

Copper ferrocyanide functionalized magnetic nanoparticles using polyelectrolyte for the removal of cesium

Hee-Man Yang*, Kune woo Lee, Bum-Kyoung Seo, Jei Kwon Moon

*Decontamination & Decommissioning Research Division, Korea Atomic Energy Research Institute, Yuseong-gu,
Daejeon 305-353, Republic of Korea*

**Corresponding author: hmyang@kaeri.re.kr*

1. Introduction

Magnetic nanoadsorbents composed of a magnetic particles core and functional shell, which adsorb the contaminants, has attracted significant attention in environmental remediation owing to their high surface area and unique superparamagnetism [1].

Since the nuclear accident at the Fukushima Daiichi nuclear power station in 2011, a huge amount of radioactive contaminants has been released into the environment. Among the various radioactive contaminants, cesium (Cs)-137 (^{137}Cs) is the most apprehensive element owing to its long half-life (30.2 years), high solubility in water, and strong radiation emission in the form of gamma rays (γ -rays).

Various methods such as ion exchange solvent extraction and precipitation are applied for the remediation of Cs-137 contaminated water [2]. In particular, metal ferrocyanides show a high selectivity toward Cs-137 [3]. However, the very fine powder form of metal ferrocyanide causes a difficult separation from water through filtration.

In the present study, magnetite nanoparticles were coated with copper ferrocyanide for the adsorption of radioactive Cs-137 in an aqueous solution through the grafting of polyethyleneimine. We describe the morphology, structure, and physical property of these nanoparticles. In addition, their ability to eliminate Cs-137 from water was also evaluated.

2. Methods and Results

The magnetite nanocrystals (MNCs) were synthesized using a modification of the method reported by Wan et al. 1 g of iron (III) acetylacetonate and 60 mL triethylene glycol were mixed, and the mixture was heated to reflux (275 °C) for 3 h under nitrogen. During this time, citric acid was dissolved in mixture of distilled water and triethyl glycol. At the end of the heating, this mixture was injected into the flask and then the system was cooled to room temperature. Excess ethyl acetate was used to wash the reactant using a magnetic separator.

100 mg of the magnetic nanoparticles (MNPs) were dispersed into water, then the nanoparticles solution and 10 wt% of polyethyleneimine in aqueous solution was mixed under sonification. The polyethyleneimine coated magnetic nanoparticles were magnetically collected,

washed with excess water, and dried. Next, 100 mg of the modified particles were dissolved in 20 mL of distilled water. This suspension was stirred for 6 h after the addition of 2 mmol of CuCl_2 . The Cu incorporated particles (Cu-MNPs) were washed with water several times, and dried. The Cu-MNPs (100 mg) were functionalized by shaking with a 20 mL solution of 0.25 M $\text{Na}_4\text{Fe}(\text{CN})_6$. The Cu and ferrocyanide incorporated nanoparticles (Cu-FC-MNPs) were washed with water several times, and dried [4,5].

3. Results

The Iron oxide nanocrystals were synthesized by a non-aqueous hydrothermal methods based on the treatment of iron (III) acetylacetonate in triethylene glycol. The as-synthesized nanocrystal were coated with citric acid to avoid the aggregation of magnetic nanoparticles. The citric acid works as a stabilizer. The citric acid coated nanocrystals were dispersible and stable in aqueous solution. However they don't have any interaction with copper ferrocyanide that can adsorb the cesium. For the contaminated water treatment application, surface modification of magnetite nanocrystals is essential to make them cesium adsorbent.

Polyethyleneimine was used to modify the surface of the nanocrystals through an electrostatic attachment of positively charged polymer on the surface of negatively charged magnetic nanoparticles, simultaneously providing surface ethylenediamine (EDA) groups for further incorporation of Cu and ferrocyanide (FC). Polyethyleneimine has excellent chelating capability for transition metal cations, making it very useful as a foundation upon which to build a metal-ferrocyanide complex [4].

To confirm the surface modification of citric acid coated magnetic nanoparticles, an FTIR spectrum of the polyethyleneimine coated magnetite nanoparticles (PEI-MNPs) was obtained. The surface of the magnetite nanocrystals was successfully coated with the polyethyleneimine. In addition, the PEI-MNPs also are stable in water. The average size distribution of the PEI-MNPs determined by dynamic light scattering was 331.8 ± 17.9 nm (Fig. 1). The zeta-potential value of the PEI-MNPs was $+48.4 \pm 0.6$ mV in water. This is attributed to the amine groups in PEI, which are present on the surface of the nanoparticles.

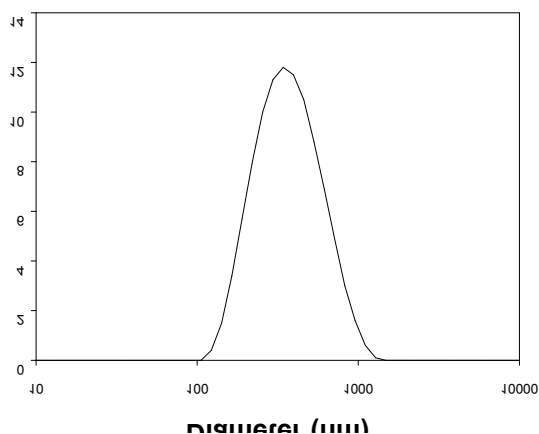


Fig. 1. Average size of Cu-FC-MNPs measured by the dynamic light scattering in aqueous solution.

In the next step, PEI-MNPs were further functionalized with Cu and ferrocyanide. Ethylenediamine(EDA) in PEI formed a Cu-(EDA)₃ complex by bonding with Cu ions. Then, ferrocyanide was immobilized on the surface of the MNPs by bonding with Cu [5]. The FTIR spectra of the Cu-FC-MNPs also showed the successful immobilization of Cu and FC (Fig. 2). A strong absorption peak of cyanide groups appears at 2050 cm⁻¹ in Cu-FC-MNPs. Therefore, it was concluded that the surface of the magnetite nanoparticles was successfully functionalized with ferrocyanide.

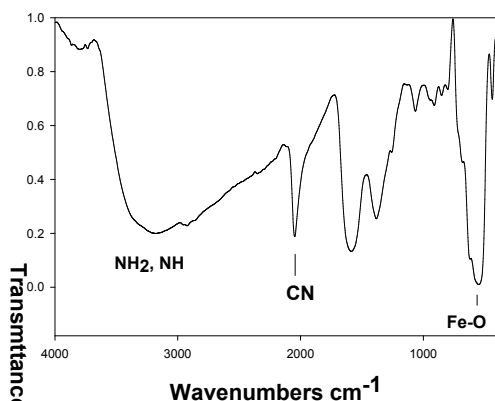


Fig. 2. FTIR spectra of copper ferrocyanide functionalized magnetic nanoparticles using polyethyleneimine.

Next, the Cs removal efficiency of the Cu-FC-MNPs was examined. Various concentrations of the Cu-FC-MNPs were mixed with an aqueous solution containing Cs. The Cu-FC-MNPs exhibited good removal efficiency even at lower concentrations.

4. Conclusions

In this study, we fabricated copper ferrocyanide immobilized magnetite nanoparticles using polyethyleneimine polyelectrolyte containing

ethylenediamine groups. The Cu-FC-MNPs have a diameter of 330 nm, exhibited easy separation ability from water by an external magnet, and showed a high removal efficiency of cesium in aqueous solutions. Therefore, the Cu-FC-MNPs demonstrated good potential for the treatment of water contaminated with radioactive cesium.

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