Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary information

Crystal structure and Chemical bonding

From the results (Fig. S1 (a)) of XRD patterns of calcium alginate, CuHCF powder and MCBs. Alginate show the broaden peaks at 2θ values 13.4°, 22.1° and 39.1° were observed. This peaks almost not confirmed in the MCBs diffraction patterns. On the other hand, the main patterns in CuHCF powder and MCBs are consistent with $Cu_3[Fe(CN)_6]_2$ having a face centered cubic structure with space group $Fm\bar{3}m$. It indicate that the crystal structure of CuHCF was not changed from powder to MCBs. Additionally, the crystallite size of the CuHCF was calculated to ca. 40nm by the half maximum full-width of the main peak near 2θ=17.6º and 25.0º which corresponds to the (200) and (220) planes, using the Scherrer equation.

The Fourier transform infrared (FT-IR) spectra of the alginate, CuHCF powder and MCBs were measured and compared as shown in Fig. S1 (b). For CuHCF powder, the presence of Cu-N bonding in the structure of CuHCF is determined by the absorption peaks at around 492 cm^{-1}. The cyanide ligands is verified by the absorption peaks at 596 and 2102 cm^{-1} that correspond to the Fe-CN bending mode and cyanide stretching mode, respectively. A broad band of maximum at 3000-3400 cm^{-1} arises from the O-H stretching vibrations of water molecules and is accompanied by the deformation mode $\delta(H_2O)$ at 1610 cm^{-1}. In the case of alginate, observed bands in 1616 and 1419 cm^{-1} were attributed to asymmetric and symmetric stretching vibrations of carboxylate salt ion, respectively. The peaks of mannuronate of alginate appeared at 1200-1000 cm^{-1} which was attributed to the C-O stretching vibrations.

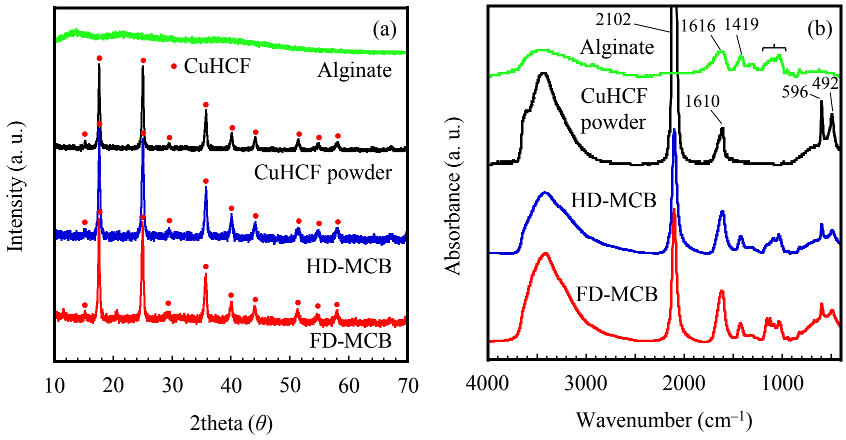

Fig. S1 X-ray diffraction patterns (a) and FT-IR spectra (b) of alginate, CuHCF powder and MCBs.

Porosity

To clarify the mechanism of the improvement of the Cs adsorption in the FD-MCB, the porosity in various scale were investigated for both MCBs by mercury intrusion porosimetry (MIP) that is widely used for characterizing pore volumes and sizes in porous materials. The pore size was calculated as a function of pressure using this equation:

$$D = \frac{-4\gamma cos\theta}{P}, \tag{1}$$

where D is the pore diameter (µm), P is the pressure, γ is the Hg surface tension (0.485 N/m) and θ is the contact angle between Hg and sample (140°).

Relationship between capillary pressure and pore size

The relationship between capillary pressure P_C and pore radius r (cm), that is given by

$$P_C = \frac{2\gamma cos\theta}{r}, \tag{2}$$

where P_C is capillary pressure (dynes/cm^2) of liquid, γ is surface tension (dynes/cm), θ is the contact angle (degrees) at which the liquid interface meets the solid surface.

Adsorption isotherm

For the evaluation of the maximum adsorption capacity (q_{max}) of the both MCBs, Cs adsorption experiments by shaker were carried out for 72 hours with various Cs concentrations. In order to calculate sorption capacity, Langmuir adsorption models have been used to describe the extraction of dissolved ions by a solid, all of which are based on the adsorption isotherms that quantify the species (Cs^+) adsorbed onto a solid (Q in mg/g) versus the concentration of the given species (Cs^+) remaining in solution at equilibrium (C in mg/L). The Langmuir model assumes that adsorption occurs at structurally homogeneous sites and all sorption sites are energetically identical:

$$Q = \frac{q_{max} K_L C_e}{1 - K_L C_e}, \tag{3}$$

where C_e is the Cs solution equilibrium concentration (mg/L) and Q is the amount of Cs sorbed per gram of CuHCF-MCB at equilibrium (mg/g). K_L is Langmuir equilibrium constant (L/g).

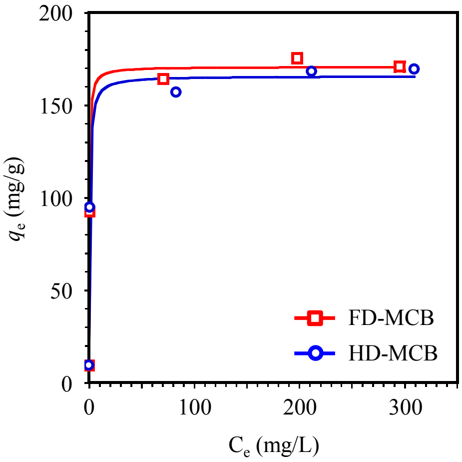

Fig. S2 Langmuir sorption isotherms of Cs ions of FD- and HD-MCB.

Adsorption kinetics

A pseudo-second order kinetic model is presented and discussed about adsorption rate using the shaking test data for 24 hours. The model is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}, \tag{4}$$

where q_e and q_t are the sorption capacities (mg/g) at equilibrium and at time t, respectively. K_2 is the rate constant of the pseudo second-order sorption process (g/mg·min). K_2 and q_e can be determined from the t/q_t versus t plot. (Figure 5 (b))

pH stability

For the pH stability, pH measurement was made with a Accumet Research AR 25 pH Meter (Fisher Scientific, USA). Total cyanide (TCN) concentration in the solution was examined on colorimetry with color reaction of 4-Pyrizine carboxylic acid-Pyrazolone method (WA-CN^{T}(L), KYORITSU CHEMICAL-CHECK Lab., Corp.). FD-MCB shows no deterioration in the pH dependence of Cs adsorption and the elution of CN^{-} ion elution, because the pH stability of products is quite important for practical applications. Although the detail of data is exhibited in Fig. S3 (a) and (b), few significant variations between FD- and HD-MCB were observed in these experiments. Both MCBs show good Cs adsorption capacity between pH 1–13, and the CN ion elution is lower than 0.5 mg/L between pH 3–10. It also indicating that the sorption capacity and CN ion elution were not so influenced by pore design using dry processes.

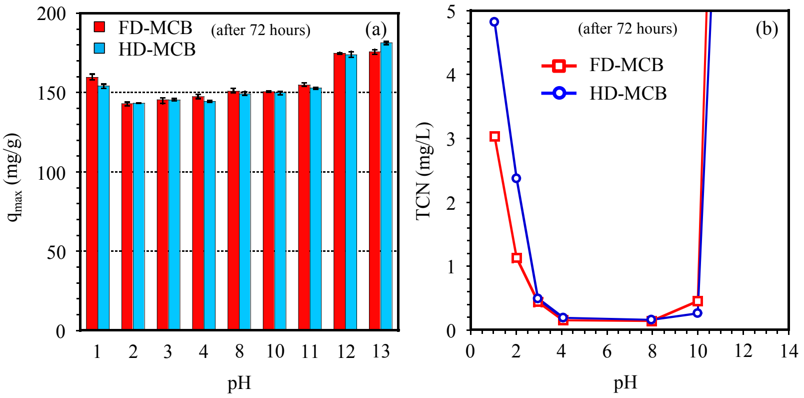

Fig. S3 Maximum adsorption capacity (a) and elution total cyanide (b) of FD- and HD-MCB at variety pH.