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Sorption properties of natural clinoptilolite modified by Fe-containing solutions

E. M. Kats and V. A. Nikashina*

*V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences,
19 ul. Kosygina, 117975 Moscow, Russian Federation.
Fax: +7 (095) 938 2054*

Sorption properties of clinoptilolite tuff modified by Fe-containing solutions were studied. The absence of sorption of monocharged anions at any pH of the solution and a high sorption capacity (up to 2.0 to 2.5 mg-eq g^{-1}) for phosphate ions at pH 10 to 11.5 were shown. Desorption of phosphates by solutions of salts and mineral acids was studied.

Key words: natural clinoptilolite, modification; Fe-containing solutions, phosphates, sorption.

Chemical modification is commonly used as a method for changing surface properties of materials in order to enlarge the areas of their application. Methods of modification of inorganic substrates by both organic and inorganic substances are known.[1–3] In particular, we have published data[4] on chemical modification of clinoptilolite-containing tuffs (CT) by an organic water-soluble amino-containing polymer. It is shown that a modified material retains the cation-exchange properties of CT and gains the anion-exchange properties of the modifying agent.

As follows from the literature data, the sorbent modified by iron ions manifests a high affinity toward multicharged oxygen-containing anions.[5] Therefore, it was of interest to study the properties of CT after their modification by iron-containing solutions.

A solution containing Fe^{3+} was chosen as a modifying agent, because Fe^{3+} ions are characterized by a high complexing ability and a tendency to form poorly soluble compounds, and Fe^{3+} hydroxide possesses amphoteric properties.

In this work, the sorption of anions, including phosphate anions, which are typical environmental contaminants of the environment, on CT modified by iron-containing solutions was studied.

Experimental

CT from the Tedzami deposit (Georgia) were chosen as the initial material for modification. An idealized composition of its unit cell can be presented by the formula $(K_2Na_2Ca)_3[Al_6Si_{30}O_{72}]\cdot 24H_2O$. It has been preliminarily shown by Mössbauer spectroscopy that Fe^{2+} and Fe^{3+} are sorbed from solutions of different compositions, including natural water, only on the clinoptilolite surface, mainly in the form of the tricharged ion.[6]

Four samples with different contents of iron were obtained for studying anion-exchange properties of modified CT. CT were treated by iron-containing solutions under static conditions changing pH and contents of iron in the solution at the phase ratio V/m = 10 (where V/mL is the volume of the solution and m/g is the mass of the sorbent). The contact time was 30 days.

The content of sorbed iron in CT was determined from the concentration differences in the initial and equilibrium solutions by the atomic absorption method. The conditions of modification and the content of iron in modified samples are presented in Table 1. Sample *5* was obtained under dynamic conditions upon purification of iron-containing ground drinking water ([Fe] = 3.0 mg L^{-1}) by CT. It is noteworthy that samples *1—5* modified by iron-containing solutions are distinguished by better mechanical properties than natural clinoptilolite.

Table 1. Conditions of modification and content of iron in modified samples with (V/m = 10)

Sample	$[Fe]_{in}$ /mg L^{-1}	$[Fe]_{eqv}$[a] /mg L^{-1}	pH_{eqv}	Content of Fe in the sorbent /mg mL^{-1}
1	0.66	0.17	3.15	4.8
2	1.98	0.90	1.95	10.8
3	6.60	4.81	1.62	17.9
4	19.80	15.70	1.28	40.7
5[b]	3.00	3.00	7.00	8.0[c]

[a] The content of Fe in the equilibrium solution. [b] The sample was transformed into the equilibrium form by iron-containing natural water. [c] The content of Fe in the modified sorbent was determined after its treatment with a 0.2 N solution of HCl.

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Results and Discussion

Sorption of monocharged (Cl^-, Br^-, and CNS^-) and multicharged (PO_4^{3-}) anions from dilute solutions (0.005 to 0.01 *N*) on modified CT samples was studied. It is shown that monocharged anions are virtually not retained by modified CT at any content of iron in the CT and pH of the solution studied. A sample of CT containing 8 mg of iron in 1 mL of sorbent (sample *5*) was used for the study of sorption of phosphate ions.

Sorption of phosphate ions was studied under static conditions within the pH range from 7 to 12, because (Fig. 1) monocharged $H_2PO_4^-$, bicharged HPO_4^{2-}, and tricharged PO_4^{3-} ions are present simultaneously in solutions at these pH values. The results of the sorption of phosphates from a 0.01 mol L^{-1} solution of Na_2HPO_4 at V/m = 200 and contact time of 18 and 40 days are presented in Fig. 2. It can be seen from Fig. 2 that in the pH range from 7.5 to 9.5 the sorbent capacity is 40 mg g^{-1} or 0.8 mg-eq g^{-1} for the HPO_4^{2-} ion. A sorption maximum is observed at pH 11 to 11.5, which comprises 70.0 to 80.0 mg g^{-1} or 1.3 to 1.6 mg-eq g^{-1} for the HPO_4^{2-} ion or 2.0 to 2.5 mg-eq g^{-1} for the $(PO_4)^{3-}$ ions, respectively. At pH > 12 the capacity for phosphate decreases sharply.

The equilibrium of sorption of phosphate ions from the 0.01 *N* solution of Na_2HPO_4 on the modified CT sample at pH 11.5 corresponding to the sorption maximum is established for approximately 40 days. The sorption isotherm of phosphates from the 0.01 *N* solution of Na_2HPO_4 on modified CT at pH 11.6 was obtained for this contact time. According to the results presented in Fig. 3, the shape of the sorption isotherm of phosphate ions is convex.

Dynamic experiments on the sorption of phosphate ions from a 0.001 *N* solution of Na_2HPO_4 at pH 9.5 and 11.5 were also carried out. The sorption of phosphate ions was studied on the sorbent with 0.3 to 0.5-mm particle size in a column 0.81 cm^2 in cross section. In the experiment at pH 9.5, the volume of the sorbent was 2.8 mL and the rate of filtration was 0.2 to 0.4 mL min^{-1}, and at pH 11.5 these parameters were 1.8 mL and 0.1 mL min^{-1}, respectively. The dynamic capacity of modified clinoptilolite for the HPO_4^{2-} ion at pH 9.5 was only 0.013 mg-eq mL^{-1} and at pH 11.5 it was 0.50 mg-eq mL^{-1} for the HPO_4^{2-} ion or 0.77 mg-eq mL^{-1} calculated per the PO_4^{3-} ion. The data obtained for the desorption of phosphate ions by a 0.2 *N* solution of HCl confirm these results.

It follows from the data presented that only insignificant sorbent capacities for phosphates can be used from weakly alkaline solutions (pH 9.5) under the conditions mentioned due to a low rate of the process, and dynamic

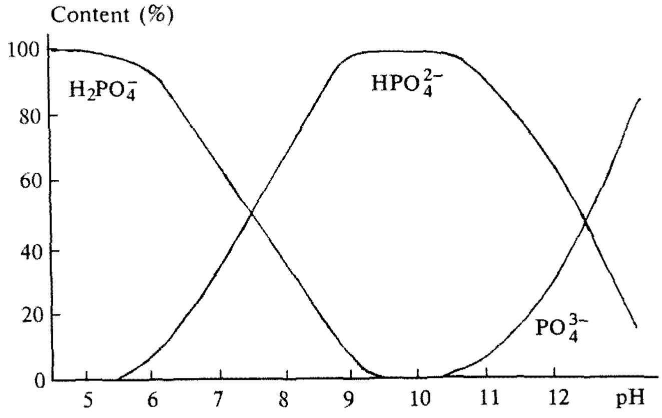

Fig. 1. Forms of phosphate ions in solution at different pH values.

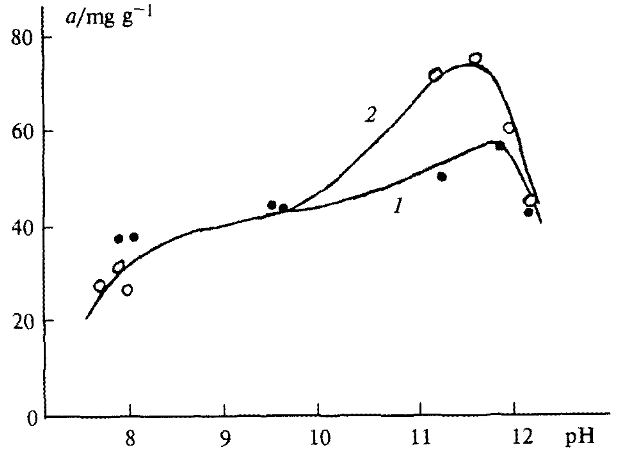

Fig. 2. Sorption of phosphate ions from a 0.01 *N* solution of Na_2HPO_4 on modified CT at different pH values (V/m = 200; *1*, contact time 18 days; *2*, 40 days).

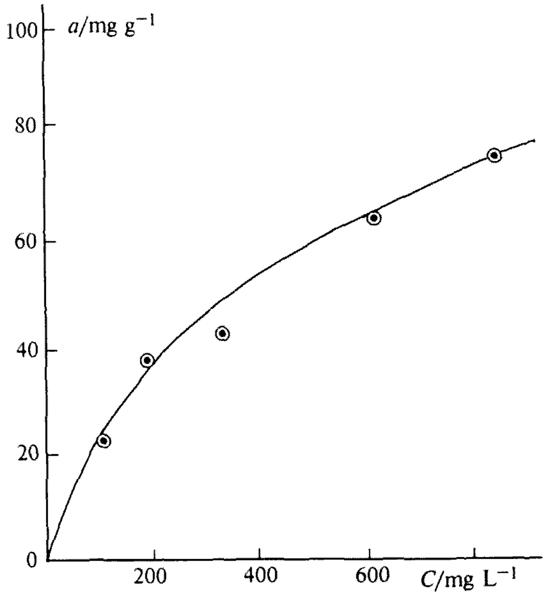

Fig. 3. Sorption isotherm of phosphate ions on modified CT (pH 11.6, contact time 40 days).

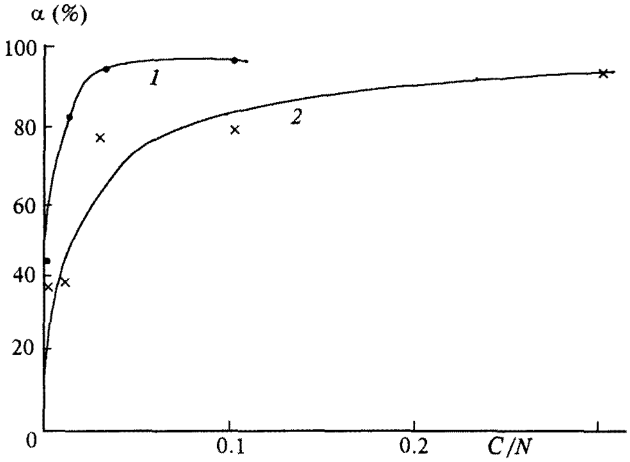

Fig. 4. Dependences of the degree of desorption of phosphate ions (*1*) and iron hydroxide (*2*) on modified CT from the concentration of HCl. Content of PO_4^{3-} ions in CT is 0.8 mg-eq mL^{-1} (V/m = 1000, contact time 12 days).

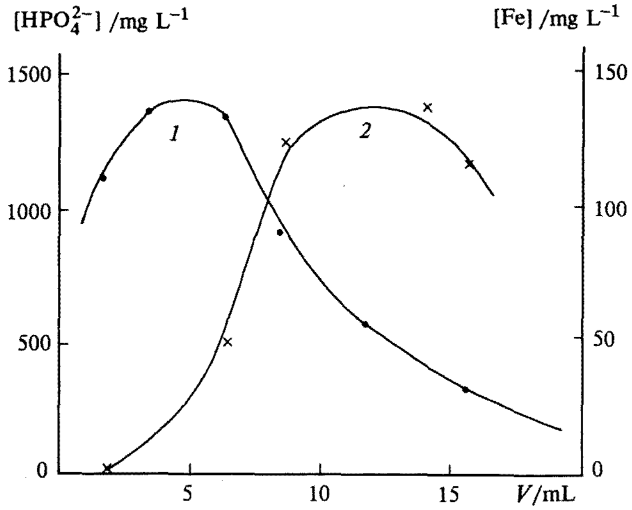

Fig. 5. Desorption of phosphate ions (*1*) and iron hydroxide (*2*) by 0.3 *N* HCl on modified CT. Content of PO_4^{3-} ions in the sorbent is 0.8 mg-eq mL^{-1}; volume of the sorbent is 0.6 mL.

capacities increase sharply when pH increases to 11.5, which testifies that modified clinoptilolite can be used for removal of phosphate ions from alkaline solutions under dynamic conditions. Application of solutions of neutral salts (1 *N* NaCl) for desorption of phosphate from modified clinoptilolite is inefficient.

Dependence of the desorption of phosphates and iron hydroxide from the CT surface by hydrochloric acid on its concentration was studied under static conditions at the contact time of 12 days and the ratio of the phase volumes of V/m = 1000. It is seen from Fig. 4 that complete removal of phosphates can be achieved at the acid concentration of 0.05 *N*, iron hydroxide is removed to a lesser extent, and the differences in the degrees of desorption of phosphate and iron hydroxide increase as the acid concentration decreases.

Desorption of phosphates and iron hydroxide by a 0.3 *N* solution of HCl under dynamic conditions is presented in Fig. 5. Almost complete desorption of phosphates takes place when 25 to 30 volumes of HCl are passed per unit volume of the sorbent. This results in the removal of only 30 % of the iron hydroxide. A 15-fold enrichment of phosphates is achieved at the maximum of the regeneration elution curve. A slower desorption of iron is likely related to higher values of the solubility product of iron hydroxide (−log SP = 38) compared to that of iron phosphate (−log SP = 22).

Phosphate ions from solutions with pH 9 to 12 are sorbed well on CT modified by iron; however, the rate of the process is low. Solutions of mineral acids (0.05—0.3 *N*) can be used for removal of phosphate ions from the sorbent. The choice of the upper boundary of the acid concentration is caused by limited stability of CT to acids. The presumable mechanism of sorption and desorption of phosphates on the modified CT could be associated with the formation of poorly soluble phosphate compounds of iron and their dissolution in acidic media. The results obtained can be used for development of the technology of purification of waste water from phosphate ions and for preparation of fertilizers based on CT.

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