

## Obtaining Neodymium-Containing Microfertilizers According to the Sorption Technology

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### Abstract

New efficient microfertilizers based on neodymium and natural zeolites are proposed. The equilibrium and kinetics of sorption of neodymium ions from the solutions of nitrate and sulphate by mordenite-containing tufa are investigated. It is established that neodymium is fully extracted from diluted solutions (<0.002 M); with an increase in concentration, sorption capacity of tufa with respect to neodymium ions is observed to decrease sharply. The kinetic parameters of sorption process are determined.

### INTRODUCTION

In Transbaikalia, a region with sharply continental climate, deep frost penetration into soil, slow thawing, a short and droughty vegetation period, an urgent task aimed at an increase in the productivity of agrocoenoses and a decrease in ripening time is search for fertilizers with high biological activity.

It is known that the compounds of rare earth elements (REE), especially the initial representatives of this row, *i.e.* lanthanum, cerium, neodymium, samarium, possess elevated biological activity and are widely used in many countries as microfertilizers [1–7].

It was established that lanthanum sulphate catalyzes fixation of atmospheric nitrogen by azotobacter in cropped legumes. Lanthanum and neodymium nitrates are efficient microfertilizers that increase germinating capacity of wheat, peas, corn, white beet seeds, increase the crop productivity by 22–40 %, the growth of the dry substance by 11–13 %, decrease ripening time by 6–10 days [2–4]. The REE compounds

participate in humus accumulation and intensify nitrogen exchange [5, 6].

The biological activity of REE compounds can be increased substantially by introducing their ions into zeolite matrix according to the sorption technology; natural zeolites can be used as sorbents. Our previous investigations [7, 8] on obtaining microfertilizers based on natural zeolites modified by lanthanum ions showed that the sorption technology is the most reasonable approach to the development of microfertilizers that stimulate the production process in the soil-plant system and decrease possible migration of microelements. The latter aspect is especially important for the soil of light granulometric composition with low biological activity.

Vegetation and vegetation-field experiments were carried out with peas, tomatoes, sweet pepper to estimate the efficiency of the effect of lanthanum and neodymium containing microfertilizers obtained according to sorption technology on the productivity and quality of agricultural plants, and on nitrification activity of chestnut soil [4, 5, 7]. It is known that

the soil concentration of nitrate nitrogen, which is a product of the live activities of nitrifying bacteria that develop under favourable conditions, can serve as a sign of ecological safety of the soil and depicts the level of its fertility [9, 10].

Investigations [7–11] showed that a micro-fertilizer based on natural zeolite modified with lanthanum ions have a durable impact on the nitrifying activity of chestnut soil [8]. The concentration of nitrate nitrogen increased up to 27 mg/kg of soil as incubation increased up to 45 days, while it decreased to 2 mg/kg of soil in the soil without lanthanum added. The crop capacity of the green mass of peas increased by 21–57 %, tomatoes by 31–35 %, sweet pepper by 29–32 %. Under the action of lanthanum, the green mass of peas exhibited an increase in the concentrations of protein nitrogen, calcium, sugar compounds and ascorbic acid [9, 10]. Natural zeolite modified with lanthanum promotes activation of microbiological activity in chestnut soil increasing total number of microorganisms and actinomycetes, fungi and yeast, within shorter time than that observed in the reference sample. An increase in the enzymatic activity of soil was also demonstrated for catalase, dehydrogenase, protease and urease as examples [11].

At present, no data on sorption of neodymium ions by mordenite-containing tufa can be found in literature. The kinetics and equilibrium of sorption in the system solution – zeolite have not been studied yet, though these data are necessary for the development of physico-chemical foundations of obtaining and application of the new neodymium-containing micro-fertilizer.

## EXPERIMENTAL

Mordenite-containing tufa of the Mukhortalin pearlite-zeolite deposit (Buryatia) was used as a sorbent in the present work. The composition of the tufa is (mass %): SiO<sub>2</sub> 70.96, Al<sub>2</sub>O<sub>3</sub> 11.97, MgO 0.18, CaO 0.92, Na<sub>2</sub>O 2.38, K<sub>2</sub>O 5.22. The ratio Si/Al = 5.2. The zeolite content of the rock was determined with the help of PTsL-2 [8]; it is 62 %. In order to study the kinetics and equilibrium of sorption of neodymium ions,

mordenite-containing tufa was ground, a fraction with the grain size of 0.25–0.5 and 1–2 mm was collected by sizing, separated from dust, and dried at room temperature for 24 h; a weighed portion was taken.

Investigation of the equilibrium was carried out under static conditions in the solutions of Nd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> × 8H<sub>2</sub>O using the constant mass procedure [13, 14]. The concentration of neodymium ions was determined by means of photometry with arsenazo III; the method is distinguished by high sensitivity and selectivity [15]. The sorption capacity was calculated on the basis of the difference in the concentrations of neodymium ions in solution before and after sorption using the results of three parallel experiments; relative error of determination did not exceed 3 %.

The kinetics of neodymium ion absorption from the solutions with different concentrations was studied under static conditions. The time of contact of solution with the sorbent varied from 5 min to 6 days. The kinetic parameters were calculated according to the procedure described in [16]. On the basis of experimental data, kinetic curves were plotted in the coordinates  $Q - \tau$ , where  $Q$  is the exchange capacity,  $\tau$  is time of contact with the sorbent. For the initial period of time, when sorption occurs on the surface of the sorbent and the process is controlled by the external diffusion mechanism, the rate constant  $R$  is calculated using equation

$$R = dQ/d\tau (1/CK) \quad (1)$$

where  $C$  is concentration of the exchanging ion in the solution,  $K$  is the equilibrium distribution coefficient.

With an increase in the time of contact, the amount of sorbed ions is determined by the rate of exchange inside the sorbent grain. To calculate the efficient diffusion coefficient  $D$  and the exchange rate constant  $B$  characterizing the internal diffusion mechanism, we used equations deduced for spherical particles:

$$F = Q_t/Q_\infty = 6/(r/\sqrt{Dr/\pi}) \quad (2)$$

$$B = p^2 D/r^2 \quad (3)$$

where  $Q_t/Q_\infty$  is the degree of ion exchange,  $r$  is mean radius of the sorbent grains.

The results are shown in Table 1 and in Figs. 1–3.

## RESULTS AND DISCUSSION

The equilibrium of neodymium ion sorption on mordenite-containing tufa was studied within a broad concentration range ( $10^{-5}$ – $10^{-2}$  M), which allowed us to reveal the changes in the initial and terminal regions of the equilibrium curves.

Figure 1 shows the equilibrium curves of neodymium ion sorption from the solutions of neodymium sulphate on natural zeolite for the grains of different size ( $\sim 0.25$ – $0.5$  and  $1$ – $2$  mm) and for different solid to liquid ratios ( $s : l$ ) equal to  $1 : 10$  and  $1 : 50$ .

One can see that the equilibrium curves are similar and depict a definite regularity in the character of interaction between neodymium ions and the zeolite phase. Isotherms exhibit the appearance of an extremum, which can be due to the formation of intermediate products of chemical reaction with respect to which the sorbent exhibits increased selectivity. The state of aqueous solutions of neodymium is characterized by the processes of hydration, hydrolysis, polymerization and complex formation. In neutral and acid solutions neodymium ions form aqua and hydroxo aqua complexes of the following types:  $[\text{Nd}(\text{H}_2\text{O})_n]^{3+}$ ,  $[\text{Nd}(\text{H}_2\text{O})_n\text{OH}]$ , where  $n = 5$ – $8$  [17, 18]. For low concentrations of sulphate ions ( $<0.03$  M), prevailing cations are  $[\text{Nd}(\text{SO}_4)]^+$  [19], though anion complexes can also be formed under the same conditions [20].

Sorption of neodymium ions is accompanied by a decrease in pH of solution by  $0.4$ – $0.6$  units. In order to reveal the reason of a decrease in pH, reference experiments were carried out in which mordenite-containing tufa was poured with distilled water. After contact for  $20$ – $24$  h, a decrease in pH by  $0.4$ – $0.6$  units was also observed in all the experiments; this occurred independently of sorption of neodymium ions and resulted from exchange between  $\text{Na}^+$  and  $\text{H}^+$  ions present in zeolites [16].

It is likely that sorption of aqua and hydroxo aqua complexes occurs prior to the extremum point, because these ions possess higher ion charge and the selectivity of zeolite toward them is increased. The proposed mechanism of exchange sorption of neodymium by substitution of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{H}^+$  by  $\text{Nd}^{3+}$  confirms the data obtained in [13].

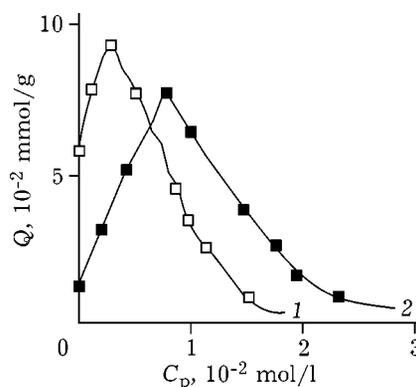


Fig. 1. Isotherms of the equilibrium sorption of neodymium from the solutions of  $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ : 1 –  $d = 0.25$ – $0.5$  mm,  $s : l = 1 : 50$ ; 2 –  $d = 1$ – $2$  mm,  $s : l = 1 : 10$ .

Grain size and the ratio of solid to liquid phase masses affect the position of maximum of the isotherms (see Fig. 1). The maximum of the exchange capacity (EC) for the grains with  $d = 0.25$ – $0.5$  mm and  $s : l = 1 : 50$  (see Fig. 1, curve 1) is shifted to smaller equilibrium concentrations. With an increase in grain size ( $d = 1$ – $2$  mm) and  $s : l = 1 : 10$ , the maximum of EC is in the region of higher concentrations (see Fig. 1, curve 2).

So, with small tufa grains, the maximal EC is achieved with lower reagent consumption. The kinetic curves of neodymium ion sorption are similar (Fig. 2).

TABLE 1

Kinetic parameters of neodymium ion sorption from sulphate solutions by natural mordenite-containing tufa

Kinetic parameter	Concentration of solution, M		
	0.001 <sup>a</sup>	0.002 <sup>b</sup>	0.003 <sup>c</sup>
$t$ , min	1540	1870	1630
$dQ/dt$ , $10^5$ mmol/(g s)	5.8	3.7	4.7
$K$ , ml/g	493	40.5	56.8
$R$ , $10^4$ s <sup>-1</sup>	4.2	3.4	4.4
$D$ , $10^8$ cm <sup>2</sup> /s	4.2	2.1	3.5
$B$ , $10^4$ s <sup>-1</sup>	8.9	7.3	8.6

<sup>a</sup> $d = 0.25$ – $0.5$  mm,  $s : l = 1 : 50$ .

<sup>b</sup> $d = 1$ – $2$  mm,  $s : l = 1 : 10$ .

<sup>c</sup> $d = 1$ – $2$  mm,  $s : l = 1 : 10$ .

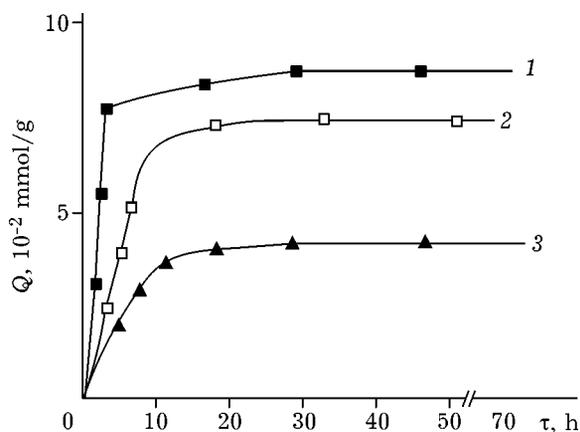


Fig. 2. Kinetic curves of neodymium (III) sorption from solutions by mordenite-containing tufa: 1 - 0.001 M,  $d = 0.25-0.50$  mm,  $s : l = 1 : 50$ ; 2 - 0.003 M,  $d = 1-2$  mm,  $s : l = 1 : 10$ ; 3 - 0.01 M,  $d = 1-2$  mm,  $s : l = 1 : 10$ .

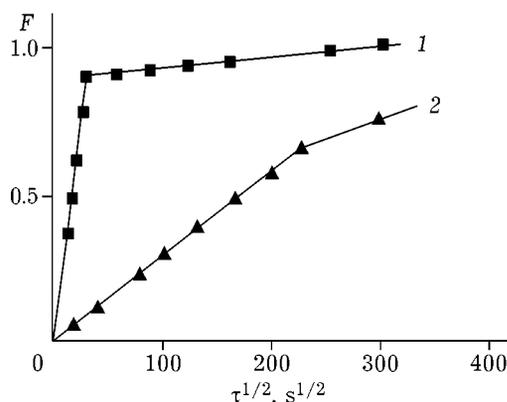


Fig. 3. Dependence of exchange degree  $F$  on time  $t$ : 1 - 0.005 M,  $d = 0.25-0.5$  mm,  $s : l = 1 : 50$ ; 2 - 0.01M,  $d = 1-2$  mm,  $s : l = 1 : 10$ .

A linear dependence of the degree of filling  $F$  for the zeolite phase *versus* time  $t$  (Fig. 3) confirms rather large contribution from the internal diffusion mechanism of sorption [20, 21].

The kinetic parameters listed in Table 1 point to the dependence of the rate of neodymium ion sorption on the size of grains of mordenite-containing tufa and on the concentration of solution. A decrease in the sorbent grain size causes increase in the surface, which affects an increase in sorption rate  $dQ/dt$  according to the external diffusion mechanism. With an increase in the concentration of neodymium sulphate solutions, time  $t$  of achieving the equilibrium state decreases, the rate constants of the external diffusion process ( $R$ ) and internal diffusion ( $B$ ) are observed to increase, so is the effective diffusion coefficient  $D$ . Rate constants  $R$  and  $B$  are of the same order of magnitude, which confirms the mixed character of sorption of neodymium ions by mordenite-containing tufa.

## CONCLUSIONS

The investigation showed that mordenite-containing tufa possesses the capacity to extract (sorb) neodymium ions from aqueous solutions. Within the concentration range  $<0.002$  M, neodymium ions are extracted completely, independently of the grain size and  $s : l$  ratio. An increase in the concentration of solution

causes changes in the selectivity of mordenite-containing tufa with respect to neodymium ions and a decrease in its sorption capacity. Sorption rate depends on tufa grain size and on the concentration of solution.

The results obtained on the sorption of neodymium ions are important for choosing the regimes of saturation of mordenite-containing tufa with the solution of neodymium salts and serve as physicochemical grounds for the sorption technology of obtaining new efficient microfertilizers with high biological activity.

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