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Samarium Sorption by Mordenite-Containing Tuff

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Abstract

Equilibrium and kinetics have been studied for the sorption of samarium ions from samarium sulphate and nitrate solutions using naturally occurring mordenite-containing tuff. It has been established that samarium can be extracted at a quantitative level from dilute solutions. With increase in the solution concentration a decrease in the sorption capacity of tuff with respect to samarium ions is observed as the concentration increased. Kinetic parameters of sorption process have been determined.

Key words: rare-earth elements, sorption capacity, natural zeolites, sorption mechanisms

INTRODUCTION

The ion exchange properties of naturally occurring zeolites with respect to rare-earth elements (REE) are studied much less than the ion exchange properties of zeolites regarding singly and doubly charged cations [1]. Naturally occurring zeolites modified by lanthanum and neodymium ions serve represent efficient micro-fertilizers due to the actvation of nitrogen and carbohydrate metabolism and the acceleration of ripening for fodder and vegetable cultivars [2–7]. Zeolites play the role of a prolonging carrier of microelements capable of evolving necessary chemical elements into the soil solution for a long time.

For today the equilibrium and kinetics for the sorption of lanthanum and neodymium ions by mordenite and clinoptilolite tuff are well studied as well as a complicated nature of interactions in the zeolite–lanthanum and neodymium ions system is demonstrated [5, 6]. At the same time there are no data available in the literature concerning the sorption of samarium ions by mordenite-containing tuff those are necessary for the estimation of REE nature influence upon the sorption equilibrium and kinetics. The aim of the present work consisted in the studies on the sorption of samarium ions by mordenite-containing tuff depending on the nature of anion, the solution concentration, the adsorbent grain size as well as upon the solid to the liquid mass ratio.

EXPERIMENTAL

In the experiments we used mordenite-containing tuff from the Mukhor-Tala perlite-zeolite deposit as an adsorbent. The tuff was characterized by the following composition, mass %: SiO_2 70.96, MgO 0.18, Al_2O_3 11.97, CaO 0.92, Na_2O_3 2.38, K_2O_3 5.22, with ratio Si/Al = 5.2. The content of zeolite in the rock determined with the use of a PTsL-2 portable zeolite laboratory [8] amounted to 62 %.

For the investigation of samarium ion absorption kinetics and equilibrium the mordenite-containing tuff was grinded. A grain fraction of 0.25–0.5 and 1–2 mm in diameter was taken using a separation method, levigated to remove dust, dried up at a room temperature during 24 h and then a weighed sample was taken. The investigation of the equilibrium was carried out under static conditions for the solutions of samarium sulphate and nitrate using a constant mass method with samarium ion concentration ranging within 0.0003–0.025 mol/L and the solid (S) to the liquid (L) ratio S/L equal to 1 : 10 and 1 : 50.

The absorption kinetics for samarium ions was studied using a limited exchange method for the solutions with the concentrations amounting to 0.01, 0.02, 0.005 and 0.007 mol/L [9]. The solution-adsorbent contact time was varied within the range from 5 min to 6 days. Basing on the experimental data kinetic curves were plotted for Q against τ, where Q is the amount of adsorbed samarium ions and τ is the contact time value for samarium solution and the adsorbent. The calculation of kinetic parameters was carried out using the technique described in [1]. For the initial period of time when the sorption occurs on the surfaces of the adsorbent and the process determined by the external diffusion mechanism, the rate constant value for the external diffusion process (R) can be determined as

$$R = \mathrm{d}Q/\mathrm{d}\tau(1/CK_\mathrm{d}) \qquad (1)$$

Here C is the concentration of an exchanging ion in the solution, mol/L; $K_\mathrm{d} = (C_0 - C_\mathrm{eq})V/C_\mathrm{eq}m$ is the equilibrium distribution coefficient, mL/g (C_0, C_eq are the initial and equilibrium concentrations of samarium ions in the solution, respectively, mol/L; V is the volume of the solution, mL; m is the mass of a weighed adsorbent sample, g).

With the increase in the contact time value the amount of ions absorbed is determined by the exchange rate inside a sorbent grain. The effective diffusion coefficient (D') and the rate constant for internal diffusion process (B) those describe the internal diffusion mechanism, were calculated according to the equations deduced for spherical particles:

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

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

Here F is the absorption level for samarium ions; r is the average radius of adsorbent particles, cm.

The rate-determining stage of the process was determined comparing the rate constant values for the external and internal diffusion mechanisms [1].

The content of samarium ions was determined using a photometry method with Arsenazo III [10]. The absorption capacity was calculated from the difference in the concentration of samarium ions before and after the sorption basing on the data of three parallel experiments; the relative error of being less than 3 %.

RESULTS AND DISCUSSION

The shape of the curves obtained for the equilibrium sorption of samarium cations from samarium nitrate and sulphate solutions on the mordenite-containing tuff under investigation indicates that there is a quantitatively complete extraction of samarium ions from dilute solutions (Fig. 1). So, the sorption from the solution

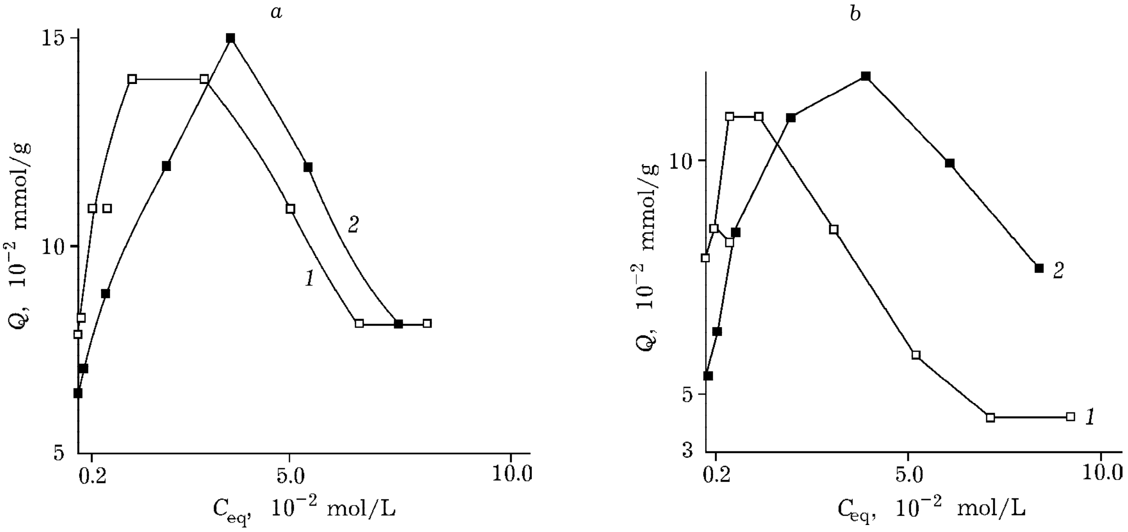

Fig. 1. Equilibrium curves for samarium sorption by mordenite-containing tuff from nitrate (*a*) and sulphate (*b*) solutions. Grain size, mm: 0.25–0.5 (*1*), 1–2 (*2*); S/L ratio: 1 : 50 (*1*) and 1 : 10 (*2*).

of samarium nitrate onto the grains of 1–2 mm in diameter at the ratio S/L = 1 : 10 results in the fact that full extraction of samarium ions occurs at the concentration of the initial solution up to 0.009 mol/L, whereas in the case of the sorption from the samarium sulphate solution under similar conditions the extraction occurs for the concentration values up to 0.0062 mol/L. Using the grains of 0.25–0.5 mm in size at the ratio S/L = 1 : 50 the samarium ions are quantitatively extracted from the solutions of samarium nitrate and sulphate with the concentration of 0.0016 mol/L. With the increase in the concentration of the solution the equilibrium curves exhibit a maximum. Further the exchange capacity (EC) of tuff with respect to samarium ions decreases.

The presence of the maximum on the equilibrium curves, to all appearance, could be connected with a pronounced tendency of REE ions to the formation of complexes. So, the authors of [13] have demonstrated the mechanism of lanthanum aqua complexes sorption onto synthetic zeolite. It is known that samarium ions in aqueous solutions exist in the form of aqua complexes such as $[Sm(H_2O)_n]^{3+}$ or $[Sm(H_2O)_nOH]^{2+}$, where $n = 5–8$ [11–14]. It is also established that in the solutions of samarium nitrate the formation of samarium complexes such as $[Sm(NO_3)_n]^{3-n}$ ($n = 1–6$) is observed, whereas in the solution of samarium sulphate the complexes such as $[Sm(SO_4)_n]^{3-2n}$ ($n = 1–3$) [14] are observed, and $[SmSO_4]^+$ ions prevail at low SO_4^{2-} concentration (<0.1 mol/L), though anionic complexes could be formed under the same conditions, too [11].

The decrease in the sorption capability of mordenite-containing tuff with respect to samarium ions, to all appearance, could be caused by so called concentration valency effect [14]. The effect is exhibited under the exchange of differently charged cations and consists in the shift of the exchange equilibrium towards a decrease in the sorption of ions with a higher charge as the solution concentration increased, as well as samarium complexes strengthening and the solution concentration growth [11].

It is established, that the anionic composition of the solution influences the EC value. So, the maximum OE value realized at the expense of samarium sorption from samarium nitrate solutions is higher as compared to that observed under the sorption of samarium ions from samarium sulphate solutions (0.145–0.152 and 0.110–0.123 mmol/g, respectively).

The position of maximum on the equilibrium curves depends on the sorbent grain size and the S/L ratio. In the case of the adsorption onto finer soprbent grains at the ratio S/L = 1 : 50 the maximum of OE is shifted towards a low equilibrium concentration range(see Fig. 1).

According to data presented in Fig. 2, the equilibrium state is established within the range from 24 to 72 h depending on sorption conditions. The results obtained (Table 1) indicate that the samarium sorption rate is determined by a mixed diffusion mechanism since the rate constant values for external and internal diffusion processes exhibit almost the same order of magnitude. A linear character of the initial part of $F - \tau_{0.5}$ curves (Fig. 3) indicates a significant contribution of the internal diffusion mechanism.

The analysis of the calculated K_d values indicates that the absorption of samarium ions from samarium nitrate solutions is more efficient as compared to samarium sulphate solutions. It has been revealed that with the decrease in the solution concentration the K_d value increases, which could be caused by a decrease in the stability of samarium complexes due to dilution. It has been established that the value of samarium adsorption rate depends on the anionic composition of the solution: samar-

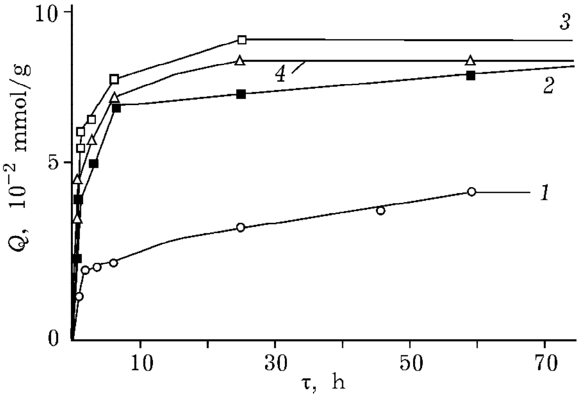

Fig. 2. Kinetic curves for samarium sorption by mordenite-containing tuff for the solutions of $Sm(SO_4)_3 \cdot 8H_2O$ (*1–3*) and $Sm(NO_3)_3 \cdot 6H_2O$ (*4*) with the concentration of 0.02 (*1*), 0.01 (*2*, *4*) and 0.005 (*3*) mol/L. Grain size, mm: 1–2 (*1*, *2*, *4*), 0.25–0.05 (*3*); S/L ratio: 1 : 10 (*1*, *2*, *4*), 1 : 50 (*3*).

TABLE 1

Kinetic parameters for samarium sorption by natural mordenite-containing tuff

Solution	τ_∞, min	$\tau_{0.5}$, min	$dQ/d\tau$, 10^{-5} mol/(g · min)	K_d, mL/g	R, 10^{-5} s^{-1}	D', 10^{-8} cm^2/s	B, 10^{-5} s^{-1}
I	1427	32	5.2	28	46	3.5	37
II	4324	173	1.3	7.6	21	4.7	9.2
III	1432	38	3.4	6.2	28	5.3	11.4
IV	2865	62	2.7	35.3	8.1	3.2	5.5

Notes. 1. I, II, III – the solutions of $Sm_2(SO_4)_3 \cdot 8H_2O$ with the concentration of 0.005, 0.01 and 0.02 mol/L, respectively; IV – the solution of $Sm(NO_3)_3 \cdot 6H_2O$ with the concentration of 0.01 mol/L. 2. Sorbent grain size is 0.25–0.5 mm for the solution I and 1–2 mm for the solutions II–IV, ratio S/L = 1 : 50 for the solution I and 1 : 10 for the solutions II–IV.

ium is faster adsorbed from the solutions of samarium nitrate since the stability of nitrate complexes is lower as compared to the stability of sulphate complexes. This fact is indicated by higher EC values (see Fig. 2), as well as by the reduction of the half-exchange attainment time $\tau_{0.5}$ as well as of the equilibrium state establishing time τ_{eq} (see Table 1).

The investigation of samarium sorption kinetics for sulphate solutions depending on the solution concentration (all other factors being equal) has demonstrated that the process rate increases with the increase in the concentration of the solution. This is indicated by the reduction of $\tau_{0.5}$ and τ_{eq} values as well as by the increase in the absorption rate for samarium ions and sizes R value. At the same time B and D' values remain almost constant. The minor variations of these values could be, to all appearance, caused by a heterogeneity of the tuff under investigation. The rate of the process in this case is also determined by a mixed diffusion mechanism.

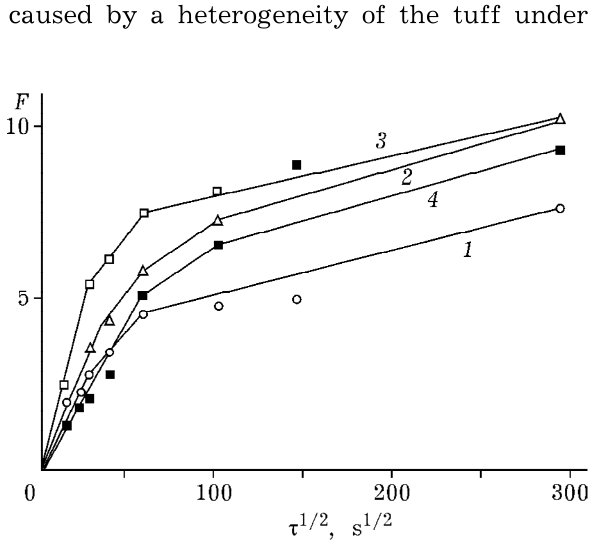

Fig. 3. $F - \tau_{0.5}$ dependence for samarium sorption by mordenite-containing tuff from $Sm(SO_4)_3 \cdot 8H_2O$ and $Sm(NO_3)_3 \cdot 6H_2O$ solutions. For designations see Fig. 2.

With the increase in the dispersity level of tuff grains and in the S/L ratio the samarium sorption rate value for dilute solution of samarium sulphate (0.005 mol/L) increases (see Table 1). A certain contribution to the acceleration of the sorption, to all appearance, is drawn by an increase in the S/L ratio and in the sorbent surface area, which could result in a more active absorption of cations.

The D' values obtained in our experiments (see Table 1) are in a good agreement with the literature data [1, 9]. Higher D' values in comparison with those obtained in the studies on kinetics of the exchange univalent and bivalent cations for mordenite [1], to all appearance, could be explained by an increased mobility of samarium ions in the presence of hydrogen ions (for the solutions 0.01 M $Sm(NO_3)_3 \cdot 6H_2O$, 0.01 and 0.02 M $Sm_2(SO_4)_3 \cdot 8H_2O$ the pH value is 5.8, 5.4 and 4.9, respectively). According to Helferich principle [15], in the exchange of the mixture of ions the more mobile among them are decelerated, whereas the less mobile ions are accelerated.

It should be noted that the sorption of samarium from samarium sulphate and nitrate solutions by mordenite-containing tuff it is characterized by higher values of EC and ion absorption rates (approximately 1.2- to 1.3-fold) as compared to lanthanum and neodymium sorption.

CONCLUSION

The analysis data concerning the studies on the equilibrium and kinetics of the sorption of samarium ions by natural mordenite-containing tuff has demonstrated the possibility of the extraction of samarium ions from aqueous solutions with the use of the sorbent. The adsorption isotherms are characterized by the presence of a maximum, which is connected with a complicated nature of interactions. The sorption rate value depends on the nature of an anion, tuff grain size of grains and the concentration of solutions.

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