



Removal of Co^{2+} , Sr^{2+} and Cs^{+} from aqueous solution by phosphate-modified montmorillonite (PMM)

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ABSTRACT

Sorptive removal of Co^{2+} , Sr^{2+} and Cs^{+} from aqueous solution by phosphate-modified montmorillonite (PMM) was studied considering the influencing factors (initial metal ion concentrations, initial solution pH and temperature). The Freundlich, Langmuir and Dubinin–Radushkevich (DR) models were used to fit single-solute sorption data. The Freundlich model was the best, indicating heterogeneous surface property of PMM. The maximum sorption capacity (q_{mL}) of Langmuir model was in the order of $\text{Cs}^{+} > \text{Co}^{2+} > \text{Sr}^{2+}$. The mean sorption energy (E) values of DR model (< 8 kJ/mol) at pH 5 for all metals indicated physical sorption. However, Cs^{+} sorption mainly occurred by chemical sorption. In bi-solute competitive sorption, the sorption of one metal ion was suppressed by the presence of competing metal ion. The Sheindorf–Rebhun–Sheintuch (SRS) model, the extended Freundlich model (EFM), the modified extended Langmuir model (MELM) and the IAST-Freundlich model predicted the competitive sorption adequately. Sorptions of Co^{2+} and Sr^{2+} were strongly dependent on the initial solution pH but that of Cs^{+} was not. The calculated thermodynamic parameters such as ΔH , ΔS , and ΔG showed that sorptions of Co^{2+} and Sr^{2+} onto PMM were endothermic, whereas that of Cs^{+} was exothermic and that all sorption occurred spontaneously.

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1. Introduction

The low-level radioactive waste (LLRW) is generated from operation and maintenance of nuclear reactors, mining and milling of nuclear fuel, and recycling the spent nuclear fuel. In general, such radioactive waste contains a variety of radionuclides that are fission byproducts generated from above processes [1]. Among the byproducts, Co^{2+} , Sr^{2+} and Cs^{+} are considered as the most dangerous radionuclides to human health due to their high transferability, high solubility, long half-lives and easy assimilation in living organisms. Several technologies such as chemical precipitations, conventional coagulation, reverse osmosis, ion-exchange and adsorption have been developed for the removal of these radionuclides present in the wastewater [2]. Out of these methods, sorption has been most widely used for the removal of these radionuclides because it is simple and cost effective with low cost sorbents.

Montmorillonite is an excellent sorbent because of high specific surface area, chemical and mechanical stability, layered structure and high cation exchange capacity (CEC). Sparks [3] reported that the high CEC for montmorillonite is due to substantial isomorphous substitution and to the presence of fully expanded interlayers that promote exchange of cations. Montmorillonite is consisted of two tetrahedral sheets, one octahedral sheet, and exchangeable cations and water

molecules located in interlayer space between sheets. Montmorillonite also has the net permanent negative charge on the surface caused by substitution of Si^{4+} by Al^{3+} in tetrahedral layer and of Al^{3+} by Fe^{2+} and Mg^{2+} in octahedral layer [4]. The net negative charge is balanced by exchangeable cations between the interlayers or around their edges [5]. Montmorillonite, therefore, has been applied for the removal of heavy metals such as Ni^{2+} and Cu^{2+} [6], Sr^{2+} [7], and Co^{2+} [8] from contaminated water.

Recently, chemical modification of natural clays such as montmorillonite and kaolinite to increase the sorption capacity by improving the clay structure has received extensive attention [5,9–12]. Acid activation followed by thermal treatment is also considered as a potential modification method to increase the sorption capacity of clays [9]. Lin and Juang [10] applied montmorillonite modified with sodium dodecyl sulfate (SDS) to remove Cu^{2+} and Zn^{2+} from aqueous solution.

Phosphate-modified kaolinite has been investigated for the sorption of heavy metals [11,12]. Unuabonah et al. [11] reported that the modification of kaolinite clay with phosphate enhanced the Pb^{2+} sorption on kaolinite, which was more endothermic and spontaneous. Adebowale et al. [11] found that modification of kaolinite with phosphate salts changed the kaolinite structure and improved the holding capacity for metal ions (Pb^{2+} and Cd^{2+}). Modification with phosphate increases the cation exchange capacity (CEC) of kaolinite and induces negative surface charge, thereby increasing sorption of heavy metal ions. However, sorptions of heavy metals onto phosphate-modified montmorillonite (PMM) were not fully understood.

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Bhattacharyya and Gupta [13] reported that the CEC of montmorillonite (153.0 meq $\text{Cu}^{2+}/100\text{ g}$) is higher than that of kaolinite (11.3 meq $\text{Cu}^{2+}/100\text{ g}$) due to difference in structures, indicating that montmorillonite would be more appropriate than kaolinite for sorption.

Sorption is considered as the most promising process for the treatment of LLRW [14]. Several sorbents such as silicotitanate [15] and ammonium molybdophosphate-polyacrylonitrile (AMP-PAN) [16] and several types of commercial inorganic ion-exchange resins [15,17] have been applied to treat the high- and low-level radioactive wastes; however, these sorbents are highly expensive.

PMM has also a promising potential for sorption of heavy metals because of high surface area and cost-effectiveness compared to the above mentioned sorbents and ion-exchange resins, however no information is currently available on the sorptive removal of Co^{2+} , Sr^{2+} and Cs^+ from LLRW by PMM. In this study, sorption of Co^{2+} , Sr^{2+} and Cs^+ from aqueous solutions onto the montmorillonite modified with KH_2PO_4 (phosphate-modified montmorillonite, PMM) was investigated. The purpose of this study is to determine the effects of operating variables such as initial metal ion concentrations, initial solution pH, temperature and presence of competing metal ion. Sorption mechanisms were discussed in detail.

2. Materials and methods

2.1. Chemicals

The montmorillonite-KSF, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (>98%), $\text{Sr}(\text{NO}_3)_2$ (>99%) and CsNO_3 (>99.9%) were purchased from Sigma-Aldrich (Seoul, Korea). KH_2PO_4 (>98%) was provided by Yakuri Pure Chemicals Co. (Japan). CH_3COONa (>98.5%), $\text{CH}_3\text{COONH}_4$ (>95%) and isopropyl alcohol (99.5%) were purchased from Duksan (Korea).

2.2. Preparation of PMM

The impurities of montmorillonite-KSF were removed by a digestion method using H_2O_2 and by washing it several times with distilled water at 60 °C. The clay suspensions were filtered with a 0.22 μm membrane filter, and the filtrate was examined for impurities using a UV-Visible spectrophotometer (Hewlett Packard, 8452A, USA). The washed montmorillonite was allowed to settle, dried in an oven at 60 °C for 24 h, and stored in a brownish bottle. The PMM was prepared by mixing 15 g of the washed montmorillonite with 1 L of 2000 mg/L of PO_4^{3-} (from KH_2PO_4) with a rotary agitator for 24 h at 200 rpm and room temperature. Thereafter, the modified clay was washed three times with 1 L of distilled and deionized water in order to remove excess H_2PO_4^- ions, air-dried for at least 3 days and kept in a brownish bottle before use.

The point of zero charge of PMM was determined by the potentiometric titration method [18]. Briefly, 4 g of air-dried PMM and 10 mL of electrolyte solution (0.1 M KCl) were added into 50 mL beakers. The solution pH was adjusted in the range of 2 to 10 using 0.1 M HCl or 0.1 M KOH and the beakers were then filled up to 25 mL with distilled and deionized water. The samples were covered and mixed in a rotary shaker for 7 days. After that, pH of the samples was measured and the amounts of H^+ and OH^- adsorbed by PMM were determined by subtracting the amount of HCl or KOH required to bring 10 mL of the blank electrolyte (0.1 M KCl) plus 15 mL of distilled and deionized water (without PMM) to the same pH. Brunauer–Emmett–Teller (BET) surface area was determined from N_2 adsorption isotherm using specific surface area analyzer (Micromeritics, ASAP-2010). Cation exchange capacity (CEC) of montmorillonite and PMM was also analyzed by sodium acetate method [19]. The sample was mixed with an excess of 1 N sodium acetate solution, resulting in an exchange of the added cations for the matrix cations. Subsequently, the sample was washed with isopropyl alcohol. 1 N ammonium

acetate solution was then added to replace the sorbed sodium with ammonium. The concentration of displaced sodium was then determined by inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin Elmer, Optima 2100DV).

X-ray diffraction (XRD) patterns were obtained using a Philips PW2273 diffractometer and $\text{Cu K}\alpha$ radiation (40 kV, 25 mA) in a range of 5–40° with a step size 0.02° and a time per step of 1 s. Scanning electron microscopy (SEM, Hitachi S-4200) was also used to examine the morphology and particle size of montmorillonite before and after modification. The chemical composition of montmorillonite and PMM was characterized by EDS analysis (Horiba E-MAX EDS detector).

2.3. Sorption experiment

For single-solute sorption experiments, metal stock solutions were prepared by dissolving $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and CsNO_3 in distilled and deionized water, respectively. The pH of the solution was measured by a pH meter (Thermo, Orion, model 720A+, USA).

Single-solute sorption experiments were conducted at 25 °C using 50 mL conical centrifuge tube (polyethylene, SPL Labware, Korea). 1 g of PMM was transferred into the tube and the pH of sorbent was adjusted to 5 by using 0.05 M MES buffer solution (heavy metal free) before the addition of metal stock solution. Thereafter, the tubes containing 1 g of PMM each were filled with approximately 50 mL of the stock solution with different initial metal ion concentrations ranging from 1 to 20 mM, in some case, to 30 mM to obtain sorption isotherms. The pH values of heavy metal solutions were also controlled at 5 ± 0.05 by using 0.05 M MES buffer. The MES buffer was used because no detectable complexation reactions occur between Co, Sr and Cs and MES buffer [20,21]. The solution pH was controlled to prevent the formation of metal hydroxides and carbonates.

The exact amount of added stock solution was determined gravimetrically. The mixture was then placed on a rotary shaker and shaken for 24 h at 200 rpm. After mixing, the tubes were centrifuged for 20 min at 3000 rpm, filtered through 0.2 μm syringe filter (Whatman, cellulose nitrate membrane filter, $\phi = 25\text{ mm}$). The metal ion concentration in the filtrate was analyzed by ICP-OES (PerkinElmer Optima 2100DV). All experiments were conducted in duplicate.

The sorbed amount of metal ion, q (mmol/g), was calculated using difference between initial and equilibrium metal concentrations.

$$q = \frac{(C_0 - C)V}{W} \quad (1)$$

where C_0 (mmol/L) and C (mmol/L) are initial and equilibrium metal ion concentrations in solution, respectively and V (L) is the volume of the solution and W (g) is the weight of sorbent.

Bi-solute competitive systems ($\text{Co}^{2+}/\text{Sr}^{2+}$, $\text{Sr}^{2+}/\text{Cs}^+$ and $\text{Cs}^+/\text{Co}^{2+}$) were prepared by mixing each metal solution of the same molar concentration in a 1:1 volume ratio for each solute. Bi-solute competitive sorption experiments were conducted in the same manner as used in the single-solute sorption experiments. The equilibrium concentrations in the mixture were also determined using the ICP-OES.

2.4. Sorption models

2.4.1. Single-solute sorption models

The Freundlich isotherm model is an empirical expression that encompasses the heterogeneity of the surface and an exponential distribution of the sites and their energies. The isotherm has been further extended by considering the influence of sorption sites and the competition between different ions for sorption on the available site [22].

$$q = K_f C_e^{N_f} \quad (2)$$

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