



Efficiency of transition metal modified akadama clay on cesium removal from aqueous solutions



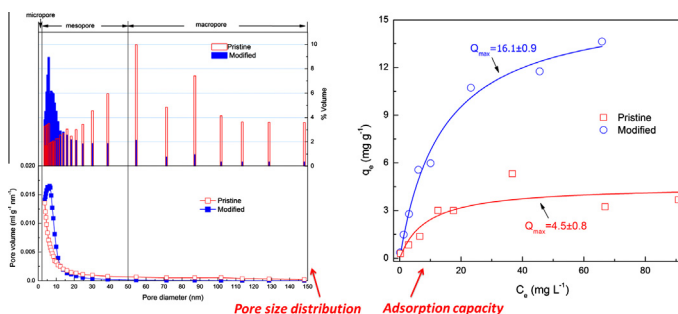
Dahu Ding, Zhongfang Lei, Yingnan Yang, Zhenya Zhang*

Graduate School of Life and Environmental Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8572, Japan

HIGHLIGHTS

- Novel transition metal modified akadama clay was prepared for the cesium removal.
- Akadama clay was transferred into a typical mesoporous material after modification.
- Modified AC had a much wider applicable pH range (5–12) than pristine one.
- The maximum adsorption capacity of modified AC was much higher than pristine one.
- Modified AC was testified as a potential efficient material for Cs⁺ removal from lake water.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this work is to develop an efficient adsorption material for cesium removal from aqueous solutions. A common and inexpensive andic soil, akadama clay (AC), was utilized in this study. In order to better its adsorption behavior, the AC was modified with nickel, a transition metal. Macropores and mesopores with diameter >20 nm in AC were transformed into smaller mesopores of diameter <12 nm after the modification. The maximum adsorption capacity increased from 4.5 ± 0.8 to 16.1 ± 0.9 mg g⁻¹. The applicable pH range (Cs⁺ removal >90%) was notably extended from pH > 11 to pH ≥ 5. Competitive ions had negative effects on the cesium adsorption especially K⁺ probably due to similar characteristics between K⁺ and Cs⁺. In addition, relatively high removal efficiency (about 85%) was achieved when the modified AC was used for lake water treatment. Desorption tests indicated that the adsorption process was relatively stable. Cs⁺ recycling could be realized by immersing the spent adsorbent into 0.1 M HCl or KCl solution for 24 h. The newly developed adsorbent is a promising efficient material for Cs⁺ adsorption from aqueous solution.

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1. Introduction

Among various radioactive nuclides, 137-cesium (¹³⁷Cs) is considered to be the most hazardous because of its large quantity and relatively long half-life (approximately 30.5 years) [1]. Accordingly, extensive research has been carried out with respect to the

adsorption of cesium on various materials [2–10]. Among these developed materials, most attention has been paid to clay materials because of their structural and economic advantages, such as large quantity, low cost, physical stability and high adsorption capacity [4,6,9]. As for most clay materials, the main mechanism occurring in the adsorption process is known as ion exchange. According to the special cubic structure and driving force caused by concentration gradients, ion exchange can be accomplished by releasing metal ions existing in clay materials into solutions (such as Na⁺, K⁺ and Ca²⁺) and adsorbing cesium ions

* Corresponding author. Address: University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8572, Japan. Tel./fax: +81 29 853 4712.

E-mail address: zhang.zhenya.fu@u.tsukuba.ac.jp (Z. Zhang).

simultaneously. Though the adsorption capacity is high, the disadvantage is low/no selectivity for ion exchange during the adsorption process. This means, not only the target metal ion but also other metal ions can be exchanged during the process, which undoubtedly leads to a waste of adsorption capacity, especially under high ionic strength conditions such as sea water. For clay materials, it is comparatively much more difficult to improve the selectivity of the ion exchange process than to increase adsorption capacity due to their complex compositions. As a result, more attention from researchers has been paid to the improvement of adsorption capacity of clay material [9,11]. Due to the special mineralization process, akadama clay (AC), which is a weakly acidic andic soil and generally used as a good medium in horticulture in Japan, contains large amount of metal ions and highly porous structure. As a result, it is a potentially ideal adsorption material compared with other kinds of clay materials.

Transition metals are known to undergo complexation with compounds containing aromatic groups based on an exchange process [12]. In addition, modification with transition metals could result in a pillared material with microporosity and mesoporosity in layered crystalline inorganic compounds [13]. ZSM-5 zeolite [14] and kaolin [15] have been successfully modified with transition metal in previous studies. Still, it is unknown whether transition metals could modify the other kinds of clay materials and whether the modification is positive for increasing adsorption capacity or not. Nickel (Ni), one of the typical transition metals and successfully used in the modification process [14], is therefore selected in this study.

The present work investigated the adsorption kinetics and capacity of the pristine and modified AC in relation to the effect of factors such as contact time, initial solution pH, adsorbent dosage, initial Cs⁺ concentration, competitive cations and temperature on their adsorption performance. In addition, in order to evaluate the feasibility of the modified AC in practice, in this study fresh lake water was chosen for the preparation of low strength Cs⁺ contaminated water due to its importance in natural waterbodies in Japan. Low strength Cs⁺ contamination is also the usual water pollution case related with radioactive accidents or leakage from the operation of nuclear power stations.

2. Materials and methods

2.1. Materials

AC used in this study was provided by Makino Store, Kiyosu, Japan. The engineering properties and chemical compositions (%) of AC were listed in Table S1 (Supplementary information). Synthetic zeolite A-4 and bentonite powder were purchased from Wako Pure Chemical Industries Ltd., Japan.

The chemicals, nickel chloride (NiCl₂·6H₂O) and sodium hydroxide (NaOH), were of A.R. grade and purchased from Wako Pure Chemical Industries Ltd., Japan. Non-radioactive cesium chloride (CsCl) purchased from Tokyo Chemical Industry Co. Ltd., Japan was used as a surrogate for ¹³⁷Cs as it has the same chemical characteristics. All the other reagents used in this study were purchased from Wako Pure Chemical Industries Ltd., Japan and used without any purification.

Deionized water (DW) generated from a Millipore Elix 3 water purification system (Millipore, USA) equipped with a Progard 2 pre-treatment pack was used throughout this study. Lake water used in this study was collected from Matsumi lake (36°6'30" N, 140°6'15" E) located in the University of Tsukuba, Japan, which mainly receives stormwater. The lake water was filtrated with a glass microfiber (Whatman, England) prior to the experiments. The naturally existing metal ions in the lake water were

determined by ICP-MS and are given in Table S2 (Supplementary information). The chemical compositions of synthetic groundwater (GW) were the same as another paper [16] and are not listed in this paper.

2.2. Modification process

The AC was ground and sieved through a No. 150 mesh. Particles with diameter below 105 μm were dried in an oven (EYELA WFO-700, Japan) at 105 °C and further used for modification. Briefly, the modification was carried out in the following three steps. Firstly, 10 g of dried akadama clay was added to 100 ml 0.5 M NiCl₂ solution and mixed thoroughly. 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). Once the first two steps were completed, the precipitate was repeatedly resuspended in DW, centrifuged and finally dried at 105 °C. As the final step, the dried precipitate was ground into powder form and heated in air at 600 °C for 1 h using a muffle furnace (TGC F-1404, Japan) in order to create a rigid, non-swelling, three dimensional zeolite-like structure [17]. The resultant modified AC was stored in an oven at 105 °C prior to the Cs⁺ removal experiments.

2.3. Cs⁺ removal studies

For the Cs⁺ removal experiments in DW, a stock Cs⁺ solution (~1000 mg L⁻¹) was prepared by dissolving 1.26 g CsCl accurately into 1 L DW. Cs⁺ solutions of desired concentrations were prepared by diluting known volumes of the stock Cs⁺ solution in DW. The solution pH was adjusted by 0.1 M HCl or NaOH solution and measured by a pH meter (Mettler Toledo SG8, Switzerland). To determine contact time and kinetic properties, 1 g of the pristine or modified AC was mixed with 200 ml of 10 mg L⁻¹ Cs⁺ solution in a 200 ml-glass flask, and the flask was shaken by a double shaker (TAITEC NR-30, Japan). Supernatants (about 1 ml for each) were retrieved at predetermined time intervals along with the initial solution (zero min point). In order to ensure reliability and improve accuracy of the kinetic data in this study, the kinetic studies were carried out in duplicate and the results reported in this study are average values with standard deviations. For the other experiments, the clay sample was added to 20 ml Cs⁺ solution in a 50 ml-polypropylene tube and placed in the double shaker for 2 h till equilibrium was reached. The contact time of 2 h is much longer than the equilibrium time determined by typical kinetic experiments (Section 3.2.1). In order to compare the adsorption capacities of the modified AC, zeolite and bentonite, namely commercial synthetic zeolite A-4 and bentonite powder were also utilized for Cs⁺ adsorption isotherm experiments. During the competitive ion experiments, two competitive ions (Na⁺ and K⁺) and three ratio levels of Na⁺/K⁺:Cs⁺ (10, 100 and 1000) at a constant Cs⁺ concentration (1 mg L⁻¹) were utilized in this study. In addition, in order to determine the thermodynamic parameters of the adsorption process, the effect of temperature (15, 25 and 35 °C) was investigated. The dosage of the modified AC was 2.5 g L⁻¹ and the initial Cs⁺ concentration was 10 mg L⁻¹.

For the experiment of Cs⁺ removal from lake water, considering the extremely low concentration of Cs⁺ in surface water (less than 1 ppb even in the case of a nuclear accident) [9] and the detection limit of ICP-MS, two low initial Cs⁺ concentrations were used in this experiment, which were 10 and 100 μg L⁻¹, respectively. The experimental conditions were similar to those in the DW tests without pH adjustment.

The whole study was conducted at room temperature (25 ± 1 °C) (except for the temperature effect section) with a shak-

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