DEPENDENCE OF GAS ADSORPTION RATES ON CARBON
GRANULE SIZE AND LINEAR FLOW VELOCITY

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1. INTRODUCTION

The modified Wheeler adsorption kinetics equation (1), initially derived from a continuity equation of mass balance between the gas entering an adsorbent bed and the sum of the gas adsorbed by plus that penetrating through the bed, shown in the polynomial form

$$t_b = \frac{W_e W}{C_o Q} - \frac{W_e \rho_\beta \ln(C_o/C_x)}{C_o k_v} \tag{1}$$

has been successfully used by Jonas and Rehrmann (2) in studies on the kinetic adsorption of gases by activated carbons. In this equation, t_b is the gas breakthrough time in minutes at which the concentration C_x appears in the exit stream, C_o the inlet concentration in g/cm^3, Q the volumetric flow rate in cm^3/min, ρ_β the bulk density of the packed bed in g/cm^3, k_v the pseudo first order adsorption rate constant in min^{-1}, W the adsorbent weight in g, and W_e the kinetic adsorption capacity in g/g at the arbitrarily chosen ratio of C_x/C_o. In Eq (1), ρ_β is determined as a property of the granular size and shape of the adsorbent when filled by gravity settling in a container column, and the parameters C_o, C_x, and Q are set by the conditions of test. A plot t_b vs W, for any fixed flow rate and temperature, yields a straight line curve from whose slope and intercept the parameters W_e and k_v can be respectively calculated. Eq (1), in its derivation, assumed constant temperature, a single effective carbon granule diameter, an invariant adsorption capacity (obtained by choosing the challenge concentration to be large enough to assure being on the plateau of the adsorption isotherm) and the absence of other parametric interrelationships.

The pseudo first order adsorption rate constant k_v in Eq (1) has recently been shown (3), in the case of benzene vapor adsorption by 12-30 mesh activated carbon granules (weighted mean diameter of 0.104 cm), to be a function of the superficial linear velocity V_ℓ of the gas-air flow into the carbon bed. The mathematical relationship found, which exhibited a 0.999 correlation coefficient with the experimental data over a 120 to 3000 cm/min (2 to 50 cm/sec) velocity range was

$$k_v = \frac{a+b}{1+(a/b)\exp[-(a+b)cV_\ell]}, \tag{2}$$

where a, b, and c were constants of the system. It is expected that one or more of these constants includes the effect of carbon granule size. Equation (2) describes a sigmoidal curve of k_v versus V_ℓ, showing a minimum value of b for k_v at low V_ℓ and a maximum value for k_v of a+b at high V_ℓ.

The purpose of this paper (in which we used dimethyl methylphosphonate) was to extend the study by investigating the dependence of the adsorption rate constant on both carbon granule size and superficial linear velocity. The granule size effect was studied over a 7-fold range from 0.019 to 0.144

cm diameter, and the superficial linear velocity was varied over a 30-fold range from 2 to 60 cm/sec, for each discrete granule size.

2. EXPERIMENTAL

The vapor used as an adsorbate was dimethyl methylphosphonate (DMMP), and the activated carbon adsorbent was a BPL grade, lot 7502, from PAC Co, Pittsburgh, PA, having a surface area of 1000 m^2/g. The carbon was sieved and ground into the discrete mesh fractions of 12-16, 16-20, 20-30, 30-40, 40-50, 50-60, 60-70, and 70-80, having mean granule diameters of 0.144, 0.102, 0.072, 0.051, 0.036, 0.027, 0.023, and 0.019 cm respectively. The kinetic adsorption tests were carried out with a gas adsorption test apparatus described in detail by Jonas and Svirbely (4). The inlet or challenge concentration was set at 2×10^{-6} g/cm^3. The vapor penetration of the bed was detected by an F&M 5750 gas chromatograph with a flame ionization detector and used a 12-ft length column of 3/16 in. diameter stainless steel tubing packed with 15% Dow-Corning silicone on a chromasorb T support. The exit air stream was monitored continually by passage into 25 cm^3 gas sampling valve of the gas chromatograph. The breakthrough time t_b was denoted as the time when the exit stream showed the presence of a gas concentration of 2×10^{-8} g/cm^3, equal to an exit to inlet concentration ratio (C_x/C_o) of 0.01.

3. RESULTS AND DISCUSSION

Each of the eight mesh fractions was tested with DMMP vapor at five linear velocities, ranging from 2 to 60 cm/sec. For each test condition the breakthrough time t_b was determined for a minimum of four different carbon weights W. Plots of t_b vs W resulted in straight line curves in accordance with Eq (1). The regression equations obtained from the t_b vs W data points had correlation coefficients (5) ranging from 0.917 to 0.999, indicating a high degree of confidence for the linear dependence of t_b on W. Values for the adsorption capacity W_e and the adsorption rate constant k_v were calculated from the slope and intercept of the regression analysis equations, in the polynomial form of Eq (1), for each velocity and carbon granule size tested. The adsorption capacity was independent of both the flow velocity and the carbon particle size, the mean capacity for the forty test conditions being 0.345 g DMMP/g carbon with a standard deviation of $\pm$ 0.040 and a coefficient of variation of $\pm$ 11.6%. The adsorption rate constant, however, was a function both of the carbon particle size and the superficial linear velocity, increasing nonlinearly with increase in velocity and decrease in particle size to a limiting value of approximately 2600 reciprocal seconds. The data for the eight carbon mesh fractions each tested at superficial linear velocities of 2, 4, 10, 30, and 60 cm/sec are shown in Table 1. A plot of adsorption rate constant vs superficial linear velocity, for the eight carbon granule

diameters tested, is shown in Fig. 1. The curves indicate that the rate constant, at least over the carbon granule diameter range 0.144 to 0.027 cm, appears to exhibit the type of nonlinear dependence shown by Eq (2). However, the k_V vs V_ℓ curve for the 0.023, and especially that for the 0.019 cm diameter granule, approach independence of linear velocity, indicating a change in the rate controlling step for the overall adsorption process. A plot of adsorption rate constant vs the reciprocal of the carbon granule diameter, for the five superficial linear velocities, is shown in Fig. 2. In this plot it can readily be seen that all curves converge to the limiting value of 2600 reciprocal seconds for the adsorption rate constant, an apparent basic characteristic of this activated carbon for DMMP vapor.

In accord with the concept of a first order heterogeneous reaction we perceive that a limit of 2600 volumes of a gas-air mixture (containing 2×10^{-6} g DMMP/cm^3), each volume equal to the volume of the carbon granular bed, can be reacted with or adsorbed by the carbon per second. Therefore, the DMMP in each such volume of DMMP-air mixture was adsorbed by the carbon in 0.00038 seconds.

TABLE 1. DMMP ADSORPTION RATE CONSTANT AT VARIOUS PARTICLE DIAMETERS AND LINEAR VELOCITIES

Mean Carbon Part. Diam. d_p (cm)	Recip- rocal Carbon Diam. $1/d_p$ (cm^{-1})	Ads. Rate Constant, k_V (sec^{-1}) at Sup. Linear Vel., V_ℓ (cm/sec)				
		2	4	10	30	60
0.144	6.94	70	101	117	187	354
0.102	9.80	92	138	188	302	421
0.072	13.89	165	244	309	401	605
0.051	19.61	211	371	485	760	805
0.036	27.78	461	619	758	1287	1430
0.027	37.04	813	974	1034	1485	1949
0.023	43.48	1509	1548	1635	1671	2313
0.019	52.63	2405	2477	2577	2628	2595

4. REFERENCES

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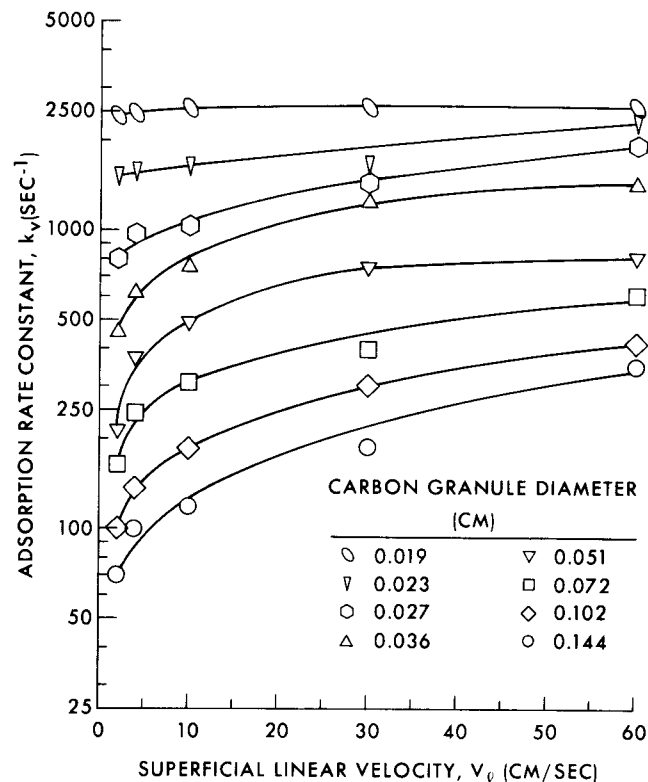
Fig. 1. DMMP adsorption rate constant as a function of linear velocity for various carbon granule diameters.
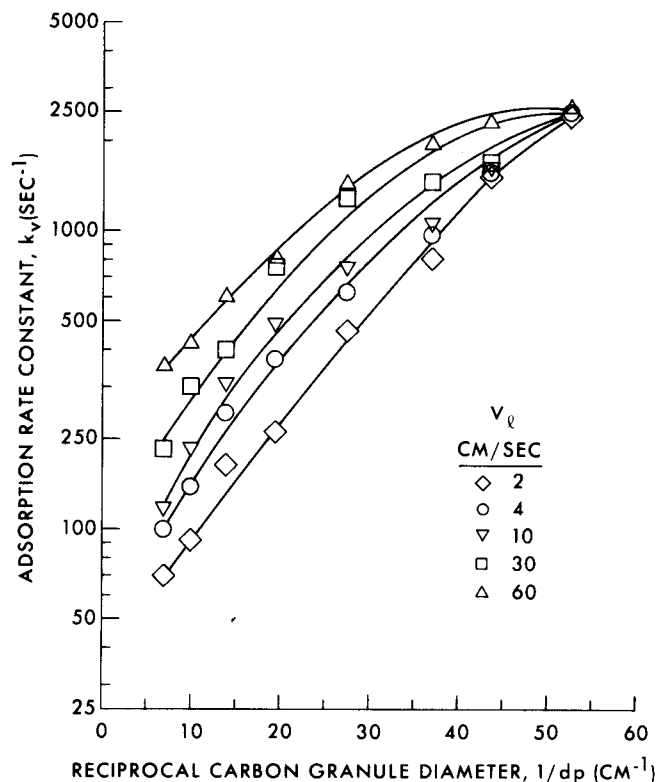

Fig. 2. DMMP adsorption rate constant as a function of carbon granule diameter for various linear velocities.