

FIXED-BED ADSORPTION OF POLYCHLORINATED DIBENZO-*p*-DIOXINS AND DIBENZOFURANS FROM THE FLUE GAS OF A MUNICIPAL SOLID WASTE INCINERATOR

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Introduction

To clarify the adsorption characteristics of polychlorinated dibenzo-*p*-dioxins and dibenzofurans to an adsorbent, we conducted an experiment with an adsorption fixed bed using the flue gas of a municipal solid waste incineration plant. Further, to analyze the adsorption distribution curve in the fixed bed, a solution for fixed-bed adsorption based on a linear mass transfer model, which adopted a linear isotherm system and a linear driving force rate equation, was applied. Using experimental data and an analytical solution, we estimated the adsorption coefficient and the overall volumetric coefficient of mass transfer for the adsorbent-adsorbate system for the flue gas of a full-scale incineration plant.

Experiment

(1) Materials

Activated coke and activated carbon were used as adsorbents in this experiment. Their shape was cylindrical (D 4 - 5 mm × L 5 - 10 mm). The Langmuir surface area of the activated coke was 260 m²/g, and that of the activated carbon was 1,250 m²/g. The cumulative pore volume by the adsorption isotherm of nitrogen and the mercury penetration method is shown in Fig. 1.

The adsorbates were tetra - octachlorinated dibenzo-*p*-dioxins and dibenzofurans. Hereafter we will use the term "DXN" to refer to both tetra - octachlorinated dibenzo-*p*-dioxins and dibenzofurans.

(2) Experimental Method

The thickness and the diameter of this experimental fixed bed were 600 mm and 100 mm, respectively. The apparatus was installed in a municipal solid waste incineration plant, whose incinerating capacity was 600 tons/24hr. The flue gas treated by an electrostatic precipitator and a wet scrubber was used as the test gas. We controlled the experimental operating conditions as follows. The temperature was 423 K, gas flow rate was 8 m³/h (at 273 K and 101.325 kPa), linear velocity was 0.25 m/s (at 273 K and 101.325 kPa), and space velocity was 1,470 h⁻¹ (at 273 K and 101.325 kPa). The DXN in the test gas at the inlet and at the outlet of the fixed bed were sampled at intervals of approximately 30 days. After experimental operations for 122 days for the activated coke and 185 days for the activated carbon, the adsorbents were sampled at intervals of approximately 50 mm of thickness to be analyzed.

Modeling of Fixed-bed Adsorption

There are few data concerning (1) equilibrium relations, (2) adsorption isotherms, (3) diffusion coefficients in gas-film and intraparticle between DXN and adsorbents, and (4) establishment of constant patterns in a fixed bed. Therefore, to analyze adsorption distribution curves in the fixed bed, modeling was based on two assumptions^{1,2)}. First, the Henry type equation was used on the adsorption isotherm between DXN and adsorbents, because DXN concentrations were on the order of ng/m³. Second, an overall volumetric coefficient of mass transfer by linear driving force was used in the rate equation, because an analytical solution could be obtained under these assumptions. For analysis of the breakthrough behavior of DXN at the outlet of the fixed bed and the profile of the amount adsorbed on the fixed bed, a step input was considered as a boundary condition at the inlet of the fixed bed.

$$c(z, t < 0) = q(z, t < 0) = 0 \quad (1)$$

$$c(z = 0, t > 0) = c_0 \quad (2)$$

$$q(z = 0, t > 0) = q_0 = \beta c_0 \quad (3)$$

where c is concentration, q is the amount adsorbed, c_0 is the concentration at the inlet, q_0 is βc_0 , β is the adsorption coefficient, t is time, and z is distance.

A set of analytical solutions under these boundary conditions is shown below.

$$\frac{c}{c_0} = e^{-X-T} I_0(2\sqrt{XT}) + \int_0^T e^{-X-T} I_0(2\sqrt{XT}) dT \quad (4)$$

$$\frac{q}{q_0} = \int_0^T e^{-X-T} I_0(2\sqrt{XT}) dT \quad (5)$$

where I_0 is the Bessel function, $X \equiv \frac{K_F a_v \times z}{u}$, $T \equiv \frac{K_F a_v \times t}{\beta \gamma}$, $K_F a_v$ is the overall volumetric coefficient

of mass transfer, u is linear velocity, and γ is packed density.

If we use the analytical solution, the equilibrium and rate parameters of the system can be determined from the experimental data.

4. Results and Discussion

The DXN concentrations at the inlet of the fixed bed were 82 - 950 ng/m³ (at 273 K and 101.325 kPa), which corresponded to 1.4 - 12 ng-TEQ/m³ based on TEF proposed by WHO/IPCS in 1988. The DXN concentrations at the outlet of the fixed bed were <0.02 - 11 ng/m³ (at 273 K and 101.325 kPa), which corresponded to <0.01 - 0.14 ng-TEQ/m³ based on TEF proposed by WHO/IPCS in 1988. Under conditions of 423 K, 600 mm, 0.25 m/s (at 273 K and 101.325 kPa), and 1,470 h⁻¹ (at 273 K and 101.325 kPa), a breakthrough curve was not observed at the outlet of the fixed bed during the 122 days for the activated coke and the 185 days for the activated carbon.

After the experimental operations of 122 days and of 185 days, the adsorbents were sampled at intervals of

approximately 50 mm of thickness to be analyzed. The DXN concentrations in the first layer were 3,000 ng/g (47 ng-TEQ/g) for the activated coke and 1,080 ng/g (11.7 ng-TEQ/g) for the activated carbon. Fig. 2 shows the DXN concentrations in the fixed bed. Large portions of the adsorbed DXN were distributed on the side of the inlet, and a constant pattern of adsorption was not observed.

The volumetric adsorption coefficient ($\beta \gamma$) and $K_f a_f$ had to be determined in Eqs. (4) and (5). But the packed density (γ) was exactly determined by another method; hence we estimated β and $K_f a_f$. The parameters were estimated on graphs whose ordinates were log scales, because the relative recovery of each homologue from the adsorbents on the removed amount from the test gas was low. The experimental data were fitted with two sets of fitting parameters, and the curves in Fig. 3 are the estimated curves. β was estimated at 80 m³/g for the activated coke and at 640 m³/g for the activated carbon. $K_f a_f$ was estimated at 9 - 11 s⁻¹ for the activated coke and at 16 - 22 s⁻¹ for the activated carbon.

Acknowledgements

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References

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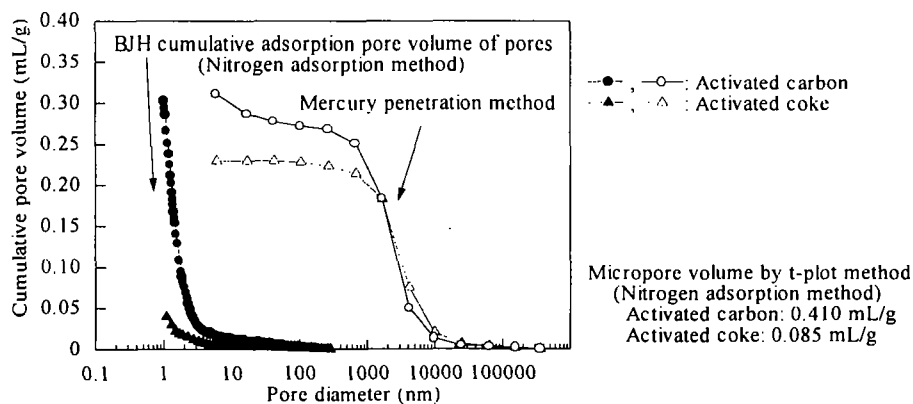


Fig. 1. Cumulative pore volume of adsorbents.

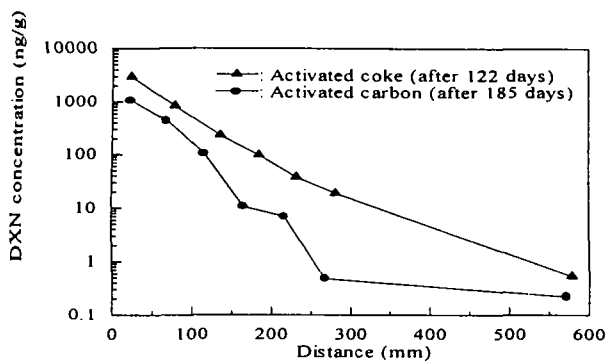


Fig. 2. DXN concentrations adsorbed in the fixed bed.

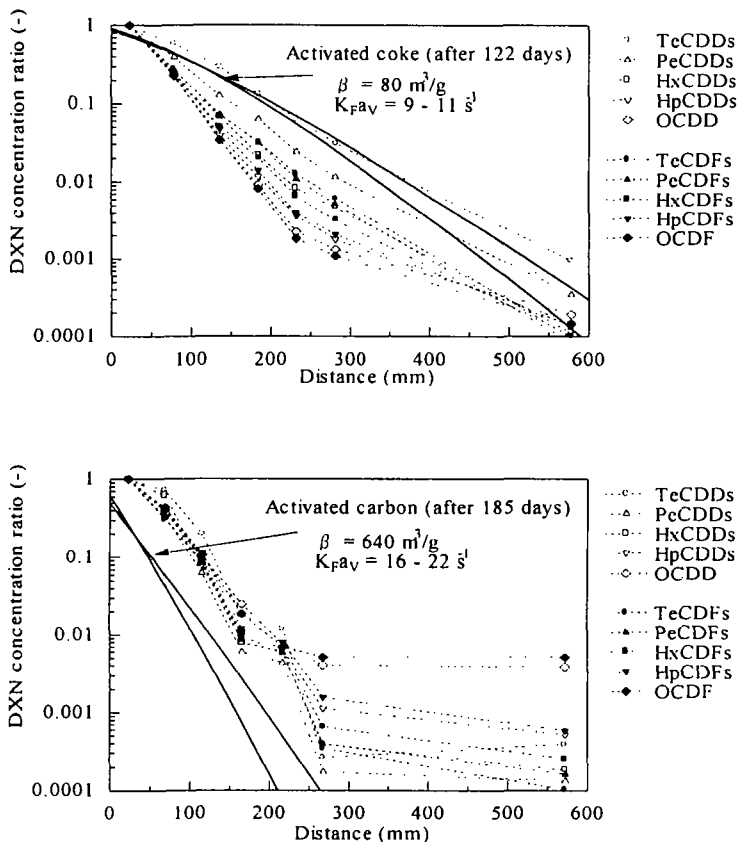


Fig. 3. Estimated adsorption front of DXN in the fixed bed.
(upper: activated coke; lower: activated carbon)