



# Selective adsorption of cesium from an aqueous solution by a montmorillonite-prussian blue hybrid

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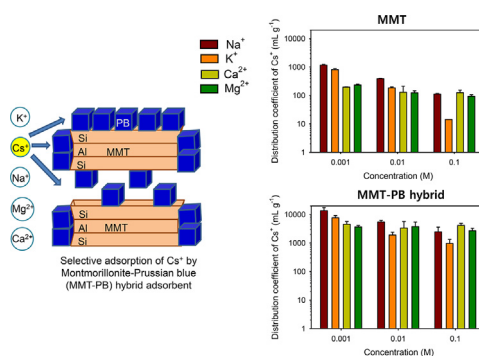
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## HIGHLIGHTS

- We synthesized montmorillonite-prussian blue adsorbent for the first time.
- Its maximum adsorption capacity for cesium was 57.47 mg/g.
- Its cesium selectivity is higher than that of most previously reported adsorbents.
- Potassium cation prevents cesium adsorption at 0.01 M concentration or above.
- Cesium adsorption occurred through both chemisorption and physisorption.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Keywords:

Caesium  
Sorption  
Removal  
Radionuclide  
Distribution coefficient

## ABSTRACT

Cesium generated from nuclear power plants is the primary source of problems for human health and environment due to its gamma radiation and high fission yield. Among the cesium removal methods, adsorption is an effective way to separating it from water. The abundance, retrievability, and selectivity of an adsorbent are crucial for its practical application in wide areas. Herein, we report a simple and environment-friendly synthesis of montmorillonite-prussian blue (MMT-PB) hybrid adsorbents and studies of the kinetic and equilibrium adsorption. Even though chemisorption (ion exchange) was dominant, physisorption (ion trapping) also occurred especially for the MMT-PB hybrid. The maximum adsorption capacity of MMT-PB was 57.47 mg/g, which was high enough as compared favorably with that of previously reported adsorbents. The distribution coefficient ( $K_d$ ) of the hybrid was examined in the presence of prevalent cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  to analyze its selectivity. The  $K_d$  value ranged from 3680 to 13700 mL/g at a cation concentration of 0.001 M. Moreover, the divalent cations prevented cesium adsorption due to its high electrostatic interactions with the adsorbent. The  $K_d$  decreased, ranging from 973 to 4160 mL/g, at a cation concentration of 0.1 M. In this case,  $\text{K}^+$  significantly prevented cesium adsorption as their hydrated radii are similar. Considering the low concentration of  $\text{K}^+$  in nature, the MMT-PB hybrid shows great promise for large-scale application in cesium removal from soil and contaminated water.

## 1. Introduction

From 1985 to 2016, the global electrical power demand of nuclear

power plants increased from 245,779 MW to 391,116 MW [1]. The high demand in nuclear power plants has caused serious problems of radionuclide contamination in soils and water. Nuclear power plants

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are the major source of radionuclide contamination of the environment – especially, cesium that has a high fission yield and long half-life – and are dangerous to the environment and human health [2]. Among all the isotopes of cesium,  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  are the most dangerous in this regard because they emit gamma radiation and have long half-lives of 2.06 years and 30.17 years, respectively [3].  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  are the most abundant species in nuclear power plants and waste repositories because of its yield of about 6% from thermal fission of  $\text{U}^{235}$  [4]. The Environmental Protection Agency (EPA) has included  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  in the National Priorities List (NPL) that targeted long-term cleanup activities involving the US Federal states [5]. The Sellafield site in the UK has been used as a nuclear fuel reprocessing and decommissioning site that discharged radionuclides to the atmosphere and sea for more than 40 years [6]. One of the major radionuclides that was discharged into the Irish Sea as part of the liquid effluent of Sellafield site was  $^{137}\text{Cs}$ , with the annual discharge from 1974 to 1978 being 4000 TBq [7]. The concentration of cesium in the earth's crust was 3 ppm on average [8]. However, the local concentration could be much higher because the radioactivity at the bottom soil in the Abukuma river of Date city near the Fukushima Nuclear Power Plant was very high: 11,000 Bq/kg of  $^{134}\text{Cs}$  and 12,000 Bq/kg of  $^{137}\text{Cs}$  on May 24, 2011 [9]. Humans can be exposed externally or internally to the gamma radiation emitted by  $^{137}\text{Cs}$ . Cesium can be transported well in the human body because it is similar to potassium in that it can enter the cells. Since April 2012, the commission implementing regulations (EU) proposed that the total maximum dose of  $^{134}\text{Cs}$  and  $^{137}\text{Cs}$  is 100 Bq/kg in the foods imported from Japan after the Fukushima nuclear power plant accident [10].

The high solubility of cesium in water makes it difficult to immobilize the metal in nuclear facilities. Many researchers have developed removal technologies for radionuclides such as extraction, ion exchange, evaporation, adsorption, and reverse osmosis. Adsorption is a popular method because it is simple to apply, has high efficiency, and can be used on a large scale. Researchers have used synthetic inorganic nanomaterials such as iron oxide, titanosilicate, manganese oxide, and prussian blue that facilitate selective removal [11,12]. Prussian blue has gathered the attention of many researchers due to its high affinity to cesium [13]. Many papers showed the evidence that prussian blue, ferrocyanide, and the prussian blue analogue are selective to cesium [13]. The crystal structure of ferrocyanide permits selectivity towards cesium due to the adsorption of hydrated cesium by the regular lattice space surrounded by cyanide bridged metal and the proton mechanism on adsorption [14]. The adsorption of cesium on prussian blue involves a combination of chemisorption ( $\text{K}^+$  exchange) and physisorption (ion trapping) [15–17]. Prussian blue had been used in pharmaceutical industries to treat cesium contamination in the Chernobyl accident [18]. However, the very fine powder of prussian blue caused problems of non-separation after the adsorption and loss to cartridge or membrane after the treatment processes [19,20]. The prussian blue containing cesium can cause secondary pollution due to its non-separation characteristics and high mobility.

Montmorillonite is a group member of smectite that has a phyllosilicate group. Montmorillonite has been used for many years in industries as fillers, carriers, absorbents, a component in drilling fluids, and most importantly as an adsorbent for nuclear waste [21–24]. Montmorillonite has a higher cation exchange capacity (CEC) and surface area compared to other clays like illite, kaolinite, chlorite, and finely milled mica [22,25]. Montmorillonite has shown better adsorption performance for cesium than other common adsorbents such as kaolinite, silicate minerals and aluminum oxides, organic matter, and hydroxyapatite [26–31]. Moreover, the presence of montmorillonite in nature is abundant in soil compared to micaceous minerals [30,32]. However, the selectivity of montmorillonite towards cesium decreased especially when there were other common cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ . Many researchers have developed montmorillonite clays to improve their performance and properties as an adsorbent for cesium removal by acid activation, pillaring, intercalating with other

metals, and by forming composites with other synthetic inorganic materials [17,20,33–35]. Researchers developed an ammonium-pillared montmorillonite/ $\text{Fe}_3\text{O}_4$  composite for cesium sorption, but the adsorption capacity did not increase significantly; further, the composite exhibited a low selectivity to cesium [36]. Previous researches also developed montmorillonite clay-based material composites with organic and inorganic materials that show a high adsorption capacity for cesium [37–40]. However, the selectivity of these materials to cesium sorption was still low.

To resolve the problems of high mobility of the nanosorbent and low selectivity of the abundant clay sorbent, in this study, we combined the advantage of the high selectivity of prussian blue with the large amount, big size, and generally good adsorbent properties of montmorillonite. To the best of our knowledge, this is the first report on a hybrid of prussian blue and montmorillonite. We synthesized this montmorillonite-prussian blue hybrid via a simple and easy in situ precipitation method at room temperature. We investigated the kinetic sorption of cesium on the hybrid and found chemisorption to be a major mechanism by evaluating the pseudo-second-order kinetic model. We also investigated the adsorption isotherm and determined the maximum adsorption capacity as 57.47 mg/g. Furthermore, the effects of competitive cations on cesium adsorption were examined, and the selectivity of this hybrid was reported to be higher than those of the previously reported materials.

## 2. Materials and methods

### 2.1. Chemicals and materials

Montmorillonite K-10 with specific surface area (SSA) 220–270  $\text{m}^2/\text{g}$  was purchased from Sigma Aldrich. Sodium hexacyanoferrate (II) decahydrate ( $\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$ , 99%) and cesium nitrate ( $\text{CsNO}_3$ , 99.8% metal basis) were purchased from Alfa Aesar. Iron (III) nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 98%), hydrochloric Acid (HCl, 37%), and calcium chloride hexahydrate ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , 97%) were purchased from Daejung. Sodium hydroxide (NaOH, 98%) was purchased from Samchun. Sodium chloride (NaCl, 99%), potassium chloride (KCl, 99%), and magnesium chloride ( $\text{MgCl}_2$ , 97%) were purchased from Sigma Aldrich. All the chemicals were used without any further purification during the experiments.

### 2.2. Synthesis of the montmorillonite-prussian blue hybrid

Two different methods to synthesize the montmorillonite-prussian blue hybrid were used to determine the optimum technique. Montmorillonite-prussian blue hybrid particles were synthesized by the precipitation method with a slight modification to a literature procedure involving the synthesis of prussian blue reported by Kaye 2007 [16]. The first method used was the montmorillonite-prussian blue ferric to cyanide (MMT-PBFC) method. In this method, 13.29 g of montmorillonite K10 particles were added to 75 mL of 0.062 M  $\text{Na}_4[\text{Fe}(\text{CN})_6]$  solution under magnetic stirring. Then, we added 75 mL of 0.082 M  $\text{Fe}(\text{NO}_3)_3$  solution dropwise to the stirred solution of montmorillonite and  $\text{Na}_4[\text{Fe}(\text{CN})_6]$ . The solution was aged with magnetic stirring for 24 h at room temperature. The second method was the montmorillonite-prussian blue cyanide to ferric (MMT-PBCF) method. In this method, 13.29 g of montmorillonite K10 particles were dispersed in a 75 mL 0.082 M  $\text{Fe}(\text{NO}_3)_3$  solution under magnetic stirring. Then, we added 75 mL of 0.062 M  $\text{Na}_4[\text{Fe}(\text{CN})_6]$  solution dropwise to the stirred solution of montmorillonite and  $\text{Fe}(\text{NO}_3)_3$ . The solution was aged with magnetic stirring for 24 h at room temperature. Both MMT-PBFC and MMT-PBCF particles were centrifuged using a 1769g-force for 15 min and washed thrice with deionized water. The wet particles were dried in a vacuum oven at room temperature.

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