

## Sorption of Lead on Na-Modified Transcarpathian Clinoptilolite

V.O. VASYLECHKO<sup>a,b</sup>, G.V. GRYSHCHOUK<sup>a</sup>,  
YA.M. KALYCHAK<sup>a</sup>, R.E. GLADYSHEVSKII<sup>a</sup>, I.P. NAVROTSKA<sup>a</sup>,  
S.R. BAGDAY<sup>a</sup> AND A.V. ZELINSKIY<sup>a</sup>

<sup>a</sup>*Ivan Franko National University of Lviv, 6 Kyryla and Mephodia Str., 79005 Lviv, Ukraine*

<sup>b</sup>*Lviv University of Trade and Economics, 9 Samchuka Str., 79011 Lviv, Ukraine*

Doi: [10.12693/APhysPolA.141.328](https://doi.org/10.12693/APhysPolA.141.328)

\*e-mail: [vasylechko@ukr.net](mailto:vasylechko@ukr.net)

The sorption properties of the Na-modified Transcarpathian clinoptilolite towards Pb(II) were studied under dynamic conditions. It was noticed that Pb(II) was sorbed with the best efficiency on the uncalcined Na-clinoptilolite samples from the solutions with pH of 7.0. The maximal sorption capacity value of the Na-clinoptilolite towards Pb(II) is equal to 65 mg/g, which is 6.1 and 1.3 times higher than the sorption capacity value of the natural and acid-modified forms of this zeolite, respectively. Lead was quantitatively removed from the solid-phase extraction column with a 2.5 M HNO<sub>3</sub> solution. The solid-phase extraction procedure with Na-clinoptilolite was used for preconcentration of trace amounts of lead ions in aqueous solutions for their final determination by the atomic absorption method. The linearity of the proposed method was evaluated in the range of 0.06–15 ng/mL with a detection limit of 0.02 ng/mL.

topics: lead, sorption, Na-modified clinoptilolite, solid-phase extraction

### 1. Introduction

Lead is a broad-spectrum toxicant. Since the permitted Pb concentration is very low, during the analysis of samples, even when using the state-of-the-art methods, there is a need for preliminary preconcentration, removal, and/or separation of Pb trace amounts [1–5]. The purification of waters and soils from this toxic element, and the regeneration of Pb from technological waste, need to be considered. The solution to this problem is connected mainly with the use of efficient sorbents of Pb.

The list of known sorbents of Pb(II) from aqueous solutions with their characteristics is described in detail [1, 4–7]. The use of sorbent of Pb(II) as common as silica gel or sorbents based on it [1, 5, 7] is problematic even in the analysis of slightly alkaline solutions because at pH ~ 8 silica gel is being partially dissolved. At pH > 9, the dissolution rate of silica gel increases extremely [8], which adversely affects the chemical and physicochemical properties of its surface.

In recent years, intensive studies of sorptive properties of natural zeolites towards Pb(II) have been carried out [9–12]. Natural zeolites combine cation exchange properties, sieve effect, and surface adsorption, which, to a certain extent, makes

it possible to affect predictably the selectivity of the substances concentration. These nanomaterials are characterized by mechanical strength, high sorption capacity and selectivity, ability to sorb trace amounts of substances, thermal stability, availability, cheapness, the possibility of modification and sorption in solutions with a wide pH range.

However, natural zeolites as sorbents of trace amounts of Pb(II) have not yet been used in the solid-phase extraction (SPE) method. Recently, in [6, 13], we investigated the sorption properties of natural and acid-modified forms of Transcarpathian clinoptilolite with respect to Pb(II) and proposed methods for concentrating trace amounts of Pb(II) from natural waters with subsequent atomic absorption analysis of the concentrate.

It is known that Na-forms of Transcarpathian clinoptilolite differ significantly from the unmodified clinoptilolite in terms of their sorptive properties, and they usually possess a higher sorption capacity towards heavy metal ions [14–17].

In this paper, we studied the sorptive properties of Na-modified Transcarpathian clinoptilolite towards trace amounts of Pb(II) in water samples and investigated the possibility of application of this sorbent in the solid-phase extraction method.

## 2. Materials and experimental details

Natural clinoptilolite was collected from the deposit near the village Sokirnytsia in the Ukrainian Transcarpathian region. The previous analysis has shown that the main component was present at 85–90 %, and the specific surface area, determined by water sorption, was 59 m<sup>2</sup>/g [18]. The composition of the oxides can be represented as follows [19]:

- SiO<sub>2</sub> — 67.29 wt%;
- Al<sub>2</sub>O<sub>3</sub> — 12.32 wt%;
- TiO<sub>2</sub> — 0.26 wt%;
- Fe<sub>2</sub>O<sub>3</sub> — 1.26 wt%;
- FeO — 0.25 wt%;
- MgO — 0.99 wt%;
- CaO — 3.01 wt%;
- Na<sub>2</sub>O — 0.66 wt%;
- K<sub>2</sub>O — 2.76 wt%;
- H<sub>2</sub>O — 10.90 wt%.

The clinoptilolite sample was grounded and sieved to 0.20–0.31 mm, washed with distilled water and dried at room temperature.

The Na-form of Transcarpathian clinoptilolite was obtained according to [20]. The powder of clinoptilolite was preconditioned with a 0.25 M HCl solution for 4 h at room temperature. Then the zeolite fraction was separated, washed with distilled water, and treated with a 1 M NaCl solution for 1–1.5 h (this part was repeated seven to eight times). The obtained Na-clinoptilolite was dried at room temperature. Previous thermogravimetric studies [15] showed that the TG and DTG thermograms of unfired samples of natural Transcarpathian clinoptilolite and its Na-form are almost identical. However, the Na-form of clinoptilolite has a more developed effective surface occupied by physically- and chemisorbed molecular water.

The Na-clinoptilolite samples were calcined at the appropriate temperatures for 2.5 h in a drying oven WSU200 (Germany) and muffle furnace SNOL 7.2/1100 (Lithuania). After heat treatment, the zeolite samples were cooled in a desiccator.

The sorption properties of Na-clinoptilolite towards trace amounts of Pb(II) were investigated by solid-phase extraction under dynamic conditions. Metal solutions were passed through a sorption cartridge filled with 0.6 g of the sorbent at a 5 mL/min velocity using the peristaltic pump. The methods of investigation under dynamic conditions are described in detail in [21]. The passage moment of Pb(II) was fixed with sulfarsazene, which creates a colored complex with Pb(II). A sulfarsazene color change from yellow to orange provides the possibility to detect the passing moment of Pb(II) ions with limit of detection (LOD) of 100 ng/mL visually and/or by DR/4000 V spectrophotometer (HACH) at a wavelength of 490 nm.

The samples containing Pb and Co were studied by X-ray fluorescence spectroscopy using the ElvaX Pro analyzer (Elvatech Ltd, Ukraine) with a fast SDD detector (area of 20 mm<sup>2</sup>). A powerful X-ray tube with Rh anode was operated at voltage 30–60 kV, current 1 mA, and power 12 W.

In order to recover the sorbed Pb from the zeolite bed, 20 mL of an eluent at a flow rate of 0.5 mL/min was passed through the sorption cartridge. The lead(II) content in eluates obtained after desorption was estimated by atomic absorption spectroscopy employing the AAS-1N spectrometer (Carl Zeiss, Jena) with a three-aperture burner with a propane/butane air flame at the wavelength of 217.0 nm.

The sorption and desorption were studied at 20 ± 1°C. All used reagents were of analytical grade. Standard aqueous solutions of lead(II) nitrate (1 mg/mL) were prepared by dissolution of metallic lead (99.9% purity, Johnson Mattley) in nitric acid (1:1).

## 3. Results and discussion

The sorption of Pb(II) was studied on Na-clinoptilolite depending on the medium acidity (Fig. 1). Appropriate pH values of Pb(II) solutions were obtained by adding diluted solutions of NaOH or HNO<sub>3</sub>. The maximum sorption capacity of Na-clinoptilolite was observed in neutral solutions of Pb(II) (pH 7.0). Trace amounts of Pb(II) in such solutions are mainly present in the unhydrolyzed cationic form Pb<sup>2+</sup> (~90%) and partly as the cationic hydroxocomplex PbOH<sup>+</sup> (~10%). In slightly alkaline solutions, a neutral soluble form of Pb(OH)<sub>2</sub> and a large polynuclear hydroxocomplex cation Pb<sub>3</sub>(OH)<sub>4</sub><sup>2+</sup> are formed. At pH > 9, trace amounts of Pb(II) form an anionic hydroxocomplex of Pb(OH)<sub>3</sub><sup>-</sup>, and in the solutions with pH > 11, there are no cationic forms of Pb(II) at all [22]. As can be seen in Fig. 1, the efficiency

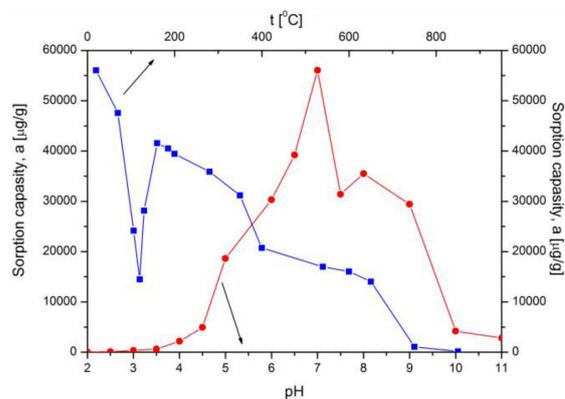


Fig. 1. The Na-clinoptilolite sorption capacity of lead(II) as function of solutions pH and thermal pretreatment of sorbents (concentration of Pb(II) — 1 µg/mL, pH — 7.0, flow rate — 5 mL/min, time of heat treatment — 2.5 h).

of Pb(II) from weakly alkaline solutions is lower compared to neutral solutions, and in the solutions with  $\text{pH} > 11$ , sorption of Pb(II) on Na-clinoptilolite is practically absent. That gives information about the ion-exchange mechanism of Pb(II) sorption on Na-clinoptilolite. The authors also mentioned in [10, 12] the ion-exchange mechanism of sorption of Pb(II) cations on the Na-form of clinoptilolite obtained from natural zeolite of Polish and Romanian deposits.

The sorption properties of Na-clinoptilolite depend on the preliminary thermal treatment, but the maximal sorption capacity was exhibited by uncalcined samples of the sorbent (Fig. 1). Water in a zeolite exists in unequal structural positions and energetic states, which leads to changes in sorption properties during the thermal treatment of samples. Water also influences the properties of exchangeable ions, their position, and migration through the zeolite channels, which will be reflected in the efficiency of heavy metals sorption. As can be seen in Fig. 1, the highest sorption capacity towards Pb(II) has the unannealed Na-clinoptilolite, and the increase of the temperature for the preliminary calcinations of the sorbent samples to  $125^\circ\text{C}$  leads to a considerable decrease in its sorption capacity towards Pb(II). A similar dependence in the temperature range of  $20\text{--}125^\circ\text{C}$  is observed during the sorption of trace amounts of Ag(I) on the Na-form of Transcarpathian clinoptilolite [14]. Only a small part of moisture is withdrawn from the Transcarpathian clinoptilolite at such temperatures [23]. Processes that occur at the low temperature stage of water thermodesorption from the zeolite lead to a decrease in its sorption capacity towards Pb(II). During zeolite dehydration, the shift of exchangeable ions takes place, which influences the channels cut [24]. Probably such channel blocking causes the weakening of Na-clinoptilolite sorption properties towards large aquacomplexes of heavy metals.

It was found that the sorption capacity of Na-clinoptilolite increases when the concentration of Pb(II) ions in the solution is decreasing (Table I). In our opinion, this is caused by the decrease in  $\text{PbOH}^+$  cation fraction and the possible formation of multinuclear cationic hydroxo complexes such as  $\text{Pb}_3(\text{OH})_4^{2+}$  or  $\text{Pb}_6(\text{OH})_8^{4+}$  while increasing the concentration of Pb(II) in the solution [22]. Since multinuclear hydroxo complexes are much bigger than mononuclear complexes, their access to zeolite grains is limited.

In order to find efficient desorbents of Pb(II) the solutions of  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_4\text{OH}$  and chlorides alkali metals have been tested. The best desorbents of Pb(II) from Na-clinoptilolite are 0.5 M NaCl, 0.5 M KCl and 2.5 M  $\text{HNO}_3$ . These desorbents remove 95–100% of sorbed Pb(II) (Table II). The concentration of Pb(II) in the eluates obtained during the effective desorption of this p-element was in the range of  $25\text{--}50 \mu\text{g/mL}$ .

TABLE I

Sorption capacity of Na-modified clinoptilolite depending on Pb(II) salts concentration ( $\text{pH} 7.0$ ).

Pb(II) concentration [ $\mu\text{g/mL}$ ]	Sorption capacity [mg/g]
0.5	65.0
1.0	56.1
3.0	13.8

TABLE II

Desorption efficiency of lead(II) from Na-clinoptilolite (flow rate of an eluent through the adsorption system — 0.5 mL/min, volume of the eluent employed — 20 mL).

Eluent	Desorption [%]
2.5 M $\text{HNO}_3$	100
7 M $\text{HNO}_3$	80
3.5 M $\text{H}_2\text{SO}_4$	12
9 M $\text{H}_2\text{SO}_4$	12
0.5 M NaCl	95–100
1 M NaCl	85
0.5 M KCl	95–100
6.5 M $\text{NH}_4\text{OH}$	8

TABLE III

Tolerance limits of some ions for lead(II) sorption from aqueous solution of Na-clinoptilolite ( $\text{pH} 7.0$ ; concentration of Pb(II) =  $1 \mu\text{g/mL}$ ).

Species	Tolerance limit [ $C_{ion}/C_{Pb(II)}$ ]
$\text{Na}^+$	1100
$\text{K}^+$	900
$\text{Mg}^{2+}$	500
$\text{Ca}^{2+}$	1200
$\text{SO}_4^{2-}$	2000
$\text{NO}_3^-$	3000

The influence of common ions of waters on the preconcentration of Pb(II) on Na-clinoptilolite has been studied (Table III). It was established that a (500–3000)-fold excess of main water components does not influence the maximum sorption capacity of Na-clinoptilolite towards Pb(II).

It is known [16] that trace amounts of Co(II) are also most efficiently sorbed by samples of Na-clinoptilolite from neutral solutions. Samples of Na-clinoptilolite calcined at  $400^\circ\text{C}$  show minimal sorption capacity with respect to Co(II) [16]. At the same time, the sorption capacity of Na-clinoptilolite samples pre-calcined at  $400^\circ\text{C}$  towards Pb(II) is  $20 \text{ mg/g}$  (Fig. 1). Such differences in the conditions of sorption of these heavy metals on Na-clinoptilolite make it possible to quantitatively separate Pb(II) from Co(II). To confirm the idea of a selective concentration of Pb(II) in the presence of Co(II), we performed X-ray fluorescence analysis of

TABLE IV

The results of X-ray fluorescence determination of lead and cobalt content in Na-clinoptilolite samples after sorption of Pb(II) from model solutions. Note: The following conditions were used in all cases: flow rate of solution through sorbent — 5 mL/min; pH 7.0; temperature of Na-clinoptilolite preliminary thermal treatment — 400°C; time of heat treatment — 2.5 h; mass of sorbent — 0.6 g; sorbent grains diameter — 0.20–0.31 mm; the volume of solution passed through the sorbent — 6000 mL.

Composition of the model solution	Proportion of sorbed Pb and Co relative to its content in the model solution [%]
1 $\mu\text{g/mL}$ Pb(II)	Pb 100
1 $\mu\text{g/mL}$ Pb(II)+0.1 $\mu\text{g/mL}$ Co(II)	Pb 100, Co 29
1 $\mu\text{g/mL}$ Pb(II)+0.5 $\mu\text{g/mL}$ Co(II)	Pb 100, Co 11
1 $\mu\text{g/mL}$ Pb(II)+1 $\mu\text{g/mL}$ Co(II)	Pb 73, Co 5.5

Na-clinoptilolite samples obtained after sorption of Pb(II) from model solutions that contained Co(II) in addition to Pb(II) in different quantities. Sorption of Pb(II) was carried out at pH 7.0 on calcined at 400°C samples of Na-clinoptilolite. The results of X-ray fluorescence analysis are given in Table IV. The data in Table IV show the incomplete separation of Pb from Co at the concentration of trace amounts of Pb(II) from a model solution containing a proportionate amount of Co(II). At the same time, from model solutions in which the concentration of Pb(II) is two and ten times higher than the concentration of Co(II), Pb(II) absorbs completely, and Co(II) absorbs only partially. Therefore, Pb(II) can be completely separated from such solutions using Na-clinoptilolite as a sorbent. Consequently, Na-modified clinoptilolite can be used in the future for extraction and separation of Pb and Co from technological solutions of enterprises utilizing galvanic elements and enterprises of radio engineering.

Summarizing the results of investigations, it can be seen that the maximal sorption capacity value of Transcarpathian clinoptilolite Na-form under dynamic conditions towards Pb(II) is equal to 65 mg/g (or 0.63 mEq/g) (Table I), which is 6.1 and 1.3 times higher than the corresponding sorption capacity of the natural and acid-modified forms of this zeolite [6, 13]. According to [24], the ion exchange capacity of Transcarpathian clinoptilolite is 1.45 mEq/g. It indicates that during the sorption of trace amounts of Pb(II) on Na-clinoptilolite under optimal conditions,  $\sim 40\%$  of the ion exchange capacity of the zeolite is involved. The optimal conditions of Pb(II) sorption on Na-clinoptilolite are as follow: the grain size of unannealed zeolite of 0.20–0.31 mm; throughput flow rate of Pb(II) solution with the concentration of 1  $\mu\text{g/mL}$  through the sorbent — 5 mL/min; pH 7.0.

A method of Pb(II) preconcentration in the solid phase extraction mode during the preparation of waters for the analysis has been proposed.

#### 4. Sample preconcentration procedure

The sorbent is prepared as follows. A sample of natural Transcarpathian clinoptilolite was grained in a ball mill. A zeolite fraction with a grain size of 0.20–0.31 mm was taken, washed with distilled water, and dried at 20°C. The clinoptilolite sample with 200 mL of 0.25 M HCl was dried at room temperature for 4 h. After that, the samples were washed with distilled water to remove traces of acid and then transformed into the Na-form by treating them with 200 mL of 1 M NaCl 7–8 times every 1–1.5 h. Next, the zeolite was washed from anions with distilled water and dried at 20°C. The solution of HNO<sub>3</sub> was added to 0.5–2.5 L of the investigated water to acidify it to pH  $\sim 1$ , and the mixture was heated in the sand bath for 1 h. After the filtration through the dense paper filter, the pH of the water was adjusted to 7.0 with a sodium hydroxide solution. The obtained solution was passed through an SPE cartridge filled with 0.6 g of the prepared sorbent at a flow rate of 5 mL/min. After loading the sample, the cartridge was washed with 50 mL of bidistilled water at the same flow rate. Whereas, lead(II) ions were desorbed with 20 mL of a 2.5 M HNO<sub>3</sub> solution at a flow rate of 0.5 mL/min. Lead content in the solution was determined by the atomic absorption method, as described in the experimental part.

In general, the proposed method for the determination of Pb(II) ions had a linearity range from 0.06 to 15 ng/mL. The detection limit was found to be 0.02 ng/mL. An enrichment factor of 125 can be achieved using the proposed method of Pb(II) preconcentration.

#### 5. Conclusions

The sorption properties of Na-modified Transcarpathian clinoptilolite regarding the aqueous solution of lead ions using the dynamic technique were investigated. It was established that Pb(II) is recovered with the highest efficiency from the neutral solutions mainly according to the ion-exchange mechanism.

The optimal conditions for the Pb(II) sorption on Na-clinoptilolite are the following: flow rate of the solution Pb(II) with the concentration of 0.5  $\mu\text{g/mL}$  through the sorbent — 5 mL/min, grains diameter of the zeolite — 0.20–0.31 mm, pH — 7.0. The maximal sorption capacity of the Na-clinoptilolite towards Pb(II) is equal to 65 mg/g, which is 6.1 and 1.3 times higher than the sorption capacity value of the natural and acid-modified form of this zeolite, respectively [6, 13].

The best desorbent of Pb is the 2.5 M solution of HNO<sub>3</sub>, by means of which 100 % of Pb concentrated on the zeolite can be desorbed.

Conditions have been found for selective withdrawal of Pb(II) and Co(II) and complete separation of these toxic metals from aqueous solutions.

The preconcentration method of Pb(II) trace amounts in the solid-phase extraction mode during the atomic absorption analysis of natural waters has been proposed. An enrichment factor of 125 was obtained under the optimum conditions. A wide range of linearity (0.06–15 ng/mL) with a detection limit of 0.02 ng/mL was achieved.

### Acknowledgments

This work was partially funded by the Ministry of Education and Sciences of Ukraine.

### References

- [1] M. Ahmadi, H. Elmongy, T. Madrakian, M. Abdel-Rehim, *Anal. Chim. Acta* **958**, 1 (2017).
- [2] S. Kagaya, E. Maeba, Y. Inoue, W. Kamichatani, T. Kajiwara, H. Yanai, M. Saito, K. Tohda, *Talanta* **79**, 146 (2009).
- [3] P. Baile, E. Fernandez, L. Vidal, A. Canals, *Analyst* **144**, 366 (2019).
- [4] Y. Wang, S. Gao, X. Zang, J. Li, J. Ma, *Anal. Chim. Acta* **716**, 112 (2012).
- [5] E.S. Yanovskaya, V.A. Tertykh, V.I. Karmanov, A.D. Dadashev, E.V. Odinets, O.Yu. Kichkiruk, *Khark. Univ. Bull. Chem. Ser.* **820**, 168 (2008).
- [6] V. Vasylechko, G. Gryshchouk, I. Neroda, *Visnyk Lviv. Univ. Ser. Khim.* **50**, 177 (2009).
- [7] M. Ghazaghi, H.Z. Mousavi, A.M. Rashidi, H. Shir Khanloo, R. Rahighi, *Talanta* **150**, 476 (2016).
- [8] F.K. Crundwell, *ACS Omega* **2**, 1116 (2017).
- [9] E. Yulianti, Abdullah, S.I. Yusniyyah, N. Aini, S.N. Khalifah, V.N. Istighfarini, *Adv. Soc. Sci. Ed. Humanit. Res.* **529**, 363 (2021).
- [10] W. Mozgawa, M. Król, W. Pichór, *J. Hazard. Mater.* **168**, 1482 (2009).
- [11] P. Kabwadza-Corner, E. Johan, N. Matsue, *J. Environ. Prot.* **6**, 45 (2015).
- [12] L. Mihaly-Cozmuta, A. Mihaly-Cozmuta, A. Peter, C. Nicula, H. Tutu, D. Silipos, E. Indrea, *J. Environ. Manage* **137**, 69 (2014).
- [13] V.O. Vasylechko, G.V. Gryshchouk, M.I. Kaminska, B.M. Stel'makhovych, *Appl. Nanosci.* **9**, 1057 (2019).
- [14] V. Vasylechko, V. Fedorenko, O. Gromyko, G. Gryshchouk, Ya. Kalychak, S. Tistechok, I. Us, A. Tupys, *Mater. Today: Proc.* **35**, 548 (2021).
- [15] O. Vyviurska, V. Vasylechko, G. Gryshchouk, Ya. Kalychak, V. Zakordonskiy, *Chem. Met. Alloys* **5**, 136 (2012).
- [16] H. Sak, V. Vasylechko, G. Gryshchouk, Ya. Kalychak, Ya. Lomnytska, *Visnyk Lviv. Univ. Ser. Khim.* **61**, 152 (2020).
- [17] V.I. Gomonyay, S.S. Milyovich, N.P. Golub, K.Yu. Sekeresh, M.I. Tegza, *Naukovij Visnik Uzhgorods'kogo universitetu Seria Himia* **6**, 187 (2001).
- [18] V.O. Vasylechko, G.V. Gryshchouk, L.O. Lebedynets, Yu.B. Kuz'ma, L.O. Vasylechko, V.P. Zakordonskiy, *Adsorpt. Sci. Technol.* **17**, 125 (1999).
- [19] Yu.I. Tarasevich, V.E. Polyakov, V.Zh. Penchev, G.N. Kirov, Kh.I. Minchev, I.G. Polyakov, L.I. Badekha, *Khim. Technol. Vody* **13**, 132 (1991).
- [20] Yu.I. Tarasevich, I.G. Polyakova, V.E. Polyakov, *Colloid. J.* **65**, 493 (2003).
- [21] V.O. Vasylechko, L.O. Lebedynets, G.V. Gryshchouk, Yu.B. Kuz'ma, L.O. Vasylechko, T.M. Bernats'ka, *Adsorpt. Sci. Technol.* **14**, 267 (1996).
- [22] C.F. Baes, R.E. Mesmer, *The Hydrolysis of Cations*, Wiley, New York 1976.
- [23] V.P. Zakordonskiy, V.O. Vasylechko, P. Staszczuk, G.V. Gryshchouk, *Visnyk Lviv. Univ. Ser. Khim.* **44**, 152 (2004).
- [24] Yu.I. Tarasevich, *Surface Phenomena on Disperse Materials*, Naukova Dumka, Kyiv 2011.