# Electrochemical Removal of Cobalt Ions from Aqueous Solution via Capacitive Deionization System

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#### 1. Introduction

Cobalt (Co), as a heavy metal, has been widely used in industrial fields such as cobalt-based alloys, cemented carbide, magnetic materials, and electronics [1]. Also, along with iron, nickel, chromium, and copper, it is used as a material for facilities in contact with coolants in nuclear power plants. However, cobalt exposed to a high-temperature and high-pressure environment during the operation of a nuclear power plant reacts with water or dissolved oxygen to form corrosion products, forming a chalk river unidentified deposit (CRUD) on coolant pipelines along with radioactive materials from nuclear fuel. form The oxide film is mainly composed of nickel, iron, cobalt, etc. [2], and is a factor that reduces the heat transfer efficiency required for cooling. In addition, cobalt present in the oxide film is Co-60, which mainly emits radiation, and causes an increase in radiation exposure of workers. Efficient management is essential for reducing the volume of radioactive liquid waste. However, the conventional evaporation treatment process requires sequential treatment facilities and operations such as an evaporator, a heater, and a condenser for the treatment of radioactive liquid waste, and additional energy is required for rapid evaporation.

Therefore, in this study, the applicability of the electrochemical method using capacitive deionization (CDI) is considered as a method of removing cobalt from wastewater generated from nuclear power plants and reducing the volume of waste.

### 2. Experimental

# 2.1 Preparation of AC and CuHCF

The commercial activated carbon (AC, P-60) powders were obtained from Kuraray Chemical Co.(Japan). The CuHCF powders were prepared through a facile wet-chemical synthetic method. 100 mL deionized (DI) water of 30 mM CuNO<sub>3</sub>· $3H_2O$  and 100 mL DI water of 20 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>] were mixed with vigorous stirring for 6 h. The obtained solution was aged for 18 h and then washed three times with DI water. The precipitates were collected by centrifugation at 4000 rpm, and then dried for 24 h at 70 °C under vacuum conditions.

#### 2.2 Structural characterization

X-ray diffraction (XRD, X-pert PRO MRD, Philips) was conducted with Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å) from 10° to 90° at a scan rate of 2° min<sup>-1</sup> over the 2 $\theta$ . The morphology of powders was analyzed by field emission scanning electron microscope (FE-SEM, Thermoscientific Cios2). Fourier transform infrared (FT-IR) measurement was carried out at room

temperature in the range of 4000 ~ 400 cm<sup>-1</sup> using a VERTEX 80 v (Bruker). The specific surface area and pore volume were determined by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analysis using N<sub>2</sub> adsorption-desorption isotherms at -196 °C, respectively (Trista II 3020).

### 2.3 Electrochemical characterization of the electrodes

To evaluate the electrochemical properties of the both electrodes, we performed a cyclic voltammetry (CV) test with a three-electrode system in a 0.5 M CoSO<sub>4</sub> solution. A platinum rod and a saturated Ag/AgCl (3 M KCl) electrode were utilized as a counter and reference electrode, respectively.

# 2.4 CDI device assembling and performance test

Deionization experiments were performed by the batch type in a flow-by mode. The CDI cell was constructed with a target cathode, a AC anode, and an anion-exchange membrane (AEM, NEOSEPTA ASE) placed adjacent to the anode. Each electrode pair was separated by a spacer (100 mesh, NBC PP) with a thickness 200  $\mu$ m in order to prevent short-circuiting. Moreover, the spacer was also used as a flow channel for the influent water within the CDI cell.

# 3. Results and discussion

Fig. 1(a) shows the XRD patterns of the AC and CuHCF powders. Activated carbon show broad peaks around 23° and 43°, which correspond (100) and (101) Bragg reflections, respectively. All diffractive peaks well match with a cubic structure (JCPDS No. 86–0513) without any other impurities. The open framework structure of CuHCF with wide ion transport channels are able to host  $Co^{2+}$  ions.

The specific surface area (S<sub>BET</sub>) was analyzed from the nitrogen adsorption/desorption isotherms of AC and CuHCF powders (Fig. 1(b), Table 1). The results showed a specific surface area of 1250.27 mg<sup>2</sup> g<sup>-1</sup> with a pore size distribution of about 1.77 nm for AC. It also showed a specific volume of 73.68 mg<sup>2</sup> g<sup>-1</sup> with a pore size distribution of about 6.75 nm for CuHCF.



Fig. 1. XRD patterns (a) and Nitrogen adsorption/ desorption isotherms (b) of AC and CuHCF powders.

Table 1 Physical properties of AC and CuHCF powders

Sample	S <sub>BET</sub> ( m <sup>2</sup> g <sup>-1</sup> )	V <sub>total</sub> (cm <sup>3</sup> g <sup>-1</sup> )	d <sub>BJH</sub> (nm)
Activated carbon (AC)	1250.2739	0.554364	1.77358
CuHCF	73.6838	0.124304	6.74799

Cyclic voltammetry (CV) was conducted to characterize the electrochemical properties of both electrodes. Fig. 2 shows the CV curves of the AC and the CuHCF at a scan rate of 1 mV s<sup>-1</sup>. The CV curve of AC represents the shape of an electric double layer capacitor is close to a rectangle, differing from CuHCF where two pair of sharp redox peaks were obviously observed. The reversible redox reaction during insertion/extraction of  $Co^{2+}$  ions with CuHCF is proposed as follows:

$$Cu_{3}^{II}[Fe^{III}(CN)_{6}]_{2} + Co^{2+} + 2e^{-}$$
  
↔ CoCu\_{3}^{I}[Fe^{II}(CN)\_{6}]\_{2} (1)



Fig. 2. CV curves of AC and CuHCF electrodes at a scan rate of 1 mV  $S^{\text{-1}}$  in 0.5 M CoSO4 aqueous solution.

Fig. 3 represents the deionization capacities and charge efficiencies of AC and CuHCF electrode in different  $Co^{2+}$  ions concentrations, respectively. Fig. 3

represents the deionization capacities and charge efficiencies of AC and CuHCF electrode in different  $Co^{2+}$  ions concentrations, respectively. The deionization capacities of the  $Co^{2+}$  ions for the AC electrode in 20 and 50 mg- $Co^{2+}$  L<sup>-1</sup> aqueous solution were 48.8 and 55.5 mg g<sup>-1</sup>, respectively, and the corresponding charge efficiencies ( $\Lambda$ ) were 0.34 and 0.41, respectively. The deionization capacities of  $Co^{2+}$  L<sup>-1</sup> aqueous solution were 141.62 and 50 mg- $Co^{2+}$  L<sup>-1</sup> aqueous solution were 141.62 and 156.85 mg g<sup>-1</sup>, respectively, and the corresponding charge efficiencies ( $\Lambda$ ) were 0.55 and 0.68, respectively.



Fig. 3. Deionization capacity and charge efficiency of AC and CuHCF electrodes under different  $Co^{2+}$  ion concentrations at 1.2 V applied voltage.

Fig. 4(a) and (b) illustrate the surface morphology of the AC electrode before and after the electrosorption of  $Co^{2+}$  ions, respectively. The surface morphology of AC shows uneven cavities and fine open pores (Fig. 4(a)). Fig. 4(b) shows the morphologies of the layered and porous structure, indicating that on the AC electrode,  $Co(OH)_2$  were grown preferentially along the layered plane to form a two-dimensional nanostructure. The inset FT-IR results are consistent with  $Co(OH)_2$ . The peak at 630 cm<sup>-1</sup> is attributed to the Co-OH stretching vibration, and the peak in the range of 1400–1500 cm<sup>-1</sup> corresponds to the bending vibration of the adsorbed water molecules.

The SEM images of the CuHCF electrode before and after electrosorption are shown Fig. 4(c) and (d), respectively. In the CuHCF electrode, granular nano-aggregates with a diameter of about 100  $\mu$ m were observed (Fig. 4(c)). After electrosorption, the morphology was similar to that of the initial electrode. Therefore, the CuHCF materials did not suffer from severe dissolution and corrosion, suggesting that it was excellent in removing Co<sup>2+</sup> ions from the aqueous solution.



Fig. 4. Morphologies of pristine for AC electrode (a) and CuHCF electrode (c), and after the electrosorption of cobalt ions for AC electrode (b) and CuHCF electrode (d). FT-IR spectrum is present in the inset of figure (b).

# 4. Acknowledgemnets

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### 5. Conclusions

This study showed that  $Co^{2+}$  ions could be removed efficiently in aqueous solutions using AC and CuHCF electrodes. It was revealed experimentally that for the AC electrode, cobalt ions are removed by the electric double layer on the surface, and for the CuHCF electrode, cobalt ions are removed by insertion into the lattice. The CuHCF electrode showed higher deionization capacity and charging efficiency than the AC electrode. Our study reveals the potential of CuHCF electrodes as a promising technology for the removal of  $Co^{2+}$  from wastewater.

## REFERENCES

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