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REMOVAL OF CESIUM FROM SEA SLUDGE THROUGH DECOMPOSITION OF ORGANIC MATTER WITH AQUEOUS HYDROGEN PEROXIDE

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ABSTRACT: The radioactive cesium scattered from the Fukushima Nuclear Power Plant has caused a pollution problem in Japan. To tackle such accidents, many technologies have been developed to remove radioactive cesium from water. However, the technology to decontaminate the sludge is much less advanced than that for water. Thus, we focus on the decomposition of organic matter by H_2O_2 for decontaminating the sludge. The maximum decontamination of the sea sludge by H_2O_2 was found to be 2.6 times higher than that by water alone, and the greatest decontamination was obtained using 34.5% H_2O_2. We believe the extent of decontamination increased for this solution because the solution pH was near the pHpzc, which would suppress the ability of the sludge to absorb Cs ions. We also examined the effect of time on the decontamination of the sea sludge; however, only a small increase in decontamination (1.7 times the initial value) was observed.

Keywords: Cesium, Decontamination, Hydrogen peroxide, Water area

1. INTRODUCTION

In 2011, the Fukushima Nuclear Power Plant was destroyed by a tsunami. Radioactive cesium was released across a wide area, contaminating soil and water. As a result, cesium was even found to be present in the sea sludge at the bottom of Tokyo Bay in concentrations that are 1.5–13 times the background level [1].

To recover from this accident, methods to remove radioactive cesium from the sea sludge are needed. There are fewer reports on the decontamination of the sea sludge than on the decontamination from water. In addition, the methods of decontaminating water cannot be simply applied to decontaminate the sea sludge. For example, iron ferrocyanide has been reported to remove Cs^+ from water; however, high concentrations of cyanide accumulated in the sludge when this method was used. Therefore, this method of decontaminating the sludge requires an additional decontamination step for the removal of cyanide [2]. Therefore, in the present study, we have studied easier methods of decontaminating the sea sludge.

1.1 Characteristics of Sea Sludge

The sea sludge absorbs cesium and iron ferrocyanide because of the clay minerals contained in the sea sludge [2]. Clay minerals contain hydroxide groups that can coordinate cations such as Cs^+ and Fe^{3+}. We examined the adsorptivity of the sea sludge for Cs^+ ions. A 10 g of the sea sludge sample was mixed with 20 mL of water containing 1000 ppm of nonradioactive cesium nitrate ($CsNO_3$). This is the same cesium isotope as the radioactive cesium that is the object of the present decontamination study. As shown in Figure 1, the adsorptivity of the sea sludge for Cs^+ in water was found to be 65.1%, and this adsorption occurred instantaneously. Moreover, the properties of the hydroxide groups in the sea sludge are changed at certain pH values. At low pH values, the hydroxide groups are protonated as OH_2^+. As a result, we assumed the adsorptivity of the sea sludge for cations would decrease. The pH value where this effect occurs is called the isoelectric point (point of zero charge; pHpzc). We assumed that the pH of the solution would affect the decontamination.

2. PURPOSE OF STUDY

In the present study, we focused on using

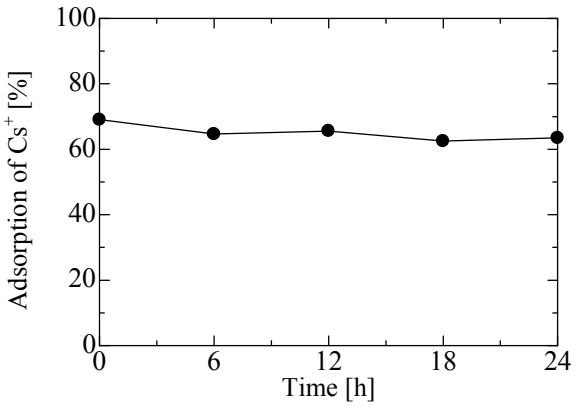

Fig. 1 Adsorption of Cs^+ by sea sludge

hydroxyl radicals as a new way to decontaminate the sludge. This idea was originated from a previous study in which Cs^+ was removed from the sea sludge, with cleaning sulfide (S) and reducing total nitrogen (T-N) by using hydroxyl radicals in micro-bubbles [3].

The authors proposed that the origin of this decontamination effect was the decomposition of organic matter by hydroxyl radicals or the decomposition of organic matter by aerobic microorganisms that were activated by the micro-bubbles. Therefore, the authors attempted decontamination using anaerobic microorganisms with the same decomposition performance as aerobic microorganisms. However, decontamination of the sea sludge by activation of anaerobic microorganisms could not be confirmed. From this result, the authors concluded that anaerobic conditions were not suitable for removal of cesium and that decontamination was most effective in aerobic conditions. In addition, the authors suggested hydroxyl radicals have shown a decomposition performance that is suitable for decontamination of the sea sludge [4].

In the present study, we studied the decontamination of the sea sludge by hydroxyl radicals. To obtain hydroxyl radicals easily and safely, we suggested using hydrogen peroxide (H_2O_2). H_2O_2 was chosen for two reasons: (i) no equipment, such as micro-bubbles, is required, and (ii) the decontamination ability can easily be compared to the change of H_2O_2 concentration. We examined the potential of hydroxyl radicals to decontaminate the sea sludge by varying the concentration of H_2O_2 and the stirring time.

3. RESULTS AND DISCUSSION

3.1 Purification of Sea Sludge by H_2O_2

First of all the ability of H_2O_2 to purify the sea sludge was examined. A 10 g sea sludge sample collected from the Funabashi port in Chiba prefecture was mixed with 20 mL of aqueous H_2O_2 with a concentration of 0%–34.5%. A powder sample was then made by filtration and drying, and the organic matter content was measured by thermogravimetry (TG) and sulfide content was determined by energy dispersive X-ray spectrometry (EDX). To compare the organic matter content, the difference in the values at 100 °C when water in the sample evaporated and 600 °C when the organic matter is burnt off was used. To compare the sulfide content, the ratio of sulfide in the sea sludge to silicon dioxide (SiO_2) in the sea sludge was used. This ratio was chosen because the content of SiO_2 in the sea sludge is not greatly affected by H_2O_2.

The change in organic matter content is shown in Figure 2. The organic matter content was found to decrease as the H_2O_2 concentration increased. The sulfide concentration, determined as the change in the S/Si ratio, was lower for all H_2O_2 concentrations studies compared with the value for 0%, as shown in Figure 3.

These results indicated that purification of the sea sludge by H_2O_2 occurs, and was similar to that observed with micro-bubbles. This result indicates that H_2O_2 could potentially be used to remove cesium from the sea sludge; thus, the decontamination ability of H_2O_2 was determined in the next experiment.

3.2 Decontamination of Sea Sludge by H_2O_2

The changes in the extent of decontamination using H_2O_2 were studied by varying the H_2O_2 concentration and the stirring time. Samples were liquids obtained by filtration and the Cs^+ concentrations were determined. Each 10 g sea sludge sample was mixed with a 20 mL solution of H_2O_2 and $CsNO_3$. The concentration of H_2O_2 was 0%–34.5%. The concentration of $CsNO_3$ was 500–2000 ppm in the experiment where the cesium concentration was varied, and was fixed at 1000 ppm in the experiment where the stirring time was varied. The Cs^+ concentration and pH in the liquid samples were measured using ion chromatography and a pH meter, respectively.

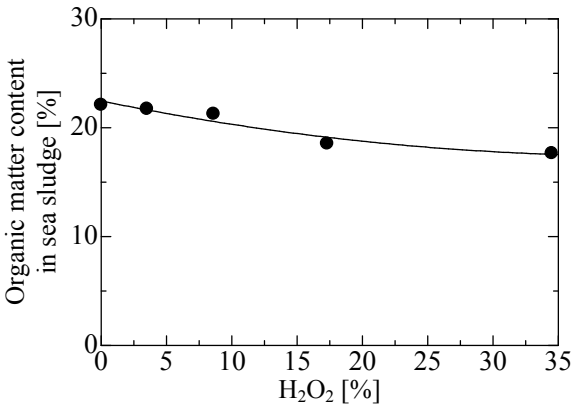

Fig. 2 Change of organic matter content

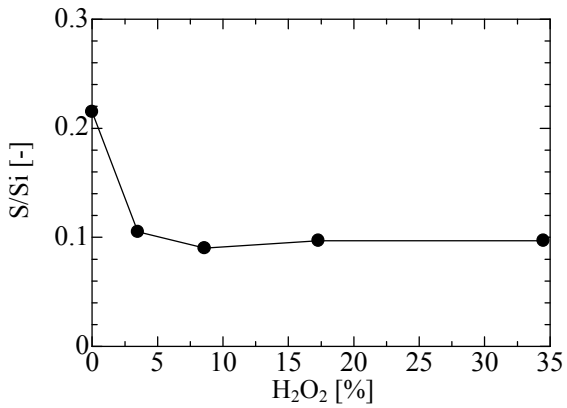

Fig. 3 Change of values in S/Si

3.3 Effect of H_2O_2 Concentration on Sea Sludge Decontamination

The ability of varied concentrations of H_2O_2 to decontaminate the sludge that contained $CsNO_3$ was examined. The dissolved Cs^+ concentrations in the liquid phases at different H_2O_2 concentrations are shown in Figure 4. The concentration of Cs^+ in the liquid phase substantially leveled when the employed H_2O_2 did not exceed 17.3% H_2O_2. The amount of Cs^+ determined in 34.5% H_2O_2 was much greater than the ones in the other conditions. By dividing the measured values by the value for 0% H_2O_2, normalized curves were obtained as shown in Figure 5. A similar trend with H_2O_2 concentration is observed for all three initial $CsNO_3$ concentrations, which indicates that the decontamination of the sea sludge by H_2O_2 was similarly effective under various conditions.

The pH values measured for these solutions are shown in Figure 6. The pH values decreased with increasing H_2O_2 concentration and were lowest for 34.5% H_2O_2. As the extent of decontamination was greatest for 34.5% H_2O_2, it is suggested that the pHpzc value of the sea sludge is between 3.6 and 4.1 in the present study.

3.4 Effect of Stirring Time on Sea Sludge Decontamination

Decontamination results obtained at various H_2O_2 concentrations (0%–34.5%) and various stirring times (0–24 h) were normalized by dividing the measured values by the value for 0 h stirring as shown in Figure 7. The values obtained for 34.5% H_2O_2 did not change significantly with stirring time. However, the other concentrations of H_2O_2 showed peaks in the graph. These peaks were observed at 18 h, 12 h and 6 h for 17.3%, 8.6% and 3.5% H_2O_2, respectively. These results indicated that the decontamination of the sludge by H_2O_2 did not change significantly with time. The peak value was only 1.5 times the 0 hour concentration for 17.3% H_2O_2 and only 1.7 times the 0 hour concentration for 8.6% H_2O_2. From these results, it is not likely that the decontamination effects would be enhanced through prolonged stirring.

3.5 Discussion

We have demonstrated the ability of H_2O_2 to elute Cs^+ from the sea sludge to water. It will be possible to remove Cs^+ from water, using the latest

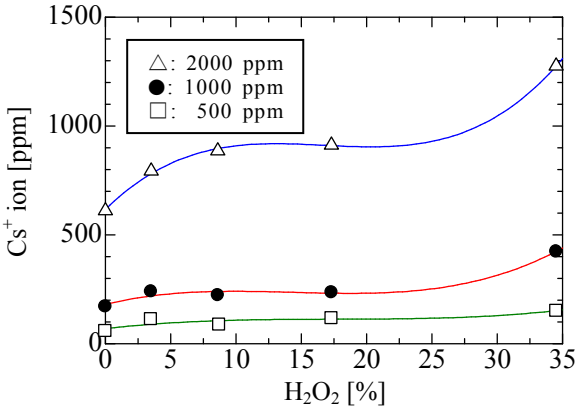

Fig. 4 Removal of Cs^+ from sea sludge by H_2O_2

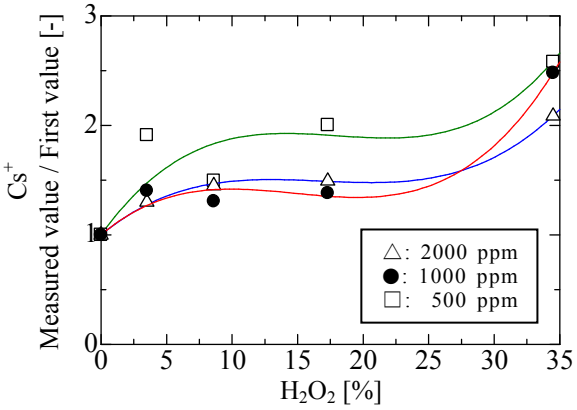

Fig. 5 Normalized removal of Cs^+ from sea sludge by H_2O_2

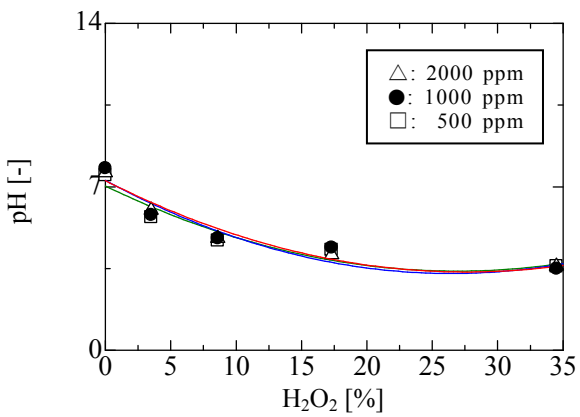

Fig. 6 Change of pH in liquid phase

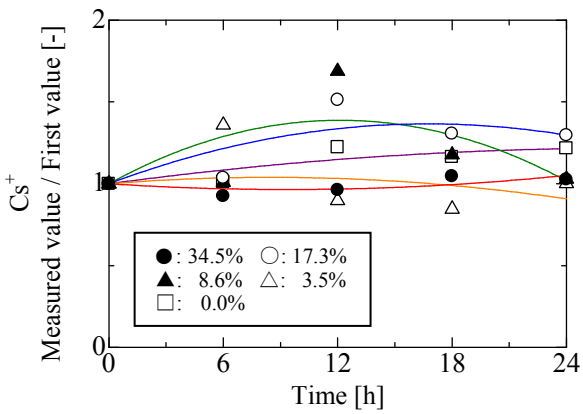

Fig. 7 Change of decontamination with time

decontamination technology, which is currently progressing [6]. From these facts, it will be possible to clean an entire body of water by combining these two technologies for decontamination of the sea sludge and water.

4. CONCLUSION

The removal of Cs^+ from the sea sludge by H_2O_2 was evidenced, and a concentration of 34.5% H_2O_2 was found to realize the highest extent of decontamination. In addition, the 34.5% H_2O_2 sample had the lowest pH value. Therefore, it is likely that the pH value in 34.5% H_2O_2 was less than or equal to the pHpzc value of the sea sludge and that the adsorptivity of the sea sludge for Cs^+ decreased at that low pH value to enhance the decontamination effect.

Decontamination of the sea sludge by H_2O_2 over time was constant for 34.5% H_2O_2, whereas an upward trend of decontamination was observed for 17.3% and 8.6% H_2O_2. However, these values were only 1.5–1.7 times the 0 hour value. The increase in the decontamination ability with time is not large, and decontamination by H_2O_2 can be considered substantially instantaneous.

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