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Removal of radioactive cesium, strontium, and iodine from natural waters using bentonite, zeolite, and activated carbon

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Key words: radioactive cesium, radioactive strontium, radioactive iodine, isotope production, bentonite, zeolite, activated carbon, adsorption

Removal of radioactive cesium, strontium, and iodine from natural waters using bentonite, zeolite, and activated carbon

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Cs-134, Sr-85, and I-131 were produced by neutron irradiation of CsCl, $SrCl_2$, and K_2TeO_3, respectively, using the Kyoto University Reactor (KUR). These radioactive nuclides were added to river water and seawater to prepare artificially contaminated samples, and the removal of these nuclides using bentonite, zeolite, and activated carbon was then investigated. In the river water samples, Cs-134 and Sr-85 were successfully removed using bentonite and zeolite, and I-131 was removed using activated carbon. In the seawater samples, Cs-134 was removed using bentonite and zeolite, whereas Sr-85 and I-131 were hardly removed at all by these adsorbents.

Introduction

A large amount of radioactive materials have been spread in the environment by the accident at the Fukushima Dai-ichi Nuclear Power Plants [1-6], and much still remains in the plants, where they remain a potential source of contamination. The migration and decontamination of these materials have been important research issues. The removal of radioactive materials from a solution has previously been investigated, using artificial polymers [7], bentonite [8], zeolite [9, 10], and activated carbon [11, 12]. In such research, radioactive traces would be suitable for use as materials because the diversity and changes in their chemical forms generally have no effect upon radiation counting and analysis. Although Sr-90 was actually released from the plants, Sr-85 was here used to the investigation taking advantage of its gamma emission property.

In this study, we first investigated the production of Cs-134, Sr-85, and I-131 and then studied the adsorption of these produced nuclides, using bentonite, zeolite, and activated carbon.

EXPERIMENTAL

Isotope production

Radioactive cesium, strontium, and iodine were produced from CsCl, $SrCl_2$, and

K_2TeO_3 [13] at the Kyoto University Research Reactor Institute. These irradiated reagents were individually dissolved in double-distilled water to prepare stock solutions whose concentrations were 2.4×10^{-4} M CsCl, 1.1×10^{-3} M $SrCl_2$, and 2.0×10^{-4} M K_2TeO_3, respectively. Their gamma activity was measured with an HPGe detector.

Iodine can exist in various chemical forms in a natural system, depending on the pH and Eh conditions. After dissolution of a tracer amount of iodine atoms produced in K_2TeO_3 salt, the speciation of iodine, whether iodide or iodade, should be investigated prior to the use of a radioactive iodine solution. Iodide and iodate have different adsorption strengths on anion exchange resin, with iodide showing strong adsorption and iodade showing weak adsorption; this adsorption behavior provides the speciation of iodine in solution [14]. The stock solution of iodine was brought into contact with a chloride-form anion exchange resin (Dowex 1x8 100 mesh), and the specific activity of the resulting supernatant and the initial stock solution was then determined to obtain adsorption ratios. For comparison, the stock solution treated with $NaHSO_3$ and NaClO was also brought into contact with a chloride-form anion exchange resin to obtain the adsorption ratio of iodide and iodade, respectively. The adsorption ratios yielded the speciation of iodine in the stock solution.

Collection of environmental water samples

Water samples of both seawater and river water were collected at two locations on June 23 and 24, 2011, respectively. The seawater was collected at Matsushita-Kaigan beach in Iwaki city, which is located at about 50 kilometers south of the disabled nuclear power plants along the Pacific Coast, where the coastal water moves southward. The river water was collected around Tone-Ohzeki, which was a weir across the Tone River between Gunma and Saitama prefectures that is connected to a water treatment plant for the district of Tokyo and its surrounding area and is located about 200 kilometers south-west of the nuclear power plants. The specific gamma activities of each of the two water samples were determined prior to their use in the adsorption experiments described below.

Determination of removal ratio for adsorbents

The removal of radioactive nuclides from artificially contaminated water samples using the commercially obtained adsorbents bentonite, zeolite, and coconut-activated carbon was investigated as follows. The water samples were filtered with qualitative filter paper No. 1 (Advantec, Dublin, CA) to remove large-size suspended solids, and then, three radionuclides were added to prepare the initial solution. The adsorbents were added to the initial solution of 200 g added; the

adsorbents weight ranged from 0.25 g to 5 g, and the mixture was then stirred for 10 min and allowed to settle for 50 min at room temperature. The mixture was then filtered with quantitative filter paper No. 5B (Advantec, Dublin, CA), which is finer than the filter paper used earlier, to prevent the percolation of fine adsorbents. The activity of an aliquot of 50 g of the resulting filtrate and the initial solution was measured to obtain the removal ratio of the radionuclides from solutions using the following equation:

$$\text{Removal ratio} = 1 - \frac{\text{Specific activity in filtrate}}{\text{Specific activity in the initial solution}}$$

RESULTS AND DISCUSSION

Isotope production

The decay product of Cs-134, Ba-134, which has a large number of energy levels that emit photons with various energies, have gamma energies and emission ratios as follows: 475 keV (1.47%), 563 keV (8.38%), 569 keV (15.43%), 605 keV (97.56%), 796 keV (85.44%), 1039 keV (1.00%), and 1365 keV (3.04%) [15]. These gamma emissions bring about the problem of the sum effect in gamma activity measurement, which makes careful analysis necessary to evaluate the absolute activity in the sample. The sum effect, however, could be cancelled in the investigation by using the relative value of the activity, for example, the distribution ratios between the solid and liquid

phase, as measured using the same solid angle as that of the samples. Figure 1 shows the measurement results for 0.3 kBq to 82 kBq Cs-134 in 500 mL as a relative strength, where the activities evaluated from the ROI, range of interest, of seven energies of photons detected was normalized by that of 605 keV at each concentration of Cs-134. These activities were in principle evaluated under consideration of their photon emission ratios, which generally means that the relative strength is expected to be independent of the photon energy. The similar tendency of the relative strength of all concentrations in Figure 1 confirms that investigations with Cs-134 using a relative value of activity can be unproblematically conducted under a specific activity ranging across at least two orders.

Among strontium nuclides, Sr-85 is actually the only nuclide that emits gamma-rays; however these energies and their emission ratio are 514 keV (95.7%) and 869 keV (0.01%) [15]; thus, only the gamma-rays of 514 keV can be used to detect Sr-85. Moreover, that energy is in the vicinity of the energy of annihilation of gamma-rays, 511 keV, which could interrupt the detection of Sr-85 in the presence of other nuclides emitting high-energy gamma-rays, and Cs-134, which is used in this study, is this type of nuclide. Figure 2 shows a gamma spectrum of Cs-134 without Sr-85, in which no significant peak is observed around 511 keV, indicating that a mixture of Sr-85 and Cs-134 nuclide was valid for this study.

The iodine adsorption ratios obtained in the original stock solution and the solution treated with $NaHSO_3$ and NaClO on the anion exchange resin were 0.97, 0.99, and 0.03, respectively; these results showed that the iodine in the original stock solution existed as iodide.

Activity of environmental samples

The specific activities of the natural samples used are listed in Table 1. The seawater sample that was collected relatively close to the disabled nuclear power plants shows the effect of the accident, whereas the river water sample collected from the Tone River shows no such effect, and the dominant gamma activity in both samples originates from K-40. Because a large amount of radioactive nuclides were added to both environmental samples, the amount of original radioactivity can be ignored.

Removal ratio for adsorbents

The removal property of Cs-134 is shown in Figure 3a. Cs-134 in river water was removed to a great degree by bentonite and zeolite, whereas it was removed to a much lesser degree by the activated carbon. The adsorption of Cs-134 in the seawater sample was less than that in river water, and in activated carbon, in particular, showed

no adsorption effect. The removal property of Sr-85 is shown in Figure 3b. Sr-85 in river water was removed by bentonite, though showing a removal property that was inferior to that of Cs-134, whereas Sr-85 in seawater was hardly removed by bentonite. Activated carbon showed almost no adsorption of Sr-85 in either the river water or the seawater. The removal property of I-131 is shown in Figure 3c. Unlike the above two nuclides, I-131 in river water was partially removed by activated carbon, whereas bentonite and zeolite showed no adsorption effect. I-131 in seawater, however, was hardly removed at all by activated carbon.

Radioactive cesium, strontium, and iodine in river water could be removed by the adsorbents that are investigated here, whereas these same elements in seawater were removed by the adsorbents to a small or negligible degree. These results confirm the concept that an increase in salt concentration suppresses adsorption [10]. The removal of Sr-85 by bentonite was inferior to the removal of Cs-134, giving results that agree with those of Khan [8]. The removal ratio of I-131 in river water by activated carbon was saturated to approximately 0.6, giving results that agree with those of Yusof [11], whereas the complete adsorption of I-131 was reported by Navarrete [12], who treated the activated carbon with 2-propanol. Although further investigations for activated carbon would be required, the agreement between the results of this study and those of other similar studies show that the radionuclides

produced here are of sufficient quality to use in tracer experiments.

CONCLUSIONS

In this paper, we showed the feasibility of the production of Cs-134, Sr-85, and I-131 at the Kyoto University Reactor (KUR), and further showed that these produced radionuclides were valid for use in studies of the environmental behavior of fission products.

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LIST OF FIGURES

Figure 1: Relative activity strength evaluated from peak area of each ROI for various Cs-134 concentrations, ranging from 0.3 kBq to 82 kBq.

Figure 2: Gamma spectrum of Cs-134 around 514 keV, at which Sr-85 emits gamma rays. The solid and dashed lines show the position on the spectrum of the gamma ray energy emitted from Cs-134 and Sr-85, respectively.

Figure 3a: Removal property of Cs-134. ●○: Bentonite; ▲△: Zeolite; and ■□: Activated carbon.. ●▲■: River water samples and ○△□: Seawater samples.

Figure 3b: Removal property of Sr-85.

Figure 3c: Removal property of I-131.

Figure 1

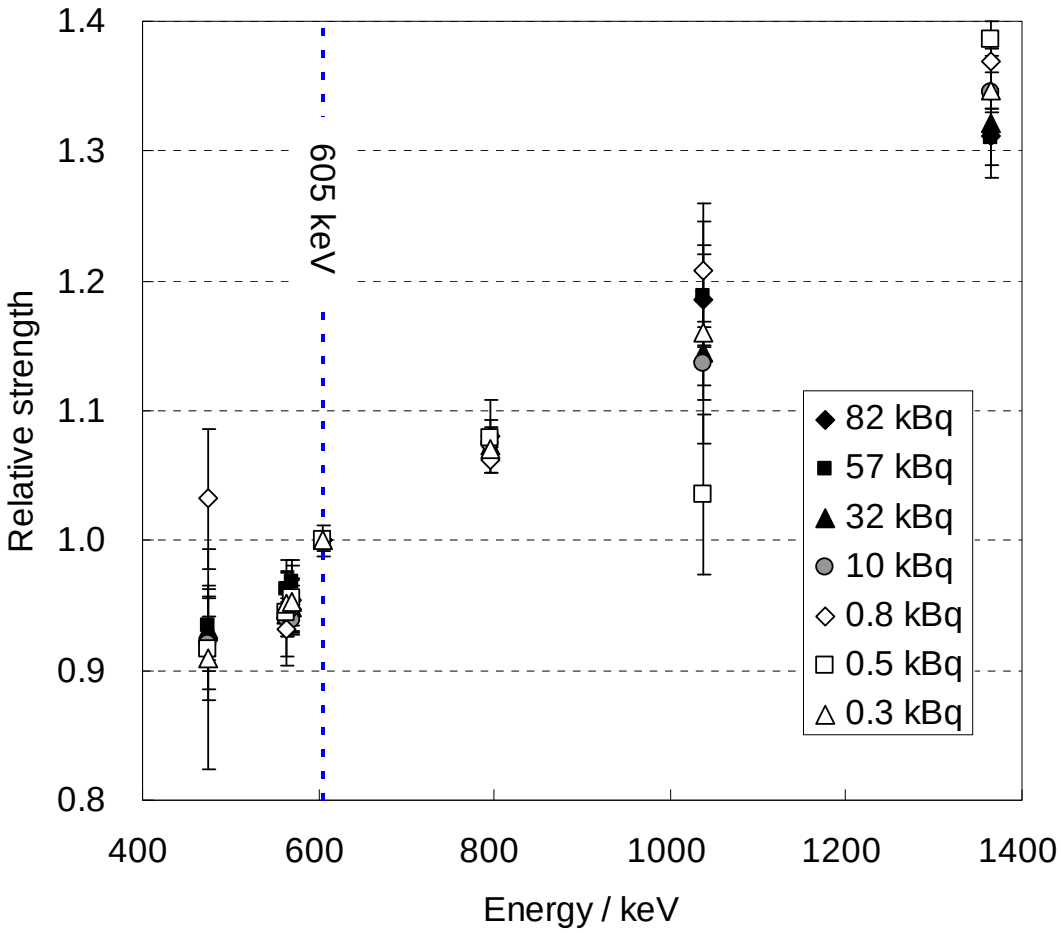

1.4
1.3
1.2
1.1
1.0
0.9
0.8
Relative strength
605 keV
400
600
800
1000
1200
1400
Energy / keV
82 kBq
57 kBq
32 kBq
10 kBq
0.8 kBq
0.5 kBq
0.3 kBq

Figure 2

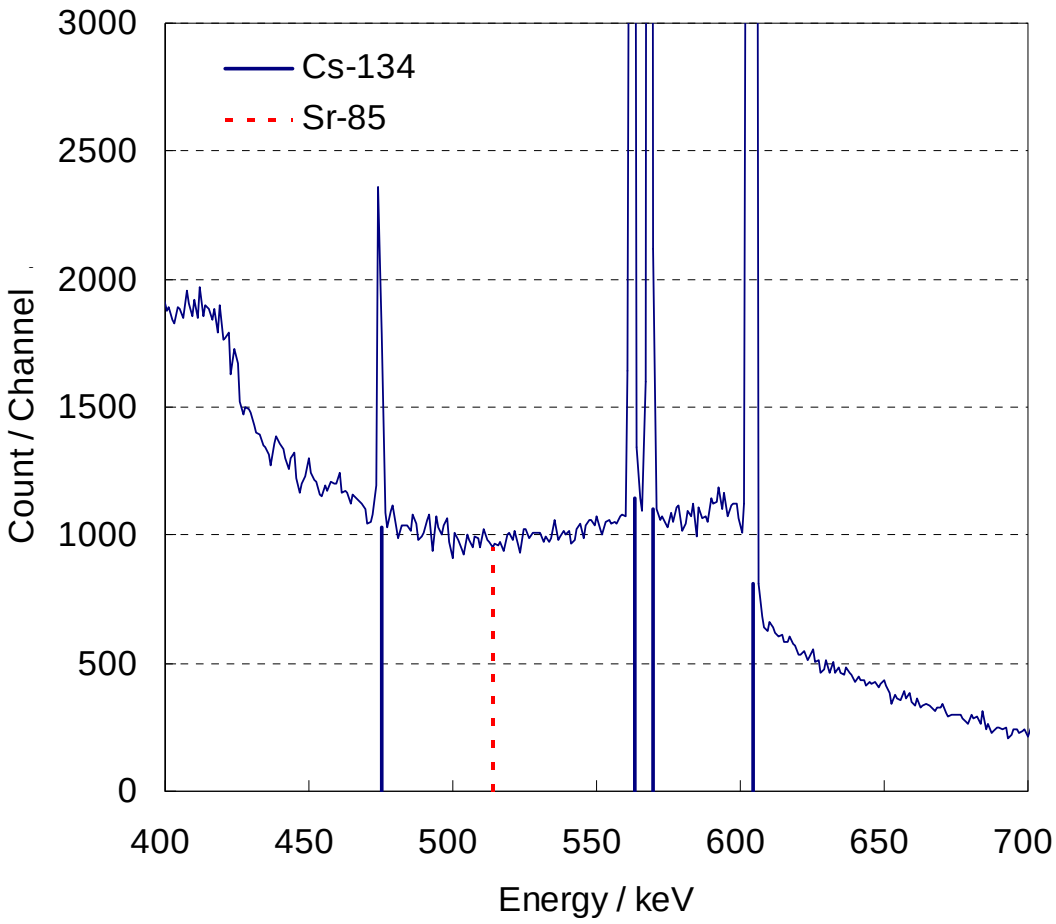

3000
2500
2000
1500
1000
500
0
Count / Channel
Cs-134
Sr-85
400
450
500
550
600
650
700
Energy / keV

Figure 3a

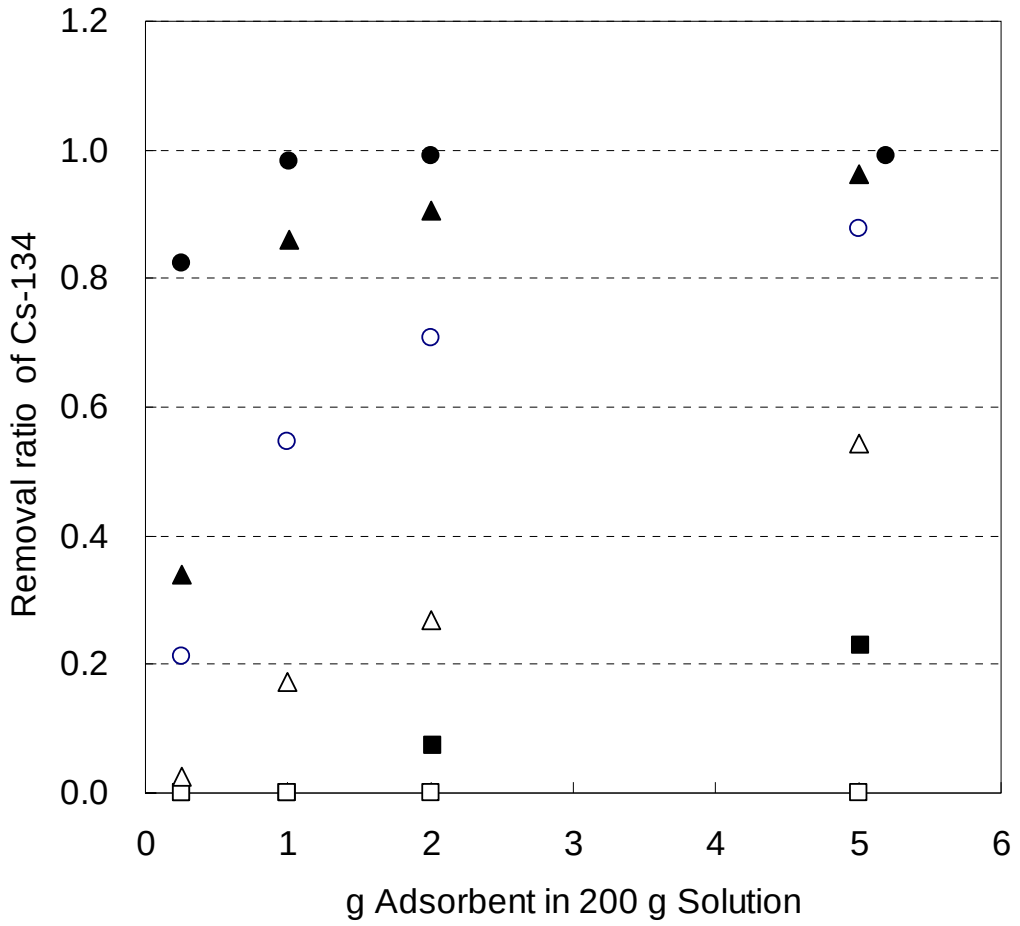

1.2
1.0
0.8
0.6
0.4
0.2
0.0
Removal ratio of Cs-134
0
1
2
3
4
5
6
g Adsorbent in 200 g Solution

Figure 3b

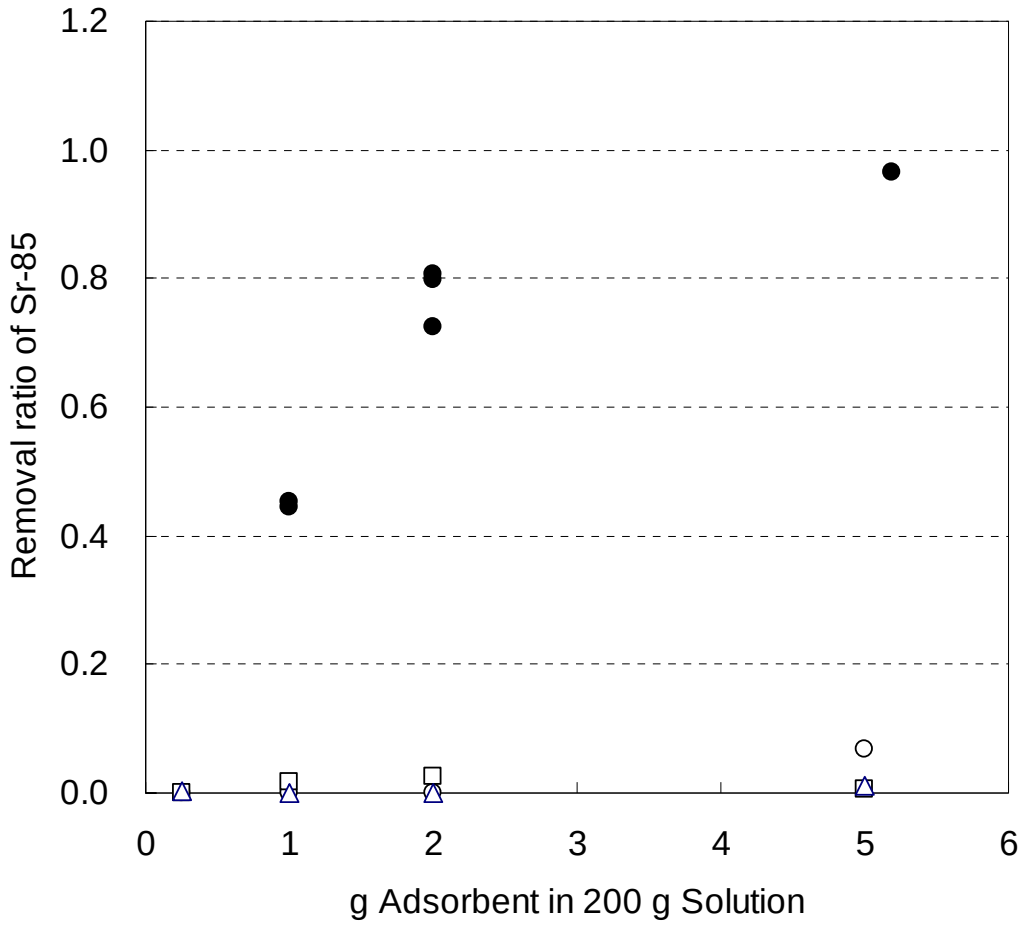
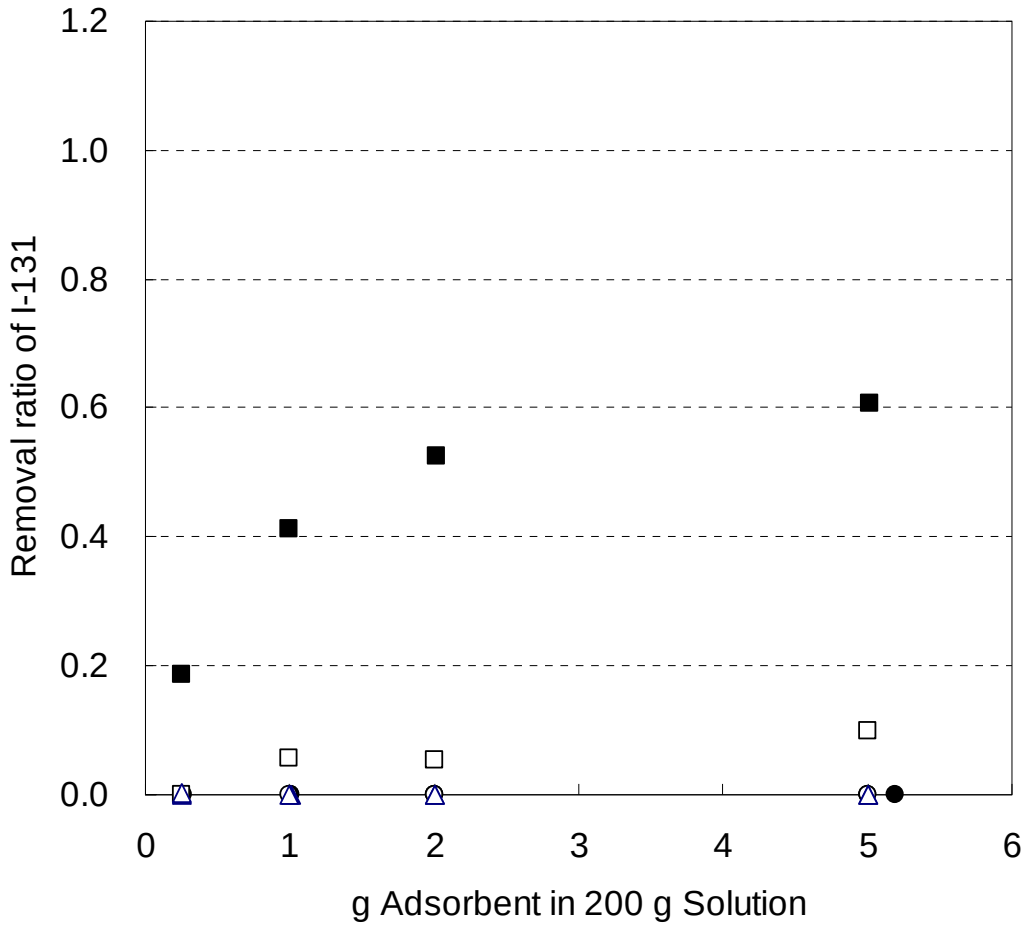

1.2
1.0
0.8
0.6
0.4
0.2
0.0
Removal ratio of Sr-85
0
1
2
3
4
5
6
g Adsorbent in 200 g Solution

Figure 3c


1.2
1.0
0.8
0.6
0.4
0.2
0.0
Removal ratio of I-131
0
1
2
3
4
5
6
g Adsorbent in 200 g Solution

LIST OF TABLES

Table 1: Specific radioactivity in natural seawater and natural river water collected at Matsushita beach in Fukushima and at the Tone River in Saitama, respectively.

Table 1

	Specific activity (Bq/L)			Date for decay correction
	Cs-134	Cs-137	K-40	
Seawater	1.6 ± 0.3	2.0 ± 0.2	13.9 ± 4.3	June 23, 2011
River water	DL (<0.8)	DL (<0.6)	7.2 ± 4.3	June 24 2011

DL: lower than the detection limit