Organic Vapor Respirator Cartridge Breakthrough Curve Analysis

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Abstract

Carbon filter beds used in organic vapor (OV) respirator cartridges and larger area filtration systems have limited service lives. Vapor breakthrough curves are measured in laboratories for quality control, development, research, and certification. The goal is often to predict efficiency and service life at the conditions of actual use. If the measured breakthrough curves can be fitted to mathematical models, more information can be derived for extrapolation to other situations (e.g., different allowable penetrations, lower challenge concentrations, or higher humidities). The simple two-parameter Reaction Kinetic model and its special case, the Wheeler equation, often do not describe measured breakthrough curves well. A four-parameter equation has now been developed which meets the following criteria: 1) it is flexible enough to fit quite asymmetric curves; 2) it reduces to the Reaction Kinetic and Wheeler equations as special cases; 3) its parameters can be assigned physical significance; 4) it has the proper range and limits; and 5) it provides consistently good fits of experimental breakthrough curve data, particularly at the more important low penetrations. The equation is presented as a tool for data analysis. Taken alone, it does not provide a correlative or predictive model for filter performance or design.

Introduction

As a carbon adsorber bed becomes loaded with the contaminant(s) removed from flowing air, removal efficiency decreases. The penetration of a contaminant consequently increases with time of bed use, until it reaches an unacceptable level. The time at which this occurs is called the service life or breakthrough time of the cartridge or other carbon bed. Service lives are dependent on both equilibrium bed capacities and dynamic mass transfer rates, which can be sorted out by making multiple service life measurements at different bed depths (Jonas and Rehrmann, 1973; Moyer, 1987; Wood and Moyer, 1989).

Alternately, entire or parts of breakthrough curves (penetration fraction vs time) are measured (Wood and Moyer, 1989; Nelson and Correia, 1976). The usual procedure is to first create a fixed challenge concentration of gas or vapor in a stream of dry or fixed humidity air by any one of a number of methods (Nelson, 1992). All or a portion of this challenge air is then passed through a prepared cartridge or test bed at a selected constant flow rate. The concentration of test vapor in the effluent air from the cartridge or bed is monitored as a function of time. The test may be terminated when a preselected break-

through concentration (or penetration fraction) is reached or continued until the challenge concentration is reached.

A breakthrough curve measurement can provide more information than a breakthrough time measurement, often at little extra effort and cost. If the critical breakthrough concentration is changed by new toxicological data or regulations, the testing may not need to be repeated. Breakthrough curves can also provide equilibrium and kinetic information that can be used for predicting or improving cartridge performance. However, before experimental breakthrough curves can be interpreted in more than a qualitative sense, they must be fit to analytical equations. If an equation fits the data well it can also be used for 1) interpolation between measured points on a breakthrough curve, or 2) smoothing and averaging of replicate breakthrough curve measurements. Figure 1

shows an example of breakthrough curves from tests run in quintuplicate, where such smoothing and averaging has been done.

If the model parameters can be assigned physical meaning, they become system descriptive parameters that can be used to 1) show trends in service life and adsorption processes as environmental and use parameters are changed, and 2) indicate possible improvements in design, components, and use procedures. Also, there is the potential of deriving such physical parameters from simpler, independent measurements or calculations.

The objective of this work was to develop a better tool (equation) for breakthrough curve analysis. The development of correlative or predictive models is beyond the scope of this paper.
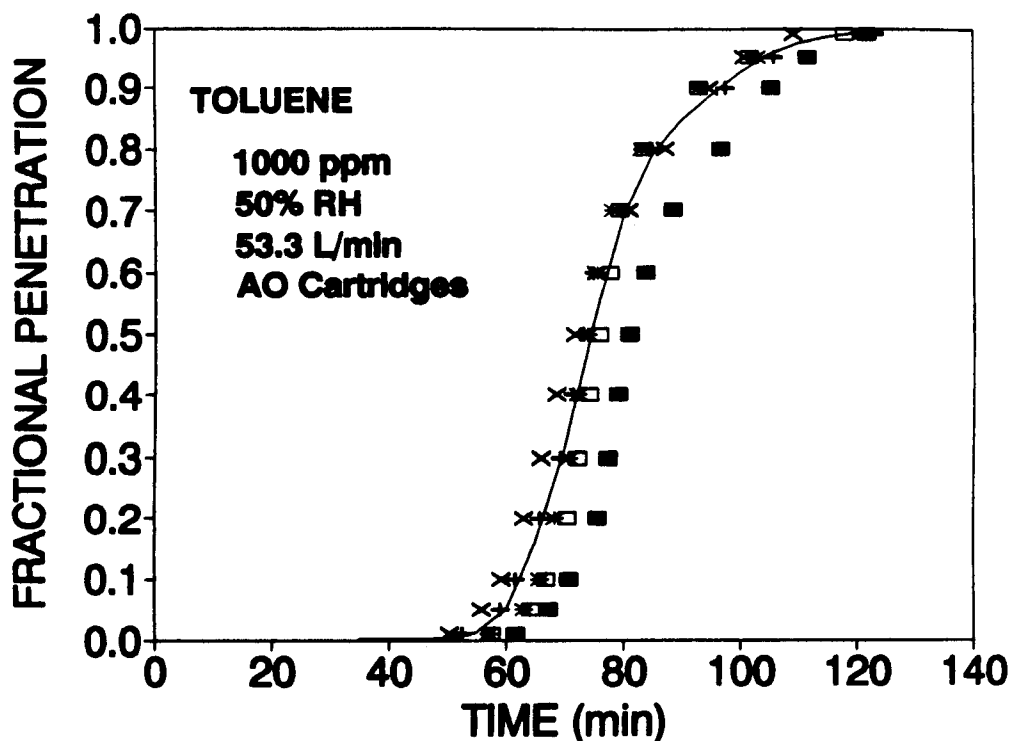

Figure 1. An example of breakthrough curves measured in quintuplicate with data smoothing for averaging and interpolation.

Previous Breakthrough Curve Equations

Several approaches to fitting breakthrough curve data have been reported. Linear combinations of statistical moments have been used (Grubner and Burgess, 1981). Rate-limited, constant-pattern solutions based on the Langmuir isotherm have been developed, including the Reaction Kinetic (RK) solution (Vermuelen et al., 1984).

The Reaction Kinetic equation can be considered the "ideal" solution, useful for describing symmetrical breakthrough curves. In terms usually associated with the Wheeler/Jonas equation (Jonas and Rehrmann, 1973), the RK equation is:

$$t = \left(\frac{W_e W}{C_o Q}\right) - \left(\frac{W_e \rho \beta}{C_o k_v}\right) \ln\left[\frac{C_o - C}{C}\right] \qquad (1)$$

where:
- t = time from start of challenge,
- C_o = constant challenge concentration,
- C = effluent vapor concentration,
- W_e = bed equilibrium capacity at C_o,
- W = weight of activated carbon,
- Q = air flow rate,
- k_v = rate coefficient for adsorption,

and
- $\rho\beta$ = carbon packing density.

Busmundrud (1991) showed that this equation can also be derived from the early work of Bohart and Adams (1920).

When experimental variables (C_o, W_e, W, Q, $\rho\beta$) are constant, Eq. (1) can be expressed in terms of adjustable curve fit parameters A and B and penetration fraction $P = C/C_o$:

$$t = A - B \ln\left[(1-P)/P\right] \qquad (2)$$

or

$$P = \frac{\exp[(t-A)/B]}{1 + \exp[(t-A)/B]} \qquad (3)$$

The Jonas modification of the Wheeler equation is widely used for correlating service life measurements (Jonas and Rehrmann, 1973). It is actually a special case of the RK, limited to low breakthrough concentrations and penetration fractions $P < 0.1$, where approximately $P = \exp[(t-A)/B]$. It is not useful for curve fitting, since it deviates more widely from data as P increases above 0.1 and predicts no limit to adsorption capacity (Nelson and Correia, 1976).

Yoon and Nelson have developed a two-parameter equation (Yoon and Nelson, 1972, 1990), which has the same form as the RK, and a three-parameter equation (YN) for nonideal breakthrough curves (Yoon and Nelson, 1988):

$$P = \left(1 + \exp[A - k'' \ln(W_a + t)]\right) \qquad (4)$$

The three curve fit parameters in the YN equation (A, k'', and W_a) are empirical, without reasonable physical meanings. Furthermore, this function is undefined for $t < -W_a$, where W_a is usually negative (Yoon and Nelson, 1988).

Desirable Characteristics of a Breakthrough Curve Equation

1. **Generalization of Simpler Equations—** One desirable characteristic of a general breakthrough curve equation is that it include more specific equations. Since some breakthrough curves may be well fit by the ideal RK equation and since the parameters of this equation have physical meaning, the general equation should reduce to the RK as a special case. This is a major shortcoming of the Yoon-Nelson three parameter Eq. (4), which leaves doubt as to which incompatible equation (RK or YN) to use.

2. **Parameters with Physical Meaning—** For the RK ideal Eq. (1) the first term corresponds to the breakthrough time if k_v were infinitely large, i.e., if adsorption and desorption were instantaneous and equilibrium was maintained at all times. For the ideal case (only) and finite k_v the first term also happens to be the time at which $P = 0.5$ and the second term in Eq. (1) becomes zero. This first term is called the stoichiometric time, t_s, and its corresponding penetration is the stoichiometric penetration fraction, P_s.

For any other (nonideal, asymmetric) breakthrough curve equation, $P = f(t)$, t_s does not correspond to $P = 0.5$, but can be calculated as the centroid of the curve by the integration:

$$t_s = \int_0^\infty (1 - P)\,dt \qquad (5)$$

Once obtained, the equilibrium capacity, W_e,(one point on the adsorption isotherm of the system) can be calculated from t_s by using the known experimental values of C_0, W, and Q: $W_e = t_s C_0 Q/W$. Therefore, a breakthrough curve equation should be in the form $P = f(t)$ for easy integration and derivation of the capacity.

3. **Proper Range and Limits**—Time and penetration fraction are always zero or positive. As time becomes very large, assuming no reaction is taking place, the bed will become used up and the penetration fraction will approach 1.0. Therefore, the third desirable characteristic of an analytical equation for breakthrough curve fitting is that it also have this range and limit. The YN Eq. (4) does not exhibit these properties, which makes regression curve fitting particularly troublesome.

4. **Good Representation of Data**—Finally, the breakthrough curve equation should provide a good fit of a variety of breakthrough curves, both over the entire curves and at low penetrations. Curve fitting is almost always done using regression (least-squares) techniques (Draper and Smith, 1980). The sum of the squares of the residuals (differences between experimen-

tal and curve values) is minimized to obtain the "best fit" values of the adjustable parameters (e.g., A and B in Eq. (3)). The best measure of the "goodness-of-fit" over the entire curve is, therefore, the value of this sum of squares of residuals (RSS) or the estimate of standard deviation (SD) that is calculated from it by (Kinniburgh, 1986):

$$SD = \left(\frac{RSS}{m - n} \right)^{\frac{1}{2}} \qquad (6)$$

where m is the number of data points and n is the number of adjustable parameters. In comparing fits of equations with differing numbers of adjustable parameters, it is best to compare only RSS values.

The form of the equation fit is also critical (Kinniburgh, 1986). The dependent (y) parameter should be the one with the most uncertainty, usually penetration fraction rather than time for breakthrough curves. Fitting a function of a parameter instead of the parameter itself (i.e., ln P instead of P) introduces a bias or weighting to the curve fitting (Kinniburgh, 1986). Whether or not this is desirable depends on the application to be made of the results. In the case of obtaining t_s by integration using Eq. (5), the points over the entire curve should be weighted equally by $y = P$, $x = f(t)$. For biasing the fit in favor of low penetration data, $y = \ln(1-P)$ could be used. Fitting $y = \ln[P/(1-P)]$ favors both the highest and lowest penetration values at the expense of the middle range of the penetration curve.

New Breakthrough Curve Equation

The breakthrough equation developed to satisfy the four desirable characteristics discussed above is:

$$P = \frac{\exp\left[\dfrac{t - A}{B + G(t - A)}\right]}{\exp\left[\dfrac{t - A}{B + G(t - A)}\right] + \left(\dfrac{1 - P_s}{P_s}\right)\left(\exp\left[\dfrac{-H(t - A)}{B}\right]\right)} \qquad (7)$$

for $t > A - (B/G)$, where A, B, G, and H are the curve-fit parameters. $P = 0$ for $t \le A - (B/G)$. The derivation of this equation is given in the Appendix.

Equation (7) reduces to the ideal RK Eq. (3) as H and G go to zero; therefore, it will always fit breakthrough curve data at least as well as the RK. It has the form of $P = f(t)$ for easy numerical

integration of Eq. (5) to give t_s. The range of P in Eq. (7) is $P \geq 0$ for all $t \geq 0$. For $H > 0$, P approaches the limit of unity as t becomes very large. At time $t = A$, $P = P_s$, so that A has the physical meaning of the stoichiometric time, $A = t_s = W_c W/C_0 Q$. The curve-fit parameter B is inversely related to the adsorption rate coefficient at the stoichiometric time by $B = W_c \rho \beta / C_0 k_v$. Therefore, at the stoichiometric time the stoichiometric rate coefficient is $k_{vs} = AQ/BV_{bed}$, where bed volume $V_{bed} = W/\rho \beta$. The parameter G represents the linear increase of k_v with $\ln[(1-P)/P]$. The parameter H is not defined at this point.

Comparisons of Equations

Since Eq. (7) is proposed as a better alternative to the RK and YN equations, the fits of all three of these equations to experimental data were compared. The breakthrough curve data used for these comparisons are from respirator cartridge breakthrough curves, measured using carbon tetrachloride and benzene vapors at several preconditioning and testing relative humidities (RH) (Nelson and Correia, 1976; Nelson et al., 1976). Although some of these data are presented only as plots in figures 4 and 8 of Nelson et al. (1976), the actual penetration fraction values measured at 5-min. intervals were provided by Gary Nelson for this study. Most of these same experiments were also analyzed in Yoon and Nelson (1988).

The nonlinear regression fits were done using a BASIC computer program on an IBM PC-XT or compatible computer. The program was based on the linearization (or Taylor series) approach to the minimum RSS (Draper and Smith, 1980). Derivatives were taken numerically. Convergence was determined by monitoring changes in the fit parameters. Alternate approaches can be used, but should give the same RSS minima. The proper functioning of the program was confirmed by comparisons with results using a commercial nonlinear curve fitting program, SYSTAT (SYSTAT, Inc., Evanston, Illinois). Two- (A,B) and three- (A,B,G) adjustable parameter programs were used for the RK and YN equations, respectively. In addition to best fit parameters, the minimum RSS was reported by the programs. As discussed above, these are one basis of comparison.

The procedure for curve fitting breakthrough data to Eq. (7) was:
1. Read data from a file. Make initial guesses of t_s and P_s, based on the data. Let $H = 0$.
2. Do a three parameter (A, B, and G) nonlinear least squares curve fit of the data to the selected equation.
3. Incrementally vary H and repeat step 2 until a minimum in RSS is passed.
4. Repeatedly change the sign of H and reduce increments to reapproach the minimum RSS with step 2 until H is determined to three decimal places.
5. Recalculate t_s using a trapezoidal approximation of Eq. (5) at one-minute intervals with P values calculated from Eq. (6) and fit parameters.
6. Recalculate P_s using Eq. (7) with fit parameters, the previous P_s, and the new t_s for t.
7. Repeat steps 2–6 until P_s converges to a constant value.

While this procedure appears tedious, it is easily accomplished on a personal computer. Fast computers and compiled versions of BASIC are recommended. Alternate equivalent curve fitting programs and procedures can be used.

Curve Fitting Results

Table 1 shows the curve fit parameters for 11 benzene and 25 carbon tetrachloride breakthrough curves at various combinations of preconditioning and experimental run relative humidities.

Figures 2–4 show sample comparisons of the curve fitting results for the RK, YN, and Eq. (7) results. Figure 2 shows a nearly ideal case, i.e., where the RK fits the data quite well over all the curve ($100 \times RSS = 0.34$). The YN overall fit is not too bad (0.64), while the Eq. (7) overall fit is slightly better (0.33). At the lowest penetrations the RK and Eq. (7) fits are best. Figure 3 shows a very unsymmetrical breakthrough, where the RK equation provides a very poor data fit overall ($100 \times RSS = 32.01$) and at low penetrations. The YN fit is much better (1.24), particularly at low penetrations, and the Eq. (7) fit is again best

Table 1. Curve fit parameters for benzene and carbon tetrachloride.

| Exp. #	Number of data	Relative humidity (percent) Precon- ditioning	Run	Curve fit parameters for Eq. (7) A	B	G	H	Stoichio- metric penetra- tion fraction
BENZENE								
1195	31	None	20	133.9	47.60	1.108	1.156	0.44
1203	32	None	50	132.3	39.46	0.982	0.858	0.64
1215	44	None	80	123.1	49.61	0.992	1.273	0.22
1197	35	50	20	130.8	34.12	0.686	0.729	0.42
1205	33	50	50	129.4	43.40	1.081	1.036	0.54
1213	43	50	80	119.9	43.13	0.814	1.036	0.24
1201	35	80	20	128.3	32.34	0.623	0.556	0.58
1207	42	80	50	131.4	196.92	2.733	5.855	0.58
1211	59	80	80	101.6	115.78	1.863	2.177	0.28
1217	59	90	50	125.1	1944.12	19.012	44.701	0.30
1209	52	90	80	82.6	109.00	1.317	1.518	0.635
CARBON TETRACHLORIDE								
1411	28	20	20	109.6	18.09	0.162	0.441	0.52
1413	24	20	50	104.5	28.39	0.533	1.400	0.60
1415	28	20	65	96.4	24.64	0.282	1.074	0.41
1417	33	20	80	96.4	16.79	0.215	0.352	0.82
1419	26	20	90	87.7	10.75	0.104	0.100	0.59
1421	45	50	20	111.5	12.66	0.121	0.000	0.02
1423	26	50	50	91.5	111.89	2.713	9.220	0.18
1425	36	50	65	103.6	11.73	0.010	0.000	0.97
1427	47	50	80	107.8	13.66	0.162	0.000	0.48
1429	28	50	90	87.5	13.28	0.184	0.199	0.92
1431	36	65	20	108.8	11.67	0.074	0.000	0.52
1433	27	65	50	100.7	23.30	0.300	0.893	0.54
1435	44	65	65	106.3	21.23	0.271	0.115	0.72
1437	50	65	80	84.5	13.64	0.167	0.000	0.56
1439	25	65	90	72.9	19.33	0.360	0.952	0.59
1441	27	80	20	110.3	12.04	0.080	0.000	0.57
1443	33	80	50	99.1	27.92	0.402	0.828	0.80
1445	40	80	65	91.1	41.52	0.682	0.865	0.25
1447	27	80	80	63.8	16.14	0.213	0.403	0.74
1449	37	80	90	59.3	13.46	0.249	0.099	0.65
1451	35	90	20	109.7	15.35	0.095	0.000	0.74
1453	49	90	50	97.7	97.17	1.434	2.358	0.94
1455	60	90	65	65.3	74.70	1.198	0.680	0.18
1457	32	90	80	33.3	15.38	0.375	0.185	0.88
1459	42	90	90	31.4	12.74	0.321	0.100	0.07
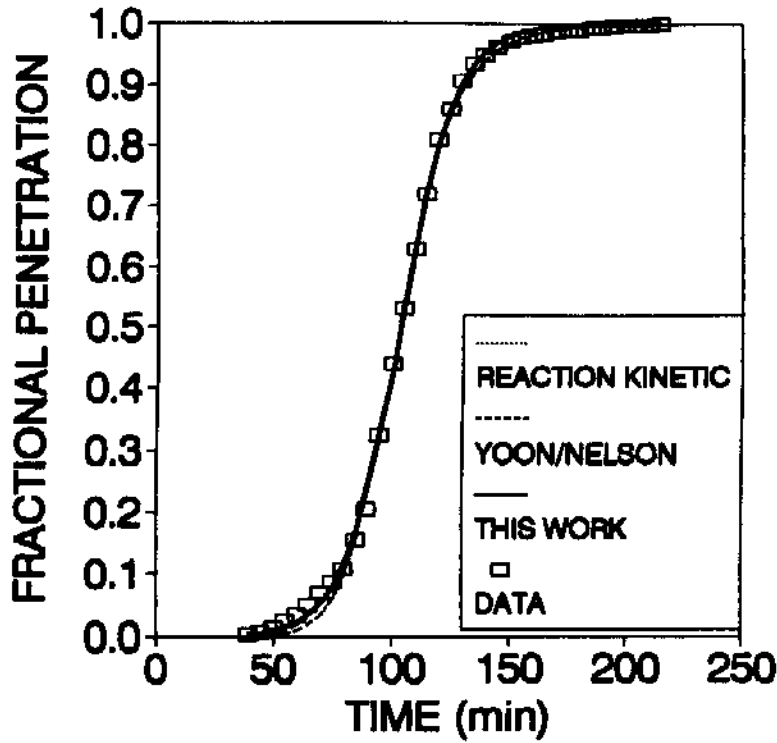
Figure 2. A nearly ideal, symmetrical breakthrough curve. 1000 ppm carbon tetrachloride, 50% RH preconditioned, 65% RH experimental, 53.3 L/min.
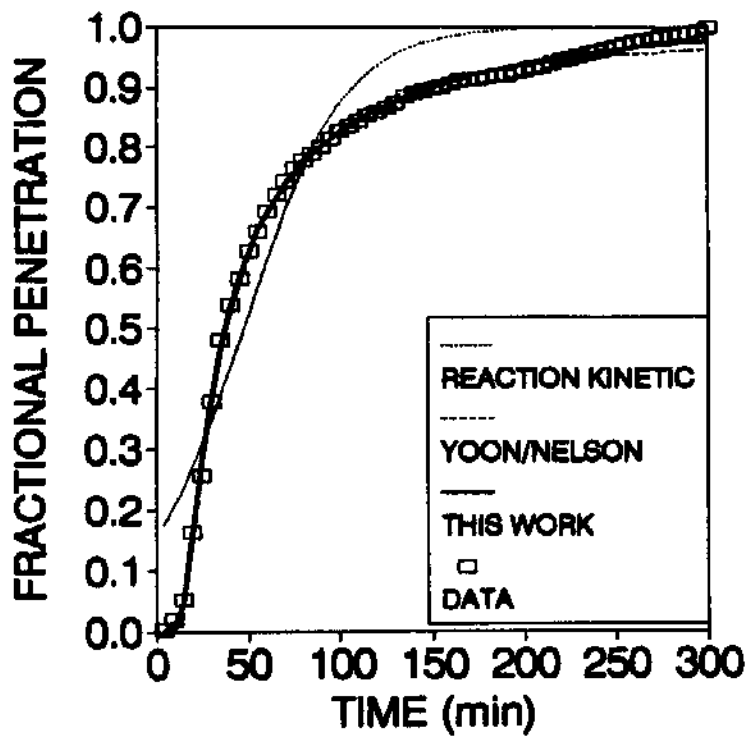

Figure 3. A very unsymmetrical breakthrough curve. 1000 ppm carbon tetrachloride, 90% RH preconditioned, 65% RH experimental, 53.3 L/min.
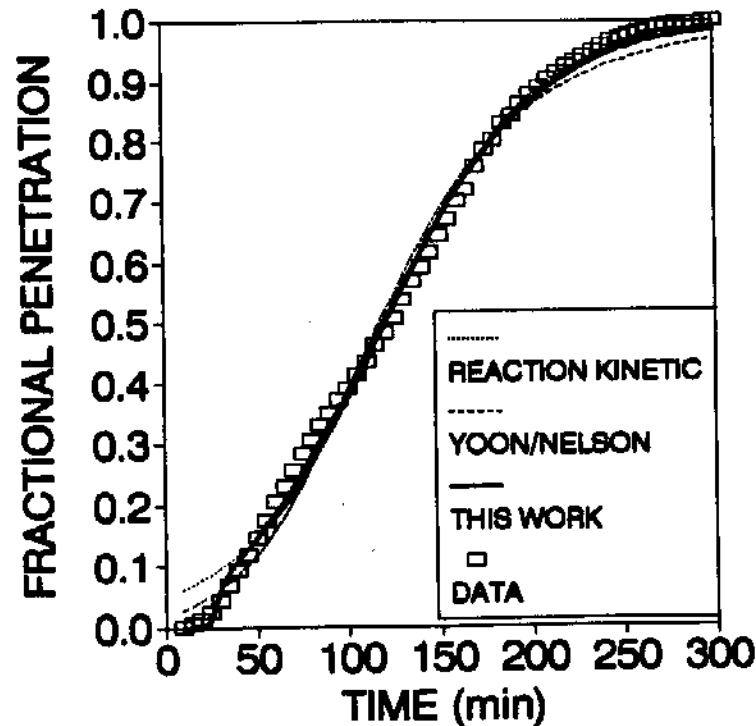
Figure 4. An unusually shaped breakthrough curve. 1000 ppm benzene, 90% RH preconditioned, 50% RH experimental, 53.3 L/min.

overall (0.45). Figure 4 shows an unusual breakthrough curve that is practically linear over its midrange. Equation (7) provides a much better overall fit (100×RSS = 1.77) and at low penetrations (<0.10) than either the RK (3.86) or the YN (5.76).

The summaries of curve fit results for benzene and carbon tetrachloride in Table 2 show that the comparisons in Figures 2–4 are typical. In none of the 36 breakthrough curves for both compounds was the RK overall fit best of all. Twice it resulted in a better fit than the YN. Equation (7) overall fits were best for all 36 breakthrough curves analyzed, including 5 times it was equal to the YN overall fit.

Another test of curve fit is the prediction of breakthrough time for a selected penetration fraction. The first experimentally detectable penetration fraction, 0.001–0.004 in these experiments, provides the most strenuous test of this. Benzene initial breakthrough times predicted by curve fits of the three equations are compared with the experimental ones in Table 3. Predictions of Eq. (7) and the YN equation were closest to the experimental initial breakthrough times, 19 times each (3 ties). The RK prediction was closest only once. The Eq. (7) predictions were never widely different as was sometimes the case with the RK and YN equations. The experimental resolution of the data was 5 minutes.

Table 2. Comparisons of breakthrough curve fits.

Experiment #	Sums of squares of residuals ($\times 100$)		
	Reaction kinetic	Yoon/Nelson	Equation (7)
BENZENE			
1195	12.10	1.7	1.0
1203	13.50	1.4	0.8
1215	7.95	0.5	0.0
1197	9.55	0.9	0.5
1205	12.21	1.4	0.7
1213	7.84	0.4	0.0
1201	11.43	0.9	0.6
1207	3.47	0.9	0.2
1211	13.51	1.7	0.0
1217	3.86	5.7	1.7
1209	17.54	2.1	0.9
CARBON TETRACHLORIDE			
1411	1.10	0.1	0.1
1413	1.51	0.1	0.1
1415	0.99	0.3	0.3
1417	2.11	0.0	0.0
1419	1.00	0.0	0.0
1421	2.65	0.9	0.6
1423	0.46	0.2	0.1
1425	0.34	0.6	0.3
1427	3.87	0.7	0.4
1429	2.30	0.0	0.0
1431	0.93	0.0	0.0
1433	1.19	0.0	0.0
1435	8.70	0.4	0.2
1437	4.15	0.2	0.0
1439	1.24	0.1	0.0
1441	1.32	0.2	0.2
1443	2.78	0.1	0.1
1445	8.37	0.6	0.3
1447	1.71	0.0	0.0
1449	5.26	0.2	0.1
1451	2.06	0.3	0.2
1453	7.50	1.5	0.5
1455	32.01	1.2	0.4
1457	7.48	0.4	0.2
1459	6.60	0.2	0.0

Table 3. Comparisons of first breakthrough times.

Experiment #	Fraction	First penetration time (min)	Calculated first penetration time (min)		
			RK	YN	Eq. (7)
BENZENE					
1195	0.001	85	12	93	96
1203	0.001	85	20	96	97
1215	0.001	75	−3	74	80
1197	0.001	85	15	89	90
1205	0.001	85	13	91	94
1213	0.001	70	−5	71	75
1201	0.001	80	10	87	86
1207	0.001	60	−51	28	64
1211	0.001	40	−104	33	44
1217	0.001	10	−158	−46	24
1209	0.002	5	−143	2	9
CARBON TETRACHLORIDE					
1411	0.002	55	33	58	59
1413	0.002	65	34	62	67
1415	0.002	40	23	45	49
1417	0.002	40	22	54	54
1419	0.002	50	27	49	48
1421	0.002	40	35	68	65
1423	0.002	45	26	38	54
1425	0.002	40	31	51	35
1427	0.002	55	30	67	64
1429	0.002	50	21	51	50
1431	0.002	55	36	60	58
1433	0.002	50	26	53	55
1435	0.002	50	3	61	56
1437	0.002	35	6	46	41
1439	0.002	30	14	36	39
1441	0.002	60	36	61	59
1443	0.002	50	9	49	52
1445	0.002	35	−30	39	43
1447	0.002	25	−6	23	23
1449	0.004	25	−1	30	27
1451	0.002	55	15	51	48
1453	0.002	30	−61	22	38
1455	0.002	5	−122	12	10
1457	0.004	5	−26	7	5
1459	0.004	5	−22	8	5

Conclusions and Discussion

The newly proposed Eq. (7) provides improved fits of breakthrough curve data compared with the ideal Reaction Kinetic equation and the three parameter Yoon-Nelson equation. It may seem obvious that a 4-parameter equation will give equal or better fits of data than a 2- or 3-parameter equation. However, this is only guaranteed if the 4-parameter is a generalization of the 2- or 3-parameter equation. The critical issue is how the additional parameters are included.

Equation (7) has the other desirable characteristics that make it useful for interpreting laboratory experiments. Once physically meaningful parameters are extracted from breakthrough curves for a variety of experimental conditions, they can be used to correlate and extrapolate to other environmental and use conditions and bed designs. The one, as yet undefined, parameter H only makes a minor contribution to the model fits and sometimes may not be needed (Wood and Stampfer, 1993).

Appendix

Equation (7) was derived on the basis of the observed functional dependence of the apparent adsorption rate coefficient k_v on $\log[P/(1-P)]$ and the requirement that $W_e W/C_o Q$ correspond to the stoichiometric time.

First, the ideal RK Eq. (1) was rearranged to give:

$$(k_v)(\tau_{res}) = \left(\frac{t_s}{t - t_s}\right) \ln\left[\left(\frac{P}{1-P}\right)\left(\frac{1-P_s}{P_s}\right)\right] \quad (8)$$

where $t_{res} = W/Q\rho_\beta$ is the bed residence time (Wood and Moyer, 1989) and the other terms are defined above. For an experiment where the flow rate, Q, the bed weight, W, and density, ρ_β, are constant, the residence time is fixed. For data covering an entire breakthrough curve, the stoichiometric time, t_s, and penetration fraction, P_s, can be estimated by numerical integration by Eq. (5) instead of curve fitting. This was done for the benzene and carbon tetrachloride breakthrough curve data. In this way an "apparent" k_v' (t_{res}), based on the ideal RK Eq. (1) was calculated. If the RK equation described the data exactly, k_v' would be constant for all values of P or any function of P alone.

Figure A-1 shows plots of the apparent k_v'(t_{res}) vs. $\log[(1-P)/P]$ from several of the breakthrough curve experiments. The value of k_v changed linearly with this function of P from the lowest penetration fraction up to P = 0.5 in every case.

This relationship deviated from linearity above P = 0.5, but this is the region of penetration having the least practical significance and a lesser effect of the rate coefficient. The conclusion, therefore, was that the adsorption rate coefficient can be expressed as:

$$(k_v)' = k_v\left(1 - G\ln[P/(1-P)]\right) \quad (9)$$

for a constant, G.

Combining Eqs. (1) and (9) and defining $A = W_e W/C_o Q$ and $B = W_e \rho_\beta/C_o k_v$ gives:

$$t = A - \frac{B}{1 - G\ln[P/(1-P)]}\ln[(1-P)/P] \quad (10)$$

And solving this for P gives:

$$P = \frac{\exp\left[\dfrac{t-A}{B + G(t-A)}\right]}{\exp\left[\dfrac{t-A}{B + G(t-A)}\right] + 1} \quad (11)$$

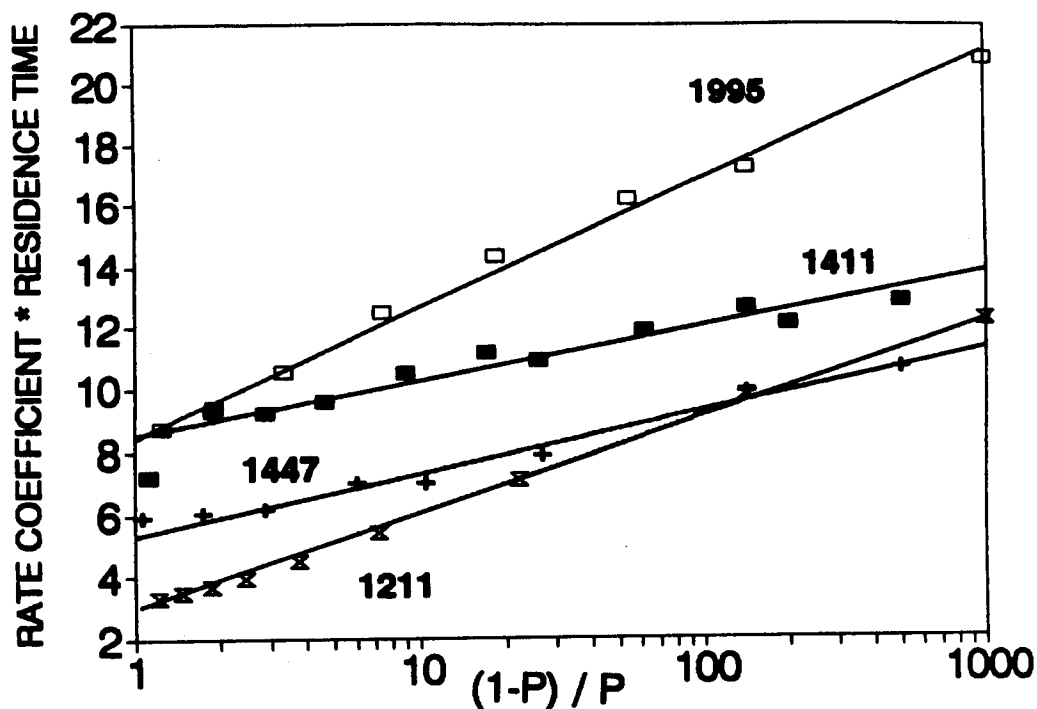For functional stability at small values of time t, a restriction must be made that P = 0 for $t \le A - (B/G)$.

Figure A-1. Semilogarithmic plots of the product of apparent adsorption rate coefficient and bed residence time vs penetration fraction function (1–P)/P. Numbers refer to experiments listed in the tables.

Second, it was observed empirically that in some cases even better curve fits could be obtained, if the second term of the denominator of Eq. (11), +1, was replaced by exp[–H(t–A)/B], where H is a fourth adjustable parameter.

$$P = \frac{\exp\left[\dfrac{t-A}{B+G(t-A)}\right]}{\exp\left[\dfrac{t-A}{B+G(t-A)}\right] + \exp\left[\dfrac{-H(t-A)}{B}\right]} \quad (12)$$

For H > 0 the second term of the denominator of Eq. (12) vanishes as time, t, gets large, so that penetration fraction, P, approaches the proper limit of unity.

Third, P should be the stoichiometric penetration, P_s, at t = A = t_s, the stoichiometric time. This was done by introducing the factor (1–P_s)/P_s into the second term of the denominator of Eq. (12). The result is Eq. (7), used for curve fitting in this paper.

References

Bohart, G.S., and E.Q. Adams, "Some Aspects of the Behaviour of Charcoal with Respect to Chlorine," *J. Am. Chem. Soc.* 42:523–544 (1920).

Busmundrud, O., "Derivation of the Yoon-Nelson Equation for Breakthrough in Carbon Beds from the Bohart-Adams Equation," *Am. Ind. Hyg. Assoc. J.* 50:A216–A217 (1991).

Draper, N.R., and H. Smith, *Applied Regression Analysis*, 2nd edition, Chapter 10, John Wiley & Sons, Inc., New York, NY (1980).

Grubner, O., and W.A. Burgess, "Calculation of Adsorption Breakthrough Curves in Air Cleaning and Sampling Devices," *Environ. Sci. Technol.* 15:1346–1351 (1981).

Jonas, L.A., and J.A. Rehrmann, "Predictive Equations in Gas Adsorption Kinetics," *Carbon* 11:59–64 (1973).

Kinniburgh, D.G., "General Purpose Adsorption Isotherms," *Environ. Sci. Technol.* 20:895–904 (1986).

Moyer, E.S., "Organic Vapor (OV) Respirator Cartridge Testing—Potential Jonas Model Applicability," *Am. Ind. Hyg. Assoc. J.* 4 8:791–797 (1987).

Nelson, G.O., *Gas Mixtures: Preparation and Control*, CRC Press, Inc., Boca Raton, FL (1992).

Nelson, G.O., and A.N. Correia, "Respirator Cartridge Efficiency Studies: VIII. Summary and Conclusions," *Am. Ind. Hyg. Assoc. J.* 37:514–525 (1976).

Nelson, G.O., A.N. Correia, and C.A. Harder, "Respirator Cartridge Efficiency Studies: VII. Effect of Relative Humidity and Temperature," *Am. Ind. Hyg. Assoc. J.* 37:280–288 (1976).

Vermuelen, T., M.D. LeVan, N.K. Hiester, and G. Klein, "Adsorption and Ion Exchange," in *Chemical Engineers Handbook*, 6th edition, Section 16, McGraw-Hill, New York, NY (1984).

Wood, G.O., and E.S. Moyer, "A Review of the Wheeler Equation and Comparison of Its Applica tions to Organic Vapor Respirator Cartridge Breakthrough Data," *Am. Ind. Hyg. Assoc. J.* 50:400–407 (1989).

Wood, G.O., and J.F. Stampfer, "Adsorption Rate Coefficients for Gases and Vapors on Activated Carbons," scheduled for publication in *Carbon* 31: No. 2 (1993).

Yoon, Y.H., and J.H. Nelson, "Application of Gas Adsorption Kinetics. I. A Theoretical Model for Respirator Cartridge Service Life," *Am. Ind. Hyg. Assoc. J.* 45:509–516 (1972).

Yoon, Y.H., and J.H. Nelson, "A Theoretical Study of the Effect of Humidity on Respirator Cartridge Service Life," *Am. Ind. Hyg. Assoc. J.* 49:325–332 (1988).

Yoon, Y.H., and J.H. Nelson, "Effects of Humidity and Contaminant Concentration on Respirator Cartridge Breakthrough," *Am. Ind. Hyg. Assoc. J.* 51:202–209 (1990).