

**Amino-functionalized magnetic chitosan beads to enhance
immobilization of potassium copper hexacyanoferrate for
selective Cs⁺ removal and facile recovery**

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1 Experimental

1.1 Chemicals

Chitosan (high molecular weight, 310,000-375,000 Da, >75% deacetylated), iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), potassium hexacyanoferrate ($\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$, $\geq 99.5\%$), and untreated seawater were purchased from Sigma-Aldrich. Acetic acid (99.7% (m/m)) and sodium hydroxide (NaOH) were acquired from JUNSEI. Methyl acrylate and cesium chloride (CsCl, 99.9%) were ordered from Alfa Aesar. Diethylenetriamine (DETA) and methanol were obtained from Daejung Chemicals and Metals Ltd. Copper (II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and hydrochloric acid (HCl) were commercially available from KANTO Chemical Co. Inc. and the OCI Company, respectively. Milli-Q deionized (DI) water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) was used for solution preparation.

1.2 Fabrication of the magnetic nanoparticle-containing chitosan beads (MC)

The magnetic nanoparticle-containing chitosan beads (MC) were prepared by a previously reported co-precipitation method.¹

Typically, 1.5 g of chitosan, 0.25 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 0.65 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved into 88 mL of acetic acid solution (4.2% (v/v)) at 30 °C. The solution was transferred into a syringe and slowly dropped into 3.4 mol L⁻¹ NaOH solution using a syringe pump. When the prepared solution was dropped into the NaOH solution, black beads were immediately formed, indicating the successful synthesis of the MC. Then, the beads were retained in the NaOH

solution at room temperature for 24 h and collected by a permanent magnet. The recovered beads were thoroughly washed with DI water followed by freeze-drying.

2 Characterization

2.1 Physicochemical characterization

The surface morphology of the beads was studied using a scanning electron microscope (SEM, Hitachi SU 8230 at 2-5 kV) coupled with an energy dispersive X-ray (EDS) spectrometer. Thermogravimetric analysis (TGA, TG209 F1 Libra) was conducted under a nitrogen atmosphere with a heating rate of 10 °C min⁻¹. The magnetic property was analyzed by a vibrating sample magnetometer (VSM, MPMS3-Evercool) at room temperature with an applied field between -20,000 and 20,000 Oe.

The X-ray diffraction (XRD, SmartLab, RIGAKU) peaks were analyzed with Cu K α radiation for a scanning range of 10° - 80° (2θ), and X-ray photoelectron spectroscopy (XPS) was conducted by K-alpha (Thermo Fisher Scientific). Fourier-transform infrared (FT-IR, Nicolet iS50, Thermo Fisher Scientific Instrument) spectra were obtained on an attenuated total reflectance (ATR) crystal in a range of frequency from 400 to 4,000 cm⁻¹. The inorganic composition of the beads was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent ICP-OES 720, Agilent) after the dissolution of the beads in a mixture of nitric acid (HNO₃) and hydrochloric acid (HCl).

2.2 Cs⁺ adsorption experiment

The effect of the adsorbent dose on the removal efficiency and adsorbed amounts was investigated for a HMC amount that ranged from 0.25 to 4 g L⁻¹ in DI water with a Cs⁺ concentration at 10 mg L⁻¹.

The pH stability of the HMC was also evaluated by immersing the HMC in a Cs⁺ solution ($C_0 = 9.69 \text{ mg L}^{-1}$) with a contact time of 24 h with a pH range of 4 to 12, in which m/V is equal to 1 g L⁻¹ (m (g) is the mass of the dried adsorbent, and V (L) is the volume of the Cs⁺ solution.). The pH of the Cs⁺ solution was determined by a digital pH meter (Mettler Toledo S220, Swiss).

To evaluate the reusability of the HMC, the adsorption process was repeated five times without the regeneration of the adsorbent in seawater ($m/V = 4 \text{ g L}^{-1}$; $C_0 = 0.86 \text{ mg L}^{-1}$). After 12 h of shaking at 200 rpm, the solution was extracted, and the concentration was measured by an ICP-MS, and the spent adsorbent was collected by a magnet to be reused for the next cycle.

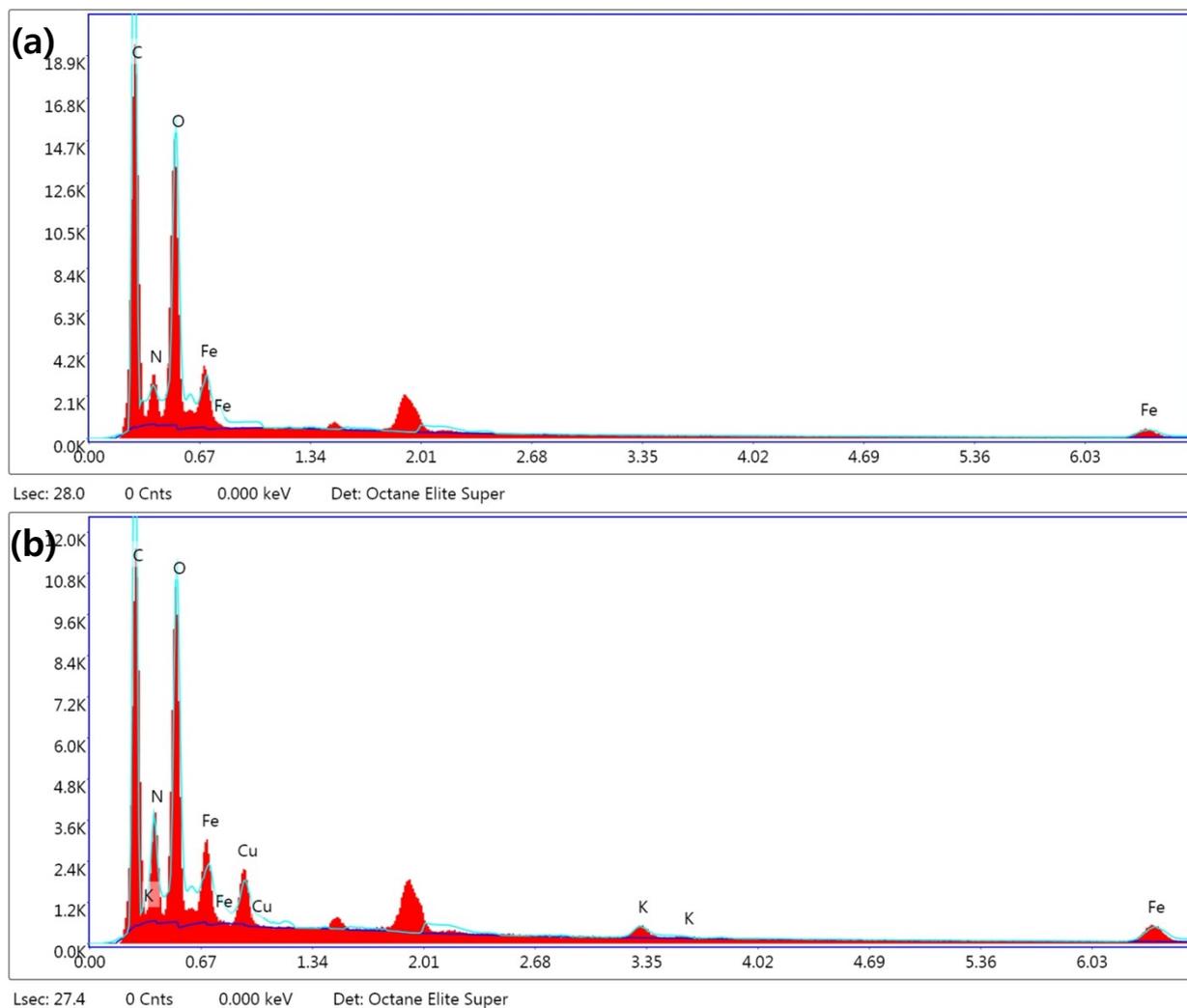


Fig. S1 The atomic compositions of the (a) MC and (b) HMC measured by SEM-EDS.

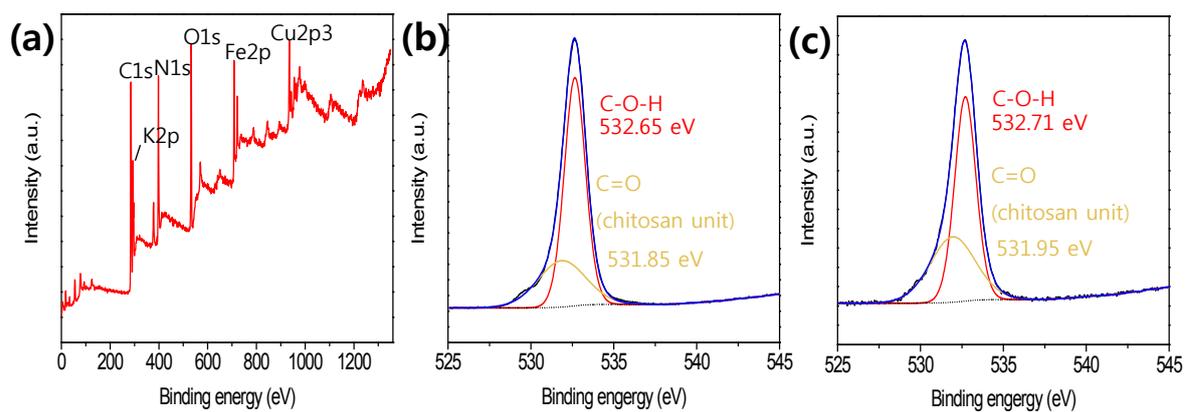


Fig. S2 The full range XPS spectrum of the (a) HMC, and the O 1s spectra of the (b) MC and (c) HMC.

Table S1 Concentration of coexisting cations in seawater.

	Na ⁺ (mg L ⁻¹)	K ⁺ (mg L ⁻¹)	Ca ²⁺ (mg L ⁻¹)	Mg ²⁺ (mg L ⁻¹)
Seawater	8247	286	179	1246

Reference

1. H. V. Tran, L. D. Tran and T. N. Nguyen, *Materials Science and Engineering: C*, 2010, **30**, 304-310.