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Investigation of Neodymium Sorption on Clinoptilolite Tuff

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Abstract

Processes of neodymium sorption from the solutions of neodymium sulphate on the natural clinoptilolite tuff were studied, and the sorption isotherms of neodymium ions were obtained. It was found that neodymium is extracted quantitatively from the dilute solutions (<0.0025 mol/l), but the exchange capacity of tuff in respect to neodymium ions decreases with increasing solution concentration. Kinetic parameters of sorption process were determined.

INTRODUCTION

Insufficient extent of investigation of ion-exchange properties of natural zeolites in relation to rare-earth elements (REE) limits the potentialities of their application. At the same time the natural zeolites modified by REE ions appear to be promising for production of effective stimulants for restorative therapy [1, 2]. With this aim the modified clinoptilolite tuffs are primarily used [3].

We have previously studied the kinetics and equilibrium of sorption of lanthanum cations by mordenite- and clinoptilolite-containing tuffs. It was established that the sorption isotherm shows a maximum attributed to a complex character of interactions in the zeolite–lanthanum ions system [4, 5]. The obtained data have become a physicochemical basis for producing food supplements and stimulants for regeneration therapy starting from lanthanum and natural zeolites. Nevertheless, the influence of REE character on the kinetics and equilibrium of sorption calls for closer inspection. With this in mind we have studied the processes of sorption of neodymium ions by clinoptilolite tuff depending on the solution concentration, the size of sorbent grains, and the relationship between the masses of solid and liquid phases.

EXPERIMENTAL

Clinoptilolite tuff of the Kholinskoye deposit was used as a sorbent of composition (mass %): SiO_2 68.11, Al_2O_3 12.84, Fe_2O_3 1.08, FeO 0.35, Mn 0.08, P_2O_5 0.05, TiO_2 0.58, CaO 4.17, MgO 2.65, K_2O 2.47, Na_2O 2.87, Cu 0.003, F 0.002; Si/Al = 5.25. The zeolite content of the tuff determined with the help of PZL-2 [6] was about 60 %.

To study kinetics and equilibrium of sorption of neodymium ions, clinoptilolite tuff was powdered, then fractions 0.25–0.5 and 1–2 mm were separated, dried at room temperature during 24 h, and samples were taken. When studying equilibrium states, sorption was carried out under static conditions from a solution of neodymium sulphate having concentrations of the determined ion in the range from 0.0003 to 0.025 mol/l and at relationships among the masses of solid (S) and liquid (L) phases 1 : 10 and 1 : 50.

The content of neodymium ions was determined by the photometric method with arsenazo III having high sensitivity and selectivity [7]. Sorption capacity was calculated from the difference of concentrations of neodymium ions before and after sorption by reference to the results of three parallel experiments; the experimental error was no more than 3 %.

The kinetics of sorption of neodymium ions was studied under static conditions by the method of limited exchange [8, 9] from solutions having concentrations 0.001 and 0.005 mol/l. The time of sorbent contact with solution varied from 5 min to 6 days. The influence of sorbent dispersity was studied on grains with diameters of 0.25–0.5 and 1–2 mm. Based on these experimental data, we have plotted the kinetic curves on the $Q-\tau$ coordinates, where Q is sorption of neodymium ions and τ is contact time of neodymium solution with sorbent. The calculations of kinetic parameters were performed according to the procedure suggested for sorption on zeolites [10]. In the early stage, while sorption takes place on the surface of sorbent and process is controlled by the external diffusion mechanism, the rate constant of this process R is defined as

$$R = dQ/d\tau(1/CK_d) \qquad (1)$$

where C is the concentration of an exchanging ion in solution, mol/l; K_d is the equilibrium coefficient of distribution, ml/g.

With time the rate of sorption of ions is coming under control of the exchange rate in the interior of sorbent grains. The effective coefficient of diffusion (D) and the rate constant of the internal diffusion process (B) can be calculated by the equations derived for spherical particles:

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

$$B = \pi^2 D/r^2 \qquad (3)$$

where F is the degree of advancement of the sorption of neodymium ions; r is the mean radius of sorbent particles, cm.

RESULTS AND DISCUSSION

The equilibrium sorption curves of neodymium cations on clinoptilolite tuff point to the quantitative sorption of neodymium ions from the diluted solutions (Fig. 1). As may be seen from Fig. 1, the most complete sorption of neodymium ions takes place at concentrations of a starting solution up to 0.0025 mol/l when using clinoptilolite grains 1–2 mm (S : L = 1 : 10) and 0.25–0.5 mm (S : L = 1 : 50) in diameter.

With a further increase in solution concentration, each of the equilibrium curves passes through a maximum and thereafter shows a drop in exchange capacity (EC) of tuff. Maximum EC is 0.118–0.131 mmol/g. The occurrence of maximum derives from the high complexing capacity of neodymium ions. It is well known that neodymium ions in the aqueous solutions are in the form of aquacomplexes $[Nd(H_2O)_n]^{3+}$ or $[Nd(H_2O)_nOH]^{2+}$, where n = 5–8 [11].

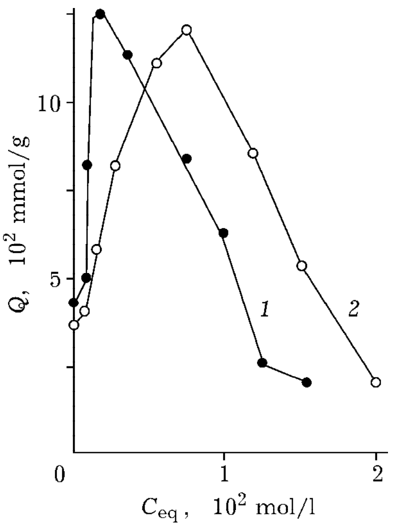

Fig. 1. Equilibrium curves of neodymium sorption from $Nd_2(SO_4)_3$ solutions by clinoptilolite tuff. Grain diameter, mm: 0.25–0.5 (*1*), 1–2 (*2*); S : L = 1 : 50 (*1*), 1 : 10 (*2*).

The solutions of neodymium sulphate can also contain complexes of composition $[Nd(SO_4)_n]^{3-2n}$, where n = 1–3. Cations $[NdSO_4]^+$ prevail at low concentrations of sulphate ions (<0.02 mol/l) [12], however anionic complexes can also be formed under conditions [13, 14]. The sorption of neodymium aqua- and hydrocomplexes is likely to take place prior to the point of maximum because the increased ability of zeolite to adsorb these complexes at the initial portion of the equilibrium curve results from their high charge. The sorption mechanism of lanthanum aquacomplexes on synthetic zeolite is discussed in [15]. This mechanism is supported by reversing sorbent selectivity with respect to neodymium ions on attainment of their fixed concentration in solution. This phenomenon owes its existence to exhibiting electroselectivity, since theoretically [8] equilibrium in a solution and sorbent system is shifted into increasing sorption of the ion having higher charge when diluting a solution, but the complete reversal of sorbent selectivity is evidenced when concentrating a solution.

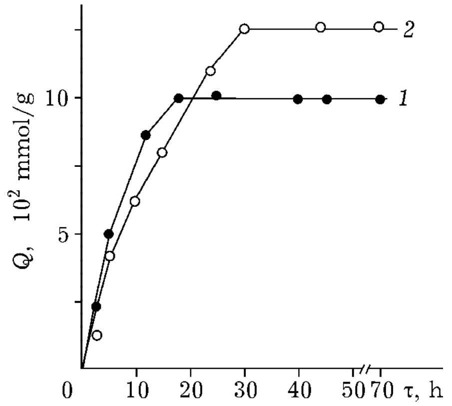

Fig. 2. Kinetic curves of neodymium sorption from 0.001 M $Nd_2(SO_4)_3$ (*1*) and 0.005 M $Nd_2(SO_4)_3$ (*2*) solutions by clinoptilolite tuff. Here and in Fig. 3 *d* (mm): 0.25–0.5 (*1*), 1–2 (*2*); S : L = 1 : 10.

The position of maximum points of equilibrium curves depends on the sorbent grain size and S : L ratio. For sorption on fine grains at S : L = 1 : 50, maximum EC is shifted in the direction of low equilibrium concentrations (see Fig. 1). Consequently, the maximum EC on fine grains can be attained at lower concentrations of solutions, which is important for a choice of the effective regime of zeolite saturation with neodymium ions when preparating the modified form of clinoptilolite tuff.

According to kinetic curves, the equilibrium state, is established during 24–32 h depending on the sorption conditions (Fig. 2), after which only an insignificant desorption of neodymium (~1.5–2 %) is observed. From the data of Table 1 it follows that the sorption of neodymium is controlled by a mixed diffusion mechanism, as the rate constants of external and internal diffusion processes are of much the same order. The linear trend of the portions of the curves in Fig. 3 points to the major contribution of the internal diffusion mechanism.

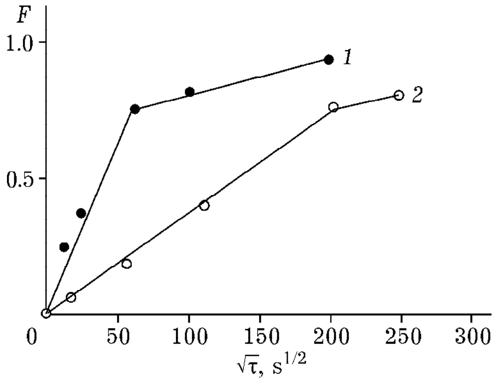

Fig. 3. Degree of neodymium ions sorption as a function of time. Designations see Fig. 2.

An increased rate of neodymium sorption from a diluted solution was noted on the grains of 0.25–0.5 mm in diameter. This is associated with increasing degree of dispersion of tuff grains and sorbent surface, which leads to an increase in the rate of sorption of neodymium ions. An increase in *R* and K_d parameters is also observed. In this case *B* and *D* parameters vary only slightly, and their small variations are apparently conditioned by the nonuniformity of the tuff used.

The obtained values of effective coefficients of diffusion (*D*) accord well with the published data [13]. Relatively high values of *D*, as compared with the data obtained in the studies of exchange kinetics of singly and doubly charged cations on mordenite [10], are most likely connected with the enhanced mobility of neodymium ions in the presence of hydrogen ions (the magnitude of pH for 0.005 M $Nd_2(SO_4)_3$ and 0.001 M $Nd_2(SO_4)_3$ solutions is 6.45 and 6.2, respectively). This is because the more mobile ions, by Helferich's principle [16], are retarded, whereas the less mobile ones are accelerated, when ion exchange takes place in solution.

It is significant that neodymium sorption from sulphate solutions by clinoptilolite tuff is characterized by increasing EC and sorption rate by a factor of about 1.2 as compared with lanthanum sorption.

TABLE 1

Kinetic parameters of neodymium sorption by a natural clinoptilolite tuff

Solution	τ_∞, min	$dQ/d\tau$, 10^5 mol/(g · min)	K_d, ml/g	*R*, 10^4 s^{-1}	*B*, 10^4 s^{-1}	*D*, 10^8 cm^2/s
I	1440	3.4	52.5	11.2	8.4	2.9
II	1920	1.9	28.7	6.9	6.2	1.7

Note. I – 0.001 M $Nd_2(SO_4)_3$ solution, *d* = 0.25–0.5 mm, S : L = 1 : 10; II – 0.005 M $Nd_2(SO_4)_3$, *d* = 1–2 mm, S : L = 1 : 10.

CONCLUSION

Analysis of the equilibrium and kinetics of sorption of neodymium ions by natural clinoptilolite tuff shows that the sorbent has the property of adsorbing neodymium ions from aqueous solutions. At a low concentration (<0.0025 mol/l) neodymium ions are adsorbed quantitatively beyond any dependence on the size of sorbent grains and the relationship among the masses of solid and liquid phases. With increasing the concentration of solution, the change of clinoptilolite tuff selectivity in respect to neodymium ions and the reduction of its sorption capacity are evidenced. The rate of sorption is a function of the size of tuff grains and the concentration of solutions.

The possibilities for production of stimulants for restorative therapy with the use of the sorption technology starting from clinoptilolite tuffs and neodymium open the outlooks for the production of effective medicinals, namely, the stimulants for restorative therapy and food supplements.

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