

Letters to the Editor

Dear Sir:

I have had an occasion recently to carefully examine the derivation by Yoon and Nelson⁽¹⁾ of a mathematical justification for the empirically observed⁽²⁾ Freundlich-type relationships, $W_e = k C_1^{1-a}$, between adsorbate vapor concentrations, C_1 , and activated charcoal cartridge capacities, W_e . This derivation was an attempt to extend the theoretical basis of their successful model⁽³⁾ of breakthrough to include contaminant concentration effects on breakthrough times.

Unfortunately, it must be reported that a fundamental assumption in the above-mentioned derivation is totally incompatible with the basis of their original model. I would like to present these observations in this forum for consideration.

Three assumptions were made (1) in deriving the Freundlich capacity expression:

1. Kinetics is of the n th order for bed breakthrough concentration, C_b , to increase from zero, *i.e.*,

$$\frac{dC_b}{dt} = k_n C_b^n \quad (1)$$

2. The half-life of the removal reaction is therefore described by

$$\tau_{1,2} \propto 1/[A_0]^{n-1} \quad (2)$$

3. $\tau_{1,2}$ corresponds to the 50% breakthrough time, τ , defined by the earlier model (3) and $[A_0] = C_1$.

It is granted that these assumptions with one restriction ($n > 1$) lead to a Freundlich isotherm expression for bed capacity,

$$W_e = K_w C_1^{1-a} \quad (a = n-1) \quad (3)$$

However, the implications of the above three assumptions must be examined.

Integrating Equation (1) from $C_b = 0$ ($t = 0$) to $C_b = C_0/2$ ($t = \tau_{1,2}$) yields the "half life,"

$$\tau_{1,2} = \frac{(2)^{n-1}}{(1-n)k_n C_1^{n-1}} \quad (4)$$

except for $n = 1$, where the integration over these limits is undefined. Note also that $n > 1$ is required to have $\tau_{1,2} > 0$. THIS IS NOT THE USUAL DEFINITION OF HALF LIFE, the time for a concentration to DECREASE from a given value, C_0 , to half that

value, $C_0/2$. For $[A_0] = C_1$, Equation (4) is equivalent to Equation (2).

The parameter τ was originally obtained⁽³⁾ by integrating the derivative expression,

$$-\frac{dQ}{dt} = k'Q P \quad (5)$$

with $P = C_b/C_1$ and $Q = 1 - (C_b/C_1)$, over the range from $C_b/C_1 = 0.5$ ($t = \tau$) to C_b/C_1 ($t = t$). At constant C_1 this becomes

$$\frac{dC_b}{dt} = k' C_b \left(1 - \frac{C_b}{C_1}\right) \quad (6)$$

Both Equations (1) and (6) describe the slope of the breakthrough curve as functions of the breakthrough concentration, but both cannot be correct. Equation (6) describes the slope of a symmetrical breakthrough curve that fits Nelson's experimental data^(1,3) very well over the range $C_b/C_1 = 0.05$ to 0.95 . Equation (6) represents adsorption kinetics first order in vapor concentration, C_b , and first order in active sites, which are depleted as C_b/C_1 increases.

Equation (1), on the other hand, describes a breakthrough curve whose slope is continuously increasing even faster ($n > 1$) than the Wheeler equation ($n = 1$). The $\tau_{1,2}$ only matches τ at $C_b/C_1 = 0.5$ by assumption 3 (above), which fixes the value of n . At all other times the two curves defined by Equations (1) and (6) cannot coincide.

The Freundlich expression can still be used to correlate concentration effects on capacities or breakthrough times over limited experimental concentration ranges.⁽²⁾ However, it must be recognized as an empirical correlation and used with caution, especially when extrapolating beyond experimental ranges. Also, the Freundlich parameters have no physical meaning, so that estimating them from independent data is impossible. Averaging them⁽²⁾ is also of questionable value.

The same capacity data of Nelson have been correlated with challenge concentrations using Dubinin⁽²⁾ and Langmuir⁽⁴⁾ isotherm expressions. These models incorporate parameters which can be given physical significance and can be estimated from independent measurements. The Langmuir model⁽⁴⁾, by the way, has the same active-site depletion mechanism as that inherent in the Yoon/Nelson model for breakthrough curves.

References

1. **Yoon, Y.H. and J.H. Nelson:** Application of Gas Adsorption Kinetics II. A Theoretical Model for Respirator Cartridge Service Life and Its Practical Application. *Am. Ind. Hyg. Assoc. J.* 45:517-524 (1984).
2. **Nelson, G.O. and A.N. Correia:** Respirator Cartridge Efficiency Studies: VIII. Summary and Conclusions. *Am. Ind. Hyg. Assoc. J.* 37:514-525 (1976).
3. **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 (1984).
4. **Wood, G.O.:** A Model for Adsorption Capacities of Charcoal Beds. II. Challenge Concentration Effects. *Am. Ind. Hyg. Assoc. J.* 48:703-709 (1987).

**Gerry O. Wood, Ph.D., CIH, CPC
Member, AIHA**

Dear Sir:

Thank you for the opportunity to respond to correspondence submitted to you by Dr. Gerry O. Wood concerning our papers published in the August 1984 issue of the American Industrial Hygiene Association Journal — References (1) and (2). In his correspondence, Dr. Wood asserts that a fundamental assumption in Reference (2) is incompatible with the work published in Reference (1). This assertion is incorrect. The assumptions we introduced in Reference (2) are, in fact, totally consistent with the theory developed in Reference (1).

It appears to us that Dr. Wood, unfortunately, has misinterpreted our second paper [Reference (2)]. It is important to note that our two papers [References (1) and (2)] address different aspects of adsorption phenomena. These differences are elaborated in the following.

Our approach in Reference (1) is based on conditions of fixed contaminant assault concentration (C_1) and variable breakthrough percentage (P). For Reference (2), the assault concentration is variable and the breakthrough percentage is fixed at $P = 1/2$. We illustrate the differences in the two approaches with a discussion of two different cases as follows:

Case 1. In Reference (1), we introduced the following expressions for contaminant breakthrough at fixed contaminant assault concentration: