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Cerium (III) Sorption by Naturally Occurring Clinoptilolite Containing Tuff

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Abstract

Cerium sulphate ion-exchange sorption by containing naturally occurring clinoptilolite tuff from aqueous solutions was studied within a wide range of concentration values (10^{-5} – 10^{-2} mol/L). Adsorption isotherms and kinetic parameters have been determined.

Key words: naturally occurring zeolite, cerium (III) ions, sorption capacity, sorption kinetics and equilibrium

INTRODUCTION

Naturally occurring zeolites modified by the ions of rare earth elements (REE) are promising for obtaining efficient stimulants for regenerative therapy and biologically active compounds. It was demonstrated that the therapeutic effect can be achieved due to the ion-exchange and sorption properties of naturally occurring zeolites those exert drainage influence to stimulate the detoxification function of lymphatic structures at the system level [1, 2]. Lanthanum and cerium introduced into zeolite matrix, exhibit a neuroprotective activity [3]. In order to reduce ischemic brain damage one considers calcium blockers to be appropriate. In biological systems, lanthanum and cerium ions displace calcium ions to inhibit the supply thereof into cells, with exerting an inhibitory effect on the development of the calcium-induced cascade of pathologic reactions inherent in brain ischemia [3].

Using sorption technologies the authors of [3] have developed efficient neuroprotective pharmaceuticals based on clinoptilolite from the Kholinskoye deposit and lanthanum. Data re-

ported in [1, 3–5] indicate that the sorption technology could enhance the biological activity of naturally occurring zeolites at the expense of introducing lanthanum and cerium ions into a zeolite matrix.

Earlier, we studied the equilibrium and kinetics of lanthanum, neodymium and samarium sorption by mordenite and clinoptilolite containing tuff [1, 4, 5]. The sorption isotherms of the mentioned REE ions exhibit maxima inherent in the interaction in the system of zeolite–REE ions. The influence of REE nature upon the sorption equilibrium and kinetics requires for deeper studying the laws of sorption in the zeolite–REE ion systems.

The purpose of this work consisted in studying the effect of solution concentration, sorbent grain size, as well as mass ratio between solid and liquid phases exerted on the sorption by cerium (III) containing clinoptilolite tuff.

EXPERIMENTAL

As a sorbent we used clinoptilolite-containing tuff having the following composition (mass %):

SiO₂ 68.11, MgO 2.65, Al₂O₃ 12.84, CaO 4.17, Na₂O 2.87, K₂O 2.47, Fe₂O₃ 1.08, FeO 0.35, P₂O₅ 0.05, TiO₂ 0.58, CuO 0.003, Mn 0.08, F 0.002; Si/Al = 5.25 [1]. Zeolite content in the rock was determined by means XRD structure analysis using a PCL-2 unit [6] to be equal to 61 mass %.

In order to study the equilibrium and kinetics for absorbing cerium (III) ions, the clinoptilolite containing tuff was grinded in a MS 23200 ball mill (Siemens), with further separating the fractions with grain diameter of 0.25–0.5, and 1–2 mm by means of sieving to remove the dust, and dried at a room temperature for 24 h, then a weighed sample portion was taken. The drying time (24 h) was chosen on the basis of the three control weighing procedures, in every three hours of drying.

The study of equilibrium was performed under static conditions in aqueous solution containing Ce₂(SO₄)₃ by means of constant mass technique at a room temperature [6, 7]. Cerium (III) ion content was determined photometrically with the use of Arsenazo III that is characterized by a high sensitivity and selectivity [8]. The absorption capacity was calculated from the difference between the concentration of cerium (III) ions in the solution before and after sorption basing on the results of three parallel experiments; the range of deviation normalized with respect to the arithmetic mean did not exceed 3 %.

The equilibrium of cerium (III) sorption onto clinoptilolite-containing tuff was studied within a wide concentration range (10⁻⁵–10⁻² mol/L),

which allowed revealing changes in the initial and final parts of the equilibrium curves.

The kinetics of cerium ion absorption was studied using a limited volume method at a ratio between the solid (S) and the liquid (L) phases S/L equal to 1 : 10 and 1 : 50, for the cerium (III) sulphate solutions with the concentration ranging within 0.001–0.003 mol/L under continuous stirring. The contact time with the adsorbent was varied from 5 min to 6 days. The effect of the sorbent grain size was investigated for the grains fractions of 0.25–0.5, 1–2 mm in diameter.

The kinetic parameters were calculated from $Q(\tau)$ curves (Q is the amount of adsorbed cerium (III) ions, mmol/g; τ is time, s) according to the procedure for the adsorption on zeolites described in [9]. For the initial period of time when the sorption takes place on the surface of the adsorbent and the process is controlled by the mechanism of external diffusion, the effective rate constant value R for all the set of external diffusion processes can be calculated according to the following equation:

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

where c is the concentration of ions in solution, mol/L; K is the effective equilibrium distribution coefficient, mL/g.

With increasing the contact time value, the amount of absorbed ions is determined by the exchange rate within the sorbent grain. The effective diffusion coefficient (D) and the rate constant for the set of all the internal diffusion processes of cerium (III) sorption (B) was calculated by the equations derived for spherical particles:

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

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

where F is the absorption level for cerium (III); r is the average radius of sorbent grain, cm.

TABLE 1

Kinetic parameters of cerium (III) sorption from sulphate solutions by naturally occurring clinoptilolite containing tuff

Parameters	Solution concentration, mol/L		
	0.001*	0.002**	0.003***
τ_∞ , min	1575	1694	1637
$dQ/d\tau$, 10 ⁻⁵ mmol/(g · s)	5.6	4.3	4.7
K , mL/g	49.4	41.7	59.3
R , 10 ⁴ s ⁻¹	4.5	4.2	4.7
D , 10 ⁸ cm ² /s	4.5	3.8	3.9
B , 10 ⁴ s ⁻¹	8.8	7.6	8.4

* $d = 0.25\text{--}0.5$ mm, S/L = 1 : 50.

** $d = 1\text{--}2$ mm, S/L = 1 : 10.

*** $d = 1\text{--}2$ mm, S/L = 1 : 10.

RESULTS AND DISCUSSION

The results obtained are presented in Table 1.

Figure 1 demonstrates the curves for the equilibrium sorption of cerium (III) from cerium sulphate solutions by naturally occurring zeolite obtained for different grain size (0.25–0.50 and 1–2 mm) at S/L ratio of equal to 1 : 50 and 1 : 10. Both equilibrium curves exhibit a

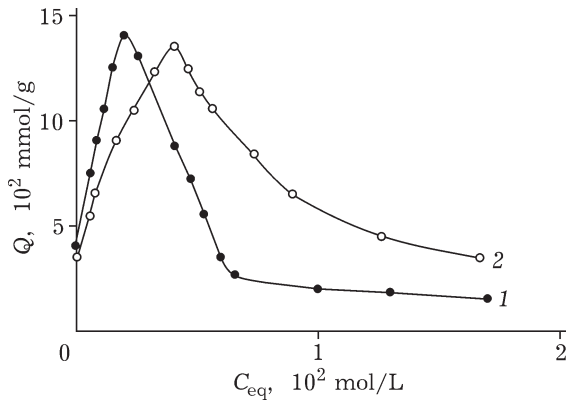


Fig. 1. Cerium sorption isotherm for cerium sulphate solution (Q is the amount of adsorbed Ce(III) ions, mmol/g; C_{eq} is the average equilibrium concentration of Ce(III) in the solution, mmol/L): 1 - $d = 0.25-0.5$ mm, $S/L = 1 : 50$; 2 - $d = 1-2$ mm, $S/L = 1 : 10$.

pronounced maximum which could be explained by REE tending to form complexes in solution. The state of aqueous cerium (III) solutions is characterized by the processes of hydration, hydrolysis, polymerization and complexation. Cerium ions in neutral and acidic aqueous solution exist in the form aqua complexes such as $[Ce(H_2O)_n]^{3+}$ and hydroxo aqua complexes such as $[Ce(H_2O)_nOH]^{2+}$, where $n = 5-8$ [10-12]. The exchange rate should be determined by the cleavage of the hydration shell. Increasing the concentration of the solution results in strengthening the REE complexes; this result in a decrease of the sorption level caused by increasing the energy of hydration shell cleavage. As

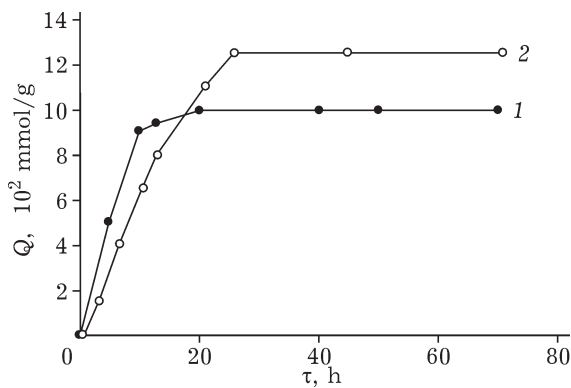


Fig. 2. Cerium (III) sorption kinetic curves for clinoptilolite containing tuff in cerium (III) sulphate aqueous solutions: 1 - $Ce_2(SO_4)_3$ concentration 0.001 mol/L; $d = 0.25-0.5$ mm, $S/L = 1 : 50$; 2 - $Ce_2(SO_4)_3$ solution concentration: 0.003 mol/L, $d = 1-2$ mm, $S/L = 1 : 10$.

far as the solutions of cerium sulphate is concerned, there is the formation of $[Ce(SO_4)_n]^{3-2n}$ complexes registered, where $n = 1-3$. At low sulphate ion concentration values (<0.03 mol/L), $[CeSO_4]^+$ cations are observed to prevail [12], although under these conditions anionic complexes could form, too [10, 13].

It can be assumed that increasing the concentration of the solution up to the extremum point results in the sorption of aqua and hydroxo cerium (III) complexes, since they have a higher ionic charge and an enhanced selectivity of zeolite thereto. The size of windows and cavities for the zeolite under investigation ranges within $5-7 \text{ \AA}$, which is to a significant extent larger than the size of aqua and hydroxo-aqua complexes. The mechanism proposed for the exchange sorption via substitution of Na^+ , K^+ , H^+ by Ce^{3+} is confirmed by data from [6, 7].

The grain size and the mass ratio between the solid and liquid phases affect the position of the maximum on the isotherms (see Fig. 1). The maximum exchange capacity (EC) for the grains with $d = 0.25-0.5$ mm and the ratio $S/L = 1 : 50$ (see Fig. 1, curve 1) is shifted towards lower equilibrium concentration values. In the case of increasing the grain size ($d = 1-2$ mm), and $S/L = 1 : 10$, the EC maximum is shifted towards higher concentration values (see Fig. 1, curve 2).

Thus, for small tuff grains the maximum EC value equal to 0.145 mmol/g is achieved at a lower level of reagent consumption.

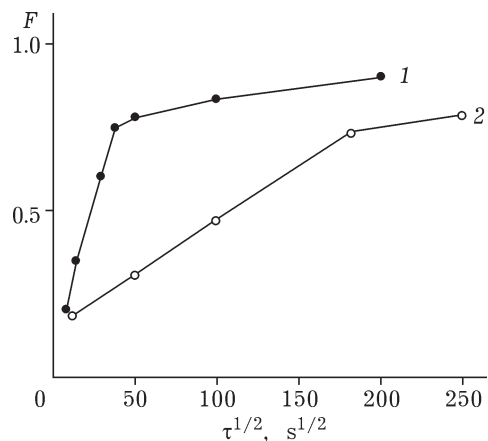


Fig. 3. Absorption level for cerium ions (F) depending on time (τ): 1 - $Ce_2(SO_4)_3$ concentration 0.005 mol/L, $d = 0.25-0.5$ mm, $S/L = 1 : 50$; 2 - $Ce_2(SO_4)_3$ solution concentration: 0.01 mol/L, $d = 1-2$ mm, $S/L = 1 : 10$.

The kinetic curves for the absorption of cerium (III) ions are similar in shape (Fig. 2).

The fact that the degree of filling the zeolite phase (F) depends on time τ in a linear manner (Fig. 3) indicates a relatively high contribution of internal diffusion sorption mechanism [6, 9, 12].

The kinetic parameters listed in Table 1 indicate the fact that the rate of the absorption of cerium (III) ions depend on the grain size of clinoptilolite containing tuff and the concentration of the solution. Reducing the size of the sorbent grains results in increasing the surface; this influences upon increasing the absorption rate dQ/dt according to the external diffusion mechanism. Increasing the concentration of cerium (III) sulphate solutions results in reducing the time to reach equilibrium τ_{∞} , one observes an increase in the rate constants external diffusion (R) and internal diffusion (B) processes, in the distribution coefficient (K), as well as in the effective diffusion coefficient (D). The constants of R and B exhibit an equal order, which confirms the fact that the mechanism of cerium (III) sorption by clinoptilolite containing tuff is of mixed nature.

CONCLUSION

In the course of contact between naturally occurring zeolite tuff and aqueous cerium sulphate solutions the sorbent exhibits the ability of extracting cerium (III) ions. At low concentration values (<0.003 mol/L), the ions of cerium (III) can be extracted quantitatively, irrespective of the adsorbent grain size and S/L ratio. With increasing the solution concentration one observes a decrease of the sorption capaci-

ty. The sorption rate depends on tuff grain size and on the concentration of the solutions.

The potentiality of obtaining neuroprotective pharmaceuticals *via* the sorption technology offers the prospects for obtaining efficient calcium channel blockers, as well as biologically active supplements.

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