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Magnetic Separation of Cesium Ion Using Prussian Blue Modified Magnetite

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Prussian-blue-modified magnetite (PB-Fe_3O_4) was prepared by a simple method. The Cs^+ sorption ability of PB-Fe_3O_4 was evaluated by batch magnetic separation. As a result, the maximum sorption amount of Cs^+ with PB-Fe_3O_4 was 16.2 mg g^{-1}, and the sorption ability was not greatly changed in the presence of high concentration of NaCl. The recovery of PB-Fe_3O_4 from water by magnet predicted that it was sufficiently applicable to treatment of water contaminated with radioactive Cs^+.

Today, Japan is faced with a critical pollution problem with radioactive species such as cesium (Cs), strontium (Sr), and iodine (I) spilled from the Fukushima nuclear power plant (NPP). Therefore, easy and safe methods to treat and analyze radioactive materials in environments of soil and water are required. Prussian blue (PB) is known as a low-cost adsorbent, which has a high selectivity for cesium (Cs) and a high stability for decomposition.[1,2] Therefore, PB has been used as an sorbent for the removal of Cs^+ uptaken into an organism.[3] The basic structure of PB is a three-dimensional polymeric network with a face-centered cubic cell consisting of alternating iron(III) (coordinated to nitrogen) and iron(II) (coordinated to carbon atom) ions linked via the bridging of cyanide ligands.[4,5] Most of sorbed Cs^+ is introduced in the lattice of PB. However, PB crystal is small, and thus the microcrystalline nature of PB is not adequate to column loading, filtration, and centrifugation after Cs^+ sorption. A magnetic separation using magnetic materials such as hematite (Fe_2O_3) and magnetite (Fe_3O_4) is an easy and quick method to collect and separate target compounds from water, and recently it has been applied to various fields such as analytical biochemistry, medical science, and biotechnology.[6–8] The magnetic separation has an advantage in the recovery of adsorbent with harmful matter without filtration and centrifugation after adsorption. Several studies on magnetic separation have been reported about the treatment methods for heavy metal ions and organic pollutants by using modified Fe_3O_4.[9–12]

The purpose of this study is to develop an easy and safe method for treatment of Cs^+ in water using PB-modified Fe_3O_4 (PB-Fe_3O_4). The column method is used widely for water treatment, and the treatment of coolant containing radioactive species at Fukushima NPP is also performed by the column method. However, use of columns requires the consideration of clogging and water leaks, and sometimes generates back pressure. Furthermore, columns constructed with several pieces of equipment are often complicated systems, and so there is a high probability of mechanical failure. Our proposed method is very simple and has few of the problems described above. Moreover, this method can be applied to turbid solutions containing many kinds of suspended matter. Since only magnetic sorbents are recovered by the magnet easily, the sorbent can be used again for treatment. So this method can be applied to not only coolant solution but also wastewater in various conditions. Thus, we prepared PB-Fe_3O_4 as follows and evaluated the magnetic method using PB-Fe_3O_4. The image of PB-Fe_3O_4 is shown in Figure 1.

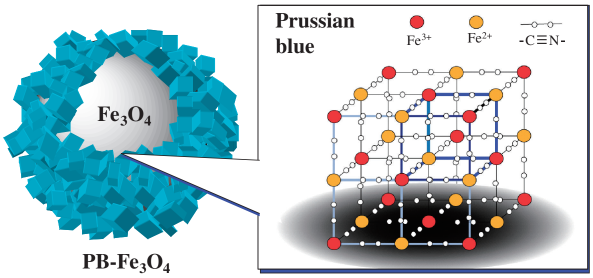

Figure 1. Schematic representation of PB-Fe_3O_4 and lattice structure of PB.

At first, Fe_3O_4 was prepared in the following manner.[13] 5.2 g of $FeCl_3 \cdot 6H_2O$ and 2.0 g of $FeCl_2 \cdot 4H_2O$ were dissolved in 25 mL of deionized water (DW), and then 0.85 mL of 12 M HCl was added in the solution. The solution was added to 250 mL of 1.5 M NaOH solution with vigorous stirring at 80 °C. After 60 min with stirring, the mixed solution was cooled by water, and then the Fe_3O_4 collected by magnet was washed with DW until the pH of supernatant was around 7. DW for preparation of solution was used after purging with N_2. The surface area of Fe_3O_4 was measured by Autosorb6 (YUASA), and the result was 7.82 $m^2\,g^{-1}$. The modification of PB on Fe_3O_4 was carried out with formation of PB on the Fe_3O_4 surface using potassium hexacyanidoferrate(II) ($K_4[Fe(CN)_6]$).[14]

100 mg of Fe_3O_4 was added into 100 mL of 2.0 mM $K_4[Fe(CN)_6]$ solution (pH 2 with HCl), and then the mixture was stirred for 3 h. The PB-Fe_3O_4 collected by magnet was washed with water three times and then dried in an oven at 40 °C for 24 h. All reagents were provided by Wako, Japan. Scanning electron microscopy (SEM, JSM-7400F JEOL) and transmission electron microscopy (TEM, JEM-2100F JEOL) images of PB-Fe_3O_4 are shown in Figure 2. Core–shell structure of PB-Fe_3O_4 and crystal of PB on Fe_3O_4 can be observed in Figures 2b and 2c, respectively. The size of PB crystal grain on Fe_3O_4 was about 100 nm, and the thickness of PB layer on Fe_3O_4 was 200–400 nm from TEM images. The presence of PB modified on Fe_3O_4 was confirmed by powder X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). The XRD pattern measurements were performed by Miniflex (Rigaku) with Ni filtered Cu Kα radiation ($\lambda = 0.154$ nm) at 35 kV, 15 mA. As shown in Figure 3a, the peaks of (220), (311), (222), (400), (422), (511), and (440) were detected as the characteristic

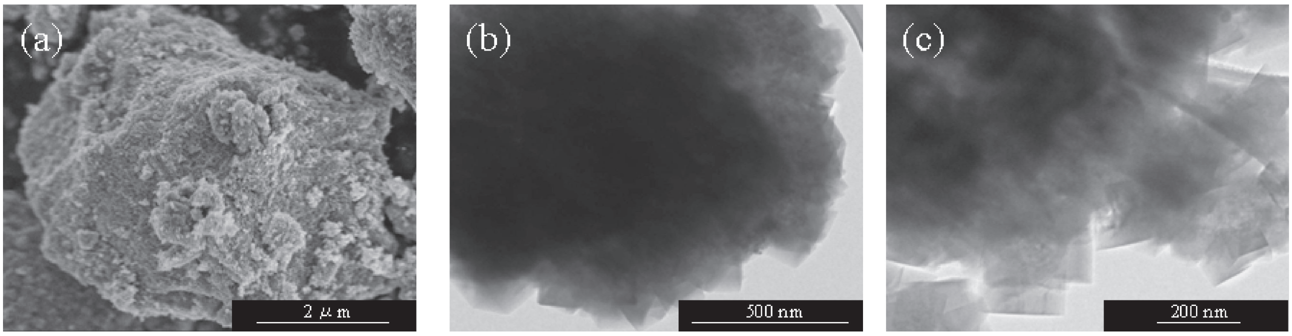

Figure 2. SEM (a) and TEM (b, c) images of PB-Fe_3O_4.

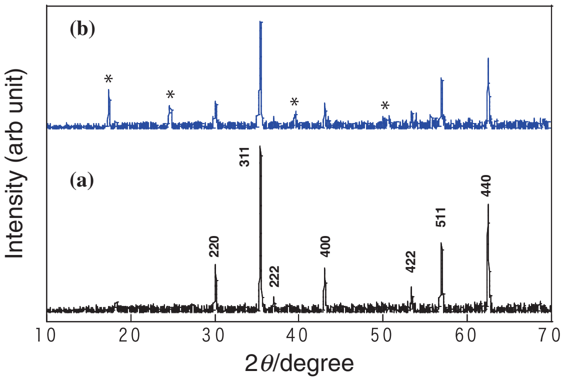

Figure 3. XRD patterns of Fe_3O_4 (a) and PB-Fe_3O_4 (b).

peaks of Fe_3O_4.[15] After PB modification, some new peaks, marked peaks of Figure 3b, coincided with the characteristic peaks of PB.[16] The FT-IR measurements were curried out with FT/IR-4100 (JASCO) in KBr pellets. In Figure S2,[20] peaks at around 1610 cm^{-1} observed in curve (a) and (b) were related to the –OH deformed vibration, and the peaks around 3400 cm^{-1} in curve (a) and (b) were assigned to the –OH stretching vibration on the surface of Fe_3O_4.[17,18] The peak of 2082 cm^{-1} in curve (b) was assigned to the CN stretching in the formed [Fe^{II}–CN–Fe^{III}] structure.[19] The size and ζ potential of Fe_3O_4 and PB-Fe_3O_4 were measured by using photon correlation spectroscopy (PCS) and electrophoretic light scattering (ELS), respectively (Delsa™ nano HC, Beckman Coulter). As a result, the average particle sizes of Fe_3O_4 and PB-Fe_3O_4 were 6.4 and 6.7 μm, respectively. The ζ potentials of Fe_3O_4 and PB-Fe_3O_4 were 20 and −79 mV at pH 5.5 (Figure S1).[20] The amount of modified PB estimated by gravimetry was 0.29 mmol g^{-1} (Figure S2 and Table S1).[20] The sorption ability of PB-Fe_3O_4 for Cs^+ was evaluated by sorption experiments. The batch experiments were carried out using 10 mL of Cs^+ solution and 10 mg of PB-Fe_3O_4 at pH 5.5 (uncontrolled) and 25 °C, and then PB-Fe_3O_4 was collected by Nd–Fe–B magnet (0.4 T, 25 × 10 × 5 mm^3) after sorption. Cs^+ concentration in supernatant was measured by ICP-MS (SPQ 6500, SEIKO). Figure 4 showed the results of sorption in various concentrations of Cs^+ (0.01–0.5 mM). The results indicated that the sorption amount of Cs^+ onto PB-Fe_3O_4 was increased with increase in the concentration of Cs^+ in the solution. The sorption results were fitted to a Langmuir model and Freundlich model to obtain the maximum sorption amount of Cs^+ onto PB-Fe_3O_4. Both fitting results were favorable to these models, but the result of Freundlich was slightly better than that of the Langmuir (the correlation coefficient with Freundlich model: 0.977 and with Langmuir model: 0.975 according to Table S2).[20] The maximum sorption amount from the fitting data of Langmuir model was 16.2 mg g^{-1}. Freundlich model is generally said to well fit the sorption on porous material such as activated carbon. On the other hand, the Langmuir model is well fitted to monolayer adsorption. Since the layer of the lattice structure of PB formed on Fe_3O_4 was relatively thin, the property of PB-Fe_3O_4 as porous material was not significantly pronounced. As a result, the sorption behavior might also fit well for the Langmuir model. Figure 5 indicated the results of sorption rate of Cs^+ onto PB-Fe_3O_4 and influence of coexisting salt on sorption of Cs^+, where concentrations were

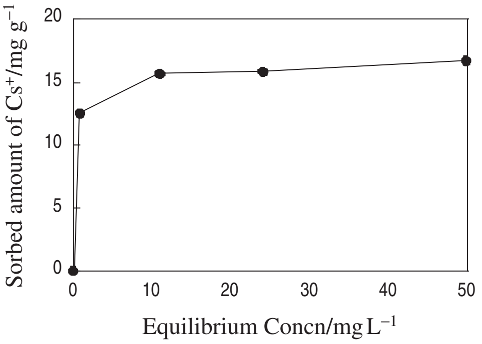

Figure 4. Adsorption isotherm of Cs^+ onto PB-Fe_3O_4.

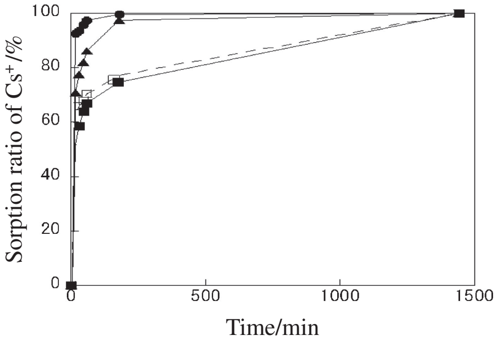

Figure 5. Kinetics of Cs^+ sorption onto PB-Fe_3O_4 on 0.001 (closed circle), 0.01 (closed triangle), and 0.1 mM (closed square) of Cs^+ with NaCl and without NaCl (open square).

0.001, 0.01, and 0.1 mM. The concentration of coexisting NaCl was 3 wt %, the same as that of seawater. According to these results, most of Cs^+ sorbed onto PB-Fe_3O_4 within the first 60 min in all cases. In 0.01 and 0.1 mM Cs^+ solution, Cs^+ sorbed slowly after 60 min. The presence of two different sorption rates of Cs^+ suggests that the sorption site of Cs^+ in the sorbent is not only the surface of PB layer but also the inside of PB lattice. Moreover, the influence of coexisting salt on the sorption of Cs^+ by PB-Fe_3O_4 was evaluated by comparison between sorption behaviors of Cs^+ in 0.1 mM Cs^+ solution with and without NaCl. The amount of sorbed Cs^+ from water containing NaCl was 91% of that without NaCl. It was found that the ability of Cs^+ sorption with PB-Fe_3O_4 was present even with low concentration Cs^+ under the high matrix conditions.

The recovery of PB-Fe_3O_4 from water by a magnet was evaluated by measuring weight of collected PB-Fe_3O_4. The recovery test was performed in the following way. First, 100 mg of PB-Fe_3O_4 was dispersed in 1 L of water. Then, the PB-Fe_3O_4 was recovered by magnet at various times with stirring. The recovered PB-Fe_3O_4 was dried at 40 °C for 24 h in an oven and then the weight measured. According to the results, the recovery ratio of PB-Fe_3O_4 was almost 100% at 6 min (Figure S3).[20] Thus, the good recovering ability of PB-Fe_3O_4 was useful in the water treatment process. If the particle size of PB-Fe_3O_4 is smaller than the case in our study, the sorption amount of Cs^+ will be increased because of increasing surface area and modified amount of PB. However, the decrease in the particle size of PB-Fe_3O_4 may lead to the reduction of recovery because of weaker magnetic strength.

Based on our study, a full automation system for treatment of contaminated water may be feasible if a hanged electrical magnet is used for collection of PB-Fe_3O_4 after sorption of Cs^+. It will make possible to treat the contaminated water with radioactive Cs^+ with few exposure.

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