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Ion-Exchange Properties and IR Spectra of Natural Clinoptilolite Modified with Titanium Hydroxophosphates

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Abstract—A method for modification of a natural zeolite, a clinoptilolite-containing tuff, with compounds based on titanium phosphate is suggested. The results obtained in a comparative study of sorption of heavy metal ions on the initial and modified clinoptilolite are presented. The modifying effect of an additive is discussed on the basis of IR and X-ray fluorescence spectroscopic data.

The selectivity of a natural zeolite, clinoptilolite, toward ions of heavy and transition metals makes promising its use for recovery of these elements from aqueous solutions, industrial wastewater, and potable water. However, the clinoptilolite-containing material is rarely used in practice in its natural form, being, as a rule, subjected to additional chemical pretreatment to improve its sorption, mainly ion-exchange properties [1].

The most widely used method for directed modification of a zeolite sorbent is cation-exchange modification, which consists in that the polycationic natural material is transformed into a monocationic (H^+, Na^+, Ca^{2+}, NH_4^+, etc.) form [2].

In contrast to the commonly accepted approach [2], in this work we examined the possibility of improving the performance of natural clinoptilolite by chemical grafting of a modifying agent with good sorption and selective properties. We believe that the most promising in this regard are compounds based on titanium hydroxophosphates [3].

EXPERIMENTAL

As starting sorbent we took samples of a clinoptilolite-containing tuff from the Sokirnitskoe deposit (Transcarpathia). The modification was performed by impregnating the polycationic matrix with a 1 M aqueous solution of $TiCl_4$ in 1 M HCl (pH 0) with subsequent drying and further treatment with a 1 M H_3PO_4 solution. The resulting sorbent was washed with distilled water to remove excess acid and salts and dried at 100–110°C.

An analysis of the elemental composition of the surface layer of the modified clinoptilolite samples by X-ray fluorescence spectroscopy (VG ESCA-3 spectrometer with reference for determining the core electrons, C1*s* line 284.4 eV) demonstrated that the Ti : P ratio is within the range (1 : 3)–(1 : 1). The observed scatter is probably due to inhomogeneity of the starting natural material.

Sorption experiments were carried out under dynamic conditions on a filtering column 0.8 cm in diameter with the sorbent bed height of 10 cm (0.5–1.0-mm fraction) and sorbent charge volume [1 c.v. (column volume)] of 5 cm^3. The filtration rate was chosen to be 2.0 $m\,h^{-1}$ (100 $cm^3\,h^{-1}$, i.e., 20 c.v. h^{-1}). Model solutions containing 1–2 $mg\,dm^{-3}$ of copper(II), lead(II), and cadmium(II) ions were prepared from potable tap water with total hardness of 3.7–4.2 mg-equiv dm^{-3}, which contained ($mg\,dm^{-3}$) 60–65 Ca^{2+} ions, 10–15 Mg^{2+} ions, and 0.3 iron ions; pH 6.8–7.1. Preliminary studies revealed that no precipitation of heavy metal ions occurs in the working range of concentrations ($\leq 10^{-5}$ M) and pH values (6.8–7.1). The results obtained are in agreement with the data of [3–5].

A comparative analysis of the output curves of sorption of copper(II), cadmium(II), and lead(II) ions, which were obtained on natural and modified clinoptilolite under the same conditions, demonstrated that the degree of recovery of these elements with a modified sorbent is 2–2.5 times that with the natural material. Data on the influence exerted by modification on the sorption of Cd^{2+}, Cu^{2+}, and Pb^{2+} ions in the dynamic mode are presented in Fig. 1. It can be seen that, even on the background of a manyfold excess (by a factor of 50–100 for Ca^{2+} only) of alkaline-earth elements present in tap water, the degree of recovery of the ions under study is sufficiently high. In this case, as also in the case of titanium hydroxophosphates, the ions can be arranged in the order of increasing degree of recovery as follows: $Cu \le Cd < Pb$.

To reveal how the modifying agent is bound to the natural zeolite, at what centers the modification occurs, and what is reason for higher sorption of heavy metal ions on the sorbent obtained, we examined the IR spectra of the starting clinoptilolite and its modified form before and after sorption of ions. Samples were in the form of KBr pellets or a mull in mineral oil. The weighed portions taken for preparing KBr pellets were chosen so that the bands under study were peaked at 80–20% transmission. The spectra were recorded on a Carl Zeiss Specord M80 instrument in the spectral range 4000–400 cm^{-1}. Since the spectral manifestation of the processes that occur on the surface is diffuse, the method of baseline and internal reference [6] was used to ensure the adequacy of the analysis performed. As the internal reference we chose the band associated with bending vibrations of water (ν ~1635 cm^{-1}) [7]. Its shape, position, and intensity are virtually the same for all of the samples studied (Fig. 2).

It is known [7] that the strongest absorption in the IR spectrum of clinoptilolite is observed in the range 900–1300 cm^{-1}. This absorption is due to intra- and extratetrahedral asymmetric stretching vibrations of O–Si(Al)–O bonds. The absorption bands in the range 400–8500 cm^{-1} range are attributed to symmetric stretching and bending vibrations of structural groups of the aluminum–silicon–oxygen framework. An isolated absorption band peaked at ν ~1635 cm^{-1} is due to bending vibrations of sorbed water, and a broad medium-intensity band of complex shape at ν ~3400 cm^{-1} is associated with stretching vibrations of hydroxy groups [7].

The results obtained in mathematical processing of the spectral data in the region of absorption associated with stretching vibrations of the O–H bonds (2900–4000 cm^{-1}) and the main absorption band of the zeolite framework (850–1550 cm^{-1}) are shown in Figs. 3 and 4, respectively. As seen from Fig. 3, modification of clinoptilolite with titanium hydroxophosphate leads to a decrease in the intensity of the high-frequency (3600–3800 cm^{-1}) wing of the absorption band associated with stretching vibrations of hydroxy groups possessing basic properties [8–10].

The modification of clinoptilolite also manifests itself in an increase in the intensity and halfwidth of the main absorption band of O–Si(Al)–O bonds, peaked at ν ~1075 cm^{-1} (Fig. 4). Figure 4 also shows the difference of the optical densities of the modified and unmodified forms of clinoptilolite, which is a

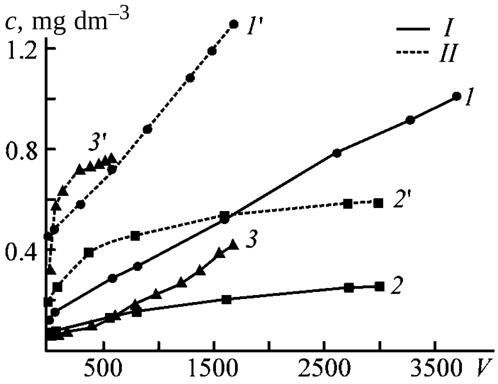


Fig. 1. Output curves of sorption of (*1*, *1'*) Cu^{2+}, (*2*, *2'*) Pb^{2+}, and (*3*, *3'*) Cd^{2+} on (*I*) natural and (*II*) modified clinoptilolite. (*c*) Concentration of Cu^{2+}, Pb^{2+}, and Cd^{2+} in solution; (*V*) number of column volumes.

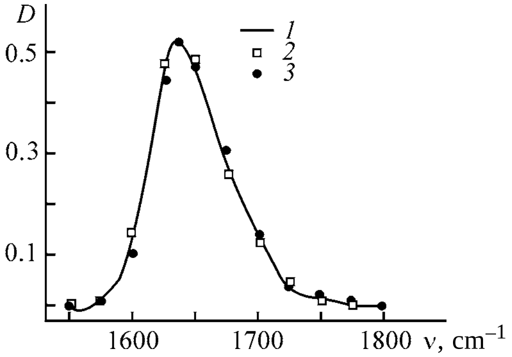


Fig. 2. Absorption associated with bending vibrations of water in (*1*) natural clinoptilolite and in its modified form (*2*) before and (*3*) after sorption of Pb^{2+}. (*D*) Optical density and (ν) wave number; the same for Figs. 3 and 4.

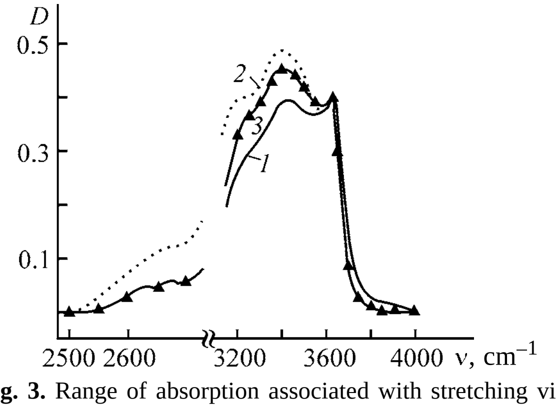


Fig. 3. Range of absorption associated with stretching vibrations of OH groups in (*1*) natural clinoptilolite and that modified with titanium hydroxophosphate, (*2*) before and (*3*) after sorption of Pb^{2+}.

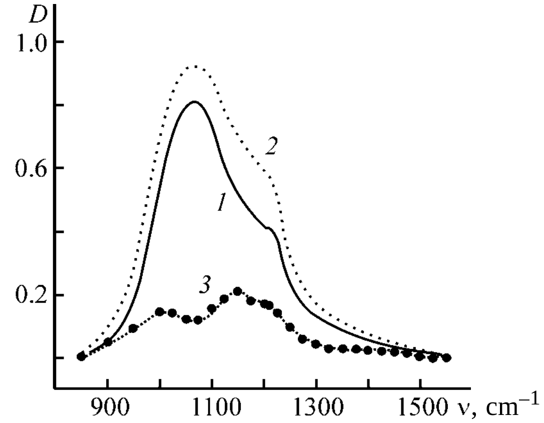


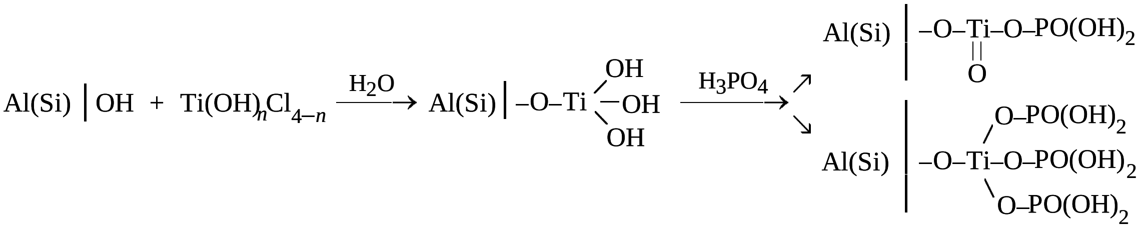
Fig. 4. Absorption bands of aluminum–silicon–oxygen framework of (*1*) natural and (*2*) modified clinoptilolite and (*3*) difference of these two.

curve with two clearly pronounced peaks. The low-frequency peak at ν ~1020 cm^{-1} is related to absorption of the modifying agent, since the main absorption band in the IR spectrum of amorphous titanium hydroxophosphate is recorded in this spectral range. The high-frequency peak (with ν ~1150 cm^{-1}) arises in the spectral range of absorption by strong aluminum–silicon–oxygen bonds of the zeolite framework. The appearance of additional O–Si(Al)–O bonds upon modification indicates that the bonding between clinoptilolite and the modifying agent is covalent.

The decrease in the amount of hydroxy groups of basic nature (Fig. 3, 3600–3800 cm^{-1}), with simultaneous appearance of additional O–Si(Al)–O bonds (Fig. 4, ν ~1150 cm^{-1}), points to the active role of these groups in the formation of covalent bonds between the modifying agent and the starting zeolite.

Figure 3 also shows that the intensity of the low-frequency wing of the absorption band associated with OH groups with pronounced protonogenic properties increases substantially in the course of modification. After the modified clinoptilolite is used as sorbent for ion recovery, the intensity of the low-frequency wing of the absorption band associated with the OH groups responsible for the acid properties of the surface decreases. This decrease is shown for the example of sorption of lead(II) ions in Fig. 3, curve *3*. The decrease (compared with the modified sample before sorption) in the intensity of the low-frequency component responsible for the acid properties of the surface points to the cationic mechanism of sorption. Here, only the following detail of interest should be noted: the stronger the hydrogen in the protonogenic OH group is covalently bound to oxygen (3500–3150 cm^{-1} range), the lower its reactivity toward cations [curve *3* occupies an intermediate position between the absorption curves of the starting clinoptilolite (*1*) and its modified form (*2*)]. With increasing ionic component in the bonding between hydrogen and oxygen (2700–2500 cm^{-1} range), all the protonogenic groups acquired in modification are "consumed" for sorption of lead(II) ions (curve *3* coincides with curve *1* of the starting clinoptilolite). It should also be noted that OH groups are not involved at all in cation sorption: the high-frequency wing (3800–3600 cm^{-1} range) of the absorption band of OH groups of modified clinoptilolite before sorption of lead(II) ions (curve *2*) completely coincides with that upon sorption of these ions (curve *3*).

The following should be taken into account when analyzing the reaction of the modifying agent with the surface of clinoptilolite: (a) IR data (role of basic hydroxy groups in grafting of the modifying agent); (b) the fact that titanium tetrachloride even at pH 0 is hydrolyzed in aqueous sulfuric acid solutions to give hydroxochlorides and hydroxo complexes [11], which form poorly soluble titanium hydroxophosphates in their subsequent reaction with phosphoric acid [3]; (c) elemental ratio Ti : P in the surface layer. Then this reaction can be represented as the following scheme:



$$\text{Al(Si)}\,|\,\text{OH} + \text{Ti(OH)}_n\text{Cl}_{4-n} \xrightarrow{H_2O} \text{Al(Si)}\,|\,\text{–O–Ti(OH)}_3 \xrightarrow{H_3PO_4} \begin{cases} \text{Al(Si)}\,|\,\text{–O–Ti(=O)–O–PO(OH)}_2 \\ \text{Al(Si)}\,|\,\text{–O–Ti(–O–PO(OH)}_2\text{)}_3 \end{cases}$$

where n = 0, 1, 2, and 3.

Additional sorption of cations on modified clinoptilolite is due to protons of grafted dibasic groups of phosphoric acid, with different dissociation constants [5]. The ionization of phosphoric acid groups mainly by the first step at working pH values of 6.8–7.1 predetermines the involvement of three equivalent protonogenic groups in the ion exchange.

CONCLUSIONS

(1) A new, highly efficient sorbent for heavy metal ions, with sorption characteristics exceeding those of the initial sorbent, was obtained by modifying a natural zeolite, clinoptilolite, with titanium hydroxophosphate.

(2) The results of IR studies, X-ray fluorescence spectroscopy, and sorption measurements led to a conclusion that the modification of clinoptilolite consists in grafting to its surface of titanium hydroxophosphate compounds with increased concentration of OH groups, which can exchange their protons for cations of heavy metals. It is the additional contribution of this cation exchange to the ion exchange commonly observed in natural zeolites that gives rise to improved sorption properties of modified clinoptilolite samples.

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