

EMISSION CONTROL, ABATEMENT TECHNOLOGIES AND REMEDICATION - POSTERS

Solvent-washing of dioxin-contaminated soil and ultraviolet treatment of the extracted dioxins

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Introduction

Dioxins are the most harmful man-made chemicals. Especially in Japan, many dioxin-contaminated sites have been found around incineration facilities (1), with the contamination levels reaching over 8,000 pg/g. Contaminated soil has been gathered and stocked in special facilities until toxicity levels decrease to less than the environmental guard line or until the soils are treated by remediation methods.

Based on recent soil analyses, that amount of contaminated soil is on the increase. Therefore, effective dioxin-treatment methods are necessary. Physio-chemical treatment methods require large amounts of energy and the construction of special facilities, but are quick and effective for treating large amounts of dioxin-contaminated soil.

Solvent extraction has been used for the cleanup of trace amounts of soil dioxins (2). This extraction, however, requires a special apparatus, a soxhlet extractor, and a harmful solvent, toluene, and it can process only a few grams of soil at a time. In addition, it takes 16 hr to complete the extraction process.

There have been some attempts to extract halogenated materials from contaminated soil. Amid et al. have used ethanol to extract pentachlorophenol (PCP) from the soil as a means of environmental restoration (3). In addition, Ri et al. have tested the ability of some solvents to extract dibenzopyrene from contaminated soil. But it takes 24 hr to extract 95% of the dibenzopyrene (4). However, to our knowledge, there have been no previous reports of solvent-washing being used for dioxin cleanup.

UV irradiation is one of the most useful methods for the treatment of solvent-soluble dioxins. There has actually been some large-scale use of the process for the treatment of dioxin-containing wastewater. In addition, Horii et. al have combined UV irradiation and hydroxyl radicals for the effective degradation of dioxins (4).

In this report we describe the extraction of dioxins from actual contaminated soil by means of solvent washing and its degradation by UV irradiation.

Materials and Methods

Chemicals

PCDD/PCDF STANDARD MIXTURE EDF-4931 (Cambridge Isotope Laboratories Inc.) was used for the quantification of dioxins. The other chemicals used in the experiment were all chemical-grade.

Apparatuses

Figure 1 shows the soil-agitation apparatus for the extraction of dioxins as well as the UV irradiation apparatus.

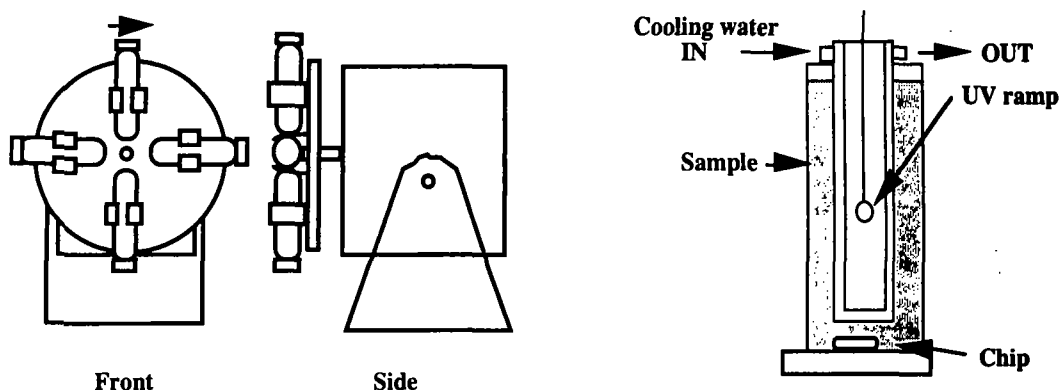


Figure 1. Soil-agitation apparatus (left) and UV irradiation apparatus (right)

Soil

The soil used in the study was an actual contaminated soil sample taken from the area surrounding the incineration institute in Nose town, Osaka, Japan. The soil sample from Nose was found to contain approximately 10,000 pg-TEQ/g (total dioxin concentration in soil approximately 1800,000 pg/g) based on data obtained in our laboratory. The soil was found to be 20% organic matter based on the heat-burning decrease percentage at 600°C. Before being using in the extraction experiment, the soil was dried and standardized by sheave using 2-mm cut mesh. Pre-treated soil was stored in a desiccator until use in the experiment.

Preparation and analysis procedure

After extraction, the soil fraction was extracted with a soxhlet extractor, and the solvent phase was extracted with 50 ml of toluene and then dried over anhydrous sodium sulfate, after which the toluene solution was washed with sulfuric acid and subjected to silica gel (3 g) column chromatography. The dioxins were eluted with 150 ml of hexane, and the volume was decreased to 100 μ l. By these procedures, approximately 100% of the spiked dioxins were recovered.

One microliter out of 100 μ l was measured by a GC-MS apparatus (ThermoQuest GCQ plus equipped with TRACE GC 2000) set to GC-MS/MS mode (6).

Results and Discussion

Solvent-washing of dioxin-contaminated soil

The extraction experiment was performed at room temperature for 10 min before the optimal conditions had been determined. The ratio of soil to solution was set to 10% (w/v) based on the solubility of dioxins in solution (7). A 3.6-g soil sample was added to a 40-ml screw-capped Teflon tube (used to avoid adsorption of dioxins). Next, 36 ml of solvent was towered in the tube. The mixture in the tube was agitated with a Rotator RT-50 (TAITEC, Co. Ltd. Japan) at 27 rpm. To separate the ethanol phase from the soil, the tube was centrifuged by a HITACH RC21 (HITACH, Co. Ltd. Japan) at 3,000 rpm and 18 °C (room temperature). The resultant clear solvent phase was decanted, and the volume was measured. Based on the withdrawal ratio of towered solution to decanted solution, the dioxin concentration of the solvent remaining in the soil was determined.

Based on the tested organic solvents, ethanol, methanol, and acetone, respectively, were found to have almost the same extraction rates (approximately 40%). We were not able to select a solvent based on the extraction efficiency, but, as ethanol is the least toxic of these solvent, we selected it as the most suitable solvent for soil washing.

The agitation time and extraction temperature were estimated. The extraction efficiency

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remained level for approximately 1 min and then decreased. An extraction rate of 36% was achieved in relation to the total dioxins. The agitation time was fixed at 1 min, and the extraction temperature was changed from room temperature (20°C) to the boiling point of ethanol (78.3°C). Finally, 76% of total dioxins were extracted in ethanol at the boiling point. With only 1 min of extraction at the boiling point of ethanol, approximately 76% of dioxins were extracted from the contaminated soil.

Although an extraction temperature of 78.6°C seems to be very energy-consuming, it is actually quite low when compared to physiological soil treatments, for example methods using supercritical fluids and burning treatments carried out at over 800°C (4). Furthermore, when ethanol is reused by withdraw via distillation, the boiling can be done after the extraction, and concentrated, small volumes of dioxins can be efficiently degraded to carbon dioxide by burning treatments carried out at high temperatures or by another physio-chemical treatment. The boiling of ethanol, therefore, is not as energy-consuming process as process engineering. We therefore fixed the extraction temperature at 78.3°C. Even with this change, however, 24% of the dioxins remained in the soil.

At the application stage, the drying of dioxin-contaminated soil is the most time- and energy-consuming part of the extract process. We therefore attempted to estimate the effects of the water percentage in ethanol on the extraction of dioxins from contaminated soil. The water percentage was changed from 0 to 40%, and the extraction rate was found to increase with decreases in the water content of the ethanol. Almost all the total dioxins were extracted with ethanol containing 20% water. At less than 10% water, however, the extraction rate was decreased. These results remained the same when dioxins were measured based on the 2, 3, 7, 8-tetrachlorinated dibenzop-dioxin toxicity equivalency quantity (TEQ). These results indicate that the dioxins extraction rate is increased when water-containing soil is treated for extraction. In advance, to estimate the water content in contaminated soil, ethanol was added to contaminated soil to bring the water-ethanol ratio to 20:80; as a result, almost all of the dioxins were extracted to the ethanol phase from the contaminated soils, indicating that the drying process is not necessary for this procedure.

Figure 2 shows the quantitative decrease in dioxins in Nose's soil under the optimal extraction conditions. In 1 min, the TEQ was decreased to less than the environmental guard line, which is actually lower than the environmental standard in Japan.

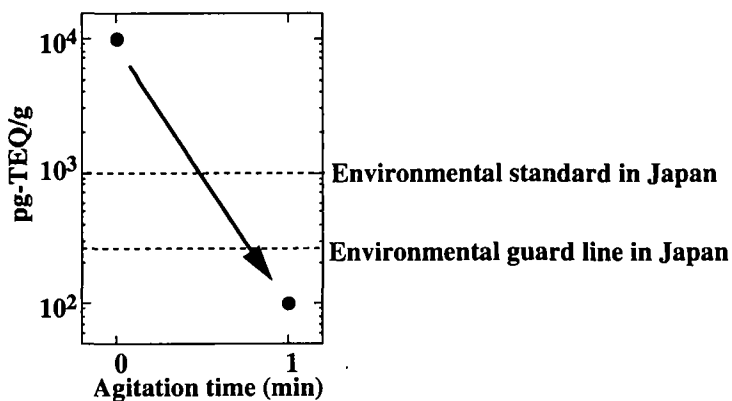


Figure 2. Decrease in dioxins in contaminated soil under optimal solvent-washing conditions.

Degradation of extracted dioxins by ultraviolet treatment

Ultraviolet treatment for the degradation of dioxins has been well studied by many researchers, and the required instruments can actually be purchased from some makers. We therefore

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attempted to degrade dioxins extracted from contaminated soil by a seldom-used high-pressure mercury ramp.

Low-pressure mercury lamps, which emit a narrow range of wavelengths, are used by many researchers. High-pressure mercury ramps, however, emit a wide range of wavelengths. In response to irradiation from this type of ramp, dioxins appear to be degraded by dehalogenation over time (data not shown). Approximately 60 min after the start of the process, dehalogenated 4-chlorinated dioxins had begun to accumulate. Then, these dioxins began to be further degraded. As a result, the toxicity was actually increased at 60 min by this method, so we decided to fix the optimum irradiation time at 90 min.

Under the above conditions, approximately 400 ng/ml (ethanol solution) of extracted dioxins were conjugated in 1 l of effluent from the landfill and allowed to react for 90 min. Table 1 shows the results of the degradation. Compared to a blank sample (0 min), the amount of TCDD+TCDF increased by 50%, indicating that dehalogenation products were accumulating as 4-chlorinated dioxins. It is possible that any materials interfering with the degradation of the dioxins were extracted with dioxins from the soil. All of these results suggest that when using UV treatments, especially those involving a high-pressure mercury ramp, we must be careful about increasing the toxicity of the soils being treated.

Table 1. UV degradation of dioxins in ethanol from contaminated soil

	Degradation (%) of				
	TCDD +TCDF	P5CDD +P5CDF	H6CDD +H6CDF	H7CDD +H7CDF	OCDD +OCDF
pg-TEQ (mg/l)	-50	68	40	57	71
Average	39				

Acknowledgements

Our study was supported by the Ministry of Health and Welfare of Japan. We would like to thank Dr. Sadayori Hoshina of Jikeikai University of Medicine and Dr. Ikuo Souda of Kanagawa Prefecture Environmental Research Center for their helpful discussion. Thanks are also due to Mr. Toshio Kawanishi of KUBOTA Co. Ltd., and Dr. Hiroshi Goda of TOWA KAGAKU Co. Ltd.

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