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Physicochemical characterization of the retardation of aqueous Cs^+ ions by natural kaolinite and clinoptilolite minerals

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Abstract

The aim of this study was to carry out kinetic, thermodynamic, and surface characterization of the sorption of Cs^+ ions on natural minerals of kaolinite and clinoptilolite. The results showed that sorption followed pseudo-second-order kinetics. The activation energies were 9.5 and 13.9 kJ/mol for Cs^+ sorption on kaolinite and clinoptilolite, respectively. Experiments performed at four different initial concentrations of the ion revealed that the percentage sorption of Cs^+ on clinoptilolite ranged from 90 to 95, compared to 28 to 40 for the kaolinite case. At the end of a 1 week period, the percentage of Cs^+ desorption from clinoptilolite did not exceed 7%, while it amounted to more than 30% in kaolinite, indicating more stable fixation by clinoptilolite. The sorption data were best described using Freundlich and D–R isotherm models. Sorption showed spontaneous and exothermic behavior on both minerals, with ΔH^0 being -6.3 and -11.4 kJ/mol for Cs^+ uptake by kaolinite and clinoptilolite, respectively. Expanding the kaolinite interlayer space from 0.71 to 1.12 nm using DMSO intercalation, did not yield a significant enhancement in the sorption capacity of kaolinite, indicating that the surface and edge sites of the clay are more energetically favored. EDS mapping and elemental analysis of the surface of kaolinite and clinoptilolite revealed more intense signals on the surface of the latter with an even distribution of sorbed Cs^+ onto the surfaces of both minerals.

Keywords: Kaolinite; Clinoptilolite; Cs^+; Sorption

1. Introduction

The reliable prediction of metal transport through the biological environment requires a thorough knowledge of the parameters which influence their migration behavior. Those parameters are mostly related with the properties of liquid and solid phases in contact. Among the properties of the liquid phase are the time of contact, pH, E_h, loading, ionic strength, and temperature. The properties of the solid phase, however, are determined by factors such as the cation exchange capacity and the particle size, which are closely related to the structural features of these solids.

Cesium, Cs, is an alkali element ($Z = 55$) that has high solubility in water. It possesses several radioactive isotopes, the most important of which are ^{134}Cs ($t_{1/2} = 2.06$ years), ^{135}Cs ($t_{1/2} = 3.0 \times 10^6$ years), and ^{137}Cs ($t_{1/2} = 30.17$ years) produced during nuclear fission processes. The fission yields of ^{135}Cs and ^{137}Cs are relatively high, 6.54 and 6.18%, respectively [1]. Due to their long half lives, both of ^{135}Cs and ^{137}Cs are principal radiocontaminants. The Cs^+ ion can be highly mobile in aqueous media due to its low hydration energy (-276 kJ/mol) as compared to elements of larger oxidation state or smaller size, for which the hydration energies can rise up to several thousands of kilojoules per mole. This property facilitates its involvement with the hydrological cycle, which has interfaces with the biological cycle and thus poses a potential detriment to man and to other living systems.

Kaolinite and clinoptilolite are two examples of aluminosilicates that are widely available as soil components. The difference in structural properties of these two minerals af-

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fects their retardation behavior of different metals. Kaolinite is a 1:1 clay mineral that possesses a tight interlayer structure with the ideal formula $Al_2Si_2O_5(OH)_4$ [2]. The sorption properties of this clay are solely determined by the nature of its surface and edges. Kaolinite possesses a variable charge that can be related to the reactions between ionizable surface groups located at the edges or at the gibbsite basal plane and the ions present in aqueous solution [3]. The same study showed that the silanol groups (Si–OH) at the crystal edges of kaolinite contribute exclusively to the negative charge, through formation of SiO^- surface complexes at moderate and high pH values. The aluminol groups at the edges are amphoteric; undergoing protonation at low pH and deprotonation at high pH, resulting in the formation of the surface complexes $AlOH_2^+$ and AlO^-. It is also stated by another study that the charge from broken edges and exposed OH planes rather than charge from Al/Si substitution determines the kaolinite CEC, even at zero point charge, and that a high CEC in some kaolinites is found to be due to smectite layers on the surface of the kaolinite crystals [4]. However, it is indicated by other researches that the negative charge on kaolinite cannot be attributed to an oxide-like source only, and the partial dissolution of structural aluminum yielding negatively charged vacant sites must also be considered [5].

Clinoptilolite is one of the most widely known zeolitic minerals. The sorption on zeolitic particles is a complex process because of their porous structure, inner and outer charged surfaces, mineralogical heterogeneity, existence of crystal edges, broken bonds, and other imperfections on the surface [6]. The elemental formula of clinoptilolite is $(Na,K)_6Al_6(Si_{30}O_{72})\cdot 20H_2O$ [7]. The cage-like structure of this mineral makes it suitable for ion exchange reactions. In the absence of steric factors that can stabilize the ions held within the cages, such a stabilization might be referred to the negative charge arising from the isomorphous substitution of Al^{3+} with Si^{4+} in the structure. Another factor could also be the deprotonation of the oxide groups if the operational pH of the medium exceeds the zero point of charge of clinoptilolite. It is also reported that the sorbed cations might be coordinated with the defined number of water molecules, and located on specific sites in framework channels [6]. Clinoptilolite has received extensive attention due to its attractive selectivity for certain heavy metal cations such as lead, cadmium, and nickel [8].

So far, a variety of studies have been devoted to characterizing various aspects of the sorption behavior of Cs^+ ion on kaolinite and on clinoptilolite, using a variety of characterization techniques [9–18]. In our earlier studies, the retention capacity of kaolinite toward Cs^+ was studied and compared with that of other clay minerals [9]. A depth profiling study was also carried out to reveal the distribution of Cs^+ across the surface of kaolinite [10]. The applicability of kaolinite as a reactive barrier for Cs^+ retention was tested by other authors and the irreversibility of its uptake by kaolinite was discussed and compared with other clay minerals [11,12]. The sorption sites and atomic dynamics of Cs^+ on kaolinite were investigated and compared with its uptake by illite and montmorillonite [13,14]. The effectiveness of clinoptilolite as countermeasure amendments against Cs^+ migration from soil into plants was reported [15]. In another study, it was documented that the addition of clinoptilolite to cements leads to a 70–75% decrease in Cs^+ release [16].

In this study, the sorption behavior of Cs^+ on natural samples dominated by kaolinite and clinoptilolite was investigated as a function of contact time, loading, and temperature using atomic absorption spectroscopy (AAS), scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDS), and X-ray powder diffraction (XRPD). The study aimed at determination of the sorption kinetics, the best fitting isotherm model(s), and thermodynamic parameters such as the activation energy, enthalpy change, entropy change, and Gibbs energy of sorption, in addition to elucidating the surface distribution of the sorbed Cs^+ using elemental and mapping analysis of EDS technique.

2. Experimental

Natural samples of kaolinite and clinoptilolite used in this study originated from the Sındırgı and Manisa regions located in the western part of Anatolia. The samples were dry-sieved and the particle size of kaolinite used in this study was <38 µm, while that of clinoptilolite was 75–150 µm. Prior to performing the sorption steps, the mineral samples were equilibrated with tap water. The pretreatment step aimed to mimic the equilibrium situation of the minerals with groundwater. In each batch of the pretreatment experiments, 10.0 g of the mineral and 1000 ml of laboratory tapwater were mixed on a lateral shaker at room temperature for 4 days. The mineral samples were then filtered and dried.

The sorption experiments were performed using 50-ml polyethylene tubes. The tubes were first cleaned, dried at 90 °C overnight, cooled, and weighed. To each tube, 0.50 g of kaolinite or clinoptilolite samples were added, followed by the addition of 50.0 ml of aqueous CsCl solution. The initial concentrations of the solutions were 10, 50, 100, and 500 mg/l. The mixtures were then mixed using a Nuve ST 402 water bath shaker equipped with a microprocessor thermostat. The experiments were carried out at 25 and 60 °C for contact periods of 5, 10, and 30 min, and 1, 2, 5, 8, 24, and 48 h. At the end of each mixing period, the samples were filtered and dried at 90 °C. The filtrate was then analyzed using flame AAS using a Thermo Elemental SOLAAR M6 Series atomic absorption spectrometer with air–acetylene flame. A Cs hollow-cathode lamp ($\lambda = 758.0$ nm) was applied as a source.

In the desorption experiments, samples of Cs-loaded kaolinite and Cs-loaded clinoptilolite, prepared previously after 48 h of mixing, were exposed to tap water and shaken for a time period that lasted for one week. Analysis of the eluted Cs^+ were performed at 10 min, 4 h, 24 h, and 7 days.