DEVELOPMENT OF A BIOREACTOR SYSTEM FOR TREATMENT OF DIOXINS-CONTAMINATED SOILS AND INCINERATED RESIDUE

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Introduction

Soil contamination caused by dioxins in and around sites of incinerators for municipal solid waste (MSW) ~~has been~~is a concern in Japan~~ed~~. For example, scattering wastewater ~~of~~ from a wet gas scrubber ~~from the top of~~at an MSW incinerator facility ~~for MSW~~in Nose, Osaka caused soil and surface water contamination ~~in Nose, Osaka, Japan~~. The concentration of dioxins in the soil was about 8,000 pg-TEQ/g. Other contamination sites include soils on which fly ash has been placed directly or improperly stored and landfill sites that have received bottom and fly ash over a long period. Some countermeasures are required immediately at these dioxins-contaminated sites.

We have previously developed bioreactor systems for dioxins-contaminated water and soil[1, 2], because biological methods are inexpensive and have a low potential to produce toxic by-products. We have shown that a fungus, *Pseudallescheria boydii (P. boydii)*, isolated from activated sludge treating wastewater that contained dioxins, can degrade highly chlorinated dioxins[2]. A reaction product of octachlorinated dibenzo-p-dioxin (OCDD) was identified as heptachlorinated dibenzo-p-dioxin[1]. Therefore, one of the pathways for degradation of OCDD by this fungus was predicted to be as follows: OCDD is transformed by dechlorination and then one of the remaining aromatic rings is oxidized.

Ishii et al.[3] showed that 1 kg of dioxins-contaminated soil (70% water content) could be treated by 5 L of bioreactor for 48 hours at 35 °C and that the degradation ratio was about 50% (initial concentration was 4,000 pg-TEQ/g). However, fly ash has not been used previously in bioreactor tests. Fly ash generally contains salts, which may inhibit the growth of *P. boydii*. Moreover, it is widely known that dioxins in fly ash are difficult to extract, which may lower the degradation ratio of *P. boydii*. The bioreactor treatment process alone may be insufficient because microorganisms cannot degrade all of the dioxins. Thus, a posttreatment process such as physiochemical treatment is needed.

This study has elucidated growth conditions for *P. boydii* in a medium containing fly ash. Bioreactor tests were carried out for three kinds of contaminated soil: (A) a soil sample from Nose, (B) soil mixed with a low dioxins concentration of fly ash, and (C) soil mixed with a high dioxins

concentration fly ash. In addition, solvent extraction was applied to the soils after the bioreactor process. Subsequently, a total bioreactor system for dioxins-contaminated soil including fly ash is proposed.

Materials and Methods

Contaminated soils: Soil A was dried at 100 °C for two hours and passed through a 2 mm mesh sieve; the concentration of dioxins were 7,310 pg-TEQ/g. Soils B and C were prepared in our laboratory by mixing uncontaminated soil with two types of fly ash. The uncontaminated soil was sampled from surface soil within the Hokkaido University grounds, and was dried and sieved. The fly ash samples were taken from electric precipitators of mechanical stoker-type incinerators. The concentrations of dioxins in the samples of soil mixed with fly ash were 173 pg-TEQ/g and 2,210 pg-TEQ/g, respectively.

Media: The medium contained glucose, 1.0 g; $(NH_4)_2SO_4$, 0.2 g; NaCl, 0.2 g; K_2HPO_4, 0.1 g; $MgSO_4 \cdot 7H_2O$, 0.1 g; $CaCO_3$, 0.2 g. It also contained 0.1 mL of a trace element solution ($FeSO_4 \cdot 7H_2O$, 0.01 g; $MnCl_2 \cdot 4H_2O$, 0.01 g and $ZnSO_4 \cdot 7H_2O$, 0.01 g per 10 mL of distilled water) per 100 mL of distilled water. In experiments to identify inhibitors of the growth of *P. boydii*, the designed amount of NaCl, $CaCl_2$, and KCl, was added to this medium.

Bioreactor test: A stainless steel cylindrical reactor (5 L), as shown in Figure 1, was used. A mixture of the respective soil and water (70% of the total mass) was agitated with an angled turbine at 200 rpm. The position of the turbine and the number of rotations was determined by preliminary experiments with a different reactor made of PVC. The reactor was controlled at 30 °C using a water jacket.

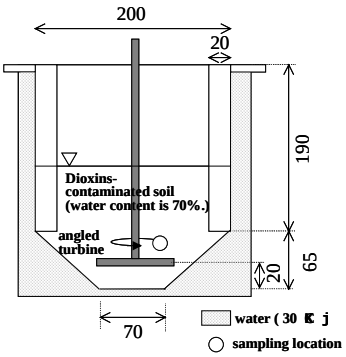

Figure 1 Schematic diagram of a bioreactor (unit: mm)

Dioxins analysis: After biodegradation tests, the culture medium, including soil, was treated with acid to extract dioxins from the cells, and the solid and liquid phases were separated with a suction funnel. The solid phase was then freeze-dried. Dioxins in the dried solid phase were extracted with toluene in a Soxhlet extractor, and those in the liquid phase were extracted with toluene three times. The extracted dioxins from the toluene phases were mixed and applied to a multi-layer silica gel column, which was filled in sequence from the bottom to the top with 0.5 g of silica gel, 3.0 g of 2% potassium hydroxide-impregnated silica gel, 0.5 g of silica gel, 4.5 g of 44% sulfuric acid-impregnated silica gel, 6.0 g of 22% sulfuric acid-impregnated silica gel, 0.5 g of silica gel, 3.0 g of 10% silver nitrate-impregnated silica gel, 0.5 g of silica gel and 3.0 g of sodium sulfate. The dioxins in the column were eluted with 150 mL of hexane, and dissolved in 0.1 mL of toluene. Analysis of dioxins was carried out with an HRGCMS apparatus. The degradation of dioxins was estimated from the decrease in the toxic equivalent quantity (TEQ) based on peaks.

Chemicals: For calibration and clean-up, a PCDD/PCDF standard mixture, EDF-4931 (CIL, Inc.), and the isotopically-labeled chlorodioxin standard, ED-900 (Wellington Lab.), were used respectively. The other chemicals were laboratory grade.

Results and Discussion

Inhibiting factors for growth of *P. boydii*

Our past study suggested that dioxins were degraded at the growth phase of *P. boydii*. Therefore, growth conditions of *P. boydii* are very important for degrading dioxins. However, monitoring the growth of *P. boydii* in soil is very difficult because *P. boydii* is a filamentous fungus. Therefore, we assumed that a decrease in glucose concentration corresponded to growth of *P. boydii*. The glucose concentration can be measured as Total Organic Concentration (TOC) because concentrations of the other organic matters are very low or negligible. The relationship between TOC concentration and weight of *P. boydii* after drying, as shown in Figure 2, suggests that a decrease in TOC concentration corresponds to growth of *P. boydii*.

To identify the inhibiting factors for growth, *P. boydii* was incubated with (1) chloride concentration control, and (2) pH control as shown, in Figure 3. The elate of the fly ash was also used for preparation of the medium. It was found that a chloride ion concentration greater than 20 g/L and a pH greater than 10 inhibited growth of P. boydii. Therefore, if the chloride ion concentration of fly ash is high, a pretreatment process is needed to reduce it before the bioreactor process. In addition, pH control is needed during operation of the bioreactor. It is noted that heavy metals in fly ash have no influence on the growth of *P. boydii*[3].

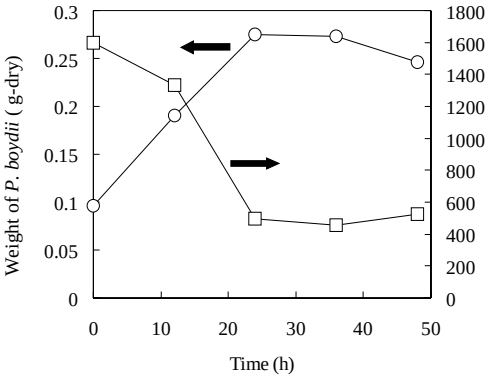

Figure 2 Relationship between TOC concentration and growth of *P. boydii*

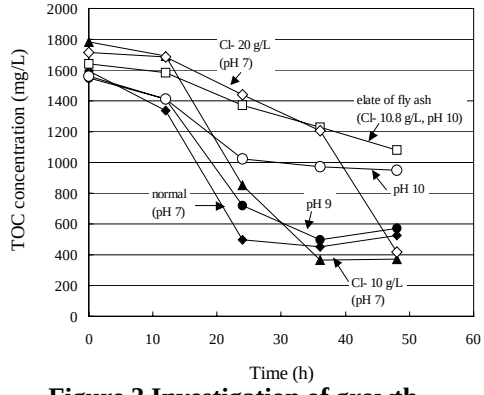

Figure 3 Investigation of growth conditions of *P. boydii*

Bioreactor tests

One kilogram of each soil (A to C) and 2.33 L of medium (water content 70%) were placed in the reactor and mixed for 96 h at 30 °C. In addition, pH was controlled below 8.0 and TOC concentration was monitored to confirm the growth of *P. boydii*.

Figure 4 shows the results of bioreactor tests. About 60% of dioxins in soil A and B, and 40% of dioxins in soil C, were degraded after 48 h. Thus, it is confirmed that *P. boydii* can be applied to soils that contain a broad range of dioxins concentration (173 pg-TEQ/g to 7310pg-TEQ/g).

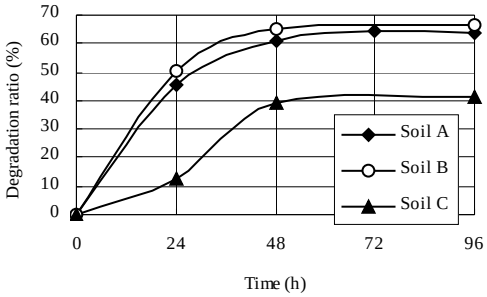

Figure 4 Results of Bioreactor tests

Post-treatment for remaining dioxins

To treat the remaining dioxins after the bioreactor process, a solvent extraction process was introduced. Nakamiya[4)] reported that ethanol (80% in water) could effectively extract dioxins from Nose's contaminated soil (soil A). Using ethanol, 70% of the remaining dioxins were extracted from soil A after the bioreactor process. In the overall bioreactor system, 92% of dioxins were removed, reducing the concentration from 7,310 pg-TEQ/g of soil treated to 580 pg-TEQ/g.

As expected, even if isopropanol or citric acid was used as a solvent, it was very difficult to extract the remaining dioxins from soil B and C.

Proposed bioreactor system for dioxins-contaminated soil and incinerated residue

Figure 5 shows the bioreactor system proposed as a result of this study. *P. boydii* is a weakly pathogenic fungus, ranked at the lowest level in Japanese guidelines. Therefore, a heating sterilizing process was added to the system. The sterilizing conditions have been reported by Ishii et al.[5)].

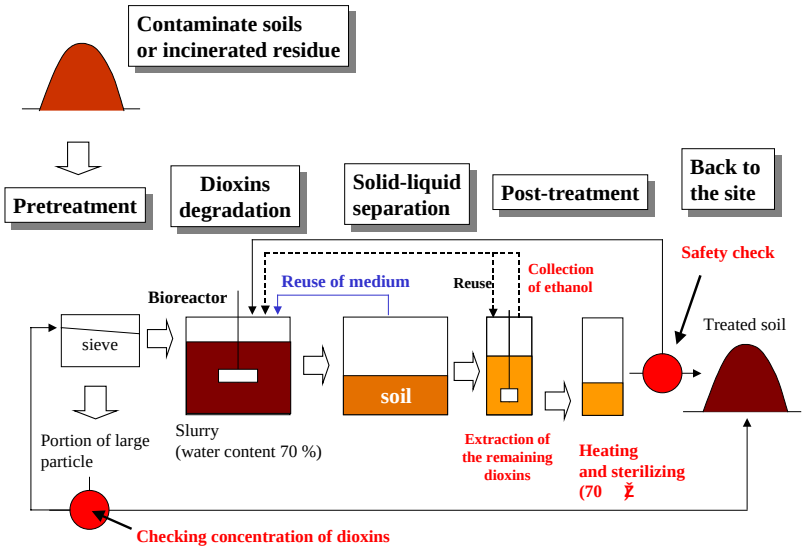

Figure 5 The Bioreactor system for dioxins-contaminated soil and

Acknowledgments

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References

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