ADSORPTION OF GASEOUS PCBs BY ACTIVATED CARBON

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Introduction

Adsorption by activated carbon is a commonly used technology for removing gas-phase toxic materials. Stringent exhaust management is required, in particular, for dioxins and PCBs; therefore, activated carbon adsorption system is absolute necessity in incinerators and PCB treatment plants. However, because of their high toxicity and the large number of isomers, difficulties exist in testing these materials, and basic knowledge on adsorption in gas phase is limited.

We have constructed a lab-scale on-column adsorption experimental equipment to attempt at clarifying adsorption of gaseous PCBs by activated carbon. Also, we compared results obtained from experiments using model materials with those obtained from calculation using an estimation formula.

Materials and Methods

1. Adsorption Experiments with KC-300

Using PCB (KC-300), adsorption of gaseous PCB by activated carbon was carried out. Fig. 1 shows the on-column experimental equipment used in the experiments. The equipment consists of a 3-necked flask, a column filled with activated carbon, and a gas collector. All glassware was connected by Teflon tubes. In a 1L 3-necked flask was added 10g of PCB (KC300), and the flask was allowed to stand for some time so as to saturate the inside of the flask with PCB vapor. This was followed by purging the activated carbon column with nitrogen as a carrier gas. The column was made by glass tube filling activated carbon and both ends were stoppered with glass wool. Nitrogen flow rate was controlled by a mass flow controller. The whole apparatus was set up in a constant temperature oven regulated at 50°C. At certain time intervals, gas samples were obtained at both ends of the activated carbon column and were analyzed for PCB. Gas samples were collected into a wash bottle in which n-hexane was placed. After stripping off some solvent, the concentrate was analyzed by quadruple GC/MS. Experimental conditions and characteristics of activated carbon used in the experiment were shown in Tables 1 and 2.

2. Adsorption of 4-Chlorobiphenyl

In experiment using KC-300, it is therefore difficult to determine the rate of adsorption or desorption due to the fact that adsorption of each isomer by activated carbon is competitive with other isomers. We therefore employed two kinds of model compounds to simplify adsorption experiments that we conducted. We used 4-Chlorobiphenyl (4-MCB, vp. 0.81Pa at 50°C) and Biphenyl (vp. 1.42 Pa at 50°C).

As in the case of KC-300 adsorption experiment, on-column adsorption equipment was used for experiments. At periodic intervals, gas sampling was done both at inlet and outlet of the column filled with activated carbon and the concentration of each gas sample was determined. By varying the column inlet concentration, equilibrium adsorption was determined for each concentration to create adsorption isotherm curves.

Results and Discussion

1. KC-300 Adsorption Experiments

Fig. 2 shows the results of the experiments. C/C0, ratio of the outlet concentration C versus the inlet concentration C, was plotted for total PCBs and for each congener to create a break-through curve. From KC-300 adsorption experiments, it was found that the break-through proceeded from di- to tri- and to tetra-chlorobiphenyls. In Fig.3, break-through curve for each isomer of tri-chlorobiphenyl was created, resulted in clear difference in break-through time among isomers. Vapor pressure of major isomers of Kanechlor is shown in Table 3[1,2]. PCBs generally have high boiling points and are non-volatile materials, however, low chlorinated PCBs have vapor pressures of 0.1~1Pa. When we focus our attention to vapor pressure and break-through time of each isomer, we find that break-through was occurring with isomers with relatively high vapor pressures, such as 2,6-di- and 2,2',6-trichlorobiphenyl.

2. Competitive Adsorption of 4-Chlorobiphenyl and Biphenyl

We first determined the equilibrium adsorption for 4-chlorobiphenyl and biphenyl by varying gas concentrations. Fig. 4 shows adsorption isotherm generated from the test results. We found that both 4-chlorobiphenyl and biphenyl fitted Freundlich's adsorption isotherm. We then mixed both 4-chlorobiphenyl and biphenyl together to perform 2-component competitive adsorption tests. The results are shown in Fig. 5. It was shown that biphenyl underwent break-through faster than 4-chlorobiphenyl. This is because of higher vapor pressure of biphenyl, similar to the results obtained for PCB congeners.

Estimation of Break-Through Curve

Using 4-MCB and biphenyl, we estimated break-through curves for 2-component competitive adsorption by activated carbon, and compared with values actually determined. We used the LDF approximation in which adsorption is assumed to be effected by diffusion transfer on the particle surface as well as the inner surface of activated carbon. Estimation of break-through curves was made by diffusion equation obtained by this method and by solving material balance formula where distribution of standard adsorption band is assumed to be generated inside the activated carbon column. As for equation of isothermal adsorption, we used Freundlich equation. Results are shown in Fig. 6. Table 4 shows parameters used for the calculation. The results indicated that break-through curve could be estimated by this method. With numerical calculation method using the LDF approximation, we could estimate break-through curves for 2-component systems.

Conclusions

We have demonstrated that adsorption of PCB in gas phase by activated carbon followed Freundlich's adsorption isotherm. Also we have found that adsorption behavior of PCB in gas phase differed by its isomers. This indicated that the break-through time for each isomer depends highly on its vapor pressure. Test results also showed that isomers with higher vapor pressure undergo break-through faster than those with a lower vapor pressure.

Using numerical LDF approximation, we could successfully estimated the break-through curves of PCB model materials (4-MCB and biphenyl) for 2-component competitive systems. The results we have obtained here show that the break-through time can be estimated with the method described.

References

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Table 1 Properties of activated carbon

	AG-100
carbon type	PAC
shape	crashed carbon
size mm	2.38-4.76
packing density g/ml	>0.4
hardness %	>95
dry reduction %	<5
pH	6.5-10
surface area m^2/g	>1000

Table 2 Experimental condition

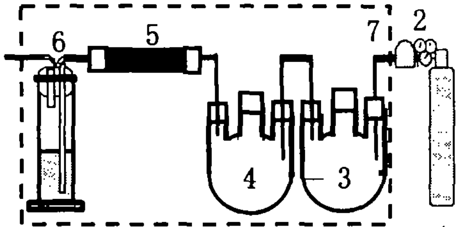
column volume	4ml (ϕ 1cm × 5cm)
AC amount	1g
gas flow rate	400ml/min
space velocity	6000 h^{-1}
adsorption temp.	50℃

Table 3 Vapor pressure of PCB isomers

isomer	vapor pressure Pa (25℃)	vapor pressure Pa (50℃)
2,6-D2CB	0.365	0.078
2,3'-D2CB	0.165	-
2,4'-D2CB	0.147	-
2,2',6-T3CB	0.167	-
2,2',5-T3CB	0.091	0.049
2,4',5-T3CB	0.058	0.029
2',3,4-T3CB	0.027	-

Table 4 Estimate condition of 2-components

concentration of 4-MCB (mg/m^3)	102
concentration of Biphenyl (mg/m^3)	165
isotherm equilibrium of 4-MCB (g/g-AC)	484
isotherm equilibrium of Biphenyl (g/g-AC)	60
viscosity of gas μ (g/m/s)	0.001
column length Z(m)	0.05
diameter of AC R (m)	0.001
packing density ρ (g/m^3)	410000
voids ratio ε (-)	0.5
surface area av (m^2/m^3)	3000
velocity of gas u (m/s)	0.3
molecule diffusion coefficient in gas phase D (m^2/s)	1×10^{-7}
ksav ($g/m^2/s$)	6×10^5
molecule diffusion coefficient in particle Ds (m^2/s)	1×10^{-9}
kfav (m/s)	501069



1 N2 gas, 2 mass flow controller,
3 three necked flask, 4 three necked flask,
5 AC column, 6 gas collector,7 thermostat

Fig.1 experimental apparatus

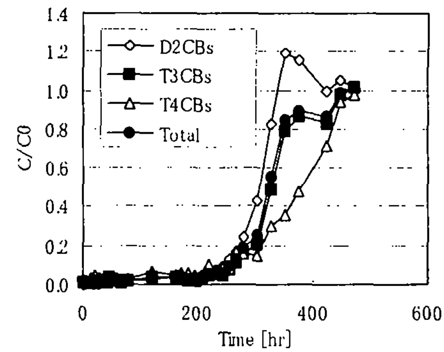


Fig.2 Breakthrough curve of KC-300

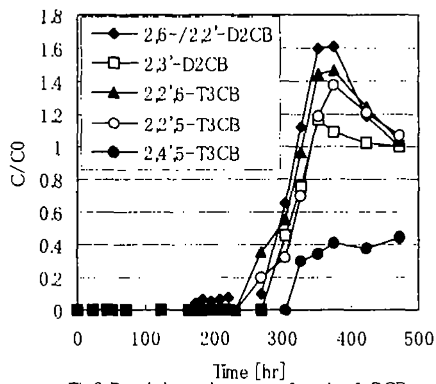


Fig.3 Breakthrough curve of each of PCB isomers

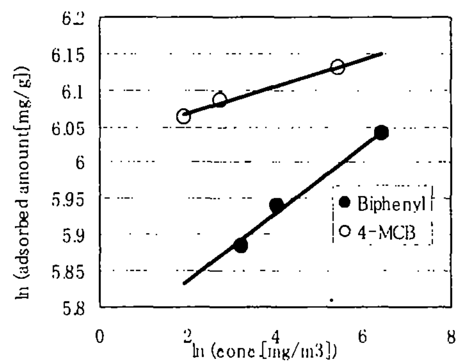


Fig.4 Adsorption isotherm of Biphenyl and 4-chlorobiphenyl

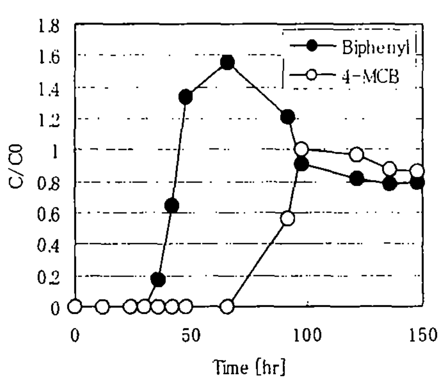


Fig.5 2-component breakthrough curves of biphenyl and 4-MCB

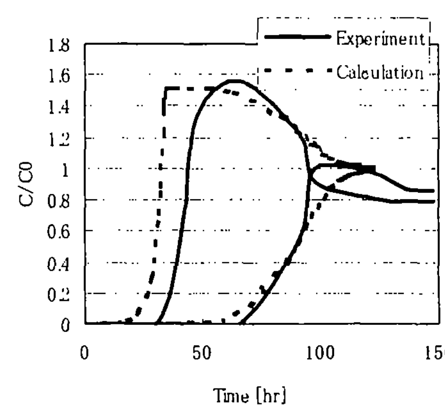


Fig.6 Estimation of breakthrough courves for 2-components