

Evaluation of nanoscale zero valent iron particles for the removal of cesium from aqueous solutions

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Abstract. The great East Japan Earthquake occurred in 2011 and seriously damaged Fukushima Daiichi Nuclear Power Plant. Large amounts of cesium was released into the environment following this accident. Therefore, this study for the first time assessed the applicability of nanoscale zero valent iron (nZVI) for the removal of cesium from aqueous solutions. The removal of cesium was investigated in a batch system with respect to initial cesium concentration, contact time, pH, temperature, competing cations and dosage of nanoparticles. The obtained results showed that nZVI displayed 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 work proved the potential utility of the nZVI in the treatment of cesium contaminated water generated after the Fukushima nuclear accident.

1. Introduction

Following the accident at the Fukushima Daiichi Nuclear Power Plant in 2011, radioactive nuclides were released into the environment in large amounts and heavily contaminated seawater, groundwater and drinking water [1]. Japanese soils were also contaminated with radionuclides. One of the various radionuclides produced by a nuclear accident, radioactive cesium (^{137}Cs) is the most hazardous element of radionuclides due to its abundance in nuclear fallout and radioactive wastewater and the hazards presented by its long half-life (about 30 years) and high emission of beta and gamma particles [2]. In food chain, radioactive liquid waste is the primary pathway of radionuclides; therefore, technologies for removing dangerous radioactive isotopes from liquid waste have received much attention.

Until today, the recovery of hazardous cesium is an unsolved problem. Different cesium adsorbents, including zeolites, Prussian blue, bentonite and aluminum molybdophosphate, were intensively investigated to remove cesium from contaminated water [3-5]. However, separation of these adsorbents from environment after use is very difficult. In recent decades, magnetic nanoparticles have been widely used in the fields of medicine, biotechnology, diagnostics and catalysis [6]. Magnetic nanoparticles compose of a magnetic based core and an outer functional shell that can sorb contaminants, which have been extensively studied for environmental remediation applications due to their quite small particle size



and large surface area to volume ratio [2]. In addition, the magnetic nanoparticles can be recovered and separated easily from medium by applying an external magnetic field due to the intrinsic magnetic feature of the nanoparticles [7].

To date, nanoscale zero valent iron (nZVI) has been shown to be efficient environmental remediator of a wide variety of contaminants involving chlorinated organics and inorganic anions [8, 9]. In addition, nZVI has also been shown to considerably remediate solutions contaminated with a variety of transition metals, such as: Cr, Co, Cu, Mo, Zn, Ni, Ag and V; post transition metals, such as: Pb, Cd and metalloids, such as: As and Se [10-12]. However, studies for the treatment of radionuclides remain less widely examined and are limited to Ba, U, Pu and TcO₄ [13, 14].

In present study, the efficiency of nZVI for the removal of cesium from aqueous solutions was evaluated. The sorption of Cs⁺ was studied in a batch system with respect to initial cesium concentration, contact time, pH, temperature, competing cations and dosage of nanoparticles. To the best of our knowledge, the feasibility of using nZVI for the removal of cesium from contaminated waters was reported in this paper for the first time.

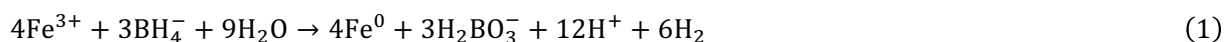
2. Experimental

2.1. Materials and chemicals

CsCl (99.9%, Wako Co., Japan) was used for preparation of the stock solution. FeCl₃·6H₂O (99%, Junsei Chemical Co., Japan), NaBH₄ (98%, Sigma-Aldrich Inc., USA) and ethanol (99.5%, Wako Co., Japan) were purchased for nanoparticles synthesis. NaCl (99.5%, Wako Co., Japan), MgCl₂·6H₂O (97%, Wako Co., Japan), KCl (99%, Wako Co., Japan) and CaCl₂·2H₂O (70–79%, Junsei Chemical Co., Japan) were purchased to prepare simulated contaminated water. HCl (35–37%, Wako Co., Japan) and NaOH (>93%, Wako Co., Japan) were used for pH adjustment. All chemicals were of analytical grade and used as received without further treatment. For all experiments, deionized deoxygenated water was used for the preparation of solutions.

2.2. Synthesis of nZVI

nZVI was synthesized following the method first proposed by Wang and Zhang [15], based on chemical reduction of FeCl₃·6H₂O using NaBH₄ as depicted in the following reaction:



Briefly, NaBH₄ (98%, 0.74 M) was pumped slowly into FeCl₃·6H₂O (99%, 0.15 M) at a rate of 1 L/h using a roller pump in 500 mL four-neck glass flask. A continuous flow of nitrogen gas was maintained during synthesis to create an anaerobic condition. The synthesis was conducted with vigorous stirring at 250 rpm and kept under constant temperature 25 ± 0.5 °C using a water bath. To complete the reaction, the synthesis was left 20 min as aging time. After reduction, the synthesized nanoparticles were washed with deionized deoxygenated water and ethanol at least three times, filtered by vacuum filtration and applied immediately in batch experiments.

2.3. Batch studies

The sorption experiments were performed under kinetic and equilibrium conditions using a batch technique at 298 K. 1 g of nZVI was contacted with 50 mL of 100 mg/L cesium solution and stirred on a magnetic stirrer at 1000 rpm for 2 h to attain equilibrium. After the experiments, the water samples were collected and filtered through 0.2 µm cellulose acetate filter. The obtained liquid were diluted with deionized water to an acceptable concentration range prior to analysis using inductively coupled plasma

mass spectrometry (ICP-MS) technique. To assess the effect of cesium concentration, the experiments were conducted at different initial concentrations of 1, 5, 50, 100, 150 and 200 mg/L. To investigate the effect of the solution pH on the cesium uptake, the initial pH was adjusted at 3–12 using dilute solution of HCl or NaOH. To examine the effect of temperature on the cesium removal, the experiments were conducted at four different temperatures ranging from 278 to 343 K. In order to investigate the effect of nanoparticles content on the sorption capacity, a series of dosage from 1 to 30 g/L was prepared. To evaluate the effect of competitive cation ions on the sorption process of cesium, different simulated waste solutions were prepared separately in the presence of Na^+ , K^+ , Mg^{2+} and Ca^{2+} . All batch experiments were carried out in triplicate and the mean values were used to evaluate sorption parameters. The amount of sorbed cesium by unit mass of the nanoparticles, q (mg/g), was calculated by the following equation:

$$q = (C_i - C_f) \times (V/m) \quad (2)$$

The percent removal of cesium, %R, was also calculated using the following formula:

$$\%R = (C_i - C_f)/C_i \times 100\% \quad (3)$$

where C_i and C_f are the initial and final cesium concentrations (mg/L) respectively, m is the amount of the sorbent (g) and V is the volume of the solution (L).

3. Results and discussion

3.1. Effect of pH

The effect of pH on the removal of cesium by nZVI was investigated over pH range from 3 to 12. As shown in Figure 1, it is obvious that cesium sorption process is a pH dependent process and the initial pH of the aqueous solution has high impact on cesium removal by nZVI. At initial pH 3, the sorption capacity of cesium by nZVI was 1.93 and the cesium removal was only 38.52%. The cesium removal by nZVI increased with the increase in the pH and the maximum removal was observed at pH 8 with cesium removal of 53.58%. At higher pH values, cesium removal by nZVI decreased to only 41.52% and the sorption capacity was 2.08. The cesium removal was inhibited in the acidic medium because the H^+ ions compete with Cs^+ ions for the sorption sites. In addition, the degradation of some fraction of the nanoparticles may occur under acidic conditions. In the strong alkaline environment, the formed passive layer of iron hydroxide precipitates can hinder further oxidation of nZVI [16].

3.2. Effect of initial cesium concentration and contact time

The effect of contact time on sorption of cesium ions onto nZVI was performed at 298 K and different initial concentrations of 1, 5, 50, 100, 150 and 200 mg/L and the results are presented in Figure 2. It is clear that the cesium sorption rate was initially very fast and the sorption amount of cesium increased with increasing the initial cesium concentration. The amount of sorbed cesium onto nZVI increased with time attaining a maximum value after 20 min. It was observed that the equilibrium time was independent on the initial cesium concentrations investigated in this study (1 to 200 mg/L). The values of maximum removal of cesium onto nZVI at 1, 5, 50, 100, 150 and 200 mg/L were 99.95%, 70.33%, 42.09%, 46.49%, 49.15% and 47.93%. The higher sorption capacity of the nanoparticles at high cesium concentrations could be attributed to higher possibility of collision between cesium ions and the nanoparticles. This behavior could also be related to the ratio of initial cesium concentration to the available reactive sites on the surface of nanoparticles.

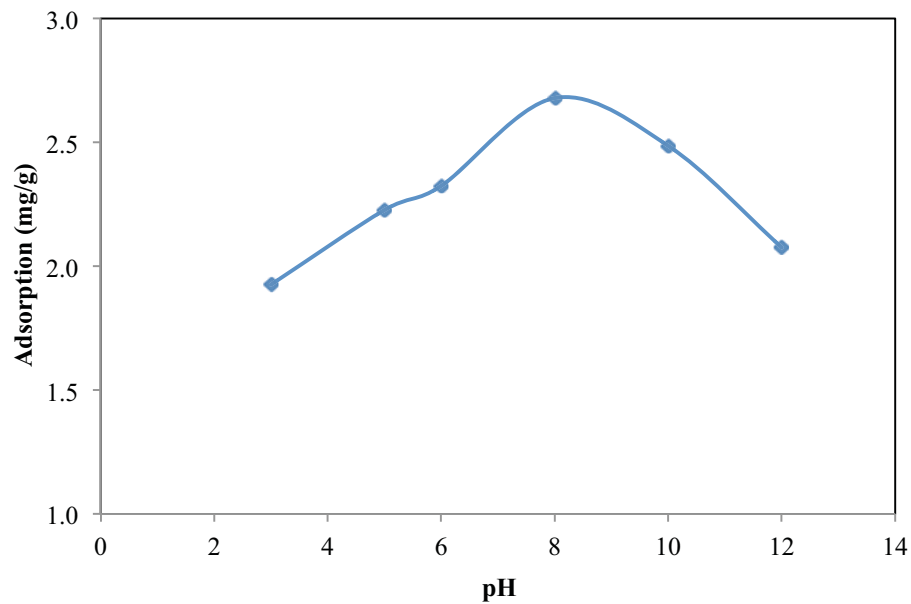


Figure 1. Effect of pH on cesium sorption by nZVI.

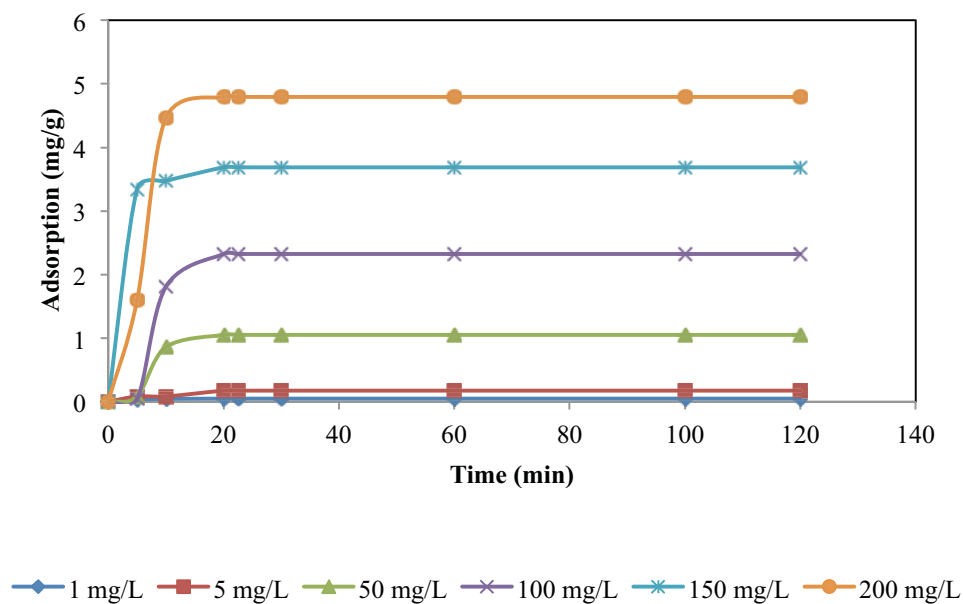


Figure 2. Effect of initial cesium concentration and contact time on cesium sorption by nZVI.

3.3. Dosage effect

The removal of cesium by nZVI was studied by a series of nanoparticles dosage in the range from 1 to 30 g/L at initial cesium concentration of 100 mg/L, initial pH of 6 and temperature of 298 K. The relation between dosage and removal of cesium is shown in Figure 3. From Figure 3, cesium removal increased with increasing the amount of the nanoparticles that more active sites were available to sorb more cesium.

With 1 g/L of nZVI, 29.54% of cesium was removed and the sorption capacity attained its maximum which was 29.54 mg/g. The removal of cesium was up to 33.43% when the dosage of nZVI increased to 2 g/L and the sorption capacity was 16.71 mg/g. These results proposed that the sorption capacity of nZVI was saturated when the dosage of nZVI was below 2 g/L in the treatment system. With 5 g/L of nZVI, the removal of cesium achieved 36.76% with the sorption capacity of 7.35 mg/g. When the addition of nZVI increased to 10 g/L, the removal of cesium achieved 47.27% and the sorption capacity was 4.73 mg/g. In the treatment system of 20 g/L of nZVI, 46.49% of cesium was removed and the removal capacity was 2.32 mg/g. The removal of cesium increased to 54.02% after the addition of 30 g/L of nZVI and the amount of cesium sorbed onto the nanoparticles was 1.80 mg/g.

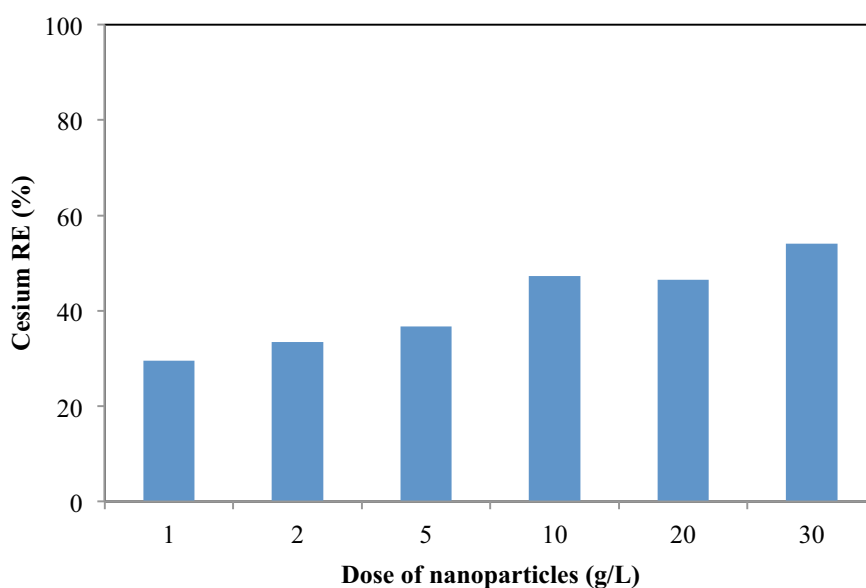


Figure 3. Cesium removal by different dosage of nZVI.

3.4. Effect of temperature

The effect of temperature on cesium sorption by nZVI was investigated at four different temperatures of 298, 313, 328 and 343 K (Figure 4). The sorption capacity decreased with increasing the temperature, suggesting that nZVI was favorable for cesium sorption at low temperatures and the sorption process was exothermic. The values of removal of cesium onto nZVI at 298, 313, 328 and 343 K were 46.49%, 45.53%, 36.36% and 21.13% and the sorption capacity was 2.32, 2.28, 1.82 and 1.06 mg/g, respectively. Results are consistent with the greater sorption of Cs^+ on natural clays [17] and Ba^{2+} on nZVI [18] with decreasing temperature.

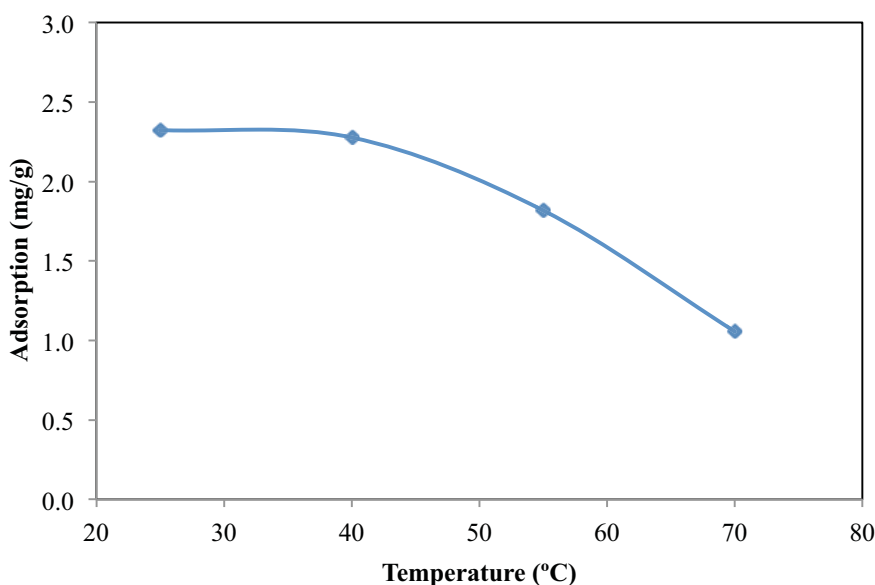


Figure 4. Effect of temperature on cesium sorption by nZVI.

3.5. Matrix effect

The effect of competing cation ions on cesium removal by nZVI at 298 K and initial pH of 6 was examined and the results are presented in Table 1. Four simulated waste solutions were prepared separately in the presence of similar concentration (20 mg/L) of Na^+ (0.87 mM), K^+ (0.51 mM), Mg^{2+} (0.82 mM) and Ca^{2+} (0.50 mM) with initial cesium concentration of 100 mg/L. It is evident that the removal of cesium were highly decreased in the presence of the competing cation. These findings confirmed that the cation ions can compete and lower the sorption of cesium on the nanoparticles. It was noted that the effect of K^+ ions on cesium removal was higher than Na^+ ions. This could be due to the close similarity in the hydration radii of K^+ and Cs^+ rather than to Na^+ [3]. In the presence of Mg^{2+} and Ca^{2+} ions, passivated precipitates such as $\text{Mg}(\text{OH})_2$ and CaCO_3 formed on the nanoparticles surfaces resulting in blocking the electron transfer from the nanoparticles cores [19].

Table 1. Effect of different competing cation ions on cesium removal by nZVI

Ions	RE (%)
100 mg/L Cs^+ (without cations)	46.49
20 mg/L Na^+	44.91
20 mg/L K^+	42.06
20 mg/L Mg^{2+}	36.38
20 mg/L Ca^{2+}	36.25

4. Conclusion

The current work evaluates the feasibility of using nZVI for cesium removal from aqueous solutions. nZVI demonstrated desirable performance for cesium removal. A minimum removal efficiency of 99% was reached at initial cesium concentration of 1 mg/L and a dosage of 1 g-nZVI/L. Solution pH is an important factor affecting sorption of cesium by nZVI. Lower temperatures are favored for enhanced removal of cesium. The obtained results demonstrated that nZVI can be used as efficient materials for

cesium removal from the contaminated solutions. Further studies are needed to assess the application of nZVI particles in a real contaminated medium.

5. References

- [1] Y. Koma, A. Shibata, T. Ashida, Radioactive contamination of several materials following the Fukushima Daiichi Nuclear Power Station accident, *Nuclear Materials and Energy*, **10** (2017) 35-41.
- [2] K.S. Hwang, C.W. Park, K.-W. Lee, S.-J. Park, H.-M. Yang, Highly efficient removal of radioactive cesium by sodium-copper hexacyanoferrate-modified magnetic nanoparticles, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **516** (2017) 375-382.
- [3] E. Borai, R. Harjula, A. Paajanen, Efficient removal of cesium from low-level radioactive liquid waste using natural and impregnated zeolite minerals, *J. Hazard. Mater.*, **172** (2009) 416-422.
- [4] G.-R. Chen, Y.-R. Chang, X. Liu, T. Kawamoto, H. Tanaka, D. Parajuli, M.-L. Chen, Y.-K. Lo, Z. Lei, D.-J. Lee, Prussian blue non-woven filter for cesium removal from drinking water, *Sep. Purif. Technol.*, **153** (2015) 37-42.
- [5] S. Gaur, Determination of Cs-137 in environmental water by ion-exchange chromatography, *J. Chromatogr. A*, **733** (1996) 57-71.
- [6] Y. Namiki, T. Namiki, Y. Ishii, S. Koido, Y. Nagase, A. Tsubota, N. Tada, Y. Kitamoto, Inorganic-organic magnetic nanocomposites for use in preventive medicine: A rapid and reliable elimination system for cesium, *Pharm. Res.*, **29** (2012) 1404-1418.
- [7] Y. Sharma, V. Srivastava, V. Singh, S. Kaul, C. Weng, Nano-adsorbents for the removal of metallic pollutants from water and wastewater, *Environ. Technol.*, **30** (2009) 583-609.
- [8] Y. Liu, S.A. Majetich, R.D. Tilton, D.S. Sholl, G.V. Lowry, TCE dechlorination rates, pathways, and efficiency of nanoscale iron particles with different properties, *Environ. Sci. Technol.*, **39** (2005) 1338-1345.
- [9] T. Shubair, O. Eljamal, A.M. Khalil, N. Matsunaga, Multilayer system of nanoscale zero valent iron and Nano-Fe/Cu particles for nitrate removal in porous media, *Sep. Purif. Technol.*, **193** (2018) 242-254.
- [10] J.T. Olegario, N. Yee, M. Miller, J. Szczepaniak, B. Manning, Reduction of Se (VI) to Se (-II) by zerovalent iron nanoparticle suspensions, *J. Nanopart. Res.*, **12** (2010) 2057-2068.
- [11] X.-q. Li, W.-x. Zhang, Sequestration of metal cations with zerovalent iron nanoparticles a study with high resolution X-ray photoelectron spectroscopy (HR-XPS), *The Journal of Physical Chemistry C*, **111** (2007) 6939-6946.
- [12] T. Scott, I. Popescu, R. Crane, C. Noubactep, Nano-scale metallic iron for the treatment of solutions containing multiple inorganic contaminants, *J. Hazard. Mater.*, **186** (2011) 280-287.
- [13] R.A. Crane, M. Dickinson, T.B. Scott, Nanoscale zero-valent iron particles for the remediation of plutonium and uranium contaminated solutions, *Chem. Eng. J.*, **262** (2015) 319-325.
- [14] J.G. Darab, A.B. Amonette, D.S. Burke, R.D. Orr, S.M. Ponder, B. Schrick, T.E. Mallouk, W.W. Lukens, D.L. Caulder, D.K. Shuh, Removal of pertechnetate from simulated nuclear waste streams using supported zerovalent iron, *Chem. Mater.*, **19** (2007) 5703-5713.
- [15] C.-B. Wang, W.-X. Zhang, Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs, *Environ. Sci. Technol.*, **31** (1997) 2154-2156.
- [16] W. Han, F. Fu, Z. Cheng, B. Tang, S. Wu, Studies on the optimum conditions using acid-washed zero-valent iron/aluminum mixtures in permeable reactive barriers for the removal of different heavy metal ions from wastewater, *J. Hazard. Mater.*, **302** (2016) 437-446.
- [17] T. Shahwan, H. Erten, Thermodynamic parameters of Cs⁺ sorption on natural clays, *J. Radioanal. Nucl. Chem.*, **253** (2002) 115-120.
- [18] O. Celebi, Ç. Üzümlü, T. Shahwan, H.N. Erten, A radiotracer study of the adsorption behavior of aqueous Ba²⁺ ions on nanoparticles of zero-valent iron, *J. Hazard. Mater.*, **148** (2007) 761-767.

- [19] B. Hu, F. Ye, C. Jin, X. Ma, C. Huang, G. Sheng, J. Ma, X. Wang, Y. Huang, The enhancement roles of layered double hydroxide on the reductive immobilization of selenate by nanoscale zero valent iron: Macroscopic and microscopic approaches, *Chemosphere*, **184** (2017) 408-416.

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