

Development of a Novel Cesium Adsorbent which Causes Minimal Hydraulic Resistance through the Immobilization of Prussian Blue Analogues in a Monolithic Silica-Alumina Microhoneycomb

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Prussian blue analogues (PBAs) such as $K_2[CuFe(CN)_6]$ are expected to become the key material for efficient cesium recovery. However to use this material efficiently, it must have a morphology that doesn't cause a severe hydraulic resistance, as a high throughput is required during recovery. This is very difficult, as this material is usually obtained in the form of small particles. In this work, we developed a cesium adsorbent with a low hydraulic resistance using PBAs as the adsorption sites. Silica-alumina was selected as the substrate. As for the morphology of the adsorbent, we adopted a microhoneycomb structure, which can be obtained by the Ice Templating Method, a new micromolding method developed in our laboratory. The obtained adsorbent showed a significantly lower hydraulic resistance than conventional adsorbents in the particle form, and could be used to continuously remove ppm-ordered cesium from solutions.

1. Introduction

Recovery of radioactive cesium, such as ^{137}Cs , from nuclear waste water is an important issue because of high radioactivity and long half-lives (30 y) of the cesium. Although the stabilization/solidification technique is suited to dispose of the nuclides in soils (Falciglia et al., 2012), it is difficult to apply the technique to huge amount of soils. In such case, adsorption and ion exchange are thought to be the proper methods to recovery the radioactive cesium from fluids which extracted from the soils. However, the resistance the adsorbents/ion-exchangers cause these fluids must be minimized as a huge amount of energy will be required if the material used for treatment causes a high hydraulic resistance. Therefore in this work, we attempted to develop a novel cesium adsorbent which only causes minimal hydraulic resistance. Various materials are known to have abilities to recover cesium from fluids, such as zeolites (Mimura and Kanno, 1985), heteropoly acid salts (Tranter et al., 2002), silicotitanates (Anthony et al., 1994), and certain PBAs such as potassium cobalt ferrocyanide (II) (Harjula et al., 1994) and potassium nickel ferrocyanide (II) (Mimura et al., 1997). Among them, we selected PBAs as the medium for recovery, as they are inexpensive and as they show a high selectivity towards cesium. PBAs which have abilities to recover cesium can be obtained by insolubilizing ferrocyanide using bivalent metal cations. However, the PBAs obtained through this method are usually in the form of fine particles, so a severe pressure drop is likely to occur when fluids are passed through them. Therefore, we dispersed such PBAs within a matrix material and molded the composite to have a morphology which only causes a minimal hydraulic resistance while still maintaining a high accessibility to the included PBAs. We selected a monolithic microhoneycomb, a miniature honeycomb having straight and aligned micrometer sized channels which are formed by walls with a thickness also in the micrometer range, as the morphology of the composite. Due to this unique morphology, a low resistance to fluid flows and short diffusion path lengths within the material are expected to be compatible, a feature which the same material in a particle form cannot

achieve. Molding was conducted using the Ice Templating method, a unique micromolding technique developed by the authors (Mukai et al., 2004).

2. Experimental

In this work, silica alumina was used as the matrix of the PBA composite (Nishihara et al., 2006). First, a silica sol, the silica source of the matrix, was prepared by diluting a sodium silicate solution with distilled and deionized water, and subsequently exchanging the sodium cations in it with protons using a strong acid ion-exchange resin. To this sol, aluminium nitrate, the alumina source of the matrix, was added so that the Si/Al molar ratio in the resulting mixture would be 5. Next, potassium ferrocyanide, the ferrocyanide source of the PBA, was added so that the Fe^*/Si molar ratio in the resulting mixture would be either 0.040, 0.050 or 0.067 (Fe^* denotes that the origin of it is ferrocyanide). Then, a compound which can release a bivalent cation was added to insolubilize the dispersed ferrocyanide. The bivalent cations used in this work were Fe^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} , and the compounds used as their sources were iron(II) sulphate, nickel(II) nitrate, copper(II) chloride and zinc(II) nitrate, respectively. Then the mixtures were transferred to polypropylene tubes and were aged at 333 K. After the mixtures transformed into gels, the tubes including them were dipped into a liquid nitrogen bath at a constant rate of 6 cm h^{-1} , and the gels were froze unidirectionally. After the gels were completely frozen, they were thawed and then thoroughly washed with distilled and deionized water. Next the water in the gels was exchanged with 2-methyl-2-propanol and then the gels were freeze-dried. Finally, cylindrical monoliths were obtained.

The morphology of the samples was directly observed using a scanning electron microscope (SEM). Elemental analyses of the samples were conducted using an inductively coupled plasma spectrometer and a CHN coder. The samples were also analysed using an X-ray diffractometer (XRD) to confirm the existence of PBAs. The porous properties of the samples were evaluated through nitrogen adsorption experiments. First, nitrogen adsorption isotherms of the samples were measured at 77 K. Next, the Brunauer-Emmett-Teller surface areas (S_{BET}) of the samples were calculated from the obtained isotherms. The cesium capacity of the samples was evaluated by measuring their cesium adsorption isotherms. Experiments were conducted at 298 K using 1 mmol L^{-1} nitric acid containing cesium carbonate. Solutions containing the samples were shaken for 7 days before determining the cesium uptake. Cesium uptake (q) was calculated using the following equation:

$$q = (C_0 - C_e) V m^{-1} \quad (1)$$

where C_0 and C_e are respectively the initial and equilibrium concentration, V the volume of the solution and m the weight of the sample.

Next, the performance of the samples in flow systems was evaluated. The hydraulic resistance the samples cause was evaluated by measuring the pressure drop which occurs when water was passed through them. The diameter and length of the samples used in this experiment were 10 mm and 10 mm, respectively. Finally, the performance of the samples as cesium adsorbents was checked in a flow system. First, 1 mmol L^{-1} nitric acid containing cesium carbonate was prepared so that the Cs^+ concentration in it would be 100 ppm (C_f). The prepared solution was passed through the samples at a flow rate of 1 mL min^{-1} , and the Cs^+ concentration at the outlet of the samples (C) was monitored periodically using ion chromatography. The ratio of C to C_f (C/C_f) was plotted against the effluent volume. The diameter and length of the samples used in this experiment were 10 mm and 20 mm, respectively. Figure 1 shows the experimental apparatus used for the measurement of pressure drop and evaluation of adsorption performance in flow systems.

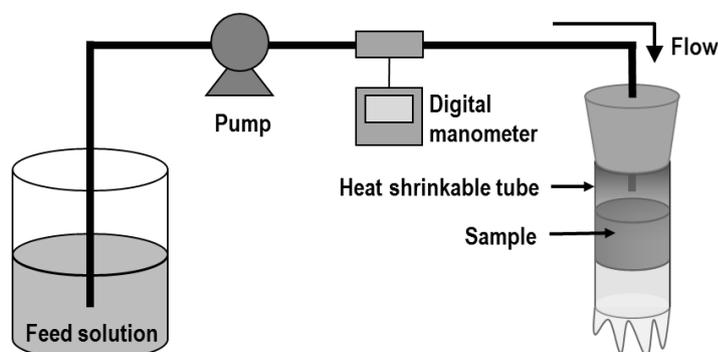


Figure 1: Experimental apparatus for flow systems

3. Results and discussion

Figure 2 shows photographs and cross sectional SEM images of typical samples obtained in this work. Basically, cylindrical samples show a characteristic color depending on the cation used for the insolubilization of ferrocyanide. Although the channels were slightly distorted, it was confirmed that the samples basically have a microhoneycomb structure, the average size of the channels being a few tens of μm . However, samples synthesized at high Fe^*/Si ratios tended to lack strength, and some of them collapsed even during analysis. Therefore, following studies were conducted using samples synthesized at a Fe^*/Si ratio of 0.050.

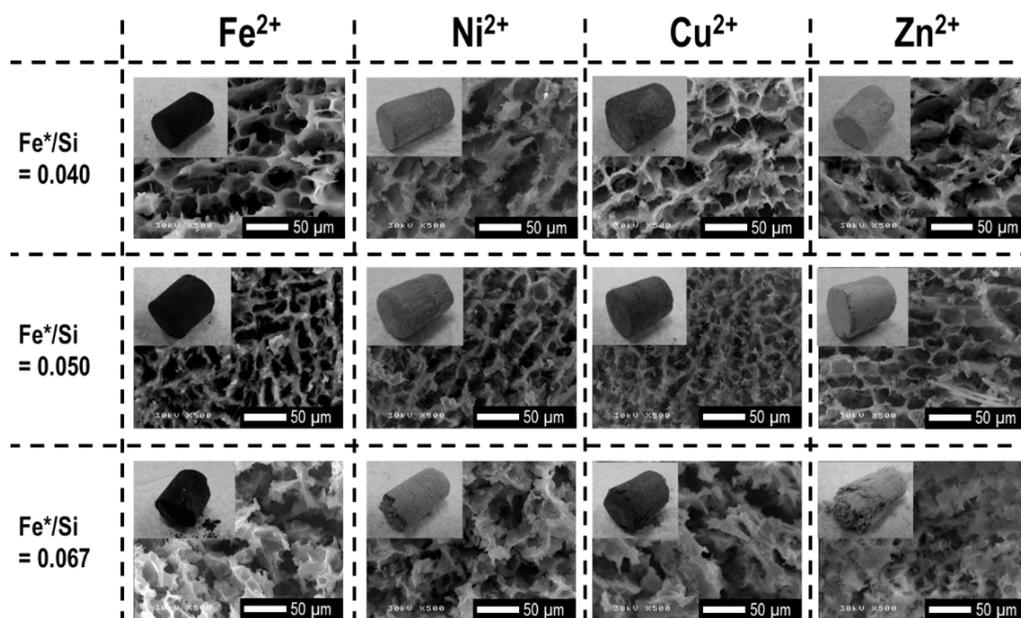


Figure 2: Photographs and cross sectional SEM images of typical samples obtained in this work

Next, the compositions of the PBAs included within the samples were verified through elemental analysis. Table 1 summarizes the results. If the desired PBAs were formed within the monolithic samples, the Fe^*/M and the $\{(\text{Fe}^*+\text{M})/2\}/(\text{N}/6)$ molar ratios should both be unity, where M ($= \text{Fe}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}$ and Zn^{2+}) denotes the amount of the cation used for insolubilization and N is amount of nitrogen atom in the sample. It was confirmed that values close to unity were achieved in all samples, indicating the high possibility of the formation of ideal PBAs in all of the samples.

Table 1. Elemental analysis results of the obtained samples

Atomic ratio	Ideal Ratio	$\text{M} = \text{Fe}^{2+}$	Ni^{2+}	Cu^{2+}	Zn^{2+}
Fe^*/M	1	1 ^a	0.93	0.97	1.02
$\{(\text{Fe}^*+\text{M})/2\}/(\text{N}/6)$	1	0.89	0.90	0.97	0.93

M : Amount of the cation used for insolubilization, Fe^* : Amount of Fe in the origin of it is ferrocyanide

^a Assumed value as Fe from iron sulphate cannot be distinguished from that from ferrocyanide

The structure of the particles included in the samples was checked using an XRD. Figure 3 shows XRD patterns of typical samples in which the ferrocyanide included in them was insolubilized using different cations. In the samples synthesized using Fe^{2+} , Ni^{2+} and Cu^{2+} for insolubilization, characteristic patterns of the corresponding PBAs were obtained, indicating the existence of the desired PBAs in them. However, this was not the case in samples synthesized using Zn^{2+} for insolubilization, which implies that either the desired PBA was not formed, or the formed PBA particles were too small to be detected. We will show later that the later seems to be the reason why Zn^{2+} based PBAs were not detected.

Next, the porous properties of the samples were evaluated through nitrogen adsorption experiments. A representative result is shown in Figure 4 where the nitrogen adsorption-desorption isotherm of a typical sample and S_{BET} derived from the isotherm is shown. Fe^{2+} was used to insolubilize the ferrocyanide in this sample. Those of a silica-alumina microhoneycomb synthesized without PBA inclusion, and of PBA particles alone is also shown for comparison. The PBA particles appeared to have a small amount of

mesopores, which is thought to actually be the pores naturally formed between the particles. On the other hand, monolithic silica-alumina microhoneycombs obtained through the Ice Templating method have developed micropores and mesopores. When PBAs were included into such microhoneycombs, a decrease in mesopore volume was observed, but the sample still showed high porosities, indicating that the accessibility to the surface of the PBA particles dispersed and immobilized in the microhoneycombs is high.

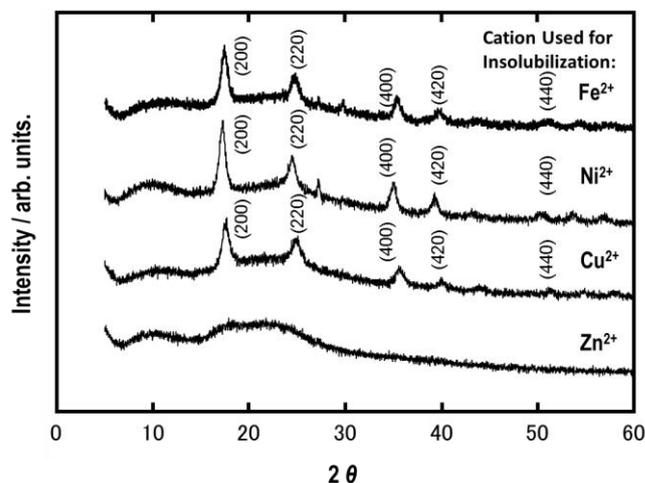


Figure 3: XRD patterns of typical samples obtained in this work

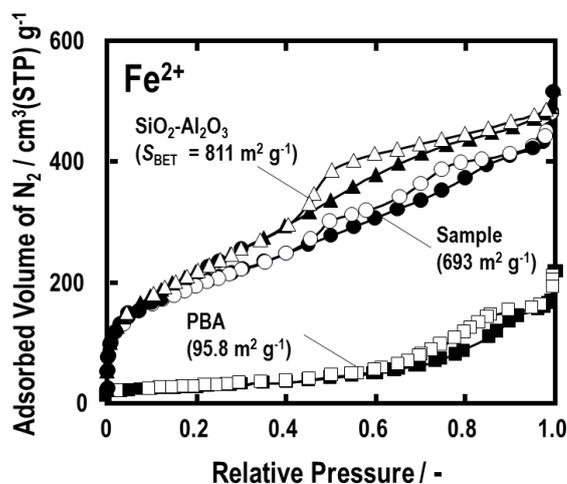


Figure 4: Nitrogen adsorption-desorption isotherms (77 K) of a typical sample insolubilized by Fe^{2+}

Figure 5 shows the cesium adsorption isotherms of samples, in which different cations were used to insolubilize the ferrocyanide included in them. It was confirmed that all of the samples possess a fairly high cesium capacity, even at low concentrations. Although the reason remains unclear at this moment, the samples synthesized using Cu^{2+} showed the highest capacity, followed by samples synthesized using Zn^{2+} , Ni^{2+} and Fe^{2+} as the metal cation for insolubilization. The theoretical ion exchange capacities of these samples, which were calculated using K^+ as the exchangeable ion, ranges from 0.843 to $0.846 \text{ mmol g}^{-1}$. The measured maximum capacity of the sample using Cu^{2+} for insolubilization was half of the theoretical value. The measured capacity was higher than the reported capacity of a similar sample synthesized using Cu^{2+} for insolubilization and polyethylenimine/silica as the matrix (0.15 mmol g^{-1}) (Bispo et al., 2002), but lower than that synthesized by using surface modification onto mesoporous silica (1.14 mmol g^{-1}) (Park et al., 2012). As Zn^{2+} -based materials also showed a high capacity, it seems safe to conclude that PBAs were also formed when Zn^{2+} was used for insolubilization.

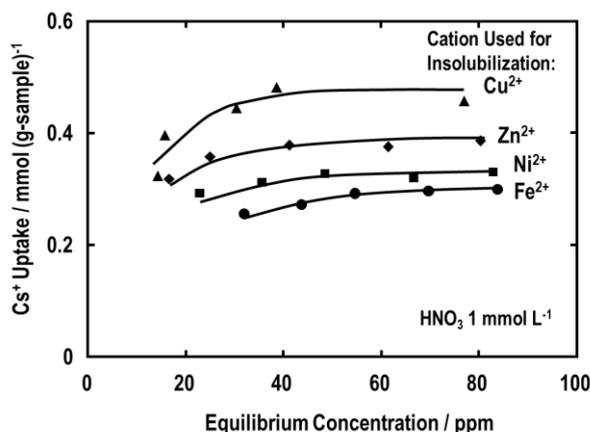


Figure 5: Cesium adsorption isotherms (298 K) of typical samples obtained in this work

Next we checked how the samples perform when they are used to recover cesium in flow systems. First, the hydraulic resistance the samples cause when water was passed through them was measured. A typical result is shown in Figure 6, where the measured pressure drop is plotted as a function of superficial velocity. It was confirmed that, as expected, the hydraulic resistance of the samples is quite low. The line in the same figure shows the predicted values of the pressure drop which occurs in a column which has the same inner diameter as the samples, and which is packed with the same amount of the same material as the samples in the form of particles. The values were predicted using the Kozeny-Carman (Carman 1937) equation assuming that the radius of the particles was 1.5 μm , same as the average diffusion path length in the microhoneycomb sample, and the void fraction of the column was 0.45, a value typical for a column packed with particles. The resistance particles having the same diffusion path lengths as the samples caused was 50-fold higher than the samples. Therefore, it was confirmed that a low hydraulic resistance and short diffusion paths are compatible in the samples synthesized in this work.

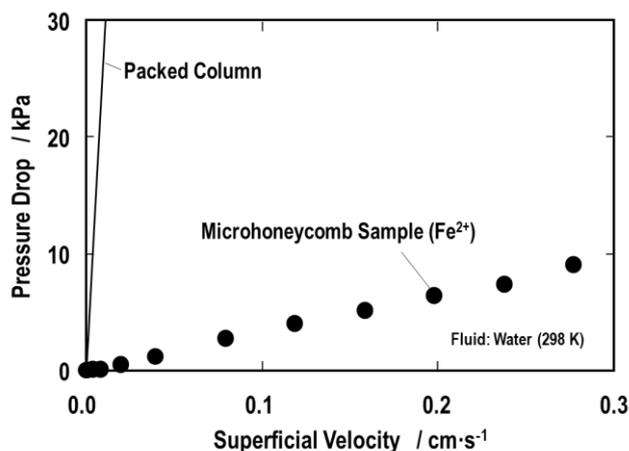


Figure 6: Hydraulic resistance of a typical sample insolubilized by Fe^{2+}

Finally, the performance of the samples as cesium adsorbents for flow systems was verified. Figure 7 shows a typical breakthrough curve of a typical sample obtained in this work. Cu^{2+} was used to insolubilize the ferrocyanide in this sample. Although the sample was short, a period of complete cesium removal was observed. Then the outlet cesium concentration started to gradually increase following a typical sigmoidal curve. From the results of this experiments, the length of the mass transfer zone of the cylindrical sample could be estimated to be about 10 mm. Due to the unique microhoneycomb morphology of the samples, this length can be maintained even when the diameter of the cylindrical sample is significantly increased, as long as the size of the channels and the superficial velocity of the fluid is the same. Therefore, such microhoneycombs are expected to be used as adsorbents for efficient cesium recovery in flow systems which require a high throughput.

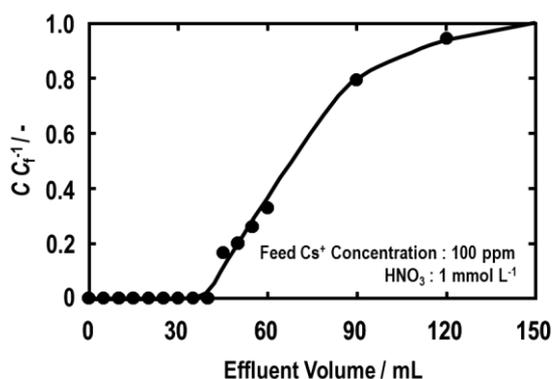


Figure 7: Breakthrough curve of a typical sample insolubilized by Fe^{2+}

4. Conclusion

In this work, cesium adsorbents were synthesized by immobilizing various PBAs in silica-alumina microhoneycombs using the Ice Templating method. Due to their unique morphology, the microhoneycombs were found to efficiently recover cesium from aqueous solutions without causing a severe hydraulic resistance. It was found that the hydraulic resistance the adsorbent causes can be reduced over 90 % by adopting a microhoneycomb morphology instead of a particle morphology. Therefore, the usage of such materials also leads to a significant decrease in the energy and operation costs required to use them. Such microhoneycomb materials have high potentials to be used not only as novel adsorbents, but also as catalysts or catalyst supporting materials for flow systems, especially when a high throughput is required.

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