A LOW-COST REMEDIATION TECHNOLOGY FOR DIOXIN CONTAMINATED SOLIDS BY UTILIZATION OF RECYCLED CHARCOAL

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Introduction

Dioxins including polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs) and coplanar biphenyls (Co-PCBs) are ubiquitous and persistent contaminants[1]. In order to combat the threat posed by these chemicals to human health and the environment, the Stockholm Convention on Persistent Organic Pollutants was adopted in 2001 and the production and usage of these compounds were heavily regulated[2]. However, these contaminants have been globally distributed in practically all environmental sectors[3]. Therefore, research and development of technologies for removal of these contaminants has gained considerable importance.

A thermal desorption technology in which dioxins-contaminated solids are being remediated by desorption and degradation is increasing used because of their high reliability and efficiency of dioxins removal[4]. However, high energy consumption during continuous heating and required cost for treatment of the effluent gas have prevented widespread implementation. In this study, a novel remediation process based on thermal desorption is proposed using cost-effective recycled charcoal as both an adsorbent and thermal source. There is no need for post-treatment of the used charcoal in the adsorption column, which saves cost. Thus, it is potentially a promising alternate to conventional dioxins remediation technologies. Main objective of the work was to examine the removal behavior and efficiency of dioxins, and to investigate feasibility of this technology.

Materials and methods

Dioxins-contaminated sediments used in this study were taken from Fugan-unga in Toyama, Japan, one of the areas of most heavily contaminated by dioxins in Japan[5]. Commercially manufactured charcoal produced from charred conifers (Ishiko Co. Ltd., Japan) was
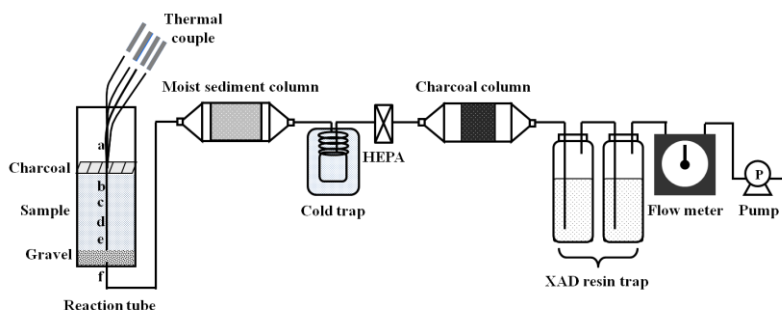

Fig. 1. Schematic diagram of the experimental apparatus

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used as an adsorbent for adsorption of dioxins in the effluent gas, which was recycled as a thermal source for continuous heating during the treatment process.

A schematic diagram of the experimental apparatus is shown in Fig. 1. Experiments were conducted in a stainless steel cylindrical reaction tube (height: 20 cm; inner diameter: 4.7 cm). Before each experiment, 50 g of gravel was placed at the bottom of the reaction tube as a substrate. Next, sediment samples mixed with charcoal at 10 wt% of the total weight (70 g) were added to the reaction tube. The procedure of thermal treatment process was as follows: 1) combustion was initiated by ignition using 20 g of burning charcoal that had been preheated at 500°C for 10 min; 2) during combustion, gas suction was applied by air (10% O_2/N_2) from the top of the reaction tube to the bottom; 3) the temperature at the top of the sample increased and the combustion gradually proceeded downward in the tube. The sediment and gas temperatures were measured using thermocouples mounted at 2, 4, 6 and 8 cm from the top of the sample and at the inlet/outlet gas lines, respectively. Effluent gas passed through a series of traps prior to its release into the atmosphere. After the treatment, samples collected from treated sediment, moist sediment and XAD traps were analyzed for dioxins by HR-GC/MS (JMS-700, JEOL, Tokyo, Japan)[6].

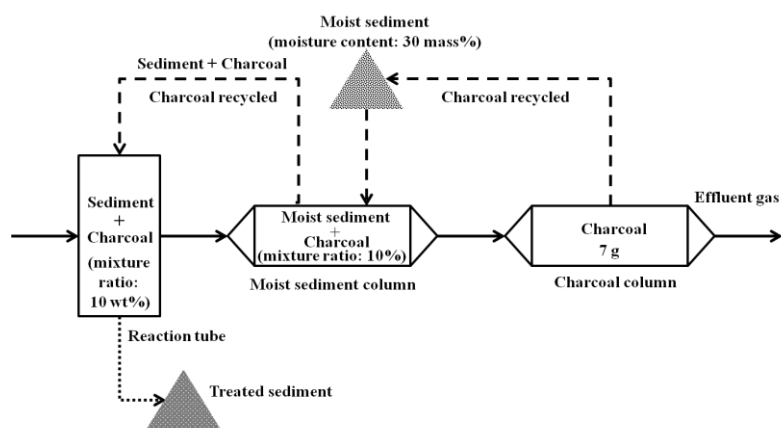The merit of this proposed process is that there is no need to treat generated secondary contaminated waste. As shown in Fig. 2, after charcoal was used for adsorption of dioxins, it can be mixed with moist sediment (contaminated sediment before dehydration) and filled in column. Eventually, charcoal can be recycled to the reaction tube as a thermal source for combustion.

Fig. 2. Schematic diagram of the charcoal recycled process

To investigate the feasibility of this proposed method for removal of dioxins from contaminated solids, experiments were carried out using recycled charcoal shown in Table 1.

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Table 1 Experimental conditions during the thermal treatment process.				
Apparatus	Conditions	Run 1	Run 2	Run 3
Reaction tube	The amount of sediment	63 g	66 g [a]	66 g [b]
	The amount of charcoal	7 g		
	Charcoal/sediment ratio	10 wt%	10 wt%	10 wt%
	Air superficial velocity	3.0 cm s^{-1}	3.0 cm s^{-1}	3.0 cm s^{-1}
Moist sediment column	The amount of moist sediment	84 g	84 g	84 g
	The amount of sediment	7 g	7 g [c]	7 g [d]
	Moisture content	25%	25%	25%
Charcoal column	The amount of charcoal	7 g	7 g	7 g
[a]: Moist sediment (including charcoal) used in Run 1 was used as a sample in Run 2 after drying for 2 h.				
[b]: Moist sediment (including charcoal) used in Run 2 was used as a sample in Run 3 after drying for 2 h.				
[c]: Charcoal filled in the adsorption column of Run 1 was recycled in the moist sediment column of Run 2.				
[d]: Charcoal filled in the adsorption column of Run 2 was recycled in the moist sediment column of Run 3.				

Results and discussion

1. PCDD/Fs

The concentrations of PCDD/Fs in the initial, treated and moist sediment of all runs are shown in Fig. 3 (Panel A, B and C). The removal efficiency calculated with concentrations of PCDD/Fs in all runs between the initial and treated sediment were higher than 99.8%. Toxic equivalency quantities (TEQ) values of PCDD/Fs were obtained by using the contents of seventeen 2,3,7,8-chlorinated
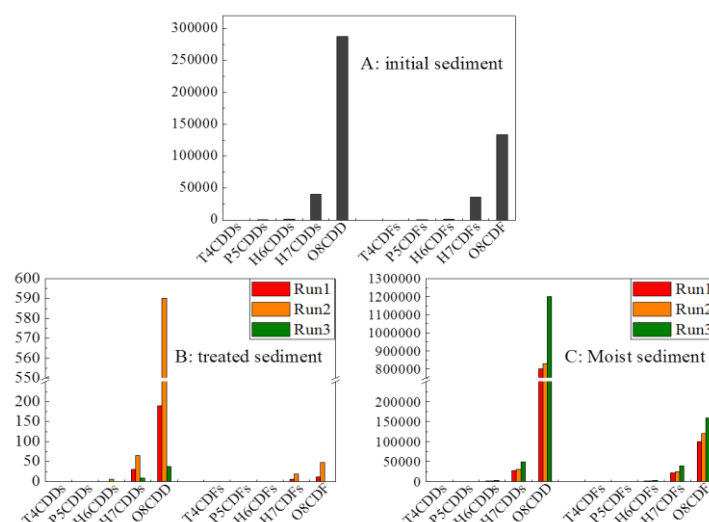

Fig. 3. Concentrations of PCDD/F homologues in all runs (pg g^{-1})

congeners and their toxicity equivalency factors (TEF), those contents in runs 1, 2 and 3 were 0.42 pg-TEQ g^{-1}, 1.5 pg-TEQ g^{-1} and 0.091 pg-TEQ g^{-1}, respectively. These values were far below 150 pg-TEQ g^{-1}, the sediment pollution standard limit in Japan[7], indicating that heating with charcoal achieved high PCDD/Fs removal efficiencies from the sediment. Additionally, as shown in Fig. 3 (Panel C), only the concentrations of O$_8$CDD in the moist sediment column significantly increased compared to those in the initial sediment, whereas other PCDD or PCDF homologues did not. The result is likely due to the reason that O$_8$CDD might be formed from pentachlorophenol (PCP), a potential precursor of O$_8$CDD, during a cooling process in a post-combustion zone[8,9], After the moist sediment column, there were no PCDD/Fs detected in the effluent gas, indicating that moist sediment column is effective for adsorption of PCDD/Fs in the effluent gas.

The homologue profiles of PCDD/Fs in the initial, treated and moist sediment are also presented in Fig. 3, respectively. In the initial sediment, as the number of chlorine atoms in the PCDD/Fs increased, their concentrations increased. O$_8$CDD/Fs were the most abundant homologue, accounting for more than 87% and

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78% of total PCDDs and PCDFs, respectively. After thermal treatment, there were no differences observed in the homologue profiles of PCDD/Fs among all three runs in the treated sediment. These suggest that decomposition was the primary mechanism during the treatment process.

2. Coplanar PCBs

The concentrations of coplanar PCBs in the initial sediment and different fractions of all runs are presented in Fig. 4. Similar high removal efficiencies were obtained as PCDD/Fs, showing above 99.9% of all runs. Adsorbed coplanar PCBs were higher in the moist sediment column than those in the initial sediment, indicating that coplanar PCBs were released from combustion sediment into the effluent gas, and then adsorbed on the moist sediment. There were also some coplanar PCBs detected in the effluent gas, which were different from the results of PCDD/Fs since no PCDD/Fs were detected in the effluent gas. These results suggest that the charcoal used in this study had better adsorption ability for PCDD/Fs than coplanar PCBs.

The isomer profiles of coplanar PCBs in all fractions are also shown in Fig. 4. PCB 118 was the predominant isomer, consistent with all runs, followed by PCB 77 and 105. The TEQ of coplanar PCBs in the effluent gas was calculated by multiplying TEF, showing the highest value was only 0.14 pg-TEQ m^{-3} in all runs. This value was far below the gas emission limit of Japan[7] (100 pg-TEQ m^{-3}).

Fig. 4. Concentrations of Co-PCB congeners in all runs (pg g^{-1} or pg m^{-3})

In summary, a novel cost-effective remediation technology was proposed for dioxins removal from contaminated solids by utilization of charcoal as an adsorbent for dioxins adsorption in the effluent gas, and recycled charcoal as a thermal source for continuous heating. There was no need for post-treatment of the used charcoal with high amounts of the absorbed PCDD/Fs, which saved cost. Results showed that higher than 99.8% of dioxins were removed from the treated sediment. The primary mechanism was decomposition since the homologue profiles after combustion were consistent with those in the initial sediment. Total TEQs in both the treated sediment and effluent gas of all runs satisfied the environmental pollution limit of Japan, no harmful contaminants were released into the environment during the treatment process. Thus, it is feasible to use this method for removal of dioxins from solids using recycled charcoal. Future research will aim to setup this method in large scale experiments.
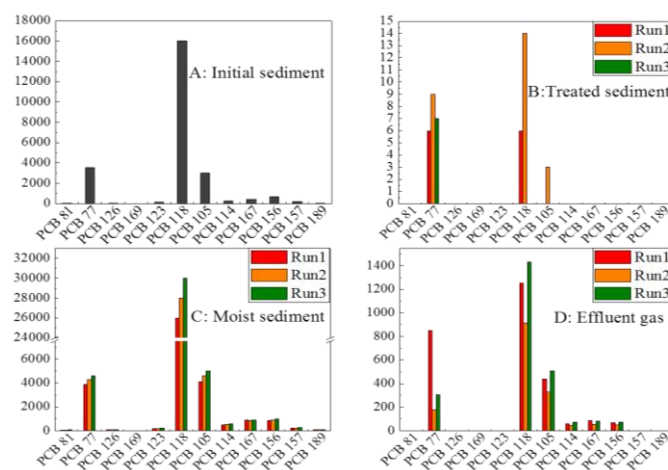
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