Supplementary information

Decontamination of very diluted Cs in seawater by a coagulation precipitation method using nanoparticle slurry of copper hexacyanoferrate

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1. Experimental procedures

1.1. Inductively coupled plasma mass spectrometry (ICP MS)

Inductively coupled plasma-mass spectrometry (ICP-MS) has been playing an increasingly important role in analytical laboratories owing to its capability of direct, simultaneous and multi-element trace analysis. The ICP-MS model used in this work is NexIon300D, Perkin Elmer, Inc., USA. The calibration curves of Cs⁺, Cu²⁺and Fe²⁺ showed excellent linearities with $R^2 > 0.99998$ for 10-fold diluted simulated seawater solution with 2% HNO₃ spiked with 20, 50, 100, 200, 500 and 1000 ng·L⁻¹ for Cs⁺ and 2, 10, 20, 50, 100 and 200 µg·L⁻¹ for Cu²⁺ and Fe²⁺, respectively. Cs analysis measurements was conducted using ICP-MS standard mode (STD). ICP-MS analysis for eluted ions in seawater with high dense concentration such as Na⁺, Mg⁺, Ca⁺, K⁺ and Cl⁻ is challenging due to the considerable influence of matrix elements in seawater. ICP-MS allows direct detection of eluted Cu²⁺and Fe^{2+} at the sub-µg·L⁻¹ level but spectral and non-spectral interferences caused by the seawater matrix elements limits direct determination by ICP-MS. Spectral interferences are caused by the presence of polyatomic species that interfere on the analyte masses. For example, copper has two stable isotopes Cu-63 and Cu-65 with relative abundances of 69.2 and 30.8%, respectively. The former nuclide (m/z= 62.93) is interfered with the polyatomic species 40 Ar²³Na on 63 Cu²⁺ of m/z= 62.95. The latter nuclide (m/z= 64.93) is interfered with 32 S¹⁶O₂ ¹H on Cu^{2+} of m/z= 64.97 which shows the apparent Cu concentrations of only 7% of the actual content of this element. Non-spectral interferences include signal suppression due to the influence of easily ionized matrix elements on the plasma (Na and K in particular) as well as signal drift caused by accumulation of salts on the cones and lenses of the ICP-MS. Simply diluting the seawater with 2% HNO₃ is a way of reducing the matrix effects. To overcome these interferences, He KED mode at a high flow rate of 4 was used to evaluate the eluted Cu²⁺ and Fe²⁺ after Cs adsorption test for quality control. High flow rate of He was recommended to

separate these interferences form the analyte peak or to remove low-molecular-weight species $(ArNa^{+} and PO_{2}^{+})$ that cause interference at m/e 63 exists in seawater.

2. Results and discussions



Figure S1. (A) XRD patterns and (B) FT-IR spectra in ambient air of the KCuHCF samples synthesized with the variation of R_{mix} using the micromixer at a flow rate of R_F = 200 mL·min⁻¹; (a & a-1) KCuHCF-0.49, (b & b-1) KCuHCF-0.42, (c & c-1) KCuHCF-0.35 and (d & d-1) KCuHCF-0.26 before and after Cs adsorption for 3 hours. The notation 'Si' indicates the diffraction peak corresponding to silicon powder mixed into the samples for the angle calibration.



Figure S2. Highly magnified SEM of KCuHCF-0.26 synthesized at synthesized with a micromixer technique at a flow rate of R_F = 200 mL·min⁻¹.



Figure S3. (a) The relation between x_{exp} and x_{obs} and (b) Relations among the factors, x, y, and z in chemical compositions of KCuHCF of x_{obs} = 0.49, 0.42, 0.35 and 0.26.

TG/DTA analysis to evaluate the interstitial water content

The interstitial water in the CuHCF lattice was evaluated from the following equation:

 $DTG = (TG_n - TG_{n-1})/(t_n - t_{n-1})$

T_{final}: final temperature of water loss

T_{final} equals the first point which DTG curve intersects with x-axis.

Tfinal= - (TG%-DTGtop x Ttop)/DTGtop



Figure S4. TG analysis for KCuHCF-NPs of x_{obs} = 0.49, 0.42, 0.35 and 0.26 under N₂ atmosphere at a flow rate of 5°·min⁻¹, and DTG analysis to evaluate the water content.

Table S1. Reynolds number (*R*e) of the KCuHCF-NPs of x_{obs} = 0.49, 0.42, 0.35 and 0.26 estimated at 21 °C and % R_h= 59%).

Samples	KCuHCF-0.49	KCuHCF-0.42	KCuHCF-0.35	KCuHCF-0.26
Flow rate (mL/min)	200	200	200	200
Hole diameter (µm)	150	150	150	150
Linear velocity (m/s)	188.72	188.72	188.72	188.72
Viscosity (mPa.s)	32.9	46.2	69.4	113
Re	6931.7	9733.89	14621.9	23808



Figure S5. (a) N₂ adsorption-desorption isotherms of KCuHCF-0.49 (black line), KCuHCF-0.42 (red line), KCuHCF-0.35 (blue line) and KCuHCF-0.26 (pink line) and (b) BET surface area dependence of chemical composition of KCuHCF with different vacancies.



Figure S6. Energy-dispersive X-ray (EDX) analysis of (a) KCuHCF-0.26 NPs, (b&c) KCuHCF-0.26 NPs after adsorption of Cs⁺ from Milli-Q water and seawater at Cs concentration of 300 mg·L⁻¹. The presence of small shoulder in EDX analysis of seawater indicates the presence of the coexistent Na ions exchangeable with K in KCuHCF-0.26.



Figure S7. Atomic ratios among metal elements of KCuHCF-0.26 NPs before and after Cs^+ adsorption in Milli-Q water and simulated seawater analysed by SEM-EDX (initial conc. Cs^+ is 300 mg·L⁻¹).



Figure S8. Coagulation and filtration experiment of KCuHCF-0.26 flocs through mesh filter (50 μ m). The KCuHCF-.026 slurry is a water-dispersed brown ink converts into KCuHCF-0.26 greenish flocs due to formation of Prussian blue after addition of flocculating agent Fe²⁺ followed by coagulation with polymolecular organic material B-2133.

Table S2. The concentrations of the eluted Cu^{2+} , Fe^{2+} and CN^- at solution to adsorbent ratio 10,000 of the KCuHCF-0.49, KCuHCF-0.42, KCuHCF-0.35 and KCuHCF-0.26 compared with standard values in seawater according to the Japanese Standard Regulations (national minimum effluent standards) after 1 hr of Cs adsorption test and filtration with 50 µm mesh filter. The concentration of polymolecular organic material coagulant (B-2133) is fixed to 20 mg·L⁻¹.

Samples	Inorganic	Concentration in the effluent			Standard value by		
	flocculant	$(mg \cdot L^{-1})$			Japanese law (mg·L ⁻¹)		
	FeSO ₄ .7H ₂ O	Cu ²⁺	Fe ²⁺	CN-	Cu ²⁺	Fe ²⁺	CN-
	$(mg \cdot L^{-1})$						
CuHCF-0.49	10	0.0187	1.108	< 0.01	3.0	10.0	1.00
CuHCF-0.42	10	0.0209	1.456	0.034			
CuHCF0.35	20	0.0219	1.682	0.021			
CuHCF-0.26	20	0.0217	2.985	0.190			



Figure S9. Elution of Cu^{2+} in the effluent after 3 hours of Cs adsorption by KCuHCF-0.26 (Cs⁺= 10 μ g·L⁻¹). The estimated Cu²⁺ concentration in seawater only is ~15 μ g·L⁻¹.



Figure S10. Adsorption efficiency of KCuHCF-NPs of x_{obs} = 0.49, 0.42, 0.35 and 0.26 for Cs⁺ in seawater after 10 min of test.