BASIC ADSORBABILITY OF DIOXIN SURROGATE COMPOUNDS ON VARIOUS ADSORBENTS

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Introduction

Many incineration plants for municipal solid wastes (MSW) and industrial wastes in Europe move to apply adsorption technology as an advanced treatment of dioxins in flue gas. Various kinds of adsorbents are developed and used in commercial plants. However, basic characteristics concerning adsorption amount and breakthrough phenomena are not well understood, because laboratory tests using dioxins are generally difficult to perform[1]. Therefore, we investigated properties of adsorbents using two surrogate compounds of dioxins. The surrogate compounds of dioxins used are 1,2,3,4-tetrachlorobenzene (T4CBz) and 1,2,3,4,5-pentachlorobenzene (P5CBz). Emphasis was placed on the amounts of adsorption and the effects of temperature, moisture content of gas and the kind of adsorbent on the amounts.

Experiments

2 . 1 Adsorbents

As shown in Table 1, one activated carbon, two activated cokes (A, B) and one inorganic adsorbent were employed in the experiments. Specific surface area and total pore volume of the activated carbon were around 150% of those of activated cokes A and B, while these values of the inorganic adsorbent were only around 10% of those of the activated cokes. All of the adsorbents were fine powder and their mean particle diameter was in the range of 10μm. The adsorbents were applied as Aktinert[2] adsorbent consisting of an inert carrier medium (mean particle diameter: 2.4mm) coated with fine-powder adsorbents.

Table 1 Typical properties of activated carbon, activated coke and inorganic adsorbent

	Activated carbon	Activated coke A	Activated coke B	Inorganic adsorbent
Mean particle diameter (μm)	9.2	9.9	11	14
Specific surface area (m^2 / g)	638	327	440	40
Total pore volume (ml/g)				
Pore diameter : < 2nm	0.22	0.13	0.18	0.01
Pore diameter : 1 - 30nm	0.20	0.11	0.04	0.03
Pore diameter : 6nm - 200μm	1.35	0.91	1.00	0.79
Water content (wt %)	2.7	1.7	5.0	7.0
Ash (wt %)	10.7	6.2	7.5	82.8
Volatile matter (wt %)	3.4	3.6	5.4	9.9
Fixed carbon (wt %)	83.2	88.5	82.1	0.3
Apparent density (g / cm^3)	0.52	0.66	0.70	1.05
True density (g / cm^3)	2.01	1.91	1.90	2.70

2 . 2 Test equipment

A schematic diagram is illustrated in Fig.1. Purified air was introduced to the diffusion tube and T4CBz or P5CBz filling the tube was diffused and mixed with the air. Then carbon dioxide and water were added to produce a model gas for the incineration flue gas. After T4CBz or P5CBz in the model gas was adsorbed on the adsorbent in the oven, the model gas was introduced to the impingers filled with water and n-Hexane. Trapped T4CBz or P5CBz in n-Hexane was determined quantitatively by a gas chromatograph with ECD.

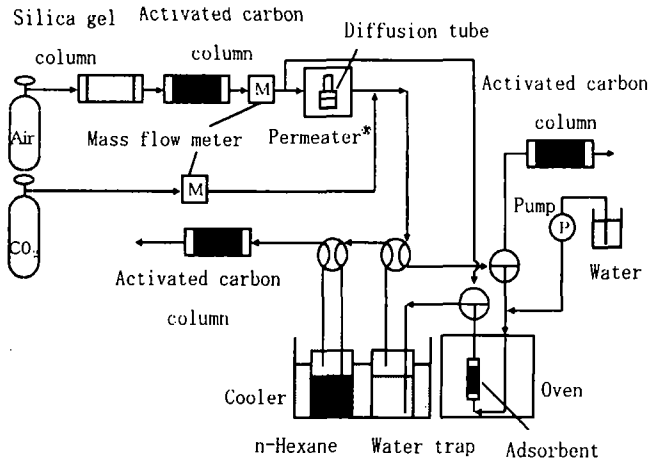

Fig. 1 Schematic diagram of adsorption test system

2 . 3 Experimental conditions

Space velocity was set at 5000h^{-1} and temperatures of the adsorbent in the oven were kept in the range of 120 - 180°C. T4CBz or P5CBz concentration was varied from 8ppb to 27ppb. Moisture content in the gas was set at 0, 20 or 40 vol%.

Results and discussion

3 . 1 Breakthrough curves

Breakthrough curves of the various adsorbents for T4CBz are illustrated in Fig.2. The breakthrough curve of the activated carbon started rising toward saturation in around 10 hours after T4CBz loading, whereas those of activated coke B and activated coke A started rising in only around half an hour and 4 hours respectively. The curve of the activated carbon reached saturation in around 70 hours and those of activated cokes A and B reached saturation in around 20 hours. Adsorption capacity of activated cokes A and B were 3.2 and 5.1 mg-T4CBz/g respectively, whereas that of the activated carbon was 18 mg- T4CBz /g, 3 - 5 times those of the activated cokes. The difference might be explained by the difference in total micro-pore volume (pore diameter: 1-30nm) of the adsorbents. Adsorption capacity of the inorganic adsorbent was very poor, compared with those of the activated carbon or activated cokes. However, the inorganic adsorbent is partly approved as an effective material for dioxins removal in Europe, therefore it will be advisable to test the material at a commercial incineration plant in Japan.

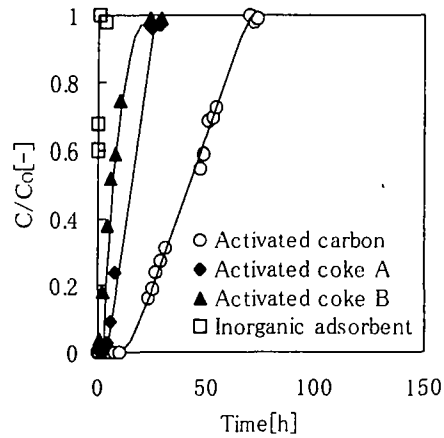

Fig.2 Adsorption curves of TCB for various adsorbents (Temp.:150℃,Moisture:40%, T4CBz:27ppb,SV:5000h^{-1})

3 . 2 Adsorption by the inert carrier medium

Adsorption characteristics of the inert carrier medium were examined without activated carbon or activated cokes to confirm the influence of Aktinert medium on adsorption. Amount of T4CBz adsorbed by the carrier was negligible in comparison with that of the activated carbon or activated cokes.

3 . 3 Influence of temperatures

Fig.3 shows the influence of the adsorption temperature on adsorbed amount. We can clearly observe that the influence is especially strong on the activated carbon and that breakthrough time at 180°C was around half of the time at 120°C. This result can be explained by a thermodynamic principle that lower temperature is more effective for adsorption, because adsorption phenomenon is an exothermic reaction. It is also interesting to observe that adsorption capacities of the two activated cokes were less influenced by temperature, compared with that of the activated carbon.

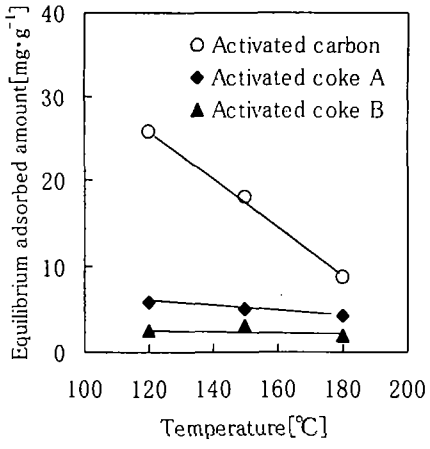

Fig.3 Influence of temperature on adsorbed amount
(Moisture:40%,T4CBz:27ppb,SV:5000h^{-1})

3 . 4 Influence of moisture content

The influence of moisture content on adsorption is shown in Fig.4. As illustrated, no clear difference in breakthrough time nor in the equilibrium adsorbed amount was seen by moisture increase in cases of the activated carbon and of activated coke A. In other words, the influence of moisture content on adsorption was comparatively small.

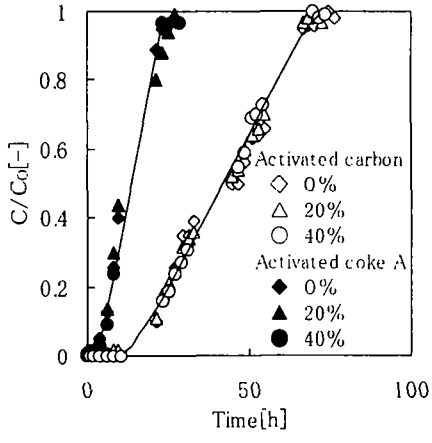

Fig.4 Influence of moisture content in gas
(Temp.:150℃,T4CBz:27ppb,SV:5000h^{-1})

3 . 5 Adsorption isotherms

As illustrated in Fig.5, the influence of T4CBz concentration was examined and the adsorption isotherms were obtained. Breakthrough time of all adsorbents decreased as T4CBz concentration increased. Adsorption isotherms were nearly straight lines for all of the adsorbents and they were well expressed as the adsorption isotherm of Freundlich formula (1) with q being equilibrium adsorbed amount and C equilibrium concentration of T4CBz.

$$\log q = \log k + 1/n \log C \quad (1)$$

Adsorption isotherm for each adsorbents can be expressed by the following equations.

$\log q = -0.36 + 0.61 \log C$ (Activated coke A)
$\log q = -0.18 + 0.62 \log C$ (Activated coke B)
$\log q = 0.34 + 0.63 \log C$ (Activated carbon)

As seen in the above equations, slope was constant for all of the adsorbents with n being 1.6. K values were 2.2 for the activated carbon, 0.67 for activated coke A and 0.44 for activated coke B. These values correspond to equilibrium adsorbed amounts of the adsorbents.

3 . 6 Adsorption characteristics of P5CBz

P5CBz was applied on activated coke A in an adsorption test and breakthrough curve of P5CBz was obtained as shown in Fig.6. As illustrated in this, the breakthrough curve of P5CBz was almost identical to that of T4CBz. The equilibrium adsorbed amount of P5CBz was around 90% of that of T4CBz.

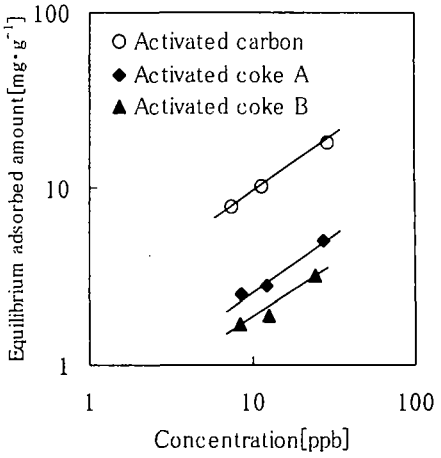

Fig.5 Adsorption isotherms of T4CBz (Temp.:150℃,Moisture:40%,SV:5000h^{-1})

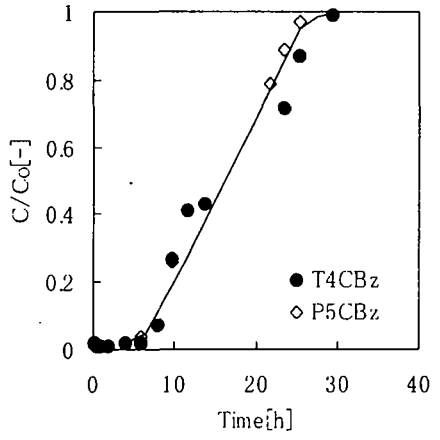

Fig.6 Adsorption curves of T4CBz and P5CBz by activated coke A (Temp.:120℃,Moisture:40%,SV:5000h^{-1})

Conclusion

1) Equilibrium adsorbed amount of T4CBz was studied by using activated cokes as cheaper organic adsorbents. 1.7 - 5.8 mg-T4CBz/g was obtained with the activated cokes, whereas 4.6 - 26 mg-T4CBz/g with the activated carbon. The adsorption capacity of the activated carbon was around 3 - 5 times that of the activated cokes, which might be explained by the difference in pore volume of adsorbents in the pore diameter range of 1-30 nm.
2) Adsorbed amount decreased as temperature increased. Adsorption capacity of the activated carbon was highly influenced by temperatures, whereas those of the activated cokes were less influenced.
3) Influence of moisture content in the flue gas was comparatively small in both cases of the activated carbon and of the activated cokes.
4) Adsorption isotherms were nearly straight lines for all of the adsorbents and they were well expressed as the adsorption isotherm of Freundlich formula (1).
5) Breakthrough curve of P5CBz was almost identical to that of T4CBz. Adsorbed amount of P5CBz was about 90% of that of T4CBz.

References

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2 W. Schüttenhelm, R. Holste : Dioxin and Furan Reduction Technologies for Municipal and Hazardous Waste Incineration Plants, *Proceeding of Korean Dioxin Control Technology Fair* (1997)