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# Modeling of dioxin adsorption on activated carbon

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## HIGHLIGHTS

- Substituent group promotes gas adsorption on activated carbon.
- Combine forces of gas and AC enhanced with increasing chlorine groups.
- Adsorption amount doubled with one chlorine substituent on benzene ring.
- Actual dioxin adsorption amount has been inferred at above 600 mg/g.

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## ABSTRACT

The adsorption of dioxin–modeling compounds on activated carbon has been investigated in this manuscript. A series of benzene compounds with different numbers and types of substituent groups were chosen as the dioxin–modeling compounds, and the gas adsorption behaviors were evaluated using a fixed-bed reactor. The adsorption results showed that the methyl, chlorine and phenolic substituent groups on a benzene ring can greatly promote gas adsorption, especially the phenolic group, the addition of which increased the adsorption capacity to more than 1.5 times that of benzene. The adsorbed AC samples were detected by TPD-MS with the combines between adsorbate and adsorbent analyzed, the methyl and chlorine groups enhanced the attraction between the gaseous compounds and AC, while the phenolic group reduced the combine force due to its oxidation on AC. The effect of an increasing number of chlorine substituents on the adsorption of gases and the combine forces were investigated. On average, the capacity of gas adsorption doubled and the desorption temperature increased by 20 K with one chlorine substituent on a benzene ring. The attachment of chlorine substituent groups to the AC lactone and quinone groups has been verified again, and the increasing chloric substituent groups consumed more oxygen groups. According to the linear relationships between gas properties and adsorption behaviors, the actual dioxin adsorption capacity has been inferred to be 600 mg/g or greater, showing that dioxin is much more easily adsorbed on AC than the conventional organic gases.



## 1. Introduction

The polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) represent a category of persistent organic pollutants (POPs), with 75 PCDD congeners and 135 PCDF congeners substituted with 1–8 chlorine atoms. PCDD/Fs are bioaccumulating, toxic, carcinogenic, mutagenic and teratogenic [1]. They are formed in low concentrations (ng TEQ/m$^3$) when chlorine species are present in post-combustion gases [2]. Activated carbon (AC) has long been used in the removal of vapor-phase organics from industrial waste gas streams [3], especially for aromatic pollutants, and has been expected to efficiently adsorb dioxins due to its high specific surface area and abundant functional groups.

The adsorption of dioxin by activated carbon from industrial flue gases was accomplished either by the use of granular activated carbon in a fixed-bed adsorber or by homogeneous injection of pulverized activated carbon into the gas [4]. The injection of activated carbon into a municipal waste incinerator has shown a removal efficiency of 96.6% for dioxin, with the dioxin effluent concentration reduced to 1.63 ng TEQ/m$^3$ [5]. The dioxin removal efficiency is directly related to the amount of AC injected. With the injection of 20, 40 and 50 kg/h of activated carbon before the bag filter, PCDD/F removals of 86%, 96% and 97% were achieved in the stack flue gas, respectively [6]. To meet the stringent emission standards and minimize the activated carbon consumption rate, various

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parameters have been investigated, including the properties of the sorbent used and the pollutant to be removed, the concentrations of other adsorbable gases and vapors, the operating temperature, and the residence time [7–9]. In any case, the properties of the adsorbent (AC) are some of the critical factors for the adsorption of PCDD/Fs.

Kawashima et al. [10] investigated the adsorption of dioxin-like polychlorinated biphenyls (DL-PCBs) on 16 different types of AC. The results showed that the AC with a surface area of 700–1200 $m^2/g$ and micropores with diameters of approximately 0.7–0.8 nm exhibited the highest adsorption activity. Similar results show high adsorption capacities for microporous ACs, indicating the necessity of micropores for the adsorption of organic pollutants [1,3,11,12]. The effects of the AC surface functional groups are not completely understood. Ghimbeu et al. [13] studied the adsorption of oxygenated hydrocarbons on AC and found that the adsorption capacities are more directly related to the chemical properties of the AC, where the number of oxygenated surface groups per carbon surface area increases the adsorption capacity. Bell et al. [14] studied the adsorption of very low concentrations (<50 ppm) of chloroaromatic gases on AC and concluded that the surface functional groups have only a relatively small effect on the adsorption characteristics.

These diverse effects of the chemical properties of the AC are closely correlated with the properties of the different adsorbates. However, because of the low volatility and high toxicity of dioxins, it is difficult to generate dioxin vapor in a stable and consistent manner in the laboratory, so it is quite hard to do bench–scale experiments to test the adsorption behavior of dioxin on ACs. PCDD/F model compounds were usually used to study the adsorption experiments, as the previous studies showed [15–17]. Chlorinated aromatic and furan compounds have been shown to be the primary precursors of dioxin formation in industrial processes [2]; therefore, this study focuses on the adsorption of a series of dioxin modelling compounds on AC. The substituent groups (including the type and number) on the benzene ring may cause the molecular diameter and polarity of these compounds to affect their adsorption. According to the adsorption behaviors of the model compounds, the adsorption capacity of the PCDD/Fs are estimated. In addition, the interactions between the PCDD/Fs model compounds and the carbon functional groups are investigated to analyze the combine forces between the adsorbed compounds and the AC surface.

## 2. Experimental

### 2.1. Materials and characterization

The coconut shell activated carbon used in the experiment was obtained from the Gongyi AC plant in Henan province. The AC was sieved and dried at 393 K for 10 h before the experiment; its properties are shown in our previous study [18].

### 2.2. Organic vapor generation and adsorption tests

The AC adsorption tests were performed in a fixed-bed reactor. This quartz tube reactor was 8 mm in diameter and 500 mm in height, with a sieve plate in the middle. Each AC sample (0.10 g) with particle sizes of 0.18–0.90 mm was loaded on the plate for each experiment. The reaction temperature was 393 ± 0.1 K. The gas flow rate was 300 ml/min at standard state, and the gaseous hourly space velocity (GHSV) was approximately 72,000 $h^{-1}$. The simulated gas consisted of the vapor of the dioxin-modeling compound and a balance of $N_2$. The benzene, chlorobenzene, phenol, toluene, 1,3-dichlorobenzene and 1,3,5-trichlorobenzene vapors were generated by bubbling $N_2$ through the compound heated on a water bath at 293, 313, 333, 293, 313, 343 ± 0.1 K, respectively. The organic vapor concentration was calibrated by a gas chromatograph (7890, Agilent) at 100 ± 5 ppm. After the gas was mixed in the mixing vessel, it was injected into the reactor with the effluent gas continuously detected by a quadruple mass spectrometer (GAM200, IPI). Before each test, the mass spectrometer was purged with high-purity nitrogen for 4 h. The benzene, chlorobenzene, phenol, toluene, 1,3-dichlorobenzene and 1,3,5-trichlorobenzene were identified using the major molecular ions with masses of 78, 112, 94, 91, 146.5, 145.5 detected by the mass spectrometer using the multiple ion detection (MID) method.

The capacities of the dioxin–modeling compounds adsorbed on the AC were calculated by numerical integration of the experimental data based on the breakthrough curves, the integration range $t$ is from 0 min to the gas saturation time, the calculation method is shown as the following equation:

$$v = \frac{F_o M}{22.4 \times m_0} \int_0^t (C_0 - C_t)dt$$

where $v$ is the adsorbent adsorption capacity (mg/g), $M$ is the mole fraction of the adsorbate (benzene-78 g/mol, chlorobenzene-112 g/mol, phenol-94 g/mol, toluene-92 g/mol, 1,3-dichlorobenzene-147 g/mol, 1,3,5-trichlorobenzene-181 g/mol), $F_o$ is the volumetric feed flow rate (ml/min), $m_o$ is the adsorbent mass (g), $C_o$ is the adsorbate feed concentration (ppm), and $C_t$ is the adsorbate concentration (ppm) at time $t$.

### 2.3. Adsorption products and fresh AC desorption tests

The method of temperature-programmed desorption coupled with mass spectrometry (TPD-MS) was used to analyze the adsorption products and the specific interactions between the AC and the adsorbate. The samples were placed in the quartz crucible of a thermogravimetric (TG) analyzer (Versa Therm HM, Thermal). The desorption process was recorded in the temperature range of 303–1273 K with a 10 K/min heating rate using argon as the carrier gas. The effluent organic gases, $CO_2$ and CO, were continuously monitored by mass spectroscopy and were identified by the molecular ions of masses 44 and 28, respectively.

## 3. Results and discussion

### 3.1. Effect of substituent group types on benzene compounds adsorption

Three different substituent group types were investigated, including chlorine, phenolic and methyl substituent groups, with benzene adsorption as a comparison. The breakthrough curves of these four gases on AC are shown in Fig. 1. Among the four organic

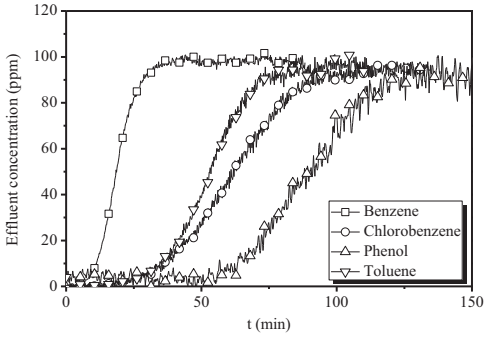


**Fig. 1.** Breakthrough curves of benzene, chlorobenzene, phenol and toluene on AC.