



Removal of cesium ions from aqueous solution by adsorption onto local Taiwan laterite

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ABSTRACT

Utilization of local Taiwan laterite (LTL) to remove aqueous cesium was investigated in this work under the conditions of various contact time, cesium (Cs) loading and temperature. Experimental results show that adsorption is instantaneous. Freundlich and Langmuir simulation results demonstrate that local Taiwan laterite has high affinity and sorption capacity for Cs at low temperatures, which may be attributed to enhanced desorption as temperature increased. Thermodynamic parameters including ΔH , ΔG and ΔS were calculated and it is indicated that Cs adsorption on LTL is an exothermic, spontaneous and physical adsorption reaction. Moreover, the adsorbed Cs is distributed evenly on the LTL surface, which is confirmed by SEM/EDS mapping images. Furthermore, the absence of apparent shifting or broadening of the kaolinite signal in XRD patterns after Cs adsorption is an indication of the non-expanding characteristic of kaolinite structure.

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1. Introduction

There is a great concern about global warming among the scientific and political communities. This “inconvenient truth” is the impetus driving development of alternative energies with minimal carbon dioxide emissions. Among many sources of power supply, nuclear energy is controversial because released radionuclides are environmentally harmful. However, as a cheap energy with no CO₂ emissions, nuclear energy plays an important role in Taiwan’s power supply system. To achieve a balance between economic and environmental concerns, extensive studies of the fate and transport of radionuclides through geological substances have been carried out.

Laterite is a kind of red soil with abundant clay minerals along with iron oxides (amorphous iron oxides, goethite, hematite etc.). These iron oxides are important sorbents regulating concentrations of heavy metals and organic contaminants in nature [1–3]. Additionally, clay minerals show a high affinity for immobilizing cationic or organic contaminants because of their large specific surface area and negatively charged surface [4,5]. With these two advantages, laterite could be a potential buffer material for use at radioactive waste repositories. Since the content of laterite may vary by loca-

tions, the laterite used in this work is designated as local Taiwan laterite (LTL).

Cesium (Cs) is the concerned contaminant due to its high yield in spent nuclear fuel and long half-life of 30 years. The transport of cesium nuclide is a key criterion for safety assessment because of its high mobility in aquifer. Although Cs nuclide is easily spread by aqueous medium, its concentration can be significantly reduced by adsorption onto surfaces of buffer material [6,7]. In this study the feasibility of using LTL as buffer material to remove Cs from aqueous solutions is estimated. A series of batch experiments are conducted as a function of contact time, Cs loading and reaction temperature. X-ray diffraction (XRD) and scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM/EDS) are also employed to identify the sorption mechanism and distribution of adsorbed Cs on LTL surfaces.

2. Material and methods

2.1. Solid characteristics

Samples of local Taiwan laterite were collected from surface soil of 2–4 m depth in Toayuan County, Taiwan. These LTL soils were sieved and the fraction of particles with diameters <0.074 mm was collected for characteristic analyses and batch experiments. The specific surface area of LTL is 32.25 m²/g (N₂-BET) and its cation exchange capacity (CEC) is 14.3 meq/100 g. The EDS (SEM/EDS,

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Leo 1530) results indicate that average elemental content on LTL surface is O (45.81%), Al (15.38%), Si (20.78%), K (2.27%) and Fe (14.12%). The major minerals in LTL determined by XRD (Philips PW1300) are quartz, kaolinite and goethite.

2.2. Batch experiments

Adsorption experiments were carried out within serum bottles (Schott, Germany) at two temperatures of 25 and 55 °C. To explore the process of cesium adsorption on LTL, 15 g of LTL was added to 450 mL deionized water (DW). The Cs concentrations (CsNO₃) of these DW solutions were 1 mM to 0.1 μM and spiked with appropriate amounts of radioactive Cs-137 tracer. The 15 g of LTL was utilized to reduce the possible influences from a laterite matrix. The mixtures were then transferred into a water bath shaker equipped with a temperature controller. These Cs solutions were collected at 1, 2, 4, 8, 12, 24, and 48 h, and 4 and 7 d. During each sampling, 1 mL of Cs suspension was collected, filtered through a 45 μm Minipore cell, and then its radioactivity was measured with an NaI detector (Wallac 1470 Wizard). After measurements, the suspension was immediately returned to the reaction serum bottle to minimize changes on experimental conditions. Decreases of radioactivity in liquid were interpreted as the amount of Cs being adsorbed to LTL. Another non-radioactive batch experiment with the same experimental conditions was conducted at 25 °C for XRD and SEM/EDS studies.

2.3. The distribution of adsorbed Cs on LTL surface

The LTL samples before and after Cs adsorption were analyzed by XRD (Philips PW1300) and scanning electron microscopes equipped with an energy dispersive X-ray spectroscopy (SEM/EDS, Leo 1530). To prepare XRD specimens, the solutions of these samples were first discarded. The solids were then dried at 45 °C under reduced pressure to prevent phase transformation at high temperatures. The XRD spectra were recorded in the range of 5–50° (2θ) by CuKα radiation (λ = 1.5406 Å) at 40 kV and 40 mA. Step size was 0.020 with a time-per-step duration of 60 s. The SEM/EDS was used to identify the locations of adsorbed Cs on LTL surface. For SEM/EDS specimens, powdered LTL samples were adhered onto a conductive carbon tape on metallic disks. Images of the LTL surface along with EDS mappings were used to identify sorption sites. The EDS mappings were carried out at a voltage of 15 kV under vacuum.

3. Results and discussion

3.1. Kinetic results

Kinetic adsorption experiments were carried out as a function of contact time under conditions of five initial Cs concentrations ranging from 10⁻³ to 10⁻⁷ M at two temperature settings, 25 and 55 °C. It is noted the adsorptions were instantaneous under given experimental conditions and all equilibria were reached within the first hour. This fast adsorption is the typical adsorption characteristic of Cs on minerals such as biotite, illite, hornblende, calcite and montmorillonite, in which fast adsorption is related to adsorption occurring on accessible sorption sites of the solid external surface [8]. By fitting kinetic results with a first-order equation, the rate constant at high and low temperature would be estimated. These rate constants could further be used to compute the activation energy (*E_a*) of adsorption (kJ/mol) by following equation:

$$\ln \left(\frac{k(T_2)}{k(T_1)} \right) = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (1)$$

Table 1

The values of *n*, ln *k* and *R*² obtained by the Freundlich isotherm and *B_{max}*, *k₃* and *R*² values by the Langmuir isotherm simulation

<i>T</i> (°C)	Freundlich isotherm			Langmuir isotherm		
	<i>n</i>	log <i>k</i> (mol/g)	<i>R</i> ²	<i>B_{max}</i> (mmol/g)	<i>k₃</i> (L/mmol)	<i>R</i> ²
55	1.657	2.47	0.999	0.2	0.12	0.999
25	1.502	2.76	0.999	0.3	0.19	0.999

where *R* is the ideal gas constant (8.314 J/mol), and *k*(*T*₁) and *k*(*T*₂) are rate constants under high and low temperatures, respectively.

Special caution should be paid to interpretation of these derived *E_a* values since there are only two data before equilibrium, one is starting concentration, and the other is the concentration after 1 h of reaction. In this case, the absolute *E_a* value obtained by modeling will be used with care. However, by only considering the *E_a* values which are very close to zero, it is recognized that Cs adsorption on LTL is physisorption, in which van der Waals force associated with weak electrostatic force induce ion-exchange reactions [9–11].

3.2. Isotherms and thermodynamic parameters

Freundlich and Langmuir isotherms are the most frequently used models for describing the relationship between adsorbed Cs on solids and remaining in solutions. Freundlich isotherm is based on concept of multilayer adsorption associated with adsorption on heterogeneous surfaces [10] and its linear form is expressed as

$$\log [Cs]_s = \log k + \frac{1}{n} \log [Cs]_i \quad (2)$$

where [Cs]_s is the amount of adsorbed Cs on a solid (mol/g), which is obtained by Eq. (3),

$$[Cs]_s = ([Cs]_0 - [Cs]_i) \times \left(\frac{V}{M} \right) \quad (3)$$

where [Cs]₀ is the initial Cs concentration (mol/L), *V* is volume of the Cs solution (L), and *M* is the mass of the LTL sample (g). The *k* value in Eq. (2) is the Freundlich constant and *n* is a constant describing adsorption linearity.

Fig. 1 plots experimental data after 7 d of adsorption, and Table 1 lists fitting results. The magnitude of the *k* value (in terms of log *k*) is referred to as the relative adsorption affinity toward Cs [8,12].

A relatively high *k* value is obtained at low temperature, indicating a high affinity of LTL toward Cs adsorption at low temperature. Additionally, a severe departure of *n* value from unity obtained in the high temperature (*n* is 1.502 at 25 °C and 1.657 at 55 °C). It means that the sorption energy barrier is increased exponentially when the neighboring sorption sites on the LTL surface are gradually occupied by Cs ions [12,13]. This entity is also accounting for the low *k* value determined at an elevated temperature.

In addition, these experimental data were also fitted by using the OneSiteBind program (a built-in fitting curve within Origin 6.0 Profession). The OneSiteBind program is a derivative of the Langmuir isotherm model that describes the concept of one site binding directly to one element. The equation of OneSiteBind program is expressed as

$$[Cs]_s = \frac{B_{max}[Cs]_i}{k_3 + [Cs]_i} \quad (4)$$

where *B_{max}* represents the maximum sorption sites and *k₃* is the Langmuir constant.

Langmuir isotherm is a physically plausible isotherm based on the following three assumptions: (a) sorption cannot proceed beyond monolayer coverage; (b) all sites are equivalent and the surface is uniform; and, (c) the possibility of a molecule to be

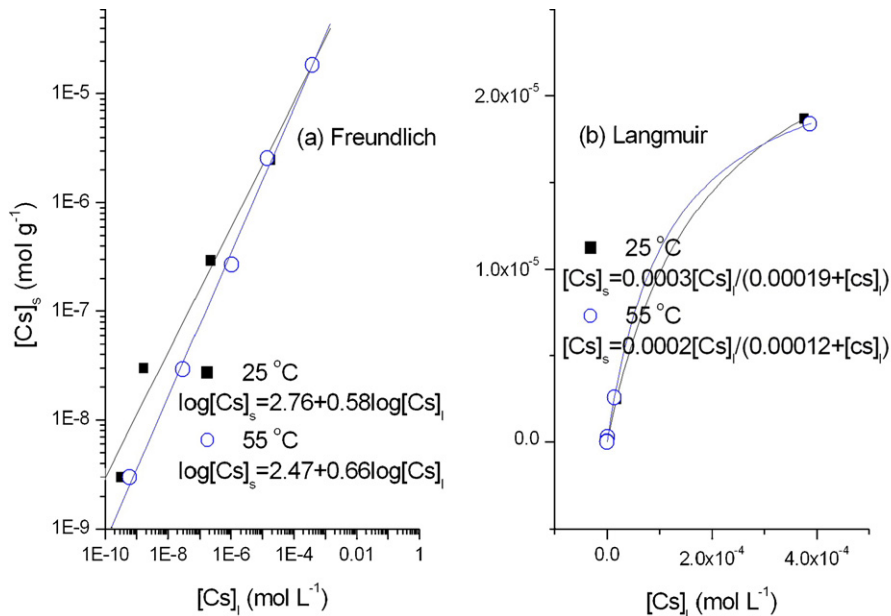


Fig. 1. Isotherm simulations at 55 and 25 °C (a) Freundlich (b) Langmuir.

adsorbed at a given site is independent of the occupation of neighboring sites [8]. Accordingly, OneSiteBind simulation is particularly informative for quantifying the sorption capacity of LTL toward Cs ions. It is observed that all R^2 values are close to unity and the B_{\max} value decreases as temperature increases (0.3 mmol/g at 25 °C and 0.2 mmol/g at 55 °C) (Table 1), indicating that roughly 33% of sorption is reduced at elevated temperatures.

This study further determines the thermodynamic parameters of Cs adsorption to LTL. By determining the K_d values in advanced from the differences of equilibrium and initial concentrations, thermodynamic parameters of enthalpy, Gibbs energy and entropy of Cs adsorption can be obtained using Eqs. (5–8) [9,11] (shown in Table 2).

$$K_d = \frac{[Cs]_s}{[Cs]_l} \text{ (L/g)} \quad (5)$$

$$\Delta H^\circ = R \ln \frac{K_d(T_2)}{K_d(T_1)} \times \frac{(T_1 T_2)}{(T_1 - T_2)} \text{ (kJ/mol)} \quad (6)$$

$$\Delta G^\circ = -RT \ln K_d \text{ (kJ/mol)} \quad (7)$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \text{ (J/mol K)} \quad (8)$$

The negative enthalpy $\Delta H^\circ < 0$ with an average value around -22 kJ/mol shows that Cs adsorption is exothermic. This observation is consistent with the isotherm result, indicating that forward reaction is favored at low temperatures. The magnitude of enthalpy change (> -25 kJ/mol) implies that an ion-exchange reaction is driven by van der Waal force [9]. The negative Gibbs energy (an average value about -19 and -18 kJ/mol for low and high temperatures, respectively) indicates that the Cs adsorption reaction is

spontaneous. Moreover, an ion-exchange mechanism is suggested by considering the magnitude of changes in Gibbs energy [12]. Negative entropy was the result of a stable arrangement of adsorbed Cs on the LTL surface [9], whereas relatively less negative entropy at elevated temperature was attributed to the increased desorption.

3.3. SEM/EDS studies of the Cs sorption

It has been reported that minerals with a sheet structure, such as kaolinite [9], illite [14], and some micaceous minerals [15–17] have excellent affinity toward Cs adsorption. In cases of LTL, the

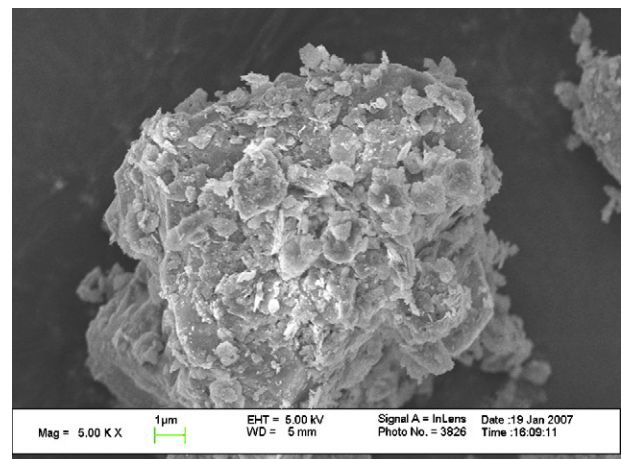


Fig. 2. The surface of Taiwan locally laterite amplified by five thousand times.

Table 2
The derived thermodynamic parameters ΔH° , ΔG° and ΔS°

Initial $[Cs]_0$	K_d (mL/g) (25 °C/55 °C)	ΔH° (kJ/mol)	ΔG° (kJ/mol) (25 °C/55 °C)	ΔS° (J/mol K) (25 °C/55 °C)
10 ⁻³ M	6.1/3.3	-16	-16/-16	-1.9/-0.2
10 ⁻⁴ M	23.0/9.5	-24	-19/-19	-16.1/-1.5
10 ⁻⁵ M	25.0/11.0	-23	-19/-19	-13.0/-1.2
10 ⁻⁶ M	25.0/11.0	-23	-19/-19	-13.6/-1.2
10 ⁻⁷ M	25.0/11.0	-23	-19/-19	-13.6/-1.2

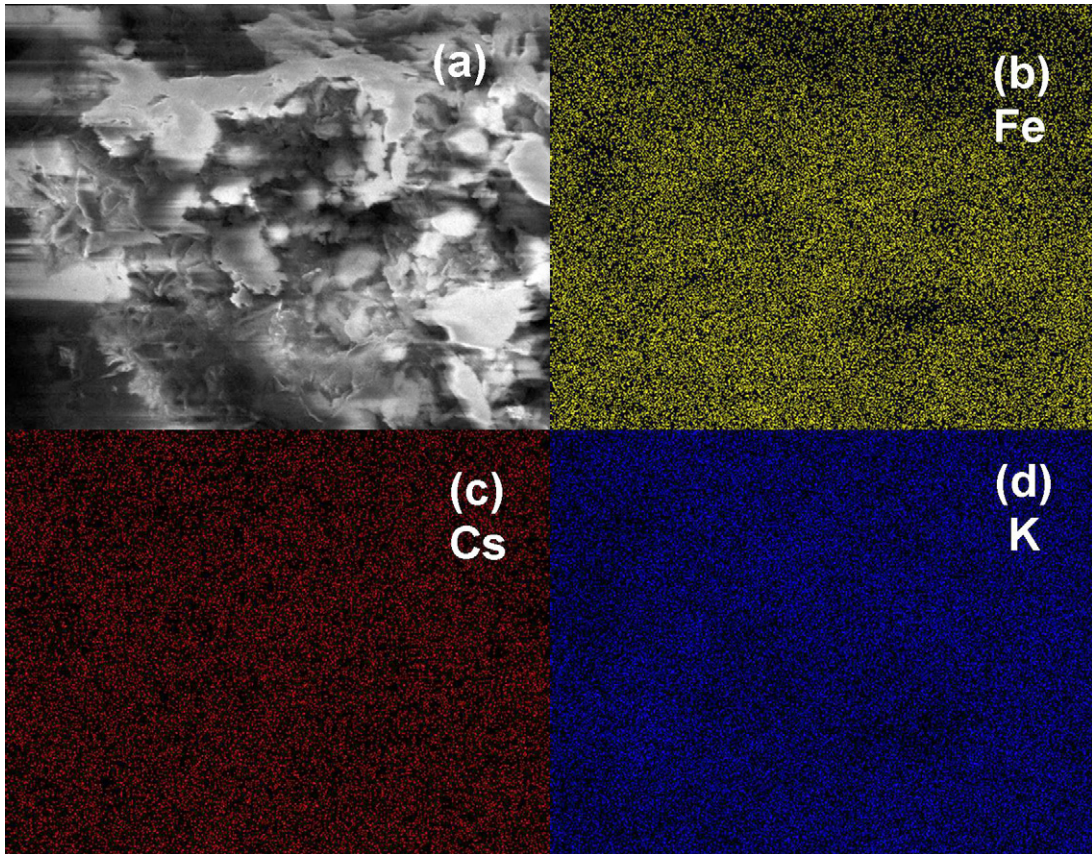


Fig. 3. The EDS mapping of Taiwan locally laterite with appearance (a), Fe signals (b), Cs signals (c), and K signals (d).

dominant sheet mineral is kaolinite. As a result, the distribution of adsorbed Cs on the kaolinite surface was analyzed via SEM/EDS images. Additionally, a mapping technique was also employed to visualize the locations of these adsorbed Cs.

The surface of kaolinite amplified by 5000 times was shown in Fig. 2. In addition to small debris along with the frayed edge on each sheet, there are still many available surfaces lying between the sheets and as a whole, increasing the number of accessible sorption

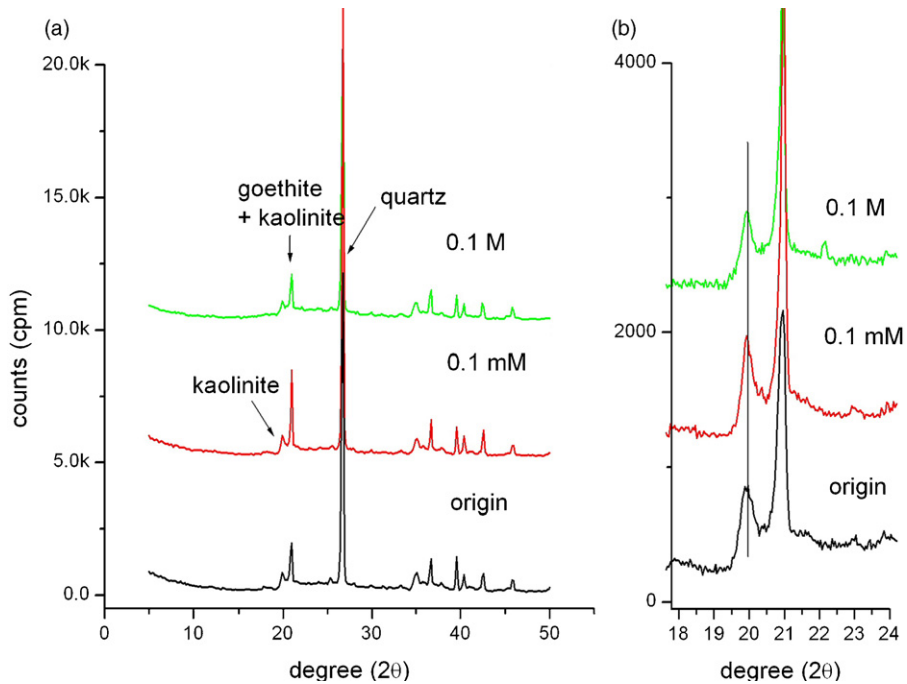


Fig. 4. XRD patterns of fresh and Cs-adsorbed LTW (a). The signals of kaolinite after filtering out the signals of quartz are especially amplified (b).

sites. The SEM image (Fig. 3a) associated with mapping results of Fe (Fig. 3b), Cs (Fig. 3c) and K (Fig. 3d) signals are presented. The adsorbed Cs (Fig. 3c) is evenly distributed over the kaolinite surface. This observation is in good agreement with the negative value for entropy change, which represents the ordered distribution of adsorbed Cs. It is noted that signals of K and Fe are also evenly distributed on kaolinite surface, demonstrating that Cs adsorption has no preferential sorption environments whether K or Fe elements are present or not.

3.4. XRD analysis of the Cs-loading LTL

Fig. 4a presents the XRD patterns of LTL before and after Cs adsorption which have been processed by commercially available program MDI Jade 6.0 to identify the mineral composition of LTL. Additionally, the pattern from high Cs-loading samples (0.1 M) was also presented for comparison. Fig. 4b shows the result for the kaolinite signal (d001) after filtering out the interference of quartz. Notably, although only the changes in kaolinite structure are considered—since it is the only recognizable clay mineral in LTL—the high CEC along with high specific surface area of LTL imply the possibility of the existence of some impurities, such as smectite or illite in LTL samples [18].

Since kaolinite is a relatively non-expanding structure, adsorption of metals on kaolinite is mainly restricted to the structure edges and surfaces [18]. However, the stress induced by adsorbed heavy metals on kaolinite is also reported, which could result in changes in swelling capacity, compaction, and the double-layer behavior of kaolinite [9,18]. In this study, there is no substantial evidence of such changes in kaolinite structure after Cs adsorption (Fig. 4b), although some fluctuations in intensity of kaolinite signal were observed (Fig. 4a) which are believed stemming from grain size orientation of the powder samples [9]. Therefore, no change happens in the interlayer space of the kaolinite structure during Cs uptake according to this XRD pattern. This fact reflects the instinct that tight hydrogen bonding between kaolinite layers restricts diffusion of adsorbed Cs to the interlayer sorption sites. This finding is in good agreement with those in other studies, in which Cs adsorption is reported occurring only at the first ten angstroms on the kaolinite surface [19].

4. Conclusions

In this work, removal of aqueous Cs by adsorption onto local Taiwan laterite (LTL) was investigated, with particular attention paid to aspects of kinetic and isotherm adsorption, and the distribution of adsorbed Cs. Kinetic studies showed that equilibriums are reached within the first hour in given conditions. Fitting isotherm results by using both Freundlich and Langmuir models showed that adsorption is favored at low temperatures. For elevated temperatures, desorption is enhanced and thus the sorption capacity is significantly reduced. Calculated thermodynamic parameters indicate

that the Cs adsorption to LTL is exothermic and spontaneous. Additionally, negative entropy change clearly suggests that adsorbed Cs is evenly distributed on LTL surface, which is in a good agreement with EDS mapping results. The XRD patterns show that no significant effect of Cs uptake on kaolinite structure.

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