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Adsorption Characteristics of Trichloroethylene Removal by 16 Kinds of Granular Activated Carbons in Gaseous Phase

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The adsorption characteristics of trichloroethylene (TCE), a major volatile chlorinated hydrocarbon, onto 16 kinds of granular activated carbons (GACs) in gaseous phase were investigated.

The amount of TCE adsorbed on GACs was proportional to the pore volume, and the adsorption was recognized to be a physical one.

Applying the Dubinin–Radushkevich (D–R) equation to the adsorption isotherms of TCE, GACs could be classified into two types: the D–R plot was either a straight line or not depending on pore size distribution. TCE was believed to be adsorbed not only into micropores but also into transitionalpores.

Keywords trichloroethylene; granular activated carbon; physical adsorption; Dubinin–Radushkevich (D–R) equation; pore size distribution; specific surface area

Trichloroethylene (TCE) is one of the major volatile chlorinated hydrocarbons and is used in factories as a cleaner, solvent, refrigerant, and desiccant. It is known to cause strong central nervous system depression when inhaled, causing vertigo, headache and fatigue at gaseous concentration of more than 50—100 ppm. The permissible concentration of TCE in the air of a work area in Japan is therefore set at 50 ppm by the Japan Association of Industrial Health.[1)]

TCE is also a contaminant of groundwater and considered to be carcinogenic so that its concentration in drinking water is regulated at 30 ppb by the Ministry of Health and Welfare of Japan.[2)] There is no regulation, however, on TCE exhaustion into the atmosphere, though this is the ultimate destination of most of produced.[3)] Thus TCE intake from the air to factories is also a matter to be addressed.

We studied the adsorption of TCE on 16 kinds of granular activated carbons (GACs) in gaseous phase, and here discuss the correlation between the pore volumes and the amount of TCE adsorbed.

Materials and Methods

Materials GACs No. 1—16 used as adsorbents in this paper are shown in Table I.

Procedure The adsorption isotherms of TCE on GACs were determined in an all-glass vacuum system of the type previously described.[4)] The specific surface area and the pore size distribution of GACs were measured by the previously described method.[4)]

The differential heat of adsorption was calculated by applying the Clausius–Clapeyron equation[5)] to the TCE adsorption isotherms at 10, 20 and 30 °C.

Results and Discussion

Physical Properties of GACs and the Adsorption of TCE on GACs Physical properties of GACs are shown in Table I. The specific surface area and the pore volume ($r < 100$ Å) of GAC No. 4 were largest, while those of GAC No. 1 were smallest. Including GAC No. 4, four kinds of GACs have no pore volume of less than 7.5 Å radii. As far as the micropore volume ($r < 20.5$ Å), which is considered to dominate the amount of TCE adsorbed, about a 1.6 times difference was observed between the maximum value (No. 4) and the minimum value (No. 5).

Figure 1 shows the adsorption isotherms of TCE on GAC Nos. 4 and 14 at 20 °C, on which adsorbed amounts were largest and smallest, respectively. GAC No. 6 was the sample produced from petroleum pitch, while the other 15 samples were from palm shell. The amounts of TCE adsorbed on GACs at 0.1, 1 and 10 Torr of equilibrium pressure are listed in Table II. In each GAC, the adsorbed amount immediately increased at very low pressure, and gradually at more than 10 Torr of equilibrium pressure. It is therefore considered that TCE

TABLE I. Physical Properties of GACs

GAC No.	Specific surface area (m^2/g)	Pore volume (ml/g)		
		$r<7.5$ Å	$r<20.5$ Å	$r<100$ Å
1	850.0	0.298	0.458	0.510
2	868.6	0.232	0.441	0.543
3	1127.1	0.149	0.553	0.662
4	1268.1	0.000	0.603	0.695
5	854.7	0.128	0.371	0.599
6	1081.1	0.000	0.512	0.595
7	970.6	0.206	0.480	0.540
8	983.8	0.000	0.469	0.603
9	965.1	0.198	0.472	0.617
10	1002.2	0.217	0.500	0.586
11	954.0	0.248	0.473	0.572
12	986.0	0.248	0.504	0.605
13	937.9	0.221	0.447	0.560
14	885.4	0.000	0.435	0.532
15	931.5	0.199	0.438	0.557
16	908.7	0.250	0.449	0.567

GAS No. 1, Activated carbon (Wako Pure Chemical Ind., Ltd.); No. 2, Charcoal activated for oxidant determination (Nakalai Tesque Inc.); No. 3, Activated carbon (Kanto Chemical Co., Inc.); No. 4, Technicoal (Bamberg Co.); No. 5, Charcoal activated (Sigma Chemical Co.); No. 6, BAC MU-1 (Kureha Chemical Ind. Co.); No. 7, Tsurumicoal (Tsurumicoal Co.); No. 10, Diasorb (Mitsubishi Chemical Ind. Co., Ltd.); No. 11, Shirasagi G2C, No. 12, Shirasagi Sx, No. 13, Shirasagi Cx, No. 14, Shirasagi G, No. 15, Shirasagi Wc and No. 16, Shirasagi Gc (all from Takeda Chemical Ind., Ltd.).

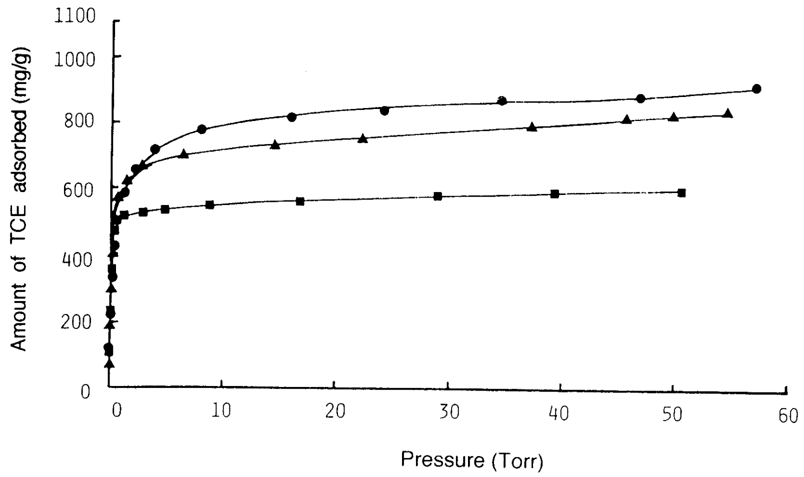

Fig. 1. Adsorption Isotherms of TCE onto GACs Nos. 4, 6 and 14 at 20°C
●, No. 4; ▲, No. 6; ■, No. 14.

Table II. Amounts of TCE Adsorbed onto GACs

GAC No.	Amount of TCE adsorbed (mg/g)		
	Q_∞ at 0.1 Torr	Q_∞ at 1 Torr	Q_∞ at 10 Torr
1	458	568	630
2	332	544	612
3	335	605	675
4	256	582	792
5	272	408	478
6	308	612	722
7	346	538	604
8	240	448	628
9	326	556	670
10	390	562	610
11	382	540	580
12	407	597	663
13	400	547	603
14	318	510	545
15	367	533	587
16	365	510	563

Table III. Correlation Coefficients between Amounts of TCE Adsorbed and Micropore Volumes of GACs

Pore radius (Å)	Amount of TCE adsorbed (mg/g)		
	Q_∞ at 0.1 Torr	Q_∞ at 1 Torr	Q_∞ at 10 Torr
7.5	0.822	0.298	0.085
8.5	0.825[a]	0.309	0.205
9.5	0.824	0.755	0.341
10.5	0.571	0.871[a]	0.656
11.5	0.321	0.838	0.792
12.5	0.176	0.779	0.815
13.5	0.106	0.738	0.819[a]
14.5	0.233	0.711	0.815
15.5	0.022	0.682	0.795
16.5	0.007	0.658	0.770
17.5	0.050	0.608	0.753
18.5	0.080	0.578	0.737
19.5	0.103	0.555	0.726
20.5	0.123	0.532	0.715

[a] $p < 0.001$.

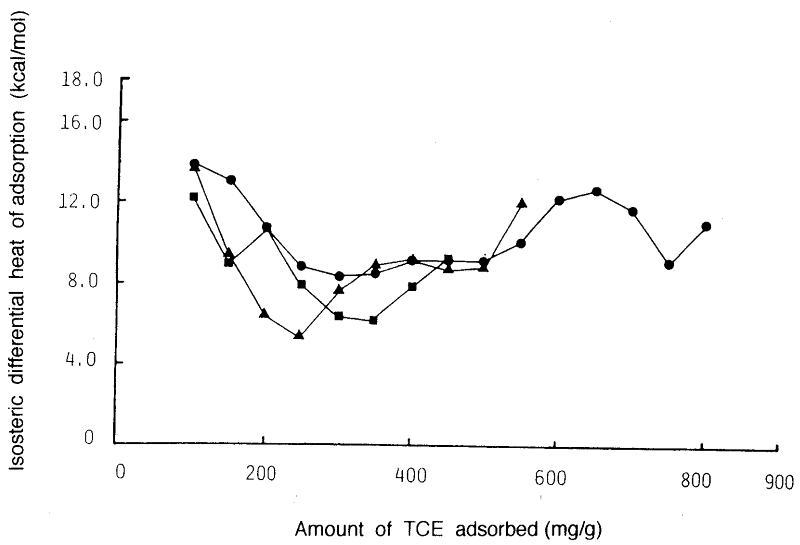

Fig. 2. Isosteric Differential Heat of Adsorption *vs*. Amount of TCE Adsorbed
●, No. 4; ▲, No. 6; ■, No. 14.

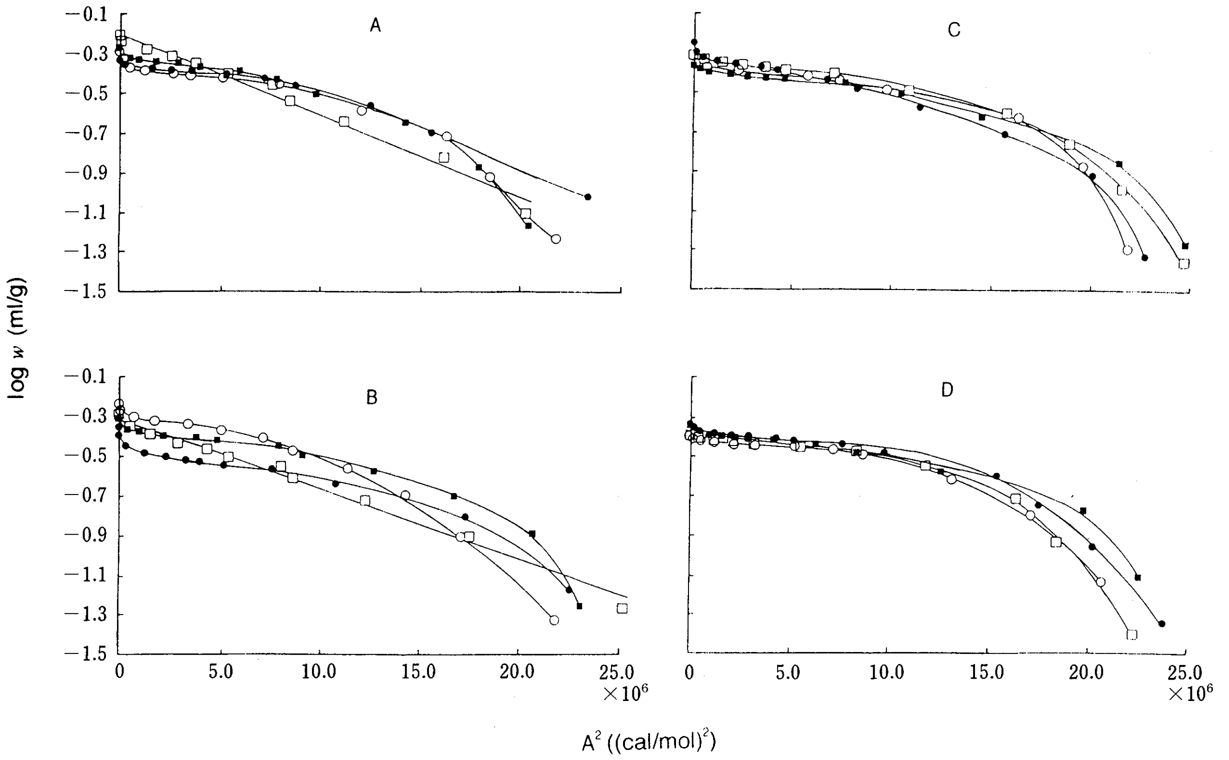

Fig. 3. Dubinin–Radushkevish Plots of Adsorption Isotherms of TCE onto GACs

A: ●, No. 1; ○, No. 2; ■, No. 3; □, No. 4, B: ●, No. 5; ○, No. 6; ■, No. 7; □, No. 8, C: ●, No. 9; ○, No. 10; ■, No. 11, □, No. 12, D: ●, No. 13; ○, No. 14; ■, No, 15; □, No. 16.

was first adsorbed into micropore. The correlation coefficients between the amount of TCE adsorbed and the micropore volumes of GACs are listed in Table III.

The dominant pore radius became larger with the increase of equilibrium pressure, so it was recognized that TCE was preferentially adsorbed into smaller pores.

Thermodynamic Properties of TCE Adsorption on GACs Thermodynamic functions were used to obtain information on the TCE–surface of the activated carbon interaction. The isosteric differential heat of adsorption of GAC Nos. 4, 6 and 14 was calculated using the Clausius–Clapeyron equation, and the results are shown in Fig. 2.

The heat of TCE adsorption of GAC No. 4 was 14—8 kcal/mol for 100—250 mg/g TCE adsorbed, that for GAC No. 6 was 14—5.5 kcal/mol, and that for GAC No. 14 was 12—6 kcal/mol. The heat of adsorption indicates the strength of the linkage force between the TCE and GACs. Thus, the TCE–GAC No. 4 binding was stronger than the TCE–GAC Nos. 6 and 14.

The isosteric differential heats of adsorption of GAC Nos. 4, 6 and 14 were below 15 kcal/mol, and this value was below the condensation heat of TCE, 31.5 kcal/mol. The adsorption heat is generally believed to be about 3 times smaller than the condensation heat of adsorbate, if the adsorption is a physical one,[6] so that the adsorption of TCE on GACs is assumed to be a physical one.

Application of the Dubinin–Radushkevich (D–R) Equation to the Adsorption Isotherms of TCE The physical adsorption in gaseous phase can be described by a theoretical model of the volume filling of pores. The D–R equation can be strictly applied to a homogeneous system of micropores.[7]

Figure 3 shows the D–R plots of the adsorption isotherms of TCE on GACs. The plots of GAC Nos. 4 and 8 were straight lines, corresponding to type A in the classification of Rand.[7] The plots of other GACs were not straight lines, deviated downward in the range above $A^2 = 10 \times 10^6$, and did not correspond to any type in Rand's classification. Thus D–R plot of GACs were of two types, and it was considered that the TEC adsorption onto GACs depends on the pore size distribution.

Conclusion

Our conclusions are as follows: (1) The TCE adsorption capacities of GACs were proportional to the pore volumes of GACs, and TCE was thought to be preferentially adsorbed into smaller pores. (2) The amounts of TCE adsorbed were larger at lower temperature, so that the adsorption was recognized to be a physical one. (3)The D-R plots of GACs could be classified into two types based on the pore size distributions. TCE was believed to be adsorbed not only into micropores but also into transitional pores.

The findings suggest that GACs rich in small micropores are more suitable for removing TCE at very low pressure with the view of preventing worker inhalation, while GACs with large pore volumes are more suitable at high pressure to prevent TCE diffusion from factories into the surrounding areas.

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