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Nano-Fe/Cu particles for the remediation of cesium contaminated solutions

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Abstract: *The great East Japan Earthquake in 2011 triggered the Fukushima Daiichi nuclear power plant accident. Large amount of cesium was released into the environment following this severe accident. Therefore, this research work evaluated the applicability of nano-Fe/Cu particles for the removal of cesium from contaminated waters for the first time. Cesium removal was investigated using batch technique with respect to initial cesium concentration, contact time, temperature, pH, competing cations and dosage of nanoparticles. The results showed that nano-Fe/Cu particles demonstrated effective performance for removal of cesium. The removal efficiency exceeded 99% at initial cesium concentration of 1 mg/L and 1 g/L dose. The removal of cesium was largely depending on the solution pH and temperature. The current study proved the potential utility of the nano-Fe/Cu particles as a promising adsorbent for the treatment of waters containing cesium.*

Keywords: Fukushima; Cesium; Treatment; Nano-Fe/Cu particles.

1. INTRODUCTION

The Great East Japan Earthquake and tsunami on 11 March 2011 severely damaged the Fukushima Daiichi nuclear plant. A very large amount of radioactive nuclides was vented into the atmosphere and subsequently caused serious radioactive contamination of the water sources over a wide region of Fukushima and neighboring prefectures [1, 2]. Radioactive cesium (^{137}Cs) is the most dangerous radioactive contaminant associated with nuclear fallout and radioactive liquid waste due to its long half-life (about 30 years) and high-energy gamma ray emissions [3]. The primary pathway of radiocesium in food chain is water; therefore its separation from the radioactive waters is important. Up to now, removal of extremely dangerous ^{137}Cs was an unresolved problem. Different Cs adsorbents, including zeolite, bentonite and aluminum molybdophosphate, were intensively applied for their ability to remove ^{137}Cs from radioactive wastes [4, 5]. However, these adsorbents were not easily collected from the environment after use. Recently, magnetic nanoparticles were extensively investigated for use in different fields, including magnetic fluids, catalysts, biotechnology and biomedical fields [6, 7]. Magnetic nanoparticles were widely analyzed for environmental treatment applications due to their high surface area to volume ratio and their ability to be separated from medium after remediation process via magnetic attraction by applying an external magnet [8].

Faghihian et al. [9] prepared a magnetic zeolite composite through the co-precipitation of Fe^{2+} and Fe^{3+} ions in the presence of zeolite and the composite was evaluated for Cs^+ and Sr^{2+} removal from aqueous solutions. Yamaguchi et al. [10] reported a carbon- γ - Fe_2O_3 nanoparticle composite for the removal radioactive material emitted after the accident at Fukushima Daiichi nuclear power plant. Hwang et al. [11] fabricated sodium-copper hexacyanoferrate-magnetic nanoparticles for the efficient removal of Cs followed by magnetic separation of the nanoparticles from water. Hong et al. [12] synthesized a highly stable 98%, Sigma-Aldrich Inc., USA) and

alginate/ Fe_3O_4 composite for Sr removal from seawater. Moamen et al. [13] examined the feasibility of using magnetic nano zeolite for the sorption of Cs and Sr ions existing in the liquid radioactive waste.

So far, nanoscale zero valent iron (nZVI) has been shown to be effective remediator of a broad range of contaminants including organic and inorganic anions [14]. It was recognized to be effective in the remediation of halogenated organic compounds, As, Cr, Pb, Cu, Zn, nitrate and phosphate [15-17]. In addition, the efficiency of nZVI to remove radionuclides was reported previously in batch experiments in many studies [18-20]. Unfortunately, nZVI suffers aggregation and consequently, decreases their efficiency by reducing surface area. To resolve this problem, a number of techniques have been developed to enhance the performance of nZVI such as synthesis of bimetallic particles. In the bimetallic system, coating nZVI using another metal such as Pd, Ni, Cu, Pt and Ag has been to be effective in the removal of a variety of contaminants [17, 21]. The improved reactivity in the bimetallic nanoparticles is attributed to catalytic hydrogenation and electrochemical effects [22].

In the work described here, the capability of nano-Fe/Cu particles for the Cs^+ removal from aqueous solutions was examined. The adsorption studies were performed using a batch technique to assess the effect of several parameters, including initial cesium concentration, contact time, pH, temperature, competing cations and dosage of nanoparticles. To the best of our knowledge, this research is the first study that investigated the feasibility of nano-Fe/Cu particles for the removal of cesium from contaminated waters.

2. MATERIALS AND METHODS

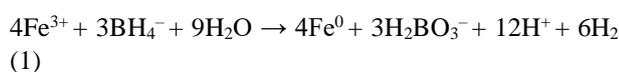
2.1. Chemicals

Cesium chloride (CsCl , 99.9%, Wako Co., Japan) was used for preparation of the stock solution. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99%, Junsei Chemical Co., Japan), sodium borohydride (NaBH_4 ,

anhydrous copper chloride (CuCl_2 , 99.9%, Aldrich Inc., USA) were purchased for nanoparticles synthesis. Sodium chloride (NaCl , 99.5%, Wako Co., Japan), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 97%, Wako Co., Japan), potassium chloride (KCl , 99%, Wako Co., Japan) and calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 70–79%, Junsei Chemical Co., Japan) were used to prepare simulated contaminated aqueous solutions. Hydrochloric acid (HCl , 35–37%, Wako Co., Japan) and sodium hydroxide (NaOH , >93%, Wako Co., Japan) were used for pH adjustment. All chemicals were of analytical grade and used as received without further purification. In all experiments, deionized degassed water was used for the preparation of solutions.

2.2. Nano-Fe/Cu particles synthesis

Nano-Fe/Cu particles were synthesized based on chemical reduction of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ using NaBH_4 as shown in the following reaction equation:



Briefly, 0.74 M of NaBH_4 solution was added slowly into 0.15 M of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution at a 1 L/h rate using a roller pump. The mixture was vigorously stirred at 400 rpm under constant temperature of 30 ± 0.5 °C. The synthesis was left 5 min as aging time in order to complete the reaction. The black solid products were washed with deionized degassed water three times and then filtered by vacuum filtration. Afterwards, the prepared nanomaterials were applied in batch experiments. The CuCl_2 was added to $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ before injecting NaBH_4 . According to Khalil et al. [23], the optimum coating ratio was 5% wt/wt of CuCl_2/Fe .

2.3. Batch studies

The adsorption behavior of Cs onto nano-Fe/Cu particles were investigated using batch technique at 298 K. 50 mL of 100 mg/L Cs^+ solution was contacted with 1 g of nano-Fe/Cu particles and placed on a magnetic stirrer at 1000 rpm (RSH-6DN, As One Co., Japan) for 120 min. At the end of the experiments, samples were collected and filtered using 0.22 μm syringe filters. Cs concentration in the filtrate was determined using inductively coupled plasma mass spectrometry (ICP-MS, model: ICPM-8500, Shimadzu Co.). To investigate the effect of pH on the adsorption process, the initial pH of the solutions was adjusted at 3–12 using 0.1 HCl and 2 M NaOH. To study the effect of nanoparticles content on Cs^+ removal, various solid to liquid ratios from 1 to 30 g/L were assessed. In order to investigate the effect of temperature on the adsorption capacity, four different temperatures from 298 to 343 K were evaluated. For kinetic experiments, the capacity of the nanoparticles was measured at different initial Cs^+ concentrations (50, 100, 150 and 200 mg/L) for different period of time (5–120 min). To examine the effect of competing cations, four simulated wastewaters were made in the presence of Na^+ , K^+ , Mg^{2+} and Ca^{2+} .

3. Results and discussion

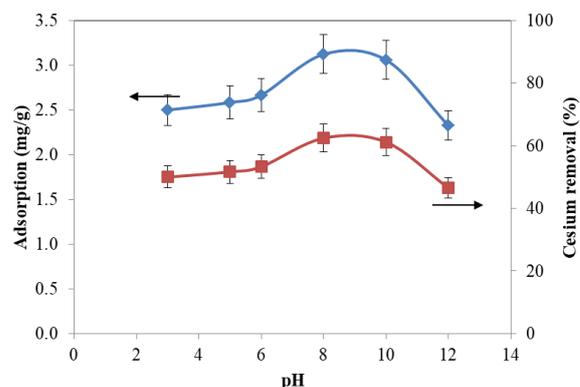


Fig. 1. Effect of pH on Cs^+ sorption by nano-Fe/Cu particles.

3.1. Effect of pH

The effect of pH on Cs^+ removal by nano-Fe/Cu particles was examined over a pH range of 3 to 12 and the results are shown in Fig. 1. It was observed that the amount of adsorbed Cs^+ increased with increase in the initial pH. The sorption amount of Cs^+ onto nano-Fe/Cu particles was 2.50 mg/g with background pH 3 and the Cs^+ removal was only 49.99%. When the initial pH was 8, the adsorption capacity of Cs^+ increased to 3.12 mg/g with 62.46% removal. At higher pH values, Cs^+ removal decreased to only 46.50% and the adsorption capacity was 2.33 mg/g, respectively. In the acidic medium, the adsorption of Cs^+ was inhibited due to the presence of H^+ ions competing with Cs^+ ions for the exchange sites of the nanoparticles [24]. The removal of Cs^+ decreased rapidly in strong alkaline environments due to the formation of Fe (oxy)hydroxide precipitates on the active sites of nano-Fe/Cu particles [25]. The maximum removal was observed at pH 8.

3.2. Effect of initial Cs^+ concentration and contact time

The effect of contact time on the amount of Cs^+ sorbed onto nano-Fe/Cu particles was studied at 298 K and different initial concentrations of 50, 100, 150 and 200 mg/L and the results are displayed in Fig. 2. The sorption process sharply increased with time and the sorption amount increased with the increase of the initial Cs concentration. This may be due to the higher possibility of collision between Cs^+ ions and the nano-Fe/Cu particles at higher concentrations [26]. The uptake of Cs^+ increased with time attaining an equilibrium value in about 10 min. This could be attributed to addition of Cu^{2+} ions to nZVI particles that decreases the agglomeration and aggregation and increases the surface area of these nanoparticles. As can be seen in Fig. 2, the equilibrium time was independent of the initial concentration. The values of Cs^+ removal at 50, 100, 150 and 200 mg/L were 53.36%, 53.33%, 47.67% and 48.22%, respectively.

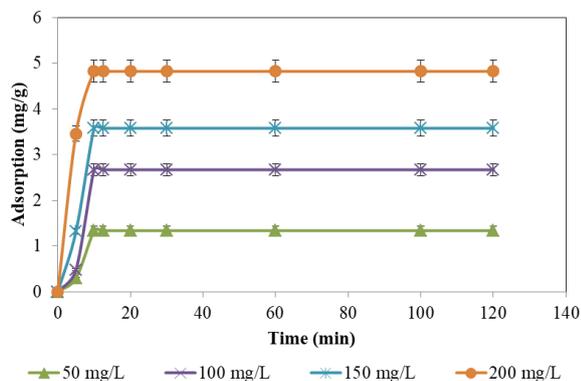


Fig. 2. Effect of initial concentration and contact time on Cs⁺ sorption by nano-Fe/Cu particles.

3.3. Effect of temperature

The adsorption removal of Cs⁺ onto nano-Fe/Cu particles was tested at four different temperatures of 298, 313, 328 and 343 K (Fig. 3). The adsorption amount of Cs⁺ decreased with increasing temperature, indicating that nano-Fe/Cu particles were favored for Cs⁺ adsorption at lower temperatures. The adsorption capacity of Cs⁺ at 298, 313, 328 and 343 K was 2.67, 2.58, 2.23 and 1.76 mg/g and the removal efficiency was 53.33%, 51.64%, 44.65% and 35.24%, respectively. Greater adsorption of Ba²⁺ on nZVI with decreasing temperature has previously been reported [27].

3.4. Amount of nanoparticles effect

The removal of Cs⁺ by the nano-Fe/Cu particles was investigated at different dosages (1–30 g/L) of nanoparticles at initial Cs⁺ concentration of 100 mg/L. As illustrated in Fig. 4, Cs⁺ removal increased with increasing amount of the nanocomposites from 1 g/L to 30 g/L because more active sites were available to adsorb more Cs⁺. The maximum uptake was achieved at 30 g/L. The values of maximum Cs⁺ adsorption at 1, 5, 10, 20 and 30 g/L doses of nano-Fe/Cu particles were 31.63, 17.39, 8.84, 4.73, 2.67 and 1.94 mg/g and the removal was 31.63%, 34.77%, 44.20%, 47.34%, 53.33% and 58.30%, respectively.

3.5. Effect of competing cations

The Cs⁺ adsorption by nano-Fe/Cu particles was tested in the presence of different competing cations at 298 K and initial pH of 6 (Fig. 5). Four simulated liquid waste were prepared separately in the presence of Na⁺, K⁺, Mg²⁺ and Ca²⁺ at similar concentration (20 mg/L) with 100 mg/L of Cs⁺ concentration.

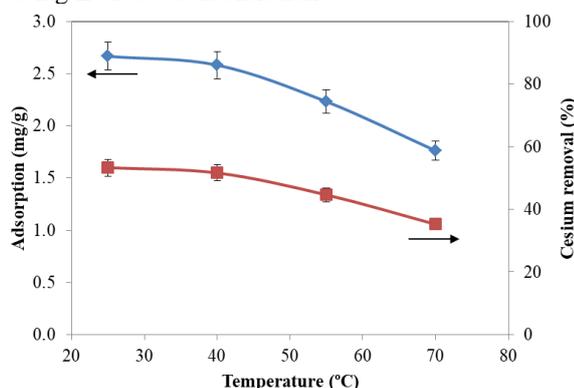


Fig. 3. Effect of temperature on Cs⁺ sorption by nano-Fe/Cu particles.

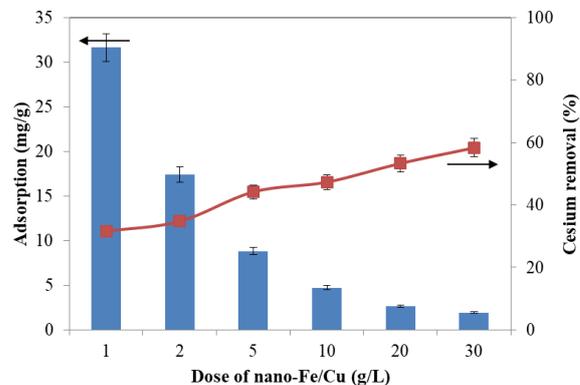


Fig. 4. Cs⁺ removal by different dosage of nano-Fe/Cu particles.

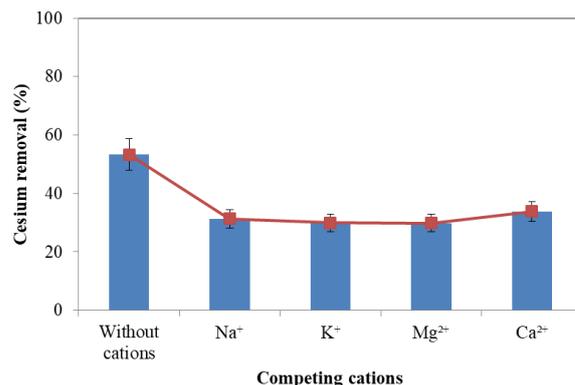


Fig. 5. Effect of different competing cation ions on Cs⁺ removal by nano-Fe/Cu particles.

It is clear that Cs⁺ removal was highly inhibited in the presence of the competing cations. These results suggested that the cation ions could lower and compete the adsorption of Cs⁺ ions.

4. Conclusion

This work investigates the efficiency of nano-Fe/Cu particles for Cs⁺ removal from waters. Nano-Fe/Cu particles showed effective performance for Cs⁺ removal. The obtained results also demonstrated that the Cs⁺ adsorption rate of nano-Fe/Cu particles was much faster than that of nZVI. In emergencies, nano-Fe/Cu particles offer a much faster method in the remediation of radioactive wastes. Solution pH is an important factor affecting adsorption of Cs⁺. Lower temperatures are favorable for improved removal of Cs⁺. These results indicated that nano-Fe/Cu particles could be used as an efficient adsorbent for removal of Cs⁺ from nuclear wastewaters.

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