Experimental Study on PCDD/Fs Adsorption onto Nano-Graphite

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ABSTRACT

The adsorption of the 17 toxic 2,3,7,8-substituted dioxin congeners onto graphite was investigated using a laboratory-scale fixed-bed adsorption system. First, the morphology and microstructure of graphite were characterized by Scanning Electron Microscopy and Brunauer-Emmer-Teller surface estimation. Removal efficiency of the 17 toxic PCDD/Fs varies from 89.31% to 99.96% and the amount adsorbed on graphite is a linear function of the inlet concentration of PCDD/Fs, as it was varied from 2.3–20.7 ng I-TEQ Nm\(^{-3}\). Operating over 3 hours, it is observed that the saturation time of fixed-bed adsorbers is less when the inlet concentration is higher. The removal efficiency of dioxin depends on vapour pressure and rises strongly with increasing chlorine substitution number. Removal efficiencies strongly correlate with vapour pressure, with \( R^2 = 0.96 \) for PCDDs and 0.99 for PCDFs, respectively. The removal efficiency of dioxin decreases linearly as the temperature increased (\( R^2 = 0.99 \)). Possibly, \( \pi-\pi \) interactions between PCDD/Fs and graphite sheets lead to a high adsorption capacity of dioxin. The high mesopores volume and pore structure of graphite are critical factors when adsorbing dioxin.

Keywords: PCDD/Fs; Graphite; Adsorption; Removal efficiency.

INTRODUCTION

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs) are commonly known as dioxin, one of the persistent organic pollutants (POPs) considered by the Convention of Stockholm (2001). The generic structure of PCDD/Fs comprises two benzene rings connected with one or two oxygen atoms, forming a C-O-C ether bridge. According to the number and position of the chlorines, there are total 210 congeners of dioxin. These PCDDs and PCDFs consist of 75 and 135 congeners, respectively; of these 17 congeners, with chlorine substitution in all of the positions 2,3,7,8, are much more harmful than others, showing dioxins-like toxicity, related with their ability to assume a planar structure. Apart from their toxicity, PCDD/Fs remain for long periods of time (persistence) in the environment, due to their physical and chemical properties (Zhao et al., 2012), their limited mobility (low vapour pressure and water solubility) and high stability. Moreover, PCDD/Fs accumulate in the food chain through absorption of high fat foods (Chao et al., 2014) of animal or marine origin, threatening ecological safety and human health (Kulkarni et al., 2008). The release of PCDD/Fs today is mainly from municipal or other waste incinerators, chemical manufacturing involving chlorophenols, metal making and reservoir resources. In China, the major source of PCDD/Fs emissions is municipal waste incineration (Zhou et al., 2015a). Adsorption on activated carbon (Everaert et al., 2003), catalytic (Yu et al., 2016a) and thermal treatment (Hung et al., 2016) and biodegradation (Mori and Kondo, 2002) were developed to control dioxin emissions. However, those technologies are expensive and generally require other pretreatment, except for adsorption.

Adsorption on carbon materials with high specific surface and multifarious functional groups is most widely applied to remove dioxin and inorganic compounds, including mercury and its compounds (Li et al., 2016). Various carbon materials, such as activated carbon (AC), lignite cokes, carbon nanotubes (CNTs) and graphene have either been applied in practice or recently proposed to reduce dioxin emission, both in engineering practice and theoretical studies. Previous study (Long and Yang, 2001) demonstrated that CNTs were much better than AC in dioxin adsorption by using temperature-programmed desorption techniques. For CNTs, a removal efficiency of PCDD/Fs over 86.8% was attained at 150°C, higher than the 70.0% and 54.2% reached for two ACs (Zhou et al., 2015b). Surface-functionalized ACs are applied to absorb and destroy dioxin indicating that different functional groups attribute to PCDD/Fs destruction, and removal efficiency was higher than 90% for all tested carbons. Graphene is a specific carbon material with a single-atom-thickness sheet (Wang et al., 2014a). Relevant study
by the density functional theory method (Zhang et al., 2014) indicated that there are chemical and electronic interactions between TCDD and intrinsic graphene. Theoretical study of the physical-chemical binding of graphite sheets and CNTs with dioxin indicated that graphite surfaces can be as efficient for dioxins removal in incineration plants (Kang, 2005) as CNTs, yet they are much cheaper.

Graphite is a layered material which consists of one-atom-thick sheets of carbon with high specific surface and superior water solubility. Those make it a promising material for environmental remediation. In previous research, the adsorption of Ag⁺, Mn²⁺, and Cr³⁺ in water was demonstrated by using nano-graphite as an adsorbent due to its excellent properties and its advantage of low cost (Wang et al., 2014b). Methyl violet removal from aqueous solution by nano-graphite indicated that π-π stacking can enhance the adsorption (Li et al., 2014). Graphite/isobutylene-isoprene rubber sorbents for organic liquid proved that graphite can modify the adsorbent and improve the sorption properties (Hu et al., 2013). Diaz et al. (2007) indicated that the adsorption capacity for volatile organic compounds (VOCs) of graphite is considerably higher than that of CNTs and carbon nano-fibers. Its adsorption rate can be amplified by raising the surface area of graphite (Lee and Kim, 2012). Meanwhile, graphite exhibits a stable and steady performance throughout the test period as an adsorbent for toxic substances. Experiments showed that the interactions between toluene or xylene and graphite in the gas phase are stronger than those for methanol and acetone and that graphite prefer to adsorb aromatic VOCs (Shinar et al., 2000).

As previously described, many studies have been conducted on the removal of PCDD/Fs by carbon materials. However, few studies have focused on the relationship between PCDD/Fs and graphite. In this study, nano-graphite powder (graphite) was applied to adsorb dioxin using a laboratory-scaled packed-bed system. The main objective of this study is to investigate the adsorption of dioxins onto graphite to obtain a better understanding of the interaction between carbon materials and dioxin. To accomplish this, the effects of dioxin’s concentration, adsorption temperature and adsorption time were investigated. Surface area, pore structure and microstructure of graphite are determined.

MATERIALS AND METHODS

PCDD/Fs Generating and Adsorption System

The experimental system is shown in Fig. 1. It is subdivided into three parts: a generator of gas-phase PCDD/Fs at steady (yet low) concentration, a dioxin adsorption unit, and the exhaust gas sampling part. The dioxin generating system was developed to supply stable gaseous and continuous PCDD/Fs (Ji et al., 2014; Yu et al., 2016a, b). The carrier gas flow (N₂:O₂ = 9) of the generator simulating incinerator flue gas is set at 1 L min⁻¹. The adsorption part consists of a quartz tube (inner diameter 20 mm, height 150 mm) with a fixed adsorption bed, heated by an electric heating jacket with temperature controller. The dioxin remaining in the off-gas is collected by adsorption on XRD-2 polymeric resin and double toluene-filled bubbling bottles.

The dioxin solution was obtained by Soxhlet extraction from fly ash of a municipal waste incinerator in Hangzhou and the extract was purified and concentrated, then solvent (n-nonane) is added to concentrated solution to adjust the concentration and obtain desirable injection liquors. The concentration was varied and adapted at three distinct levels, i.e., 2.3 (C1), 9.5 (C2) and 20.7 (C3) ng I-TEQ Nm⁻³.

Before the test, graphite was dried at 105°C for 24 hours. In each experiment, 0.1 g graphite is placed in the adsorption tube and then fixed by quartz wool. The reaction temperature was adjusted between 150°C and 190°C by the temperature controller. The concentration of the 17 toxic dioxin supplied was varied from 2.3 ng I-TEQ Nm⁻³ to 20.7 ng I-TEQ Nm⁻³. It is difficult to continuously detect the concentration of the outlet PCDD/Fs in present technologies. Therefore, the dioxin present in the off-gas was collected during a fixed period of 1 hour. Thus, the adsorption experiments were carried out for the same 1 hour at specific conditions, except when studying the time effect (3 hours).

![Fig. 1. PCDD/Fs adsorption system.](image-url)
Characteristics of Graphite

The nano-graphite powder (prepared by detonation splitting technique and average particle size smaller than 30 nm) was purchased from Nanjing XFnano Materials Tech Co. Ltd in China. The pore structure and microcosmic surface of graphite were characterized by SEM (Scanning Electron Microscopy) and the BET (Brunauer-Emmett-Teller) surface area, using a Hitachi SU-70 scanning electron microscopy and a Micromeritics Tristar 3020 instrument, respectively. Nitrogen adsorption isotherms of graphite at 77 K and pore size distribution is shown in Fig. 2(a). According to the classification of International Union of Pure and Apply Chemistry (Sing, 1985), the adsorption isotherm of graphite belongs to the type IV. The characteristic feature of type IV isotherm is a hysteresis loop, associated with capillary condensation taking place in mesopores. The hysteresis loop of graphite is observed with aggregates of plate-like particles giving rise to slit-shaped pores. The graphite pore sizes are concentrated in a range of 2–20 nm. Its BET surface area is 438 m² g⁻¹ and average particle size is 10.4 nm, respectively. The mesopores volume of graphite is 1.12 cm³ g⁻¹. These indicate that graphite is a typical mesoporous carbon materials. The SEM images reported in Fig. 2(b) show that graphite is well organized, featuring a spongy structure and loose with abundant pore space. The morphologies of graphite conform well to nitrogen adsorption isotherm analysis that graphite is plate-like particles with slit-pores.

Sample Analysis

The tail gas concentration of PCDD/Fs was analysed after absorption on XRD-2 and in toluene. The pretreatment of dioxin samples includes acid washing, purification on two chromatographic columns, evaporation, concentration and labeling, according to Method 1613 from US Environmental Protection Agency (USEPA). The dioxin analysis was performed by a high-resolution gas chromatography (HRGC)/high-resolution mass spectrometer (HRMS) (JMS-800D, JEOL, Japan) with a DB-5 capillary column (60 m × 0.25 mm × 0.25 µm). In this study, only the 17 toxic congeners of PCDD/Fs are quantified and discussed. The recovery of standards for PCDD/Fs ranges from 78%–125%, all within the acceptable 40%–150%. The removal efficiency of the PCDD/Fs is referred to as “RE”, and calculated as follows

\[
RE = \frac{PCDD/F_{\text{inlet}} - PCDD/F_{\text{off-gas}}}{PCDD/F_{\text{inlet}}} \quad (1)
\]

![Fig. 2. Characteristics of graphite: (a) Nitrogen adsorption isotherms of graphite at 77 K and pore size distribution and (b) SEM images of graphite.](image-url)
RESULTS AND DISCUSSION

The Effect of Initial Concentration on the Removal of PCDD/Fs

The concentration was varied at 2.3 (C1), 9.5 (C2) and 20.7 (C3) ng I-TEQ Nm⁻³ during adsorption at 150°C with a duration of one hour. All initial concentrations are average values of three samples. The distribution of 17 toxic PCDD/Fs congeners is shown in Table1, nearly similar with previous investigation (Ji et al., 2014; Karademir et al., 2004; Yu et al., 2016b). The I-TEQ concentration of PCDFs is higher than PCDDs and 2,3,4,7 and 8-PeCDF is the dominant I-TEQ contributor.

As the condition described above, the removal efficiency of PCDFs is 9.15% higher than PCDDs at concentration C1, and removal efficiency of PCDFs at C2 and C3 are only 0.34% and 1.24% higher than for PCDDs, respectively (Table 2). This is probably influenced by the different concentration of PCDDs and PCDFs in the initial concentrations (Zhou et al., 2016). Dioxins solution is extracted from fly ash, and the total concentration of PCDDs is lower than PCDFs (Table 1). The distribution of 17 toxic PCDD/Fs in the tail gas shows similar fingerprints with the initial concentrations and no change in the congener fingerprints with the addition of graphite was observed.

With the increase of concentration, removal efficiency of PCDD/Fs surges from 89.31% at C1 to 99.96% at C2 at first and then decreases to 96.77% at C3. Fig. 3(a) describes the removal efficiency of 17 dioxin congeners at different concentrations with temperature 150°C. In fact, there is no obvious disciplinary between removal efficiency and initial concentration of PCDD/Fs. But we can still get that the removal efficiency of PCDD/Fs increase at first and then decrease with concentration of dioxin increase. In this study, the low concentration of PCDD/Fs means the mass of PCDD/Fs in flue gas would become lower and the partial pressure of PCDD/Fs molecules could become smaller in flue gas, which leads to small contact area between graphite and PCDD/Fs. The contact area is not enough to remove dioxin efficiently at low concentration. In this study, the relationship between inlet amount of PCDD/Fs and removed amount by graphite is linear as shown in Fig. 3(b). It is clearly that there exists a concentration below which no adsorption occurred, which could be caused by the insufficient contact time at low concentration. Previous study (Hung et al., 2011) indicated that contact time is one of the important factor affecting the removal efficiency, and the outlet concentration of PCDD/Fs increases as the contact time is decreased. In present study, the contact time is fixed due to constant flow rate of carrier gas. And the low removal efficiency of PCDD/Fs at low concentration may be attribute to that the contact time is not enough long for the adsorption of dioxin at lower concentration level (Karademir et al., 2004). Both of them explain that small contact area and short contact time can result in low RE at low concentration. On the other hand, adsorption is a process that molecules accumulate on the free surface area of an adsorbent, which caused by the saturation of free bonding forces (Mohan et al., 2009).

Table 1. Initial concentrations from dioxin generating system (pg I-TEQ Nm⁻³).

<table>
<thead>
<tr>
<th>Toxic PCDD/Fs</th>
<th>C1 (average)</th>
<th>C2 (average)</th>
<th>C3 (average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2378-TCDD</td>
<td>92.9</td>
<td>367.8</td>
<td>800.3</td>
</tr>
<tr>
<td>12378-PeCDD</td>
<td>206.2</td>
<td>849.9</td>
<td>1849.3</td>
</tr>
<tr>
<td>23478-HxCDD</td>
<td>34.0</td>
<td>141.7</td>
<td>308.3</td>
</tr>
<tr>
<td>123678-HxCDD</td>
<td>70.3</td>
<td>291.9</td>
<td>635.1</td>
</tr>
<tr>
<td>123789-HxCDD</td>
<td>50.0</td>
<td>210.1</td>
<td>457.1</td>
</tr>
<tr>
<td>1234678-HpCDD</td>
<td>35.5</td>
<td>147.6</td>
<td>321.2</td>
</tr>
<tr>
<td>OCDD</td>
<td>3.4</td>
<td>14.2</td>
<td>30.9</td>
</tr>
<tr>
<td>2378-TCDF</td>
<td>72.2</td>
<td>280.9</td>
<td>611.3</td>
</tr>
<tr>
<td>12378-PeCDF</td>
<td>50.0</td>
<td>204.5</td>
<td>445.1</td>
</tr>
<tr>
<td>23478-PeCDF</td>
<td>905.8</td>
<td>3734.1</td>
<td>8125.3</td>
</tr>
<tr>
<td>123478-HxCDF</td>
<td>221.3</td>
<td>899.5</td>
<td>1957.3</td>
</tr>
<tr>
<td>123678-HxCDF</td>
<td>196.3</td>
<td>814.7</td>
<td>1772.7</td>
</tr>
<tr>
<td>234678-HxCDF</td>
<td>96.7</td>
<td>398.7</td>
<td>867.6</td>
</tr>
<tr>
<td>123789-HxCDF</td>
<td>217.4</td>
<td>887.9</td>
<td>1932.1</td>
</tr>
<tr>
<td>1234678-HpCDF</td>
<td>54.3</td>
<td>224.7</td>
<td>489.0</td>
</tr>
<tr>
<td>1234789-HpCDF</td>
<td>6.5</td>
<td>27.1</td>
<td>58.9</td>
</tr>
<tr>
<td>OCDF</td>
<td>1.6</td>
<td>6.5</td>
<td>14.2</td>
</tr>
<tr>
<td>PCDDs</td>
<td>492.2</td>
<td>2023.1</td>
<td>4402.3</td>
</tr>
<tr>
<td>PCDFs</td>
<td>1822.1</td>
<td>7478.7</td>
<td>16273.6</td>
</tr>
<tr>
<td>PCDD/Fs</td>
<td>2.3 × 10³</td>
<td>9.5 × 10³</td>
<td>20.7 × 10³</td>
</tr>
</tbody>
</table>

Table 2. Removal efficiency for PCDD/Fs at different initial concentrations with temperature 150°C.

<table>
<thead>
<tr>
<th>Initial concentration, ng I-TEQ Nm⁻³</th>
<th>2.3 (C1)</th>
<th>9.5 (C2)</th>
<th>20.7 (C3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE for PCDDs</td>
<td>82.23%</td>
<td>99.30%</td>
<td>95.79%</td>
</tr>
<tr>
<td>RE for PCDFs</td>
<td>91.38%</td>
<td>99.64%</td>
<td>97.03%</td>
</tr>
</tbody>
</table>
Porous adsorbents are used and the adsorption capacity is mainly determined by pore volume and surface area (Zhou et al., 2014). For a given amount of graphite, the pore volume and surface area are determinate. Therefore, the removal efficiency would decline when the concentration exceeds a certain concentration.

The Effect of Adsorption Time on the Removal of PCDD/Fs

The variation of removal efficiency of PCDD/Fs with concentration and test duration is also discussed: we increased the test duration from 1 hour to 3 hours (adsorption temperature at 150°C). Fig. 4 shows removal efficiency of PCDD/Fs with time at 150°C for three different concentrations. Apparently, the removal efficiency trends of PCDD/Fs exist differences between varied concentrations. The removal efficiency at C2 changes very little over time (from 99.56% in the 1st hour to 97.78% in the 3rd hour). It is seemed that these different trends result from concentration. In fact, the saturation is the main reason (Mohan et al., 2009; Zhou et al., 2015a). It is well known that adsorption and desorption occur simultaneously during adsorption period. It will be saturated when the adsorption velocity equals to desorption velocity. At low concentration, active sites of graphite are abundant and the removal efficiency increase at first. With the process goes on, the RE would decrease due to active sites of graphite become less and desorption velocity increase. From the three concentrations it is observed that the saturation time of fix-bed is less when the concentration is higher. This is because at high concentration more molecules compete for active site of adsorbent at a given amount graphite and hence the saturation become earlier.
150°C, 170°C and 190°C. With temperature rising from 150°C to 190°C, the removal efficiency of PCDD/Fs in this study decreases from 96.77% to 91.18%. The empirical relationship between adsorption temperature and removal efficiency is shown in Fig. 5. The figure suggests that the RE of dioxins decreases linearly with rising temperature, and the correlation coefficient ($R^2$) is 0.99. Dioxin is classified as semi-volatile organic compounds, temperature can affect the vapour pressure of dioxin. High temperature provides high vapour pressure of PCDD/Fs, and gas phase of PCDD/Fs was found to increase with the increase of temperature. Hence more PCDD/Fs molecules would probably evaporate to the gas phase and escape un-adsorbed as temperature increase (Zhao et al., 2012; Lee et al., 2016). On the other hand, adsorption is an exothermic process, RE of dioxin by graphite would decrease as the temperature increases (Hung et al., 2011).

Fig. 6 shows that the removal tendencies of the 17 PCDD/Fs congeners are similar at different temperature and declining with increase of adsorption temperature. RE values of PCDD/Fs are around 91.8–98.6%, 90.1–97.7% and 84.5–95.5% at 150°C, 170°C and 190°C, respectively. Low-chlorinated congeners are less adsorbed on graphite than high-chlorinated congeners. Relative study (Lee et al., 2016) also showed that higher chlorinated PCDD/Fs are much easier captured by particle. Probably, vapour pressure plays a dominant role (Karademir et al., 2004; Hung et al., 2011; Ji et al., 2014; Yu et al., 2016a). Generally, high chlorinated PCDD/Fs with lower vapour pressure have lower gaseous fractions at a specific temperature as compared to low chlorinated ones. Hence, low chlorinated PCDD/Fs usually tend to partition to the gas phase compared to the high chlorinated ones (Zhang et al., 2015). The removal efficiency of PCDD/Fs would increases as the chlorine number increase.

Fig. 7 shows a linear relationship between the RE and the vapour pressure of various PCDDs and PCDFs at 150°C, respectively. It illustrates that removal efficiency strongly depends on vapour pressure. The removal efficiencies of PCDDs and PCDFs are increased with the increasing substitution level of chlorine (declined with vapour pressure). The correlation ($R^2$) is 0.96 for PCDDs and 0.99 for PCDFs, respectively.

### Adsorption Mechanism

According to previous studies (Nagano et al., 2000; Inoue and Kawamoto, 2005; Chi et al., 2006; Zhou et al., 2014), there are three main factors of adsorbent to effect the remove efficiency: (1) Mesopores volume. A higher mesopores volume increases the adsorption ability of PCDD/Fs and facilitates the internal diffusion of PCDD/F-molecules. (2) Pore size. The pore size of 2–20 nm is a critical factor for PCDD/Fs adsorption capacity. Thus, the pore size of graphite should larger than 2 nm. (3) Micropores volume and specific surface area, and BET surface area should be larger than 500 m² g⁻¹. Previous study indicated that specific surface area was proportional to the micropores volume, and micropores volume is perhaps the most important factors governing the adsorption capacity. As previously described, graphite contains mesopores within the range of 2–20 nm, and mesopores volume is 1.12 cm³ g⁻¹. Compared to usual activated carbon the BET surface of graphite is small with 438 m² g⁻¹. However the RE of dioxins can reach 80.6% after three hours at a high concentration of 20.7 ng I-TEQ Nm⁻³. According to the pore size distribution in Fig. 2 (a), there is no distribution of micropores on the surface of graphite. We can conclude that the RE of PCDD/Fs correlates strongly with mesopores volume and pore structure, other than with micropores volume.

Graphite can be applied within a wide range of temperature for adsorption. The removal efficiency of PCDD/Fs drops 5.59 points as the temperature increasing from 150°C to 190°C. All results show that graphite performs excellent on the removal of PCDD/Fs. Compared to other adsorbents, such as AC and CNTs (Long and Yang, 2001; Zhou et al., 2015b), the removal efficiency of PCDD/Fs by graphite can achieve almost 100%. It can be attributed to the unique structure of graphite except for the pore structure. Nano-graphite is one type of material in the nano-scale and contains hexatomic rings with sp² hybridized carbon atoms as the basic units, which is a layered material. Relevant research has indicated that π–π interactions, formed by graphite sheets and compounds with benzene rings, play important roles in the adsorption process (Shinar et al., 2000; Wang et al., 2014a). Wang et al indicated that the high affinities of polycyclic aromatic hydrocarbons (PAHs) to graphite sheets are dominated by π–π interactions. PAHs are...
also one class of semi-volatile organic compounds (Cheruiyot et al., 2015). Dioxin, is one of the organic compounds, which contains π electrons that can interact with π electrons of benzene rings of graphite sheets by means of π-π interaction (Wang et al., 2014b). We propose that π-π interactions between π-electron-rich PCDD/Fs rings and π-electron-depleted regions of graphite sheets surface was another important mechanism for the removal of PCDD/Fs. This
also suggests that graphite is a promising adsorbent to remove dioxin and might be able to be used in incineration plants. Since it is available in much larger amounts as well as much cheaper than other nano-materials (such as CNT and graphene) (Kang, 2005; Wang et al., 2014b).

**CONCLUSIONS**

In this study, graphite was engaged to adsorb dioxin in a laboratory-scale packed-bed system and adsorption was investigated at different concentrations, temperature and time periods. With the increase of concentration, the RE first enhances from 89.31% to 99.96%, yet then declines to 96.77%. At low concentration the removal efficiency of PCDD/Fs augmented by 7.26 points over 3 hours, but dropped by 1.78 points and 16.15 points with time, respectively at medium or high concentration. The RE-values show that RE decreases in proportion to temperature, with R² (0.99). The relationship of vapour pressure and RE indicates that RE would decline with the increase of vapour pressure. These preliminary results suggest graphite is an outstanding adsorbent to adsorb dioxin. According to the performance of graphite, it seems that mesopores volume and abundant pore structure are important to remove dioxin. Apart that π-π interactions between PCDD/Fs and graphite sheets is another reason leads to a high adsorption capacity of dioxin.

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