

Adsorption of OCDD on Different Materials

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Introduction

The concentration of PCDDs/PCDFs in flue gas from incineration has been limited to 0.1 ng TEQ/Nm³ in Japan, European Union and other countries. In response to strict legislation limiting the dioxin emissions, municipal waste incinerators (MWI) are commonly equipped with one or more techniques for PCDDs/PCDFs removal, such as dry sorbent injection, fixed or moving-bed adsorption and selective oxidation catalytic reactor *etc.*^{1,2}. Up to now, none of these abatement techniques has been generally accepted, and it is comparatively expensive to achieve the goal, due to the problem of collecting the diffused dioxins³. Spray dryer and fabric filter combination have been employed to control air emissions of PCDDs and PCDFs from MWIs^{4,5}. Adsorption of PCDDs/PCDFs and PCBs onto activated carbon and calcium (Ca)-based sorbents is of interest in the fields of air pollutant emission control and of contaminated soil treatment.

Although activated carbon *etc.* has long been used as adsorbent for removal of dioxins, there is lack of equilibrium adsorption information for dioxin congeners, because experimental technique developed for measuring adsorption for such low-volatile high-toxicity organic compounds is scarce. A simple method based on Knudsen effusion technique is developed here for evaluating and quick screening of adsorbents.

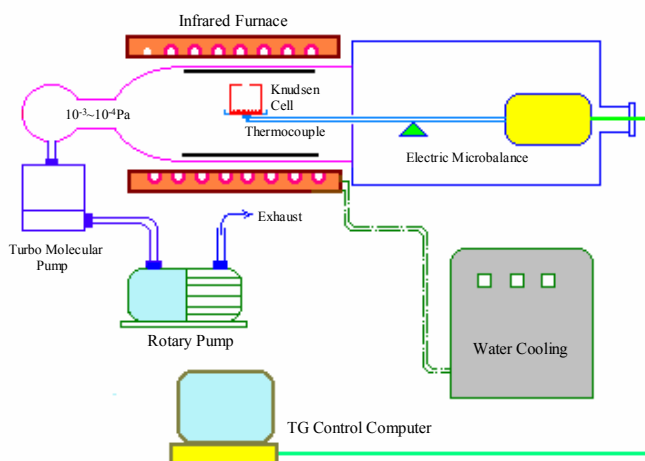


Fig 1 Apparatus diagram of dioxin congeners adsorption

Experimental

The Knudsen effusion method was employed to examine the adsorption capacity of adsorbents on OCDD vapor. The apparatus of adsorption study was shown in Fig 1. The Knudsen cells are 4.4 mm in internal diameter, 4.6 mm in depth and 0.1 mm in wall thickness. There is an effusion hole (diameter: 0.05~0.20 mm) coaxially located at the lid of the cell. The small size of the effusion cell requires only a small amount of sample (1-2mg) for one experiment.

After weighting, the powder OCDD and adsorbent were mixed together thoroughly, and charged and compressed in a thin layer on the bottom of the Knudsen effusion cell, so as to get a flat surface and a good heat transfer. After charging sample, the Knudsen cell was hermetically sealed by a special presser, and was put on the holder of the electric microbalance hand. The precision of the calibrated microbalance is of 1 microgram. The experimental temperature of the effusion cell is controlled by an infrared furnace, which cooled by a recycle water-cooling equipment. The accuracy of temperature control is of ± 0.1 °C in the temperature range of room temperature to 1000 °C. A high vacuum (10^{-3} to 10^{-4} Pa) of the system was established by a rotary pump and a turbo molecular pump. Weight change and temperature profile were continuously collected and record by the data system on line in real time.

From the kinetic theory of gases, the vapor pressure inside the cell, p , is given by

$$p = \{\Delta m / (A_0 \cdot K_C \cdot t)\} \cdot (2 \cdot \pi \cdot R \cdot T / M)^{1/2} \quad (1)$$

where Δm is the mass loss of the samples, A_0 is the area of the effusion orifice, K_C is the Clausing factor, t is the effusion time period, R is the universal gas constant, T is the experimental temperature of the samples, and M is the molecular mass of the effusing vapor. Accurate K_C is cited in the literature ⁶.

The crystalline sample of OCDD was made by AccuStandard Inc., its purity was 98.2%. The samples used as adsorbents in this study are calcium hydroxide ($\text{Ca}(\text{OH})_2$), hematite (Fe_2O_3), zinc oxide (ZnO), graphite and activated carbon. They are all pure chemical compounds. The size and specific surface area analyses of those adsorbents are summarized in Table 1.

Table 1 Size and specific surface of adsorbents

Adsorbent	Fe_2O_3	$\text{Ca}(\text{OH})_2$	ZnO (coarse)	ZnO (fine)	Graphite	Activated carbon
Mean particle size (μm)	2.6	6.7			12.8	90.3
Specific surface area (m^2/g)	4.35	12.49	2.25	9.63	7.9	1163

Results and discussion

OCDD vapor adsorbing effect of $\text{Ca}(\text{OH})_2$: The blending ratio of OCDD to calcium hydroxide were changed from 3:1 to 1:10. The effusion rate results of OCDD vapor from the orifice of Knudsen cell at different temperatures were shown in Fig 2. Figure 2 shows that the apparent vapor pressure of OCDD decreases as the blending ratio of $\text{Ca}(\text{OH})_2$ to OCDD increases, and the apparent vapor pressure changes is not significant when the ratio over 3:1. In the case of the ratio of

OCDD to Ca(OH)_2 is 1:10, the apparent vapor pressure at 235.6 °C decreases significantly due to the OCDD sample near exhausting of vaporization.

OCDD vapor adsorbing effect of different adsorbents: The experimental blending ratio of OCDD to adsorbent is fixed at 1:3. The apparent vapor pressure of OCDD with hematite, graphite, and zinc oxide at different temperatures were shown in Fig 3. For comparing, the results with Ca(OH)_2 are also shown in the same figure.

It can be easily concluded from Fig 3 that the adsorption capacity sequence on OCDD vapor is $\text{ZnO(coarse)} < \text{Fe}_2\text{O}_3 < \text{ZnO(fine)} < \text{graphite} < \text{Ca(OH)}_2$. Although the mean particle size of Fe_2O_3 is more fine than that of Ca(OH)_2 and graphite, the specific surface area of Fe_2O_3 (4.35 m^2/g) is lower than the values of Ca(OH)_2 (12.49 m^2/g) and graphite (7.9 m^2/g). It seems that adsorption capacity depends on the specific surface area of adsorbent. The results show the adsorption capacity of fine ZnO is stronger than that of coarse ZnO, but weaker than that Ca(OH)_2 .

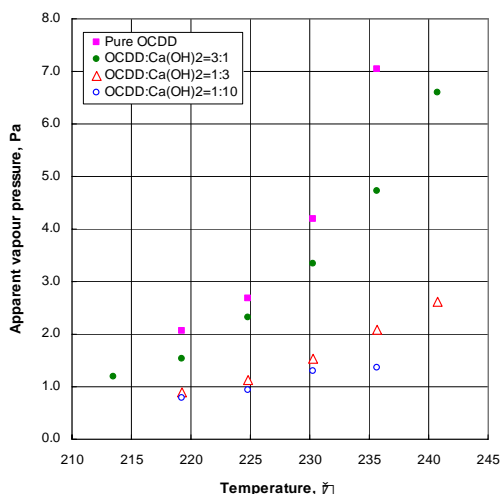


Fig 2 The adsorbing effect of Ca(OH)_2 on OCDD vapor

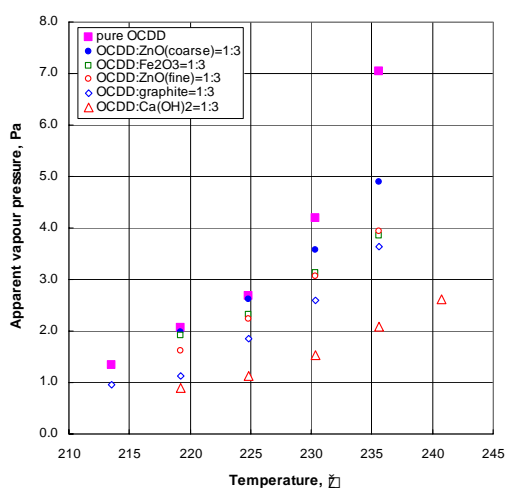


Fig 3 Comparison of adsorbing effects of different adsorbents on OCDD vapor

It appears that the adsorption capacity sequence of those adsorbents is almost the same as their specific surface area sequence, except graphite and fine ZnO.

Adsorption capacity: $\text{ZnO(coarse)} < \text{Fe}_2\text{O}_3 < \text{ZnO(fine)} < \text{graphite} < \text{Ca(OH)}_2$
 Specific surface area: $\text{ZnO(coarse)} < \text{Fe}_2\text{O}_3 < \text{graphite} < \text{ZnO(fine)} < \text{Ca(OH)}_2$
 (m^2/g): (2.25) (4.35) (7.9) (9.63) (12.49)

It means that the adsorption capacity of graphite is stronger than zinc oxide.

OCDD vapor adsorbing effect of activated carbon: Activated carbon (AC) is the common adsorbent used frequently. At first, the blending ratio of OCDD to AC was set at 1:3. The apparent vapor pressure of OCDD at different temperatures decreased dramatically even at much higher temperature, as shown in Fig 4.

It is obvious that activated carbon is far stronger than the other adsorbents although its particle size is much coarse than the others. It should be noted that the specific surface area of activated carbon (1163 m²/g) is much larger than those of the other adsorbents.

To see the effect of blending ratio, the ratio of OCDD to AC was changed from 1:3 to 1:1 and 2.2:1, the results were shown in Fig 5. It is apparent that when the blending ratio of OCDD to AC increases to 2.2:1 the apparent vapor pressure of OCDD increases significantly as temperature increases at first, and then decreases sharply and maintain a stable very low pressure. It appears that there is too much ‘free’ solid OCDD on the surface of effusion sample layer when the ratio of OCDD to AC over than 1:1, the effusion rate is very higher at first. After the ‘free’ solid OCDD sample on the surface evaporated out, the vapor dropped to a very low pressure.

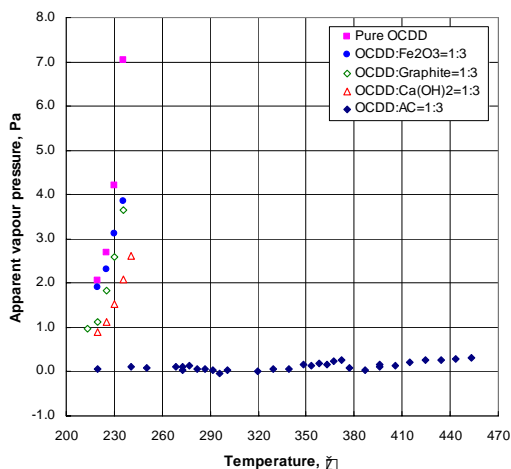


Fig 4 Adsorbing effects comparison of activated carbon and other adsorbents

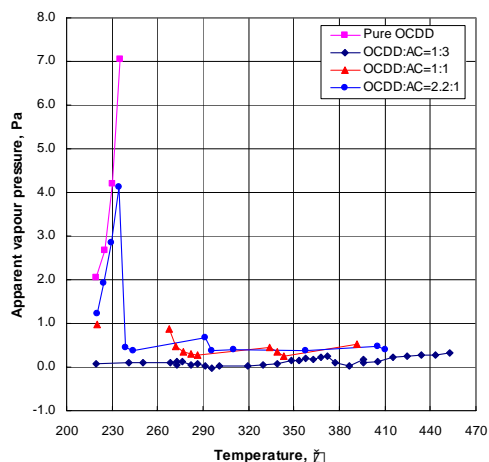


Fig 5 The adsorbing effects of activated carbon on OCDD vapor

It demonstrates that activated carbon has excellent adsorption capacity to dioxin congeners, and the adsorption capacity of adsorbents mainly depend on their specific surface area.

Conclusions

The adsorption capacity of OCDD vapor on different substances was studied using the Knudsen effusion technique. Experiments were carried out by mixing adsorbent with OCDD. Due to the presence of adsorbent, the apparent vapor pressure of OCDD inside the Knudsen cell was

changed. By measuring the apparent vapor pressure, the adsorbabilities of different substances could be judged easily.

It was indicated that the blending ratio of adsorbent to OCDD could affect the apparent vapor pressure of OCDD, but the influence became insignificant as the ratio over 3:1. It was determined that the adsorption capacity sequence of adsorbents used here is as the follow (It is almost the same as their specific surface area sequence, except graphite and fine ZnO).

ZnO(coarse)<Fe₂O₃<ZnO(fine)<graphite<Ca(OH)₂<<activated carbon.

It could be concluded that activated carbon has excellent adsorption capacity to dioxin congeners, and the adsorption capacity of adsorbents mainly depend on the specific surface area.

Acknowledgements

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