Simultaneous Removal of PCDD/Fs, PCP and Mercury from Contaminated Sediment via Pyrolysis

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Introduction

PCDD/Fs, PCP and mercury coexist with relatively high concentrations in the sediments collected from An-Shun site due to previous operation of a PCP plant and chlor-alkali process. Various soil and sediment remediation techniques including photoremediation, landfarming, soil washing, bioremediation, and thermal processes have been developed to remediate the contaminated soil and sediment. In general, thermal treatments can be divided into two groups, i.e.,(i) combustion in the presence of oxygen and (ii) pyrolysis in the absence of oxygen. Due to the low heating value of sediment, oxidation of its organics cannot generate enough heat to sustain thermal oxidation so that pyrolysis is better than thermal oxidation. Moreover, a lower gas flow rate reduces the loading of air pollution control devices (APCDs). Based on the same treating capacity of contaminated sediment, the sizes of a continuous thermal system with oxygen-deficient condition and its APCDs are much smaller compared with those for thermal oxidation. Chang and Yen (2006) applied thermal desorption technology for remediating mercury-contaminated soils and indicated that higher than 98.78% of mercury removal efficiency could be achieved at a temperature higher than 650^{o}C. Hu et al (2006) indicated that a removal efficiency of 99.9999% for total dioxins could be achieved with a pyrolysis system operated at 800^{o}C. A continuous pyrolysis system (CPS) has been developed for effective removal of PCP and PCDD/Fs from contaminated soil and the discharges including both the remediated soil and the exhaust are <0.03% and 1.14% of the input for PCP and PCDD/Fs, respectively (Hung et al., 2016). For effective remediation of highly contaminated sediment of this site, a CPS is designed and tested in this study.

Materials and methods

Sediments were taken from An-Shun site in southern Taiwan for experiment. Two types of sediment collected from a seawater pond and the river nearby, respectively, were tested. The properties of the sediments are shown in Table 1. Because most sediments contain a mixture of sand, silt and clay in different proportions in natural environments, contaminated sediment needs to be pretreated before the experiment. The contaminated sediment after natural drying was sieved and collected with the size less than 10 mesh for testing with CPS which is shown in Fig. 1. Nitrogen (N_2) was applied as carrier gas to maintainan oxygen-deficient condition and the N_2 flow rate was controlled at 10 L/min. The pyrolysis temperatures was regulated with the temperature controllers of the tubular furnace. The feeding rate of sample was controlled at 2 kg/hr by means of a rotary valve. Operating temperatures were adjusted to 550, 600 and 650^{o}C, respectively, and the retention time was fixed at 46 min. In the CPS, contaminated sediment was stirred with inner blades to ensure the homogeneity of temperature and well mixing of sediment. As for APCDs, a bag filter/quench tower/multi-layer activated carbon adsorption bed (MAB)/wet scrubber (WS) system was applied to remove secondary pollutants in flue gas. The samples after thermal treatment were spiked with a Method 1613 labeled standard and a Method 23 internal standard following quantification standards, respectively, before Soxhlet extraction and then analyzed for PCDD/Fs with a high resolution gas chromatography/high resolution mass spectrometer. For PCP analysis, samples were spiked with the labeled standards (Wellington Laboratories Inc.) prior to the Soxhlet extraction and analyzed with HRGC/HRMS. Quantification of mercury in contaminated/ remediated sediment and exhaust followed the USEPA Methods 7471B and 101.

Table 1. Characteristics of the sediments collected from seawater pond and river, respectively.

Measurements (N=3)	Seawater pond	River
Sand (%)	46	31
Silt (%)	12	11
Clay (%)	42	58
Size	<10 mesh	<10 mesh
Moisture content (%)	15.6	14.5
pH	6.6	6.9
Organic matter (%)	2.83	4.38
Cation exchange capacity (CEC) (cmol/kg)	4.87	6.28
Total Sulfur (%)	0.23	0.49
Chloride (mg/kg)	1612	781
Mercury (mg/kg)	112.4	56.3
PCP (mg/kg)	19.49	28.65
PCDD/Fs (ng-TEQ/kg)	8,723	15,345

N: samples analyzed

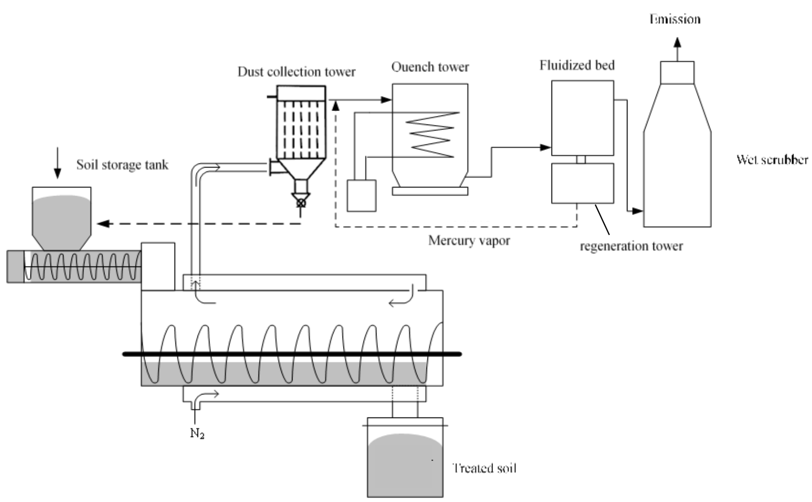

Figure 1. Schematics of the continuous pyrolysis system (CPS) combined with the APCDs consisting of bag filter, quench tower, AC adsorption bed and wet scrubber for sediment remediation.

Results and discussion

The effects of the pyrolysis temperature (ranging from 550ºC to 650ºC) on the removal efficiencies of pollutants were evaluated with the sediments collected from the seawater pond and the river nearby, respectively. The residual concentrations in remediated sediments and removal efficiencies of PCDD/Fs, PCP and mercury achieved are presented in Fig. 2. The operating parameters include 2 kg/hr of sediment treatment capacity, 46 min of residence time, and 10 lpm of N_2 flow rate. Initial PCDD/Fs concentration of seawater pond and river sediments were 8,723 and 15,345 ng-TEQ/kg, respectively. The destruction efficiencies of PCDD/Fs in seawater pond and river sediments increased from 96.2% to 98% and from 96.8% to 98.6%, respectively, as the operating temperature was raised from 500ºC to 650ºC. However, operating the system at 550ºC results in 98.3 and 142.2 ng-TEQ/kg of PCDD/Fs remaining for the remediated sediments, respectively, which are well over the PCDD/Fs limit of sediment (68.2 ng-TEQ/kg) promulgated by Taiwan EPA. The trends of destruction efficiencies of PCP were similar to PCDD/Fs in both seawater pond and river sediments. At 600ºC, the destruction efficiencies of PCP even achieved 99.3% for river sediment. For mercury, the removal efficiencies were higher than 99.22% and 98.68% for two types of sediments. Regarding the removal of mercury from contaminated sediment, desorption is the most important mechanism since mercury cannot be destroyed. In addition, elemental mercury may be transformed into oxidized mercury of higher melting point. However, operating the system at 550ºC resulted in 1.06 and 0.9 mg/kg of mercury remaining in the remediated soil, which are well over the upper limits of mercury in sediments (0.87 mg/kg) as regulated by Taiwan EPA. Operating the CPS at a temperature higher than 600ºC is needed to ensure that PCDD/Fs and mercury concentrations in the remediated sediments fulfill the regulation limits.

Compared with mercury, the removal mechanisms of PCDD/Fs and PCP from contaminated sediments are more complex: desorption, dechlorination, destruction and other unknown reactions may take place simultaneously in the pyrolysis system and it is difficult to pinpoint the exact mechanism and reaction pathway leading to PCDD/F and PCP degradation. However, the results obtained in this study indicate that the CPS developed is in effective in simultaneous removal of PCDD/Fs, PCP and mercury from contaminated sediment if the system is properly operated.

Moreover, the results of flue gas sampling/analysis indicate that bag filter can effectively remove particulate matter (PM) and keep the PM concentration lower than 3 mg/Nm^3. Furthermore, removal efficiencies of PCDD/Fs and mercury achieved with the quench tower increase with decreasing operating temperature and MAB is highly efficient to ensure that emission concentrations of PCDD/Fs and mercury are lower than the emission standards with the AC replacing rate of 1 cm/day. However, SO_2 is significantly found in the exhaust of CPS. WS with NaOH as scrubbing liquid can efficiently remove more than 90% SO_2 from the exhaust.

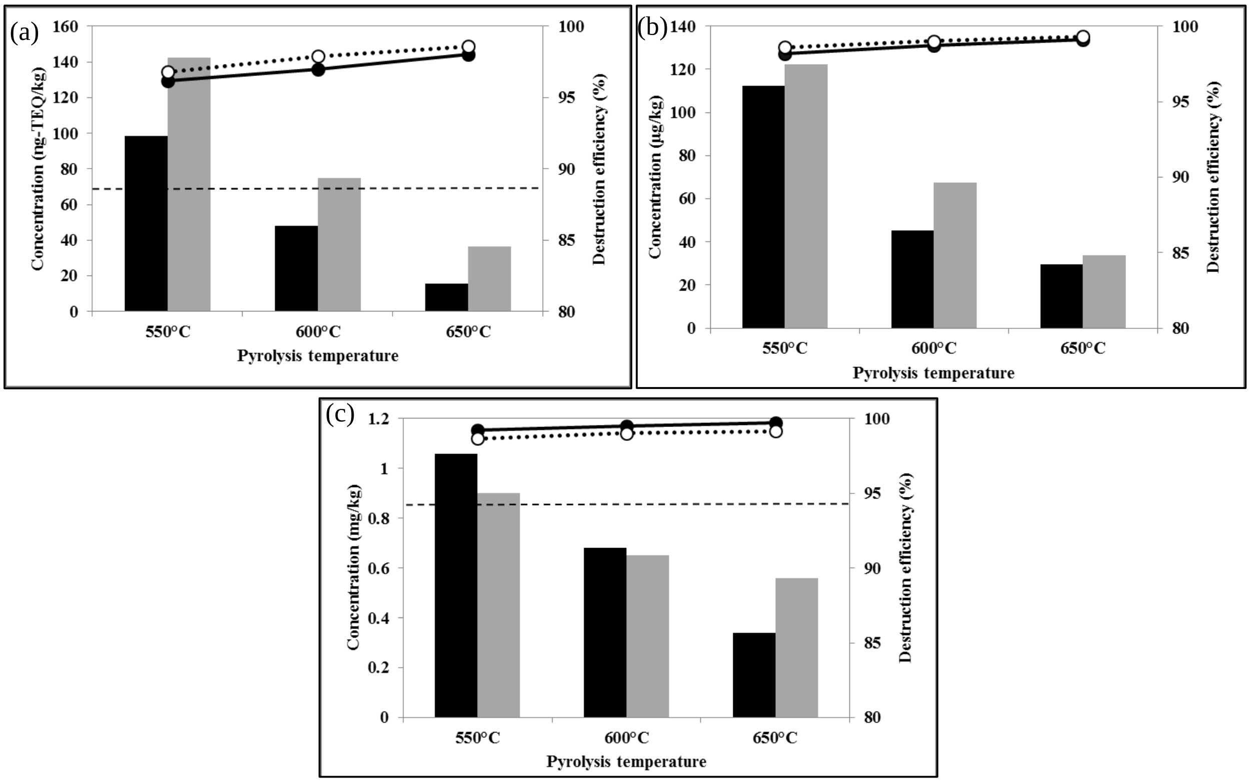

Figure 2. Effect of operating temperature on (a) PCDD/Fs, (b) PCP and (c) mercury removal achieved with the CPS. Black and gray bars represents the residual concentrations of pollutants in remediated seawater pond and river sediments, respectively. Solid and dotted lines represents the efficiencies of pollutants removal for seawater pond and river sediments, respectively. The horizontal dotted line represents the upper limit concentration of sediment as regulated by Taiwan EPA.

Acknowledgments

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Reference

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