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Removal of Thorium Ions from Simulated Wastewaters onto Callovo Oxfordian Clay

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Abstract: The adsorption of Th(IV) from simulated waters onto clay as a function of sorbent mass, Th concentration, pH, temperature was studied by using the batch technique under ambient condition in the absence of any ionic competition. The results indicate that the adsorption of Th(IV) onto Callovo Oxfordian clay depends on pH, and the adsorption of Th(IV) increases with increasing clay mass. Thermodynamic parameters, the Gibbs free energy, enthalpy and entropy were also calculated.

Keywords: Mineral clay; Thorium ions; Wastewaters; Sorption properties.

Introduction

In recent years inorganic exchange materials have being used for liquid radioactive waste treatment and spent fuel reprocessing.

These materials have a number of advantages making them preferable to the organic materials: they are very resistant towards radiation damage, and have high thermal and chemical stability.[1,2]

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Both the cation exchange capacity of clays and the availability at low cost are the main reason for their applicability in radionuclide immobilization and consequently in decontamination of radioactive wastewaters.

It is known that the kinetics of ion exchange process can be affected by a number of parameters, such as the nature of the exchanger, the nature of the counter ions, the extent of agitation, the concentration of the counter ions, etc.[3-5]

The aim of the present study was to investigate the removal of thorium ions from simulated waters onto Callovo Oxfordian clay. The effect of contact time, initial thorium concentration and solid/liquid ratio was investigated.

Results and discussions

The effect of the contact time was studied at a pre-established concentration of radioactive solution (0.50 mg/mL) at room temperature (20 ºC) onto the 0.63 mm diameter fraction. As presented in Figure 1, the sorption increased with the contact time and the equilibrium is reached after 120 h.

The variation of Th^{4+} ions sorption onto the mineral clay with the initial concentration of solution was studied at 20 ºC varying the concentration of the radioactive ions from 0.25 to 0.75 mg/mL and keeping constant all the other parameters. Figure 2 shows that the amount of sorbed radioactive ions increases with increasing of the initial concentration in the solution up to 0.50 mg/mL, and an opposite effect at higher concentrations.[6,7]

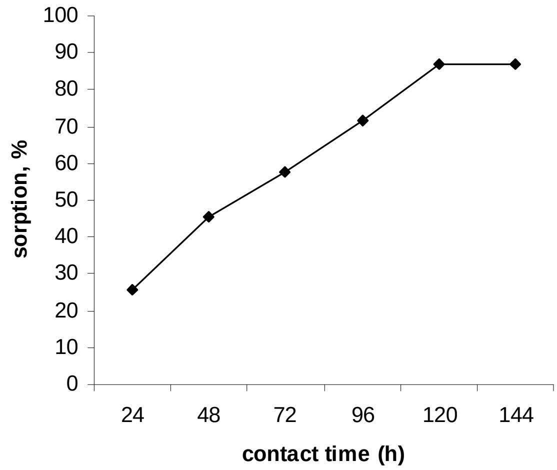

Figure 1. Variation of the sorption versus contact time.

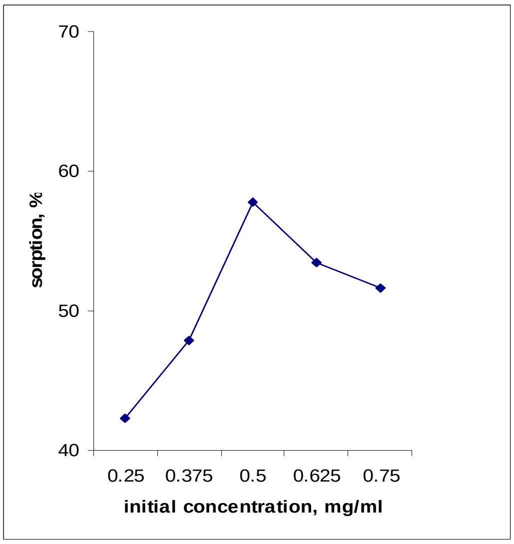

Figure 2. Sorption as a function of the radioactive solution concentration.

Figure 3 presents the dependence of the sorption on pH.

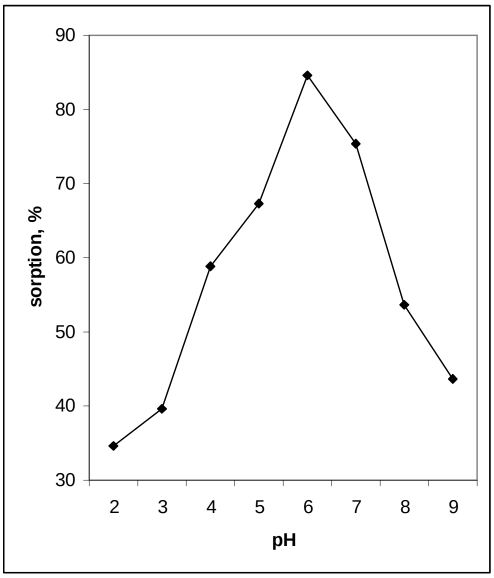

Figure 3. Effect of pH on Th^{4+} removal.

The temperature effect on the sorption process was studied in the range of 20-60 ºC. The obtained data presented in Figure 4 illustrates that the sorption linearly increases with increasing of temperature.[8,9]

The thermodynamic parameters ΔH^o and ΔS^0 were calculated from the slopes and intercepts of the linear variation of lnK vs. 1/T by:

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (1)$$

where K_d is the distribution coefficient, T is the absolute temperature (K) and R is the ideal gas constant.

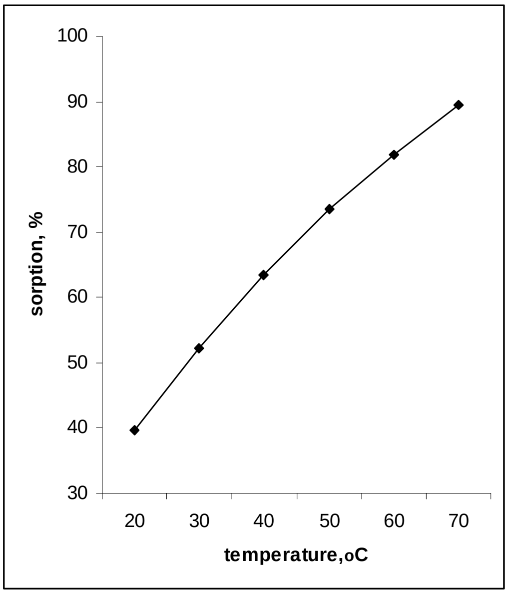

Figure 4. Effect of temperature on the sorption process.

The Gibbs free energy values were calculated by equation (2):

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (2)$$

The calculated thermodynamic parameters for the thorium sorption process on clay materials are summarized in Table 1. The positive values of both ΔH^0 and ΔS^0, and the negative value of ΔG^0 indicate an endothermic and, respectively a spontaneous adsorption process.

Table 1. Thermodynamic parameters for the sorption of Th(VI) on the clay materials.

Clay materials	ΔH^o, J/mol	ΔS^o, J/mol·K	ΔG^o, kJ/mol				
			293	303	313	323	333
Callovo Oxfordian	12.32	49.79	-14.57	-15.07	-15.57	-16.06	-16.56

Experimental

The Callovo Oxfordian clay sample was obtained from the borehole EST 104 at 494 m depth.[10]

The Callovo-Oxfordian formation is a complex mineral assemblage where phyllosilicates, quartz and feldspars are cemented by carbonates (calcite and dolomite). Small proportions of Fe-rich minerals (pyrite, siderite and Fe oxide and hydroxides) and organic matter are also present.[11] The mineralogical composition of Callovo-Oxfordian clay is given in Table 2.[12]

The clay was milled and sieved and the 0.63 mm granulometric fraction was used in the sorption experiments. The specific surface area of the clay was measured by nitrogen adsorption based on Brunauer-Emmett-Teller (BET) surface area equation and it was found to be 17.0021±0.1714 m^2/g.

The simulated wastewater was prepared by dissolving $Th(NO_3)_4 \cdot 5H_2O$ (A.R. reagent) in distilled-deionised water. The concentration of Th^{4+} ions was spectrophotometrically determined with Arsenazo III, at $\lambda = 660$ nm. Concentrations of Th^{4+} between 0.25-0.75 mg/mL were determined.

The adsorption of thorium was studied using a batch-mode technique. A weighted amount of clay was equilibrated with a volume of radioactive solution of known concentration at a pre-established temperature.

Table 2. Molar composition of Callovian-Oxfordian clays.

Mineral	Formula	Amount (%)
Kaolinite	$Si_2Al_2O_5(OH)_4$	2.2
Biotite	$K(Si_3Al)(Mg_{1.5}Fe^{2+}_{1.5})O_{10}(OH)_2$	27.8
Chlorite	$Si_3Mg_5Al_2O_{10}(OH)_8$	2.2
Illite	$K_{0.9}(Mg_{0.5}Fe_{0.05})(Si_{3.25}Al_{2.55})O_{10}(OH)_2$	38.2
Quartz	SiO_2	7.5
Montmorillonite	$Ca_{0.083}Na_{0.133}(Al_{1.667}Mg_{0.333})(Si_4)O_{10}(OH)_2$	20.6
K-feldspar	$KAlSi_3O_8$	1.5

The results of performed experiments were expressed as:

$$sorption = \frac{C_0 - C_e}{C_0} \cdot 100 \qquad (3)$$

where:

C_0 – initial concentration of the radioactive solution, mg/mL;

C_e – equilibrium concentration of the radioactive solution, mg/mL.

Conclusions

The present study indicates that the adsorption of thorium ions from aqueous solution depends on concentration of thorium in simulated wastewaters, on contact time, temperature and on pH. Th(IV) is very well retained onto the studied clay, both physical and chemical processes being involved. The process is strongly dependent on temperature and pH.

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