



Neodymium sorption on the Na-form of Transcarpathian clinoptilolite

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ABSTRACT

The sorption properties of Na-modified Ukrainian Transcarpathian clinoptilolite towards neodymium aqueous solutions under dynamic conditions have been investigated. The sorption capacity of the Na-form of Transcarpathian clinoptilolite towards Nd(III) significantly depends on the concentration of neodymium salt, the pH of the solution, and the heat treatment temperature of the sorbent. Nd(III) is most efficiently sorbed from slightly alkaline solutions (pH 8.5), mainly by adsorption of neutral hydrolyzed forms of Nd(OH)₃ on the surface of Na-clinoptilolite samples preheated at 75 °C. During the passage of an Nd(III) solution with a concentration of 1 μg mL⁻¹ through the sorbent at a rate of 3 mL min⁻¹ under optimal conditions, the sorption capacity of Na-clinoptilolite is 7.2 mg g⁻¹, which is in 4 and 2.3 times higher than that of natural and acid-modified forms of this zeolite. It is shown that under the experimental conditions with an increase in the flow rate, the thickness of the stationary surface layer decreases, which leads to a decrease in the sorption capacity of Na-clinoptilolite. The best Nd(III) desorbents are solutions of mineral acids and acidified solutions of alkali metal salts (except NaCl), which provide 93–98 % extraction of lanthanide from the zeolite matrix. The method for neodymium trace amounts preconcentration from aqueous solutions in a solid-phase extraction mode with a further determination of this rare earth element by a spectrophotometric method was developed. The detection limit of this method is 0.75 ng mL⁻¹ and the linearity was evaluated in the range of 2.5–500 ng mL⁻¹.

1. Introduction

Neodymium is one of the most popular elements of the cerium subgroup lanthanides (Ln). This lanthanide, along with other rare earth elements (REE), is widely used as a component of alloys that are used in the production of data storage devices and magnets, lasers, and glass coloring (tinting). Neodymium is also used in nuclear power engineering, electronics, and medicine [1–4].

Neodymium as a trace element has been detected in seawater, river, and lake sediment samples [5,6]. The content of Nd and other

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REEs in bentonite-clarified wines is proposed to be used as a “fingerprint” in the authentication of Hungarian wines [7].

When analyzing various objects for Nd content, it is frequently necessary to pre-concentrate, separate, and/or isolate this lanthanide. There is also the problem of extracting Nd from process solutions. One of the ways to solve these analytical and technological problems is the search and research effective selective sorbents of this REE. In recent years, sorbents have been increasingly used in the analytical chemistry of lanthanides [5,6,8–10]. Application of the solid-phase extraction method makes it possible to reduce sample preparation time, reduce the amount of toxic organic solvents used, and simplify their disposal after analysis. This method makes it possible to automate the sample preparation stage during analysis [9,11]. REE are mainly concentrated on modified silica gels, polymer sorbents, activated carbon, aluminium oxide, carbon nanofibers, zirconium phosphates, and fullerenes. Natural REE sorbents include Spirulina biomass [12], cherty rocks [13], algal biomass [14,15], and modified chitosans [16–18].

Among the most common sorbents used in the solid phase extraction method are zeolites [8,19–23]. The sorption properties of natural zeolites in Nd(III) aqueous solutions are poorly studied. There are known works [3,4] that investigated the sorption capabilities of heulandite and natrolite towards this lanthanide. However, natural zeolites as sorbents of trace amounts of Nd(III) have not yet been used in the solid-phase extraction method. Among natural zeolites, clinoptilolite is the most common. We recently investigated the sorption properties of natural and acid-modified forms of Transcarpathian clinoptilolite towards Nd(III) and proposed methods for concentrating trace amounts of Nd(III) from aqueous solutions with subsequent spectrophotometric analysis of the concentrate [24, 25].

Various researchers have shown that pretreating clinoptilolite by first completely Na-exchanging it increases cation exchange performance [26–28]. Two possible reasons exist why Na will exchange out of samples faster than Ca. The first could be explained by the structural location of Na and Ca in the sample and the second by the difference in the hydration spheres associated with each. Exchangeable Na^+ cations in clinoptilolite are mostly located near the intersection of channels A and C, and Ca^{2+} cations are located in channel B [26,28]. Sodium bonds to two framework O atoms and five channel water molecules. Calcium bonds to three framework O atoms and five channel water molecules, that is, Ca has more bonds to the framework, which may hold it more tightly in the structure [26]. Also of importance, no doubt, is the bonding of the water molecules to the exchanging cations. The monovalent cations with fewer, more weakly bonded waters are actually smaller and more mobile than the divalent cations with larger, more tightly bonded water molecules [26,29]. Therefore, the low-silicon calcium variety of clinoptilolite, to which Transcarpathian clinoptilolite belongs, after converting it into the sodium form, shows increased efficiency of cation exchange, in particular, increased selectivity to multi-charged cations. It is well known that Na-forms of clinoptilolite have markedly different sorptive characteristics than unmodified clinoptilolite, and they typically have a greater sorption capacity towards cations of d- and f-transition elements [30–36].

We evaluated the sorptive capabilities of Na-modified Transcarpathian clinoptilolite towards trace levels of Nd(III) in water samples and the feasibility of using this sorbent in the solid-phase extraction method in this work.

2. Materials and methods

2.1. Materials and reagents

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 $59 \text{ m}^2 \text{ g}^{-1}$ [37]. The clinoptilolite formula in the oxide form (mass fraction) is (in %): SiO_2 , 67.29; TiO_2 , 0.26; Al_2O_3 , 12.32; Fe_2O_3 , 1.26; FeO , 0.25; MgO , 0.99; CaO , 3.01; Na_2O , 0.66; K_2O , 2.76; H_2O , 10.90 [38]. The clinoptilolite sample was ground and sieved to 0.20–0.31 mm, washed with distilled water, and dried at room temperature.

The Na-form of clinoptilolite was obtained according to Ref. [39]. 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 (repeated seven to eight times). The obtained Na-clinoptilolite was dried at room temperature.

The thermogravimetric investigations that have been carried out earlier [32] showed that TG and DTG thermograms of unannealed samples of natural Transcarpathian clinoptilolite and its Na-form are practically identical. However, the Na-form of clinoptilolite has a more developed effective surface occupied with physically and chemically sorbed water molecules. Based on the TG curve for a Na-form sample of Transcarpathian clinoptilolite [32], the water content in this sorbent is 11.4 %. Based on previously proposed approaches for determining the specific surface area of zeolite samples [21,22,37] and data from thermogravimetric studies of the Na-form of Transcarpathian clinoptilolite given in Ref. [32], we performed calculations to determine the specific surface area of this modified form of clinoptilolite, determined by water sorption is $65 \text{ m}^2 \text{ g}^{-1}$.

The Na-clinoptilolite samples were calcined at the appropriate temperatures for 2.5 h in a drying oven WSU200 (Germany) and muffle furnace SNOL February 7, 1100 (Lithuania). After heat treatment, the zeolite samples were cooled in a desiccator.

All reagents used were of analytical grade: $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (99.5 %, Sigma-Aldrich), HNO_3 (65 %, Lachema, Czech Republic), sulfarsazene (p.a. for spectrophotometric det. Fluka), arsenazo III (98 %, Sigma-Aldrich), HCl (37 %, Sigma-Aldrich), tris(hydroxymethyl)aminomethane (99 %, Sigma-Aldrich), H_2SO_4 (93.6–95.6 %, Sumykhimprom, Ukraine), NaOH (97 %, Sigma-Aldrich), KCl (99 %, Sigma-Aldrich), NaCl (98 %, Sigma-Aldrich), KNO_3 (99.8 %, Hemel, Ukraine), NaNO_3 (98 %, Sigma-Aldrich), NH_4NO_3 (98 %, Sigma-Aldrich), H_3PO_4 (85 %, Sigma-Aldrich), RbNO_3 (99.7 %, Sigma-Aldrich), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99 %, Chemical Elements, Ukraine), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99 %, Sigma-Aldrich). Standard aqueous solutions of neodymium nitrate (with a concentration of 1.0 mg mL^{-1}) were prepared by dissolving the metallic neodymium (99.9 % purity, Johnson Mattley) in the nitric acid solution (1:1). The working solutions of Nd(III) were prepared by the appropriate dilution of the standard solution. The 0.05 % solution of sulfarsazene was prepared using a 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$ aqueous solution. Bidistilled water was used for all reagent solutions.

2.2. Methods

2.2.1. Potentiometric titration

The acid-base properties of clinoptilolite samples were investigated by potentiometric titration [40] carried out in a cell thermostated at 25.0 ± 0.1 °C using an automatic DL25 titrator (Mettler-Toledo, Switzerland). Before titration, 0.2 g of the sample was equilibrated in 20 mL of 0.1 M NaCl solution for 5 h. Then the sample was titrated with 0.1 M NaOH or 0.1 M HCl solution, adding 0.01 mL every 90 s. The concentration of protons was monitored using an LL pH combined glass electrode (Metrohm, Switzerland). The equilibrium concentrations of ions in the solution at each point during titration and correction of possible carbonate and/or silicate contamination were calculated using the EST software [41]. The Proton Affinity Distribution (PAD) was calculated from proton-binding isotherms by solving the adsorption integral equation using the CONTIN method [42,43].

2.2.2. Zeta potential

The zeta potential of natural and Na-form clinoptilolite was measured using a Zetasizer Nano ZS series (Malvern Instruments, Malvern, Great Britain). The device automatically calculates the electrophoretic mobility of the particles and converts it to the zeta potential using the Smoluchowski equation. Clinoptilolite samples were ground into a powder with a fraction of 0.02 mm. The surface charge was determined for diluted colloidal particles of clinoptilolite ($m_{\text{sample}} = 1$ mg) in doubly distilled water ($V = 2$ mL) with pH values from 2 to 12 after sonication for 5 min. Before adding the sorbents, the pH of each solution was adjusted to the required value by adding 0.1 M NaOH or 0.1 M HNO₃. Each measurement was repeated three times. All measurements were carried out at 20–22 °C and the zeta potential values were obtained within the experimental error of ± 2 % [25].

2.2.3. Adsorption of Nd(III)

The sorption properties of Na-clinoptilolite were studied under dynamic conditions in the solid-phase extraction mode. A sorption cartridge which consists of a quartz tube (7 mm in diameter and 20 mm in length) filled with Na-clinoptilolite was used. The tube was closely retained in a poly (vinyl chloride) frame which allowed the passage of solution in and out of the Na-modified sample. The solution of Nd(III) salt was passed through a cartridge for preconcentration filled with 0.6 g of the sorbent at a 5 mL min^{-1} flow rate using a peristaltic pump. The passage moment of Nd(III) ions was fixed by the photometric method using the reaction of Nd(III) with sulfarsazene. It is a highly sensitive method of Nd(III) determination ($\text{LDL} = 100 \text{ ng mL}^{-1}$). This allowed determine the passage point of Nd(III) using a DR/4000 V spectrophotometer (HACH) at a wavelength of 540 nm. The methods of investigation performed under dynamic conditions are described in detail in the paper [25].

2.2.4. Desorption of Nd(III)

To recover the sorbed Nd(III) ions from the zeolite bed, 10 mL of eluent was passed through the sorption cartridge at the flow rate of 0.5 mL min^{-1} . The eluates were collected in 25 mL volumetric flasks and the volume was adjusted to the mark by adding double distilled water. Since solutions of mineral acids and pre-acidified solutions of alkali metals are efficient desorbents of Nd(III) from Na-clinoptilolite, the solutions obtained after the Nd(III) desorption contained a much higher concentration of metals (components of sorbent) than the matrix solutions obtained after Nd(III) sorption. Besides, the spectrophotometric method based on the arsenazo III is much more selective than the technique with sulfarsazene. That is why we used this particular method to determine the content of the desorbed Nd(III) in the solution. The solution absorbance was measured at $\lambda = 650 \text{ nm}$ using a spectrophotometer. To eliminate the interfering influence of Fe(III), Al(III), Mg(II), and Ca(II) ions, ascorbic and sulfosalicylic acid, and Rochelle salt were additionally introduced into the system. The desorption studies were conducted at a temperature of 20 ± 1 °C [25].

During the study of various dependencies, two parallel experiments were conducted. The values of parallel experiments differed by

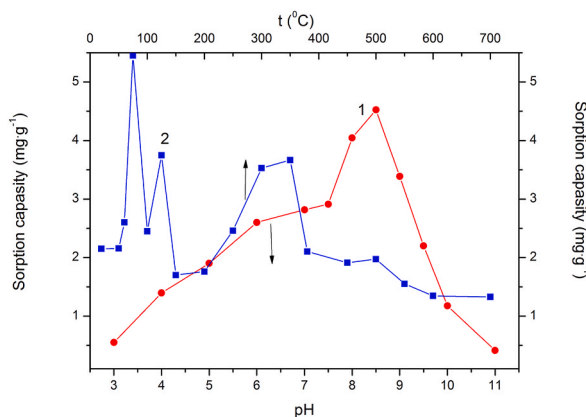


Fig. 1. Dependence of the sorption capacity of Na-clinoptilolite towards Nd(III) on the pH value of the aqueous solution (1) and on the heat treatment temperature (2) (pH 8.5, $1.3 \cdot 10^{-4}$ M borate buffer solution; concentration of Nd(III) – $1 \mu\text{g mL}^{-1}$; time of heat treatment – 2.5 h; flow rate – 5 mL min^{-1}).

no more than ± 5 %. Average values from parallel experiments are presented in the article.

3. Results and discussion

3.1. Optimization of the experimental procedure

The sorption of Nd(III) was studied on Na-clinoptilolite depending on the medium acidity (Fig. 1). Appropriate pH values of Nd(III) solutions were obtained by adding diluted solutions of NaOH or HNO₃. The results obtained confirm that Nd(III) is not sorbed by Na-clinoptilolite in a strong acid medium. Starting from pH 3 the sorption of Nd(III) is growing rapidly and reaches its maximum in a weakly alkaline solution at pH 8.5. In more alkaline solutions, the sorption of Nd(III) decreases sharply. It is known [30,31,33,44] that the sorption-active centers of the Na-form of Transcarpathian clinoptilolite concerning most heavy metals are mostly surface OH groups. That is why the character of the Nd(III) sorption process can be caused by the chemical features of the Na-clinoptilolite surface and by possible forms of Nd(III) in aqueous solutions at different pH values. The dissociation of surface hydroxyl groups of the sorbent is almost completely stopped at low pH values which causes a relatively small value of Na-clinoptilolite sorption capacity towards Nd(III). The dissociation of surface OH groups grows as pH rises, and consequently, so does the value of sorption. The form of Nd(III) in the solution also changes simultaneously with an increase in pH. At a low total concentration of Nd(III), which is comparable to its concentration in the solutions in which the sorption properties of the zeolite were studied, in a solution with a pH of 8.5, Nd(III) is mainly in the form of Nd(OH)₃ (~85 %) and partially in form of Nd(OH)₂⁺ (~15 %) [25]. Therefore, under optimal conditions, the sorption of Nd(III) on the Na-form of Transcarpathian clinoptilolite occurs, mainly, by adsorption of soluble neutral hydroxide Nd(OH)₃ on the surface of the zeolite. Anionic complexes, which are known to be almost completely unsorbed on zeolites, will likely predominate in more alkaline solutions. Natural and H-form of Transcarpathian clinoptilolite sorb Nd(III) from neutral solutions mainly according to the ion exchange mechanism [24,25].

Since Na-clinoptilolite most efficiently sorbs Nd(III) from weakly alkaline solutions (pH 8.5), it is advisable to use a buffer solution rather than an alkali solution to ensure the stability of the pH, and therefore to improve the metrological characteristics of the concentration during the preparation of the investigated solutions for analysis. For this purpose, the possibility of using borate and Tris-buffered solutions was investigated. It was discovered that the maximal sorption capacity of Na-clinoptilolite for Nd(III) in the medium of both borate and Tris-buffered solutions is 50 % of the sorption capacity, which is attained from a solution of Nd(III) with a pH of 8.5, that was prepared using a NaOH solution. Since the pH value of the Tris buffer solution depends to a greater extent on temperature than for most other buffer solutions, we chose a borate buffer for the Nd(III) concentration. In addition, the use of a buffer solution provides a constant ionic strength of the solution, which, in turn, minimizes the influence of various impurities on the Nd(III) concentration.

It was determined that the sorption capacity of the Na-form of Transcarpathian clinoptilolite increases with an increase in Nd(III) concentration up to 2 $\mu\text{g mL}^{-1}$. However, with a further increase in the concentration of Nd(III) to 10 $\mu\text{g mL}^{-1}$, a significant decrease in the sorption efficiency of Na-clinoptilolite is observed (Table 1).

Usually, the adsorption capacity increases with an increase in the concentration of the adsorbed substance. However, during the sorption of trace amounts of substances, the opposite dependence can be observed [22,23,31,45–49]. In particular, the work [47] presents the results of experimental studies, which show that the efficiency of adsorption of Au(III) on In(OH)₃ in a certain concentration range increases with the dilution of Au(III) solutions. The authors of this work also performed calculations according to the Langmuir and Frumkin equations, taking into account the degree of filling of the adsorbent surface and the attraction constant, which takes into account the interaction between particles that are sorbed. These calculations also showed that the amount of sorption should increase with a decrease in the initial concentration of the component that is sorbed. We believe that the different sorption capacity of Na-clinoptilolite concerning low and high concentrations of Nd(III) is also related to the different ability to form hydroxo-complexes at low and high concentrations.

The sorption properties of Na-modified Transcarpathian clinoptilolite also depend on thermal pre-treatment [30–33,44]. That is why the Na-clinoptilolite samples were heated to different temperatures for 2.5 h and after cooling in a desiccator their sorption capacity towards Nd(III) was determined.

The dependence of the sorption capacity of Na-clinoptilolite on the preheating temperature of the sorbent in the low-temperature region is quite complex. At 75 °C, a clear maximum appears, at which the maximum value of the sorption capacity (5.45 mg g^{-1}) is recorded. A characteristic maximum is observed in the high-temperature region, where in the range of 300–350 °C the sorption capacity is ~70 % of its maximum value (Fig. 1). It is known [40] that at temperatures ≤ 100 °C, removal (evaporation) of the surface film

Table 1
Dependence of the sorption capacity of Na-clinoptilolite on Nd(III) concentration (pH 8.5, bufferless solution).

Nd(III) concentration, $\mu\text{g mL}^{-1}$	Sorption capacity, mg g^{-1}
0.25	3.045
0.5	3.045
1.0	4.525
2.0	5.190
5.0	3.225
10.0	2.490

of liquid water is observed in clinoptilolite. This is the external diffusion region of the thermodesorption process, in which only 1–2% of the moisture bound to the zeolite is removed. However, the processes of this stage of thermodesorption of water likely cause an increase in the sorption capacity of samples of Na-clinoptilolite preheated at 75 °C, compared to not heated samples. As the temperature increases from 200 °C to 350 °C, the sorption capacity of Na-clinoptilolite gradually increases. The sorption-active centers of Transcarpathian clinoptilolite concerning heavy metals are mainly surface OH groups, therefore, the increase in the sorption efficiency of Na-clinoptilolite samples calcined in this temperature range is associated with an increase in surface OH groups of zeolite water molecules, as well as surface silanol groups (Si–OH) [50]. A decrease in the sorption efficiency of Na-clinoptilolite at higher temperatures occurs due to the processes of deep dehydroxylation of the zeolite surface and its partial amorphization [32]. It is known [32, 33] that the common lanthanide Tb is most efficiently sorbed on Na-modified Transcarpathian clinoptilolite calcined at 475–700 °C, and the sorption of the transition metal Co on the Na-form calcined at 300 °C of this zeolite is minimal. At the same time, as can be seen from Fig. 1, Nd(III) is practically not sorbed by Na-clinoptilolite calcined at 600 °C but is sufficiently effectively sorbed by Na-clinoptilolite calcined at 300 °C. Such significant differences in the sorption of Nd(III), Tb(III), and Co(II) on thermally modified Na-clinoptilolite samples provide a fundamental opportunity to quantitatively separate Nd from Tb and Co. Such a need may arise during the analysis of solutions for the content of lanthanides in the presence of other REE, as well as during the extraction of Nd, Tb, and Co from spent technological solutions. These three metals are used, in particular, for the production of magnetic materials.

It was important to search for effective desorbents. Acidified solutions of NaCl, KCl, KNO₃, and RbNO₃ salts, as well as solutions of HNO₃, HCl, H₂SO₄, and H₃PO₄ acids were tested. Apart from the NaCl solution, all other tested solutions of salts and acids were effective Nd(III) desorbents, which ensure 93–98 % extraction of lanthanide from the zeolite matrix (Table 2). In the proposed method of Nd(III) concentration, we chose a 2.4 M HCl solution as a desorbent.

The influence of some “common” ions from natural and waste waters on the Nd(III) sorption by Na-form of clinoptilolite was also investigated. Permissible multiple contents ($C_{ion}/C_{Nd(III)}$) of these ions did not change the maximum breakthrough by more than 5 % (Table 3). When preconcentrating trace amounts of Nd(III), there is no need to achieve the maximum breakthrough capacity of Na-clinoptilolite. That is, if the water macro components exceed the allowable multiple quantities, resulting in a drop in adsorption effectiveness, the residual breakthrough capacity value is quite sufficient for the concentration of Nd(III).

The dependence of the sorption capacity of the Na-form of Transcarpathian clinoptilolite on the flow rate of the Nd(III) salt solution with pH 8.5 through the sorbent was investigated (Table 4). The results of this dependence show that a decrease in the flow rate of the Nd(III) solution through the sorbent from 5 to 3 mL min⁻¹ leads to an increase in the sorption capacity of Na-clinoptilolite by 1.3 times. As mentioned above, ~85 % of Nd(III) in solutions at pH 8.5 is in the form of a soluble neutral hydrolyzed form of Nd(OH)₃. Therefore, sorption of Nd(III) from slightly alkaline solutions mainly occurs by adsorption of Nd(OH)₃ on the surface of Na-clinoptilolite. In acidic and neutral solutions, trace amounts of Nd(III) exist almost entirely in the non-hydrolyzed cationic form Nd³⁺ [25]. Therefore, it is obvious that the sorption of Nd(III) from such solutions occurs according to the ion-exchange mechanism with somewhat lower efficiency (Fig. 1).

In order to confirm the priority of the ion-exchange mechanism of sorption of Nd(III) by Na-form clinoptilolite from neutral solutions, studies of the release of ions from the sorbent during the sorption process were conducted. In parallel, similar studies were conducted during the sorption of Nd(III) from a weakly alkaline solution at pH 8.5. It is known [21,22,38] that the exchangeable complex of Transcarpathian clinoptilolite mainly includes Ca²⁺, K⁺, Na⁺ and Mg²⁺ ions. In order to study the efficiency of exchangeable ions of Na-form clinoptilolite during Nd(III) sorption, the mother solutions obtained after mixing zeolite with a solution of Nd(III) at pH 7.2 and 8.5 on an electronic vibrator with a vibration frequency of 4 s⁻¹ were investigated. After 3 h the mother solutions were separated from the solid phase and analyzed on the content of the main exchangeable ions Ca²⁺, K⁺, Na⁺ and Mg²⁺. For blank experiments water solutions (pH 7.2, Tris buffer solution and pH 8.5, borate buffer solution) without Nd(III) ions were used. Calcium and magnesium contents in the solutions were determined by the atomic absorption method using the C•115 M1 spectrometer (Selmi, Ukraine) at a wavelength of 422.7 and 285.2 nm, respectively. Sodium and potassium concentration were determined on the same device, but in emission mode. The completeness of Nd(III) sorption was confirmed spectrophotometrically using sulfarsazene. To calculate the efficiency of the exchangeable cations of Na-form clinoptilolite, the difference between concentrations of studied cations in mother solutions of work and blank experiment were applied. The method for calculating the efficiency of the exchangeable cations was described in detail in Ref. [21].

As expected, Na⁺ ions are the most efficient ions for neodymium (III) sorption on Na-form clinoptilolite. Efficiency of the

Table 2
Desorption effectiveness of neodymium (III) from Na-clinoptilolite.

Eluent	Desorption (%)
2.4 M HCl	98
3.5 M H ₂ SO ₄	98
2.9 M HNO ₃	97
2.9 M H ₃ PO ₄	97
1 M RbNO ₃ , acidified to pH 4.0 with HNO ₃	95
1 M KCl, acidified to pH 4.0 with HCl	93
1 M KNO ₃ , acidified to pH 4.0 with HNO ₃	93
1 M NaCl, acidified to pH 4.0 with HCl	65

Flow rate of eluent through the adsorption system = 0.5 mL·min⁻¹, volume of the eluent employed = 10 mL.

Table 3

Tolerance limits of some ions for neodymium (III) sorption from the aqueous solution of Na-clinoptilolite (concentration of Nd(III) – 1 $\mu\text{g mL}^{-1}$; pH 8.5, $1.3 \cdot 10^{-4}$ M borate buffer solution).

Admixture	Tolerance limit ($C_{\text{ion}}/C_{\text{Nd(III)}}$)
Na^+ , K^+	45
Ca^{2+}	15
NH_4^+	10
Mg^{2+}	4

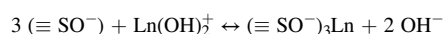
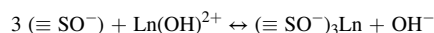
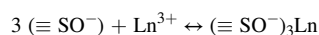
Table 4

Adsorption capacity of Na-clinoptilolite at various neodymium (III) flow rate through the adsorbent (Neodymium (III) concentration = 1 $\mu\text{g mL}^{-1}$; pH 8.5, $1.3 \cdot 10^{-4}$ M borate buffer solution; Na-clinoptilolite preliminary thermally treated at 75 °C).

Flow rate ($\text{mL} \cdot \text{min}^{-1}$)	Adsorption capacity ($\text{mg} \cdot \text{g}^{-1}$)
5.0	5.450
4.0	6.880
3.0	7.185

exchangeable Na^+ cations exceeds 50 % (Tables 5 and 6).

The percentage of ion exchange in neodymium (III) sorption on Na-form of Transcarpathian clinoptilolite can be calculated from received data. From the data of the article [25] it can be seen that three forms of Nd(III) ions: Nd^{3+} , NdOH^{2+} and $\text{Nd}(\text{OH})_2^+$ are present in the solutions during the sorption process. Ion-exchange sorption of different form Ln (III) ions from solution on the natural aluminosilicates can be represented by the following scheme [51]:



Thus, the values of equivalents are stable for different forms of lanthanides under sorption conditions. Considering this fact and taking into account that 500 μg neodymium was sorbed on the Na-form of clinoptilolite, the amount of sorbed lanthanide in μequiv is the following

$$\frac{500}{48} = 10.4.$$

As can be seen from the data (Table 5), the total quantity of ion-exchangeable cations in mother solution obtained after sorption of Nd(III) ions on Na-clinoptilolite from neutral solution (pH 7.2), is 10.33 μequiv . This indicates that the sorption of Nd(III) on the Na-form of clinoptilolite from neutral solutions occurs according to the ion-exchange mechanism.

In the case of sorption of Nd(III) on Na-clinoptilolite from a weakly alkaline solution (pH 8.5), the total quantity of ion-exchangeable cations in mother solution obtained after sorption of Nd(III) ions is only 3.64 μequiv (Table 6). This indicates that the share of ion exchange during the sorption of Nd(III) on Na-clinoptilolite from weakly alkaline solutions is insignificant.

Table 5

Composition of mother solution and efficiency of exchangeable cations of Na-clinoptilolite during neodymium (III) sorption from the solution at pH 7.2^a.

Cation	Concentration of cation in the solution ($\mu\text{g} \cdot 50 \text{ mL}^{-1}$)	Concentration of exchangeable cation in the solution ($\mu\text{equiv} \cdot 50 \text{ mL}^{-1}$)	Efficiency of the exchangeable cation (%) ^b
Na^+	120	5.21	50.4
K^+	17	0.44	4.3
Ca^{2+}	75.5	3.78	36.6
Mg^{2+}	11	0.9	8.7
Σ		10.33	100

^a The time contact of sorbent with neodymium (III) solution – 3 h; concentration of neodymium (III) in the initial solution – 10 $\mu\text{g mL}^{-1}$; pH of the neodymium (III) solution – 7.2 ($2 \cdot 10^{-3}$ M Tris buffer solution); volume of neodymium (III) solution – 50 mL^{-1} ; temperature of the solution – (20 ± 1) °C; mass of sorbent – 0.600 g; diameter of zeolite grains – (0.20–0.31) mm.

^b The efficiency of exchangeable cation was calculated using the ratio of concentration of definite exchangeable cation to total concentrations of exchangeable cations ($\mu\text{equiv} \cdot 50 \text{ mL}^{-1}$).

Table 6

Composition of mother solution and efficiency of exchangeable cations of Na-clinoptilolite during neodymium (III) sorption from the solution at pH 8.5^a.

Cation	Concentration of cation in the solution ($\mu\text{g}\cdot 50\text{ mL}^{-1}$)	Concentration of exchangeable cation in the solution ($\mu\text{equiv}\cdot 50\text{ mL}^{-1}$)	Efficiency of the exchangeable cation (%) ^b
Na ⁺	53	2.31	63.5
K ⁺	13	0.34	9.3
Ca ²⁺	13	0.66	18.1
Mg ²⁺	4	0.33	9.1
Σ		3.64	100

^a pH of the neodymium (III) solution – 8.5 ($1.3\cdot 10^{-4}$ M borate buffer solution). All other experimental conditions were the same as in the case of neodymium (III) sorption from a solution at pH 7.2 (see Table 5).

^b The efficiency of exchangeable ions was calculated similarly to that presented in Table 5. Table 7 presents the results of the study of the dependence of the ion-exchange sorption capacity of Na-clinoptilolite on the flow rate of the Nd(III) solution with pH 7.2 through the sorbent. In the sorption capacity of the adsorbent, two components can be distinguished – ions that are bound to the solid surface and counterions in the stationary surface layer (Fig. 2).

Table 7

Ion exchange sorption capacity of Na-clinoptilolite at various neodymium (III) flow rates through the adsorbent (Nd(III) concentration = $1\ \mu\text{g mL}^{-1}$; pH 7.2, $2\cdot 10^{-3}$ M Tris buffer solution; Na-clinoptilolite thermally pre-treated at 75 °C).

Flow rate ($\text{mL}\cdot\text{min}^{-1}$)	Sorption capacity ($\text{mg}\cdot\text{g}^{-1}$)
5.0	3.310
4.0	4.180
3.0	4.365

$$E = A_0 + A_i,$$

where E – is the sorption capacity, A_0 – is the number of ions that are bound to the solid surface, A_i – is the number of ions that are in the stationary surface layer of thickness x_i .

It can be seen from Table 5 that the sorption capacity decreases with an increase in the flow rate of the initial solution. Such a decrease is related to a change in the sorption conditions. With an increase in the solution supply rate in the adsorption system, some changes may occur that affect the amount of adsorption, namely.

- 1) destruction of the primary structure of the adsorbent (sealing),
- 2) formation of regions of closed air,
- 3) moving the boundary of the stationary liquid layer closer to the solid surface.

Among these three possible scenarios of changes in the adsorption system, the third is the most likely, so we will consider it in more detail. sorption conditions may occur in case of an increase in the flow rate of the initial solution.

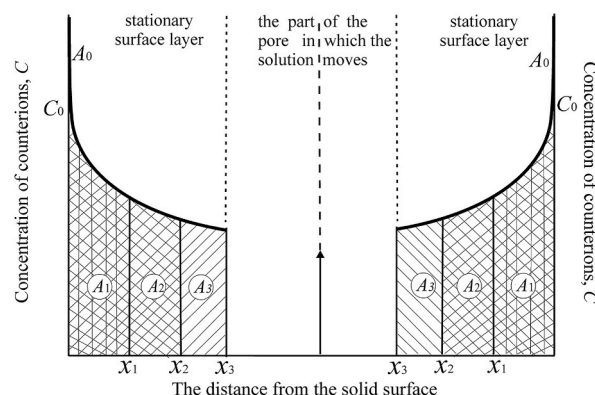


Fig. 2. Schematic representation of the pore and the distribution of counterions in the stationary surface layer.

1. The thickness of the stationary surface layer decreases and the cross-sectional area of the pore in which the solution moves increases, and the flow rate of the fluid in the pore remains unchanged.
2. The thickness of the stationary surface layer and the cross-sectional area of the pore in which the solution moves do not change, and as a result, the flow rate of the fluid in the pore increases.
3. The thickness of the stationary surface layer, the cross-sectional area of the pore in which the fluid moves and the speed of the fluid movement change simultaneously.

To confirm these changes in the sorption conditions, consider the balance of the sorption capacity for three flow rates of the initial solution:

$$E_1 = A_0 + A_1,$$

$$E_2 = A_0 + A_2,$$

$$E_3 = A_0 + A_3,$$

where indices 1, 2, and 3 indicate the experiment number and are related to the flow rate of the initial solution according to [Table 7](#). The number of ions in the stationary surface layer can be found from the distribution of ions in the electric double layer:

$$A_i = \int_0^{x_i} a e^{-bx} dx = \frac{a}{b} [e^{-bx_i} - 1]$$

where a and b are the counterion distribution parameters in the electric double layer.

Next, we searched for the theoretical ratio of differences in the number of counterions for three possible combinations of the flow rate of the initial solution:

$$P_1 = \frac{A_1 - A_2}{A_1 - A_3} = \frac{e^{-bx_1} - e^{-bx_2}}{e^{-bx_1} - e^{-bx_3}} = \frac{D_{12}}{D_{13}},$$

$$P_2 = \frac{A_1 - A_2}{A_2 - A_3} = \frac{e^{-bx_1} - e^{-bx_2}}{e^{-bx_2} - e^{-bx_3}} = \frac{D_{12}}{D_{23}},$$

$$P_3 = \frac{A_1 - A_3}{A_2 - A_3} = \frac{e^{-bx_1} - e^{-bx_3}}{e^{-bx_2} - e^{-bx_3}} = \frac{D_{13}}{D_{23}}.$$

From the given equations, we find that

$$D_{12} = P_1 D_{13}, D_{12} = P_2 D_{23}, D_{13} = P_3 D_{23}.$$

From here, we have what

$$P_1 D_{13} = P_2 D_{23}, D_{13} = \frac{P_1 \cdot P_3}{P_2} D_{13}.$$

Therefore, according to the theory, in the case when the thickness of the stationary surface layer decreases with an increase in the flow rate of the initial solution, and the flow rate of the fluid in the pore does not change, the condition is fulfilled that:

$$\frac{P_1 \cdot P_3}{P_2} = 1.$$

Let's check this for the obtained experimental results from [Table 7](#):

$$P_1 = \frac{3.310 - 4.180}{3.310 - 4.365} = 0.825,$$

$$P_2 = \frac{3.310 - 4.180}{4.180 - 4.365} = 4.703,$$

$$P_3 = \frac{3.310 - 4.365}{4.180 - 4.365} = 5.703,$$

$$\frac{P_1 \cdot P_3}{P_2} = \frac{0.825 \cdot 5.703}{4.703} = 1.0.$$

Thus, the conditions of the first variant of changes that occur in the case of an increase in the flow rate of the initial solution are fully confirmed by experimental results.

An interesting question is the determination of the fraction of the number of ions that are in the stationary surface layer in the total

sorption capacity of the adsorbent. But to determine it, it is necessary to know the thickness of the stationary surface layer under experimental conditions. This thickness must be determined by independent experiments, which will be the subject of further research.

The generalized conditions for the effective sorption of trace amounts of Nd(III) on Na-clinoptilolite under dynamic conditions are presented in Table 8.

Summarizing the results of the investigation, it can be seen that the maximal sorption capacity of Na-form of Transcarpathian clinoptilolite under dynamic conditions towards Nd(III) is equal to 7.2 mg g^{-1} (Table 8), which is 4 and 2.3 times higher than the corresponding sorption capacity of the natural and acid-modified forms of this zeolite [24,25]. Among the known Nd(III) sorbents used in the solid-phase extraction method are polyhydroxamic acid [5], bydi (2-ethylhexyl)phosphoric acid grafted nanoparticles Fe_3O_4 , TiO_2 [6], diglycolamide-grafted Fe_3O_4 /polydopamine nanomaterial [52]. Sorption capacities of bydi (2-ethylhexyl)phosphoric acid grafted nanoparticles Fe_3O_4 , TiO_2 and Na-form of Transcarpathian clinoptilolite with respect to Nd(III) are comparable. The sensitivity of determination and the range of determined concentrations of Nd(III) according to the method using diglycolamide-grafted Fe_3O_4 /polydopamine nanomaterial and our proposed method based on Na-clinoptilolite are also comparable. The sorption capacity of polyhydroxamic acid in relation to Nd(III) is 135 mg g^{-1} , which exceeds the value of the sorption capacity of the Na-form of Transcarpathian clinoptilolite. However, the synthesis and modification of Nd(III) sorbents proposed by the authors [5,6,52] are complex procedures that require the use of organic substances and toxic solvents.

3.2. Potentiometric titration

The interaction at the clinoptilolite/water interface comprises ion exchange at ion exchange centers, proton attachment to the surface OH groups, and surface OH group dissociation. The proton-binding isotherms for natural and Na-form of clinoptilolite are shown in Fig. 3a. The ion exchange centers (permanent charge) are compensated by Na^+ , K^+ , and Mg^{2+} ions for natural clinoptilolite and Na^+ ions for the Na-form and do not interact with the aqueous solution of the electrolyte in the studied pH range. The proton-binding isotherms for both natural and Na-form of clinoptilolite are in both the positive region (proton uptake) and the negative region (dissociation). The point of zero charge (PZC), where the sorption of protons is zero, for natural clinoptilolite is 6.04, for Na-clinoptilolite – 3.19, for heat-treated Na-clinoptilolite – 3.15. The proton affinity distributions of surface groups (Fig. 3b) show two main peaks with pK 0.62–0.80 and 11.4. The first group corresponds to the beginning of the exchange of metal cations to protons in acid media while the second group is the result of the partial dissolution of clinoptilolite in an alkaline environment.

3.3. Zeta potential

The zeta potential of zeolites is significantly affected by the pH of the solution in which the particles of these aluminosilicates are [53–56]. Therefore, the change in pH in the solution will affect the efficiency of ion exchange of zeolites, which is largely related to electrostatic forces. The zeta potential of natural and Na-form Transcarpathian clinoptilolite is negative in the entire studied pH range (Fig. 4). This indicates that both forms of clinoptilolite are capable of sorbing cationic forms of metals from solutions of different acidity. The negative charge of clinoptilolite is the result of the isomorphous substitution of Si^{4+} by Al^{3+} in the lattice [53–55]. The increase in the negative charge with increasing pH is a consequence of the dissociation of surface silanol groups. Although the nature of the zeta potential dependence curves on pH for the natural and Na-form of clinoptilolite is generally similar, for the Na-form of clinoptilolite, significantly higher values of the negative surface charge can be traced over almost the entire studied pH range (Fig. 4). This fact is probably one of the reasons for the increased sorption efficiency of Na-clinoptilolite in relation to metal cations in comparison with the natural form of clinoptilolite. We can recommend Na-clinoptilolite to recover Nd(III) from aqueous solutions and pre-concentrate Nd(III) ions at the stage of water sample preparation for analysis.

The proposed method for detecting the trace Nd(III) levels in the solid phase incorporates a spectrophotometric method using arsenazo III.

3.4. Sample preconcentration procedure

In a previous work [25], we described in detail the procedure of Nd(III) pre-concentration on acid-modified clinoptilolite in the mode of solid-phase extraction and subsequent spectrophotometric determination of this REE with arsenazo III.

The procedure and algorithm for the Nd(III) sorption-spectrophotometric determination using Na-modified clinoptilolite are same

Table 8
Optimal conditions for sorption of trace amounts of Nd(III) on Na-clinoptilolite under dynamic conditions.

Temperature heat treatment of Na-clinoptilolite:	75 °C
Time of Na-clinoptilolite pretreatment:	2.5 h
pH of the aqueous solution:	8.5
Concentration of borate buffer solution:	$1.3 \cdot 10^{-4} \text{ M}$
Velocity of Nd(III) solution passing through sorbent:	3 mL min^{-1}
Nd(III) concentration in solution:	$1 \text{ } \mu\text{g mL}^{-1}$
Sorption capacity:	7.2 mg g^{-1}

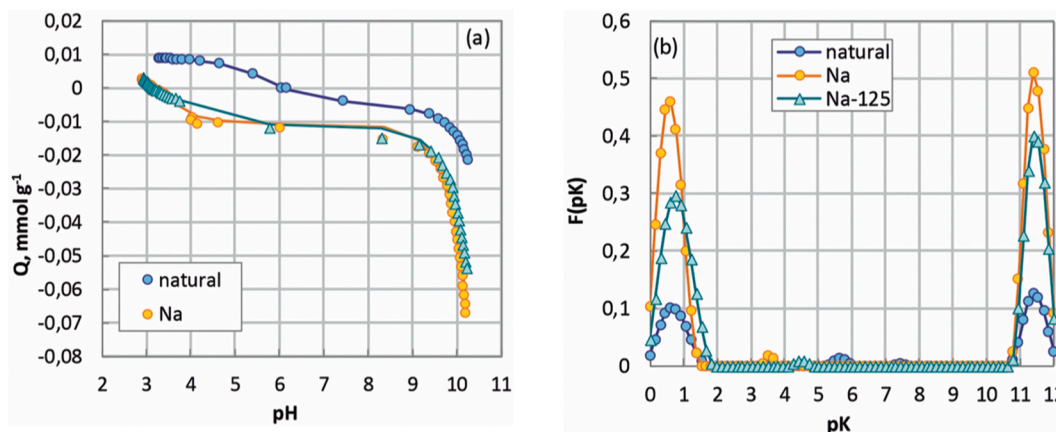


Fig. 3. Proton-binding isotherms (a) and proton affinity distributions (b) for natural clinoptilolite, Na-clinoptilolite, and Na-clinoptilolite calcined at 125 °C.

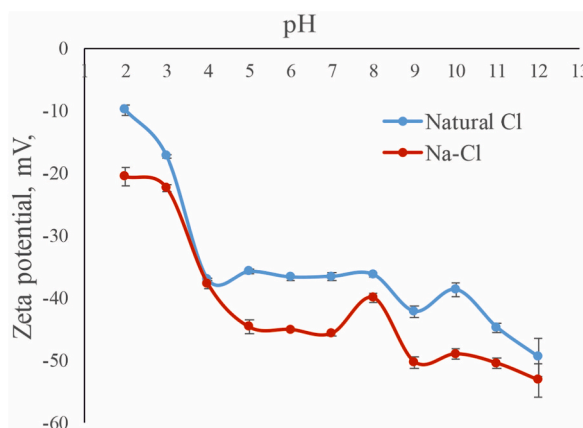


Fig. 4. The variation of the zeta potential of natural and Na-form clinoptilolite (Cl) versus pH.

as in to case of acid-modified clinoptilolite. However, the optimal conditions for Nd(III) sorption and desorption when using these both modified forms of clinoptilolite are different. Therefore, in the proposed method of Nd(III) concentration, the analyzed acidified solution after heating was filtered, the next was neutralized with NaOH solution to pH 7.0, and then the borate buffer solution with pH 8.5 was added. The concentration of the borate buffer in the final volume should be equal to $1.3 \cdot 10^{-4}$ M. Then, this solution was passed through the SPE cartridge filled with 0.6 g of the Na-clinoptilolite samples preheated at 75 °C using the peristaltic pump with a flow rate of 3 mL min^{-1} . Nd(III) ions were desorbed by 10 mL of 2.4 M HCl at the flow rate of 0.5 mL min^{-1} . The Nd(III) amount in the eluate was determined by spectrophotometric method using arsenazo III as reagent. In general, the proposed method of the Nd(III) determination had a linearity range from 2.5 to 500 ng mL^{-1} . The detection limit was found to be 0.75 ng mL^{-1} .

The proposed method of the Nd(III) preconcentration and determination was tested in the analysis of tap water with the additional input of Nd(III) ions. As can be seen from Table 9, the components of water do not have a considerable effect on the determination of trace amounts of neodymium.

4. Conclusions

The results obtained in this work confirmed that the Na-modified Transcarpathian clinoptilolite is an effective sorbent for the solid phase extraction of a trace amount of Nd(III) from aqueous solutions. It was established that Nd(III) is most efficiently sorbed from weakly alkaline solutions (pH 8.5), mainly by adsorption of neutral hydrolyzed forms of $\text{Nd}(\text{OH})_3$ on the surface of Na-clinoptilolite samples preheated at 75 °C. Sorption of Nd(III) from acidic and neutral solutions occurs by the ion-exchange mechanism, but with lower efficiency. During the passage of an Nd(III) solution with a concentration of $1 \mu\text{g mL}^{-1}$ through the sorbent at a rate of 3 mL min^{-1} under optimal conditions, the sorption capacity of Na-clinoptilolite is 7.2 mg g^{-1} , which is in 4 and 2.3 times higher than the sorption capacity of natural and acid-modified forms of this zeolite. The best Nd(III) desorbents are solutions of mineral acids and acidified solutions of alkali metal salts (except NaCl), which provide 93–98 % extraction of lanthanide from the zeolite matrix.

Table 9

Determination of Nd(III) ions in the tap water with an additional introduction of Nd(III) ions after preconcentration using Na-clinoptilolite (n = 3, P = 0.95).

Volume of water sample (mL)	Enrichment factor ^a	Concentration of Nd(III) (ng·mL ⁻¹)		Recovery (%)	RSD (%)
		Added	Found		
250	25	500	475 ± 65	95	5.5
500	50	100	90 ± 13	90	6.0
1000	100	50	47 ± 11	94	9.6
1500	150	25	24 ± 5.3	96	8.9
2000	200	10	9.8 ± 2.3	98	9.5
2000	200	0	ND ^b		

RSD relative standard deviation.

^a Enrichment factor = volume of sample/volume of eluent.

^b ND < detection limit.

Differences in the optimal conditions of sorption of Nd(III), Tb(III), and Co(II) on the Na-form of clinoptilolite provide a fundamental opportunity to separate these metals, which are common components of magnetic materials.

The decrease in the sorption capacity of the studied sorbent with an increase in the flow rate of the initial Nd(III) solution was determined to be caused by a decrease in the thickness of the surface layer and an increase in the cross-sectional area of the pore in which the solution moves.

The preconcentration method of Nd(III) trace amounts in the solid-phase extraction mode during the spectrophotometric analysis of natural waters has been proposed. An enrichment factor of 200 was obtained under the optimum conditions. A wide range of linearity (2.5–500 ng mL⁻¹) with a detection limit of 0.75 ng mL⁻¹ was achieved.

Ethics approval and consent to participate

Not applicable.

Data availability statement

Data included in article/supp. material/referenced in article.

CRedit authorship contribution statement

Emilia T. Stota: Writing – original draft, Methodology, Investigation. **Volodymyr O. Vasylechko:** Writing – review & editing, Writing – original draft, Validation, Supervision, Project administration, Conceptualization. **Zinoviy M. Yaremko:** Writing – review & editing, Writing – original draft. **Svitlana R. Bagday:** Writing – original draft, Visualization. **Olga Poddubnaya:** Validation, Supervision, Investigation. **Alexander M. Puziy:** Writing – review & editing, Visualization, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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