Improvement of the Cobalt ion Adsorption Performance of δ-MnO_2 Nano particle through Aging Optimization

Hye Jin Jang, Ji Chan Kim, Sung Oh Cho*
Dept. of Nuclear & Quantum Engineering, Korea Advanced Institute of Science & Technology, Daejeon, Republic of Korea, 34141
**Corresponding author: socho@kaist.ac.kr*

Keywords : δ-MnO_2, Aging Effect, Cobalt Removal, Adsorption, CVCS

1. Introduction

Cobalt ions generated from corrosion in nuclear reactor primary systems are activated into radioisotopes such as ^{60}Co, increasing radiation levels in the Chemical and Volume Control System (CVCS). Layered δ-MnO_2 is a promising adsorbent due to its high surface area and strong affinity toward divalent metal ions. This study investigates the effect of aging time (0, 6, 12, 24 h) on structural evolution and Co^{2+} removal performance.

.

2. Method

2.1 Synthesis of δ-MnO_2 Nanoparticle

δ-MnO_2 nanoparticles were synthesized via a controlled redox precipitation method under ambient pressure conditions. Potassium permanganate ($KMnO_4$) was used as the manganese precursor, and a reducing agent was introduced to induce the formation of layered manganese dioxide.

In a typical synthesis, an aqueous $KMnO_4$ solution was prepared using deionized water (resistivity ≥ 18.2 MΩ·cm). Under continuous magnetic stirring, the reducing agent solution was slowly added dropwise into the $KMnO_4$ solution to initiate the redox reaction. Upon addition, the solution immediately turned dark brown, indicating the formation of MnO_2 precipitates. The reaction mixture was further stirred to ensure homogeneous nucleation and particle growth.

After completion of the reduction reaction, the suspension was subjected to thermal aging at **60 °C** for different durations (0, 6, 12, and 24 h). The aging process was carried out in a temperature-controlled water bath while maintaining mild magnetic stirring to prevent sedimentation. The elevated aging temperature was selected to promote structural rearrangement, crystallization, and stabilization of the layered δ-MnO_2 phase.

Following the aging treatment, the precipitates were collected by vacuum filtration and repeatedly washed with deionized water to remove residual ions and by-products. The filtered solids were dried in a convection oven at 60 °C for 12 h. The dried materials were gently ground into fine powders using an agate mortar and pestle and stored in airtight containers prior to characterization and adsorption experiments.

The crystalline structure of the synthesized samples was analyzed by X-ray diffraction (XRD), while the morphology and nanosheet structure were examined using transmission electron microscopy (TEM). The specific surface area and textural properties were evaluated by nitrogen adsorption–desorption isotherms (BET method), and surface charge characteristics were determined via zeta potential measurements. In addition, the cobalt ion concentration was quantified using inductively coupled plasma (ICP) analysis.

2.2 Batch Adsorption Experiments

Batch adsorption experiments were conducted to evaluate the cobalt ion (Co^{2+}) removal performance of δ-MnO_2 samples aged for different durations.

A stock solution of cobalt was prepared by dissolving cobalt chloride ($CoCl_2 \cdot xH_2O$) in deionized water. Working solutions with an initial concentration of **50 mg/L** were obtained by appropriate dilution. All adsorption experiments were performed at room temperature (25 ± 2 °C).

For each experiment, **0.3 g** of δ-MnO_2 powder was added to **100 mL** of the cobalt solution in a glass beaker. The suspension was magnetically stirred at a constant speed to ensure uniform dispersion of the adsorbent particles and to minimize external mass transfer limitations.

At predetermined time intervals, aliquots of the suspension were withdrawn and immediately filtered through a 0.22 μm membrane filter to remove suspended solids. The residual cobalt concentration in the filtrate was quantified using inductively coupled plasma optical emission spectroscopy (ICP-OES).

The removal efficiency (R, %) was calculated according to:

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100$$

where C_0 is the initial cobalt concentration (mg/L) and C_t is the concentration at time t.

All experiments were conducted at least in duplicate to ensure reproducibility, and average values were reported. The influence of thermal aging time on adsorption kinetics and equilibrium removal efficiency was systematically evaluated and correlated with structural evolution and surface properties of δ-MnO_2.

3. Results

3.1 Cobalt Adsorption Capacity Results

3.1.1. BET Analysis

BET analysis (Fig. 1) shows that the specific surface area increases from 0 h to 6–12 h and then decreases at 24 h. The 6–12 h aged samples exhibit the highest adsorption volume, indicating enhanced surface area development at intermediate aging times. This behavior is attributed to increased edge exposure of nanosheets at moderate aging, followed by restacking and aggregation at longer aging times.

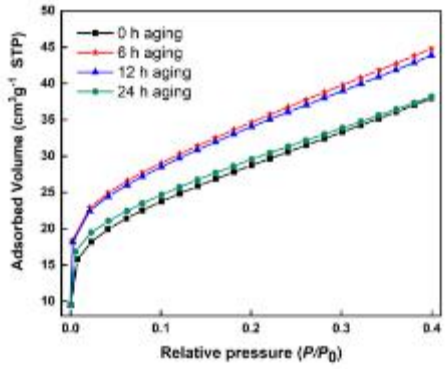

Figure . N_2 Adsorption isotherms of delta-MnO_2 aged for 0-24 h

Aging time	BET(m^2/g)
0 h	104.78
6 h	125.20
12 h	123.20
24 h	107.13

3.1.2 XRD Analysis

XRD patterns (Fig. 2) confirm that all samples maintain the layered δ-MnO_2 structure without phase transformation. However, peak sharpening with increasing aging time indicates enhanced crystallinity and improved layer stacking order.

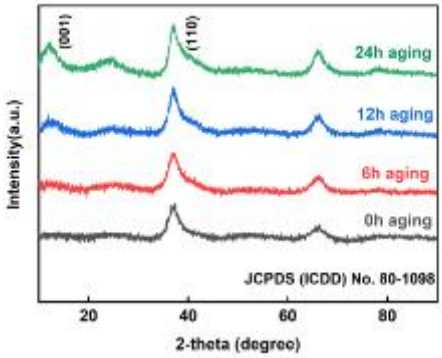

Figure . XRD patterns of dleta-MnO_2 as a function of aging time

3.1.3 Zeta potential

Zeta potential results (Fig. 3) show that the surface charge becomes progressively more negative with increasing aging time. This trend is attributed to the deprotonation of surface hydroxyl groups (Mn–OH → $Mn–O^-$), leading to an increase in negatively charged sites. As a result, the electrostatic attraction between the δ-MnO_2 surface and Co^{2+} ions is enhanced.

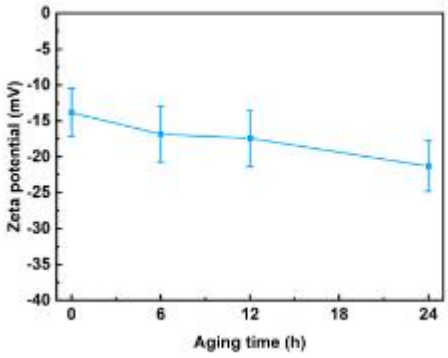

Figure . Zeta potential variation with aging time

3.1.4 TEM analysis

TEM images(Figure 4) show the structural evolution of δ-MnO_2 nanosheets with increasing aging time. The 0 h sample exhibits aggregated and disordered nanosheets. At 6–12 h, more defined nanosheet structures with increased edge exposure are observed. In contrast, the 24 h sample shows pronounced restacking and aggregation, indicating reduced accessible surface area due to structural densification.

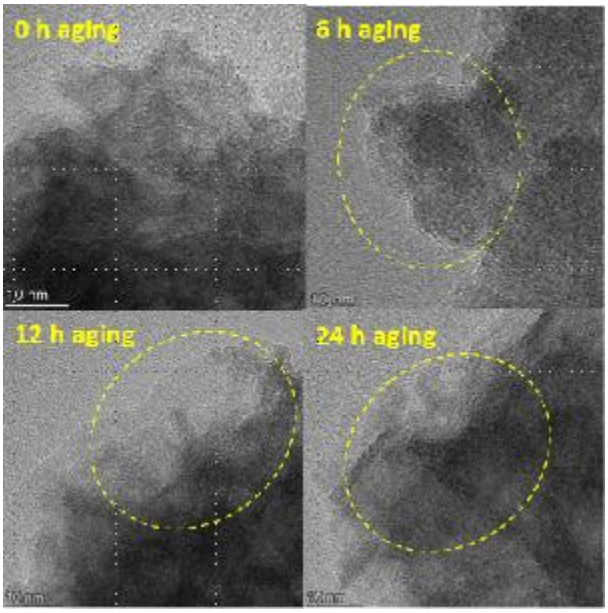

Figure 4. TEM images of δ-MnO_2 nanosheets as a function of aging time (0–24 h)

3.1.5 ICP Analysis

The effect of contact time on Co^{2+} removal efficiency is shown in Fig. 5. All samples exhibit rapid adsorption within the initial stage, followed by a plateau indicating equilibrium. The 12 h aged sample shows the highest removal efficiency over the entire time range, suggesting superior adsorption performance. This behavior indicates that adsorption is dominated by fast surface reactions in the initial stage, followed by gradual diffusion-controlled processes.

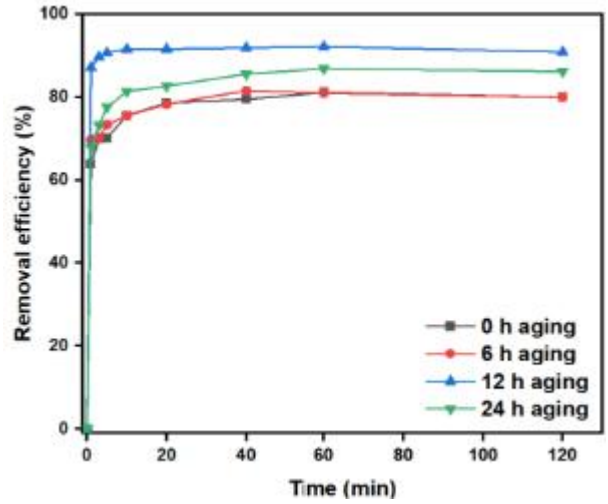

Figure 5. Effect of Adsorption time on Co^{2+} removal efficiency of δ-MnO_2 with different aging times

Fig. 6 shows the effect of initial Co^{2+} concentration on removal efficiency. As the initial concentration increases, the removal efficiency decreases for all samples due to the saturation of available adsorption sites. Among the samples, the 12 h aged δ-MnO_2 consistently exhibits the highest removal efficiency, indicating an optimal balance between surface properties and available active sites.

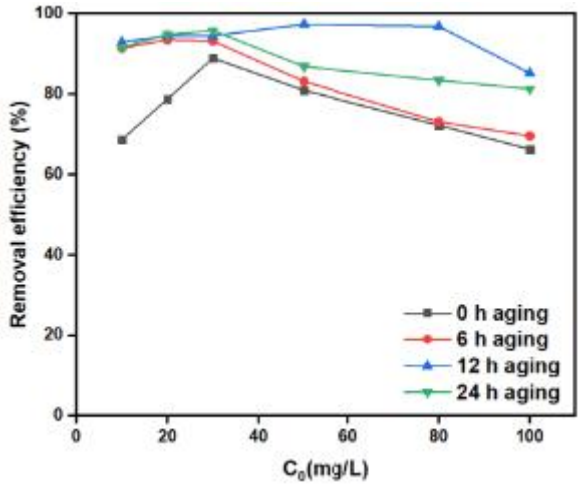

Figure 6. Effect of initial Co^{2+} concentration on removal efficiency of δ-MnO_2

The effect of solution pH on Co^{2+} removal efficiency is presented in Fig. 7. The removal efficiency increases with pH and reaches a maximum around neutral conditions. At low pH, competition between H^+ ions and Co^{2+} reduces adsorption efficiency, while at higher pH, enhanced electrostatic attraction between negatively charged δ-MnO_2 and Co^{2+} ions improves removal performance.

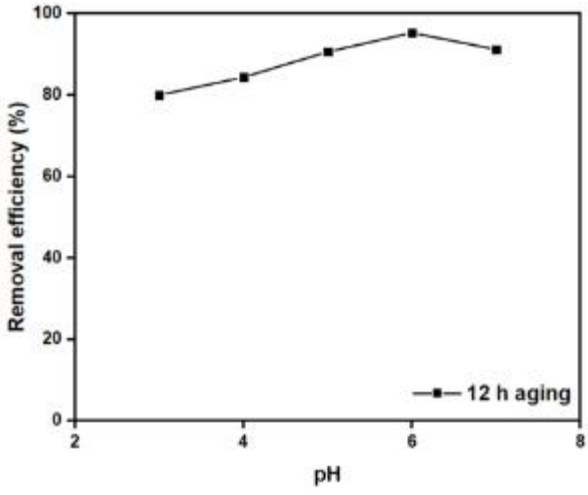

Figure 7. Effect of pH on Co^{2+} removal efficiency using 12 h aged δ-MnO_2

4. Conclusions

In this study, the effect of aging time on the structural and adsorption properties of δ-MnO_2 was systematically

investigated. The results show that moderate aging (12 h) provides the optimal balance between surface area, surface charge, and structural stability, leading to the highest Co^{2+} removal performance. Excessive aging induces restacking and reduces accessible active sites. These findings demonstrate that aging is a critical parameter for optimizing MnO_2-based adsorbents for cobalt removal.