

ADSORPTION PROPERTIES OF SUPPORTED SUPERACTIVATED CARBON

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INTRODUCTION

All adsorbent fabrics used for protection against percutaneous exposure to toxic vapor contain activated carbon fibers or particles on a suitable air permeable support material. Vapor penetration occurs under dynamic conditions such that the observed barrier performance is dependent on both the mass transfer kinetics and the adsorption capacity of the carbon. Several methods are available for analysis of the vapor breakthrough curve (BTC) which allow separation of these parameters, and determination of their relationship to bed characteristics and carbon properties.

This study relates the performance of superactivated carbon (SAC) having micropore volumes ≥ 1 ml/g to that of conventional activated carbon (AC), in the form of adsorbent fabric or packed granular beds. A computer model is described which simulates expected mass transfer behavior including the effects of axial dispersion.

ADSORPTION EXPERIMENTS

Fabric disks (100 cm²) consisting of partially reticulated polyester polyurethane foam impregnated with powdered AC or SAC in a polymeric binder formulation (80 wt% carbon) were challenged with carbon tetrachloride vapor in dry nitrogen at 32°C in a gas-tight flow cell. Granular carbon samples packed in cylindrical beds were similarly exposed to vapor challenge. Carbons used in this study are described in table 1.

The effluent concentration was monitored by either an MTI Model M200 gas chromatograph or an HNU Systems Model 101 photoionization detector. Vapor concentration and linear velocity were varied from the standard condition of 10 g/m³ and 10 cm/min. Dependence of the dynamic adsorption capacity (A_d) and pseudo first order rate constant (k) on temperature, vapor concentration, and velocity was determined statistically for AC adsorbent fabric in a central composite design experiment. Equilibrium adsorption isotherms were determined at 32°C for all adsorbents using a Cahn Model D200 digital recording balance. Constant weight was obtained in less than one hour at all but the lowest partial pressures ($p > 0.1$ torr) for fabric or particulate carbon specimens exposed to carbon tetrachloride vapor in nitrogen in a flow system similar to that used for dynamic challenge. Adsorption breakthrough was simulated in a computer model of a segmented packed bed for which adsorption and flow parameters can be varied independently.

Both actual and simulated dynamic adsorption experiments were analysed according to equation 1, a semi-empirical expression based on a modified Wheeler equation which accurately describes the sigmoid breakthrough curve (BTC) obtained with all carbon containing fabrics and granular beds.

$$t = [A_d/C_0Q] [W - \sigma Q \ln\{(C_0/C) - 1\}/k\tau^{\delta}] \quad (1)$$

$$\tau = t/\delta, \text{ with } \delta, \text{ residence time} = \epsilon L/v$$

Where t is adsorption time, C_0 and C are challenge and effluent

vapor concentration, A_d is the dynamic adsorption capacity, Q is volumetric flow rate, W is weight of adsorbent, σ is bed density, k is the apparent rate constant, ϵ is the void fraction and L is the bed length, v is flow velocity, and a is an empirical curve fitting constant introduced to compensate for axial dispersion and channeling in the bed.

At $C_0/C = 2$, eqn. 1 gives a rate-independent solution for A_d :

$$t = t_{1/2} = A_d W / C_0 Q \quad (2)$$

Rearranging eqn. 1 and substituting vA (A is specimen area) for Q we get

$$C_0/C = 1 + \exp[(\sigma A)^{-1} k' (t/L)^{\delta} (W - C_0 A v t / A_d) v^{\delta-1}] \quad (3)$$

which yields the net rate constant, k' after selection of the value for a which provides the best fit to the experimental BTC data.

Table 1. Properties of Carbon Adsorbents

Carbon	Form/Origin	Pore Volume, ml/g		Mean Size, mm
		Micropore	Total	
SuperA ^a AX21 ^a	P/ Coal Char	1.02	1.6	0.025
Maxsorb ^b 30AW ^b	P/ Petrol. Coke	1.13	1.57	0.015
Type PCB-G ^c	P/ Coconut char	0.4	0.72	0.004
Renoves ^d M-40 ^d	P/S Coal Tar Pitch	1.11	2.60	0.05
Maxsorb ^b Pellets ^b	C/ Petrol. Coke ²	0.96	1.13	1.5
SARATOGA ^e	S/ Coal Tar Pitch	nd	0.7	0.3

Producers: a - Anderson Development, b - Kansai Coke & Chemical, c - Calgon Carbon, d - Osaka Gas, e - Kureha

1. P = fine powder, S = sphere, C = cylinder, F = fractal particle
2. Pellet contains 30 wt% Kaolin as binder.

ADSORPTION CAPACITY

It is assumed that the equilibrium adsorption capacity (A_e) is the maximum adsorption at any vapor concentration, and that A_d could be decreased by time constraints, and in the case of impregnated fabric, by partial pore blockage by binder. This assumption is tested in Table 2 which compares A_e with A_d for powdered SAC and AC, both as a thin layer of dry powder and incorporated in fabric. Adsorption capacities were determined at a carbon tetrachloride vapor concentration of 10.0 g/m³ ($P/P_0 = 0.00793$). A small but significant extent of pore exclusion is found at equilibrium for the four carbons, ranging from 10% to 16%, whereas inspection of A_d/A_e indicates about a 10% decrement due to kinetically limited adsorption. Thus, thermodynamic data for the pure carbon can provide a reliable estimate and upper bound for A_d of a carbon containing fabric.

Table 2. Adsorption Capacity

Carbon	A_d , g/g	A_s , g/g
AX-21	0.84	0.75
AX-21/fabric	0.71	0.62
30AW	0.91	0.81
30AW/fabric	0.82	0.74
M-40	0.88	0.77
M-40/fabric	0.79	0.77
PCB-G	0.51	0.45
PCB-G/fabric	0.43	0.38

APPLICATION OF BTC EQUATION

Equation 3 provides a good fit ($r^2 > 0.99$) to experimental data from both adsorbent fabrics and beds. A typical example is shown in Fig. 1 for an adsorbent fabric under standard test conditions. A_d is relatively invariant for a given AC or SAC at constant temperature and concentration, whereas k and a vary with the physical form of the specimen and flow velocity. These effects were confirmed in a central composite design experiment with PCB-G fabric over the range: 5-30 g/m³ CCl₄ vapor, 0-40°C, and linear velocities of 240-4000 cm/min. ANOVA disclosed no significant interactions, with major effect probabilities (alternative hypothesis) shown in Table 3.

Table 3. Dependence of BTC Parameters

Factor	C_0	T	v
A_d	<0.001	<0.001	0.76
k	0.54	0.002	<0.001
a	0.04	0.14	0.1

As expected, A_d is strongly dependent on C_0 and T, a consequence of its relationship to the thermodynamic capacity, A_s . Although k increases moderately with T, it is primarily dependent on v which is consistent with vapor phase mass transfer as the rate controlling step in the overall adsorption process. None of the tested variables appears to have more than a weak influence on a indicating that this curve fitting constant compensates for axial broadening due to heterogeneity and channeling within the fabric or granular bed. In support of this hypothesis, studies with adsorbent fabrics show that a is a function of fabric thickness and binder content. The combined effect of flow variations on the BTC is illustrated for a SAC in Fig. 2. Axial broadening within the bed causes increased skew at higher flows although, as predicted by eqn. 2, the curves intersect at $t_{1/2}$ when normalized to total challenge.

SIMULATION OF THE BTC

A computer model of the adsorbent bed was formulated as a series of parallel axial columns within which individual bed characteristics could be altered according to a preselected continuous or step function. A preliminary evaluation indicated that at least seventeen parallel segments are required to generate a BTC using eqns. 1 or 3 which is relatively insensitive to the number of additional segments. This model is used to characterize bed performance, as for example, to determine the effect of variation in adsorbent packing or distribution on a when

A_d , k , and operating conditions are held constant. Adsorbent distribution and vapor velocity were varied continuously across the bed via a uniform incremental change in bed density. The resultant BTC for a 34% variation in density is displayed in Fig. 3. The apparent rate constant, $k_v = k\tau^a$, associated with this computer derived BTC is compared with the empirical k_v for the typical adsorbent fabric BTC shown in Fig. 3. The similarity in time dependence of k_v attests to the significant role played by bed heterogeneity in determining BTC characteristics.

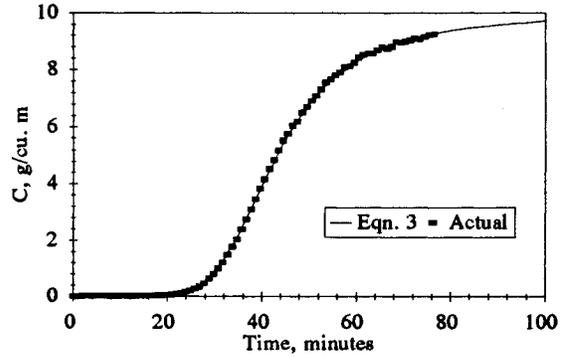


Fig. 1 BTC for PCB-G Fabric

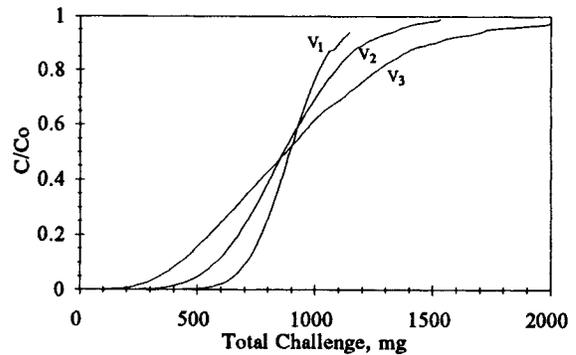


Fig. 2 Effect of Velocity on BTC for Maxsorb Pellets
 $V_1 = 750$ cm/min, $V_2 = 1515$ cm/min, $V_3 = 3170$ cm/min

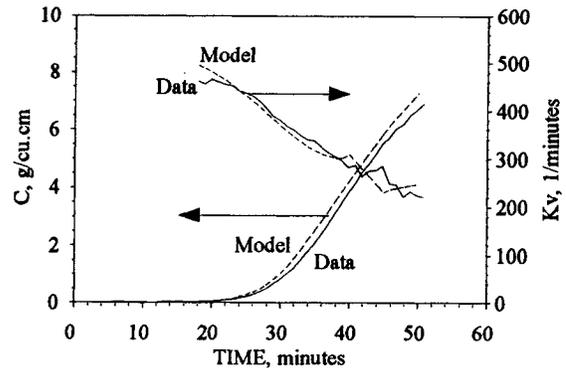


Fig. 3 Test of Computer Model - BTC and K_v