

Purification of waste waters containing $^{60}\text{Co}^{2+}$, $^{115\text{m}}\text{Cd}^{2+}$ and $^{203}\text{Hg}^{2+}$ radioactive ions by ETS-4 titanosilicate

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The sorption of $^{60}\text{Co}^{2+}$, $^{115\text{m}}\text{Cd}^{2+}$ and $^{203}\text{Hg}^{2+}$ from diluted solutions (as analogues for radioactive waste waters) on ETS-4 microporous titanosilicate was studied at 277, 293, 313 and 333 K by measuring the sorption kinetics using a batch-method. The sorption of these radiocations was compared by means of the distribution coefficient and of the sorption capacity. The maximum sorption capacities follow the order: $^{203}\text{Hg}^{2+} > ^{115\text{m}}\text{Cd}^{2+} \geq ^{60}\text{Co}^{2+}$. The thermodynamic functions of the sorption processes have been estimated. The increase of the absolute value of ΔG° with increasing temperatures shows that higher temperatures favor ionic exchange.

Introduction

Because of nuclear weapons tests, the nuclear accidents and long-term operation of radiochemical and nuclear fuel cycle facilities, very high levels of artificial radionuclides have been accumulated in the environment. The accidental releases of man-made radiotoxic substances into aquatic systems remain an important health and scientific issue.¹

According to TYKVA and BERG,² the main part of the radioactivity in the waste solutions of pressurized water reactors (PWR) consists of the isotopes of cobalt (^{58}Co and ^{60}Co), by more than 50% and in boiling water reactors (BWR) by 87%. ^{60}Co is an important gamma-ray source, and is extensively used as a tracer and a radiotherapeutic agent, it is a corrosion product in nuclear power plant also. A number of radioisotopes of cadmium and mercury appear as result of the fission process. Although there are not so long lived, their presence in environment is a potential health hazard.^{2,3} The maximum permissible limit of the corresponding non-active elements into drinking water is Hg $0.001 \text{ g}\cdot\text{dm}^{-3}$, Cd $0.01 \text{ g}\cdot\text{dm}^{-3}$ and Co $0.05 \text{ g}\cdot\text{dm}^{-3}$.⁴

Consequently, different techniques for their removal were proposed during the last decades: (1) liquid-liquid solvent extraction, (2) anion exchange (very effective, since Cd and Hg form many stable anion complexes), the best anion-exchange resins are of the strongly basic type like the quaternary ammonium salts of polystyrene divinyl benzene (Dowex 1 and 2, Amberlite IRA-400), (3) cationic exchange on sulphonated phenolic resins (Amberlite IR-100) or the sulphonated hydrocarbon chain or the divinyl benzenes (Amberlite IR-120, Dowex 50).⁵ In addition, cellulose acetate, alumina, or even some natural zeolites were successfully used as cation exchangers.^{6–9}

These studies lead us to idea of the utilization of the titanosilicates for removal of the radiocontaminants from waste waters. From the environmental point of view, information relating to the scavenging of toxic radioisotopes by novel inorganic materials is very useful. This is why we start a systematic study of individual radionuclides on titanosilicates of Engelhard class. The sorption of some $\beta+\gamma$ -radioisotopes from low radioactive waste waters on ETS-10 titanosilicate was earlier reported by our group.¹⁰ The synthetic titanosilicates were previously utilized by other scientists for heavy metals^{11,12} and radiocations^{13–15} removal from solution.

Due to the specific properties related to the framework structure and high ion exchange capacity (ca. $6.0 \text{ meq}\cdot\text{g}^{-1}$, hydrous basis), ETS-4 titanosilicate is especially recommended for safe storage and removal of radioactive elements from nuclear waste. The ETS-4, patented by KUZNICKI,¹⁶ is a member of the Engelhard Titanium Silicate family having uniform pore size of ca. 4 \AA . According to PHILIPPOU and ANDERSON,¹⁷ this material is structurally very interesting and is related to mineral zorite, although not its synthetic counterpart.

Since the waste solutions are very different of one another, it is impossible to study all the possibilities, predictions being necessary. This is why we investigate in a model study the sorption of $^{60}\text{Co}^{2+}$, $^{115\text{m}}\text{Cd}^{2+}$ and $^{203}\text{Hg}^{2+}$ radiocations from simulated waste waters onto ETS-4 using a batch-type technique. Furthermore, kinetic and thermodynamic aspects are studied, as very important for the optimization of the sorption process.

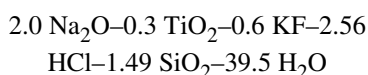
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Experimental

Materials

Chloride solutions of $^{60}\text{Co}^{2+}$ ($T_{1/2}=5.27$ y, specific activity = 641 ± 12 MBq·cm $^{-3}$), $^{115\text{m}}\text{Cd}^{2+}$ ($T_{1/2}=44.6$ d, specific activity = 96 ± 6 MBq·cm $^{-3}$), and $^{203}\text{Hg}^{2+}$ ($T_{1/2}=46.6$ d, specific activity = 188 ± 10 MBq·cm $^{-3}$) were procured from the Institute of Atomic Physics, Magurele, Romania. As non-active carriers, CdCl_2 , HgCl_2 (Fluka) and CoCl_2 (Chemapol Prague) were used. Solutions of $5\cdot 10^{-3}$ mol·dm $^{-3}$ were prepared by dissolving appropriate amounts of their carriers in double distilled water, labelled with the corresponding radionuclide and standardized by titration with EDTA. The specific activity of the diluted solutions at the beginning of the experiment was 250 ± 20 Bq·cm $^{-3}$. The pH of the obtained solutions was adjusted at 4.0 using acidic buffer.

The hydrothermal synthesis of ETS-4 titanosilicate ($\text{K}_{1.13}\text{Na}_{3.92}\text{Ti}_{3.07}\text{Si}_{8.17}\text{O}_{25}\cdot 8.64\text{H}_2\text{O}$) was carried out according to the procedure previously described^{18,19} from starting gels with the molar composition:



The reaction gel was prepared by mixing an acidic aqueous solution (A) obtained from KF (40 wt.%, Panreac), TiCl_4 (50 wt.%, Merck), HCl (37 wt.%, Riedel de Haën) and distilled water with a basic aqueous solution (B) obtained from sodium silicate (8 wt.% Na_2O , 27 wt.% SiO_2 , Merck) and NaOH (50 wt.%, Carlo Erba). The synthesis was carried out in PTFE-lined Morey type stainless steel autoclaves without stirring at 463 K for 3 days. The products were recovered by filtration, washed with deionised water and dried at 363 K for 12 hours. The physical and chemical characterisation of this material was presented extensively in numerous papers.^{20,21}

Instruments

In order to test the stability of ETS-4 to the external irradiation, a ^{60}Co γ -irradiation source with a total activity of $1.85\cdot 10^{15}$ Bq and a nominal dose of $8.612\cdot 10^4$ Gy·h $^{-1}$ had been used. The X-ray diffraction patterns of the ETS-4 titanosilicate before and after irradiation were recorded on a Philips PW 1830 X-ray powder diffractometer (Cu K_α radiation) with a scan rate of 0.02 °s $^{-1}$ ($2\theta=5-45^\circ$). The morphology and the dimensions of the crystals were evaluated by scanning electron microscopy on a Microspec WDA-2A microscope at 25 kV. The amount of exchangeable cations (Na^+ and K^+) from ETS-4 was determined using a Shimadzu AA-660 atomic absorption spectrometer.

The radioactivity measurements were carried out by γ -radiation spectrometry using a high efficiency NaI(Tl) detector connected to a Canberra Omega 1 multichannel analyzer. The activities of $^{60}\text{Co}^{2+}$, $^{115\text{m}}\text{Cd}^{2+}$ and $^{203}\text{Hg}^{2+}$ were determined by evaluation of the peaks 1173.0 keV, 993.6 keV and 279.1 keV corresponded to $^{60}\text{Co}^{2+}$, $^{115\text{m}}\text{Cd}^{2+}$ and $^{203}\text{Hg}^{2+}$, respectively. Due to relatively low activity, the measuring time was established for all the samples and standards at $6\cdot 10^2$ seconds. The relative standard deviation of the measured activities was $\pm 10\%$.

Batch mode adsorption

Parallel solutions series were set up in Berzelius flasks, introducing in each 100 cm 3 of CdCl_2 , HgCl_2 or CoCl_2 solution ($5\cdot 10^{-3}$ mol·dm $^{-3}$). Consequently, the initial number of miliequivalent gram of cation was one in each sample. The series were thermostated at 293, 313 and 333 K using a Messgeräte-Werk Lauda bath thermostat and at 277 K by using a commercial refrigerator. Afterwards, 0.1 g of ETS-4 titanosilicate was added, the contacting moment was considered the starting time for the sorption experiment. The experiment was conducted under intermittent shaking.

The sampling procedure and the preparation of the samples and standards were described in a previous article.¹⁰ All the measurements of standards and samples were performed at the end of the experiment in order to avoid the error resulted from the radioactive decay.

The batch distribution coefficient (K_d) and the amount of radioactive ion sorbed (q_e) were calculated as:

$$K_d = \frac{A_i - A_t}{A_t} \cdot \frac{V}{m} \text{ cm}^3\cdot\text{g}^{-1} \quad (1)$$

$$q_e = (C_i - C_e) \cdot \frac{V}{m} \text{ mmol}\cdot\text{g}^{-1} \quad (2)$$

where C_i and C_e represent the initial and equilibrium concentrations of various metal ions in aqueous phase, respectively, A_i and A_t are the initial activity and the activity of the solution at the sampling time t , m and V denote the weight of dry ETS-4 and the volume of aqueous phase used in the experiments.

Results and discussion

Characterization

Figure 1 shows the X-ray powder diffraction patterns of the ETS-4 titanosilicate as synthesized above and after 72 hours of γ -irradiation with the ^{60}Co source. The patterns are very similar, with no extra diffractions and with a very small reduction of the intensity of the peaks after irradiation. The SEM analysis before (Fig. 2) and

after irradiation (pictures not shown) indicates that the morphology and the elemental composition of the crystals did not change after irradiation. This behavior of the ETS-4 titanosilicate is very favorable for our purpose.

The ion-exchange capacity was expressed as the sum of Na^+ and K^+ cations determined by AAS, after the dissolution of the sample in hydrofluoric acid and distilled water. A value of $6.3 \text{ meq}\cdot\text{g}^{-1}$ (based on the anhydrous mass of the ETS-4) was obtained, in good agreement with that reported by KUZNICKI et al.²²

Kinetic considerations of the sorption process

The effects of the contact time and of the temperature onto the distribution coefficients of $^{60}\text{Co}^{2+}$, $^{115\text{m}}\text{Cd}^{2+}$ and $^{203}\text{Hg}^{2+}$ radioisotopes on ETS-4 titanosilicate, for a bath factor of $1 \text{ dm}^3\cdot\text{g}^{-1}$, are presented in Fig. 3. In all the studied systems, the K_d values increase proportionally with the increases of sorption temperature. We can note that in the case of $^{115\text{m}}\text{Cd}^{2+}$ the temperature play an important role in the sorption process, being observed important differences between the distribution coefficients. After 168-hour contact time in the sorption batch, the equilibrium was not reached for $^{60}\text{Co}^{2+}$ and $^{203}\text{Hg}^{2+}$ at 277 K. In all the other cases, a rapid increase of K_d take place in the first hours, and after about 24 hours, the systems reaches the stationary state. It seems that the sorption process is not as fast as the sorption of heavy metal lead on ETS-10 titanosilicate.^{12,23}

At 293 K, the distribution coefficients are increasing in the series:

$$^{203}\text{Hg}^{2+} > ^{115\text{m}}\text{Cd}^{2+} \geq ^{60}\text{Co}^{2+}$$

accordingly with the hydration energies and the hydrated radius of the corresponding ions.²³

In Table 1, the maximum distribution coefficients for the studied cations on ETS-4 (present study) and ETS-10 (taken from Reference 18) microporous titanosilicates (in the same working conditions) are presented.

It can be noted that the K_d values are not essentially different from the values obtained for the sorption of the same radiocations on the ETS-10 titanosilicate,¹⁸ although the theoretical exchange capacity of the dehydrated ETS-10 ($4.47 \text{ meq}\cdot\text{g}^{-1}$) is smaller than the one of the dehydrated ETS-4 ($5.15 \text{ meq}\cdot\text{g}^{-1}$).

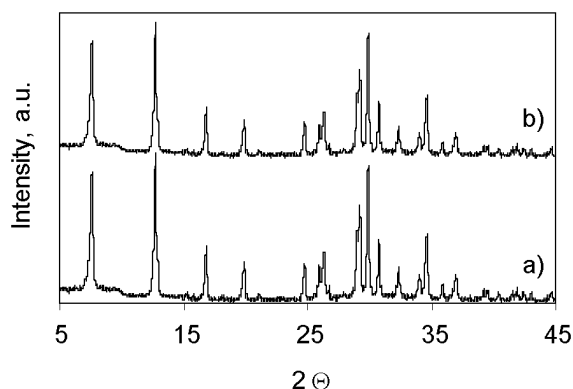


Fig. 1. X-ray diffraction patterns of the ETS-4 titanosilicate before (a) and after 72-hour γ -irradiation (b)

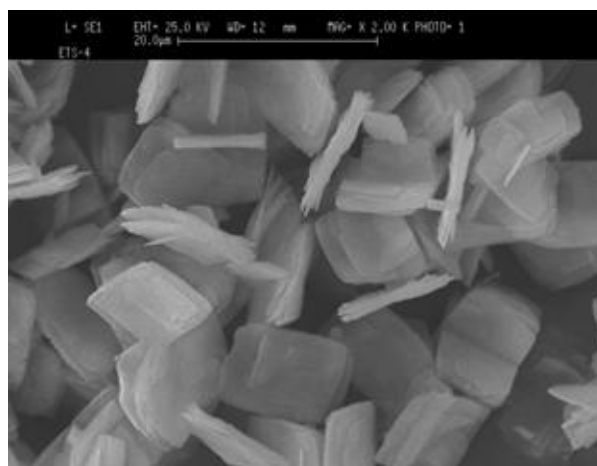


Fig. 2. SEM image of the ETS-4 titanosilicate

Table 1. Distribution coefficients of $^{60}\text{Co}^{2+}$, $^{115\text{m}}\text{Cd}^{2+}$ and $^{203}\text{Hg}^{2+}$ on ETS-4 and ETS-10 titanosilicates

Cation	Titanosilicate	$K_d, \text{ cm}^3\cdot\text{g}^{-1}$			
		277 K	293 K	313 K	333 K
Co^{2+}	ETS-4	536	593	625	649
	ETS-10 ^a	436	733	760	— ^b
Cd^{2+}	ETS-4	583	651	693	750
	ETS-10 ^a	631	791	811	— ^b
Hg^{2+}	ETS-4	644	778	801	810
	ETS-10 ^a	341	627	808	— ^b

^a From Reference 18.

^b There are no data for 333 K.

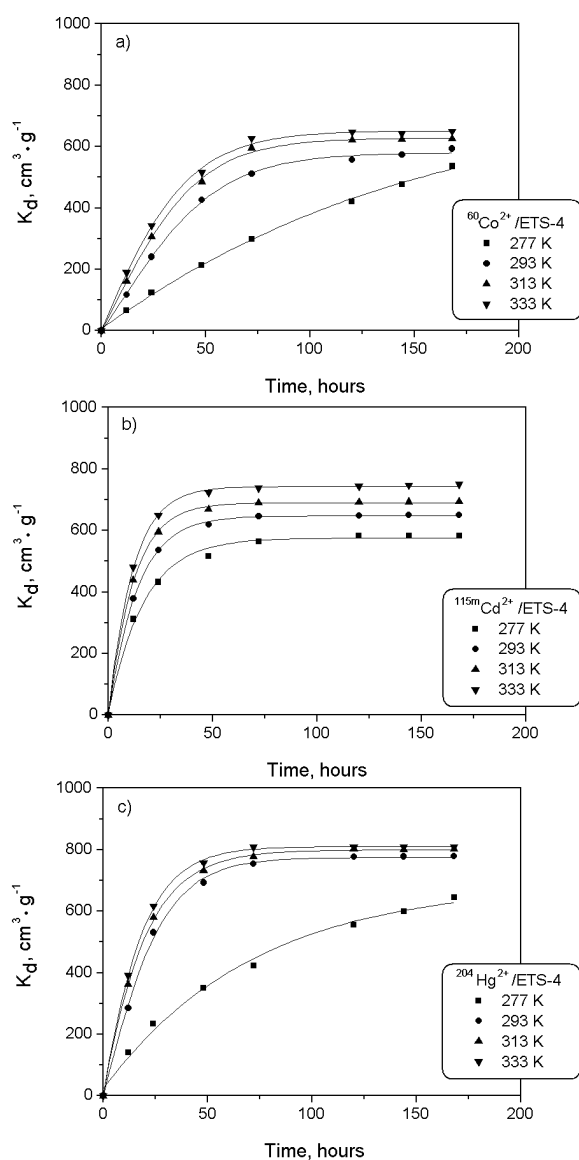


Fig. 3. Kinetics of the distribution coefficient of $^{60}\text{Co}^{2+}$ (a), $^{115\text{m}}\text{Cd}^{2+}$ (b) and $^{203}\text{Hg}^{2+}$ (c) at various temperatures

AL-ATTAR and DYER¹⁴ explain a similar situation (sorption of uranium) based on the structure of the considered titanosilicates. The ETS-10 has a structure in which chains of corner sharing TiO_6 octahedra are linked to tetrahedral silicate units, generating a three dimensional 12-membered ring pore system. The presence of tetravalent titanium in octahedral coordination, $[\text{TiO}_6]^{2-}$, generates a formal negative charge on the unit cell, which is balanced by exchangeable cations. The presence of octahedral titanium in the ETS-10 composition generates opportunities for the ionic exchange. The ion exchange capacity, chemical and thermal stability, framework resistance to radiation and the pore size ($\sim 8 \text{ \AA}$), higher to

that of metal hydrated ions could explain the good performances of ETS-10 for the retention of toxic and radioactive metal ions from the waste waters. ETS-4 contains two orthogonal sets of channels with pore size of ca. 4 \AA , formed by 12-membered Si/Ti rings and 8-membered Si rings with octahedral $[\text{TiO}_6]^{2-}$ and semi-octahedral $[\text{TiO}_5]^-$ titanium atoms. The main structural difference of these two titanosilicates consists in the type and effective pore size. ETS-4 behaves as a small-pored material, with a pore size comparable to zeolite A, since ETS-10 is a large-pored material. Hence, the heavy cations (having the ionic radius of 0.74 , 0.97 and 1.10 \AA for $^{60}\text{Co}^{2+}$, $^{115\text{m}}\text{Cd}^{2+}$ and $^{203}\text{Hg}^{2+}$, respectively) diffusing into the 8 \AA pore size channel would have to make detours through the 4 \AA one in order to pass freely.

Even if the distribution coefficient indicates the affinity of the solid sorbent toward the solute at equilibrium, the concept can be extended for non stationary states also. This procedure provided us the possibility to establish quickly at which moment the equilibrium is reached. Nevertheless, in the thermodynamic calculations only the saturation values of the exchanger were considered.

The Langmuir equation has been used by many authors to describe ion exchange systems.²⁵ This theory did not present interest for our systems, such time it was derived to describe monolayer absorption. The rate of $^{60}\text{Co}^{2+}$, $^{115\text{m}}\text{Cd}^{2+}$ and $^{203}\text{Hg}^{2+}$ sorption by ETS-4 titanosilicate at 293, 313, 333 K (and 277 K for $^{115\text{m}}\text{Cd}^{2+}$) tends to follow the Lagergren's first order equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_s}{2.303} \cdot t \quad (3)$$

where q_t is the amount of radiocations sorbed at the time t , q_e is the amount of radionuclide sorbed at the equilibrium and k_s is the sorption rate constant. As shown in Fig. 4, linear plots were obtained by representing $\log(q_e - q_t)$ function on time (indicating the applicability of the first order kinetics). Only the points corresponding to a temperature where the equilibrium was established were used for the calculation.

Thermodynamic considerations on the sorption process

The sorption rate constants, k_s , determined from the slopes of the plots are presented in Table 2. The activation energy was derived from the Arrhenius equation:

$$k_s = k_0 \cdot e^{-\Delta E_a / R \cdot T} \quad (4)$$

where k_s is the sorption rate constant, k_0 is the Arrhenius constant, E_a is the activation energy, R is the gas

constant and T is the absolute temperature. The calculated values are also presented in the Table 2.

The used procedure to determine the activation energy may not be applicable to many physical systems where the surface diffusion contribution is significant.²⁴ As expected, the activation energies for $^{115\text{m}}\text{Cd}^{2+}$ and $^{203}\text{Hg}^{2+}$ sorption on ETS-4 were found to be very closed (0.101 kJ·mol⁻¹ and 0.096 kJ·mol⁻¹, respectively). In agreement with SCHNEIDER and SMITH²⁶ the contribution of external surface diffusion is negligible as compared with the pore diffusion and so, because the activation energy for diffusion is much lower than the energy of sorption and ionic exchange.

The increase of the values of the distribution coefficient calculated by (1), with the temperature, prove the endothermic nature of the sorption.

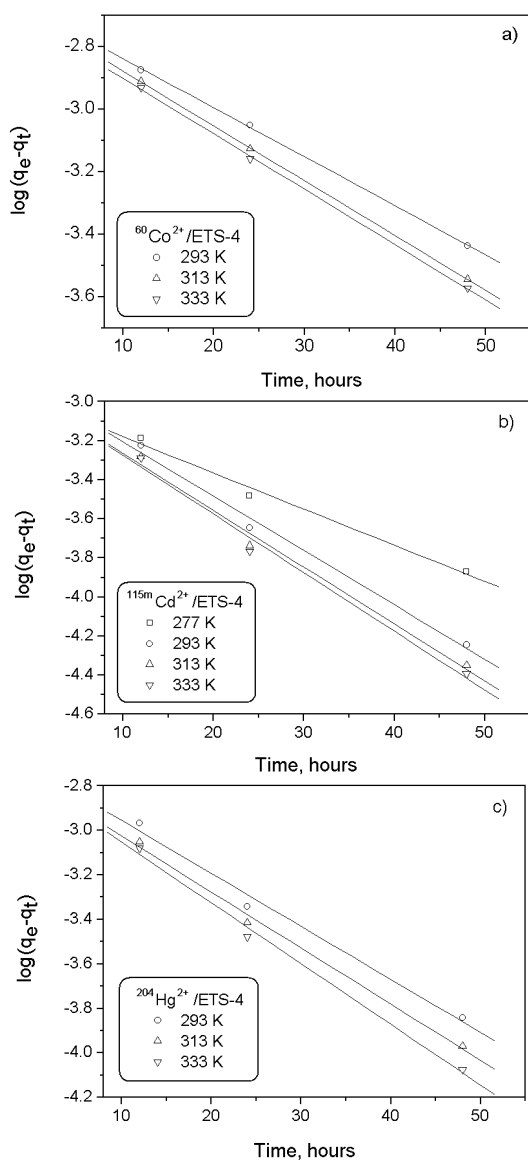


Fig. 4. Lagergren equation for $^{60}\text{Co}^{2+}$ (a), $^{115\text{m}}\text{Cd}^{2+}$ (b) and $^{203}\text{Hg}^{2+}$ (c) sorption on ETS-4 titanasilicate

The values of ΔH° and ΔS° were calculated from the slopes and intercept of linear regression of $\ln K_d$ vs. $1/T$ (Fig. 5) by:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (5)$$

where K_d is the distribution coefficient (cm³·g⁻¹), ΔS° the standard entropy, ΔH° the standard enthalpy, T the absolute temperature (K) and R the gas constant (kJ·mol⁻¹·K⁻¹).

The standard free energy values, ΔG° , were calculated using:

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ \quad (6)$$

The values of ΔH° , ΔS° and ΔG° are given in Table 3. ΔH° is positive for the sorption of $^{60}\text{Co}^{2+}$, $^{115\text{m}}\text{Cd}^{2+}$ and $^{203}\text{Hg}^{2+}$ radiocations on ETS-4 and the process is endothermic.

The results show an endothermic heat of sorption (ΔH° varies between 0.821 and 3.337 kJ·mol⁻¹), and negative free energy values, indicating that the radiocations are preferred in the solid phase. The free energy values for all the systems are negative and the increase of the absolute value of ΔG° with increasing temperatures shows that higher temperatures favour the ionic exchange. When the hydrated ions are sorbed on the ETS-4 surface, water molecules previously bonded to the metal ion are released and dispersed onto solution; this results in a slight increase of the entropy.

Table 2. The sorption rate constants and the activation energies for $^{60}\text{Co}^{2+}$, $^{115\text{m}}\text{Cd}^{2+}$ and $^{203}\text{Hg}^{2+}$ sorbed on ETS-4

Temperature, K	k_s, h^{-1}		
	$^{60}\text{Co}^{2+}$	$^{115\text{m}}\text{Cd}^{2+}$	$^{203}\text{Hg}^{2+}$
277	0.0138	0.0426	0.0193
293	0.0361	0.0641	0.0548
313	0.0404	0.0670	0.0580
333	0.0408	0.0691	0.0628
$E_a, \text{kJ}\cdot\text{mol}^{-1}$	0.161	0.101	0.096

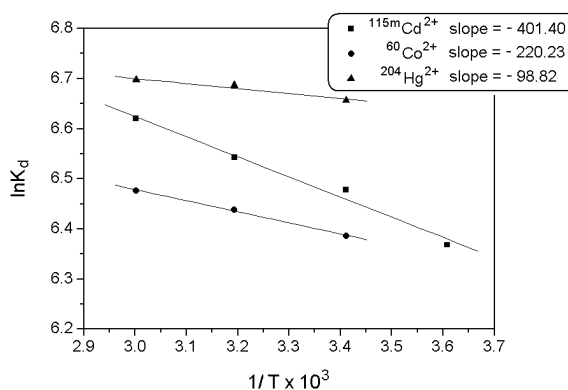


Fig. 5. Relation between $\ln K_d$ and the sorption temperature

Table 3. Thermodynamic parameters for the sorption of $^{60}\text{Co}^{2+}$, $^{115\text{m}}\text{Cd}^{2+}$ and $^{203}\text{Hg}^{2+}$ on the ETS-4 titanosilicate

Radiocation	ΔH° , kJ·mol ⁻¹	ΔS° , kJ·mol ⁻¹ ·K ⁻¹	ΔG° , kJ·mol ⁻¹			
			277 K	293 K	313 K	333 K
$^{60}\text{Co}^{2+}$	1.831	0.059	-14.51	-15.45	-16.63	-17.81
$^{115\text{m}}\text{Cd}^{2+}$	3.337	0.065	-14.68	-15.71	-17.01	-18.31
$^{203}\text{Hg}^{2+}$	0.821	0.058	-15.24	-16.17	-17.33	-18.49

Conclusions

ETS-4 titanosilicate has an important ability to remove radiocations from their aqueous solutions (as models for radioactive waste waters). In batch systems, the maximum sorption capacities of the studied ions on ETS-4, without ionic competition, follow the order: $^{203}\text{Hg}^{2+} > ^{115\text{m}}\text{Cd}^{2+} \geq ^{60}\text{Co}^{2+}$. The obtained values are slightly smaller than the ones obtained for the sorption of the same cations on ETS-10.

The sorption dependence on time and temperature, as well as the thermodynamic functions of the sorption process were presented. The sorption rate is not so high, our results indicating a time of ca. 24 hours to reach the equilibrium.

The sorption efficiencies of the ETS-4 (present work) and ETS-10¹⁸ titanosilicates for $^{60}\text{Co}^{2+}$, $^{115\text{m}}\text{Cd}^{2+}$ and $^{203}\text{Hg}^{2+}$ radioisotopes encouraged the further study on the selectivity of these materials on real radioactive waste waters. The influence of pH and competitive ions will be studied in depth, column sorption studies should be performed to demonstrate application on real waste solutions.

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