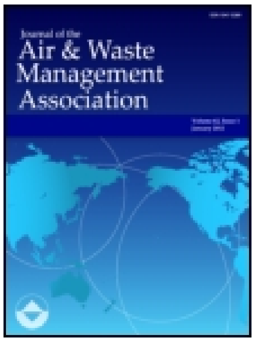

Journal of the Air Pollution Control Association

ISSN: 0002-2470 (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/uawm16

Modeling Adsorption Bed Behavior Using a Microcomputer

Sharon L. Forbes & Dwight W. Underhill

To cite this article: Sharon L. Forbes & Dwight W. Underhill (1986) Modeling Adsorption Bed Behavior Using a Microcomputer, Journal of the Air Pollution Control Association, 36:1, 61-64, DOI: 10.1080/00022470.1986.10466047

To link to this article: https://doi.org/10.1080/00022470.1986.10466047

panding when sampled for analysis. With time, increases in dry mass would further reduce the foliar concentration of F expressed as μg per gram dry mass (ppm).

Keller[4] placed seedlings of elm (*Ulmus scabra*) and black locust (*Robinia pseudoacacia*) trees near an industrial source of fluoride for 20 weeks during dormancy (November to April) and then transferred the plants to a greenhouse for bud break and growth. After three weeks, elm leaves and entire new shoots of black locust were analyzed for F. The mean concentrations of F in tissues developed in pollutant-free air were reported to be "more than double" those of the controls. However, the actual differences for control and exposed plants, respectively, were 2.5 and 8.0 ppm F in black locust shoots and 6.2 and 13.3 ppm F in elm leaves. The levels of F in these two species, which are considered to be relatively tolerant of atmospheric fluoride,[8] are within the background range and probably below the threshold necessary for adverse foliar effects.

Norway maple and lilac are considered to be of intermediate susceptibility to HF.[8,9] In our experiments, the mean concentrations of F in post-exposure growth from shoots exposed to high concentrations of HF continuously for 12 days during dormancy were relatively low. All were <9 ppm F and within the range of natural concentrations found in most plants where there are no anthropogenic sources of F.[1,8]

Conclusion

Results from continuous exposure of Norway maple and lilac for 12 days to high concentrations of HF indicate that significant concentrations of F may be absorbed (or adsorbed) during the winter by tissues exposed directly to the pollutant (bark, buds, etc.). Only a small fraction of the F accumulated during dormancy is recovered in new growth that emerges in the spring, and these concentrations are usually too low to cause direct effects on the plant. We conclude that deleterious direct effects from exposures of these two, and possibly, many other deciduous species to realistic doses of HF during winter dormancy are unlikely. Whether or not they lead to indirect effects, however, is uncertain. The suggestion by Keller[10] that exposures to HF during dormancy may increase the susceptibility of plants to spring frosts should be tested experimentally.

References

1. L. H. Weinstein, "Effects of Fluorides on Plants and Plant Communities: An Overview," in *Fluorides-Effects on Vegetation, Animals and Humans*, J. L. Shupe, H. B. Peterson, N. C. Leone, eds., Paragon Press, Salt Lake City, 1983, pp. 53–59.
2. D. C. MacLean, "Air quality standards for fluoride to protect vegetation: regional, seasonal, and other considerations," *JAPCA* **32:** 82 (1982).
3. T. Keller, "Translocation of fluoride in woody plants," *Fluoride* **7:** 31 (1974).
4. T. Keller, "Wintertime atmospheric pollutants—do they affect the performance of decidous trees in the ensuing growing season?" *Environ. Pollut.* **16:** 243 (1978).
5. R. H. Mandl, L. H. Weinstein, G. J. Weiskopf, J. L. Major, "The Separation and Collection of Gaseous and Particulate Fluorides," in *Proceedings of the Second Clean Air Congress*, H. M. Englund, W. T. Beery, eds., Academic Press, New York, 1971, pp. 450–458.
6. "Analysis for Fluoride Content of the Atmosphere and Plant Tissues (Manual Procedures)," in *1976 Annual Book of ASTM Standards*, American Society for Testng and Materials, Philadelphia, 1976, pp. 697–712.
7. D. A. Levaggi, W. Oyung, M. Feldstein, "Microdetermination of fluoride in vegetation by oxygen bomb combustion and fluoride ion electrode analysis," *JAPCA* **21:** 277 (1971).
8. *Biologic Effects of Atmospheric Pollutants—Fluorides*, National Academy of Sciences, National Research Council, Washington, DC, 1971, 295 pp.
9. P. W. Zimmerman, A. E. Hitchcock, "Susceptibility of plants to hydrofluoric acid and sulfur dioxide gases," *Contrib. Boyce Thompson Inst.* **18:** 263 (1956).
10. T. Keller, "Zur Fluor-Translokation bei Waldbäumen," *Mitt. Eidg Anstalt. Versuchswesen Forstl.* **51:** 335 (1975).

Dr. MacLean and Ms. Hansen are with the Environmental Biology Program at Boyce Thompson Institute, Cornell University, Ithaca, NY 14853. This note manuscript was peer reviewed.

Modeling Adsorption Bed Behavior Using a Microcomputer

Sharon L. Forbes and Dwight W. Underhill
Graduate School of Public Health
University of Pittsburgh
Pittsburgh, Pennsylvania

Gas adsorption beds range in size from small gas sampling cartridges to large tanks containing many tons of charcoal for the control of radioactive offgases from nuclear reactors. In these, and the many other applications where the breakthrough of only a small fraction of the input could be harmful, the need for a simple procedure to predict performance as a function of time is self-evident. Yet some mathematical models in current use inadequately describe the breakthrough of contaminant as a function of time. As an example of poor fit of a theoretical curve to experimental results, Figure 1 shows the fit of the Mecklenberg and Wheeler equations[1] to a breakthrough curve obtained from a respirator cartridge. Only from zero to 40 percent breakthrough can these equations be considered adequate, and even in this range there are difficulties caused by the fact that both the Mecklenberg and Wheeler equations give a poor prediction of the rate of increase in breakthrough as a function of time. More importantly, calculations of the capacity of an adsorption bed, as well as determining the efficiency of mass transfer within an adsorption bed, depend on fitting an equation

---

to the entire breakthrough curve, and for this purpose both the Mecklenberg and Wheeler equations are totally inadequate.

The *J* Function

Chemical engineers, when required to describe a breakthrough curve, very often use a mathematical expression known as the *J* function.[2] Figure 2 shows data fitted by the *J* function. There is no question that here, as well as for most adsorption data, the *J* function gives a far better representation of the data than can the Mecklenberg equation. For the data in Figure 2, the overall difference between the measured and calculated values is about 3 percent, which is within the accuracy that the concentration could be measured.

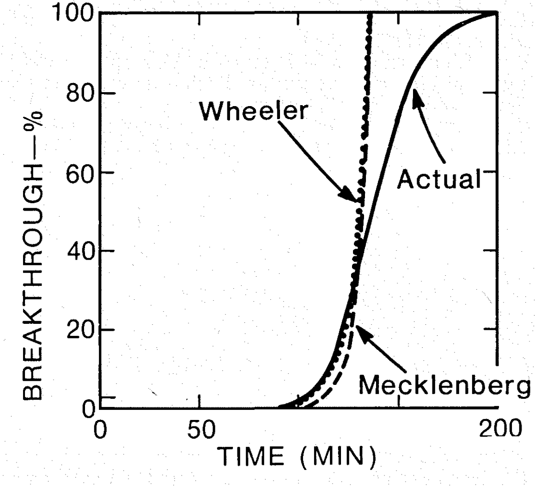

Figure 1. Comparison of calculated and experimental breakthrough curves for toluene. Tests were made at 1000 ppm, 50% relative humidity and 53.3 L/min. The calculated curves closely approximate the shape and magnitude of the experimental data only from 0–40% breakthrough. (From Nelson and Correia[1])

Yet it might also appear that the *J* function, given in the Appendix, is too complex for practical use. Inspection of this equation shows it to be an infinite integral of a modified Bessel function. In practice, graphical procedures can be used. For example, one can try to fit the curves in Figure 16–18 of the *Chemical Engineers' Handbook* to the experimental data, or use the graphical procedure advocated by Hougen and Marshall.[3] As this latter procedure is based on determining the slope of the breakthrough curve at a selected point, the results obtained depend somewhat on which data points are selected for analysis. In practice, either procedure can be time-consuming and subjective.

Use of the Microcomputer

With the microcomputer, there is commonly available the means for a simple, rapid, and objective determination of the best fitting *J* function. It is shown here how this may be accomplished using a microcomputer program written in BASIC. This computer program carries out the following calculations:

1) As this program is written, the *J* function, Equation A1 in the Appendix, is approximated by Equation A2, an integral error function also given in the *Chemical Engineers' Handbook*. Most BASIC programs for the microcomputer do not have as a standard subroutine the integral error function, but this may be calculated rapidly with an error $\leq 1.5 \times 10^{-7}$ using the approximation given in Equation 7.1.26 of Abramowitz and Stegun.[4]

2) To use this program, first the data pairs giving the time and the corresponding concentration of test agent in the effluent are entered. The program then finds the best values for t_h, the mean holdup time, and for N, the number of theoretical plates, which are the two factors needed to define the *J* function. As an initial guess the program assumes t_h to be a time near the point of 50 percent breakthrough. The initial value for N is arbitrarily assumed to be 200. The program next calculates the predicted concentration for each time the concentration was measured and sums the squares of the differences between the measured and predicted concentrations. This procedure is repeated as t_h and N are varied until a minimum is found in the sum of the squares of the differences between the predicted and the measured concentrations. With 30 pairs of time-concentration data, the compiled program takes about five minutes on an IBM-AT personal computer to determine the values of t_h and N giving the optimum fit.

Analysis of Individual Breakthrough Curves

The values of t_h and N obtained in the preceding analysis can be used to characterize the performance of an adsorption bed. The mean holdup time, t_h, gives the time that the adsorption bed could operate, assuming that none of the input passed out in the effluent, before the bed became saturated with the inflowing contaminant. This is a function of the adsorptive capacity of the bed and does not depend on the shape of the bed. Suppose, for example, it was desired to operate an adsorption bed for 24 hours, and it turned out that t_h was equal to 20 hours. Then we know that a simple rearrangement of the shape of the adsorption bed may change the shape of the breakthrough curve, but could not raise the effective operating time to 24 hours. An adsorption bed that could meet the above requirement must contain more adsorbent than the bed that was tested. In other cases the design criteria might be met by changing the shape of the bed without necessarily having to add more adsorbent. For example, suppose it were required to operate an adsorption bed for 20 hours *without* significant breakthrough. Then the bed described above could meet this requirement *if* the number of theoretical plates (primarily determined by bed

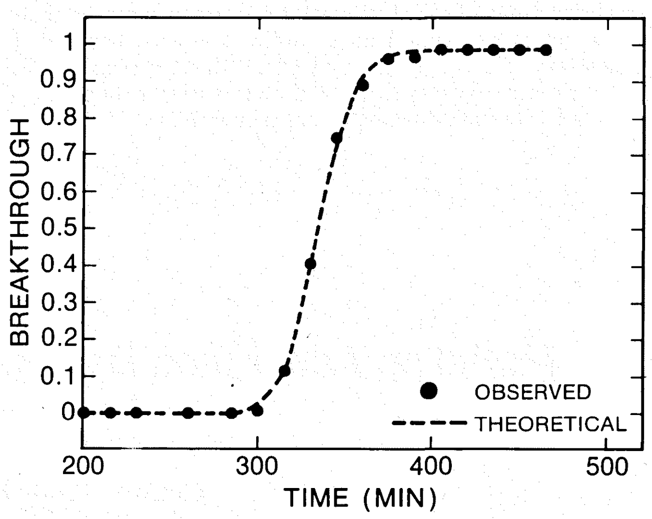

Figure 2. The *J* function fitted to experimental data.

geometry) were sufficiently high. Figure 3 illustrates these two cases.

Correlation of Adsorption Data

If it is desired to correlate adsorption bed performance over a wide range of conditions, the "J" function may still be useful if the factors t_h and N are determined as functions of whatever parameters are varied. For example, in the study in which Figure 2 was taken, it was desired to determine the performance of respirator cartridges as a function of the concentration of the challenge agent. The best fitting J function was determined for each run, and then t_h and N determined as a function of input concentration. It was found that the mean holdup time, t_h, could be calculated from the equation:

$$t_h = aC^{-b} \tag{1}$$

where: C = input concentration of challenge agent, mg/m^3, and
a, b = constants derived from a log-log plot of t_h vs. C.

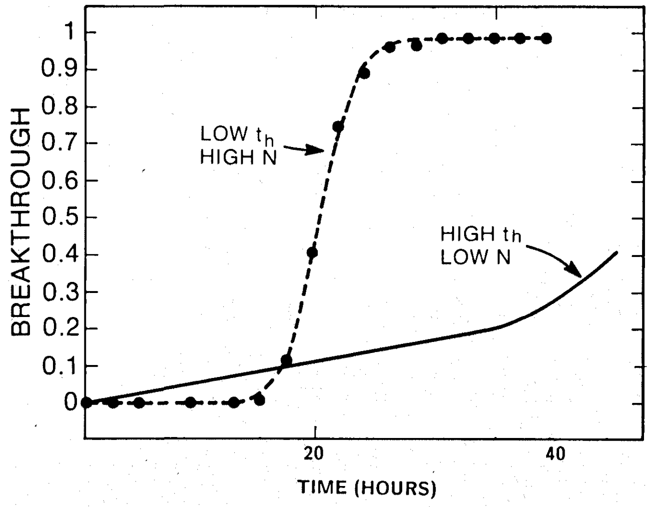

Figure 3. Effect of mass transfer on use time. For the bed having the low number of theoretical plates, if the bed geometry were changed to give a higher number of theoretical plates, the effective use time could be increased greatly. For the bed with the higher number of theoretical plates, the effective use time is already near t_h, which here is 20 hours. Increasing the number of theoretical plates could not increase the effective use time to over 20 hours.

Equation 2 is equivalent to fitting the adsorption data to a Freundlich isotherm. If it is known from static tests that some other adsorption isotherm might be more appropriate, then Equation 1 may be altered to use that particular isotherm. The key factor to remember in deriving an alternative for Equation 1 is that the mean holdup time should be inversely proportional to the partition coefficient.

The number of theoretical plates was found by a very similar regression of the number of theoretical plates vs. input concentration. Here we used the equation:

$$N = a'C^{-b'} \tag{2}$$

where: C = input concentration of challenge agent, mg/m^3, and
a', b' = constants derived from a log-log plot of N vs. C.

the values of a' and b' were determined by linear regression, which minimized the sum of the squares of the difference between the logarithms of the predicted and measured values of N. Thus, once the constants in Equations 1 and 2 are known, if the input concentration is specified, t_h and N may be predicted from the above two equations and these values used with the J function to calculate breakthrough as a function of time.

Calculation of Adsorption Bed Efficiency

Ideally, the adsorbent would become saturated with vapor before permitting any contaminant to break through into the effluent stream. This corresponds to an adsorption bed having an infinite number of theoretical plates. This ideal situation never occurs in real adsorption beds, where there is always some breakthrough of contaminant before the bed is completely saturated. The J function allows a calculation of the degree to which saturation was attained before the adsorption bed has lost its effectiveness. Table I gives the theoretical plates corresponding to a given degree of adsor-

Table I. Calculation of adsorption bed efficiency from the number of theoretical plates.

Fraction of ideal use time	Percent breakthrough 1%	2%	5%	10%
90%	1037	810	524	320
80%	247	194	126	78
70%	104	82	54	34
60%	55	44	29	18
50%	33	26	17	11

Appendix

Approximation of the *J* Function

The J function:

$$J(N,Nt') = 1 - \int_0^N \exp(-Nt' - z)I_0(2\sqrt{Nt'z})dz \tag{A1}$$

where I_0 = modified Bessel function of the first kind
N = number of theoretical plates
t = time from beginning of test challenge
t_h = mean holdup time
$t' = t/t_h$

This equation can be approximated by

$$J(N,Nt') = \tfrac{1}{2}\left\{1 - \operatorname{erf}[\sqrt{N}(1 - \sqrt{t'})] + \frac{\exp[-N(1-\sqrt{t'})^2]}{\sqrt{\pi N}(\sqrt{t'} + \sqrt[4]{t'})}\right\} \tag{A2}$$

The integral error function , erf, was approximated by:

$$\operatorname{erf} x = 1 - (a_1t + a_2t^2 + a_3t^3 + a_4t^4 + a_5t^5)e^{-x^2} \tag{A3}$$

where $t = \dfrac{1}{1 + px}$

$a_1 = 0.254829592$
$a_2 = -0.284496736$
$a_3 = 1.421413741$
$a_4 = -1.453152027$
$a_5 = 1.061405429$
$p = 0.3275911$

bent saturation before a fixed degree of breakthrough occurs. Note that a high number of theoretical plates, corresponding to highly efficient mass transfer, permits a more effective use of the adsorbent before breakthrough occurs.

Conclusions

When this study began, we thought that procedures such as described here would require more computational power than available in a microcomputer, but this was not the case: microcomputers which are now in common use can process rapidly a vast amount of adsorption data, and determine from them the fundamental parameters which describe the operation of an adsorption bed.

The computer program used in these calculations is available from the authors on request.

Acknowledgment

This study was supported by NIOSH Grant 1 RO1 OHO1644-01. These results were orginally reported at Ventilation-85, a conference held at Toronto, Canada, October 1985.

References

1. G. O. Nelson, C. A. Correia, "Respirator cartridge efficiency studies: VIII. Summary and conclusions," *Am. Ind. Hyg. Assoc. J.* **37:** 514 (1976).
2. R. H. Perry, *Chemical Engineers' Handbook*, 6th Ed., McGraw-Hill, New York, 1984.
3. O. A. Hougen, W. R. Marshall, Jr., "Adsorption from a fluid stream flowing through a stationary granular bed," *Chem. Eng. Progress* **43:** 197(1947).
4. M. Abramowitz, I. Stegun, *Handbook of Mathematical Functions*, National Bureau of Standards, Applied Mathematics Series 55, U.S. Government Printing Office, Washington, D. C., sixth printing, 1967.

Sharon Forbes is currently at the Koppers Company, Inc., Science and Technology Center, Monroeville, PA, and Dr. Underhill is an associate professor in the Department of Industrial Environmental Health Sciences, University of Pittsburgh, Graduate School of Public Health, Pittsburgh, PA 15261.
