Fabrication and Cs Removal Performance of Various Metal-ferrocyanide Functionalized Magnetic Adsorbents

Kyu Sun Hwang, Chan Woo Park, In-Ho Yoon, Kune-Woo Lee, and Hee-Man Yang*

Korea Atomic Energy Research Institute, 111, Daedeok-daero 989beon-gil, Yuseong-gu, Daejeon, Republic of Korea

*hmyang@kaeri.re.kr

1. Introduction

A huge amount of radioactive contaminants have leaked and spread over a large area of soil and water from the nuclear accident sites at Fukushima Daiichi nuclear power station in 2011.

Radioactive cesium (^{137}Cs) is the most dangerous radioactive contaminant associated with nuclear fall out and radioactive liquid waste due to its long half-life (30.2 years), high-energy gamma ray (γ-ray) emissions, and biological interactions, which are similar to those of potassium [1].

A variety of cesium adsorbents, including zeolites, ammonium molybdophosphate (AMP), silicotitanate (CST), and metal-ferrocyanide were extensively investigated for their ability to remove radioactive cesium from water [2].

Metal-ferrocyanide; such as iron ferrocyanide (prussian blue) is known as a low cost adsorbent which has a high selectivity for cesium and high stability for decomposition. However, very fine powder forms of metal-ferrocyanide are difficult to collect the adsorbents used after applying them into the environment [3].

In the present study, metal-ferrocyanide functionalized magnetic nanoclusters were fabricated for the removal of cesium and rapid magnetic separation of absorbent from contaminated water.

2. Materials and methods

2.1 Fabrication of magnetic adsorbents

The procedure used to synthesize the MFC-MNCs (M = Co, Ni, Cu) for the removal of Cs is illustrated in Fig. 1. First, the as-synthesized magnetic nanoclusters (MNCs) were synthesized via a hydrothermal reaction in the presence of succinic acid (SA), 1,6-Hexanediamine (HMD), and citric acid (CA) as a capping ligand. Naming the SA-MNCs, HMD-MNCs, and CA-MNCs, respectively.

Succinic acid (SA) with the carboxylate have strong coordinative affinity towards metal ions. In case of SA-MNCs, the negatively charged carboxylate ions. These carboxylate ions capture the toxic metal ions by forming chelate complexes.

Polyethyleneimine (PEI) was employed as a foundation material to functionalize the surfaces of the HMD-MNCs and CA-MNCs with CuFC due to the outstanding adsorption properties of PEI toward heavy metals, such as Cu ions.

After immobilizing the MFC onto the SA-MNCs and PEI-MNCs surfaces, we conducted adsorption tests using inactive and radioactive cesium (^{137}Cs) to evaluate their cesium removal performance.

2.2 Characterization of magnetic adsorbents

The fabricated CoFC-MNCs, NiFC-MNCs, CuFC-MNCs-1, and CuFC-MNCs-2 were characterized by X-ray diffractometer (XRD), Fourier transform infrared spectroscopy (FTIR), Transmission electron microscopy (TEM), and Dynamic light scattering instrument (DLS), vibrating sample magnetometer (VSM).

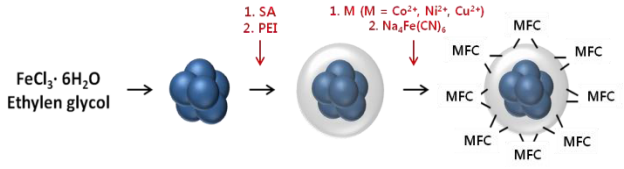

Fig. 1. Synthesis of magnetic adsorbents for the removal of cesium.

3. Results and Discussion

The crystalline structure of the MCNs was determined by XRD, as shown in Fig. 2. The XRD analysis revealed six characteristic peaks at 2θ = 30.1, 35.5, 43.1 53.4, 57.0, and 62.6°, corresponding to the (220), (311), (400), (422), (511), and (440) phases of Fe_3O_4, respectively, indicating that the magnetic

nanoclusters consisted of a Fe_3O_4 phase. The peaks in the XRD results confirmed that the Fe_3O_4 in the SA-MNCs, HMD-MNCs, and CA-MNCs had a high crystallinity.

FTIR analysis also revealed the successful coating of CoFC, NiFC, and CuFC onto the MNCs surfaces. As shown in Fig. 3, a strong absorption peak corresponding to the cyanide groups of hexacynoferrate appeared at 2100 cm^{-1} in the FTIR spectra, indicating that the CoFC-MNCs, NiFC-MNCs, CuFC-MNCs-1, and CuFC-MNCs-2 were successfully functionalized with MFC.

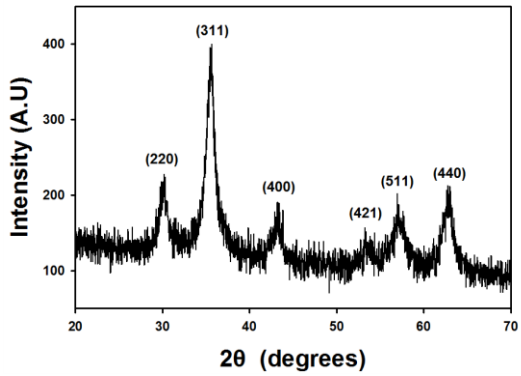

Fig. 2. XRD patterns obtained from the MNCs.

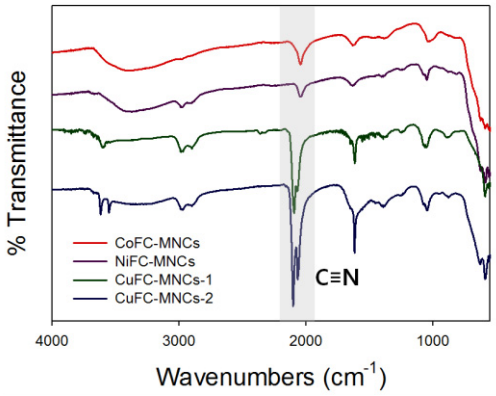

Fig. 3. FTIR spectra of the MFC-MNCs.

The Cs removal performance of the MFC-MNCs were evaluated by measuring the adsorption isotherms using inactive Cs. The experimental isotherm data were analyzed as Langmuir isotherm (Fig. 4). The excellent fit to the Langmuir isotherm curve suggested monolayer adsorption of Cs onto the MFC-MNCs surfaces. The maximum adsorption capacity (q_{max}) of the adsorbents were 15.63 mg/g (CoFC-MNCs), 12.11 mg/g (NiFC-MNCs), 125 mg/g (CuFC-MNCs-1), and 166.7 mg/g (CuFC-MNCs-2), respectively

The MFC-MNCs provided a high removal efficiency exceeding 99.09% of the ^{137}Cs.

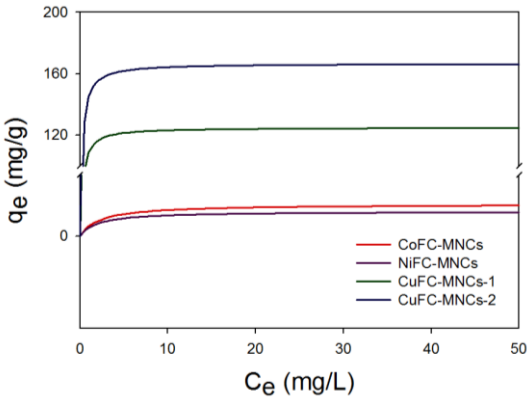

Fig. 4. Adsorption isotherm data obtained from the MFC-MNCs. The curve fits were obtained from the Langmuir isotherm.

4. Conclusions

In this study, we successfully fabricated metal-ferrocyanide modified magnetic nanoclusters (MFC-MNCs). The MFC-MNCs exhibited high removal efficiency of cesium in water and showed rapid magnetic separation of the adsorbents from the water after treatment. They have great potential for the treatment of liquid waste containing radioactive cesium (^{137}Cs). The magnetic adsorbents can be easily recovered once spread into an open environment.

REFERENCES

[1] Brumfiel G, "Fukushima set for epic clean-up", Nature, 472, 146-147 (2011).

[2] E.H.Borai, R.Harjula, L.Malinen and A.Paajanen, “Efficient removal of cesium form low-level radioactive liquid waste using natural and impregnated zeolite minerals”, J. Hazard. Mater, 172(1), 416-422 (2009).

[3] P .A. Hass, “A review of information on ferrocyanide solid for removal of cesium from solutions”, Sep. Sci. Technol, 28, 2479-2506 (1993).