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Reduction of dioxin emission by a multi-layer reactor with bead-shaped activated carbon in simulated gas stream and real flue gas of a sinter plant

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ABSTRACT

A laboratory-scale multi-layer system was developed for the adsorption of PCDD/Fs from gas streams at various operating conditions, including gas flow rate, operating temperature and water vapor content. Excellent PCDD/F removal efficiency (>99.99%) was achieved with the multi-layer design with bead-shaped activated carbons (BACs). The PCDD/F removal efficiency achieved with the first layer adsorption bed decreased as the gas flow rate was increased due to the decrease of the gas retention time. The PCDD/F concentrations measured at the outlet of the third layer adsorption bed were all lower than 0.1 ng I-TEQ Nm^{-3}. The PCDD/Fs desorbed from BAC were mainly lowly chlorinated congeners and the PCDD/F outlet concentrations increased as the operating temperature was increased. In addition, the results of pilot-scale experiment (real flue gases of an iron ore sintering plant) indicated that as the gas flow rate was controlled at 15 slpm, the removal efficiencies of PCDD/F congeners achieved with the multi-layer reactor with BAC were better than that in higher gas flow rate condition (20 slpm). Overall, the lab-scale and pilot-scale experiments indicated that PCDD/F removal achieved by multi-layer reactor with BAC strongly depended on the flow rate of the gas stream to be treated.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are commonly known as dioxin which has been listed as one of the persistent organic pollutants (POPs). Relevant study (Quaß et al., 2004) indicates that emission of PCDD/Fs originate mainly from municipal waste incinerators and metal smelting processes including electric arc furnace, secondary zinc production and iron ore sintering plant. Iron ore sintering plants are associated with the production of iron and steel, often in integrated steel mills. Since the steel-making process is regarded as one of the most important anthropogenic sources of PCDD/Fs, Taiwan government set the PCDD/F emission limit for newly built sinter plants (0.5 ng-TEQ Nm^{-3}) in June 2004. In the meantime, Taiwan government also set 2.0 ng-TEQ Nm^{-3} as the PCDD/F emission limits for existing sinter plants starting from January 2006 and then more stringent standard of 1.0 ng I-TEQ Nm^{-3} was in effect starting from January 2008. In general, dioxins can be generated during the thermal process, requiring the installation of additional air pollution control devices (APCDs) to reduce PCDD/F emissions. However, previous study (Guerriero et al., 2009) indicated that the PCDD/F removal efficiencies of a sinter plant achieved with the electrostatic precipitator and wet scrubber were relatively low, being 41.4% and 68.4%, respectively.

Activated carbon injection (ACI) could effectively remove air pollutants, such as PCDD/Fs, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) (Cudahy and Helsel, 2000) and heavy metals (Hg in particular) from incineration processes. Activated carbon can generally be applied in three ways, i.e. entrained flow or called activated carbon injection (ACI), fixed bed and moving bed adsorption (Buekens and Huang, 1998). In the activated carbon injection method, powder activated carbon (PAC) is injected upstream of the baghouse filter (BF) and accumulates on the filter bag surface, and flue gases are made to pass through the AC + residual dust layer. Previous study (Karademir et al., 2004) indicates that most PCDD/Fs in the vapor phase penetrate through filter bag without ACI, while PCDD/Fs in solid phase are effectively removed by the BF. Previous studies also indicate that about 95.5% PCDD/Fs and 99.7% PCBs in the flue gases can be removed by ACI + BF in MWI and PCDD/F removal efficiency can reach 97.6–98.3% be achieved with ACI + BF in the Waelz process (Chi et al., 2006, 2007). Although AC injection technology can effectively reduce PCDD/F concentrations in flue gas, previous study (Chi et al., 2005) indicates that it may actually increase the total PCDD/F discharge (including that in fly ash and flue gas) from MWIs. As a result, Taiwan EPA has started to regulate PCDD/F content in fly ash with the allowable limit of

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1.0 ng I-TEQ g^{-1}. Thus, ACI would face serious challenge of the high PCDD/F content in fly ash associated. In this study, potential application of the multi-layer adsorber to reduce gas emissions without increasing dioxin content in ash is investigated. Multi-layer adsorption technology has a high mass transfer and high gas–solid contact which can greatly enhance the pollutant removal efficiencies (Chiang et al., 2003). Therefore, this study is motivated to investigate the feasibility of applying commercial BACs as adsorbents for reducing PCDD/F emission. Fundamental properties of BACs were examined before PCDD/F adsorption experiment. Experimental tests were conducted with the laboratory-scale multi-layer reactor for PCDD/F adsorption at various operating conditions including gas flow rate, inlet PCDD/F concentration, operating temperature and water vapor content of the gas stream. Furthermore, the removal efficiency of vapor-phase PCDD/Fs achieved with multi-layer reactor with the real flue gas streams of a sinter plant was also investigated.

2. Materials and methods

2.1. Characteristics of bead-shaped activated carbon

Commercial bead-shaped activated carbons (BACs) produced by Kureha Co., Ltd., were used as the adsorbent in this study. The ranges of BAC diameter and bulk density were 0.59–0.84 mm (0.72 mm in average) and 0.54–0.56 g cm^{-3}, respectively. The characteristics including Brunauer–Emmett–Teller (BET) specific surface area, average pore diameter, pore volume distribution and trace metal contents (Fe, Cu and Cr) of BAC are reported in Table 1 (Chang et al., 2008). The results revealed that the BAC is mainly of micro-porous structure. Ramirez et al. (2004) indicated the pore volume diffusion related to the molecular size of the contaminant to be removed. The adsorption capacity of adsorbents depends on the BET specific surface area, which is closely related to micropore volume and relatively independent of the mesopore and macropore volume (Inoue and Kawamoto, 2005). In addition, this study also measured the BAC wall friction and internal friction coefficients which were the major parameters affecting particles flow property, and were compared with commercial granular activated carbon (GAC) as also listed in Table 1. The results revealed that the angles of wall friction of both BAC and GAC on stainless steel were quite close, indicating both BAC and GAC on stainless steel wall sustained almost equivalent frictions. Additionally, the internal friction is the friction formed by static mechanical stress and kinetic stress between particles and particles. The results reveal that the angle of internal friction of GAC is larger than that of BAC. It implies that the flow property of BAC is superior to GAC and may be more suitable in multi-layer adsorption application.

Table 1
Characteristics and internal/wall friction coefficient of bead-shaped activated carbon (Chang et al., 2008).

Material	Coal
BET specific surface area ($m^2\ g^{-1}$)	1138
Micropore (pore diameter <2 nm) ($cm^3\ g^{-1}$)	0.50
Mesopore (pore diameter 2–50 nm) ($cm^3\ g^{-1}$)	0.05
Average pore diameter (Å)	19.3
Cu content (ppm)	2360
Fe content (ppm)	37 000
Cr content (ppm)	1260
Angle of internal friction	17° (BAC) 29° (GAC)
Angle of wall (stainless steel) friction	6.2° (BAC) 7.2° (GAC)

2.2. Laboratory-scale multi-layer reactor system

The laboratory-scale multi-layer reactor (height = 30 cm and inner diameter = 2.5 cm) was made of glass and was divided into three layers with BACs (5 g) being used as the adsorbent and the bed height was 2 cm. The laboratory-scale multi-layer reactor was placed in an oven with the temperature ranging from 20 to 200 °C. The gas stream from the outlet of each layer was collected with XAD-2 resin, which was cooled to 5 °C to avoid PCDD/F penetration. This study employed the BAC as the adsorbent and applied the laboratory-scale multi-layer reactor to adsorb PCDD/Fs at different operating conditions, including gas flow rate, temperature and water vapor content. In order to simulate the full-scale activated carbon control unit, the operating temperature was controlled at 150 °C, 180 °C and 200 °C and the water vapor content was adjusted to 0% (without water vapor addition), 5% and 15%, respectively. The reactor was installed in an electric furnace and the temperature was controlled by a regulator. The temperature of the multi-layer reactor was monitored with a *K*-type thermocouple located in the middle of the reactor.

2.3. Dioxin-containing gas stream generating system

The experimental tests were carried out in a continuous gas flow system. The dioxin-containing gas stream generation system developed consists of the PCDD/F stock solution injector, temperature-controller, evaporator and gas flow rate controllers (Yang et al., 2008). The experimental setup is schematically shown in Fig. 1a. With different types of PCDD/F stock solutions being injected into the system, the distributions and concentrations of PCDD/F congeners in the gas stream can be varied. The PCDD/F stock solution used in this study was prepared by the extraction of fly ash collected by EP of the sinter plant investigated. The extract of the EP ash has subjected to the clean-up procedures without the addition of PCDD/F standards ($^{13}C_{12}$-2,3,7,8-substituted congeners). The PCDD/F contents of real extract being injected were analyzed before the test of the PCDD/F removal in the lab-scale reactor. The reproducibility tests indicated that the PCDD/F recovery efficiencies were between 89% and 108%. For simulating the PCDD/F emission from the sintering process, the PCDD/F inlet concentrations of 410 and 550 ng I-TEQ Nm^{-3} were examined. The lab-scale PCDD/F adsorption experiments were carried out for 3 h at specific operating conditions except for the testing of water vapor content effect which were performed for 1 h.

2.4. Pilot-scale multi-layer reactor system

The sinter plant investigated was equipped with electrostatic precipitator (EP) and selective catalytic reduction (SCR) as APCDs for controlling particulate and gaseous pollutant emissions. The capacity of the sinter plant investigated was 250 tons day-$unit^{-1}$. A pilot-scale multi-layer reactor system was constructed for the evaluation of PCDD/F removal with real flue gases withdrawn from the sinter plant investigated. The pilot-scale system consists of two Graseby Anderson Stack Sampling Systems (MST 2010) as shown in Fig. 1b. The real flue gas stream for pilot-scale system testing was taken from the flue gas at EP outlet of the sinter plant investigated. The solid-phase PCDD/Fs and particulate matter in the flue gas had been removed by fiber glass filter installed in front of the pilot-scale system and only vapor-phase PCDD/Fs passing through the multi-layer reactor were concerned. One stack sampler located upstream of the multi-layer reactor was used to collect vapor-phase PCDD/Fs with XAD-2 as inlet concentration (baseline sample) while the other stack sampler was located downstream