

# Sorption of Neodymium and Gadolinium on Transcarpathian Clinoptilolite

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The sorption properties of Transcarpathian clinoptilolite towards Nd(III) and Gd(III) under dynamic condition have been studied. Nd(III) was sorbed with the best efficiency on the uncalcined clinoptilolite samples from the solutions at pH 6.5. Clinoptilolite samples that were previously calcined at 250 °C exhibit the maximal sorption capacity towards Gd(III) from the solutions at pH 9.5. Nd(III) and Gd(III) sorption on clinoptilolite mechanisms are different: Nd(III) is sorbed according to the ion-exchange mechanism, and the sorption of Gd(III) is carried out mainly by means of the adsorption of soluble hydrolyzed forms of Gd(III) on the zeolite surface. The differences in sorption mechanisms of these lanthanides give an opportunity to separate Nd(III) and Gd(III) from the solutions at pH 9.5. The maximal sorption capacity of the clinoptilolite regarding Nd(III) and Gd(III) at the optimal conditions was found to be 1810 and 6500 µg/g. The best desorbent of Nd from the clinoptilolite is 7 M HNO<sub>3</sub> solution. The best desorbent of Gd is 1 M solution of KCl acidified to pH 2.6, which provides a 100% withdrawal of Gd from the zeolite matrix. Transcarpathian clinoptilolite is proposed as a sorbent for the preconcentration of trace amounts of Nd(III) and Gd(III) from aqueous solutions in a solid phase extraction mode.

DOI: [10.12693/APhysPolA.133.794](https://doi.org/10.12693/APhysPolA.133.794)

PACS/topics: 68.43.-h, 07.60.Dq, 82.75.Vx

## 1. Introduction

Neodymium and gadolinium are ones of the most popular elements of cerium and yttrium subgroups, respectively. These lanthanides (Ln) have been widely used in the electronics, nuclear power, as components of magnetic alloys, phosphors, hydrogen accumulators, and data storage media. The zeolite compositions with these REE have the biological activity.

Most of the lanthanides (Ln) are closely similar in their chemical properties that causes difficulties in separation and quantitative determination of these elements. The number of highly sensitive and selective methods of analysis for the detection and quantitative determination of Ln is not enough. In most cases, the quantitative determination methods include the pretreatment procedure of samples such as separation, concentration and removal of REE. There is also a problem with the withdrawal of rare metals from the technological solutions.

Solid-phase extraction with the application of different sorbents is one of the ways to solve the pretreatment problem of the technological solutions and wastewaters. More often natural zeolites are used for this purpose, which have several advantages in comparison with other sorbents. For example, these natural aluminosilicates have mechanical strength, good stability in aggressive medium and under thermal treatment, ability to sorb the trace amounts of analytes, high sorption capacity and

selectivity, possibility of easy modification and regeneration of the sorbent, low cost and accessibility.

Sorption properties of zeolites in aqueous solutions of Nd(III) and Gd(III) are investigated insufficiently. There are known works [1–4], in which compositions Nd–Gd–synthetic zeolite were studied. Sorption of Ln in most cases was carried out from their nitric or chloride solutions. However, synthetic zeolites are not applied in order to concentrate trace amounts of Nd and Gd. Usually synthetic zeolites containing Nd and Gd are investigated in terms of their luminescent properties. Among natural zeolites only heulandite was studied as a sorbent for Nd(III) [5, 6]. Nd(III) is sorbed on heulandite from the neutral solutions. The sorption capacity of this natural zeolite towards Nd(III) is not high, also the completeness of the withdrawal of Nd(III) from solutions is not provided. Particularly, heulandite withdraws only 55% of Nd(III) from solutions with the concentration of this Ln 10 mg/l [6].

The aim of this paper is to examine the influence of various factors (pH, preliminary thermal treatment of sorbent, nature of the buffer solution) on sorption of Nd(III) and Gd(III) on Transcarpathian clinoptilolite and to investigate the possibility of application of this sorbent in solid phase extraction.

## 2. Materials and experimental details

The clinoptilolite used in this investigation was obtained from the deposit near the village of Sokirnytsia in Ukrainian Transcarpathian region. The previous analysis has shown that the main component was present

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at 85–90%, the specific surface area, determined by water sorption was  $59 \text{ m}^2/\text{g}$  [7]. The chemical composition of Transcarpathian clinoptilolite is (in %):  $\text{SiO}_2$ , 67.29;  $\text{TiO}_2$ , 0.26;  $\text{Al}_2\text{O}_3$ , 12.32;  $\text{Fe}_2\text{O}_3$ , 1.26;  $\text{FeO}$ , 0.25;  $\text{MgO}$ , 0.99;  $\text{CaO}$ , 3.01;  $\text{Na}_2\text{O}$ , 0.66;  $\text{K}_2\text{O}$ , 2.76;  $\text{H}_2\text{O}$ , 10.90 [8].

The zeolite samples were grained in a ball-mill, after that the grain fraction of size 0.20–0.31 mm was selected, washed with distilled water and dried at room temperature. The thermal treatment of clinoptilolite was performed for 2.5 h at required temperature in the oven.

The sorption properties of clinoptilolite were studied under dynamic conditions in a solid phase extraction mode. Metal solutions were passed through a sorption cartridge filled with 0.6 g of the sorbent at 5 ml/min velocity using the peristaltic pump. The methods of investigation under dynamic conditions are described in detail in [9]. The passage moment of Nd(III) and Gd(III) ions was fixed by the photometric method by means of the reaction of Ln(III) with sulfarsazene. It is a highly sensitive method of Nd(III) and Gd(III) determination ( $\text{LDL} = 100 \text{ ng/ml}$ ). This makes it possible to establish the passing moment visually and/or by means of a DR/4000 V spectrophotometer (HACH) at a wavelength of 540 nm.

In order to recover the sorbed Nd and Gd from the zeolite bed, 15 ml of an eluent at a flow rate of 1 ml/min (desorption of Nd) and 0.5 ml/min (desorption of Gd) were passed through the sorption cartridge. The eluates were collected in the volumetric flasks of 25 ml and made-up to the mark with double distilled water.

As solutions of mineral acids or acidified solutions of alkaline metals salts are effective desorbents of Nd and Gd from the clinoptilolite, solution obtained during the desorption of Ln contain much higher concentrations of metals present in the sorbent composition than matrix solutions obtained during the sorption of Ln(III) on clinoptilolite. This is the reason why the selectivity of the spectrophotometric determination of Ln(III) with sulfarsazene proved to be not enough for the analysis of filtrates obtained during the desorption. That is why to determine the content of the desorbed Nd(III) and Gd(III) in the solution we applied a spectrophotometric method based on the arsenazo III, which despite the lack of sensitivity is much more selective than the method with the application of sulfarsazene. In order to eliminate the interfering influence of  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  ascorbic and sulfosalicylic acids, EDTA and Rochelle salt were additionally introduced into the system.

The sorption and desorption were studied at a temperature of  $20 \pm 1^\circ\text{C}$ . All used reagents were of analytical grade. Standard aqueous solutions of neodymium and gadolinium nitrate ( $\text{Ln}^{3+}$  concentration was 1 mg/ml) were prepared by dissolving the metallic neodymium and gadolinium (99.9% purity) in the solution of  $\text{HNO}_3$  (1:1).

### 3. Results and discussion

It was found that the sorption efficiency of Nd(III) and Gd(III) depends significantly on the acidity of Ln

solutions (Fig. 1). The trace amounts of Nd(III) most effectively are sorbed on the zeolite from the neutral medium at pH 6.5. However, the best concentration of Gd(III) occurs from the low basic solutions at pH 9.5. It is known [7, 10–13] that OH-groups are predominantly sorption active centers of Transcarpathian clinoptilolite towards heavy metals ions. In our opinion, the sorption process of the studied Ln is caused by both chemical specificity of zeolite surface and dominant forms of Nd(III) and Gd(III) species in water solutions at various pH values. Dissociation of hydroxyl groups on mineral grains surface, which is responsible for sorption of heavy metals ions from the solutions, is almost completely inhibited at low pH values. This is the reason for low value of clinoptilolite sorption capacity towards Ln(III) ions. Moreover, at these conditions the competing reaction of ion exchange on protons is taking place. Increasing pH facilitates the dissociation of surface OH-groups and has a positive influence on the sorption capacity.

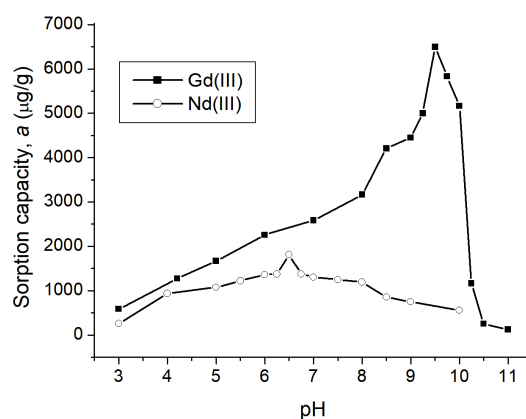


Fig. 1. Dependence of the sorption capacity,  $a$ , of clinoptilolite towards neodymium(III) and gadolinium(III) on the pH value of the aqueous solution.

At different pH values existing forms of Nd(III) and Gd(III) in the solution are changed. Currently the hydrolysis of Nd(III) and Gd(III) is studied poorly. We have carried out the calculation of the distribution of different forms of Nd(III) and Gd(III) in aqueous solutions at different pH values. The system of equations that describes equilibria of Ln(III) hydrolysis is the following:

$$K_{11} = \frac{[\text{LnOH}^{2+}][\text{H}^+]}{[\text{Ln}^{3+}]}, \quad (1)$$

$$K_{12} = \frac{[\text{Ln}(\text{OH})_2^+][\text{H}^+]^2}{[\text{Ln}^{3+}]}, \quad (2)$$

$$K_{22} = \frac{[\text{Ln}_2(\text{OH})_2^{4+}][\text{H}^+]^2}{[\text{Ln}^{3+}]^2}, \quad (3)$$

$$C_M = [\text{Ln}^{3+}] + [\text{LnOH}^{2+}] + [\text{Ln}(\text{OH})_2^+] + 2[\text{Ln}_2(\text{OH})_2^{4+}] + [\text{Ln}(\text{OH})_3], \quad (4)$$

$$K_S \geq [\text{Ln}^{3+}][\text{OH}^-]^3. \quad (5)$$

In Eq. (4) (the material balance of Ln) the neutral hy-

droxoform  $[\text{Ln}(\text{OH})_3]$  appears. Probably at the negligible total concentration of Ln the formation of this form will not cause the appearance of a solid phase of the hydroxide and it will remain in a soluble state.

Since it is not known beforehand whether  $\text{Ln}(\text{OH})_3$  will be formed or not (will the  $K_s$  condition be fulfilled), the solution of the system of equations was carried out in two steps. At first it was assumed that the condition of  $\text{Ln}(\text{OH})_3$  formation is not fulfilled, so the equilibrium state was calculated assuming that  $[\text{Ln}(\text{OH})_3] = 0$ . At this stage for each pH value the equilibrium concentrations of  $\text{Ln}^{3+}$ ,  $\text{LnOH}^{2+}$ ,  $\text{Ln}(\text{OH})_2^+$  and  $\text{Ln}_2(\text{OH})_4^{4+}$  forms were found. Then for each pH value the condition of neutral hydroxide formation ( $[\text{Ln}^{3+}] \cdot [\text{OH}^-]^3 \geq K_s$ ) was checked. If the condition was obeyed, then the solution was carried out according to all four equations and beside forms mentioned above the equilibrium concentration of  $\text{Ln}(\text{OH})_3$  was found, too. At conditions of our investigations the concentration of foreign electrolytes did not exceed 0.01 mol/l, so we used average values of constants for calculations found at the low ionic strength of the solution ( $\mu < 0.01$ ) [14–18]. Graphs with the distribution of different forms of Nd(III) and Gd(III) are given in Fig. 2 and Fig. 3. Our calculations show that pH value, at which the formation of a neutral hydroxide  $\text{Ln}(\text{OH})_3$  and maximal fractions of charged hydroxoforms are reached, for Gd are bigger, than for Nd (presumably on 0.2–0.3). In general the shape of distribution curves of different forms of metals depending on pH at various values of the total concentration is similar for both of these Ln. While increasing the total concentration of the metal the formation of  $\text{Ln}(\text{OH})_3$  begins at the lower pH value. At the low total concentration of the metal (Figs. 2, 3) the form  $\text{Ln}_2(\text{OH})_4^{4+}$  is practically not formed (the maximal fraction does not exceed 0.045%).

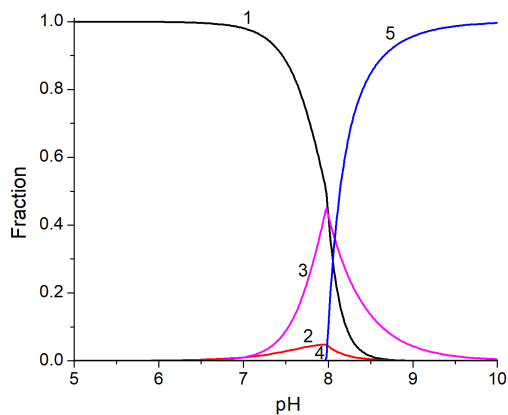


Fig. 2. Dependence of the Nd(III) species fraction on pH (1 —  $\text{Nd}^{3+}$ , 2 —  $\text{NdOH}^{2+}$ , 3 —  $\text{Nd}(\text{OH})_2^+$ , 4 —  $\text{Nd}_2(\text{OH})_4^{4+}$ , 5 —  $\text{Nd}(\text{OH})_3$ ).

The trace amounts of Nd(III) mainly exist in the cationic forms of the aqueous complexes  $[\text{Nd}(\text{H}_2\text{O})_9]^{3+}$  in the solutions at pH 6.5. Weakly alkaline solutions of Gd(III) contain the neutral hydroxocomplex  $[\text{Gd}(\text{OH})_3(\text{H}_2\text{O})_5]$  (95%) and a negligible content of the

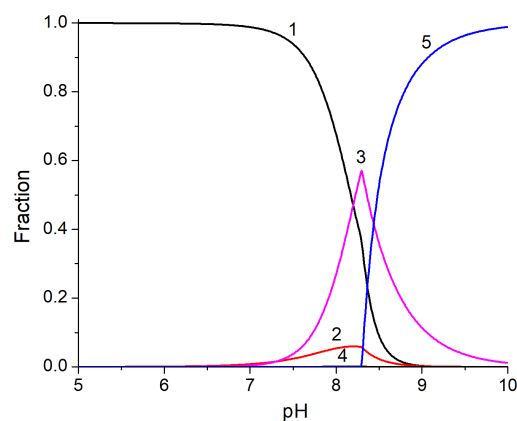


Fig. 3. Dependence of the Gd(III) species fraction on pH (1 —  $\text{Gd}^{3+}$ , 2 —  $\text{GdOH}^{2+}$ , 3 —  $\text{Gd}(\text{OH})_2^+$ , 4 —  $\text{Gd}_2(\text{OH})_4^{4+}$ , 5 —  $\text{Gd}(\text{OH})_3$ ).

cationic hydroxocomplex  $[\text{Gd}(\text{OH})_2(\text{H}_2\text{O})_6]^+$  (5%) at pH 9.5. It has been shown that Nd(III) is sorbed on the clinoptilolite using the ion-exchange mechanism. The sorption of Gd(III) on this zeolite is generally achieved by means of the adsorption of soluble hydrolyzed forms of Gd(III) on the surface of the aluminosilicate. The differences on the sorption mechanisms of these Ln give the possibility to separate Nd(III) and Gd(III) in the solutions at pH 9.5. At this optimum condition the clinoptilolite mostly sorbs Gd(III) and practically does not sorb Nd(III).

The buffer solutions have been used to maintain the constant value of pH, ionic strength of the solutions and to improve the metrological characteristics of pre-concentration methods of Ln. In the case of the concentration of Nd(III) the best results have been obtained with thrys-buffer solution. The trace amounts of Gd(III) most effectively are sorbed with borate buffer solution.

Despite the sorption capacity of the clinoptilolite depends on the temperature of its previous thermal treatment [7, 10–13], Nd(III) most effectively is sorbed at the uncalcined clinoptilolite samples. On the curve showing the dependence of sorption capacity of the clinoptilolite towards Gd(III) on the temperature of the previous thermal treatment of zeolite samples, two maxima are observed at temperatures of 250 °C and 500 °C, respectively (Fig. 4). It is known that closest neighbors of Gd in the periodic table Tb and Eu practically do not sorb on the Transcarpathian clinoptilolite calcined at 250 °C [12, 19], that gives a fundamental possibility of quantitative separation of Gd from Eu and Tb.

It was determined that the most effective desorbents of Nd from the clinoptilolite are solutions of mineral acids. The solution of 7 M  $\text{HNO}_3$  provides a 98% withdrawal of Nd from the zeolite matrix. 100% withdrawal of Gd from the clinoptilolite is achieved by the application of 1 M solution of KCl as a desorbent, acidified to pH 2.6.

The influence of water macrocomponents on the sorption of Nd and Gd on the clinoptilolite was studied, too. Obtained data confirm that the Transcarpathian clinop-

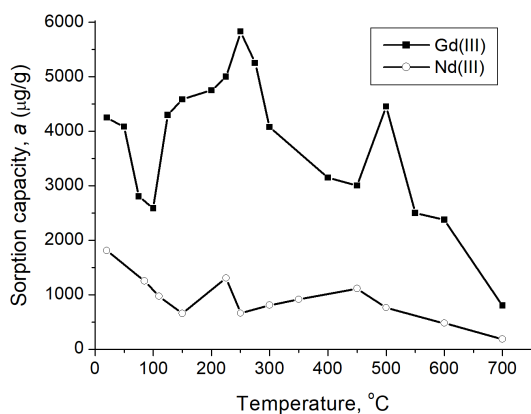


Fig. 4. Dependence of the sorption capacity,  $a$ , of clinoptilolite towards neodymium(III) and gadolinium(III) upon thermal treatment carried out in the range from 20 to 700 °C.

tilolite could be used for the withdrawal of trace amounts of Nd and Gd from aqueous solutions.

#### 4. Conclusions

The results of the investigation confirm that the Transcarpathian clinoptilolite is an effective sorbent for the pre-concentration of trace amounts of Nd(III) and Gd(III) from aqueous solutions.

The optimal conditions for the Nd(III) sorption on clinoptilolite are the following: flow rate of the solution of Nd(III) with the concentration of 1.0 µg/ml through the sorbent — 5 ml/min, grains diameter of the zeolite 0.20–0.31 mm, pH 6.5. The maximal sorption capacity of the clinoptilolite towards Nd(III) is equal to 1810 µg/g. The best desorbent of Nd is the 7 M solution of HNO<sub>3</sub>, by means of which 98% of Nd concentrated on the zeolite can be desorbed.

The optimal conditions for Gd(III) sorption on clinoptilolite are the following: the temperature of preliminary thermal treatment of 250 °C; flow rate of the solution of Gd(III) with the concentration of 1.0 µg/ml through the sorbent — 5 ml/min; grains diameter of the zeolite 0.20–0.31 mm; pH 9.5. The maximal sorption capacity of clinoptilolite towards Gd(III) is 6500 µg/g. The most effective desorbent of Gd is a 1 M solution of KCl, acidified to pH 2.6, by means of which 100% of Gd is desorbed from the zeolite matrix.

It was found that Nd(III) is sorbed on the clinoptilolite according to the ion-exchange mechanism, and the sorption of Gd(III) is achieved mainly by means of the adsorption of the soluble hydrolyzed forms of Gd(III) on the aluminosilicate surface. The differences on the sorption mechanisms of these Ln give the possibility to separate Nd(III) and Gd(III) in solutions at pH 9.5.

#### Acknowledgments

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

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