

Effect of Nanodiamond on Removal of Cesium from Soil by Potassium Ferrocyanide

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Abstract

Detonation nanodiamond (DND) was examined for its effect on soil Cs⁺ removal by precipitation with Prussian Blue and its analogues. In a preliminary experiment using a synthetic sea-water sample added with 6.6 % of Cs⁺, it was found that addition of DND, CuCl₂, and potassium ferrocyanide in this order to the solution removed Cs⁺ with more than 99.9 % efficiency in the supernatant. Based on this finding, Cs⁺ in soil slurry of Fukushima prefecture after the nuclear power plant accident, was treated in the same way as above, and the supernatant was measured for ¹³⁷Cs γ -ray. The result showed that Cs⁺ was removed to a non-detected level. Since the separation and settling of the precipitation is rapid and coagulation occurs effectively well, filtration is also rapid and can be easily compared to that of the conventional process. Such effect of DND can be due to adsorption of Cs-containing Prussian Blue onto the surface of DND, which finally accelerates precipitation of the Prussian Blue and soil slurry.

Keywords

Soil cesium removal, Prussian Blue, soil slurry, detonation nanodiamond.

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Introduction

A detonation nanodiamond (DND) is synthesized by detonation of explosives in a large pressure-resistant chamber. DND is different from other synthetic diamonds such as HTHP (high-temperature high-pressure) static-synthesis diamond or CVD (chemical vapor deposition) diamond. The structure of DND after purification of raw detonation soot consists of several aggregated primary diamond spheres of 4–6 nm in diameter, covered with graphite-like carbon layers on the surface. After strong oxidative purification of the soot, the diameter of DND becomes 200 μ m or less. This aggregate can be dispersed stably in water, since the particles have covalently-bonded surface polar functional groups, such as carboxylic, hydroxyl, ketonyl, and ester groups [1–3].

Owing to presence of the surface polar groups, DND is reasonably expected to act as an adsorbent and

ion-exchanger. So far, however, only a few applications have been reported for metal adsorption and ion-exchange: selective preconcentration of tungstate in water for ICP-AES (Inductively Coupled Plasma – Atomic Emission Spectrometer) measurement [4], and adsorption of several metal ions, especially of radio active nuclide Cs on DND [5]. In Cs adsorption, the effect of surface modification was extensively studied, which is informative for practical application in removal of radio nuclides, on the one hand, and for a valuable understanding of the relation between surface functional groups and the functional efficiency as an adsorbent, on the other hand.

As for metal ion adsorption, several mechanisms have been suggested: 1) coordination of metal ions onto the surface functional groups; 2) ion-exchange reaction on the functional groups; 3) adsorption onto the surface graphite; 4) intercalation into the surface graphite; 5) crosslinking adsorption and coordination

of a metal ion between multiple particles forming an aggregation. However, no detailed study has been carried out on the real mechanism occurring in the metal adsorption and ion-exchange [1–3].

The earthquake and Tsunami disaster in Fukushima nuclear power plant a few years ago urged us to develop an efficient and effective method for removal of radio-active nuclides such as cesium, strontium, iodine, and several others. Prussian Blue ($\text{Fe}[\text{Fe}(\text{CN})_6]$) is a well known selective adsorbent for Cs^+ , and many applications are reported for Cs^+ removal in a variety of environmental samples. In the present experiment, the effect of DND addition in the Cs removal by potassium ferrocyanide and its analogue was examined in a soil sample, and the effect of DND was evaluated in terms of removal efficiency, process speed, and easy handling of the precipitate. DND has the advantage of being heat-resistant, radio-activity resistant and chemically stable in comparison with other common adsorbents and ion-exchange resins. It is known that during storage of processed precipitate containing radio-active elements, radio-activity of the precipitate emits heat and gradually decomposes the precipitate. If Prussian Blue is gradually decomposed, cyanide is possibly leached out, which is a serious problem that needs to be solved by a new technology. Unlike Prussian Blue, DND is far more stable towards radio-activity, heat, and chemical reactions, thus it is more stable in long-term storage of radio-active materials. In the present study, the effect of DND in adsorption of soil Cs with Prussian Blue was studied.

Experimental

Reagents and samples

1 % water dispersion of DND from Vision Development Co., Ltd. was used as received. The DND had an approximate diameter about 100 nm according to the specification document. Although the dispersion seems to be stable for several months, ultrasonic irradiation was applied to the dispersion for a few minutes before use. Before treating a soil sample, a water solution containing non-radioactive Cs in sea-water matrix was prepared, and the effect of DND in Cs removal by Prussian Blue was examined. The solution was prepared by dissolving commercial sea-water salt powder (“Nuchimasu” from Nuchimasu Co.) into pure water to 0.07 w/v%. This concentration was selected so that Cs can be measured on ICP-AES without any interference of sodium ion. At this

concentration, the sea water contains about 175 ppm of Na. To the sea water solution, a commercial standard 1000 ppm Cs solution (Wako Pure Chemical Industries Ltd., Japan) was added to 6.6 ppm (pH 7.6).

A soil-containing slurry sample used in the present experiment was prepared from a soil of Fukushima prefecture and processed to a slurry by preliminary treatment with high temperature and high pressure. The slurry contained 5 % soil and was measured and analyzed for decontamination efficiency with ^{137}Cs γ -ray measurement, before and after treatment with the present Prussian Blue-DND precipitation method. The slurry sample was a stable dispersion, being turbid even after several hours standing, whose filtering as it is without any treatment with a paper of pore size less than 1 μm caused clogging.

In several cases of the treatment, an inorganic coagulant (Supernammit TN315NY-T3 from Noatech Co.) was used. All of the reagents used were of reagent grade and were used without further purification.

Instrument

The ICP-AES instrument was from Seiko Instruments Co. with a CCD (charge-coupled device) camera and a nebulizer for dispersion solutions. The ^{137}Cs γ -ray activity was measured with a Ge semiconductor detector from Ortec Co. FT-IR (Fourier transform infrared) spectrum of DND as KBr pellet was measured on JASCO FT/IR-6100 spectrometer as KBr pellet in N_2 by a diffusion-reflection method. The zeta-potential of DND was measured as a 0.1 % aqueous suspension based on DLS (dynamic light scattering) on Zetasizer NanoZS from Malvern Instruments Ltd.

Procedure

Treatment of Artificial Sea-water to remove Cs^+ . To 80 ml of sea water of 6.6 ppm Cs there was added 0.2 ml of 1 % DND dispersion and the solution was stirred for a min. The solution became grey and slightly turbid. 0.2 ml of 0.1 mol/l solution of CuCl_2 was added to the solution, and it was stirred for 5 min. After stirring, 0.2 ml of 0.05 mol/l of potassium ferrocyanide was added and the solution was stirred for 30 min. After being left standing for 30 min, precipitate appeared and settled to the bottom. The supernatant was taken and measured for ^{137}Cs activity.

For comparison, CoCl_3 and FeCl_3 were added instead of CuCl_2 in the above procedure, and the efficiency of Cs removal was measured. Since CuCl_2 gave the best removal efficiency among the three transition metal chlorides, all the following experiments were carried out with CuCl_2 addition. The total weight of the final air-dried precipitate when using CuCl_2 was 16 mg.

Treatment of soil slurry to remove Cs. The procedure for addition of DND, CuCl_2 , and potassium ferrocyanide was the same as for artificial sea-water sample above, and in addition, in several cases, either a coagulant (Supernammit TN315NY-T3 from Noatech Co.) was added to 500 ppm, or a 0.22 μm filter (Millipore Co.) was used, or both were used after the chemical precipitation process. The supernatant was obtained either by filtration or when filtering was not applied, was pipetted out from the above. The ^{137}Cs γ -ray activity of the supernatant was measured with Ge semiconductor detector.

Results and Discussion

IR spectrum and zeta potential of DND

The IR spectrum of DND is shown in Fig. 1, in which two absorption bands are observed at around 1700 cm^{-1} to 1600 cm^{-1} . It is reported that free carboxylic groups ($\sim 1700\text{ cm}^{-1}$), ketones, and several carboxyl-related groups such as lactones ($\sim 1600\text{ cm}^{-1}$) exist on the surface of DND [1–3]. Phenolic hydroxyl and water O-H are also observed in $\sim 1600\text{ cm}^{-1}$ and $\sim 3100\text{ cm}^{-1}$ regions. These spectral features are common to all DNDs, but the relative intensities of the groups are different depending on the method of detonation and purification of soot to obtain final DND. The present DND has a relatively strong absorption band around 1700 cm^{-1} relative to 1600 cm^{-1} .

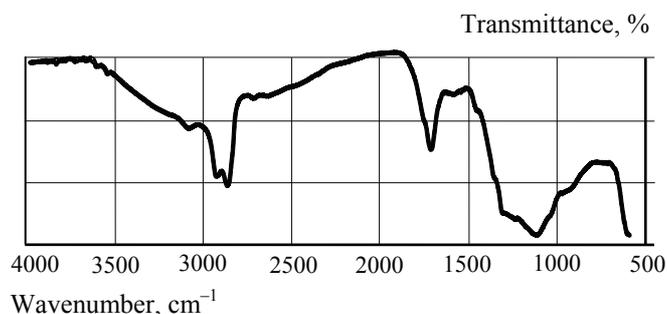


Fig. 1. Zeta potential of the DND dispersion (0.1 %) in water was +46 mV

Removal of Cs^+ in Artificial Sea-Water

Literature survey showed that not only Prussian Blue ($\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6]_3$) [6, 7] but also several other analogous ferrocyanide complexes of the type $\text{K}_x\text{M}_y[\text{MFe}(\text{CN})_6]$, where M is Co^{3+} [6–8] Cu^{2+} [6–14], Ni^{2+} [6–9, 15–20], and Zn^{2+} [6, 7, 13, 17], are active adsorbents for Cs^+ in water and sea water. These analogues of Prussian Blue are mostly synthesized by addition of MCl_2 or MCl_3 to a solution of potassium ferrocyanide, and all of them are moderately to remarkably effective to remove Cs^+ , with the efficiency depending on M^{II} . Therefore, in the current experiment, the effect of DND addition was examined by varying M^{II} ($0.25\text{ mol}\cdot\text{l}^{-1}$) in Cs^+ removal by potassium ferrocyanide. The results of Cs removal in artificial sea water showed that CuCl_2 (Cs removal over 99 %) gave the best removal efficiency, followed by Fe^{3+} (72 %) and Co^{3+} (67 %). Therefore, the following experiments were carried out with CuCl_2 . In order to obtain high removal efficiency, it was necessary to add DND, CuCl_2 , and potassium ferrocyanide stepwise in the order described in the experimental section. The addition of DND later than others decreased Cs removal efficiency. The results of the final Cs concentration in the supernatant after several different treatments are listed in Table 1, in which Cs is most effectively removed when all of the three reagents are added (run 3).

It is obvious that adding DND in addition to CuCl_2 and potassium ferrocyanide gives better results than simply adding only potassium ferrocyanide and CuCl_2 . Sodium concentration does not change in all of the cases, showing that sodium ion is not adsorbed in the precipitate. It is noteworthy that Cu^{2+} is also removed from the solution when all of the three reagents are added (run 3), however, Cu^{2+} is only partially removed when DND is not added (run 4).

Table 1

Various treatments of Cs removal in artificial sea-water spiked with Cs

Addition to sea-water			Conc. in supernatant, ppm				Cs removal ratio, %
DND, mg/l	CuCl_2 , μM	KFC*, μM	Cs	Na	Cu	Fe	
0	0	0	6.6	175	N.D.	N.D.	0
0.25	0	0	4.1	177	N.D.	0.03	38
0.25	50	25	0.003176	N.D.	N.D.	0.01	99.9
0	50	25	1.5	178	1.2	0.14	77

* Potassiumferrocyanide.
N.D., not detected.

It is also noteworthy that when all of the three reagents are added, Fe^{3+} is more effectively removed than when DND is not added (runs 2, 3, and 4). This fact suggests that cyanide is probably mostly removed by addition of DND. All of these facts prove that DND is a superior material and reinforces Cs^+ as well as ferrocyanide removals in the traditional ferrocyanide decontamination system.

As for the mechanism of Cs^+ precipitation by potassium ferrocyanide and CuCl_2 , it is known that Cu^{2+} partially substitutes positions of Fe^{2+} in the cubic lattice framework of $[\text{Fe}(\text{CN})_6]^{4-}$, and Cs^+ ion enters into the void within the cubic lattice, being trapped into the void, and precipitates $\text{Cs}_4[\text{Cu}_x\text{Fe}_{1-x}(\text{CN})_6]$. Copper ion partially substitutes positions of Fe^{2+} in the cubic framework to adjust the void volume, so that it fits best to Cs^+ diameter.

Based on this mechanism, the effect of DND in the Cs removal was approximately considered as follows. From run 2, it is evident that UDD (ultradispersed detonation diamond) itself has adsorption and precipitation property for both Cs^+ and Fe^{2+} . This is due to the surface carboxylic and phenolic groups for metal coordination, as well as the positive zeta-potential of DND, which affects electrostatic attraction of negative species, such as $[\text{Fe}(\text{CN})_6]^{4-}$ or $[\text{Cu}_x\text{Fe}_{1-x}(\text{CN})_6]^{2-}$. These two opposite charge effects of the present DND are notable and should be compared to those of another detonation nanodiamond

having diameter of 4 nm and zeta-potential of +55 mV. This nanodiamond is manufactured in Nano Carbon Research Institute Co., and is reported to adsorb only negative ions, being especially a good adsorbent to tungstate anion [4]. For our DND, both positive and negative ions were adsorbed and precipitated together with DND. In the present procedure for Cs^+ removal, it is not clear whether DND adsorbs Cs^+ or Cu^{2+} . But it is certain that Cu^{2+} reacts with $[\text{Fe}(\text{CN})_6]^{2-}$ to form $[\text{Cu}_x\text{Fe}_{1-x}(\text{CN})_6]^{4-}$ while incorporating Cs^+ . It was certain that DND does not adsorb preformed $[\text{Cu}_x\text{Fe}_{1-x}(\text{CN})_6]^{2-}$, since Cs^+ removal was appreciably decreased when DND was added after both Cu^{2+} and potassium ferrocyanide had been added. Copper ion must be added just after DND addition prior to potassium ferrocyanide. Formation of $[\text{Cu}_x\text{Fe}_{1-x}(\text{CN})_6]^{2-}$ is hindered, judging from the color, if potassium ferrocyanide is added after DND and prior to copper chloride. It seems that ferrocyanide adsorbed on DND does not react with copper ion to produce $[\text{Cu}_x\text{Fe}_{1-x}(\text{CN})_6]^{2-}$.

Removal of Cs^+ from soil slurry

The soil slurry contained 5 v/v % fine powder (the photo shown in Fig. 2 a). After addition of DND, CuCl_2 , and potassium ferrocyanide, the solution produced precipitate and supernatant (Fig. 2 b).

This precipitate solution was filtered (ϕ 0.22 μm) to give a dark-brown transparent filtrate shown in Fig. 2 c.

As it is obvious in Table 2, Cs can be removed to some extent only by coagulant and filtration (run 2) or by DND and coagulant alone (run 3). However, addition of DND, CuCl_2 , and potassium ferrocyanide in addition to coagulant and filtration gave the best result (run 4 and 5), and radio-activity was not detected. It is notable that only filtration with a less than 1 μm filter without addition of any reagents or coagulant, resulted in clogging of the filter. This fact and the experimental observation described earlier show that addition of DND, CuCl_2 , and potassium ferrocyanide facilitates growing and coagulation of precipitate particles in a shorter time, and makes filtration procedure practically possible.

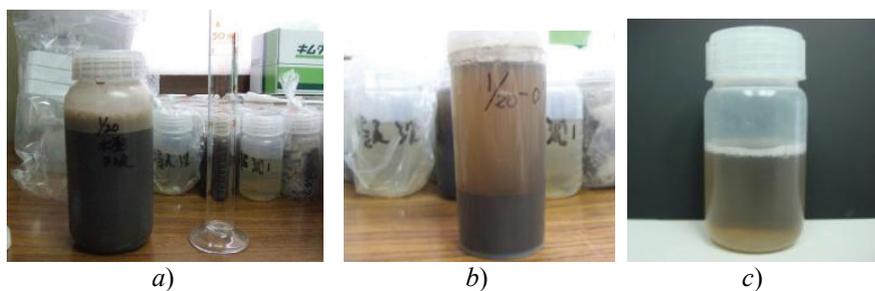


Fig. 2. The filtrate was subjected to ^{137}Cs γ -ray measurement. The results are shown in Table 2

Table 2

Run	DND, mg/l	CuCl_2 , mM	$\text{K}_4[\text{Fe}(\text{CN})_6]$, mM	Coagulant	Filter (0.22 μm)	^{137}Cs , Bq/kg
1	0	0	0	–	–	1075
2	0	0	0	+	+	87
3	2.5	0	0	+	–	138
4	2.5	0.5	0.25	+	+	N.D.
5	2.5	2.5	1.25	+	+	N.D.

N.D., not detected.

Conclusion

Although DND alone was previously reported to be an effective adsorbent of Cs^+ , the present experiment showed that DND, if used together with Cu^{2+} and potassium ferrocyanide, becomes even more powerful, almost perfect adsorbent of Cs^+ . In addition, DND removes Fe^{2+} and ferrocyanide ion in solution, which is a valuable property to avoid possible cyanide contamination of environment. Application of the present technology to other elements can be worthy of research and will expand further applications of DND.

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