



Electrochemical synthesis and immobilization of a beadwork-like Prussian Blue on carbon fiber and the removal of cesium



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ABSTRACT

Beadwork-like Prussian blue (PB) crystals were immobilized on a carbon fiber (CF) surface using an electrochemical modification method. The modification condition of PB on CF was investigated by changing the applied potential and modification time. Potentials from 0.35 V to 0.5 V provided a stable deposition of PB on the CF sheet. The PB-modified CF (PB-CF) was characterized by cyclic voltammetry, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopic mapping. The SEM images of the PB-CF prepared at potentials of 0.2 V and 0.35 V showed a beadwork-like structure. In contrast, PB formed an island structure on CF at potentials of 0.5 V and 0.6 V. The adsorption ability of PB-CF for Cs ions was estimated at different pH values and for different modification potentials. The adsorption ratios for 5 ppm Cs⁺ were about 60% at pH 1 for 48 h, and more than 90% at pH 5.6. The adsorption ability of PB-CF remained under basic conditions. The specific structure of PB-CF was useful to adsorb Cs⁺ from solutions at a wide range of pH values.

1. Introduction

On March 11, 2011, a massive earthquake caused an accident at the Fukushima Daiichi Nuclear Power Plant; the loss of electricity disabled the reactor cooling systems. The accident led to the release of various radionuclides, such as cesium, strontium, and iodine, into the environment. This caused water and soil pollution over a wide area. In particular, the long-term influences of radioactive ¹³⁷Cs are of great concern because ¹³⁷Cs has a long half-life (thirty years). In the environment, Cs exists as a monovalent cation, which is similar to other alkali metal cations, such as K⁺ and Na⁺. Cs⁺ is captured by soil particles or organic matters with negative charges [1,2]. In addition, Cs⁺ is strongly intercalated into the layers of clay minerals, such as vermiculite and illite. Once it is intercalated, it is difficult to desorb Cs⁺ from these clay minerals [3,4]. Therefore, the removal of Cs⁺ from water is necessary before it is immobilized on soil.

Many studies have suggested that adsorption is one of the promising methods for Cs⁺ removal from aquatic environments [5,6]. Prussian blue (PB) is an adsorbent with a selective adsorption ability for Cs [7,8]. PB is a blue dye, and the structure of PB is a cubic cell of ferric and ferrous ions linked by bridging cyanide ions [9,10]. Cs⁺ can be strongly adsorbed into the lattice of the PB structure. In addition, PB can be easily synthesized, by mixing Fe²⁺ or Fe³⁺ with [Fe(CN)₆]³⁻ or [Fe

(CN)₆]⁴⁻, respectively. However, it is difficult to collect fine particles of PB crystals after they are used for Cs⁺ removal by adsorption from aquatic environments. Therefore, it is necessary to immobilize fine PB crystals on the surface of another substance to facilitate their collection after Cs⁺ adsorption from water.

In some studies, PB or PB analogs such as nickel [11], cobalt [12], and copper hexacyanoferrates [13], were prepared for use as Cs⁺ adsorbents. PB analogs also have a high selectivity and adsorption ability for Cs⁺. Therefore, some methods, such as coating PB analog ink onto metallic substances and staining clothes with PB analogs, were developed, and these materials have been used for the attempted removal of Cs⁺ [14–16]. However, these methods have some disadvantages, e.g., it takes a long time to prepare the adsorbent because the pretreatment processes require long treatment times and the modification processes must be repeated many times until sufficient amounts of PB analogs are immobilized.

The electrochemical method has some advantages; for example, the PB modification can be controlled by the potential without adding any specific chemicals. Some papers have reported the electrochemical modification of PB on Pt, carbon, SnO₂, and indium tin oxide electrodes [17–19]. In particular, PB that was electrochemically modified on carbon materials, such as grassy carbon or carbon fiber (CF), was used for sensing glucose and H₂O₂ [20–23]. In these studies, cyclic potential

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scans or a constant potential was used for PB modification. However, these studies focused on biosensing, not removing Cs^+ . Therefore, the amount of PB modified on the electrode was not sufficient for the removal of Cs^+ in aquatic environments. Using PB-modified carbon materials as adsorbents has not been investigated. In addition, the stability of the modified PB has not been considered.

In this study, electrochemical immobilization of PB on a sheet of CF was investigated for the removal of Cs^+ in aqueous environments. CF has a high surface area, conductivity, and chemical stability. From these properties, CF has been used as an electrode material for the removal of pollutants [24–26]. The immobilized amounts of PB can be significantly increased using a sheet of CF as a modification substance for PB. The chemical properties and stabilities of PB-modified carbon fiber sheets (PB-CF) were investigated by controlling the modification potentials and scanning potential in water at several pH values. The removal of Cs^+ in water was also investigated using the electrochemically prepared PB-CF.

2. Materials and methods

2.1. Materials

Iron(III) chloride hexahydrate and potassium hexacyanoferrate(III) were used for the preparation of PB-CF and were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Sodium dihydrogen phosphate was purchased from Wako Pure Chemical Industries, Ltd., and disodium hydrogen phosphate dodecahydrate and ethanol were purchased from Junsei Chemical Co., Ltd. (Tokyo, Japan). The alkali metal salts used for the adsorption experiment, a cesium standard solution (1000 mg/L) and cesium chloride were purchased from Junsei Chemical Co., Ltd. Hydrochloric acid and sodium hydroxide for pH adjustment were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan) and Junsei Chemical Co., Ltd., respectively. Potassium chloride for Cs analysis by atomic adsorption spectroscopy (AAS) was purchased from Junsei Chemical Co., Ltd. Oxalic acid was purchased from Wako Pure Chemical Industries, Ltd. All reagents were of analytical grade and used without any prior treatment.

2.2. Modification of prussian blue on carbon fiber

The modification of CF with PB was performed using an electrochemical redox reaction in a three-electrode system. A potentiostat-galvanostat HA-301 (Hokuto Denko Ltd., Japan) was used to apply a constant potential. A CF (0.5-mm diameter; Hokuto Denko Ltd. Tokyo, Japan) were used as the working electrode. A platinum wire and Ag/AgCl (Bioanalytical Systems Inc. (BAS), USA, and International Chemistry Co., Ltd., Japan) were used as a counter electrode and a reference electrode, respectively. Before use, the CF was dipped in ethanol and then sonicated in ultra-pure water for 15 min; the ultra-pure water was changed every 5 min during the sonication.

The pretreatment of CF and electrochemical modification of PB were performed according to the procedure shown by Ricci et al. [27] and Karyakin et al. [28]. For the electrochemical pretreatment of the CF, a constant potential of 1.7 V vs. Ag/AgCl was applied for 3 min in 0.1 M KCl and 0.1 M phosphate buffer (pH 6.8). After the pretreatment, a constant potential vs Ag/AgCl was applied in the mixed solution of 2 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$, 2 mM FeCl_3 , 0.1 M KCl, and 3 mM HCl. Then, the scan between -0.05 V and 0.35 V was repeated for 10 cycles in a solution of 0.1 M KCl, and 3 mM HCl, and the PB-CF was washed with ultra-pure water. The prepared PB-CF was dried at 80°C for 30 min and stored in the dark at room temperature. The chemical modification of PB on CF was performed according to the report by Sun et al. [15]. First, a CF sheet (1 cm \times 5 cm) was immersed in ethanol overnight. After that, the CF was placed in a solution of 50 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ containing ethanol. Then, the CF was moved into a 50 mM FeCl_2 solution containing ethanol. After modification, PB-CF was dried at 80°C .

2.3. Effect of the modification potential

A constant potential between -0.2 V and 0.8 V was applied in the mixed solution of 2 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$, 2 mM FeCl_3 , 0.1 M KCl, and 3 mM HCl. Then, the solution after applying the potential was used to measure the absorbance at 710 nm, which is proportional to the amount of PB produced in the solution. The absorbance at 710 nm was plotted against the potential.

2.4. Amount of PB on the CF

The amount of modified PB on the CF was estimated by measuring the weight of PB-CF before and after elution of PB from CF. The elution of PB was carried out by immersing a 1 cm \times 1 cm piece of PB-CF in a 0.1 M oxalic acid solution and slowly stirring; then, the piece of CF was washed with deionized water and dried at 80°C overnight. The weight measurement was performed after cooling to room temperature.

2.5. Characterization of PB-CF

The characterization of PB-CF was carried out by cyclic voltammetry (CV), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS). A CV-50W voltammetric analyzer (BAS, USA) was used for CV analysis. The morphological structure of the modified CF with PB was observed by a low vacuum-SEM (JSM-6360LA, JEOL, Japan).

2.6. Influence of pH on the stability of PB-CF

A 2 cm long thread of PB-CF as a working electrode was immersed in 15 mL of 0.1 M KCl; the solution pH was adjusted from 1 to 11, and the CVs were measured after a constant interval using the thread. The stability of PB on the CF surface was estimated by measuring the decrease of the oxidation peak current and the observation of the surface of the PB-CF.

2.7. Adsorption of cesium on PB-CF

Adsorption experiments were performed using the batch method with 10 mL of a 5 ppm Cs^+ solution; the pH and concentration of the solution were adjusted to obtain adequate conditions for Cs^+ removal. An electrochemically prepared PB-CF sheet (1 cm \times 1 cm) was immersed in the Cs^+ solution for a constant time at room temperature. Then, the PB-CF was removed from the solution. The remaining Cs^+ in the solution was measured by AAS (A-2000 HITACHI, Japan) at 852.11 nm with air-acetylene gas. Distribution coefficients (K_d , mL/g) of Cs^+ were measured in batch tests with 5–100 ppm Cs^+ concentrations. A 1 cm \times 1 cm PB-CF sheet prepared by applying 0.35 V for 10 min was immersed in the 10 mL of the Cs^+ solution, and shaken for 72 h at room temperature.

3. Results and discussions

3.1. Modification of PB on carbon materials

3.1.1. Modification potential

The simplest method to modify PB on a piece of CF cloth is chemical modification by immersing it in a solution containing the ingredients of PB [15,29]. The modification of PB on CF by this method required a lot of time to immerse in the solution or to repeat the cycle of dipping to immobilize sufficient PB on the CF surface. The electrochemical modification is an excellent method to obtain stable PB on CF in a short time. The process of electrochemical modification of PB on CF in a FeCl_3 and $\text{K}_3[\text{Fe}(\text{CN})_6]$ mixed solution is shown in Scheme 1. It is based on the reactions of $[\text{Fe}(\text{CN})_6]^{3-}$ with Fe^{2+} produced by the reduction of Fe^{3+} at the electrode. That is, Fe^{3+} in the solution is firstly reduced to

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