

## Sorption of ammonium and phosphate ions from aqueous solutions by carbon and mineral sorbents

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**Abstract:** A search for a sorbent capable of simultaneously extracting both phosphate anions and ammonium cations from a highly competitive medium like the biological environment of the human's body was realized. For this purpose a comparative study of a sorption of ammonium and phosphate ions from aquatic environments in the absence of any backgrounds electrolytes and from Ringer's solution by activated charcoal, its oxidized forms and mineral amorphous sorbents – powdered titanium silicate, as well as spherically granular hydrous zirconium silicate and titanium dioxide, obtained by original methods of synthesis, as well as some of their ion-substituted forms in comparison with commercially available silica gel was carried out. The features of the sorption of ammonium cations and phosphate anions by the studied sorbents are discussed. It was established that sorption properties of the sorbents depend strongly from their chemical nature. It determines a selectivity of ion-exchange and a possibility of chemisorption processes in Ringer's solution. A relationship between the sorption of calcium cations and phosphate anions from Ringer's solution was supposed which made it possible to assume the chemisorption mechanism. Based on the sorption mechanism understanding the sorption properties of titanium silicate with respect to phosphate anions were considerable improved by converting the initial sample into Ca- and Ce-ion-substituted forms without significant loss of its high sorption properties toward ammonium cations.

**Keywords:** sorption, ammonium cations, phosphate anions, Ringer's solution

### 1. Introduction

Sorption processes are used in various areas of human activity that are not directly related to chemistry, for example, medicine (Ash et al., 2015; Chang et al., 2017; Mikhalovsky et al., 2012). Further purposeful development of the technologies requires, first of all, most complete understanding of physical and chemical processes occurring in a system of interest. In a case of a violation of the normal functioning of the kidneys or liver, metabolic products accumulate in the human biological medium. These compounds can be conditionally divided into substances of organic and inorganic nature. Among the latter, an excess of phosphate ions and, especially, ammonium ions are dangerous.

In chronic renal failure, various methods of renal replacement therapy are used, among which the dialysis has gained preference. But this membrane technology has a number of irreparable shortcomings which make it possible to operate dialysis units only in specialized centres. Considering a possibility of creating portable devices for dialysis, the author of work (Agar, 2010) concluded that sorption purification is promising method. At the same time, it should be considered that the direct contact with blood requires high biocompatibility of a sorbent, so a range of hemosorbents is very limited (Chang et al., 2017).

Currently, it is believed that the least traumatic sorption method for a human body is the continuous purification of circulating dialysate (contaminated dialysis solution). Thanks to this

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technique a range of potential sorbents has been significantly expanded. As follows from the reviews (Agar, 2010; Bazaev et al., 2018; Bazaev et al., 2018), three types of cartridges, containing selective mineral sorbents, are most often used in experimental devices of the so-called "artificial" kidney. There are hydrous zirconium phosphate and dioxide to remove metabolic products of inorganic nature in cation- and anion-exchange forms and activated charcoal for organic uremic toxins. More complex combinations have been also proposed (Bazaev et al., 2018). So a content of the adsorptive cartridge can be optimized in the direction of reducing the types of sorbents used.

The efficiency and safety of the sorption purification procedure are determined by the absorptive and toxicological properties of sorbents used. The latter is also important for membrane methods, but it refers to water quality. The ISO 23500-3:2019 standard lists metal ions with proven toxicity, their content is normalized in dialysis solutions: Mn, Fe, Al, Cu, Zn. Based on this, a range of sorbents was formed in presented work. At the same time, most synthetic mineral sorbents have an underdeveloped surface, but a pronounced selectivity (Celestian et al., 2007). On the contrary, the well-known inert silica gel has high specific surface area ( $S_{sp}$ ) and porosity ( $V_s$ ), due to which it exhibits good sorption properties with respect to urea, comparable to activated carbon (Wee-KC et al., 2018). For this reason silica gel has prospects for use in medicine (Diab et al., 2017).

The purpose of this work is to search for a sorbent capable of simultaneously extracting both phosphate anions and ammonium cations from a highly competitive medium like the biological environment of the human's body. As a subtask, it was also necessary to find out how expedient it is to use a selective sorbent in comparison with silica gel, an inexpensive adsorbent with a developed surface as a component of the sorption cartridge. For realization of this purpose a comparative study of a sorption of ammonium and phosphate ions from aqueous solutions by charcoals and mineral sorbents synthesized at the Institute for Sorption and Problems of Endoecology of National Academy of Science of Ukraine according to original methods was carried out.

## 2. Materials and methods

In this work commercially available silica gel, synthetic charcoals – activated and oxidized to various degrees (the latter was determined by the value of the sorption exchange capacity (SEC) for  $\text{Na}^+$  ion), as well as mineral amorphous sorbents – powdered titanium silicate, spherically granulated hydrous zirconium silicate and titanium dioxide were used as the basic sorbents.

One of the main requirements for medical sorbents is the absence of changes in pH value of the biological environment which should be 7.4. The initial samples of silica gel, activated charcoal, titanium silicate, zirconium silicate, and titanium dioxide, which were washed after synthesis to  $\text{pH} \approx 7.4$ , correspond to this condition. The samples of oxidized charcoals need to be brought into equilibrium with 0.1 M NaCl solution with  $\text{pH} \approx 7.4$ ; pH value was corrected using 0.1 M NaOH before sorption experiments. Therefore, mixed Na-, H-forms of oxidized charcoals were obtained as initial ones. Titanium and zirconium silicates were in the same form, since their synthesis was carried out in NaOH solution.

The chromatographic silica gel, used in experiment, was produced by ROCC (Belgium), ( $\text{SiO}_2$ , sample no. 1, Tables 1, 2). The activated charcoal sample (AC, no. 2, Tables 1, 2) was synthesized by additional activation of commercially available AC from coconut husk 607C Aquacarb (China) in accordance with patent UA 108785. This sample of AC was oxidized with  $\text{HNO}_3$  at boiling for a time sufficient to reach the following values of SEC, mmol/g ( $\text{Na}^+$ ): 0.6, 2.0, 2.8 (OC-0.6, 2.0, 2.8; nos. 3, 4, 5, Tables 1, 2, respectively) as it is described elsewhere (Jaramillo et al., 2010). The powder-like amorphous titanium silicate (TiSi, no. 6, Tables 1, 2) was synthesized by the hydrothermal synthesis in accordance with patent UA 76886. This material was obtained under milder hydrothermal conditions compared to those required for the synthesis of crystalline forms. It has a nonstoichiometric composition  $x\text{TiO}_2 \cdot y\text{SiO}_2 \cdot n\text{H}_2\text{O}$ , and is known in the literature as titanosilicate or silicotitanate (Strelko et al., 2015).

A series of sorbents was obtained in Ca- and Ce-ion-exchange forms. TiSi sample was transferred to the Ca-ion-exchange form in two ways: 1) by contacting the sample in its original form with a 0.05 M  $\text{CaCl}_2$  solution (TiSi(Ca)-1, no. 7, Tables 1, 2); 2) TiSi sample was first converted into H-form in 0.1 M HCl, then it was transferred into 0.05 M  $\text{CaCl}_2$ . This solution was gradually alkalized with 0.1 M NaOH to  $\text{pH} \approx 7.4$  (TiSi(Ca)-2, no. 8, Tables 1, 2). Samples of TiSi,  $\text{SiO}_2$ , and OC-2.8 were obtained in

the Ce ion-exchange form by contacting the initial forms with a 0.01 M solution of  $\text{CeCl}_3$  (TiSi(Ce),  $\text{SiO}_2(\text{Ce})$ , and OC-2.8(Ce); nos. 9, 10, and 11, Tables 1, 2, respectively, sorption capacity (A) towards  $\text{Ce} \approx 85 \text{ mg/g}$ ).

The amorphous spherically granulated hydrous zirconium silicate (ZrSi, no. 12, Tables 1, 2) was obtained by the sol-gel method using the technology of continuous synthesis [Strelko, 2013, patent UA 105999]. The initial molar ratio Zr:Si was 0.6, the general formula of the sample is  $x\text{ZrO}_2 \cdot y\text{SiO}_2 \cdot n\text{H}_2\text{O}$ . The amorphous spherically granulated hydrous titanium dioxide,  $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ , was also synthesized by the same method (HTD, no. 13, Tables 1, 2).

Table 1. Some characteristics of studied samples

No.	Sorbent	Abbreviation	Physical form	$S_{\text{sp}}$ , $\text{m}^2/\text{g}$	$V_s$ , $\text{cm}^3/\text{g}$
1	silica gel	$\text{SiO}_2$	fine-grained	500	0.75
2	activated charcoal	AC	irregular granule	1770	0.90
3	oxidized charcoal	OC-0.6			
4		OC-2.0			
5	oxidized charcoal	OC-2.8	powder	150	0.60
6	amorphous titanium silicate	TiSi			
7	amorphous titanium silicate	TiSi(Ca)-1			
8	in Ca-ion-exchange form	TiSi(Ca)-2			
9	amorphous titanium silicate in Ce-ion-exchange form	TiSi(Ce)	fine-grained	500	0.75
10	silica gel in Ce-ion-exchange form	$\text{SiO}_2(\text{Ce})$			
11	oxidized charcoal in Ce-ion-exchange form	OC-2.8(Ce)	irregular granule	1770	0.90
12	amorphous hydrous zirconium silicate	ZrSi	spherically similar granule	220	0.15
13	hydrous titanium dioxide	HTD		120	0.25

For sorption experiments two types of solutions were prepared. They are based on: /i/ pure water; /ii/ Ringer's solution, which simulates a dialysis solution ( $\text{NaCl}$  - 9,  $\text{KCl}$  - 0.42,  $\text{CaCl}_2$  - 0.24,  $\text{NaHCO}_3$  - 0.15  $\text{mg}/\text{cm}^3$ ).  $\text{NH}_4\text{Cl}$  or  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  salts were added to both types of solutions in an amount of 0.2  $\mu\text{mol}/\text{cm}^3$  in terms of  $\text{NH}_4^+$  or phosphorus. A determination of concentrations of ammonium and phosphate ions in a solution was performed using colorimetric methods – with Nessler's reagent or vanadate-molybdate, respectively.

The study of sorption was carried out under static conditions with stirring a sample on a shaker; the weight of a sorbent was 0.025 g, the sieve grain size was 0.16–0.25 mm, the volume of the solution was 50  $\text{cm}^3$  (S:L = 1:2000). The pH of a solution was controlled and, if necessary, maintained during the entire experiment at a level of  $7.4 \pm 0.2$  using 0.1 M HCl or NaOH solutions. A sorption equilibrium was fixed by periodic sampling. An equilibrium sorption capacity ( $A(\text{P})$  or  $A(\text{NH}_4^+)$ ) was calculated from a difference in concentrations of phosphate or ammonium ions in the initial and equilibrium solutions and was given in  $\text{mmol}/\text{g}$ . A study of sorption kinetics was carried out in a similar way, solution samples were taken at regular intervals. The studies were carried out without considering the temperature factor, under normal conditions, while dialysis is carried out at the human's body temperature. All of the reagents used in the experiments were of chemical purity.

### 3. Results and discussion

In the course of the studies, the influence of the following factors on the sorption of ammonium and phosphate ions was assessed: 1) the presence/absence of a background electrolyte; 2) the chemical nature of the sorbent; 3) oxidation states for OC; 4) ion-substituted form.

At first the results for silica gel will be consider.  $\text{SiO}_2$  is characterized by one of the highest sorption capacities among the studied ion-exchangers with respect to phosphate and ammonium ions during sorption from a background-free solution. It demonstrates the ability to absorb both anions and

cations under these conditions (1, Table 2). The good sorption properties of SiO<sub>2</sub> are explained by its high values of S<sub>sp</sub> and V<sub>s</sub> (Table 1). However, in Ringer's solution, SiO<sub>2</sub> is characterized by a "classical" for ion exchange decrease in the sorption capacity for ammonium ions by almost 3 times due to the competitive sorption of Na<sup>+</sup> ions. Furthermore, it can be seen that adsorption centres of SiO<sub>2</sub> do not show selectivity with respect to phosphate anions against significant amount of Cl<sup>-</sup> anions in Ringer's solution at all (1, Table 2).

Table 2. Sorption capacity of studied samples

No.	Sample	Sorption capacity, mmol/g			
		Phosphate anions		Ammonium cations	
		Pure water	Ringer's solution	Pure water	Ringer's solution
1	SiO <sub>2</sub>	0.31	0	0.40	0.14
2	AC	0.068	0.032	0.17	0.021
3	OC-0.6	0.038	0.019	0.29	0.056
4	OC-2.0	0.038	0.025	0.44	0.11
5	OC-2.8	0.026	0.019	0.45	0.17
6	TiSi	0.077	0.11	0.38	0.20
7	TiSi(Ca)-1	0.16	0.19	0.37	0.20
8	TiSi(Ca)-2	0.21	0.24	0.35	0.17
9	TiSi(Ce)	0.33	0.36	0.36	0.18
10	SiO <sub>2</sub> (Ce)	0	0	0.063	0
11	OC-2.8(Ce)	0.32	0.38	0.061	0
12	ZrSi	0.25	0.29	0.21	0.079
13	HTD	0.20	0.32	0.13	0.053

Charcoal sorbents are time-tested hemo- and enterosorbents. It was shown that the AC sample, studied in this work, can absorb some aminoacids, which simulate one of the types of uremic toxins [Isaieva et al., 2019]. The possibility of sorption on AC, as well as on SiO<sub>2</sub>, of another type of uremic toxin, urea, has also been noted [Wee-KC et al., 2018]. Therefore, AC is an essential element of a potential sorption system for dialysate purification from uremic toxins of organic origin. At the same time, the test showed that AC is poorly suited for purifying Ringer's solution from inorganic ions (2, Table 2). However, under these conditions, AC is a more "universal" sorbent than SiO<sub>2</sub>, since it absorbs as ammonium cations, so as phosphate anions. In the absence of competition, sorption capacity of AC with respect to phosphate anions and, especially, ammonium cations, is several times higher, but still remains significantly lower than that of SiO<sub>2</sub>. As a result, for the complex purification of dialysate one more sorbent is needed, which would removal inorganic ions, for example, oxidized carbon.

In turn, OC samples are characterized by low sorption capacities for phosphate anions in both types of solutions (3-5, Table 2). A(P) weakly depend on SEC value of OC sample and they are slightly higher than for SiO<sub>2</sub> and slightly lower than for AC in Ringer's solution. Therefore, the OC in the initial state (Na-, H-form) does not fully meet the goal. Towards ammonium cations, the sorption properties of OC expectedly improve with increasing SEC, but only for the sample with SEC = 2.8 mmol/g (Na<sup>+</sup>) the value of A(NH<sub>4</sub><sup>+</sup>) slightly exceeding SiO<sub>2</sub> in water and Ringer's solution (3-5, Table 2).

Therefore, a number of synthetic selective mineral sorbents was included in this study. First, a sample of amorphous powder-like TiSi. With respect to ammonium cations, its sorption capacity is close to that of SiO<sub>2</sub> and OC-2.8 in both types of solutions (6, Table 2), despite the lower values of V<sub>s</sub> and S<sub>sp</sub> (Table 1). Towards phosphate anions in water, TiSi is characterized by a significantly lower A(P) value compared to those for SiO<sub>2</sub> (6, Table 2). In other words, cation-exchange properties dominate in this type of a sorbent. At the same time, A(P) value of TiSi in the Ringer's solution is several times higher than the results of SiO<sub>2</sub> and OC. It indicates a high selectivity of TiSi anion-exchange centres with respect to phosphate anions.

Another important feature of the uptake of phosphate anions on TiSi is that its sorption from a background-free medium is lower than from a Ringer's solution. This can be explained by the superposition of two sorption mechanisms. The first one is the sorption of phosphate anions on the

primary TiSi anion-exchange centres, which is typical for a background free medium. Conditions for the second mechanism are created in Ringer's solution, since they are most likely associated with the adsorption of  $\text{Ca}^{2+}$  ions. The newly formed Ca-ion-substituted cation-exchange functional groups form secondary sorption centres for phosphate anions. The authors of [Strelko et al., 2018] believe that this mechanism is based on the ion-exchange self-assembly of apatite. However, it can also be considered from the point of view of chemisorption, since the chemical affinity in the sorbent-adsorbate system plays a significant role. Previously, we experimentally showed that sorption capacity of a sorbent exceeds its ion-exchange capacity for  $\text{Na}^+$  ions in a case of a theoretical possibility of a formation of a poorly soluble compound between an element of a sorbent matrix and a sorbate. For example, a correspondence between the observed sorption capacity and the reference value of the solubility of the corresponding phosphates was noted during the sorption of  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ , and U(VI) ions on amorphous spherically granular titanium phosphate obtained by the same method as ZrSi and HTD [Zakutevskyy et al., 2012].

Such sorption behaviour of TiSi with respect to phosphate anions in the background-free medium and Ringer's solution sharply differs from AC, OC, and, especially,  $\text{SiO}_2$  (1–5, Table 2). This may be due to the insufficient selectivity of the active centers of AC, OC,  $\text{SiO}_2$  towards both phosphate anions and  $\text{Ca}^{2+}$  cations. It manifests itself in the predominant sorption of  $\text{Cl}^-$  and  $\text{Na}^+$  ions, respectively, due to their greater amount in Ringer's solution. In the case of TiSi, the established nature of the sorption makes it possible to improve the absorption capacity with respect to phosphate anions by using not Na-, but a more complex Na-, Ca-ion-substituted form. This may also prevent the unwanted removal of vital  $\text{Ca}^{2+}$  ions from the biological medium.

Therefore, in order to study the influence of the chemical nature of active sites on the sorption of phosphate anions and ammonium cations, the initial TiSi sample was converted into Ca- and Ce-forms (7–9, Table 2). Ce(IV) compounds are known for their positive effect on biochemical processes in the human's body [Abuid et al., 2019]. Compared to the initial TiSi sample (Na-, H-form), the ion-substituted forms do increase the uptake of phosphate anions in both water and Ringer's solutions. At the same time: 1) Ce-form coordinates phosphate anions better than Ca-forms (9 and 7, 8, Table 2). This most likely correlates with the solubility of the corresponding phosphates; 2) TiSi sample, converted to Ca-form after preliminary soaking in 0.1 M HCl (successive replacement of  $\text{Na}^+$ - $\text{H}^+$ - $\text{Ca}^{2+}$  ions), is characterized by a higher sorption capacity with respect to phosphate anions than the sample contacted with  $\text{CaCl}_2$  solution only (8 and 7, Table 2). This can be explained by a large number of Ca-substituted centers in the first case; 3) the influence of adsorbed  $\text{Ca}^{2+}$  and  $\text{Ce}^{3+}$  ions on the sorption of ammonium ions is practically absent (6–9, Table 2); 4) based on the multiple increase in A(P) values, it can be concluded that phosphate anions are adsorbed mainly not by primary, but by Ca- and Ce-ion-substituted active centers.

The transformation of TiSi into the Ce-ion-substituted form makes it possible not only to increase the equilibrium sorption capacity with respect to phosphate anions as compared to the initial sample, but also to significantly improve its sorption kinetics (1–3, Figure). For comparison, the Figure also shows the curves for amorphous spherically granular ZrSi and HTD, since the sorption of phosphate anions on the initial TiSi sample in the time interval of this Figure is negligible. The acceleration of the sorption of phosphate anions on TiSi(Ce) can be associated with a sharp increase in the number of readily accessible surface active centers ( $\text{Ce}^{3+}$  ions adsorbed on primary cation-exchange centers). This is radically different from the slow sorption of phosphate anions on ZrSi and HTD.

Attention should also be paid to the significant increase in the rate of sorption of phosphate anions on the same TiSi(Ce) sample from Ringer's solution compared to pure water (2 and 3, Figure). These data confirm the previously stated assumption about the parallel sorption of phosphate anions on the initial anion-exchange, Ce- and Ca-ion-substituted centers. The latter are additionally formed in Ringer's solution after the sorption of  $\text{Ca}^{2+}$  ions by the initial cation-exchange active sites.

The influence of the amount of adsorbed  $\text{Ce}^{3+}$  ions on the sorption of phosphate anions was also studied. For this, TiSi samples were obtained with the following approximate values of  $A(\text{Ce}^{3+})$ , mg/g: 10; 25; 50 and 85. Sorption properties of TiSi(Ce) samples with  $A(\text{Ce}^{3+}) < 50$  mg/g differ little from the initial one. With the next successive increase in the content of adsorbed  $\text{Ce}^{3+}$  ions, an improvement in the sorption of phosphate anions is observed (1 and 2, Fig. 1). It confirms the relation-

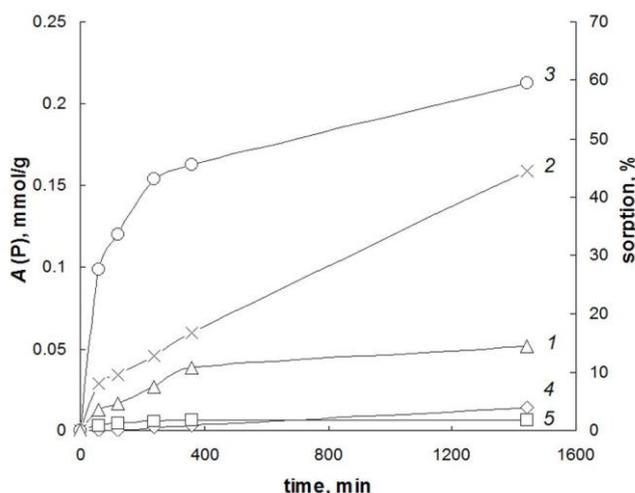


Fig. 1. Kinetic curves of sorption of phosphate anions from water (1, 2, 4, 5) and Ringer's solution (3): 1-3 – TiSi(Ce),  $A(\text{Ce}^{3+})=50$  (1) and 85 (2, 3) mg/g; 4 - HTD; 5 - ZrSi; the right axis is the percentage of the equilibrium sorption capacity of the sample

ship between the amounts of Ce-ion-substituted active surface sites of TiSi(Ce) sample and adsorbed phosphate anions.

The sorption behaviour of Ce-ion-substituted forms of OC and SiO<sub>2</sub> differs from that of TiSi(Ce). Only tentative assumptions can be made about the reason for this difference within the framework of this article. SiO<sub>2</sub>(Ce) (10, Table 2) sharply reduces its sorption capacities with respect to ammonium cations and phosphate anions compared to the initial SiO<sub>2</sub> in both types of solutions. The first possible explanation is that on the nonspecific sorbent, silica gel, a loss of the majority of selective with respect to phosphate anions adsorption centers occurs. This is due to the ion-exchange substitution of Ce<sup>3+</sup> ions by Na<sup>+</sup> ions. Na<sup>+</sup> ions also compete with ammonium cations, as it is observed for the initial SiO<sub>2</sub>. But from this position it is difficult to explain the decrease in the sorption of ammonium and phosphate ions in pure water. These results are more consistent with the assumption that Ce<sup>3+</sup> ions form coordinatively saturated surface complexes on the SiO<sub>2</sub> surface. By this reason Ce-ion-substituted centers are not active with respect to phosphate anions and simultaneously prevent the sorption of ammonium cations.

On OC-2.8(Ce) sample, the observed pattern is more complicated than on SiO<sub>2</sub>(Ce). OC-2.8(Ce) (11, Table 2) is characterized by a radical increase in the equilibrium sorption capacity towards phosphate anions in comparison with the initial sample OC-2.8 (5, Table 2), which almost reaches the value equal the best sample TiSi(Ce) (9, Table 2). However, this is accompanied by a deterioration in the sorption of ammonium cations (11, Table 2) on a scale similar to that of SiO<sub>2</sub>(Ce). Some decrease was also observed in the case of the TiSi(Ca) and TiSi(Ce) samples (6 and 8, 9, Table 2). It is explained by some decrease in the number of cation-exchange centers, which are active with respect to ammonium cations. The difference in the degree of negative effect can be associated with a significant proportion of micropores (Kang et al., 2017) in the porous structure of the OC. The micropores are blocked by adsorbed Ce<sup>3+</sup> ions that prevent further penetration of ammonium cations.

At the end of experiment discussion, let us consider the sorption properties of ZrSi, as well as HTD, one of the widely known inorganic ampholytes [Xu et al., 2010]. Their undeniable advantage compared to powdered mineral materials lies in spherically granular form, which is more convenient for practical use in a sorption column.

Studies have shown that, despite the different chemical nature, ZrSi and HTD have similar adsorption properties. Thus, in terms of A(P) values in pure water, they are second only to SiO<sub>2</sub> of all unmodified samples, i.e. anion-exchange centers dominate in their chemical structure (12, 13, Table 2). In Ringer's solution an increase is observed, especially for HTD, in the sorption of phosphate anions almost to the level of the TiSi(Ce) sample. It indirectly indicates a considerable sorption of Ca<sup>2+</sup> cations by these sorbents. The high sorption of Ca<sup>2+</sup> cations is apparently due to the occurrence of ion-

exchange and chemisorption processes. The last one lies in the formation of surface compounds like calcium titanate, but the overall process is more complex, since it also includes phosphate anions. However, with respect to ammonium cations, ZrSi and HTD are characterized by the lowest sorption capacities of all studied mineral sorbents in both types of solutions (12, 13, Table 2). Their values correspond to the level of weakly oxidized coal. In this case, ZrSi also demonstrates a higher sorption activity compared to HTD.

The array of experimental data obtained makes it possible to suppose the chemical nature of selective sorption centers. The inflections on the curves of the pH-metric titration of a crystalline sample of TiSi with 0.1 M NaOH solution [Bortun et al., 1996] suggest the existence of three types of functional groups on its surface: Si-OH ( $pK \leq 2$ ) and Ti-OH ( $pK_1 \approx 5.6$  and  $pK_2 \approx 10.5$ ). From the given data on sorption on SiO<sub>2</sub> it can be concluded that Si-OH groups selectively adsorb ammonium cations and non-selectively phosphate anions. Therefore, the Ti-OH and Zr-OH groups are responsible for the selective sorption of phosphate anions on TiSi, HTD, and ZrSi. These assumptions correspond to: 1) moderate sorption of ammonium cations on HTD, on the surface of which Si-OH groups are absent; 2) higher sorption of phosphate anions from a background-free solution on ZrSi compared to HTD due to their joint ion-exchange sorption by Si-OH and Zr-OH groups. As follows from these considerations the studied Zr-Si sample is closer in chemical structure to hydrated zirconium dioxide (the predominance of Zr-OH groups). As a consequence, in order to obtain more balanced cation/anion exchange properties (improved sorption of ammonium cations), the ratio of components in the synthesis should be used less than Zr:Si = 0.6, although the values of  $S_{sp}$  and  $V_s$  may decrease in this case. For amorphous spherically granular titanium phosphates, this issue was considered in more detail in [Strelko, 2013].

#### 4. Conclusions

It was established that sorption properties of the studied sorbents towards phosphate anions and ammonium cations depends strongly from their chemical nature. The silica gel demonstrates high sorption capacities with respect to ammonium cations and phosphate anions in pure water. At the same time, it has a low selectivity for phosphate anions in Ringer's solution. Oxidized charcoal does not effectively purify Ringer's solution from phosphate anions and activated charcoal from all studied ions.

Mineral sorbents have more pronounced amphoteric properties, which makes it possible for them to sorb both ammonium cations and phosphate anions from solutions with  $pH \approx 7.4$ . But ion-exchange properties of spherically granulated amorphous hydrous zirconium silicate and titanium dioxide towards ammonium cations are not sufficiently pronounced. Amorphous powdered titanium silicate has the most balanced sorption properties in relation to the ions of interest.

At the same time it was found that a significant complication of adsorption processes in comparison with individual solutions of NH<sub>4</sub>Cl or NaH<sub>2</sub>PO<sub>4</sub> salts due to the addition of chemisorption to ion-exchange in Ringer's solution takes place. Based on the sorption mechanism understanding, the sorption properties of titanium silicate with respect to phosphate anions were considerably improved by converting the initial sample into Ca- and Ce-ion-substituted forms along with the preservation of its high sorption properties toward ammonium cations.

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