trade names “ферроцин”, “ferrotsin”, “ferrocin” is used even to remove radiocesium from the human body, that is, as a radioprotector [1,47]. The disadvantage of iron ferrocyanide is its low hydrolytic stability in weak alkaline and even in neutral media [48]. As noted above, titanium silicates also are known as good adsorbents to cesium and strontium radioisotopes. Ion exchangeable titanium silicates are crystalline powder compounds having in their structure exchangeable alkali metal ions (sodium, potassium) or protons. One of the founders of the work in this direction is Clearfield [39,41]. The classical synthesis of the crystalline powder ion-exchangeable titanium silicates consists in the hydrothermal treatment of a mixture of solutions of titanium and silicon compounds. As titanium compounds the peroxide or other complexes of titanium are usually used. Sodium or potassium liquid glass is generally used as silicon compounds for synthesis. Increased temperature and duration of hydrothermal treatment helps to obtain titanium silicates with greater crystallinity and a large grain size. Onto the best samples of titanium silicates obtained in a similar way, it is possible to carry out the adsorption of cesium ions with distribution coefficients close to 1,000,000. The selectivity of the strontium ions adsorption on the alkaline and alkaline earth salts background is significantly less. As disadvantages of the synthesis method described above, it is necessary to note the relatively high energy consumption and complexity of the equipment [39–43]. Another drawback is the difficulty of separating the adsorbent powder after adsorption from the equilibrium solution, especially when it comes to radioactive solutions. At the same time, to clean various environmental objects (water, soil) from cesium and strontium radioisotopes, cheap, eco-friendly and highly efficient adsorbents are needed. We first proposed to precipitate titanium ion-exchangeable silicates on products of thermochemical processing of rice husk [49]. Rice husk contains a large amount of silicon dioxide and is a large-tonnage waste of agricultural production [50]. In accordance with the technology proposed, at the first stage of the synthesis, rice husks are treated with acidic titanyl sulfate with weak heating. Acid titanyl sulfate, as an intermediate product of the sulfuric acid technology for the synthesis of titanium rutile white pigment, is quite cheap. At the second stage, the acid excess is neutralized with an alkaline reagent. After acid excess neutralizing the hydrothermal treatment of the product obtained should be carried out in various ways. At the final stage of the synthesis, the adsorbent obtained is washed from salts excess and dried. The result is an adsorbent, wherein ion-exchangeable titanium silicate is distributed on the surface of the carbon carrier pores. It was found that the type of hydrothermal treatment, its temperature, and duration determine the porosity of the adsorbent and its adsorption properties. Two rows of such adsorbents in sodium and potassium ion-exchangeable forms were synthesized and investigated. Potassium forms in general have the best adsorption properties, therefore, only potassium forms of adsorbents are presented in this article. Adsorbents based on carbon matrices and other solid adsorbent materials for adsorption of radionuclides were synthesized and investigated by Wang, X.K. et al. [51–58].

2. Materials and Methods

2.1. Reagents

All reagents used were of Sigma-Aldrich analytical grade. For the adsorption experiments, cesium and strontium chloride salts were dissolved in distilled water. For the synthesis of titanium silicates, titanyl 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. For analysis, double distilled deionized water was used.

2.2. Synthesis of Titanium Silicates

Two different methods were used to synthesize the titanium silicates precipitated on the products of thermochemical processing of rice husk. The first method is as follows. At the first stage, the rice husk in a closed heat-resistant chemical glass was heated in a water bath with a solution of titanyl sulphate for 10 h. At the second stage, the product obtained in the first stage was mixed with a solution of potassium alkali or with a solution of potassium liquid glass (silicate). Then, sulfuric acid was neutralized with alkali and the reaction mixture was heated. Neutralization was carried out in closed vessels with cooling in order to avoid water boiling and evaporations from the reaction mixture. At the third stage, this neutralized mixture was placed in steel autoclaves with Teflon liners and sealed. Next, the autoclaves were heated in a heating chamber for 10 h at a temperature of 150 °C, or at a higher temperature. When this happened, the hydrothermal treatment of the reaction mixture in an alkaline aqueous medium takes place. After that, the autoclaves were cooled, opened, the reaction products were washed from excess salts and alkali with distilled water and dried in a heating air oven at a temperature of 120 °C. The second method is as follows. The first stage of processing the rice husk with titanyl sulfate and the second stage of neutralizing the reaction mixture formed in the first stage with potassium alkali or silicates were the same as in the first method. On the third stage of the second method, the neutralized reaction mixture was placed in a tube furnace in a tube of thermally and chemically resistant stainless steel. This reaction mixture in the tube was heated at a temperature of 400, 500, 600, 700, 800 °C at one temperature for each experiment for 2–3 h with continuous blowing through the tube of water vapor. After cooling the tubular furnace, the obtained products were washed and dried as in the first method of synthesis.

2.3. Adsorption Experiments

The adsorption of Cs⁺ and Sr²⁺ cations onto the precipitated on the rice husk biochar titanium silicates were carried out at room conditions to determine their respective adsorption capacity and distribution coefficient. Adsorption of cations from 0.01 M NaCl water solution as a background electrolyte by the adsorbents was carried out under static conditions at a constant ratio of the volume of the solution to the mass of the adsorbent with constant stirring. The weight ratio of the adsorbent to the solution was 1:500 (0.1 g of adsorbent, 50 milliliters of solution). The contact time of the adsorbent with the solution was 48 h at constant stirring. After reaching the adsorption equilibrium, adsorbents were filtered out from equilibrium solutions. The calculation of the adsorption isotherms is carried out as follows. The concentration of the metal in the equilibrium filtrate is determined by atomic absorption spectroscopy. Then the amount of metal adsorbed by 1 g of adsorbent is calculated. As a result, an adsorption isotherm is constructed: the dependence of the amount of adsorbed metal as a function of the metal concentration in the corresponding equilibrium solution. The magnitude of the Adsorption (A) of metals (Uptake) was calculated by the formula (1):

$$A = \frac{(C_{init.} - C_{equil.})V}{1000m} \quad (1)$$

where A (Adsorption) is the metal cation uptake by adsorbent (mg/g); C_{init.} and C_{equil.} are initial and equilibrium concentrations of metal cations (mg/L) respectively; V is the volume of solution for adsorption (mL); m is the mass of adsorbent (grams). The distribution coefficients of cesium and strontium between the adsorbent and the equilibrium solution were calculated with the formula (2):

$$Kd = \frac{V(C_{init.} - C_{equil.})}{mC_{equil.}} \quad (2)$$

where Kd is the distribution coefficient (mL/g); C_{init.} and C_{equil.} are initial and equilibrium concentrations of metal cations (mg/L) respectively; V is the volume of solution for adsorption (mL); m is the mass of adsorbent (grams).

The distribution coefficient K_d characterizes the degree of ion extraction by the adsorbent from solution.

2.4. Analytic Methods

The specific surface area, pore volume, and samples pore volume distribution by effective radii was performed via nitrogen adsorption-desorption measurements using Gemini -02 “Micromeritics” (Micromeritics Instruments Corporation, Norcross, GA, USA) porozimeter. The outgas temperature was 160 °C. XRD studies were performed using DRON-3 (Bourestnik, Inc., St. Petersburg, Russia) Cu $K\alpha$ XRD spectrometer. pH measurements were conducted using И-160-M (Gomel Plant of Measuring Equipment, Gomel, Belarus) pH-meter. Electron and optical microscopy were performed using JEOL JSM-840A (JEOL, Ltd., Tokyo, Japan) electron microscope and OLYMPUS (Olympus Corporation, Tokyo, Japan) optical microscope. Atomic absorption spectrometer used was AA 6300 SHIMADZU (Shimadzu Corporation, Tokyo, Japan).

3. Results and Discussion

3.1. Physical-Chemical Characterization

The original rice husk is a hard-rigid flake. It has a bumpy surface. Its appearance is shown in Figure 1 (middle and right images—electron microscopy).

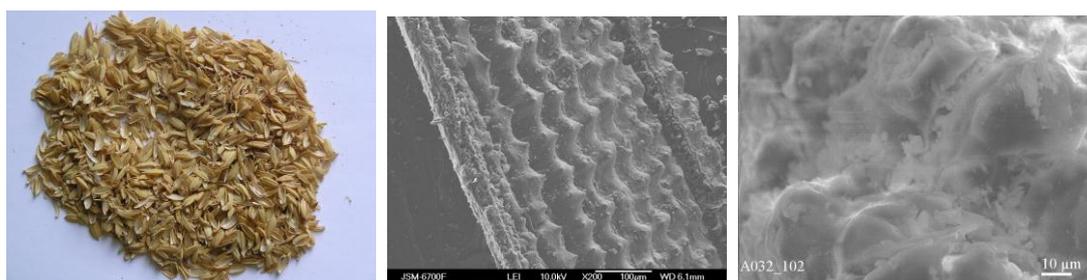


Figure 1. Original rice husk images.

During thermo-chemical treatment, thermolysis of the main organic components of the husk, cellulose and lignin, occurs. In the presence of oxygen or air, a simple burnout of the organic components takes place. If the thermo-chemical treatment is carried out without the presence of oxygen, or when steam is blown through a sample, the formation of porous carbon with macropores with a diameter of more than one micron is possible (Figure 2). At the syntheses by both methods, a product consisting two fractions is formed—a gray-brown powder-TiSi fraction and a carbon-TiSi fraction (Figure 3). These two fractions have different physicochemical and ion exchange properties. Using the first method, adsorbent 7 was synthesized at a temperature of 200 °C. After the salts excess washing off and drying, the 7 TiSi-powder fraction was analyzed using X-ray phase analysis, which showed the presence of a weak crystallinity of the sample (Figure 4). Using the second synthesis method, four samples were synthesized with steam blowing. When blowing with steam, the samples were heated in a tube furnace to temperatures of 150, 400, 600, and 800 °C, respectively. The X-ray phase analyses of the last three samples were performed and are presented in Figure 5, showing the presence of the amorphous phases.

Samples obtained with both methods were synthesized in potassium form, when potassium reagents were used for the syntheses. During the synthesis with the second method, the alkali content in the reaction mixture was higher than the same during the synthesis with the first method. This explains the fact that the first method yielded a weak crystallinity even at a temperature of 200 °C, while at the second method, amorphous samples were obtained at higher temperatures (Figure 5).

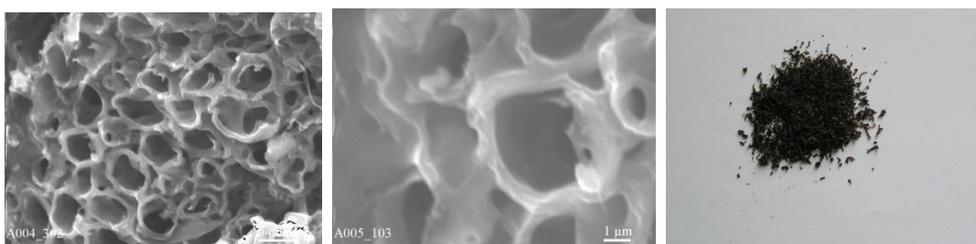


Figure 2. High porous charcoal prepared at thermal treatment of rice husk (left and middle images—electron microscopy, right—usual without magnification).



Figure 3. A gray-brown powder-TiSi fraction (left) and a carbon-TiSi fraction (right)—the products of titanium silicates precipitated on the rice husk biochar (usual images at small magnification).

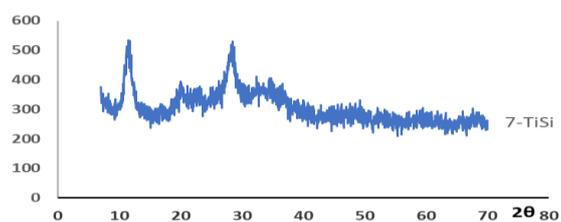


Figure 4. X-rays diffraction analysis of the TiSi-powder fraction of the sample 7 (Cu $K\alpha$).

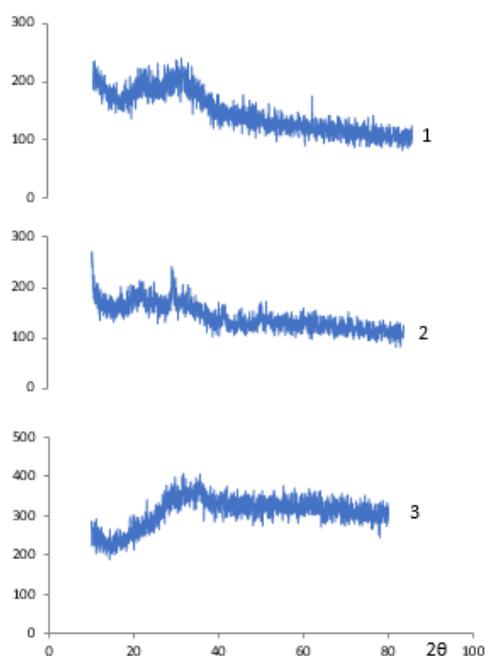


Figure 5. X-ray diffraction analysis of the TiSi-powder fractions prepared at steam blowing at 400 °C (1), 600 °C (2), and 800 °C (3) (Cu $K\alpha$).

Despite a weak crystallinity, it is very difficult to identify the crystal structure of the sample's 7 powder-TiSi fraction. Figure 6 presents the nitrogen adsorption-desorption isotherms and the functions of pore volume distribution by the pore radius for sample's 7 TiSi-powder fraction and for sample's 7 carbon-TiSi fraction. It should be noted here that the distribution of pores for the powder and for the carbon fractions are close, but not the same. Basically, both fractions contain pores with radii within 10–35 angstroms. Pure microcrystalline ion exchange titanium silicates (sample's 7 TiSi-powder fraction) have a specific surface area much less (only the surface of the crystals or of the amorphous particles). We can assume that our materials are complex organo-mineral composite or organo-mineral chemical compounds. Moreover, the powder-TiSi and the carbon-TiSi fractions are different in composition, in porosity and in ion-exchange properties (this will be shown later). The specific surface of the powder-TiSi fraction is more than six times greater than that of the carbon-TiSi fraction, and the total pore volume is more than seven times greater.

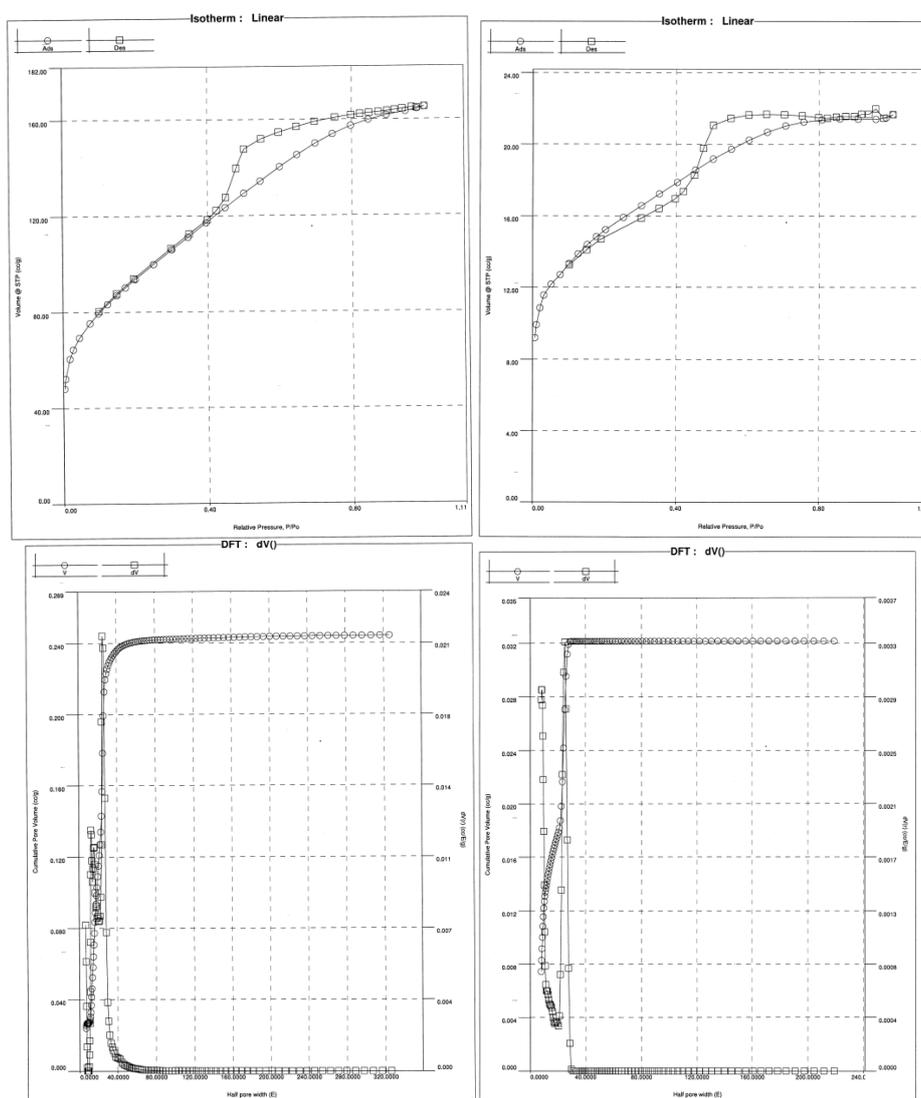


Figure 6. Nitrogen adsorption-desorption isotherms and the functions of pore volume distribution by the pore radius for sample 7 TiSi-powder fraction and sample 7 carbon-TiSi fraction: Top left, lower left, isotherms and distribution accordingly to TiSi-powder fraction sample; top right, lower right, isotherms and distribution accordingly to carbon-TiSi fraction sample. For sample's 7 TiSi-powder fraction $V_S = 0.25 \text{ cm}^3/\text{g}$, $S_{sp.} = 326 \text{ m}^2/\text{g}$. For sample's 7 carbon-TiSi fraction $V_S = 0.033 \text{ cm}^3/\text{g}$, $S_{sp.} = 53 \text{ m}^2/\text{g}$.

3.2. Ion-Exchange Properties

On the synthesized silicates of titanium in the potassium form, ion-exchange adsorption of ions of stable cesium and strontium isotopes was studied. Adsorption was carried out on a saline background of a 0.01 molar solution of sodium chloride. The adsorption of cesium and strontium ions was studied under static conditions. According to those results, adsorption isotherms were constructed at different initial ion concentrations, the ion adsorption values and the ion distribution coefficients between the adsorbent phase and the equilibrium solution were calculated (Tables 1–3, Figures 7 and 8).

Table 1. Strontium adsorption (A) and distribution coefficients (Kd) from the background 0.01M NaCl solution onto Carbon-TiSi and Powder-TiSi fractions of the sample 7.

Fraction	pH		Sr ²⁺ , mg/L			A		Kd
	Initial	Equil.	Cin.	Ceq.	ΔC	mg/g	mg-eqv./g	
CarbonTiSi	6.62	6.94	9.64	0.01	9.63	4.82	0.11	4.8 × 10 ⁵
	6.64	7.27	30.2	0.97	29.23	14.62	0.33	1.5 × 10 ⁴
	6.37	7.0	50.5	6.2	44.3	22.15	0.51	3.6 × 10 ³
	5.99	6.87	76.75	19.65	57.1	28.6	0.65	1.5 × 10 ³
	6.06	6.74	107.88	39.1	68.78	34.4	0.79	0.9 × 10 ³
Ti-Si powder	6.62	6.88	9.64	0.04	9.6	4.8	0.11	1.2 × 10 ⁵
	6.64	6.85	30.2	1.44	28.76	14.38	0.33	1.0 × 10 ⁴
	6.37	6.74	50.5	3.44	47.06	23.5	0.54	6.8 × 10 ³
	5.99	6.67	76.75	9.26	67.49	33.7	0.77	3.6 × 10 ³
	6.06	6.54	107.88	35.9	71.98	36.0	0.82	1.0 × 10 ³
	6.38	6.65	185	108.6	76.5	38.3	0.87	352
	6.14	6.48	373	293	80	40	0.91	137

Studies have shown that the materials investigated have good ion-exchange properties and therefore are very promising. It should be noted that for the purpose of cleaning environmental objects from cesium and strontium radionuclides, the most important property of a sorbent is the ability to separate ions as much as possible between the phase of the adsorbent and the equilibrium medium (water, soil, etc.) at the lowest initial concentrations of these ions. Such distribution coefficients at the smallest concentrations of cesium and strontium ions for all the studied adsorbents are given in Table 3. The titanium silicate (TiSi-powder fraction) obtained by autoclave synthesis at a temperature of 200 °C has the highest degree of cesium ions extraction (the highest distribution coefficients) among the studied adsorbents (sample 1, Table 3), Kd = 26,500. This is a low result when compared with the best known adsorbents for cesium. For other adsorbents obtained by blowing steam into a tube furnace, the results for cesium are even lower.

However, the greater difficulties arise at cleaning environmental objects from strontium. Adsorbents for strontium are either expensive or have low selectivity. As can be seen from Table 3, even adsorbent 1 (synthesis in an autoclave) achieved a good result in the adsorption of strontium, Kd = 120,000. However, the best results on the adsorption of strontium were found for adsorbents obtained with blowing steam (samples 3,4) with Kd = 2,095,000–1,396,000. The result Kd = 2,095,000 was found for the sample with not the highest treatment temperature. This is the synthesis at 400 °C. It is difficult to unequivocally answer the question why the best result was achieved at this temperature. Considering the adsorption isotherms of cesium and strontium in the carbon-TiSi and powder-TiSi fractions of adsorbent 7 (autoclave synthesis) (Tables 1 and 2, Figures 7 and 8), it is necessary to note quite high values of exchange capacities of both fractions and for both cations. Adsorbent 7 (powder fraction) in Table 3 is sample 1.

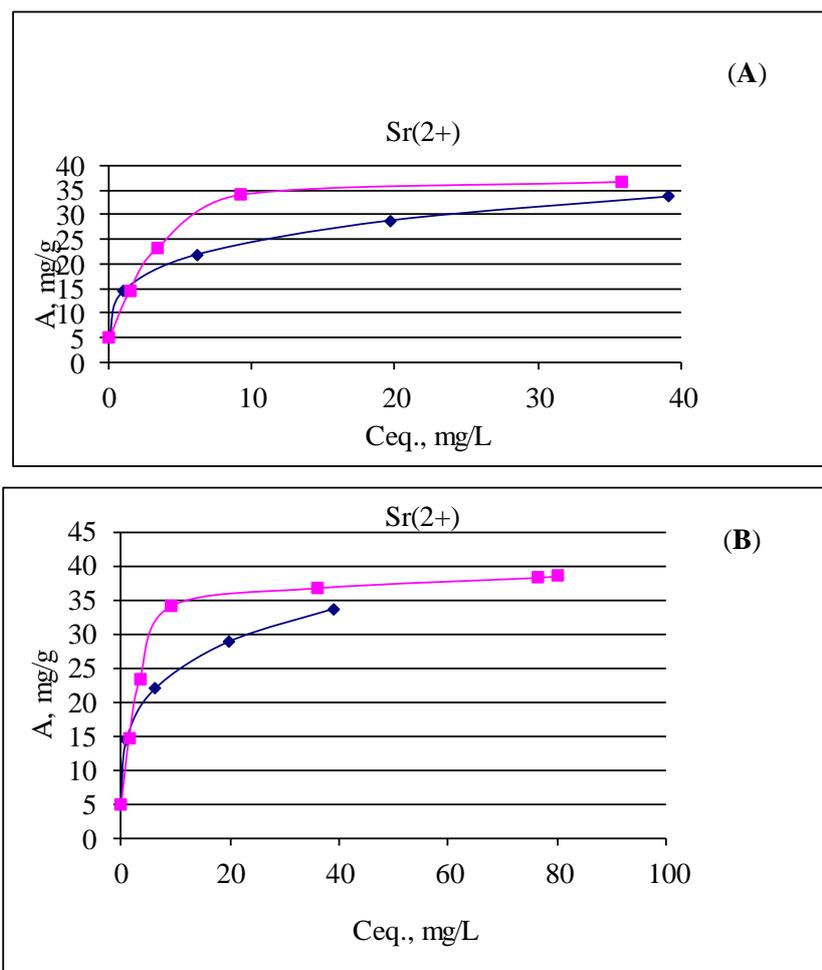


Figure 7. Strontium adsorption isotherms from the background 0.01M NaCl solution by sample 7. □—TiSi-powder fraction; ◇—Carbon-TiSi fraction; at low concentrations (A); at middle concentrations (B).

Table 2. Cesium adsorption (A) and distribution coefficients (Kd) from the background 0,01M NaCl solutions onto the simple's 7 Carbon-TiSi and Powder-TiSi fractions.

Fraction	pH		Cs ⁺ , mg/L			A		Kd
	Initial	Equil.	Cin.	Ceq.	ΔC	mg/g	mg-eqv/g	
Carbontisi	6.68	6.87	10.8	0.74	10.06	5.03	0.038	6.8×10^3
	6.79	7.18	32.3	3.4	28.9	14.45	0.109	4.3×10^3
	6.76	7.16	51.0	7.15	43.95	21.98	0.165	3.1×10^3
	6.41	7.13	85.88	20.3	65.58	32.8	0.247	1.6×10^3
	6.33	7.15	107.75	33.2	75.55	37.78	0.284	1.1×10^3
	6.68	6.75	10.8	0.2	10.6	5.3	0.04	2.7×10^4
Ti-Si powder	6.79	6.88	32.3	1.1	31.2	15.6	0.117	1.4×10^4
	6.76	6.90	51.0	2.24	48.76	24.4	0.18	1.1×10^4
	6.41	9.80	85.88	5.28	80.6	40.3	0.30	7.6×10^3
	6.33	6.89	107.75	7.76	100.99	50.5	0.38	6.5×10^3
	6.68	7.24	237.5	42.3	195.2	97.6	0.73	2.3×10^3
	6.70	7.01	463	202.5	260.5	130.3	0.98	6.4×10^2
	6.62	6.38	686	371.5	314.5	157.3	1.18	423
	6.45	6.32	968	623	345	172.5	1.30	277

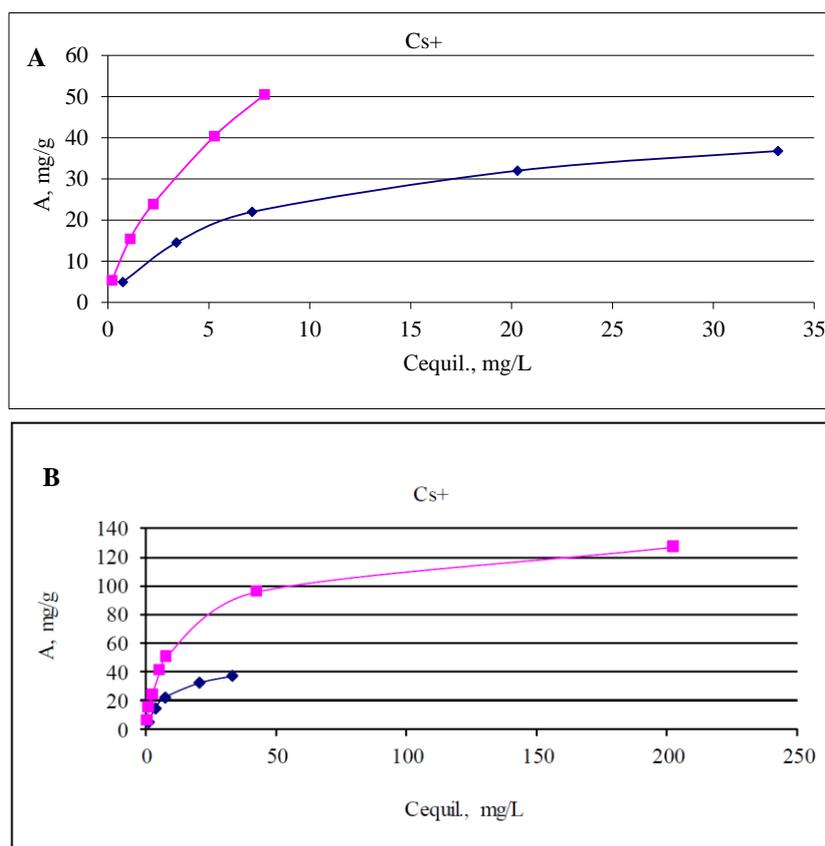


Figure 8. Cesium adsorption isotherms from the background 0.01M NaCl solution by sample 7. □—TiSi-powder fraction; ◇—Carbon-TiSi fraction; at low concentrations (A); at middle concentrations (B).

Table 3. Adsorption properties of the samples TiSi-powder fraction prepared by various hydrothermal treatment.

No.	Sample	Cesium: Concentration, mg/L; Kd, mL/g, and Adsorption, mg/g				Strontium: Concentration, mg/L; Kd, mL/g; and Adsorption, mg/g			
		Cin.	Ceq.	A	Kd	Cin.	Ceq.	A	Kd
1	200 °C TiSi powder autoclave 10 h	10.8	0.2	5.3	27,000	9.64	0.04	4.8	120,000
2	Blowing steam TiSi powder 150 °C, 2 h	10.18	3.01	3.59	1200	7.2	0.04	3.58	90,000
3	Blowing steam TiSi powder 400 °C, 2 h	10.66	2.77	3.95	1424	8.38	0.002	4.19	2,095,000
4	Blowing steam TiSi powder 600 °C, 2 h	10.66	3.56	3.55	1000	8.38	0.003	4.19	1,396,000
5	Blowing steam TiSi powder 800 °C, 2 h	10.66	4.79	2.94	613	8.38	0.05	4.17	83,300

It is important to consider the sorbent's 7 powder-TiSi and carbon-TiSi fractions using the results of ion exchange. According to the porozimetry of the carbon-TiSi and powder-TiSi fractions of the sorbent 7 (Figure 6), it can be seen that the specific surface of the powder-TiSi fraction is six times larger, and the pore volume is more than seven times larger than for the carbon-TiSi fraction. The macroporous structure of the carbon-TiSi fraction is not taken into account here, because it is not determined by the

used porozimetry method. At the same time, the exchange capacity for cesium (Table 2, at the same initial concentrations of cesium, 107.75 mg/L) for the powder-TiSi fraction is only just (50.5:37.78) = 1.34 times larger. The exchange capacity for strontium (Table 1, with the same initial concentrations of strontium 107.88 mg/L) for the powder-TiSi fraction (36.0 mg/g) is almost the same as for the carbon-TiSi fraction (34.4 mg/g). Moreover, with the same smallest initial concentrations of strontium (9.64 mg/L) for the carbon-TiSi fraction, the distribution coefficient K is even higher than for the powder-TiSi fraction (480,000 and 120,000, respectively, Table 1). This once again unequivocally confirms that powder-TiSi and the carbon-TiSi fractions of the adsorbent 7 contain in their composition various ion-exchange phases with different ion-exchange properties. Pure biochar practically does not adsorb cesium and strontium. All calculations of adsorption isotherms (Figures 7 and 8) and distribution coefficients K_d (Tables 1–3) were performed in accordance with the description and formulas 1,2 in Section 2.3. *Adsorption experiments*. You can compare these results with similar ones for similar adsorbents [59]. As it was noted in the article [59] the K_d values ranged from 390 to 160,000 mL/g for Sr and from 6 to 41,000 mL/g for Cs.

4. Conclusions

Using two different methods of synthesis, the ion exchangeable titanium silicates precipitated on the products of the thermo-chemical treatment of rice husk were synthesized. It was found that in both cases the products of the synthesis are represented by the powder and carbon fractions, which have different physicochemical and ion-exchange properties. It was established that titanium silicates obtained by steam blowing at 400 °C, 2 h have the highest degree of strontium ions extraction (K_d = 2,095,000), and those obtained by autoclaving at 200 °C, 10 h have the highest degree of cesium ions extraction (K_d = 26,500).

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Conflicts of Interest: Author declares no conflict of interest.

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