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Catalytic hydrodechlorination of PCDD/Fs from condensed water with Pd/γ-Al_2O_3

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HIGHLIGHTS

- In the liquid-phase catalytic hydrodechlorination is applied for removal of PCDD/F from condensed water which the concentration of tar is high.
- PCDD/F removal efficiency achieved with catalytic hydrodechlorination is higher than carbon adsorption.
- Compare the PCDD/F removal efficiencies by two sources of hydrogen are available for hydrodechlorination.
- Dechlorination is an important pathway for PCDD/F degradation.

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ABSTRACT

A continuous pyrolysis system (CPS) with effective air pollution control devices (APCDs) is designed and constructed to remediate the soil containing high-concentration PCDD/Fs. The quench tower of the APCDs system can capture the pollutants of high boiling points from the flue gas of CPS and produces condensed water of high PCDD/Fs concentration (16–44 ng I-TEQ/L), and needs further treatment. First, the result of activated carbon adsorption test displays the PCDD/Fs toxicity concentration of effluents meet the regulatory standards as the liquid to solid ratio is controlled at 3: 1. However, large amount of activated carbon need to achieve the high removal efficiency leads to high cost, so catalytic hydrodechlorination technology with Pd/Al_2O_3 as catalyst is applied to treat the condensed water. The PCDD/Fs mass removal efficiency achieved without the reducing agent is 53.21% with the operating time of 180 min. As 5% reducing agent (methanol) is added, the removal efficiency increases to 71.86%. In addition, to better understand the differences between molecular hydrogen and hydrogen donor, the condensed water was pre-aerated with hydrogen and catalytic hydrodechlorination test with palladium as catalyst was conducted. The results show that the PCDD/Fs mass removal efficiency increases to 97.34% with the operating time of 180 min, demonstrating the high PCDD/Fs removal efficiency of catalytic hydrodechlorination.

1. Introduction

Soils containing extremely high concentrations of PCDD/Fs (as high as 86,700 ng-TEQ/kg) are found in An-shun site of Taiwan due to the previous operation of a PCP plant (Soong et al., 2006; Huang et al., 2011). For effective remediation of contaminated soil in An-shun site, a continuous pyrolysis system (CPS) equipped with effective air pollution control devices (APCDs) including baghouse, quench tower and multi-layer activated carbon adsorption system is designed and adopted to remediate the soil and to control the air pollutants discharged from the CPS. CPS had been proved effective for the removal of PCDD/Fs from contaminated soil (Hung et al., 2015). Also, APCDs adopted can efficiently remove PCDD/Fs from gas streams to meet the emission limits. Quench tower effectively condenses the water vapor of gas stream to maintain a high removal efficiency of PCDD/Fs with activated carbon adsorption bed thereafter. However, pollutants of high boiling points such as PCDD/Fs are effectively condensed as well, so high concentration PCDD/Fs inevitably remain in condensed water.

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are a group of structurally related chemicals which persist in the environment, bioaccumulate in the food chain and are extremely toxic. Congeners containing chlorine at 2,3,7,8

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positions (7 PCDDs and 10 PCDFs) have been identified as more toxic to exposed organisms. Various methods for removing PCDD/Fs from wastewater have been consequently developed, such as activated carbon adsorption, photocatalytic degradation (Gunlazuardi and Lindu, 2005; Wu et al., 2005; Lu et al., 2011), bioremediation (Nam et al., 2005, 2008), zero-valent metal process (Choi et al., 2009) … etc. However, activated carbon adsorption produces secondary waste, other methods require harsh reaction conditions with special facilities, and many of them are frequently incomplete. Among these methods, reductive dechlorination that involves hydrogen cleavage of one or more C–Cl bonds to the formation of lower chlorinated organic compounds and preventing the formation of hazardous by-products is considered as an effective method to detoxify PCDD/Fs.

Generally, two sources of hydrogen are available for hydrodechlorination i.e., molecular hydrogen and a hydrogen donor. Catalytic transformations of 1,2-dichlorobenzene, chlorobenzene, 4-chlorobiphenyl, g-hexachlorocyclohexane (Lindane), naphthalene and phenanthrene have been studied over Pd/Al_2O_3 in hydrogen-saturated water at room temperature and ambient pressure (Schüth and Reinhard, 1998). The results showed that the chlorinated benzenes and Lindane were rapidly hydrodechlorinated and partial or complete hydrogenation was observed for biphenyl and polycyclic aromatic hydrocarbons (PAHs). However, the applicability of the molecular hydrogen treatment for removing these contaminants over Pd/Al_2O_3 from aqueous waste streams remains to be evaluated under actual treatment conditions. On the other hand, previous study indicates that alcohols (mainly methanol, ethanol and isopropanol) are the most commonly used solvent and reducing agent (hydrogen donor) for liquid-phase hydrodechlorination (Urbano and Marinas, 2001). In order to distinguish hydrogen-transfer, catalytic dechlorination was carried out with four kinds of deuterium-labeled isopropanol (Ukisu and Miyadera, 2003), and the results indicate that the α-hydrogen of isopropanol transfers preferentially to the organic chlorines and the OH group of isopropanol is a minor hydrogen source. Mitoma et al. (2006) indicate that highly efficient degradation of polychlorinated aromatic compounds including PCDD/Fs, and co-PCBs can be achieved with reductive dechlorination via catalytic reduction with Rh/C catalyst which generates hydrogen donor, without external addition of hydrogen (Mitoma et al., 2006).

In this study, the effectiveness of a catalytic system developed for hydrodechlorination of high-concentration PCDD/Fs in condensed water is evaluated. We also compare the PCDD/Fs removal efficiencies of two sources of hydrogen, including molecular hydrogen adding and a hydrogen donor.

2. Methods and sample analysis

2.1. Materials

5% (wt.) $Pd/\gamma\text{-}Al_2O_3$ was purchased from Acros Organics, USA (Code: 293030100). The catalyst was not pre-treated before all experiments and kept in a hermetical desiccator. Methanol as the hydrogen donor was purchased from Tedia, USA. Condensed water containing PCDD/Fs was obtained from the quench tower which is a part of APCDs designed for the removal of gaseous PCDD/Fs from CPS (see Fig. 1).

2.2. Catalyst characterization

5% (wt.) $Pd/\gamma\text{-}Al_2O_3$ catalyst prepared was first characterized with different techniques. The nitrogen adsorption and desorption isotherms of the catalysts were carried out at 77 K using a Micromeritics ASAP-2010 analyzer, while the surface areas, pore diameter, and pore volume were measured by applying the Brunauer Emmett Teller (BET) method. The XRD patterns were obtained with a D8AXRD diffractometer using a Cu Kα monochromatic X-ray, operated at 40 kV and 40 mA over the scattering angle of 2θ from 5° to 80° with a step of 0.05°/s.

2.3. General procedure

2.3.1. Activated carbon adsorption process

Activated carbon is packed into a column with the diameter of 1 cm, and then 5 mL of condensed water flows through the column with the L/S ratio of 3, 7, 13 and 20, respectively, to test PCDD/Fs adsorption efficiency.

2.3.2. Catalytic hydrodechlorination of condensed water pre-aerated with hydrogen

Initially, the condensed water was pre-aerated with hydrogen gas for 2 h, and then 20 mL condensed water was added into a 40 mL vial. Supported palladium catalyst (100 mg) was then added to the solution, and the mixture was stirred at a speed of 250 rpm. All experimental tests were carried out at the condition of room temperature and ambient pressure. No further hydrogen was added during the experiment.

2.3.3. Catalytic hydrodechlorination of condensed water with methanol

Methanol was dissolved in the condensed water (1%, 5% methanol, respectively), and 20 mL condensed water was added to a 40 mL vial. 100 mg supported palladium catalyst was then added to the solution, and the mixture was stirred at a speed of 250 rpm. All experimental tests were carried out at the condition of room temperature and ambient pressure.

Removal efficiency is defined as the percentage of the contaminant removed from the original contaminated wastewater by adsorption or hydrodechlorination treatment. During hydrodechlorination treatment, part of organic contaminants is destroyed and other part is adsorbed on the catalyst. In order to better understand the characteristics of contaminant destruction, destruction efficiency is further applied to account for the contaminants adsorbed on the catalyst. Relevant definitions are listed as below:

$$\text{Removal efficiency}(\%) = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%$$

$$\text{Destruction efficiency}(\%) = \frac{C_{in} - (C_{out} + C_{adsorb})}{C_{in}} \times 100\%$$

where C_{in} and C_{out} are the pollutant concentration of raw condensed water and treated condensed water, respectively. C_{adsorb} represents the pollutant adsorption concentration on the catalyst after hydrodechlorination.

2.4. Extraction and analysis

After reaction, catalyst samples were recovered by filtration. Solid samples were soxhlet extracted with toluene for 24 h and condensed water was liquid extracted and the extracts were transferred to graduated vials to obtain an exact volume. Samples were spiked with known amounts of Method 23 internal standard and Method1613 labeled standards, following quantification standards, respectively, and then analyzed for the 17 2,3,7,8-substituted PCDD/F congeners with high-resolution gas chromatography (HRGC, Thermo Trace GC)/high-resolution mass spectrometer