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Experimental investigation of radiocesium sorption on ceramic clay using a batch method

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Abstract In this study, radiocesium sorption on ceramic clay was investigated as a function of particle size and initial ^{137}Cs concentration using a batch method. Ceramic clay samples taken from the Söğüt(İnisar) clay deposit were composed of kaolinite, dickite and quartz. The equilibrium time and the liquid–solid ratio were determined as 60 min and 250 mL g^{-1}, respectively. The distribution coefficients (K_d) for variable liquid–solid ratio and the percentage adsorption (P_{Ad}) were calculated. The values of K_d and P_{Ad} ranged from 483 to 3165 mL g^{-1} and 34–93%, respectively. The K_d and P_{Ad} values increased with increasing particle size, but decreased with increasing initial concentration. The sorption data were interpreted in terms of a Langmuir isotherm. The results indicated that the Söğüt(İnhisar) ceramic clay has good sorption capacity for cesium.

Keywords Cesium · Sorption · Batch method · Clay · Distribution coefficient

Introduction

A nuclear reactor produces numerous fission products (radiocesium, radiostrontium, etc.). Radiocesium (^{137}Cs, $T_{1/2} = 30.07$ years; ^{135}Cs, $T_{1/2} = 2 \times 10^6$ years; ^{134}Cs, $T_{1/2} = 2.4$ years) is important in nuclear waste effluents because of high yields in the nuclear fission process. Therefore, knowledge of the mobility of radiocesium in natural materials such as soil, rock, clay, etc. is essential to assess the impact of its release from waste disposal sites or geological locations considered as potential sites for radioactive waste disposal. Sorption is an important process controlling the mobility or transport of radionuclides through natural materials. Understanding of sorption behavior is necessary to evaluate radionuclide migration to the biosphere. Many studies have been conducted on the adsorption behavior of fission products, particularly radiocesium, on natural materials especially clays, which are good sorbents because of their ability to adsorb cations, thermal stability and wide availability [1–9].

Söğüt clay deposits are an important source of raw materials for the ceramics industry of Turkey. Söğüt has a reserve estimated of 1 million tons (Mton) kaolin and 16.2 Mton clay [10]. Ceramic clay samples used in this study originated from the İnhisar clay deposit of Söğüt. The Söğüt (İnhisar) ceramic clay comprises of kaolinite, dickite and quartz.

A few studies have been carried out of the sorption of radionuclides (radiocesium, radiostrontium and radiobarium) on Turkish clays [11–15]. The present study was conducted to investigate the radiocesium sorption behavior on the Söğüt(İnhisar) kaolinite clay as a function of particle size (ranging from 0.125 to 0.500 mm) and initial ^{137}Cs concentration (ranging from 1.68×10^{-4} to 5.88×10^{-4} M) using a batch method with ^{137}Cs as a radiotracer. The Langmuir isotherm model was used to describe the sorption of behavior of radiocesium and assess the sorption potential of radiocesium on the Söğüt(İnhisar) ceramic clay.

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Experimental

Sample and sample preparation

The natural ceramic clay sample investigated in this study was taken from the clay deposit of İnhisar in the region of Söğüt. The elemental concentration in the Söğüt(İnhisar) ceramic clay sample was determined using X-ray fluorescence (XRF) spectrometry (RIGAKU RIX2000) and is presented in Table 1. On the basis of X-ray diffraction (XRD) analysis, the Söğüt(İnhisar) ceramic clay sample consisted of kaolinite, dickite and quartz [16].

The raw ceramic clay sample was passed through standard sieves to get a size range between 0.125 and 0.500 mm, washed with distilled water and dried in a temperature-controlled furnace at 80 °C for 24 h. The cation exchange capacity of the clay sample was determined to be 1.30 meq g^{-1} by using the Cu-trien method [17].

The radiotracer of ^{137}Cs supplied from Amersham (UK) with carrier of CsCl was prepared to form tracer solution with an initial concentration varying from 1.68×10^{-4} to 5.88×10^{-4} M.

Batch method

The sorption experiment was executed using a batch method under normal laboratory conditions (oxic atmosphere, 25 °C, pH 6.4). 0.02 g of absorbent sample of each particle size and 5 mL of ^{137}CsCl solution were combined in a 20 mL shaking tube. The mixture was then shaken periodically and in selected time intervals in a thermostatic water bath. The aliquots of solution were taken for activity measurement after centrifugation at 3500 rpm for 30 min. The activity of ^{137}Cs in the supernatant solution was measured using a gamma-ray spectrometer with coaxial high purity germanium (HPGe) detector which has a relative efficiency of 16% and an energy resolution of 1.9 keV at the 1332.5 keV of ^{60}Co. The sorption was determined in terms of distribution coefficient (K_d) and was calculated from the following equation:

$$K_d\left(\text{mL g}^{-1}\right) = \frac{(A_0 - A_1)}{A_1} \times \frac{V}{m} \quad (1)$$

where A_0 is the initial activity of the solution, A_1 is the activity of the solution after sorption, V is the volume of the sorbate solution in mL and m is the mass of the sorbent in g.

The percentage adsorption (P_{Ad}) is related to K_d by the following equation:

$$P_{Ad}(\%) = \frac{100 \times K_d}{K_d + V/m} \quad (2)$$

Table 1 Chemical analysis of the ceramic clay sample investigated in this study

Composition	Content (wt%)
SiO_2	64.24
Al_2O_3	20.95
TiO_2	1.87
Fe_2O_3	2.06
CaO	0.92
MgO	0.33
Na_2O	1.78
K_2O	1.66
LOI	6.19

Results and discussion

In this study, radiocesium adsorption on the ceramic clay was studied as a function of particle size (0.125, 0.149, 0.210, 0.354 and 0.500 mm) and initial concentration of ^{137}CsCl solution (1.68×10^{-4}, 2.52×10^{-4}, 3.36×10^{-4}, 4.20×10^{-4}, 5.04×10^{-4} and 5.88×10^{-4} M).

Determination of equilibrium time and liquid–solid ratio

The equilibrium time and the ratio of volume of the solution to mass of solid was determined using the batch method for different times varying from 1 min to 16 h at a fixed temperature 25 °C, pH 6.4 and an initial Cs concentration of 5.88×10^{-4} M. The batch experiment described above was conducted for each particle size of the clay sample. Figure 1 depicts the variation of the percentage adsorption (P_{Ad}) against shaking time for the clay samples of the five particle sizes. The results in Fig. 1 indicate that uptake of Cs was rapid and that the percentage adsorption attained almost its maximum value after 60 min and did not change thereafter up to 16 h. Thus, the equilibrium time could be set at 60 min for the determination of sorption isotherms.

The effect of the change in solid to liquid ratio on the distribution coefficient (K_d) was studied by varying the amount of the ceramic clay sample from 0.01 to 0.4 g at the constant volume of 5 mL of ^{137}CsCl solution at a concentration of 5.88×10^{-4} M (Fig. 2). It is seen from Fig. 2 that the K_d increased rapidly with an increasing ratio of V/m up to the value of 250 mL g^{-1} and then remained unchanged between 250 and 500 mL g^{-1}. One of the reasons for the lower K_d at the smaller V/m ratio is higher concentration of the competing cations (e.g., K+ and Na+ etc.) leached from the clay to the solution, since the experiments were not carried out at a constant ionic

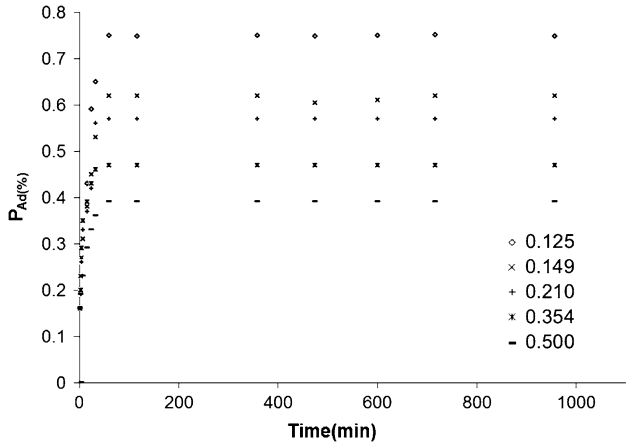


Fig. 1 Variation of the percentage adsorption (P_{Ad}) with time at different particle sizes

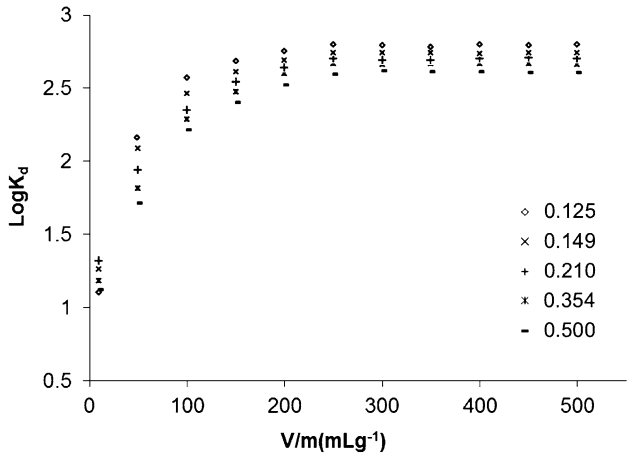


Fig. 2 Variation of the distribution coefficients (K_d) calculated each particle size with *V/m* ratio at 25 °C

strength. When all of the available adsorption sites are occupied by ^{137}Cs, further increase in the V/m ratio does not change the K_d considerable. As a result the liquid–solid ratio was set to 250 mL g^{-1} for the determination of sorption isotherms.

Effect of initial concentration

One of the most important parameters that can affect the sorption behavior of radiocesium is initial radiocesium concentration. The batch experiment described above was conducted for each particle size and initial concentration of radiocesium. Figures 3 and 4 show the relationship between P_{Ad} and the initial concentration, and between the K_d and initial concentration, respectively. It is observed from Figs. 3 and 4 that the values of P_{Ad} and K_d decreased with increasing initial radiocesium concentration and particle size.

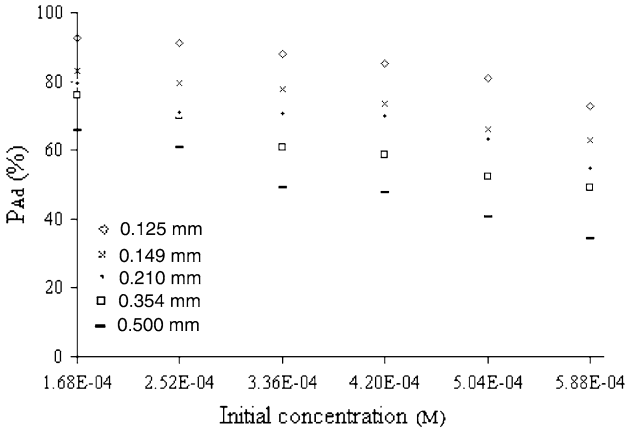


Fig. 3 Relation between the percentage adsorption (P_{Ad}) and initial concentration

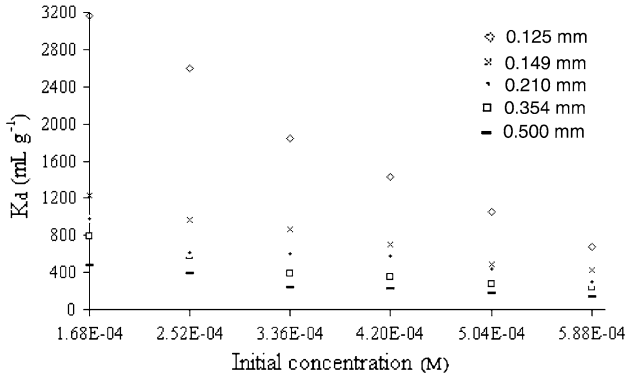


Fig. 4 Relation between the distribution coefficients (K_d) and initial concentration

Adsorption isotherm

Sorption data for wide range of sorbate concentrations are conventionally described by adsorption isotherms such as Langmuir, Freundlich and Dubinin–Radushkevich, permitting the calculation of adsorption capacity and mean adsorption energy. Data obtained for sorbate concentrations varying from 1.68×10^{-4} to 5.88×10^{-4} M were analyzed in terms of these isotherms. Best results were obtained using a Langmuir isotherm which is the simplest theoretical model. The applicability of the basic Langmuir equation to the adsorption experiment may be written in the following form to make a graph of the data by using the linear form of the basic Langmuir equation:

$$\frac{C_E}{C_{Ads}} = \frac{1}{b \cdot Q} + \frac{C_E}{Q} \quad (3)$$

where C_E is the equilibrium concentration of Cs in solution (mol L^{-1}), C_{Ads} is the amount of Cs adsorbed on the sorbent (mol g^{-1}), b is the Langmuir adsorption constant and Q is the sorption capacity, i.e., the amount of Cs that can be absorbed (mol g^{-1}). The plots of C_E/C_{Ads} against C_E are

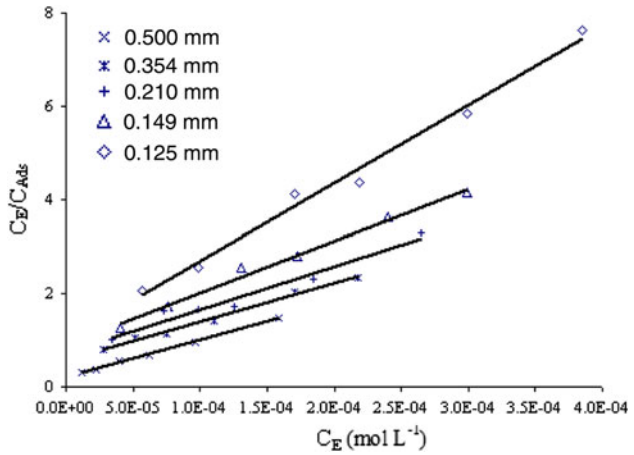


Fig. 5 Langmuir isotherm for adsorption of Cs on the ceramic clay sample at different particle sizes

Table 2 Parameters from Langmuir isotherm equation for adsorption of Cs on the ceramic clay sample

Particle size (mm)	$Q \times 10^3$	b	R^2
0.125	8.39	0.015	0.9963
0.149	11.42	0.018	0.9931
0.210	13.41	0.022	0.9974
0.354	14.93	0.029	0.9881
0.500	17.56	0.038	0.9989

linear (Fig. 5) and the values of b and Q were determined from the slope and intercept of the plots using the method of least squares and are given Table 2. It can be seen from Table 2 that the value of the Q increased with increasing particle size.

Conclusions

The sorption behaviour of radiocesium on the natural Söğüt(İnhisar) ceramic clay sample was studied as a function of the particle size of sorbent and the initial concentration of sorbate using a static batch method. The experiments were performed under laboratory conditions in ambient atmosphere. The distribution coefficients (K_d) and the percentage adsorption (P_{Ad}) of Cs have been found to be influenced by the particle size and initial concentration. Experimental data were fitted to Langmuir isotherms. It was found that the adsorption capacity increased with increasing particle size. Overall, the present study shows that the Söğüt(İnhisar) ceramic clay has a good sorption capacity and a rapid sorption rate for Cs.

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