Adsorption and Desorption of Benzene in Two Soils and Montmorillonite Clay

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■ The adsorption, desorption, and possible degradation of benzene in two silty clay loam soils and montmorillonite clay saturated with either aluminum (Al^{3+}) or calcium (Ca^{2+}) ions were studied. With benzene concentrations in water of 10, 100, and 1000 ppb, it was found that sorption was minimal for the soils and the Ca-saturated clay. Benzene sorption on the Al-saturated clay was seven times greater than for the soils and three times greater than for the Ca-saturated clay. Once sorbed, benzene tends to resist desorption. The most likely route of benzene loss from soils appears to be by volatilization. In addition, soil may provide a medium for the degradation of benzene.

Statistical analyses by Cross and Wiersma (1) of cancer incidence by county and other supportive studies suggest a relationship between cancer mortality rates and the production of organic chemicals. Many organic chemicals are known carcinogens and have been ranked by Geomet, Inc. (2) by importance factors such as production, release, and volatility. Benzene was ranked by that group as the number one chemical of concern.

Very little is known about the environmental fate of benzene (3). Recently, the sorption of benzene and other hydrophobic compounds to natural aquatic sediments has been studied (4). This work indicated that the sorption of benzene to both sediment and terrestrial soil should be similar when data is adjusted on an organic carbon basis. This possibility, as well as the overall fate of benzene in soil, has not been investigated. Accordingly, a study was initiated to determine the adsorption-partition constants of benzene in soils and clay. The extraction of benzene from those adsorbents was also investigated. The information produced from this study will be useful in delineating the movement and fate of benzene in soil.

Materials and Methods

Two air-dried soils (Overton series from southeastern Nevada and Hastings series from Nebraska) and montmorillonite clay (montmorillonite 25, Upton, Wyo., Wards Natural Science Establishment) were studied. Before use, the clay was saturated with either Al^{3+} or Ca^{2+} ions by adding 50 g of dry clay to 500-mL aqueous solutions, either 1 N $AlCl_3$ or 1 N $CaCl_2$. These mixtures were blended with an ultrasonic probe until all of the clay was in solution. The solutions were placed into dialysis tubing and washed with distilled water until Cl^- ion could no longer be detected, thus indicating the removal of excess Al^{3+} or Ca^{2+} ions. Washed clay was then freeze-dried to obtain the final clay powder used for the experiments. Chemical and physical properties of these adsorbents are found in Table I.

Benzene was obtained from New England Nuclear premixed in distilled H_2O. Each sealed ampule contained benzene uniformly labeled with 0.10 mCi of ^{14}C (specific activity of 54.0 mCi/mmol) mixed with 20 mL of H_2O. New England Nuclear analyzed this mixture after we had stored some of the solutions for over 1 year and found no deterioration of the labeled benzene.

Before use, the radiolabeled benzene from an ampule was diluted to 210 mL with distilled water, and this stock solution was stored in a 210-mL amber bottle with a screw cap having a Supelco mininert valve. The valve allowed the use of a syringe to remove solution in any desired amount.

A 10^5-ppb stock solution of stable benzene was made by mixing 0.1 g of benzene with 1 L of distilled water. Labeled benzene solutions used in the studies were made by mixing, in sealed serum vials, stock solutions of labeled and stable benzene with a required amount of water.

The batch equilibration sorption study was conducted with 1 g of soil and 0.5 g of clay at a ratio of 1:25 or 1:50 adsorbent:water–benzene solution, respectively. These ratios were necessitated by the requirement for a minimal headspace in the 25-mL centrifuge tubes that were used, because a restrictive headspace reduced the volatile loss of benzene from solution during shaking.

Three solution concentrations of benzene were used for the sorption study. These concentrations were 10, 100, and 1000 ppb of benzene in 25 mL of liquid. After the soil or clay solutions were incubated at 25 °C, with shaking, for the desired period of time (1, 16, 42, 64, or 136 h), the soil or clay was removed from solution by refrigerated centrifugation (5 °C). Benzene remaining in the supernate was determined by liquid-scintillation counting of 5 mL of the liquid. After the solution was decanted from the centrifuge tube, the tube and its contents were weighed to determine the amount of solution remaining in the pellet. The calculated amount of benzene entrapped in the soil or clay pellet was then determined, and this value was used as a correction to obtain the amount of benzene which was actually on the adsorbents.

Benzene associated with the adsorbent was determined by first oxidizing the organic materials in the pellet at 900 °C in a stream of oxygen. Gases from the oxidizer were bubbled in a CO_2-gathering liquid-scintillation cocktail. The amount of ^{14}C was then determined by liquid-scintillation analysis. The liquid-scintillation cocktail was made by mixing 900 mL of a stock cocktail (1.5 g of bis-MSB, 7.0 g of 2,5-diphenyloxazole (PPO), 1 L of p-xylene, and 400 mL of Triton N-101) with 100 mL of Packard Carbo-Sorb.

Adsorption-partition constants were determined for benzene by use of the following log form of the Freundlich isotherm:

$$\log (x/m) = 1/n (\log C) + \log K$$

where x is the weight of benzene sorbed (ng), m is the weight of adsorbent (g), C is the equilibrium concentration of benzene in solution (ng/mL), K is a constant, and $1/n$ is a constant. The constants, K and $1/n$, were determined by linear regression. K is a measure of the degree or strength of adsorption, while $1/n$ is used as an indication of whether adsorption remains constant ($1/n = 1$) or decreases with increasing adsorbate concentrations ($1/n \neq 1$).

To check the methods used in the sorption studies, activated charcoal ground to pass a 5-mm sieve was used as an adsorbent. A batch equilibration study using 50-mg quantities of charcoal was incubated at 25 °C for 16 h with 2500 ng of benzene. It was found that 98% of the benzene was sorbed, indicating that the methods used for the batch equilibration provided sufficient opportunity for benzene to be sorbed. In addition, it was found that benzene did not adsorb to the glass centrifuge tubes.

Other studies were conducted to determine the amount of benzene which could be desorbed (extracted) from the adsorbents used for the batch equilibration study or from those being maintained at less than 100% of their moisture-holding

Table I. Physical and Chemical Properties of Adsorbents

adsorbent	% sand	% clay	% organic carbon	cation exchange capacity, mequiv/100 g	pH
Hastings silty clay loam	1	31[a]	2.6	17	5.6[c]
Overton silty clay loam	15	34[a]	1.8	29	7.8[c]
Al-saturated montmorillonite	0	100	0[b]	80[b]	4.2[d]
Ca-saturated montmorillonite	0	100	0[b]	80[b]	6.6[d]

[a] Montmorillonitic in character. [b] Assumed value. [c] 1:5 soil–water solution. [d] 1:50 clay–water solution.

Table II. Freundlich Constants for Benzene Sorption after 16 h of Incubation

adsorbent	K	$1/n$
Hastings silty clay loam	2.4	0.89
Overton silty clay loam	1.8	0.94
Al-saturated montmorillonite	30.9	1.08
Ca-saturated montmorillonite	4.4	0.99

Table III. Sorption of Benzene-Derived ^{14}C [a] in Sterile and Sterilized Reinoculated Soils during 136 h

adsorbent	sterilized, pCi	reinoculated, pCi
Hastings silty clay loam	580 ± 67	7495 ± 193
Overton silty clay loam	318 ± 117	7480 ± 430

[a] 30 694 pCi of ^{14}C initially added to solution.

capacity (MHC). Three replicates were used for the experiments in each study.

Extraction of sorbed benzene from batch-equilibrated adsorbents was performed on adsorbent pellets obtained by the methods outlined. After the amount of residual equilibrium solution was determined gravimetrically, a water extract (25 mL) of benzene-free soil was used to replace the decanted equilibrium solution. The adsorbent pellets were dispersed in the new solution and shaken for the desired time period. Determinations of the corrected amount of benzene in the extraction solution and on the adsorbent were carried out in the usual manner. Three concentrations of benzene were used: 10, 100, and 1000 ppb (250, 2500 ng, and 25 000 ng total).

In the second desorption study, the dry adsorbents were wet to less than 100% MHC by using a water–benzene solution. This was accomplished by placing 1 g of soil or 0.5 g of clay into a 25-mL centrifuge tube. To the soils was added 0.5 mL of water containing 1000 ng of tagged benzene. The clay was similarly treated with 0.5 mL of water containing 500 ng of labeled benzene. After treatment, the tubes were tightly capped to prevent the loss of moisture. Gravimetric measurements at the times the tubes were opened showed that there had been no moisture loss during incubation. The ^{14}C content of the benzene–water solutions was verified at the time of addition by analyzing duplicate samples of each solution by liquid-scintillation counting. After the desired period of incubation, 25 mL of distilled water was added, and the tubes were shaken for prescribed times. Benzene in the water extract and on the adsorbents was determined as outlined. This work and all other work involving incubation were carried out in the dark at 25 °C.

The study was repeated on sterile soils to determine if biological degradation of benzene was taking place. These soils were autoclaved in 100-g quantities every 3 days for a total of three 6-h treatments. In addition, H$_2$O and centrifuge tubes were autoclaved. All autoclaving was done at 121 °C and 15 psig. Sterile soils were reinoculated by the addition of 1 mL of a nonsterile soil–water extract to the batch equilibration solutions. Benzene solutions used in sterility studies were sterilized by passing them through a 0.22-μm membrane filter. Sterility of the adsorbents and solutions was verified by streaking samples on nutrient agar and observing for any microbial growth.

A determination of the possible degradation of benzene as a result of oxidation was made on the 1000-ppb benzene-treated samples after each incubation period. Testing was done by equally dividing the supernate remaining in each centrifuge tube after removal of the initial 5 mL. Half of the supernate was adjusted either to less than pH 3 with 1 N HCl or to more than pH 10 with 0.2 N NaOH. Five milliliters of

p-xylene was then added to each solution, and the resulting mixture was shaken for 1 min in a separatory funnel. The amount of ^{14}C-labeled oxidation product in the p-xylene was determined by liquid-scintillation counting. If no oxidation of the benzene occurred during incubation, equal amounts of ^{14}C were found in both p-xylene samples. However, if oxidation products were present, more ^{14}C was found in the acidified supernate.

Results and Discussion

Initial benzene sorption on soil and clay was determined after 16 h of incubation. Table II contains the Freundlich constants determined for the adsorbents. The $1/n$ values are at unit or very close to it, indicating that sorption should be linear within the range of increasing benzene concentrations used for this study.

This assumption was shown to be correct when plots of the Freundlich isotherms were made (Figures 1–4). The importance of the K and $1/n$ data will be discussed later. Mass balance calculations showed that all benzene was accounted for either in the solution or on the adsorbents. Other incubation periods were tested to determine if sorption was time dependent.

Figures 5 and 6 are plots of the Freundlich K values with time. Both soil adsorbents had increasing K values with time (Figure 5). However, for the clays, maximum K values occurred by the 16-h sampling period. These values remained approximately the same for each subsequent sample (Figure 6). These data indicate that maximum sorption on the clay adsorbents occurred by 16 h. The apparent increase in sorption on the soil adsorbents shows that more benzene was being sorbed with increased time. However, it also suggests that there may have been a degradation of benzene occurring with the resultant ^{14}C-labeled product(s) being more readily sorbed by the soils. Indeed, unidentified oxidation products from benzene were found after 16 h in the water solution containing the soil adsorbents. No such compound(s) were found in the extracts of the clay adsorbents.

Since microbial degradation of benzene by oxidation is known to occur (5–9), the possibility of microbial metabolism of benzene was studied by incubating sterilized soils with 1000-ppb sterilized benzene solutions for 136 h. As a control, sterilized soils reinoculated with microbes were also incubated. Data from this study (Table III) show that 2 and 1% of the benzene were sorbed to the sterilized Hastings and Overton soils, respectively, while 24% of the carbon from the original
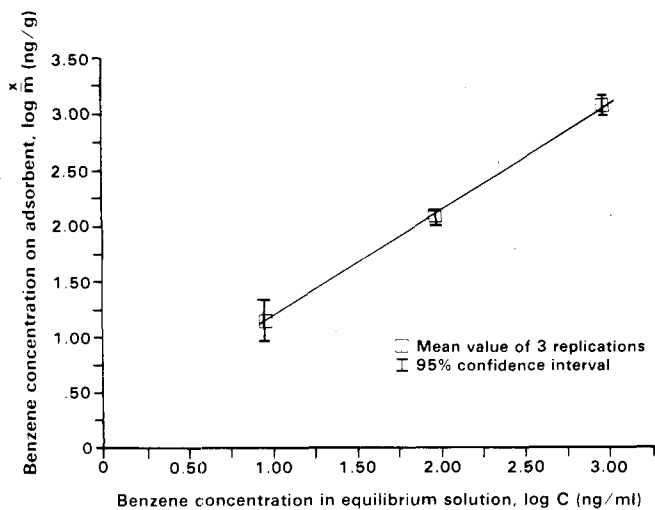
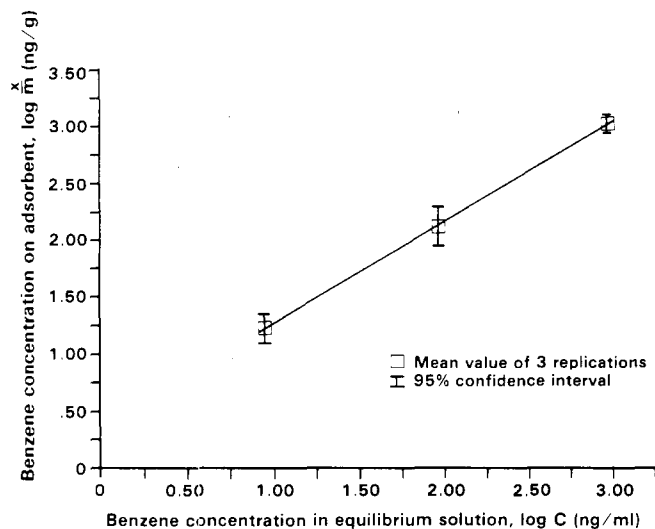**Figure 1.** Freundlich plot for benzene on Overton silty clay loam

Figure 2. Freundlich plot for benzene on Hasting silty clay loam
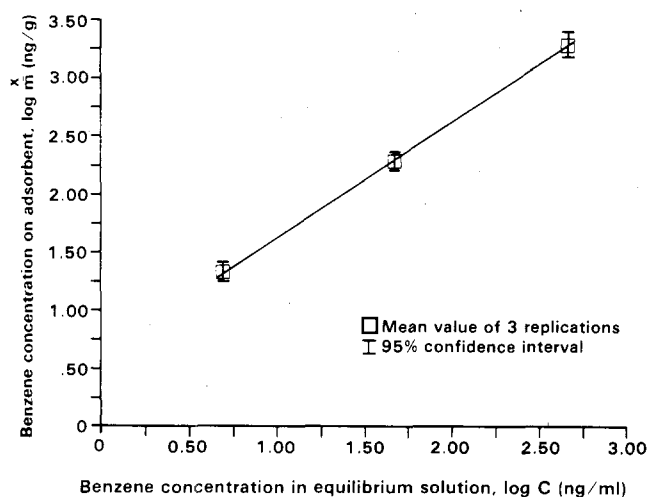

Figure 3. Freundlich plot for benzene on Ca-saturated montmorillonite clay

benzene was sorbed to the nonsterile soils. In the initial study, after 136 h the apparent increased sorption of benzene by the nonsterile soils (Figure 5) resulted in 25 and 33% of the ^{14}C being sorbed to the Hastings and Overton soils, respectively. These data implicate microbes as the source of benzene degradation, and suggest that decay products, rather than benzene, are the primary residues sorbed on soils that have been incubated for extended periods of time.
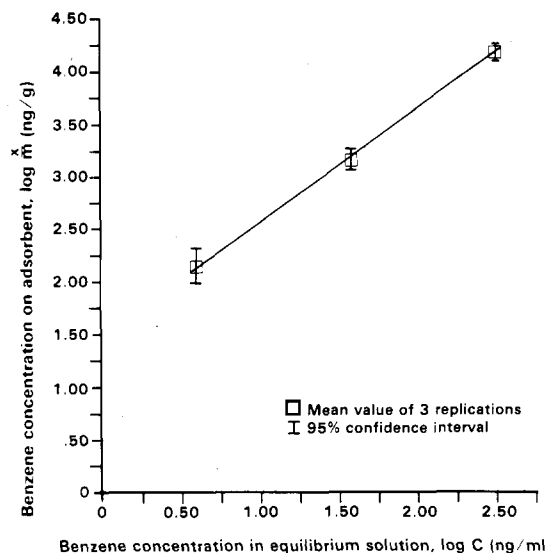

Figure 4. Freundlich plot for benzene on Al-saturated montmorillonite clay
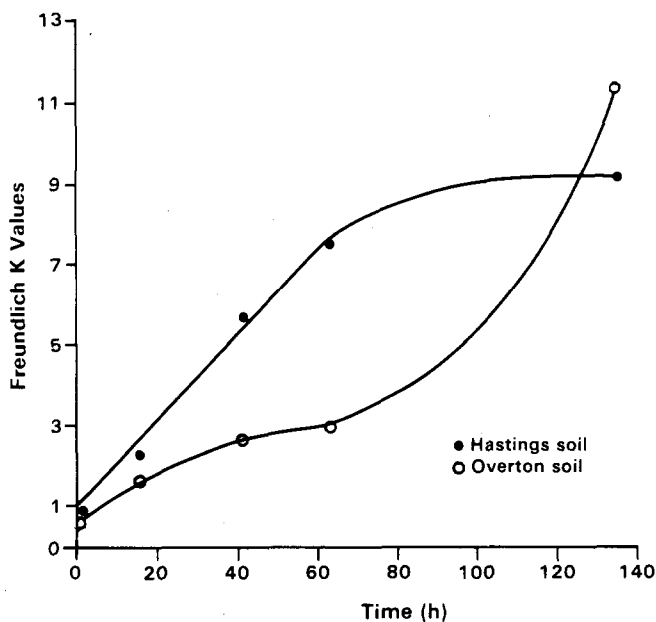

Figure 5. Freundlich K values for benzene with increasing time

The Freundlich $1/n$ values (Table II) suggest that all of the adsorbents used in this study sorbed increasing concentrations of benzene in a linear fashion. However, the small K values for the soils and Ca-saturated clay indicate minimal sorption, while more sorption would be expected for the Al-saturated clay because of the larger K value. These values have relevancy when compared with the amount of benzene sorbed. After 16 h of batch equilibration, the Al-saturated montmorillonite clay sorbed 3% of the available benzene. The Ca-saturated montmorillonite benzene sorption was 4%, while the Overton and Hastings soils each sorbed 5% of the benzene.

A correlation of benzene sorption and soil organic carbon content was obtained by use of the following equation:

$$K_{oc} = \frac{K_f 100}{\% \text{ oc}}$$

where K_f is the Freundlich constant and % oc is the percent soil organic carbon. The K_{oc} values for the Overton and Hastings soils were calculated by this method to be 92 and 100, respectively. Karickhoff and Brown (4) obtained an average K_{oc} value of 85 in a study of benzene sorption by sediments. The data for the soils and sediments appear to be reasonable

Table IV. Benzene Sorbed to and Extracted from Moist Adsorbents with Time (ng)

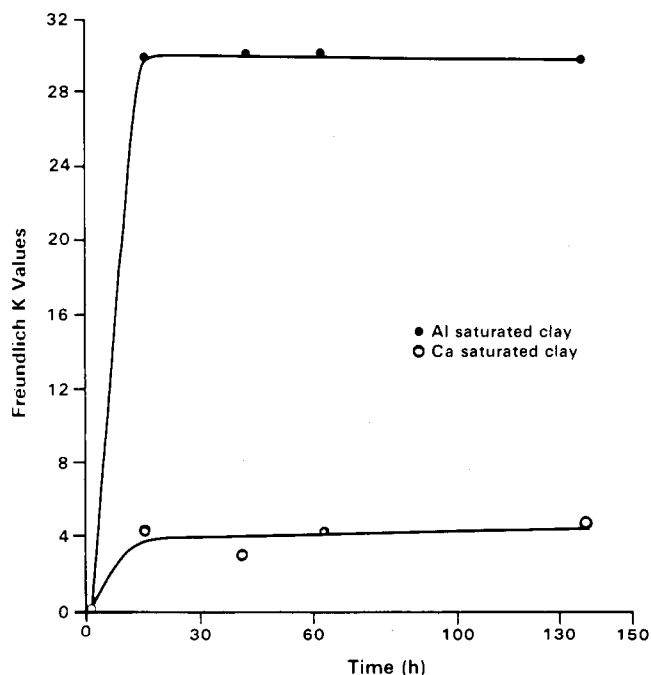| time, [a] h	Hastings silty clay loam		Overton silty clay loam		Al-saturated montmorillonite		Ca-saturated montmorillonite	
	sorbed	extrac.	sorbed	extrac.	sorbed	extrac.	sorbed	extrac.
16	85	31	43	23	8	9	6	5
42	66	8	23	6	5	5	4	3
64	70	3	26	3	8	3	5	3
136	64	2	20	2	8	2	7	3

[a] Time after amendment with benzene.

Figure 6. Freundlich K values for benzene with increasing time

since K_{oc} values for a chemical on soils from different areas generally vary by a factor of 2 or 3 (10).

The mechanism causing the increased sorption of benzene in the Al-saturated clay was not determined. Since both clays were identical prior to cation treatment and were handled in the same manner during the Al^{3+} and Ca^{2+} saturation, washing, and freeze-drying, it appears that the difference in benzene sorption was solely the result of the Al^{3+} treatment. In other work with copper-saturated montmorillonite clay (11), it was found that 50 mg of the clay was able to sorb 4% of the 8750 μg of benzene available in a benzene–water solution. All of these data indicate that montmorillonite saturated with metals is capable of sorbing varying amounts of benzene depending on the metal and the concentration of benzene in solution.

Sorbed benzene appeared to be tightly bound. When the adsorbents were extracted with the prepared soil solutions, desorbed benzene was not detected. In this study, 3% of the initial benzene remained sorbed to the two soils; 32% remained in the Al-saturated and 1% on Ca-saturated clays.

Adsorbents maintained in the moistened condition were also able to retain benzene after a 10-min extraction with water (Table IV). The length of time before the adsorbents were extracted with water had no effect on the amount of benzene sorbed to the Al- and Ca-saturated clays. The two soils decreased in sorbed benzene between 16 and 42 h, but they had a minimum of change thereafter. No benzene degradation was detected in the extraction water obtained from the adsorbents. A mass balance calculation for the benzene indicated that from 88 to 99% of the 1000 ng of benzene applied to these adsorbents was lost within the first 16 h. This

loss was attributed to volatilization of the benzene.

In another study, the moistened adsorbents with added benzene were incubated for 16 h and then extracted with distilled water for 16 h (instead of the 10-min washing used previously). The amount of benzene remaining sorbed to the Al and Ca clays was the same as that found in the previous study (Table IV). The Overton soil retained 46 ng and the Hastings soil retained 26 ng of benzene. The increased period of extraction (16 h) appears to have resulted in an increased desorption of the benzene from the soils. This desorbed benzene was not found in the extraction solution, and we presume that it was lost by volatilization.

Retention of benzene by the moistened soils and Ca-saturated clay in these studies was similar to that of the batch equilibrium studies. The amount of benzene sorbed by the Al-saturated clay was only about 1% compared to about 33% in the batch equilibrium studies reported. These data indicate that either the increased water and/or the increased benzene–clay contact time in the batch equilibration solution resulted in the increased sorption of benzene in Al-saturated clay.

Summary

The results of this study indicate that sorption of benzene is not the major effect of soil on benzene. Rather, soil may provide a medium for the degradation of benzene. Although sorbed benzene tends to resist desorption, a minimal amount of benzene sorbed to soil would be lost to water. The more likely route of benzene loss appears to be via volatilization.

Montmorillonite clay saturated with Ca sorbed less benzene than the soils; however, Al-saturated clay, for some unexplained reason, was able to sorb and retain much more benzene than could the soils.

Literature Cited

(1) Cross, A. J., Wiersma, G. B., "Preliminary Analysis of Cancer Rates in Organic Chemical Producing Counties", EPA Research Series, EPA-600/1-79-022, June 1979.
(2) "Second Quarterly Progress Report Prepared for U.S. EPA, Las Vegas, Nevada", Geomet, Inc., Gaithersburg, Mo., April 1, 1977–June 30, 1977.
(3) Miller, T. A., Ed., "Problem Definition Studies on Potential Environmental Pollutants. IV. Physical, Chemical, Toxicological and Biological Properties of Benzene; Toluene; Xylenes; and p-Chlorophenyl Methyl Sulfide, Sulfoxide, and Sulfone", U.S. Army Medical Bioengineering Research and Development Laboratory, Report No. Ad A040435, Fort Detrick, Md., 1976.
(4) Karickhoff, S. W., Brown, D. S., *Water Res.*, 13, 241–8 (1979).
(5) Rhodes, R. C., Belasco, I. J., Pease, H. L., *J. Agric. Food Chem.*, 18, 524–8 (1970).
(6) Somerville, H. J., Mason, J. R., Ruffell, R. N., *Eur. J. Appl. Microbiol.*, 4, 75–85 (1977).
(7) Dagley, S., *Am. Sci.*, 63, 681–9 (1975).
(8) Dagley, S., Chapman, P. J., Gibson, D. T., Wood, J. M., *Nature (London)*, 202, 755–8 (1964).
(9) Marr, E. K., Stone, R. W., *J. Bacteriol.*, 81, 425–30 (1961).
(10) Hamaker, J. W., Thompson, J. M., "Organic Chemicals in the Soil Environment", Vol. 1, Goring, C. A. I., Hamaker, J. W., Eds., Marcel Dekker, New York, 1972.
(11) McBridge, M. B., Pinnavaia, T. J., Mortland, M. M., "Fate of Pollutants in the Air and Water Environments", Part 1, Vol. 8, Suffet, I. H., Ed., Wiley, New York, 1977.