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# Nickel Oxide Grafted Andic Soil for Efficient Cesium Removal from Aqueous Solution: Adsorption Behavior and Mechanisms

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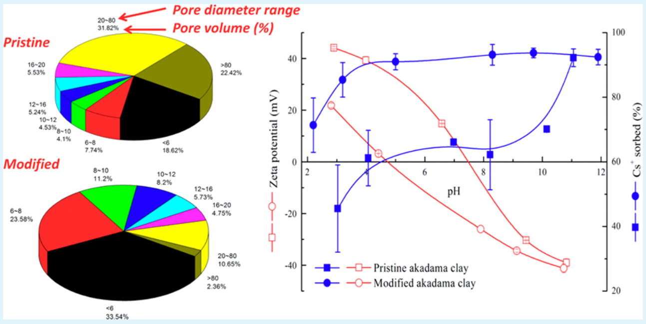
*Supporting Information*

**ABSTRACT:** An andic soil, akadama clay, was modified with nickel oxide and tested for its potential application in the removal of cesium from aqueous solution. Scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS), and powder X-ray diffraction (XRD) results revealed the nickel oxide was successfully grafted into akadama clay. $N_2$ adsorption−desorption isotherms indicated the surface area decreased remarkably after modification while the portion of mesopores increased greatly. Thermogravimetric-differential thermal analysis (TG-DTA) showed the modified akadama clay had better thermostability than the pristine akadama clay. Decreases in cation exchange capacity (CEC) and ζ-potential were also detected after the modification. Adsorption kinetic and isotherm studies indicated the adsorption of $Cs^+$ on the modified akadama clay was a monolayer adsorption process. Adsorption capacity was greatly enhanced for the modified akadama clay probably due to the increase in negative surface charge caused by the modification. The adsorption of $Cs^+$ on the modified akadama clay was dominated by an electrostatic adsorption process. Results of this work are of great significance for the application of akadama clay as a promising adsorbent material for cesium removal from aqueous solutions.



**KEYWORDS:** *andic soil, cesium, adsorption isotherm, electrostatic adsorption, ion exchange*

## 1. INTRODUCTION

With the development of nuclear power, large amount of nuclear wastes are generated not only from routine operation of nuclear power stations but also from big accidents, such as the most recent Fukushima Daiichi accident. The regulated wastes are generally classified into four categories: high-level wastes (HLWs), transuranic wastes (TRUs), uranium mill tailings, and low-level wastes (LLWs).[1] Radionuclide of major concern is cesium-137 ($^{137}Cs$) because of its hazardous to public health and relatively long half-life of 30.2 years.[1] One of the effective strategies to deal with the remediation of a radiocontaminated ecosystem and the management of nuclear wastes is adsorption.[2−4] Three kinds of adsorbents are mainly applied for the removal of radio-cations: natural and modified clay minerals,[2,4−6] synthetic selective adsorbents,[3,7,8] and biosorbents.[9,10] Compared with the other two kinds of adsorbents, natural and modified clay minerals possess advantages, such as large amounts, easy availability, low cost, high stability, etc. Thus, extensive research has been conducted on the removal of radionuclides by using various kinds of clay materials.[4−6,11−16]

According to the energy white paper in Japan, seventeen nuclear power stations were under operation in Japan and produced $48.847 \times 10^6$ kW, 29.2% of the total electric power supply in 2009.[17] In addition, Fukushima nuclear power station was the largest nuclear power station in the world. Despite the serious nuclear accident caused by the earthquake and tsunami in Fukushima, the nuclear electricity net generation decreased to $15.478 \times 10^6$ kW in 2011, which still ranked the top five all over the world and occupied approximately 14.7% of the total electricity net generation in Japan.[18] Therefore, it is urgent to find a proper way to treat the large amount of radioactive wastes in Japan, especially after the big nuclear accident. Natural zeolite is well regarded as an efficient adsorbent for radioactive wastewater treatment and has been put into practice for the environmental remediation after the Fukushima nuclear accident. However, the main disadvantage of its application is the competitive interactions with other monovalent cations, in particular $Na^+$ and $K^+$ in waste effluents that can considerably block $Cs^+$ adsorption.[5,19−21] On the other hand, Japan is an island country with limited natural resources. Therefore, the most valid strategy of coping with the large amount of radioactive wastewater in Japan is to find or develop another abundant and low cost clay as an alternative adsorption material with improved adsorption capacity after some appropriate modification.

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Akadama clay, a weakly acidic andic soil usually used as a good medium in horticulture in Japan, has been investigated for the removal of various pollutants through much effort of our laboratory.[22−24] It has the common advantages of clay materials mentioned above. In addition, because of the specific mineralization process, large amount of metal ions and highly porous structure are present in this kind of clay material.[23] As a result, it probably possesses a high cation exchange capacity (CEC) and is a potentially ideal adsorption material compared with other kinds of clay materials. Noteworthily, it is not expandable clay. On the other hand, nano-sized transition metal oxides have been widely used for their potential ability in removing heavy metals.[25−28] Much attention is now paid to finding or developing porous supports for the fine or ultrafine particles of transition metal oxides.[28] In addition, nickel hexacynofferate has been demonstrated as an efficient and selective adsorbent for $Cs^+$ removal.[9,29,30] In this study, we evaluated the feasibility of akadama clay as a support for nickel oxide in treating radioactive wastewater and developed a novel modification process for akadama clay. As described above, $^{137}Cs$ is a major concerned radionuclide,[1] which was also detected in drinking water after the explosion occurred in Fukushima Daiichi accident.[31] $^{137}Cs$ seems to be the most common radionuclide and is therefore selected as the target radionuclide in this study by using non-radioactive cesium chloride (CsCl) as surrogate. The objective of this study is to investigate the adsorption performances of pristine and modified akadama clays in removing $Cs^+$ through batch adsorption experiments. The possible reason for the different adsorption behaviors is also explored along with some surface characterization techniques. In addition, much effort has been undertaken to determine the adsorption mechanism of $Cs^+$ on the modified akadama clay, which is especially important for its further performance improvement and practical application, through adsorption kinetic, isotherm, and desorption studies.

## 2. MATERIALS AND METHODS

**2.1. Reagents.** The chemicals nickel chloride ($NiCl_2 \cdot 6H_2O$) and sodium hydroxide (NaOH) were of A.R. grade and purchased from Wako Pure Chemical Industries Ltd., Japan. CsCl was purchased from Tokyo Chemical Industry Co. Ltd., Japan. All the other reagents were purchased from Wako Pure Chemical Industries Ltd., Japan, and were used as received without further purification. Deionized water (DW) generated from a Millipore Elix 3 water purification system (Millipore, U.S.A.) equipped with a Progard 2 pretreatment pack was used throughout this study.

**2.2. Modification of Akadama Clay.** Akadama clay used in this study was provided by Makino Store, Kiyosu, Japan. The clay material was ground and sieved through no. 150 mesh, and those particles with diameter less than 105 μm were dried at 105°C and used for further modification. Briefly, the modification process of akadama clay included overall three steps. Firstly, 10 g of dried akadama clay was added to 100 mL of 0.5 M $NiCl_2$ solution and mixed thoroughly for about 10 min. Secondly, 100 mL of 1 M NaOH solution was added into the mixture slowly. The resultant mixture was left to react for 1 h under vigorous stirring at 70 °C in a thermostated shaking machine (IKA RET basic, Germany). The resulted akadama clay was repeatedly washed (to nearly neutral), centrifuged and finally dried at 105 °C. Finally, the dried clay was ground into powder form and heated in air at 600 °C for 1 h in a muffle furnace (TGK F-1404, Japan).

**2.3. Batch Adsorption and Desorption Studies.** Batch experiments were conducted in this study to evaluate the $Cs^+$ adsorption behavior on the pristine and modified akadama clays. A stock $Cs^+$ solution (~1000 mg $L^{-1}$) was prepared by dissolving 1.26 g of CsCl accurately into 1 L DW. $Cs^+$ solutions of desired concentrations including standard solutions were prepared by diluting known volumes of the stock $Cs^+$ solution in DW. To investigate the adsorption performance and mechanisms, adsorption kinetic (along with competitive ions effect), isotherm (including adsorption capacity evaluation), and desorption studies were carried out as follows.

For kinetic analysis, 1 g of modified clay was mixed with 200 mL of 10 mg $L^{-1}$ $Cs^+$ solution (dosage of 5 g $L^{-1}$) under vigorous shaking (200 rpm). Water samples including initial solution (as zero point) were collected at determined time intervals (5, 10, 20, 30, 60, 90, and 120 min). Nonlinearized pseudo-first-[4] and pseudo-second-order[32] kinetic models corresponded to eqs 1 and 2, respectively, were adopted to investigate the kinetic behavior of $Cs^+$ on the modified akadama clay.

$$q_t = q_e(1 - e^{-k_1 t}) \tag{1}$$

$$q_t = \frac{k_2 {q_e}^2 t}{1 + k_2 q_e t} \tag{2}$$

where the rate constant $k_1$ ($h^{-1}$) and the equilibrium capacity, $q_e$ (mg $g^{-1}$) were determined as free parameters by nonlinear fitting using Origin 7.5 software. $k_2$ (g $mg^{-1}$ $h^{-1}$) is the rate constant of second-order adsorption. Effect of competitive ions was also investigated by using $Na^+$ and $K^+$ at different concentrations (10 100 and 1000 mg $L^{-1}$), while keeping $Cs^+$ at a constant concentration (1 mg $L^{-1}$). Dosage of 2.5 g $L^{-1}$ was selected in this experiment.

For adsorption isotherm determination, 0.05 g of the modified akadama clay was mixed with 20 mL of $Cs^+$ solution (dosage of 2.5 g $L^{-1}$) in a 50 mL-polyethylene centrifuge tube (Violamo, Japan) and placed in a double shaker (Taitec NR-30, Japan) at 200 rpm for 1 d, which is much longer than the equilibrium time (Supporting Information Figure S5). Adsorption isotherms play an important role in determining the adsorption mechanisms because of their abilities in providing much information about adsorption process. In this study, six different adsorption isotherms were adopted, including Langmuir, Freundlich, Dubinin−Radushkevich (D−R), Temkin, Redlich−Peterson, and Langmuir−Freundlich isotherms. For lots of explanations on the normal isotherms could be found in previous studies,[4,9,33] much details were not given in this study except for the equations (given in Table 4). Specifically, it is worth noting that the first four isotherms have two parameters and are more widely used than the latter two ones, which have three parameters.[33]

In addition, desorption study usually could give meaningful results for understanding the adsorption mechanisms during an adsorption study. In the present work, three kinds of desorption solutions, 0.1 M HCl (acidic solution), 0.1 M NaOH (alkaline solution), and 0.1 M KCl (strong ion exchange solution) were prepared to determine the adsorption mechanism and evaluate the stability of $Cs^+$ adsorbed on the modified akadama clay with DW as reference. 0.2 g of the modified akadama clay was firstly contacted with 40 mL of 10 mg $L^{-1}$ $Cs^+$ solution for 1 d under vigorous shaking and then separated by centrifugation. The resultant $Cs^+$ loaded clay sample was later resuspended into 50 ml of the prescribed desorption solution with no shaking for 1 d.

All the water samples were collected by filtering supernatants through 0.22 μm mixed cellulose ester membrane (Millipore, Ireland), diluted with DW to a proper extent (less than 1 mg $L^{-1}$) into 15 mL-polypropylene centrifuge tubes (Violamo, Japan), respectively, and finally stored at 4°C in a refrigerator prior to concentration measurement. All the experiments were conducted at room temperature (25 ± 2°C) and without pH adjustment except for the investigation on the effect of pH variation on adsorption performance, which was adjusted with 0.1 M HCl and NaOH solutions.

**2.4. Analysis and Characterization.** *2.4.1. Elemental Analysis.* Point (or surface) elemental analysis was performed with an energy dispersive X-ray spectroscopy (EDS) equipped with a JSM 7000F field emission scanning electron microscope (FE-SEM) operated at an acceleration voltage of 20.0 kV. In addition, elemental mapping technology was applied to determine the distribution of elements on the surface of samples.

Table 1. Elemental Analysis of Pristine and Modified Akadama Clays by EDS[a]

| element (at %[b]) | O | Si | Al | Fe | Mg | K | Ca | Na | Ni |
|---|---|---|---|---|---|---|---|---|---|
| pristine akadama clay | 56.8 ± 10.1 | 24.5 ± 2.4 | 13.9 ± 5.4 | 2.4 ± 1.4 | 0.69 ± 0.05 | 0.44 ± 0.04 | 0.17 ± 0.14 | 0.14 ± 0.03 | [c] |
| modified akadama clay | 55.6 ± 4.6 | 5.3 ± 3.2 | 8.1 ± 5.7 | 1.4 ± 0.6 | 0.44 ± 0.07 | 0.11 ± 0.16 | 0.07 ± 0.08 | 3.2 ± 2.7 | 23.9 ± 9.1 |

[a] Data were collected from two sampling sites and given as mean ± standard deviation. [b] Atom percentage. [c] Not detected.

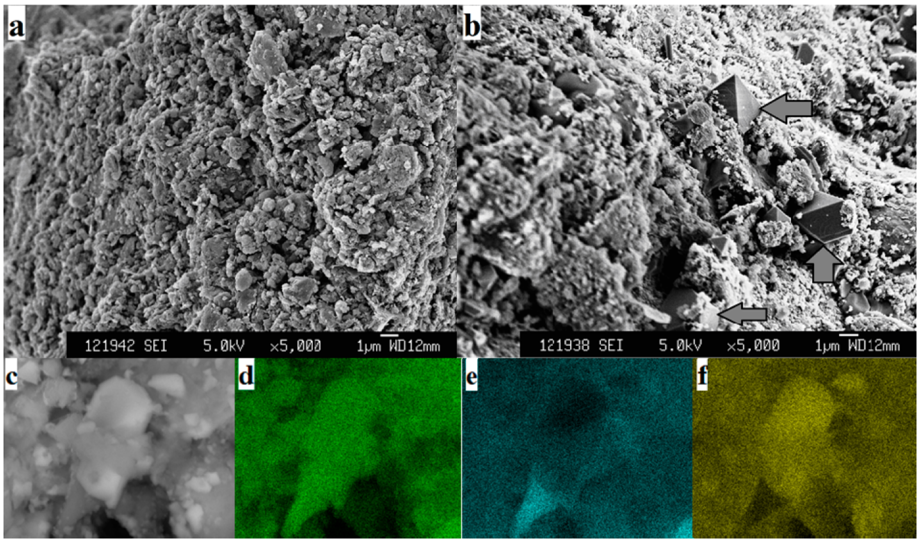

**Figure 1.** SEM images of pristine (a) and modified (b) akadama clays at the acceleration voltage of 5.0 kV and magnification of 5000×, elemental mapping images of modified akadama clay (c, raw, d, O signal, e, Si signal; f, Ni signal) at the acceleration voltage of 20.0 kV and magnification of 10000×.

*2.4.2. Scanning Electron Microscope (SEM).* The surface morphology of the pristine and modified akadama clays was observed by a JSM 6330F SEM. The samples were put onto a conductive carbon tape adhered to the metal stub and coated with a thin layer of platinum for charge dissipation during SEM imaging. Acceleration voltage of 5.0 kV and magnification of 5000× were applied.

*2.4.3. Powder X-ray Diffraction (XRD).* The XRD patterns were recorded on a computer controlled Rigaku X-ray diffractometer with CuK$\alpha$ radiation source ($\lambda$ = 1.540562 Å) at operation conditions of 40 kV and 150 mA. A step of 0.02° and a scan speed of 10° $\text{min}^{-1}$ were selected. The databases in the joint committee on powder diffraction standards (JCPDS) were used to verify the crystal structure.

*2.4.4. Surface Area and Pore Size Distribution.* The specific surface area and pore size distributions were measured by $N_2$ adsorption-desorption isotherms at −196°C (77 K) after out-gassing the powder clay samples for 90 min at 120°C with a Coulter SA3100 specific surface area analysis device. The Brunauer−Emmett−Teller (BET) equation was used for the determination of the specific surface area ($S_{\text{BET}}$), while the Kelvin equation was used to determine the Barrett−Joyner−Halenda (BJH) pore size distribution and pore volume. The total pore volume ($V_t$) was calculated from the volume adsorbed at $P_s/P_o$ = 0.98 in the desorption branch of the isotherm and the micropore volume ($V_{\text{mic}}$) was calculated by means of the *t*-plot method.

*2.4.5. Thermogravimetric-Differential Thermal Analysis (TG-DTA).* Simultaneous thermogravimetric and differential thermal analysis of the pristine and modified akadama clays was carried out using an Exstar TG/DTA 7300 thermal analyzer (Japan). About 7 mg of each sample was placed into a platinum pan and heated up to 1000°C in air (carrier gas, 200 mL $\text{min}^{-1}$) atmosphere at a rate of 20 °C $\text{min}^{-1}$ for thermal analysis.

*2.4.6. Cation Exchange Capacity (CEC) Determination.* The CEC of the pristine and modified akadama clays was determined according to the sodium acetate method (EPA method 9081, U.S.A.).

*2.4.7. Surface Charge (SC) Determination.* The SC of the pristine and modified akadama clays was determined according to the colloid titration technique described by Kawamura and Tanaka.[34] Polybren and potassium polyvinyl sulfate (PVSK) were used as the standard cationic and anionic colloids.[35] A known weight (0.05 g) of the sample was suspended in DW (20 mL) and mixed with excess 0.001 N polybren then titrated against 0.001 N PVSK until electrical neutrality was reached. Equal volumes of polybren in distilled water were used as blanks. The colloid charge expressed as milliequivalents per gram of positive or negative colloid charge can then be determined from the expression given below:

$$\text{SC (mequiv/g)} = \frac{(A - B) \times N}{M} \tag{3}$$

where *A* (mL) and *B* (mL) represents the volumes of PVSK added to the sample and blank respectively, *N* represents the normality of PVSK (0.001 N), and *M* (g) represents the mass of sample used.

*2.4.8. ζ-Potential Determination.* Samples for ζ-potential determination were prepared by suspending 0.01 g of clay in 40 mL of DW containing 1.0 mM $NaNO_3$. The suspensions were shaken at a speed of 200 rpm for 2 h to be dispersed completely. Suspension pH was adjusted to 2.0−12.0 using 0.1 M $HNO_3$ or NaOH solutions. After equilibrating for 24 h, the ζ potential was measured using a Malvern zetasizer (Malvern, England).

*2.4.9. Inductively Coupled Plasma Mass Spectrometer (ICP-MS).* The concentration of metal ions was analyzed by using a fully quantitative analytical method on an ICP-MS (Perkin Elmer Elan DRC-e, U.S.A.) in standard mode throughout this study. ICP-MS tuning solution (1 ppb) was used as the calibration solution to monitor the quality of the ICP. Each sample was set to be analyzed 5 times with average being used.

## 3. RESULTS AND DISCUSSION

**3.1. Characterization of Pristine and Modified Akadama Clays.** Energy dispersive X-ray spectroscopy (EDS) patterns of the pristine and modified akadama clay were given in the Supporting Information (Figure S1). It is clearly indicated from Table 1 that Ni was successfully

Table 2. Material Properties of the Pristine and Modified Akadama Clays

| samples | $S_{BET}$ ($m^2$/g) | $V_t$ (mL/g) | $V_{mic}$ (%) | $V_{mes}$ (%) | $V_{mac}$ (%) | CEC (mequiv/g) | $pH_{pzc}$ | SC (mequiv/g) |
|---|---|---|---|---|---|---|---|---|
| pristine akadama clay | 174.3 | 0.1920 | 4.08 | 58.7 | 37.2 | 6.97 ± 0.35 | 6.9[a] | −0.018 ± 0.001[c] |
| modified akadama clay | 64.3 | 0.1298 | 0 | 96.9 | 3.1 | 3.35 ± 0.11 | ∼5[b] | −0.086 ± 0.002[c] |

[a] Data is provided by manufacturer. [b] Estimated from Figure 5. [c] The negative value of SC denotes that the surface of clay particles is negatively charged and the absolute value represents the amount of negative charge.

introduced into the akadama clay through modification. As a predictable result, most of the other elements were reduced, especially for Si and Al, which were the main elements in the pristine clay. Meanwhile, it is worth noting that the point elemental analysis by EDS mainly reflect the composition of elements on the surface of clay samples. Generally speaking, the modification process may change the surface characteristics of the clay as anticipated.

A significant difference could be found between the surface morphologies of the pristine and modified akadama clays (Figure 1). Many clear crystals appeared and were grafted into the surface of the akadama clay after modification. Some formed crystals embed in the clay with only part of themselves remaining on the surface, as the arrows indicated in Figure 1b. On the basis of the results of elemental analysis by EDS, these crystals are possibly composed of Ni. To confirm this hypothesis, elemental mapping results were performed in this figure (Figures 1c, d, e, and f). The elemental mapping results were obtained by 10000× magnification of a surface site containing the crystal (Figure 1c). The results showed that O and Ni were clearly contained in the crystal, indicating that the crystal is possibly an oxide of Ni. To further determine the oxide of Ni, an XRD analysis was performed as follows.

The XRD results show that the pristine akadama clay is mainly composed of quartz (JCPDS 65-0466), while the peak of quartz is suppressed remarkably after modification (Supporting Information Figure S2). Nickel oxide (JCPDS 44-1159) was detected in the modified akadama clay through XRD pattern analysis (Supporting Information Figure S2b), indicating the crystals in Figure 1b should be NiO. The XRD results confirm the successful “grafting” modification of nickel oxide into the akadama clay.

The modified akadama clay had better thermostability than the pristine akadama clay, as the TG curves showed (Supporting Information Figure S3). The pristine akadama clay exhibited a rapid TG loss (about 20%) under 500°C, which could be attributable to the evaporation of adsorbed water. However, a relatively less TG loss (about 10%) was observed in the modified akadama clay at the temperature of about 900°C.

As we know that only part of the $S_{BET}$ is accessible for the solute molecules. Moreover, adsorbents with higher mesoporosity area are desirable.[36] It is obvious from Table 2 that the $S_{BET}$ and $V_t$ of akadama clay decreased after modification, especially for the former. The proportion of mesopores (pore diameter of 2−50 nm[37]), however, increased a lot. This observation could be attributed to the occupation of macropores by NiO during the modification process. From the results it can be concluded that the irregular porous akadama clay was transformed into a typical mesoporous material after modification, favoring the mass transfer during adsorption process. Figure 2 shows the comparison of pore size distribution between the pristine and modified akadama clays in detail. Most of the pores in the pristine akadama clay had pores with diameter between 20 and 80 nm, in contrast with less than 6 nm in the modified akadama clay.

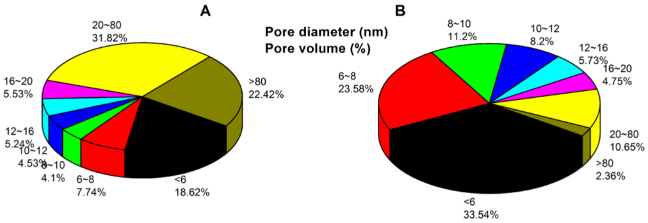

**Figure 2.** Comparison of pore size distribution in the pristine (A) and modified (B) akadama clays.

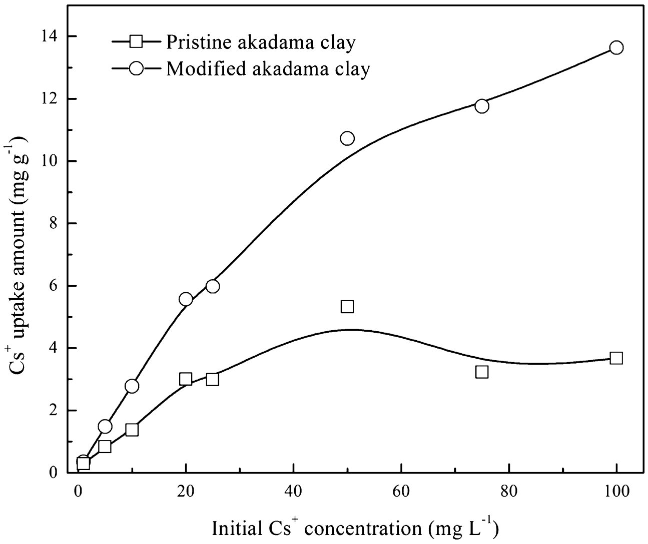

**Figure 3.** Comparison of cesium uptake amount on the pristine (square) and modified (circle) akadama clays at the dosage of 2.5 g $L^{-1}$.

**3.2. Adsorption Performance and Kinetics.** As shown in Figure 3, the $Cs^+$ adsorption performance was enhanced significantly after modification. With the increase in initial $Cs^+$ concentration, the gap in $Cs^+$ uptake amount between the two clays increased. As reported,[38] different adsorption behaviors is probably caused by the different surface properties of adsorption materials. Seen from the SEM images (Figure 1), distinctive difference did exist between the surfaces of the prinstine and modifiec akadama clays. Taking the results of XRD into consideration, it is verified that the crystal of nickel oxide has been successfully introduced into the akadama clay through modification. However, as listed in Table 2, after modification the $S_{BET}$ and $V_t$ decrease obviously, indicating these two parameters have less impact on the adsorption performance of akadama clay. On the other hand, the macropores in the pristine akadama clay were transformed into mesopores during the modification, resulting in a relatively homogeneous mesoporous material for the modified clay (portion of $V_{mes}$ = 96.9%, Table 2), which adds the accessibility of molecular species to adsorption sites.[39] In addition, a clear increase in negative surface charge was also observed for the modified akadama clay (Table 2). Therefore, it can be deduced that the modification by nickel oxide could transform the pristine akadama clay into a homogeneous mesoporous material with increased negative surface charge and as a result, enhance the $Cs^+$ adsorption behavior.

The possible negative effects brought by competitive ions were also investigated and the results are given in Supporting Information Figure S4. Distribution coefficient ($K_d$) is applied in this experiment because it is an important value for evaluating the selectivity adsorption of a material. The equation for the $K_d$ value calculation was reported in many literatures[4,5,9,10,29] and provided in the Supporting Information. The results indicate that the modified clay material exhibits better performance than the pristine one under high ionic strength conditions. $K^+$ exerts a stronger negative effect than $Na^+$ during the $Cs^+$ adsorption process probably due to its much more similar radius (1.33 Å) and hydration energy with $Cs^+$ (1.69 Å) , which was also observed by other researchers.[4,5,10]

It is shown in Supporting Information Figure S5 that the $Cs^+$ adsorption on modified akadama clay is a rapid process and accomplished in less than 10 min. In addition, the rate constants of the pseudo first and second order kinetic models are 49.9 ± 2.2 $h^{-1}$ and 406.8 ± 85.5 g $mg^{-1}$ $h^{-1}$, respectively, indicating the adsorption process progresses very fast. Both kinetic models gave similar equilibrium adsorption capacity from the experimental data. Overall, the two kinetic models well fitted the experimental data with correlation coefficients ($R^2$) of nearly 1 and the chi-square/degrees of freedom ($\chi^2$/DoF) of nearly 0 (Table 3). Therefore, it is deduced that both physical and chemical adsorption processes occur during $Cs^+$ adsorption on the modified akadama clay. Because of their similar fitting results, it is hard to determine which one dominates the adsorption process only through the above kinetic analysis.

**Table 3. Adsorption Kinetic Parameters of Pseudo-First- and Second-Order Models for the Modified Akadama Clay**

| parameter | pseudo-first-order kinetic model | pseudo-second-order kinetic model |
|---|---|---|
| $q_{eexp}{}^{a}$ (mg $g^{-1}$) | 1.76 ± 0.01 | 1.76 ± 0.01 |
| $q_{ecal}{}^{b}$ (mg $g^{-1}$) | 1.76 ± 0.00 | 1.76 ± 0.00 |
| $k_1$ ($h^{-1}$) | 49.9 ± 2.2 | |
| $k_2$ (g $mg^{-1}$ $h^{-1}$) | | 406.8 ± 85.5 |
| $R^2$ | 1 | 1 |
| $\chi^2$/DoF[c] | $2 \times 10^{-5}$ | $3 \times 10^{-5}$ |

[a] Equilibrium adsorption capacity estimated from the experimental data. [b] Equilibrium adsorption capacity calculated from the kinetic model. [c] $\chi^2$ value/degrees of freedom.

### 3.3. Adsorption Isotherm.

All the nonlinear fittings and the statistical analysis were performed with Origin 7.5 software. The estimated model parameters with $R^2$ and $\chi^2$/DoF calculated for the different isotherms by the software are given in Table 4. On the basis of the physical meanings of these two parameters, a higher $R^2$ and lower $\chi^2$/DoF values usually mean a better isotherm fit. It is shown that the experimental data of $Cs^+$ adsorption on the modified akadama clay could be well fitted by these isotherms except Temkin isotherm with the lowest $R^2$ and highest $\chi^2$/DoF values. According to the assumption of Temkin isotherm, it can be deduced that the heat of adsorption of all the molecules in the layer does not decrease linearly with coverage. As shown in Supporting Information Figure S6, the isotherm curves of Langmuir, Redlich−Peterson, and Langmuir−Freundlich almost coincide with each other. It is interesting to point out that the three-parameter isotherms provide better fitting in terms of $R^2$ and $\chi^2$/DoF values than most of the two-parameter isotherms (except Langmuir isotherm), which agrees well with the finding of Zeng et al.[33] Among the isotherms applied, Langmuir isotherm gave the highest $R^2$ and lowest $\chi^2$/DoF values, signaling the adsorption of $Cs^+$ on the modified akadama clay is probably a monolayer adsorption process.

Although the fits of adsorption data to these adsorption isotherms are more mathematically meaningful and don't reflect the actual adsorption process, some of the isotherm parameters are helpful to interpret the adsorption mechanisms. The essential characteristic of the Langmuir isotherm may be expressed in terms of a dimensionless equilibrium parameter $R_L$, which is defined as[40]

$$R_L = \frac{1}{1 + K_L C_0} \tag{4}$$

where $K_L$ is the Langmuir constant and $C_0$ is the initial solute concentration (initial $Cs^+$ concentration in this study). For the value of $K_L$ in this study is 0.07, which is a positive value, the calculated $R_L$ certainly lies between 0 and 1. Similarly, when using the constant of Langmuir−Freundlich isotherm, the expression for $R_{L-F}$ can be modified as[33]

$$R_{L-F} = \frac{1}{1 + b{C_0}^{1/n}} \tag{5}$$

where $b$ and $n$ are the Langmuir−Freundlich constants and $C_0$ is the initial solute concentration. Given the fact that $b$ is a positive value (0.08), the $R_{L-F}$ should range between 0 and 1. In any case, the values of $R_L$ and $R_{L\text{-}F}$ in this study fall between 0 and 1, indicating a favorable adsorption of $Cs^+$ on the modified akadama clay. Another important parameter, $Q_L$ or $q_m$ in Langmuir or Langmuir−Freundlich isotherm, representing the maximum adsorption capacity of $Cs^+$ on the modified akadama clay, were 16.1 ± 0.9 and 16.6 ± 2.5 mg $g^{-1}$, respectively. It is worth noting that the maximum adsorption capacity of clay material prepared in this study is comparatively lower than some well-known clay materials such as zeolite[5] and montmorillonite,[4] whose adsorption capacities are approximately 100 mg $g^{-1}$. However, it is relatively higher than those of natural soils and rocks such as ceiling tiles (0.21 mg $g^{-1}$),[13] bure mudrock (13.3 mg $g^{-1}$),[11] and ain oussera soil (4.31 mg $g^{-1}$).[6] In addition, the clay material used in this study has not been well explored for other applications except horticulture and it is widely distributed in Japan. Compared with zeolite and montmorillonite, it has much more meaning to expand the application of this clay material. Therefore, this study will contribute to its application in environmental remediation. On the other hand, this alternative clay material would also save zeolite and montmorillonite, which have much more other applications such as catalysis and medicine industries.

### 3.4. Desorption Study.

It is well believed that the surface of clay material is positively charged at acidic conditions (pH < $pH_{pzc}$). As shown in Figure 4, a large portion (approximately 70%) of adsorbed $Cs^+$ was desorbed into 0.1 M HCl (acidic solution), indicating a reversible adsorption of $Cs^+$ on the modified akadama clay. This phenomenon is probably brought

**Table 4. Estimated Isotherm Parameters for Cesium Adsorption on Modified Akadama Clay (Dosage = 2.5 g $L^{-1}$)**

| | parameters related | | | fitting of data | |
|---|---|---|---|---|---|
| isotherms | symbol | unit | estimated value | $R^2$ | $\chi^2$/DoF |
| Langmuir $q = Q_L K_L C_e/(1 + K_L C_e)$ | $Q_L$ | mg $g^{-1}$ | 16.1 ± 0.9 | 0.988 | 0.336 |
| | $K_L$ | L $mg^{-1}$ | 0.07 ± 0.01 | | |
| Freundlich $q = K_f {C_e}^{1/n}$ | $K_f$ | mg $g^{-1}$ $L^{1/n}$ $mg^{-1/n}$ | 2.19 ± 0.4 | 0.965 | 1.00 |
| | $n$ | | 0.45 ± 0.05 | | |
| Dubinin−Radushkevich isotherm $q = Q_m \exp[-\beta(RT \ln(1 + 1/C_e))^2]$, $E = 1/(2\beta)^{1/2}$ | $Q_m$ | mg $g^{-1}$ | 12.04 ± 1.04 | 0.901 | 2.88 |
| | $\beta$ | $mol^2/J^2 \times 10^{-6}$ | 6.68 ± 2.3 | | |
| | $E$ | kJ $mol^{-1}$ | 0.27 | | |
| Temkin isotherm $q = a + b \ln C_e$ | $a$ | | 2.55 ± 0.96 | 0.862 | 4.02 |
| | $b$ | | 2.21 ± 0.36 | | |
| Redlich−Peterson isotherm $q = aC_e/(1 + b{C_e}^n)$ | $a$ | | 1.22 ± 0.34 | 0.988 | 0.400 |
| | $b$ | | 0.09 ± 0.08 | | |
| | $n$ | | 0.97 ± 0.17 | | |
| Langmuir−Freundlich isotherm $q = q_m b{C_e}^{1/n}/(1 + b{C_e}^{1/n})$ | $q_m$ | mg $g^{-1}$ | 16.6 ± 2.5 | 0.988 | 0.399 |
| | $b$ | L $mg^{-1}$ | 0.08 ± 0.02 | | |
| | $n$ | | 1.04 ± 0.21 | | |

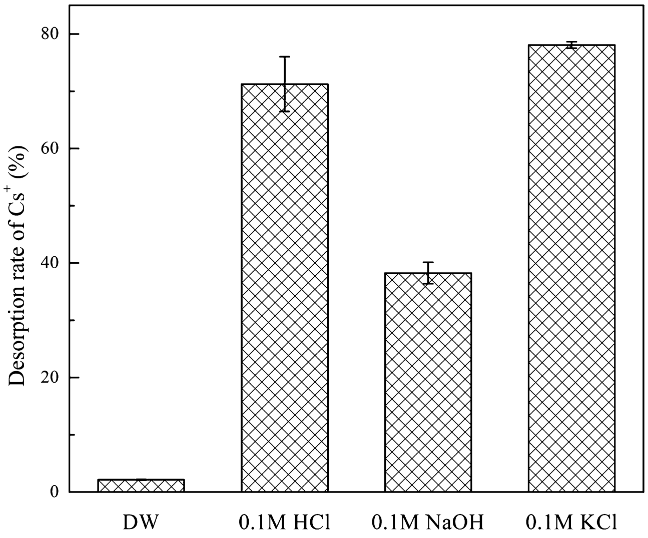

**Figure 4.** Desorption rate of cesium-loaded modified akadama clay at different desorption solutions. (clay/solution = 4 g $L^{-1}$, desorption time = 1 day, no stirring).

about by the electric repulsion between the positively charged surface and adsorbed $Cs^+$ on the surface of the modified akadama clay. In addition, this phenomenon seems lead to a conclusion that electrostatic adsorption might be the dominant process during the $Cs^+$ adsorption on the modified akadama clay, which is in agreement with the relationship between the increase in negative charge (Table 2) on the surface of modified akadama clay and the adsorption performance. On the other hand, approximately 40% of adsorbed $Cs^+$ was desorbed into 0.1 M NaOH (alkaline solution), implying that other mechanism might concur with the electrostatic adsorption during the adsorption process of $Cs^+$ on the modified akadama clay. In addition, a similar desorption result was obtained between 0.1 M HCl and 0.1 M KCl (Figure 4), a strong ion exchange solution, signaling the existence of exchange between $Cs^+$ and $K^+$ ions during the $Cs^+$ adsorption on the modified akadama clay. Finally, as shown in Figure 4, little $Cs^+$ was desorbed from the modified akadama clay into DW, indicating the stability of the adsorbed $Cs^+$. Above all, the desorption results reveal that the adsorption of $Cs^+$ onto the modified akadama clay is contributed by electrostatic adsorption and ion exchange processes. Further investigation is necessary to distinguish which one dominates the whole process.

**3.5. Adsorption Mechanisms Speculation.** As a clay material with complex composition, it's possible for several adsorption mechanisms to occur simultaneously during $Cs^+$ adsorption on the modified akadama clay. As deduced from the kinetic analysis, there might be both physical and chemical processes in the $Cs^+$ adsorption onto the modified akadama clay. Adsorption isotherm studies gave the conclusion that this process was probably a monolayer adsorption process and the isotherm parameters indicated a favorable adsorption of $Cs^+$ on the modified akadama clay. Furthermore, the followed-up desorption study probed into the adsorption mechanisms further, which might include electrostatic adsorption and ion exchange processes.

$\zeta$-Potential, an important indicator for the stability of colloidal dispersions, can be used to indicate the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particles. On the other hand, surface charge is an indicator of electric charge present at the surface of the clay particles during the adsorption. As well known, both of them have close relationship with the electrical characteristics of the surface of clay materials, that is, with the electrostatic adsorption. As shown in Figure 5, the zeta potential of akadama clay colloid decreased after the modification, probably contributed by the grafting of positive $Ni^{2+}$ and loss of some alkali-earth metals. In addition, the change of clay surface properties could reduce the $\zeta$-potential of the modified clay. Besides, the differences of $\zeta$-potential between the pristine and modified akadama clays decreased with the increase of pH. A similar phenomenon is observed for the $Cs^+$ removal efficiency, indicating a close relationship existed between zeta potential and $Cs^+$ removal efficiency during the adsoprtion. When pH value is approaching 11.0, no obvious difference in zeta potential and $Cs^+$ removal efficiency is observed between the two clays, indicating the consistence between the variation of zeta potential and $Cs^+$ adsorption performance, which is opposite. Furthermore, the adsorption performance is found to be favored at alkaline and suppressed at acidic conditions (Figure 5). This phenomenon could be related with the change in surface charge under these two conditions. It is well believed that low pH value ($pH < pH_{pzc}$)

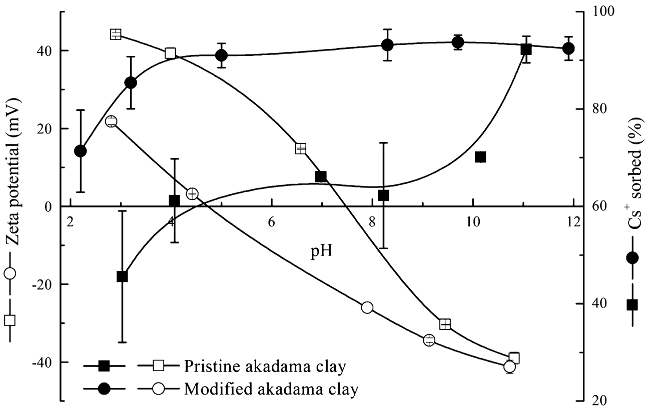

**Figure 5.** $\zeta$-Potential of pristine (square) and modified (circle) akadama clays in 1 mM $NaNO_3$ and variation of cesium (1 mg $L^{-1}$) sorbed with pH value (clay dosage = 5 g $L^{-1}$).

could result in positive surface charge, which is not favorable for the adsorption of positive $Cs^+$ based on the electrostatic adsorption theory; whereas high pH value ($pH > pH_{pzc}$) is benefitial for the adsorption of $Cs^+$. As shown in Figure 5, there is an obvious decrease in adsorption performance when at $pH < 5$, which is well agreed with the $pH_{pzc}$ value of the modified akadama clay (Table 2). As listed in Table 2, the surface charge of the pristine and modified akadama clay is negative at neutral conditions. In addition, an obvious increase in negative surface charge was found on the surface of the modified akadama clay under neutral condition, well agreed with the decrease of its $pH_{pzc}$. On the basis of the electrostatic adsorption theory in addition to the results of this study, the enhanced adsorption performance of the modified clay is most probably attributed to the increased negative charge on the surface of the modified akadama clay (Figure 3).Restated, according to the desorption study and surface charge analysis, the most probable mechanism should be electrostatic adsorption during $Cs^+$ adsorption onto the modified akadama clay, and the enhanced $Cs^+$ adsorption performance is probably resulted from the increase in negative charge on the surface of the modified akadama clay.

As deduced from the desorption study, ion exchange might occur during $Cs^+$ adsorption on the modified akadama clay. Ion exchange process is a common mechanism in metal ion adsorption onto clay materials.[5,20,41] It is hypothesized that if adsorption is mainly caused by ion exchange reaction, then the quantity of the released cations (in gram-equivalent) would be close to that of the adsorbed target ions. Interestingly, the quantity (in gram-equivalent) of adsorbed $Cs^+$ was much less than that of released cations (Table 5). However, the increase in initial $Cs^+$ concentration enhanced the release of cations, indicating that there was but not just ion exchange mechanism during $Cs^+$ adsorption on the modified akadama clay. It is also observed that large amount of $Na^+$ was released into DW (no $Cs^+$ condition) (Table 5), probably due to the dissolution of soluble sodium compounds from the clay. A similar phenomenon was also reported by Miah et al.,[13] who used ceiling tiles as adsorbent for cesium removal. The authors found that cations released into solutions were much more than the adsorbed cesium ions. As an important indicator for the ion exchange process, CEC values of the pristine and modified akadama clays were determined and listed in Table 2. The results showed that the CEC value of akadama clay decreased after modification, implying that ion exchange is not dominant process during $Cs^+$ adsorption on the modified akadama clay. The increase in negative charge and decrease in CEC seems to be conflicted, because increased negative charge would generally promote the cation exchange process. In this study, however, the metal ions present in the modified akadama clay and $S_{BET}$ are greatly decreased after modification (Tables 1 and 2), possibly attributable to the reduction in CEC and the increase in negative charge. Therefore, electrostatic adsorption other than ion exchange is the dominant process during the adsorption of $Cs^+$ onto the modified akadama clay.

**Table 5. Comparison between Amounts of Adsorbed Cesium and Released Ions during Adsorption onto the Modified Akadama Clay (Dosage = 5 g $L^{-1}$)**

| | adsorbed (×$10^{-3}$ mequiv) | released (×$10^{-3}$ mequiv) | | | | |
|---|---|---|---|---|---|---|
| solution | $Cs^+$ | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $Ni^{2+}$ |
| 10 mg $L^{-1}$ $Cs^+$ solution | 1.4 | 26.6 | 0.47 | 0.32 | 0.84 | 0.02 |
| 100 mg $L^{-1}$ $Cs^+$ solution | 11.4 | 39.3 | 2.8 | 9.6 | 12.2 | 0.08 |
| DW | | 34.7 | 0.55 | 0.3 | 0.36 | 0.02 |

## 4. CONCLUSIONS

The results of this study indicate that akadama clay could be transformed into an efficient adsorbent for cesium removal from aqueous solution through nickel oxide grafting. BET surface, total pore volume, cation exchange capacity and $\zeta$-potential are decreased after modification while the quantity of Ni and proportion of mesopore increased. The maximum adsorption capacity of the modified akadama clay for $Cs^+$ is greater than 16 mg $g^{-1}$, much higher than the pristine akadama clay probably due to the increase in negative surface charge. $K^+$ has a much stronger negative effect than $Na^+$ on $Cs^+$ adsorption. High pH value is preferred for $Cs^+$ adsorption on the modified akadama clay because of increased negative surface charge. Adsorption isotherms indicate the $Cs^+$ adsorption onto the modified akadama clay is a monolayer adsorption process. Electrostatic adsorption might be the dominant process for the $Cs^+$ adsorption onto the modified akadama clay.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Equation of distribution coefficient ($K_d$), EDS patterns of pristine and modified akadama clays, powder X-ray diffraction patterns of pristine and modified akadama clays, TG curves of pristine and modified akadama clays obtained at the heating rate of 20 °C $min^{-1}$ in air (carrier gas, 200 ml $min^{-1}$) atmosphere, Effect of competitive ions on cesium adsorption on pristine and modified akadama clays, application of non-linearized pseudo-first- and second-order kinetic model to cesium adsorption by modified akadama clay, and application of adsorption isotherms to cesium adsorption on modified akadama clay. This information is available free of charge via the Internet at http://pubs.acs.org/.

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**Notes**

The authors declare no competing financial interest.

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