STUDIES ON THE STRIPABILITY OF PRIORITY

POLLUTANTS IN SEEDED AND NON-SEEDED

ACTIVATED SLUDGE

SYSTEM

By

YU-PING CHUNG

Bachelor of Science in Agriculture

National Taiwan University

Taipei, Rep. of China

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Dedicated to my Parents

Kuo-Tong and Chiou-Fang Chung

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Thesis Approved:

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Thesis Adviser

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Dean of the Graduate College

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CHAPTER I

INTRODUCTION

A great number of the waste water treatment plants currently in the United States are activated sludge plants which provide secondary treatment to meet the effluent standards required by the Environmental Protection Agency (EPA). The reasons for its popularity are (1) low capital cost and low operation and maintenance cost when compared to chemical and physical treatment processes, (2) high treatment efficiency under proper control and (3) excellent flexibility of treating highly variable wastewaters generated by both municipal and industrial sources.

As petrochemical and other industries produce new organic compounds, the characteristics of their wastewaters are simultaneously changing and the treatment of those wastewaters becomes more and more complex. A certain level of analysis of the wastewater quality has to be done in order to obtain the best treatment efficiency. The volatile organic compounds are often found in the petrochemical industrial waste and they can escape from the aqueous waste into the atmosphere due to the aeration and the agitation mechanisms. The aeration mechanism is vital to the activated sludge process in regard to providing both the oxygen requirement and the completely mixed environment for the microbial population. The escape of such compounds to the atmosphere during treatment by the activated sludge process may constitute a

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health hazard to the plant personnel, as well as adding to the complexity of describing the course of purification.

The objective of this work was to determine and compare the stripability of selected priority pollutants in seeded and unseeded activated sludge reactors.

CHAPTER II

LITERATURE REVIEW

General

The application of microorganisms in the treatment of wastewater
can be traced back many decades. Yet, the development of mathmetical
descriptions for the functional behavior of this process did not
receive much attention until the late fifties. During the early years,
the basic design parameter was the hydraulic detention time which
describes the physical characteristics of the incoming wastewater
without considering the behavior of microorganisms. In 1942, Monod
(1, 2, 3) developed a mathmetical model to describe the growth character-
istic of bacteria. In this model, the growth rate of the microorganisms
is a hyperbolic function of the initial substrate concentration. The
relation between the growth rate and the substrate concentration is
a decreasing first order curve. Steming from this concept, researchers
have derived different models for designing the activated sludge process
(1, 4). A common starting point for these models is a mass balance of
the substrate:

$$V \left(\frac{dS}{dt} \right)_R = F S_i - F S_e - \left(\frac{dS}{dt} \right)_B V \qquad (1)$$

rate of change of substrate in reactor	substrate inflow to reactor	substrate outflow from reactor	substrate biologically oxydized

When a continuous flow system reaches steady state, the rate of change of the substrate in the reactor is zero, i.e., $(\frac{dS}{dt})_R = 0$. All the other terms on the right hand side of Eq. 1 are fixed as soon as the system reaches steady state.

Physical and chemical activities can also play significant roles in organic removal when aeration device are employed to provide oxygen demand and mixing requirement. Prather (5) found that chemical oxygen demand (COD) can be more efficiently removed from refinery wastewaters by a dissolved air flotation clarification process. His results indicated that COD removal can be increased from 70 percent to as much as 92 percent. Also, Prather and Gaudy (6) attempted to design an experiment aimed at determining the roles of stripping and chemical oxidation in the purification of refinery wastes. This experiment was conducted in a plant scale pressure flotation unit. They concluded that both chemical autoxidation and stripping were operative in the experiment on whole wastes under the condition employed and that the biological activity played a minor role in reducing the COD. The supporting evidences they found were an increase of the concentration of hydroperoxides which are one of the primary products of many autoxidation reactions and the subsequent decrease of the hydroperoxides concentration due to stripping.

Whenever the stripping of volatiles from the aeration tank is mentioned, the related air pollution and the health hazards to the treatment plant personnel can not be overlooked. Ledbetter (7) reviewed the air pollution aspects of aerobic waste water treatment processes. It is his conviction that the offensive odor prevailing in the

neighborhood of aerobic waste water treatment plant was due to the volatilization of complex organics and intermediate derivatives.

Fundamental Theory of Stripping

Stripping has been defined by Haney (8) as "negative adsorption". Adsorption is defined as addition of gas to liquid. In other words, stripping involves removal of gases from the liquid. Eckenfelder, Kleffman, and Walker (9) defined stripping as a process of mass transfer from the liquid phase to the gas phase.

Haney (6) has done an excellent review on the aeration theory. In his review, he covered the two film theory which is now the most recognized and accepted theory. The two film theory assumes that at the interface between a gas and a turbulent liquid there exists a thin film of gas and another of liquid. Gases pass through these films from either direction by the relatively slow rate of molecular and eddy diffusion caused by the concentration difference of the gases studied. A fundamental equation for gas adsorption is given by Lewis and Whitman (10),

$$\frac{1}{A} \left(\frac{dW}{dt} \right) = k_L \left(C_i - C_L \right)$$
$$= K_g \left(P_g - P_i \right) \tag{2}$$

For most hydrocarbons which are only sparingly water soluble and have high value of Henry's constant, the transfer rate is controlled by the liquid phase. Similarly, for solvents having high water solubility, the transfer rate is controlled by the gas phase. The equation describes the rate of gas release is given by Haney (6),

$$-\frac{dC_t}{dt} = k_L \times 10^{-6} \left(\frac{A}{V} \right) \left(C_t - C \right) \tag{3}$$

where k_L is the transfer coefficient through the liquid film (cm/hr).
A final applicable gas release equation after integrating Eq. 3 is given as follow:

$$\log_{10} \left(C_t - S \right) = -k \left(\frac{A}{V} \right) t + \log_{10} \left(C_o - S \right) \tag{4}$$

where $k = \dfrac{k_L \times 10^{-6}}{2.303}$

Haney also indicated that factors influencing the rate of gas exchange include temperature, extent of agitation, film thickness, gas partial pressure, and depth of basin.

Stripping Kinetics of Volatile Organic Compounds in Batch Studies

Eckenfelder, Klefman, and Walker (9) investigated gas film stripping studies on solvents and mixtures of solvents. Their study was conducted in one-liter cylinders in a temperature controlled water bath. Reduction in solvent concentration was measured using a modified COD method. Based on Eq. 4, the methodology employed in their study for analyzing data was to calculate the rate constant K by plotting the logrithm of COD remaining in the aqueous phase against the time of operation. An assumption was made in the calculation that the equilibrium concentration at the interface is negligible with respect to the concentration in the bulk of solution, i.e., $\log(C_t) = -Kt$. The primary

variables influencing the rate of solvent stripping investigated in their experiment were temperature, the ratio of interfacial area to liquid volume, and the physical and chemical nature of the solvent. They found that the transfer coefficient K increased exponentially with increasing temperature. The K value for methyl-ethyl-ketone (MEK) at an air flow rate of 200 - 300 cc/min/l increased from 0.06/hr to 0.18/hr when the temperature was increased from $20^{\circ}C$ to $60^{\circ}C$. It was concluded that the increase in transfer coefficient correspondingly represent the increase in gas-liquid interfacial area. They also found that the relationship between the transfer coefficient and air flow rate could be described by the equation $K = C Q^{n}$ where K is the overall transfer coefficient, C is a constant depending on the solvent investigated and the temperature, Q is the air flow rate, and n is a function of the physical aspect of the equipment. In their studies conducted on pure solvents n was 0.35, and those on mixed chemical waste n has a value of 0.15. For mixed solvent solutions, they concluded that the overall COD reduction depends on the rate of removal of the least volatile component. A conclusion was also made that reduction in K is largely due to changes in viscosity and surface tension in the solution which create interfacial diffusion barriers, reduce the bubble size generated and reduce the rate of interface renewal.

Some of the basic considerations requiring experimental proof for use in studying the stripping of volatile waste compounds have been presented by Engelbrecht, Gaudy and Cederstrand (11). They employed a vertically placed 48-in high Lucite tube having an inside diameter of foru inches and containing eight liters of liquid. The kinetic expression used by these authors was in line with those detailed by

Haney (8) which was described previously. COD was used as the parameter for evaluating the stripping of transfer constant for acetone and butanone from observed data with different air flow rates, different initial concentrations, and inorganic salts necessary for biological treatment. It was found that both acetone and butanone were stripped in accordance with first order kinetics. An arithmetic relationship was developed between the transfer coefficient and unit air flow rate. Using their notation, the relationship was described as follow:

$$K_a = K_{ao} + R Q_o \qquad (5)$$

where R is the slope of the line or rate of change in the removal constant K_a with respect to unit air flow Q_o. The theoretical intercept on the K_a axis, K_{ao}, respresents the removal constant due to mixing alone in the absence of diffused aeration. K_{ao} is a function of temperature and physical characteristics of the system, and has been proven by these authors to be experimentally attainable. This linear expression contrasted to the exponential function derived by Eckenfelder, et al (9). However, it was concluded that both expressions can be practically applied in engineering field. It was also concluded that initial concentration of compounds has no effect on K_a.

Gaudy, Engelbrecht, and Turner (12) examined other compounds and considered factors affecting the course of stripping process. They carefully compared the applicability of exponential and mathmetical stripping models. The observed data indicated that it can not be assumed that all volatile compounds will be stripped according to first order kinetics. Autoxidation was suspected to be the reason for this phenominon. These authors felt that the emperical expression,

Eq. 5 is a more generally applicable relationship than the expression $K_a = C Q^n$ in studying the joint action of stripping and biological activities. They concluded that temperature, unit air flow rate, and tank geometry are three factors most prominently affecting the stripping of a specific volatile compound.

Gaudy, Turner, and Pusztaszeri (13) also studied the removal of acetone and butanone by running experiments in the Warburg apparatus where biological activity was the only removal mechanism, and in an activated sludge aeration tank where both biological metabolisms and physical stripping were involved. The basic kinetic assumptions as stated by the authors were

1. The kinetic order for both stripping and biological removal remains constant at all substrate concentrations.
2. The numerical value of the kinetic constant is the same for all substrate concentrations.
3. As a corollary to 1 and 2 the kinetics of both mechanisms of substrate removal operate entirely independently to each other. (p. 76)

Two kinetic expressions were developed by these authors. First, assuming both stripping and biological substrate removal follow first order kinetics, the substrate remaining in the system at any time is

$$- \frac{dC}{dt} = (K_a + K_{b1}) C$$

and its integration is

$$C = (C_o) e^{-(K_a + K_{b1}) t} \tag{6}$$

Second, assuming stripping follows first order kinetics and biological removal follows zero order kinetics, the rate of disappearance of the substrate is

$$- \frac{dC}{dt} = K_a C + K_{bo}$$

and its integration is

$$C = C_o \left(e^{(K_a t)} \right) + \frac{K_{bo}}{K_a} \left(e^{(-K_a t)} - 1 \right) \qquad (7)$$

With carefully designed experiment procedures and apparatus, the authors were able to attain representative biological removal constants which are either first order or zero order kinetics. Combining the biological removal rate constants determined in their study and the rate constants for stripping determined in separate studies into either equation 6 or 7, the authors plotted a theoretical curve along with the data obtained from the dual removal system. Their results showed that the removal of acetone and butanone in an activated sludge aeration tank due to both stripping and biological metabolism can be predicted very well by equation 7 when the substrate concentration is not lower than the residue concentration.

Stripping Kinetics of Volatile Compounds
in Continuous Flow System

The stripping studies reviewed so far were all conducted in batch systems. Goswame (14) studied the stripping constant obtained from both batch and continuous flow systems. By using batch studies, he was able to predict the amount of substrate stripped in continuous activated sludge system. For continuous flow system, the rate of change of volatile compound was expressed as follow:

$$V \left(\frac{dS}{dt} \right)_R = F S_i - F S_e - \left(\frac{dS}{dt} \right)_s V$$

where $\left(\frac{dS}{dt} \right)_s$ followed a first order kinetics. Therefore, $\left(\frac{dS}{dt} \right)_s$

equals to $K_a S_e$. At steady state, $(\frac{dS}{dt})_R$ equals to zero. If S_i and S_e are known, the stripping constant can be determined as follow:

$$K_a = \frac{(S_i - S_e) F}{S_e V} \qquad (8)$$

If k_a is known, the substrate concentration in the aeration tank can be predicted from the same equation as follow:

$$S_e = \frac{S_i F}{K_a V + F}$$

Furthermore, the author concluded that the stripping constants obtained from batch and continuous flow operation were the same as long as these two systems have the same aeration volume, unit air flow, and aeration tank (where tank geometry does not affect the results).

Freeman, Schory, Klieve, and Archer (15) recently studied the rate of stripping of acrylonitrile for both sterile and seeded activated sludge systems. They used three continuous-flow bench-scale biological reactors which were designed to operate at 50 %, 100 %, and 150 % recycle rates. By varying the dissolved oxygen content in the seeded activated sludge reactor from 1 mg/l to 4 mg/l, they found that acrylonitrile concentration in effluent samples was below detection level (0.5 mg/l). These systems were then maintained at a DO content of 2.0 mg/l through the entire experiment period. The air and liquid samples were collected at the same time. The concentration of acrylonitrile was found below the detection limit in both cases. It was concluded that 99.96 % of acrylonitrile can be removed by activated sludge system. In addition to this, the possibility of formation of polyacrylonitrile was also tested. A negative result was found, which indicated that acrylonitrile was only biologically degraded. They

also found that 18 % of acrylonitrile entering the sterile reactor was stripped.

Recently, Pellizzari and Little (16) developed an analytical method for the analysis of volatile priority pollutants in airstreams passing through wastewater using a Tenax GC cartridge in conbination with gas chromatography/masspectrometry/computer. Their study is very similar to that conducted in this work. It is of particular interests to study and describe their work in detail. A sampling system was designed and field tested for sampling airstreams passing through grit chambers and activated sludge systems. Recovery of the volatile priority pollutants was accomplished by thermal desorption, purging with helium into a liquid-nitrogen-cooled nickel capillary trap, and introducing the vapors onto a gas chromatographic column, where they were separated from each other. Characterization and quantification of the priority pollutants was accomplished by mass spectrometry using mass fragmentography. The areas of investigation included (a) recovery studies of priority pollutants from distillwater, raw wastewater and activated sludge using laboratory-simulated conditions, (b) a methods-of-addition study for priority pollutants in raw wastewater and activated sludge, and (c) the application of the developed methods for the analysis of priority pollutants in air surrounded raw wastewater and activated sludge treatment system.

The percent recovery of priority pollutants from deionized-distilled water was conducted by using three different vessel configurations. Two of these vessels permitted the water to be circulated in a manner similar to aeration ponds at municipal treatment plants. A third vessel was used; in this case a sintered glass frit created a fine

bubble dispersion of the air stream as it passed into the liquid column. The standard solution of priority pollutants were prepared in methanol and added to distilled water to produce the desired final concentration. Purging of the airstream through these three vessels was conducted using an air/liquid volume ratio of two to one. The rate was 80 ml/min. The percent recovery of some selected priority pollutants is shown in Table I.

TABLE I

PERCENT RECOVERY OF PRIORITY POLLUTANTS FROM
DEIONIZED-DISTILLED WATER

priority pollutant	vessel-1	vessel-2	vessel-3
1,2-DICHLOROETHANE	79± 7	84± 8	83± 7
1,2-DICHLOROPROPANE	84± 8	66±20	94±16
1,2-DICHLOROBENZENE	33± 2	47±13	69± 2
ACRYLONITRILE	47± 9	37± 9	42±11
ACROLEIN	40± 5	41±13	36± 3
BENZENE	115±27	ND	103± 8

In general, the vessel with glass frit (vessel 3) gave the highest recovery. The authors found a trend that those compounds which have lower vapor pressures also subsequently have lower recoveries. Furthermore, those compounds which were water soluble were difficult to purge from the aqueous medium.

They also studied the percent recovery of priority (purgeable) pollutants from raw wastewater and activated sludge for three different

wastewater treatment plants. It was concluded that generally the
recoveries of priority pollutants from raw wastewater decreased as the
level of the added priority pollutants decreased. The recoveries of
priority pollutants from the activated sludge generally were lower than
those from the raw wastewater.

Results of the methods-of-addition study for priority pollutants
in raw wastewater and activated sludge indicated possible sorption of
the priority pollutants to organic solids. The authors suggested that
it is difficult to extrapolate from airstream concentration in the raw
wastewater using percentage recoveries.

Houel, Pearson, and Selleck (17) studied the removal of chloroform
by air stripping in a contercurrent stripping tower to meet the
requirement for public drinking water supplies. Their results showed
that with an initial concentration of 834 ug/l, 97.5 % to 99.98 % of
chloroform was removed. Concerned with the health risk due to the
removal of volatile organic compounds by air, they concluded that the
concentration of chloroform in the exausted air was lower than the
EPA and OSHA's limitation.

Singly, Ervin, and Williamson (18) have done a study on the
stripping of chlorinated organic compounds in water. It was indicated
that the minimum air to water ratio (l/l) for reduction of chloroform
at 25°C to 50 ug/l from any initial concentration higher than 400 ug/l
is 5 l/l to 6 l/l. The same ratio for reduction of 1,2-dichloroethane
and cis-1,2-dichloroethante at 25°C to 0.5 ug/l when the initial
concentration was higher than 10 ug/l were 18 l/l and 3 l/l respectively.

Background of Priority Pollutants

In this work, the compounds studied are all listed as priority pollutants by the EPA except ethyl acetate. Most of them are purgeable compounds. It is of interests to have some idea about the historical development and the characteristics of the priority pollutants. Keith and Telliard (19) have presented an detailed review on the historical origins of the EPA's priority pollutants. Resulting from the "EPA Consent Decree" EPA was required to publish a list of toxic pollutants which technology-based effluent limitation and guidelines would be required for. After a period of discussion, some criteria were employed to prioritize and to select specific representative compounds for each classified toxic group. These criteria are (1) all compounds specifically named in the Toxic Pollutant List were automatically included, (2) all compounds except those listed as Toxic Pollutant were considered if they were found with a frequency of greater than five percent of the total known listings for that class of compounds, (3) chemical production data was used as a guide when they were available. Finally, 129 compounds were named as priority pollutants and they were divided into nine groups: metals, asbestos, total cyanides, pesticides, acidic extractable compounds, basic extractable compounds, neutral extractable compounds, total phenols, and purgeable compounds.

CHAPTER III

MATERIALS AND METHODS

Treatment of Stripable Compounds by Stripping and

Biological Degradation in Continuous

Flow Reactors

Experimental Apparatus

The continuous flow reactor used in this study shown in Figure 1
is made of stainless steel. The system is composed of aeration and
sedimentation compartments with internal recycle. A baffle between
these two compartments was used for adjusting the internal recycle rate
of biological solids. Both compartments have a stainless steel cover.
The activated sludge reactor (aeration compartment) had two glass-made
diffusers and had a volume varying from 3.04 l to 3.26 l. The settling
compartment had a volume of 3.23 liters. The synthetic wastewater was
pumped from a scaled 55 liters tank by Milroyal D controlled volume
pump. The elevation of entire system was arranged so that the flow of
wastewater was driven only by pumping and not by gravity.

All continuous flow experiments were conducted at a nominal
hydraulic detention time of eight hours (dilution rate 1/8 hr^{-1}), and at
a feed flow rate of 6.25 ml/min. Aluminum tube was used instead of
traditional tygon tube to eliminate the possibile chemical reactions
between specific compounds and tygon tube. The feed line was cleaned

every day to prevent in-line contamination by using 2 % (by volume)
chlorox solution. The 55-liter feed tank was cleaned with cleaning
solution every other day. Compressed air was supplied at a rate varying
from 1.5 l/min to 2.5 l/min. The air flow rate was measured by Bendix
flow meter.

The apparatus used for off-air sampling is also shown in Figure 1.
The off-air trap was made of a 1/8 inch stainless steel tube packed
with six inches of Tenax and four inches of silica gel. On the cover
above the aeration compartment, there were four openings. Two of them
were used for connecting air compresser to air diffusers. One was used
as influent port. The other one was used for off-air sampling. During
the operation of off-air sampling, the slit between the cover and
compartment was not sealed. The slit was used as an opening for excess
aeration air to escape when the opening on the cover was used for air
sampling. The pressure produced by compressed air is larger than that
of atmosphere, therefore, the atmosphere air can never mixed with the
air inside aeration compartment. Thus, air samples were ensured from
containing any foreign air from atmosphere. Constituents of the
synthetic wastewater are listed in Table II.

TABEL II

CONSTITUENTS OF BASE MIX

ethylene glycol	113.0 mg/l	phosphoric acid	15.74 mg/l
ethyl alcohol	113.0 mg/l	Salts	
glucose	113.0 mg/l	$CaCl_2$	8.0 mg/l
glutamic acid	113.0 mg/l	$MnSO_4$	8.0 mg/l
acetic acid	113.0 mg/l	$FeCl_3 \cdot 6H_2O$	0.4 mg/l
phenol	22.6 mg/l	$MgSO_4 \cdot 7H_2O$	80.0 mg/l
ammonium sulfate	100.0 mg/l		
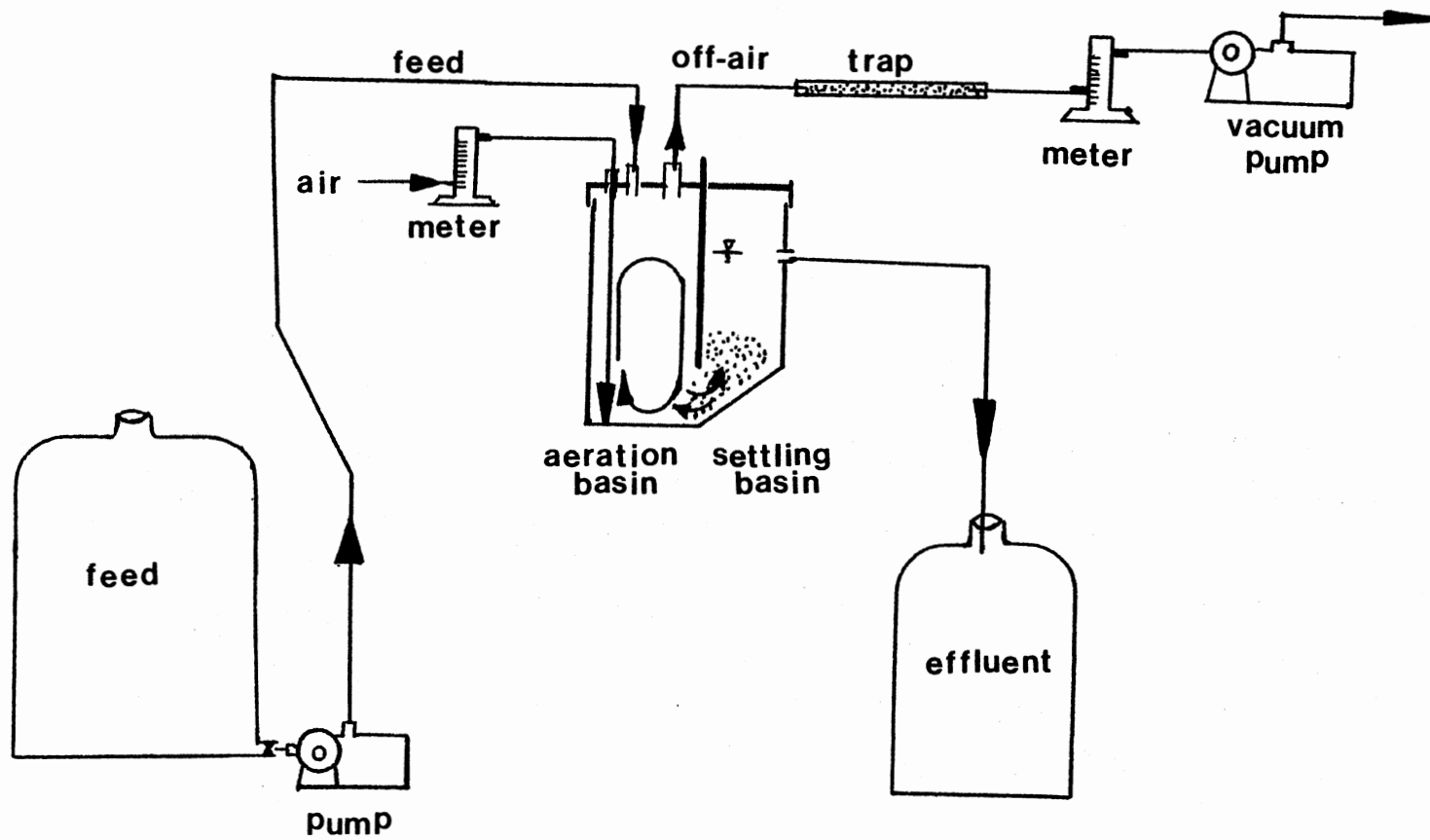
Figure 1. Schematic Diagram of Laboratory Scale Activeted Sludge Unit With Off-Air Sampling Device

Operation Procedures

To initiate the system, biological suspended solids obtained from the domestic sewage treatment plant at Ponca City, Okalhoma, was trans- fered into the reactor and fed with full strength base mix. The systems were maintained at three different sludge ages, 2, 4, and 6 days. After one week of acclimation, a specific priority pollutant was gradually added into the system. Ideally, the amount of specific compound should be added gradually in two weeks up to a point where the specific compound contributes 75 % of chemical oxygen demand of the feed sloution. However, it happened sometimes that low maximum solubility prohibited the compound from disolving to such extent. In such case, the maximum solubility was applied. For low solubility compounds, such as 1,2-dich- lorobenzene, a stirrer was employed in order to ensure complete disolution. Since volatile compounds were subject to stripping when exposed to stirring, the duration of stirring was fixed so that the specific compound concentration would not vary.

Samples for specific compound analysis were taken from the feed and effluent once every week for an eight week period. To avoid volatilization, liquid samples were collected in 100 ml bottles without any void space. The duartion of collecting off-air samples varied from one to two hours depending on the stripability of each compound. Vacuum rate was set at 20 ml/min for maintaining a moderate air flow through the packing materials.

Treatment of Stripable Compounds by Stripping

Alone in Continuous Flow Reactors

The system employed was exactly the same as the stripping and
biological degradation system except that no biological solids was
introduced into the system and that the feed consisted of only one
specific compound at a nominal concentration of 300 mg/l with no base
mix. The inflow rate was set at 6.25 ml/min. Since there was no
biological solids in this system, volume of the whole system in terms
of dilute-in was 6.23 liters; 3.0 liters of aeration compartment and
3.23 liters of settling compartment. This volume was apparently greater
than that of biological system. Therefore, the detention time was
accordingly larger and was 17.6 hr^{-1}. Although a baffle was seating
between compartments, the reactor was still applicable to meet the
required dilute-in characteristics. This was demonstrated by the result
obtained from running the dilute-in test of phenol as shown in Figure 2
and Figure 3.

Operation Procedures

To initiate this experiment, the stripping reactor was filled with
distilled water. The baffle was adjusted as it had been usually set in
biological units, i.e., about one-half to 3/4 inch. Feed was pumped
into the reactor at a rate of 6.25 ml/min. Effluent samples of dilute-
in test were collected directly from the effluent tube every two hours
during the first forty-eight hour period, then every three or four
hours during the next forty-eight hour period. Feed samples were
analyzed at times to check if the concentration was consistent. Total

organic carbon analysis was employed for developing the dilute-in curve. Based on the dilute-in curve, the time needed for reaching steady state and the amount of compounds removed by stripping can be determined. After the system had reached steady state, off-air, influent and effluent samples were collected at the same time for specific compound analysis.

Dilute-In Test

A theoretical dilute-in equation has been developed by Komorit and Gaudy (20),

$$C_t = C_o \left(1 - e^{-Dt} \right) \tag{9}$$

where C_t = conc. at time t (mg/1)

C_o = initial conc. (mg/1)

D = dilution rate (hr^{-1})

t = time (hr)

As demonstrated in Figures 2 and 3, the tank geometry and air diffusers applied in this study performed very well in terms of complete mixing. By comparring theoretical curve with experimental curve, the amount of compound stripped can be easily determined. From equation (9), the following experssion was derived,

$$\ln \left(1 - \frac{C_t}{C_o} \right) = -D\, t \tag{10}$$

If a volatile compound is partially stripped, the dilution rate (D) will be smaller than the theoretical D value. If the compound is completely stripped, the D value will be zero. Steady state can also be determined
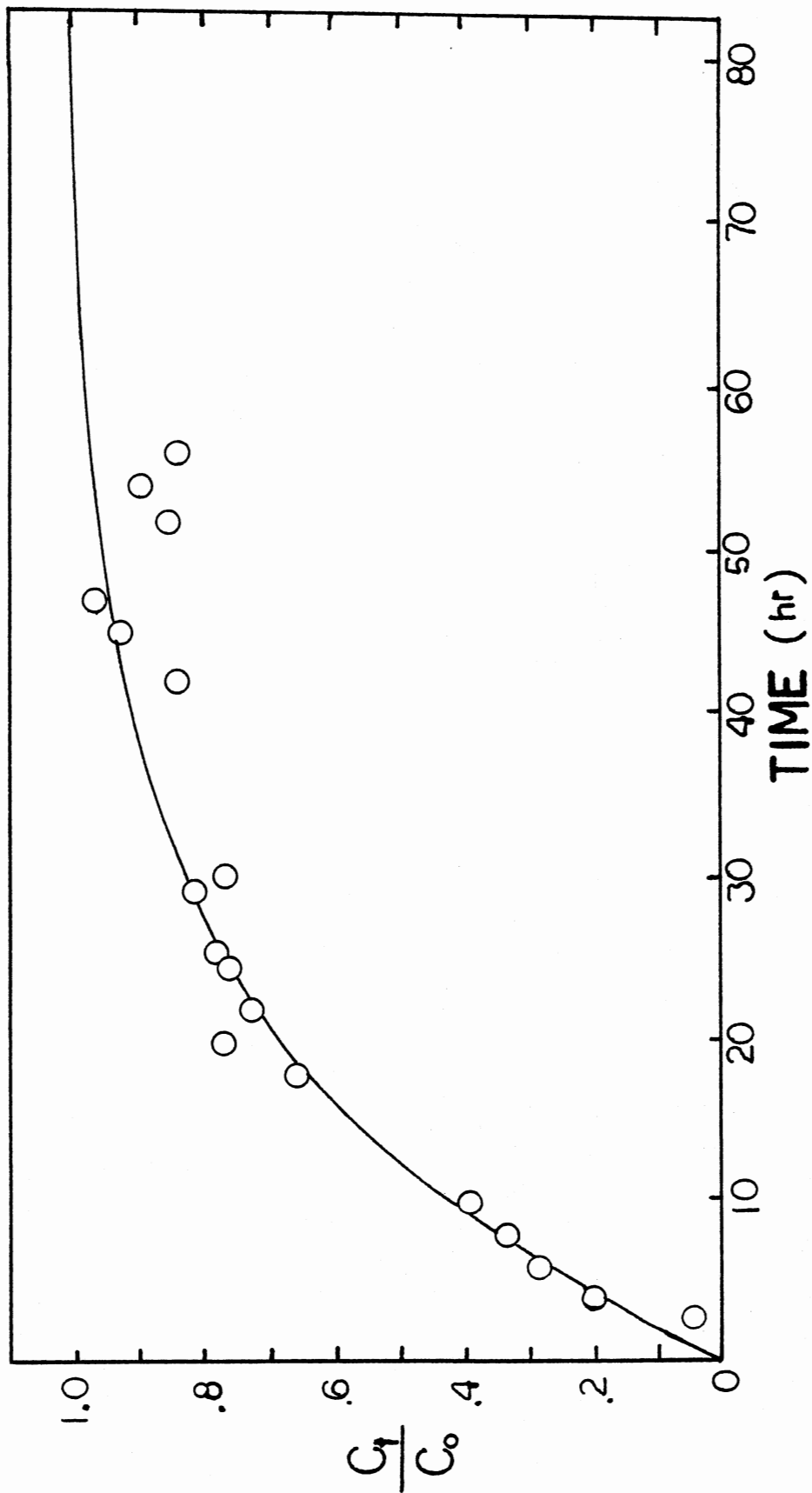
Figure 2. Dilute-In Cruve of Phenol Based on TOC Analysis
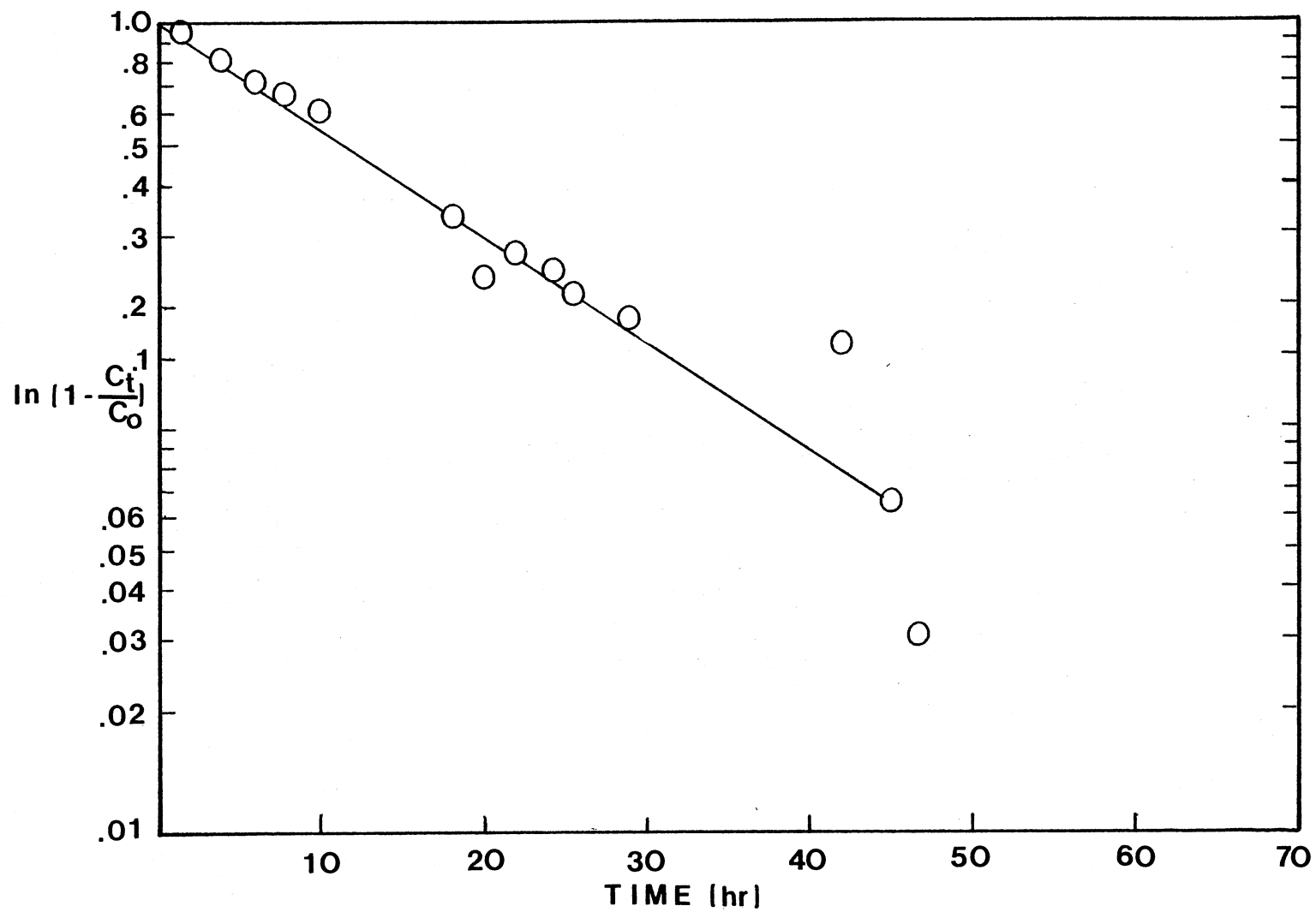
Figure 3. Semilog Plot of Dilute-In Test of Phenol

by this experiment. When the effluent concentration of the stripping unit do not change with time, the system is said to be at steady state.

Gas Chromatograph Analysis

In this study particularly dealing with stripable compounds, a purge-and-trap device (Tekmar, Liquid Sample Concentrator, Model LSC-1) was connected to the gas chromatograph instrument. The whole system is shown in Figure 4. The instrument employed was F&M Scientific Corporation Model 810. A 25 ml liquid sample was introduced into a glass holder. This sample holder has a porcelain sieve which breaks carrier gas into fine bubbles. After sample holder had been tighlty connected to purging line, the liquid sample was purged by passing carrier gas through the sample for 12 minutes. In this experiment, the carrier gas was nitrogen. For desorbing the compound absorbed in the trap, the heating element surrounding the trap was turned up to a temperature higher than the boiling point of the compound investigated.

Traps filled with off-air sample were connected directly onto the purge-and-trap line for GC analysis. Specific conditions of each compound for GC analysis are listed in Table III. A computerized integrater was also employed which can print out directly the detention time and area corresponding to compounds analyzed.

Mass Balance

A mass balance for the activated sludge system can be described as follow:

$$V \left(\frac{dS}{dt} \right)_R = F S_i - F S_e - V \left(\frac{dS}{dt} \right)_r \qquad (11)$$
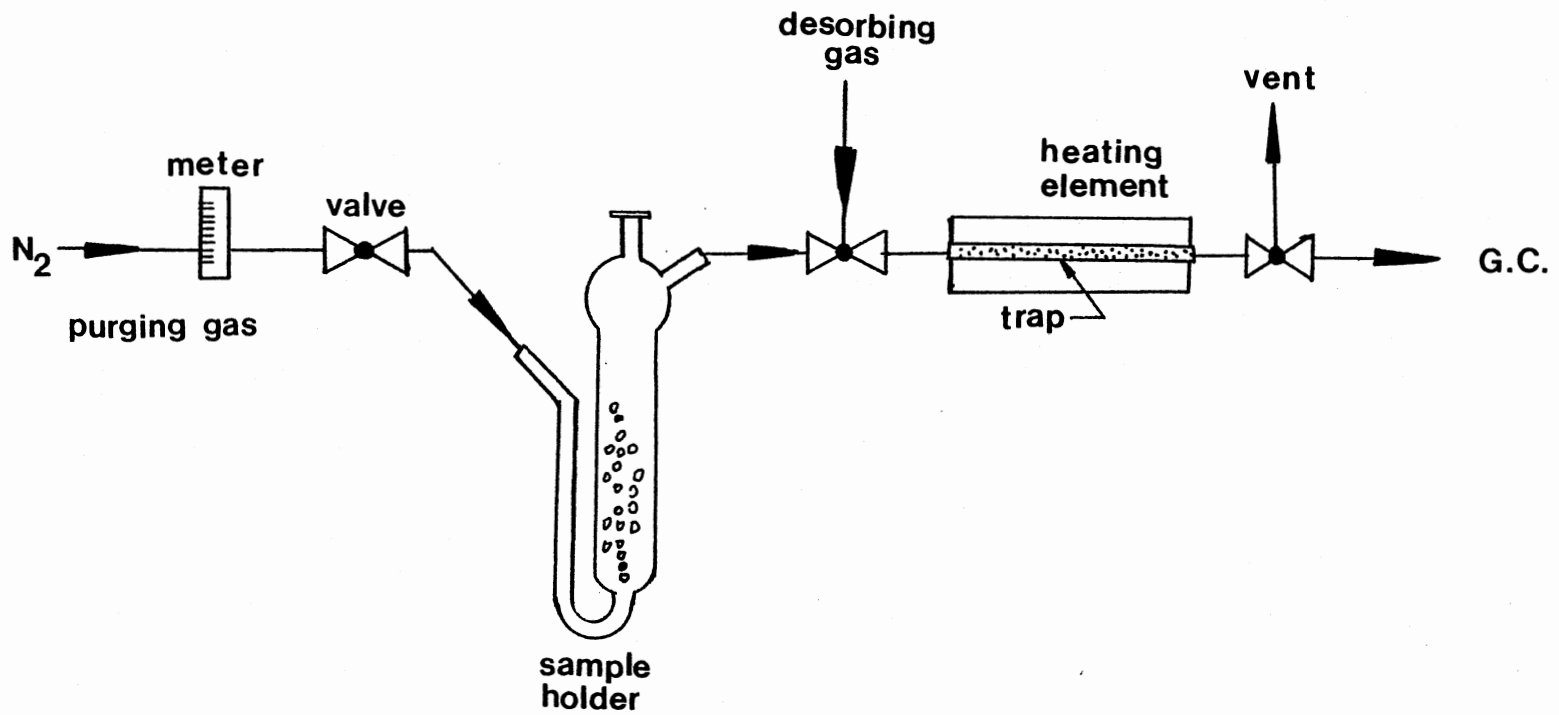
Figure 4. Schematic Diagram of Purge-and Trap System Connected to GC Instrument

TABLE III

SPECIFIC CONDITION FOR GC ANALYSIS OF EACH COMPOUND

Compound	PURGE-AND TRAP		GAS CHROMATOGRAPHY				
	Desorb Temp °C	Carrier Gas ml/min	Separation Column	Oven Temp °C	Detector Temp °C	Inject Port °C	Carrier Gas ml/min
Acrolein	175	60	50/80 mesh poropack N	90	260	130	20
Acrylonitrile	175	60	50/80 mesh poropack N	90	260	130	20
1,2-Dichloropropane	175	60	50/80 mesh poropack N	90	260	130	20
Benzene	175	60	chromosorb & carbowax	120	260	130	20
Methylene Chloride	150	60	chromosorb & carbowax	153	375	130	20
Ethyl Acetate	90	60	chromosorb & carbowax	90	260	283	20
1,2-Dichloroethane	150	60	poropack	105	270	220	20
Phenol	190	60	SP 1240 DA	70	260	260	40
1,2-Dichlorobenzene	150	60	1% SP 2250	75	260	260	15

where $(\frac{dS}{dt})_R$ = rate of change of specific compound in reactor

S_i = specific compound in influent

S_e = specific compound in effluent

$(\frac{dS}{dt})_r$ = specific compound removed totally

Furthermore, $(\frac{dS}{dt})_r$ can be broken into two parts, $(\frac{dS}{dt})_s$, substrate removed by stripping, and $(\frac{dS}{dt})_b$, substrate removed by biodegradation.

The term "recovery" (from air at steady state) used through this study was defined as follow:

$$\text{recovery} = \frac{(\frac{dS}{dt})_s}{(\frac{dS}{dt})_r}$$

$$= \frac{(\frac{dS}{dt})_s}{FS_i - FS_e} \tag{12}$$

CHAPTER IV

RESULTS AND DISCUSSION

Treatment of Stripable Compounds by Stripping
Alone in Continuous Flow Reactors

All physical stripping experiments were conducted in a continuous
flow unit with a volume of 6.23 liters. The detention time averaged
17.6 hours (dilution rate 0.0568 hr^{-1}) varying from 16.2 to 17.9 hours.
The influent flow rate was approximately 6.0 ml/min varying from 5.8
ml/min for one compound to 6.4 ml/min for three of the compounds. The
air flow varied from 1.5 l/min to 3.0 l/min. The feed concentration of
each compound is shown in Table IV. Due to the stripability and
solubility of these compounds, the nominal feed concentration, 300 mg/l
was not easily acheived and it varied from 72.0 mg/l for 1,2-dichloro-
benzene to 362 mg/l for phenol. Temperature was not controlled but it
was always in the range of 20°C to 25°C.

The theoretical dilute-in curve without any removal mechanism
involved and the experimental dilute-in curve with stripping in the
continuous flow reactors are shown in Figure 5 to Figure 14.

Table IV gives the air flow rate, influent flow rate, average
value of the specific compound analysis, and recovery of the compound
from air. Table V gives the percentage of compound stripped based on
specific compound analysis and on TOC analysis.

TABLE IV

SPECIFIC COMPOUND MASS BALANCE OF NONBIOLOGICAL STRIPPING SYSTEMS

Compound	Aera-tion Rate 1/min	Inflow Rate ml/min	Inf. Conc. mg/l	Eff. Conc. mg/l	Off-Air Conc. mg/l$_{air}$	Inf. mg/min	Eff. mg/min	Off-Air mg/min	% Recovery from Air
ACRO	2.0	6.2	314.0	118.0	0.570	1.974	0.755	1.140	95.6
ACRYLO	3.5	6.0	241.0	58.0	0.039	1.446	0.348	1.356	123.5
1,2DCP	2.5	6.4	141.0	2.13	0.033	0.903	0.014	0.819	92.1
MC	3.0	5.8	342.0	2.0	0.073	1.984	0.012	2.110	107.0
BENZENE	2.75	5.8	236.0	1.9	0.045	1.369	0.011	1.125	92.1
EA	2.0	6.4	236.0	76.0	0.502	1.510	0.486	1.004	98.0
1,2DCE	2.0	6.0	275.0	10.8	0.484	1.650	0.065	0.967	61.0
PHENOL	2.0	6.0	362.0	355.0	0.0	2.172	2.130	0.0	-
1,2DCB	2.0	6.0	72.0	10.0	0.217	0.432	0.060	0.433	116.4

TABLE V

PERCENT OF PRIORITY POLLUTANTS STRIPPED IN NONBIOLOGICAL SYSTEMS

Compound	Based Upon TOC			Aeration	Based Upon Specific Compound Analysis		
	INF mg/l	EFF mg/l	% stripped	Rate l/min	INF mg/l	EFF mg/l	% stripped
Base Mix	312.5	257.3	17.66	2.5	–	–	–
Acrolein	208.0	86.0	58.65	2.0	314.0	118.0	62.42
Acrylonitrile	200.0	51.0	74.59	3.5	241.0	58.0	75.93
1,2-Dichloropropane	96.0	1.0	98.96	2.5	141.0	2.13	98.49
Methylene Chloride	49.0	1.0	97.96	3.0	342.0	2.0	99.42
Benzene	100.0	1.0	99.00	2.75	236.0	1.9	99.19
Ethyl Acetate	150.0 163.0	36.5 67.4	75.4 58.65	2.0 1.2	236.0 236.0	76.0 32.0	67.8 54.17
1,2-Dichloroethane	69.0	4.6	93.99	2.0	275.0	10.8	96.07
Phenol	230.0	203.0	0.0	2.0	362.0	355.0	1.93
1,2-Dichlorobenzene	44.0	1.0	97.73	2.0	72.0	10.0	86.11

Base Mix

Figure 5 shows the completely mixed dilute-in characteristics of base mix based on TOC at an aeration rate of 2.5 l/min. Base mix is composed of compounds required for microbial growth. In order to eliminate the interferance due to the presence of the microorganisms, the whole stripping system was sterilized before operation. As shown in Figure 5, no compound was removed until twenty-third hour. After the system reached steady state, 17.66 percent of total TOC was removed by stripping when compared with the theoretical dilute-in curve. GC analysis was not performed on this test because of the difficulties of detecting the multicomponents liquid sample.

Acrolein

Figure 6 shows the comparison of theoretical and stripping dilute-in curves of the nonbiological system. This figure clearly demonstrates the stripability of acrolein. At steady state, the average effluent concentration of acrolein was 86 mg/l TOC. Compared with the theoretical curve, 58.65 % of acrolein was removed by stripping at an air flow rate of 2.0 l/min. Off-air samples were taken during steady state with a vacuum pump rate of 20 ml/min for thirty minutes. By running specific compound analysis, the recovery of acrolein from air was found to be 95.6 % which indicates the capability of the absorbant (Tenax and silica gel) in the off-air sampling trap. This also indicates that no other interfer reaction was involving, such as oxidation, in the removal of acrolein. Referring to Table IV, it can be clearly seen that both
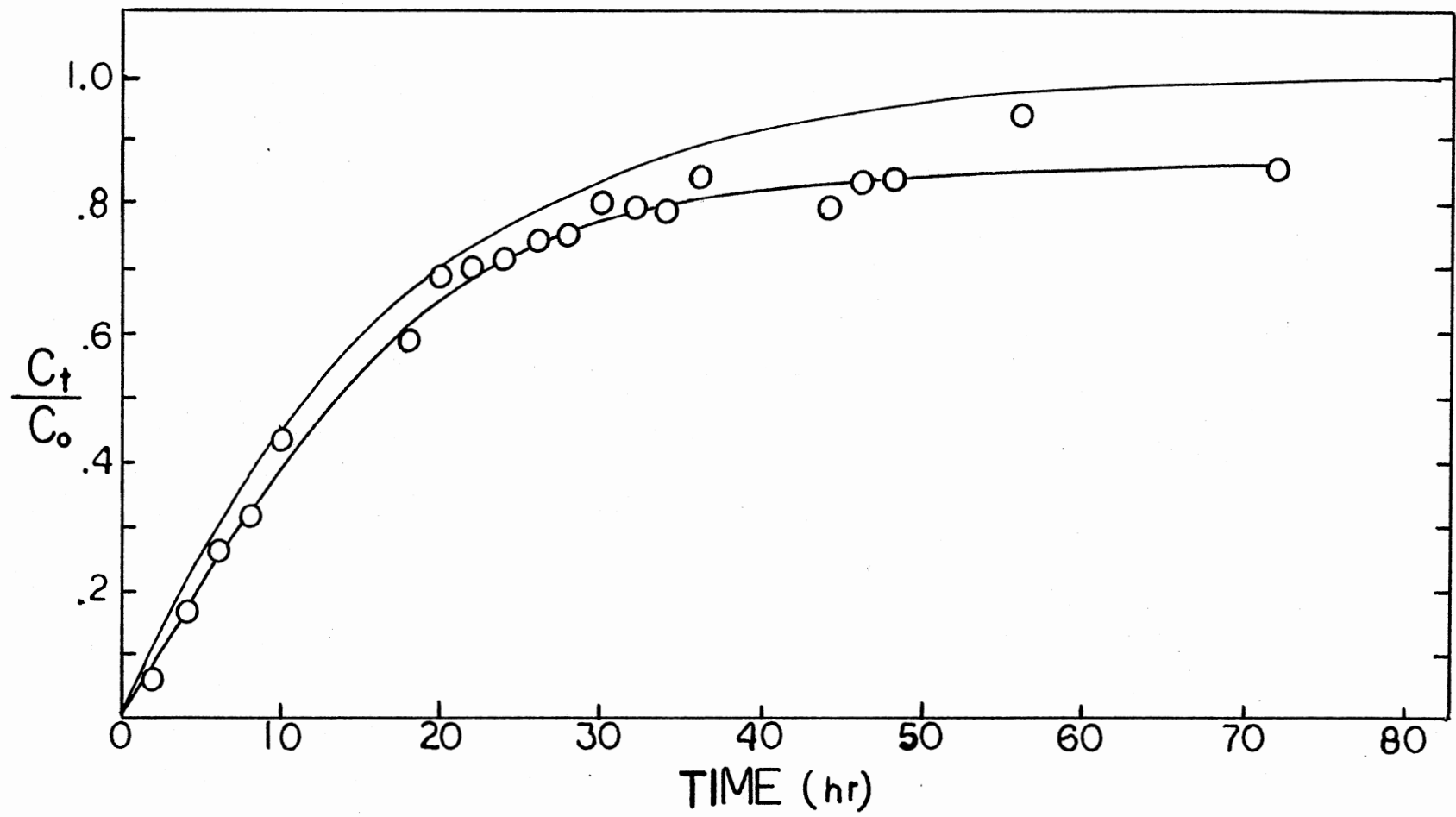
Figure 5. Completely Mixed Dilute-In Curve of Base Mix; Theoretical Curve Without Stripping and Experimental Curve With Stripping
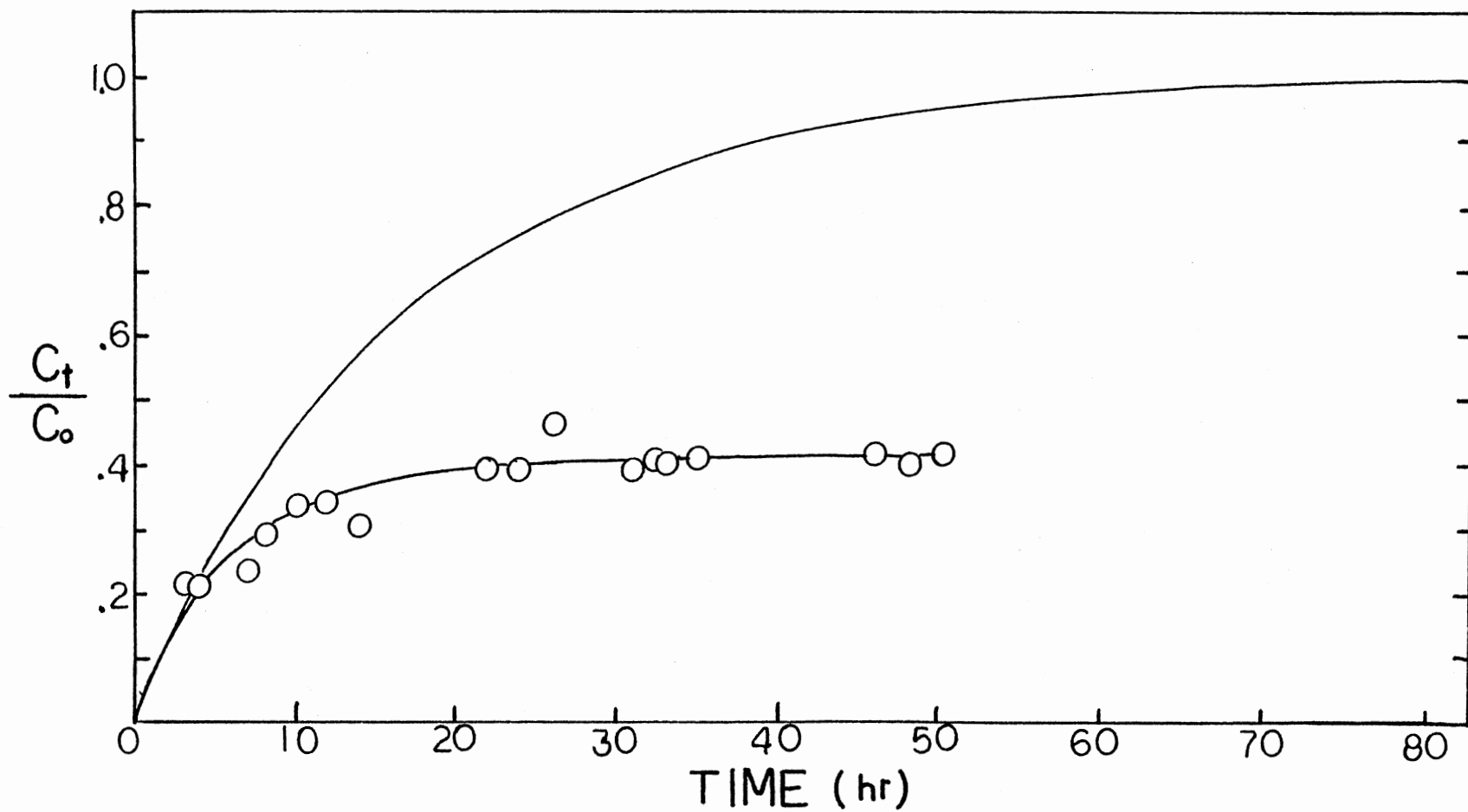
Figure 6. Completely Mixed Dilute-In Curve of Acrolein; Theoretical Curve Without Stripping and Experimental Curve With Stripping

parameters, TOC and specific compound analysis, are comparable with each other in terms of stripping efficiency.

Acrylonitrile

The continuous flow stripping system reached steady state at around the eighteenth hour as shown in Figure 7. As shown in Table V, the average effluent concentration at steady state was 51.0 mg/l TOC. This indicates 74.59 % of initial feed concentration was stripped at an aeration rate of 3.5 l/min. Acrylonitrile recovered from air samples was 123.5 % as shown in Table IV. In Tabel V, percentages of acrylonitrile stripped based on TOC and specific compound analysis were 74.59 % and 75.93 % respectively.

1,2-Dichloropropane

Figure 8 shows that 1,2-dichloropropane was stripped as soon as it was fed into the system. The effluent concentration of 1,2-dichloropropane was below the detection limit of TOC analyzer (1.0 mg/l). By running specific compound analysis, the effluent concentration was found to be 2.13 mg/l. More than 99 % of the compound was stripped based on TOC and 98.49 % of the compound was stripped based on specific compound analysis as shown in Table V. The off-air recovery given in Table IV was 92.1 %.

Methylene Chloride

Acting like 1,2-dichloropropane, methylene chloride was stripped from the liquid in the aeration tank as soon as it was fed into the system. Figure 9 gives the results obtained from dilute-in-stripping
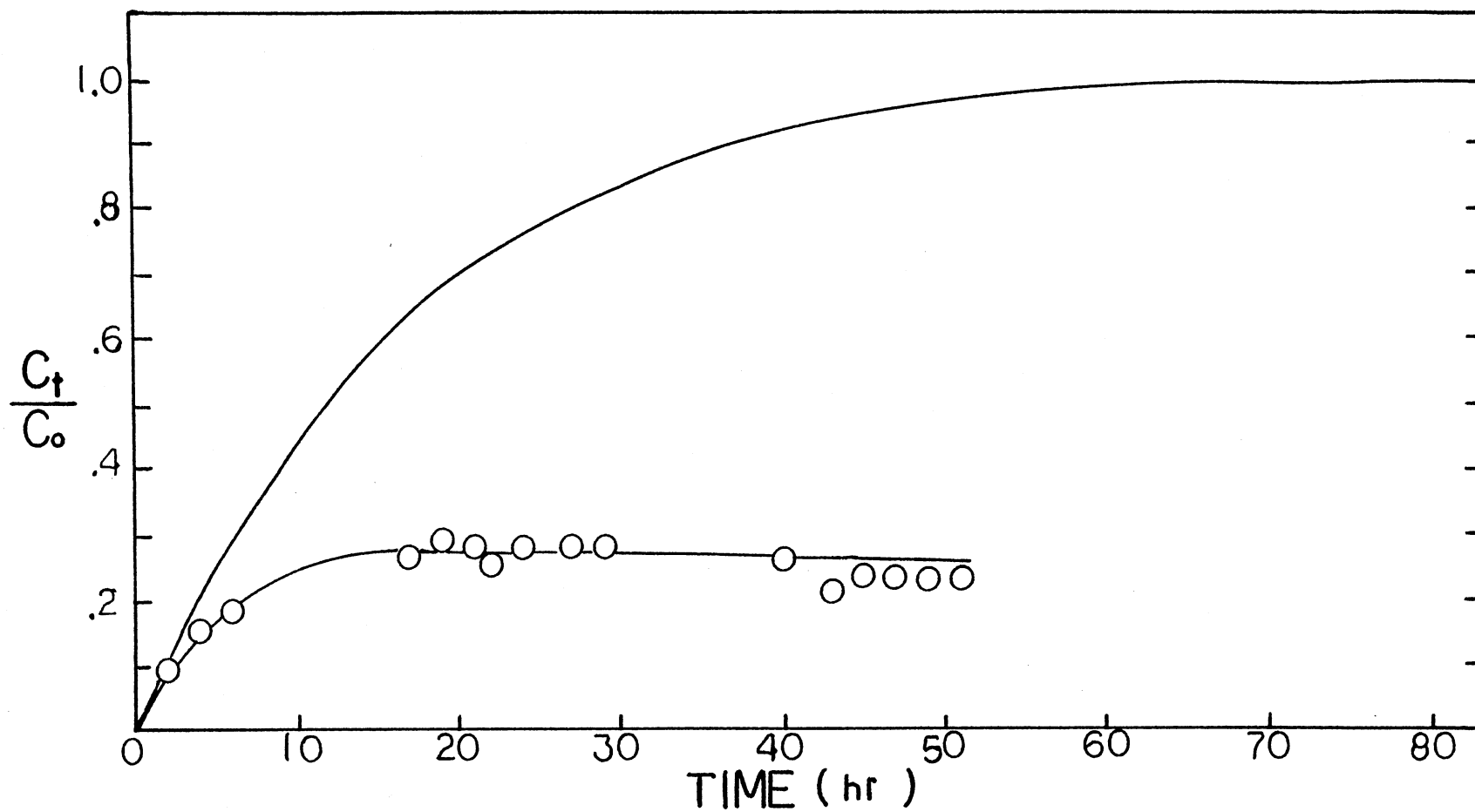
Figure 7. Completely Mixed Dilute-In Curve of Acrylonitrile; Theoretical Curve
Without Stripping and Experimental Curve With Stripping
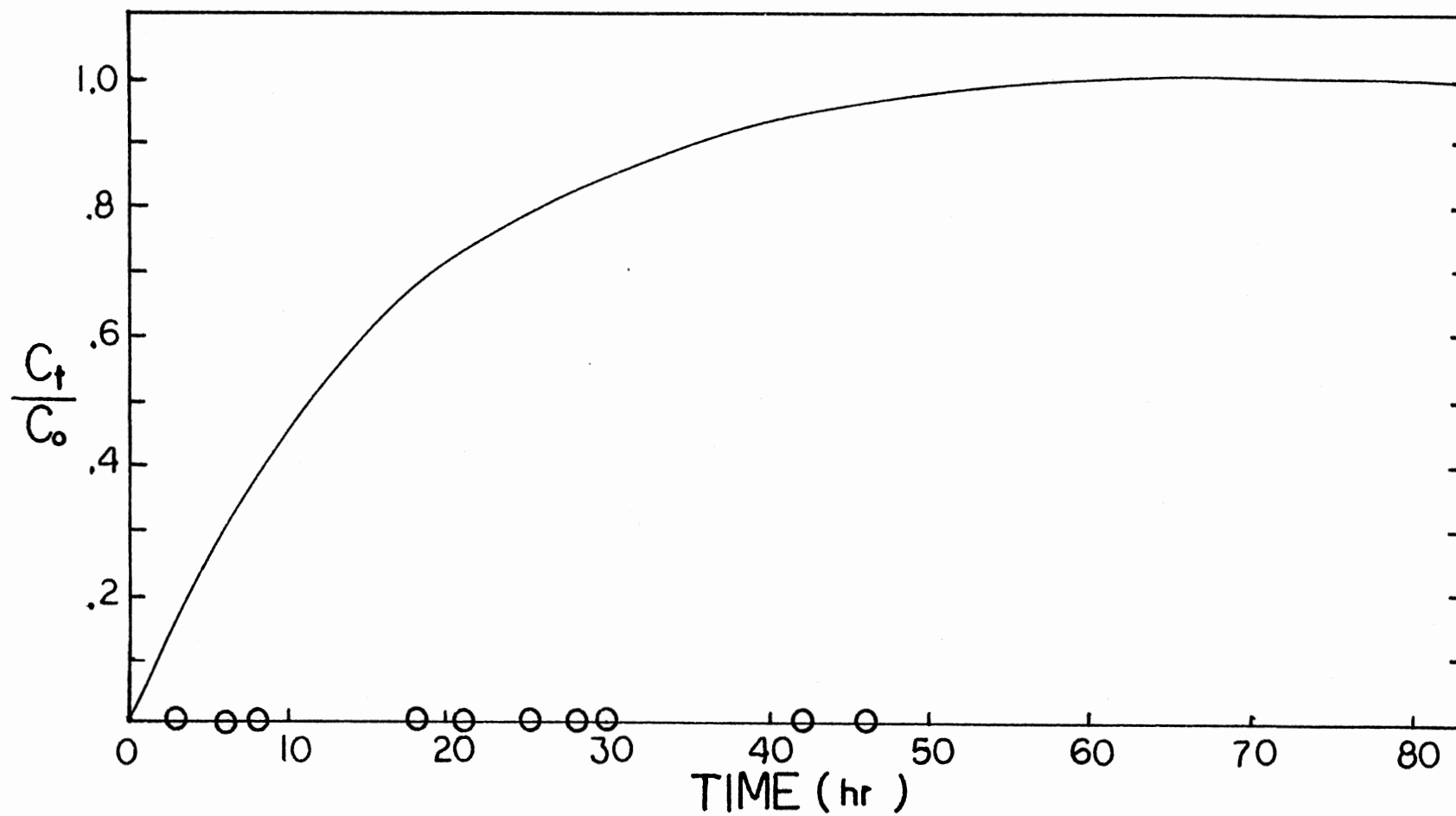
Figure 8. Completely Mixed Dilute-In Curve of 1,2-Dichloropropane; Theoretical Curve Without Stripping and Experimental Curve With Stripping

test. The concentration of methylene chloride in the effluent was below TOC detection limit. The overall TOC removal was greater than 97.96 %. Based on specific compound analysis, 2.0 mg/l of the compound was detected in the effluent and 99.42 % of the initial concentration was stripped at an aeration rate of 3.0 l/min. The recovery of methylene chloride from air was 107 %.

Benzene

Figure 10 indicates that benzene was also highly stripable. The benzene concentration in the effluent was less than 1.0 mg/l TOC. More than 99 % of initial TOC was stripped. Specific compound analysis showed that the effluent concentration was 1.9 mg/l. This result indicates that 99.19 % of benzene in the feed solution was removed as soon as it was pumped into the aeration tank at an aeration rate of 2.75 l/min.

Ethyl Acetate

Stripping tests at two different aeration rates were studied for the nonbiological continuous flow stripping reactor. Figure 11 shows the effect of aeration rates on stripability. At an aeration rate of 2.0 l/min, the system reached steady state at the fifteenth hour. The average effluent concentration during steady state was 36.5 mg/l TOC while the influent concentration was 150 mg/l TOC. This indicates that 75.5 % of the initial TOC was stripped. Based on specific compound analysis, 67.8 % of ethyl acetate was stripped. Recovery of the compound from air samples was 98 %.

Figure 9. Completely Mixed Dilute-In Curve of Methylene Chloride; Theoretical Curve
Without Stripping and Experimental Curve With Stripping

Figure 10. Completely Mixed Dilute-In Curve of Benzene; Theoretical Curve Without
Stripping and Experimental Curve With Stripping

Figure 11. Completely Mixed Dilute-In Curve of Ethyl Acetate; Theoretical Curve Without Stripping and Experimental Curve with Stripping at Two Different Aeration Rates

At an aeration rate of 1.5 l/min, the system reached steady state at the twentyninth hour. The average effluent concentration during steady state was 67.4 mg/l TOC while the influent concentration was 163.0 mg/l TOC. It indicates that 58.65 % of initial TOC was stripped. It is seen that more ethyl acetate is stripped at the higher aeration rate.

1,2-Dichloroethane

Figure 12 shows that the continuous flow system reached steady state at the fourth hour at an aeration rate of 2.0 l/min, and that 99.33 % of initial TOC in the influent was stripped. Specific compound analysis indicated that the recovery of 1,2-dichloroethane from air was only 61.01 %. However, the differences between observed concentration of 1,2-dichloroethane in the influent and effluent obtained from TOC analysis and specific compound analysis were very close; 93.33 % based on TOC and 96.06 % based on specific compound analysis of initial concentration was stripped.

Phenol

Phenol is not an easily stripable compound as shown in Figure 13. The observed data of continuous flow stripping system shows that the dilute-in curve fit very well to the theoretical curve. The aeration rate was 2.0 l/min. Specific compound analysis by GC also gave the same result. Both the influent and effluent have the same phenol concentration and nothing was detected from air samples at steady state.
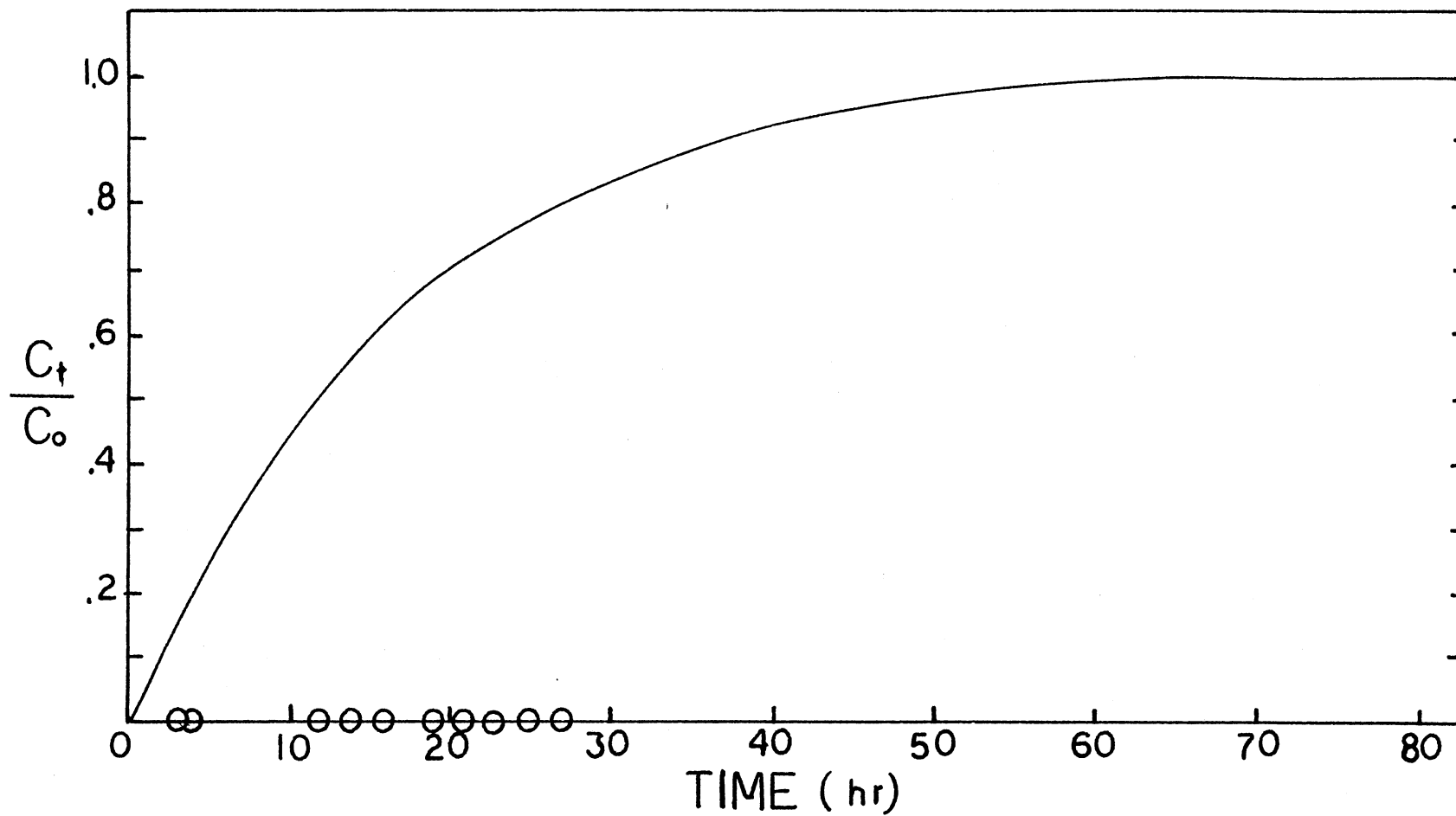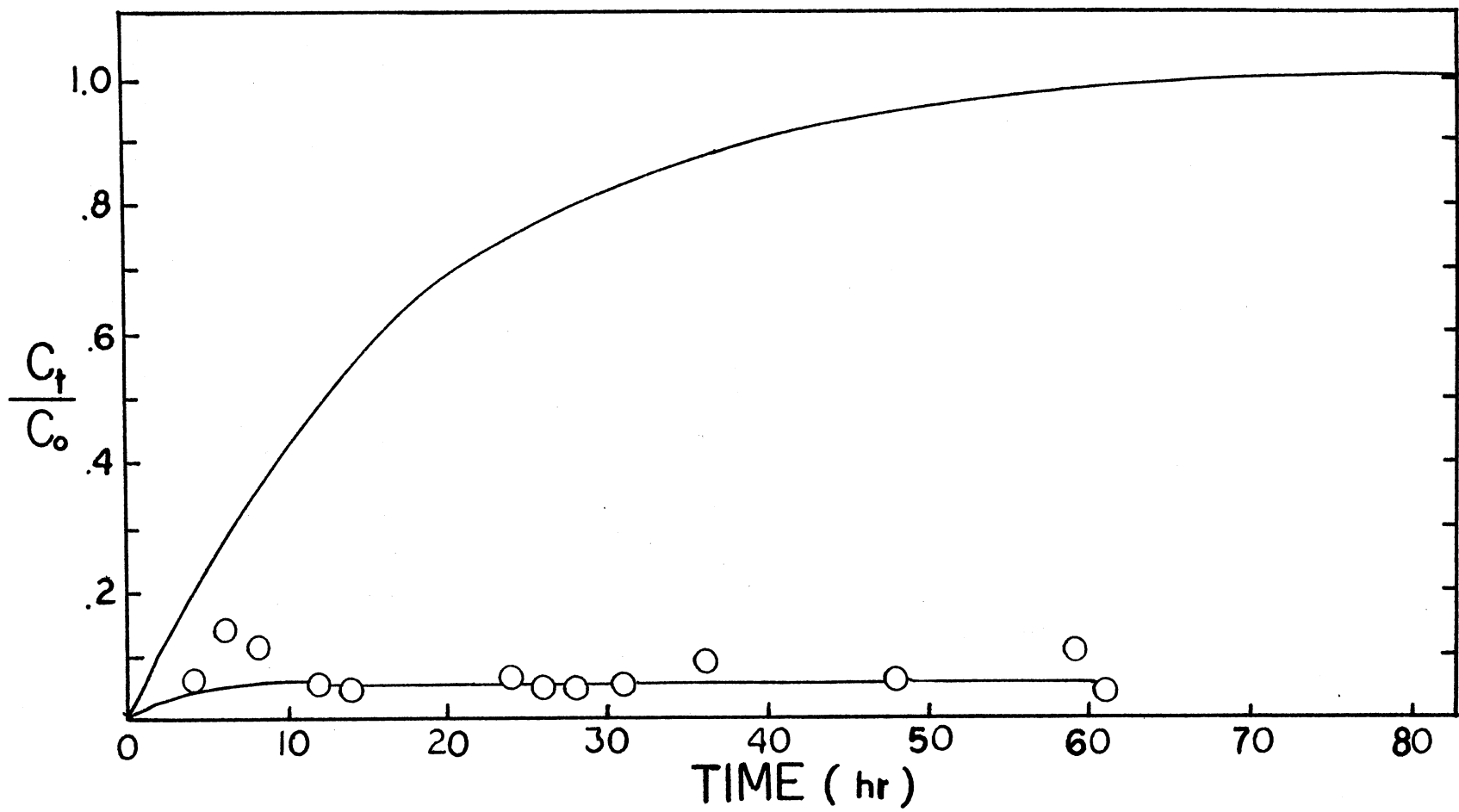
Figure 12. Completely Mixed Dilute-In Curve of 1,2-Dichloroethane; Theoretical
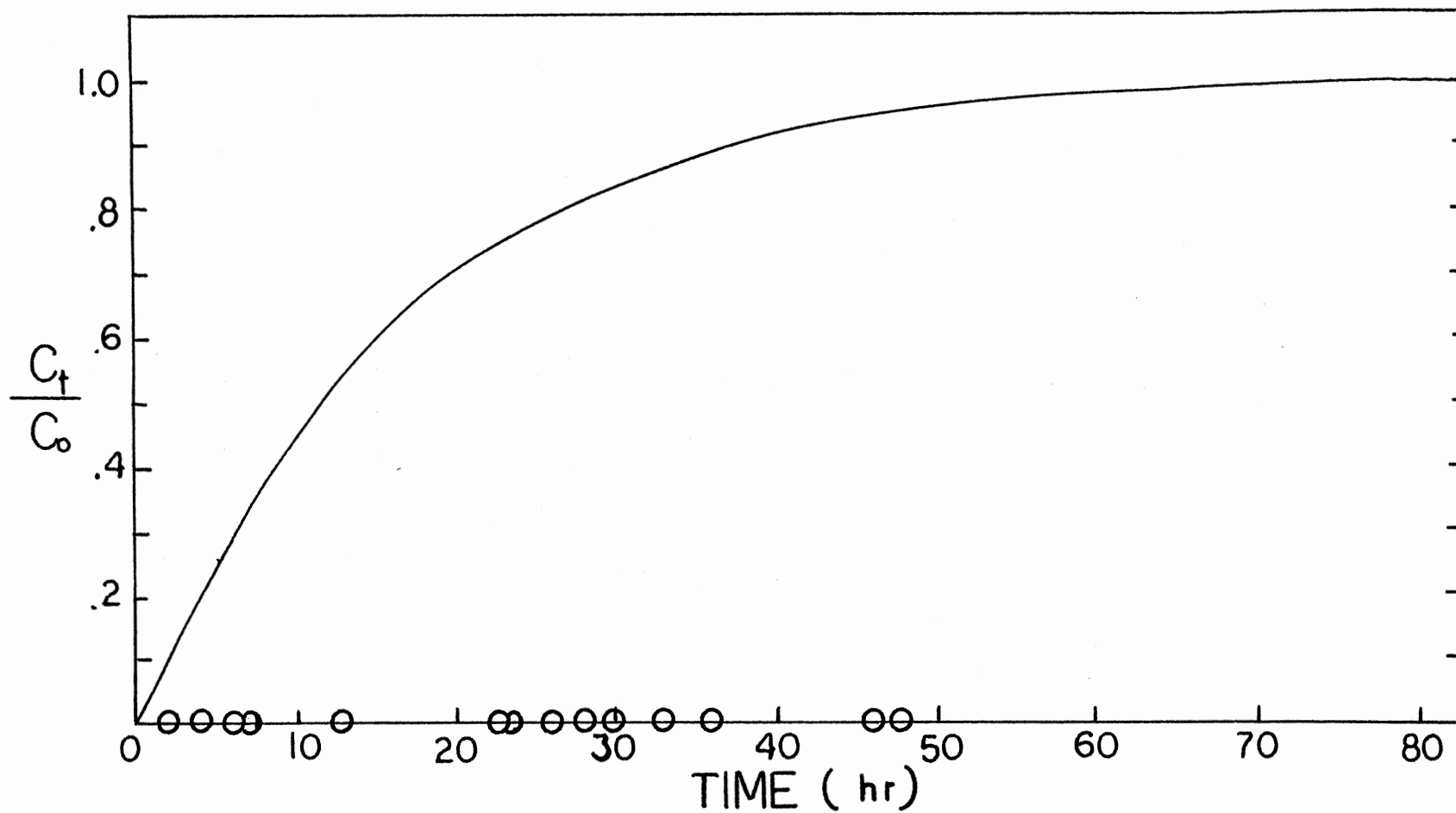Curve Without Stripping and Experimental Curve With Stripping
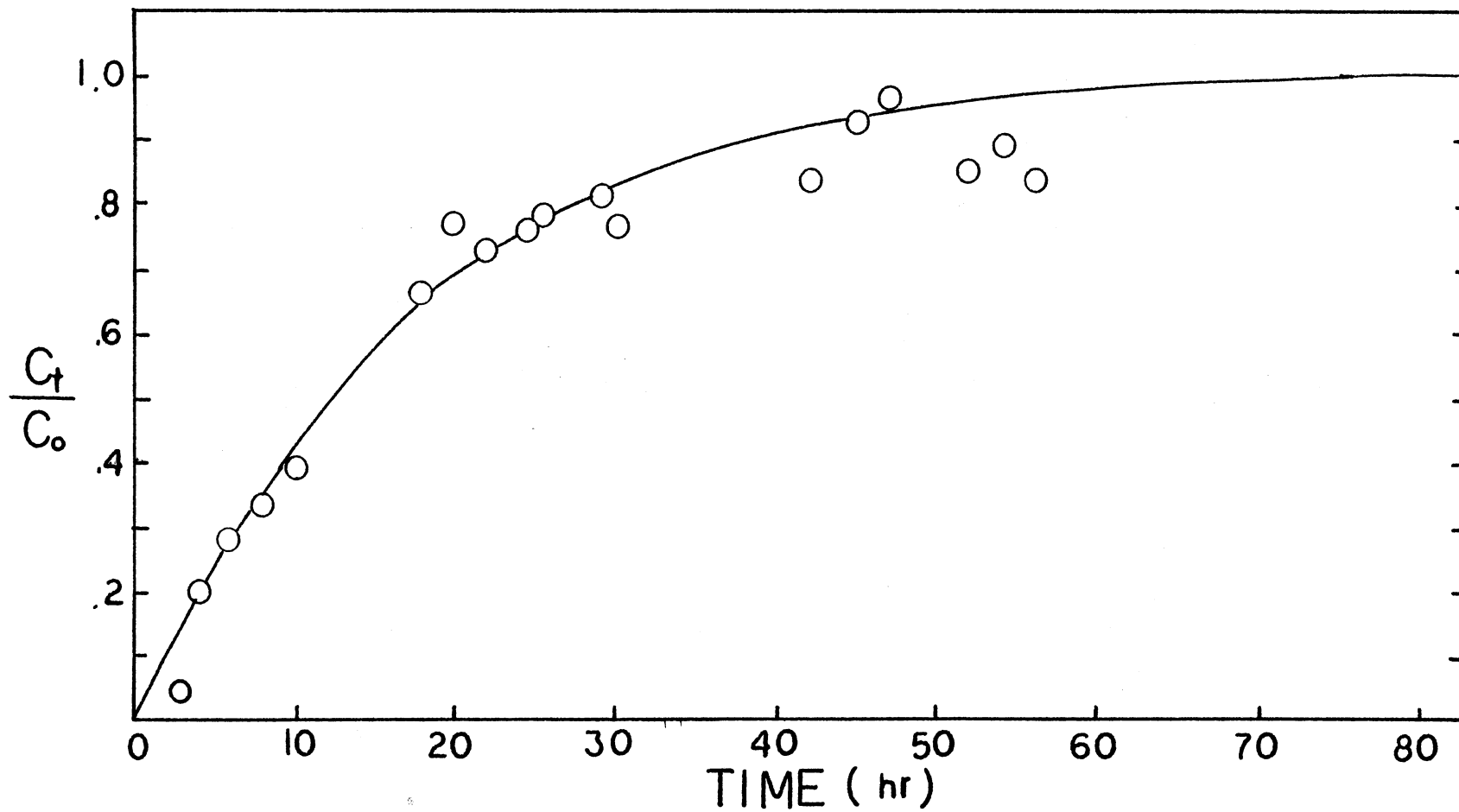
Figure 13. Completely Mixed Dilute-In Curve of Phenol; Theoretical Curve Without
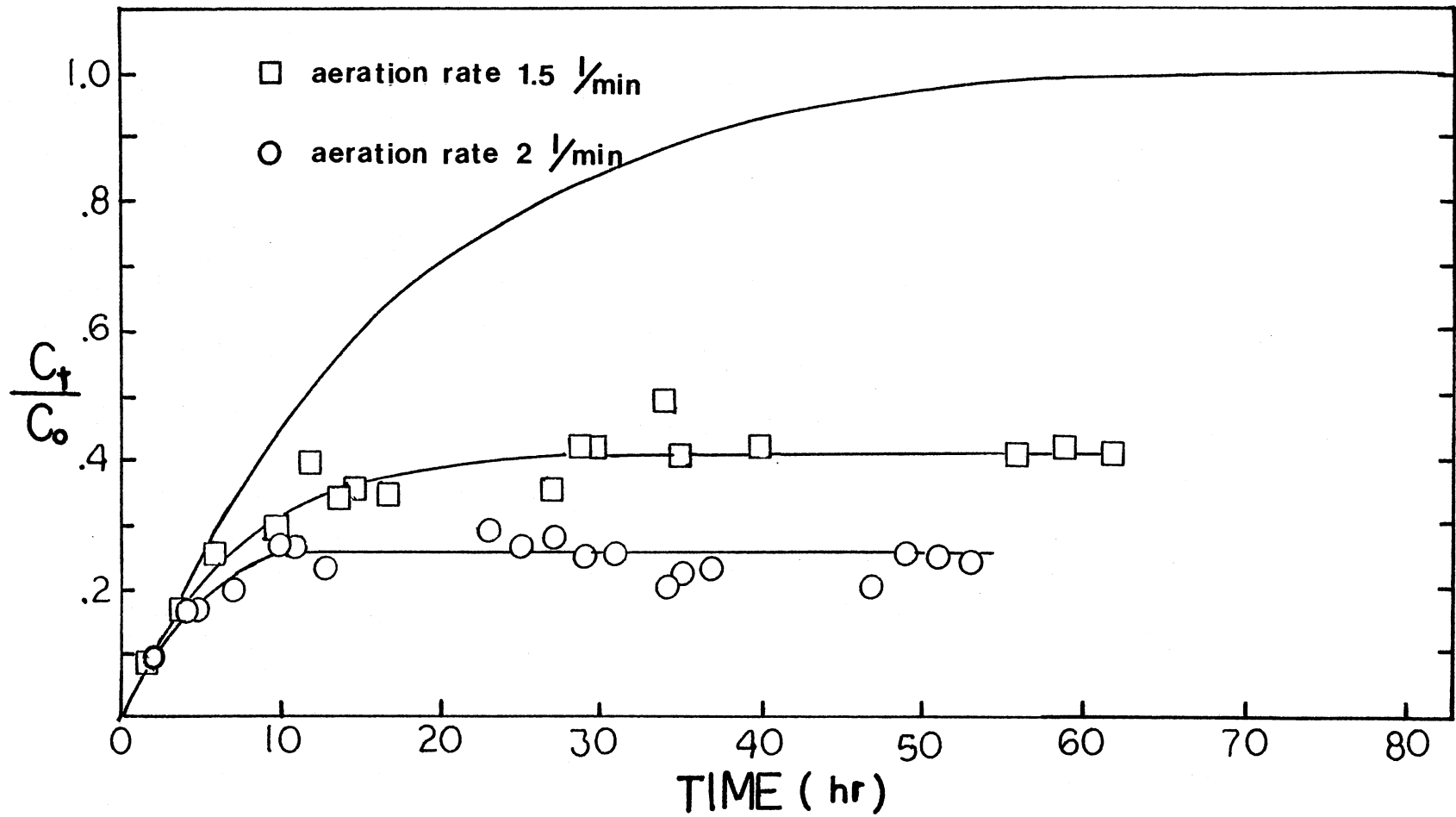Stripping and Experimental Curve With Stripping
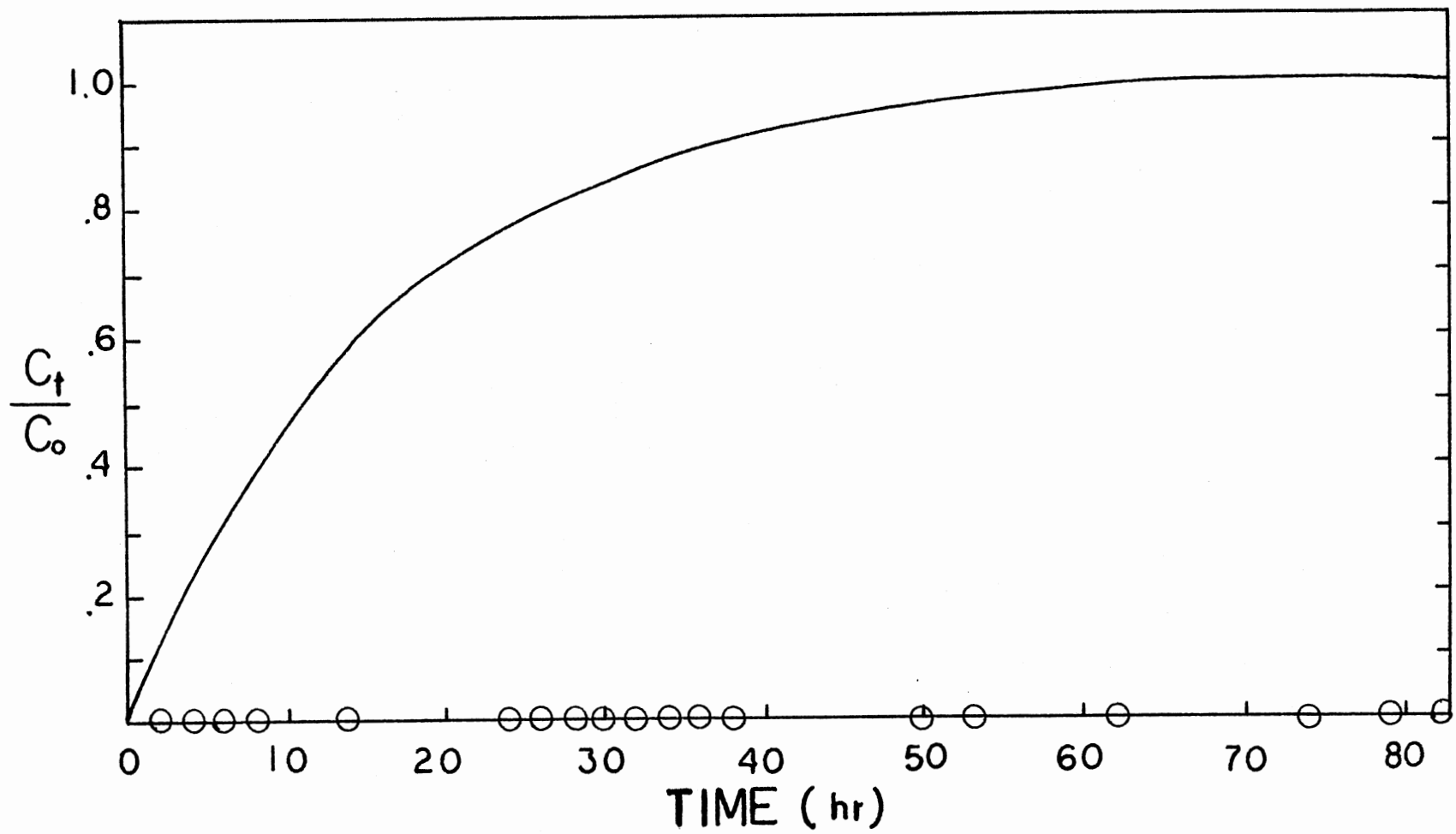
Figure 14. Completely Mixed Dilute-In Curve of 1,2-Dichlorobenzene; Theoretical
Curve Without Stripping and Experimental Curve With Stripping

<u>1,2-Dichlorobenzene</u>

Figure 14 indicates that at an aeration rate of 2.0 l/min, the concentration of 1,2-dichlorobenzene in the effluent were below TOC detection limit, and that more than 97.73 % of initial TOC was stripped. Although 1,2-dichlorobenzene was not detected in the effluent when measured as TOC, specific compound analysis by GC did show that there was 10.0 mg/l in the effluent samples. It is shown in Table IV that 86.11 % of the compound was stripped and the recovery of the compound from air was 116.4 %.

Referring to Table I and Table IV, it is found that for those listed compounds the trend of stripability agreed very well. Benzene has the highest stripability and acrolein has the lowest stripability. However, the stripping efficiency were different due to the differences in configuration of reactors, aeration rate, and A/V ratio.

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Treatment of Stripable Compounds by Stripping and

Biological Degradation in Continuous

Flow Reactors

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The biological activated sludge units were operated at three different sludge ages, 2, 4, and 6 days, for each compound for a period of three months. The hydraulic detention time was eight hours varing from 8.0 hr to 8.7 hr. The influent flow rate varied from 6.08 ml/min to 6.39 ml/min. Concentration of each specific compound in feed solution was different. The reason is that microorganisms in the activated sludge might not be able to withstand these priority pollutants at a concentration as high as 300 mg/l which was used for nonbiological system.

Another reason is that compounds which have high COD value will contribute 75 % of total feed COD at a low concentration level. Therefore, specific compound concentration in the feed, as shown in Table VI, was lower than that of nonbiological stripping units. The stripping theory, discussed in Chapter II, states that the initial concentration of substrates does not affect the stripping characteristic. Results obtained by running stripping tests at different initial specific compound concentration in the biological units and in the nonbiological units are thus comparable with each other.

The aeration rates of each biological units were not the same. It varied from 1.5 l/min to 2.0 l/min due to the differences in the oxygen demand of microorganisms and the extent of complete mixing. Aeration rate is an important controlling factor affecting the stripping efficiency. From the engineering standpoint, the aeration rates applied in this work were in a reasonable range so that the test results were comparable.

Table VI gives the operation conditions of all the biological activated sludge units. Table VII gives the overall removal efficiency and physical stripping efficiency. Here, the overall removal efficiency is defined as the disappearance in quantity of priority pollutants from liqiud phase through any kind of mechanism. In this study, biological oxidation and physical stripping were two major mechanisms in removing the priority pollutants from the liquid phase.

Table VII indicates that nearly 100 % of the priority pollutants were removed either by biodegradation or by stripping. The last column of Table VII gives the percentage of priority pollutants stripped from the activated sludge aeration tank. It was found that the system

TABLE VI

OPERATION CONDITIONS OF ACTIVATED SLUDGE SYSTEMS

compound	θ_c day	aeration tank volume l	inflow rate ml/min	detention time hr	dilution rate hr^{-1}	pollutant in feed mg/l
ACRO	1.73 3.66 5.62	3.13 3.14 3.04	6.21 6.23 6.17	8.4 8.4 8.2	0.1190 0.1190 0.1219	62.4
ACRYLO	1.75 4.06 6.13	3.14 3.04 3.16	6.17 6.21 6.26	8.5 8.2 8.4	0.1176 0.1220 0.1190	151.8
1,2DCP	1.98 3.73 6.27	3.13 3.05 3.26	6.14 6.18 6.21	8.5 8.3 8.7	0.1176 0.1204 0.1149	159.4
MC	2.05 4.22 6.08	3.14 3.04 3.16	6.19 6.27 6.19	8.5 8.1 8.5	0.1176 0.1235 0.1176	127.3
BENZENE	2.01 4.00 6.20	3.13 3.05 3.26	6.10 6.27 6.13	8.6 8.1 8.8	0.1163 0.1235 0.1136	151.3
EA	2.03 3.86 5.78	3.13 3.14 3.04	6.21 6.21 6.24	8.4 8.4 8.4	0.1190 0.1190 0.1235	167.3
1,2DCE	2.01 4.07 5.96	3.13 3.14 3.04	6.19 6.39 6.25	8.4 8.2 8.1	0.1190 0.1220 0.1235	257.5
PHENOL	2.04 4.11 6.18	3.13 3.04 3.16	6.08 6.16 6.14	8.6 8.1 8.6	0.1163 0.1235 0.1163	172.9
1,2DCB	1.99 4.04 5.86	3.13 3.05 3.26	6.25 6.23 6.30	8.3 8.2 8.6	0.1204 0.1220 0.1163	55.3

TABLE VII

SPECIFIC COMPOUND MASS BALANCE AND REMOVAL EFFICIENCY
OF ACTIVATED SLUDGE SYSTEMS

COMPD	θ days	INF mg/min	EFF mg/min	OFF-AIR mg/min	OVERALL REMOVAL %	RECOVERY %
ACRO	1.73	0.388	0.0003	–	99.9	–
	3.66	0.389	0.002	–	99.5	–
	5.62	0.385	0.006	–	98.4	–
ACRYLO	1.75	0.937	0.002	–	99.8	–
	4.06	0.943	0.002	–	99.8	–
	6.13	0.950	0.002	–	99.8	–
1,2DCP	1.98	0.925	0.006	0.813	99.4	87.9
	3.73	0.922	0.008	0.813	99.1	88.2
	6.27	0.914	0.009	0.813	99.0	88.9
MC	2.05	0.992	0.005	0.046	99.5	4.2
	4.22	1.149	0.006	0.037	99.5	3.6
	6.08	1.159	0.006	0.079	99.5	6.8
BENZENE	2.01	0.941	0.001	0.157	99.9	16.7
	4.00	1.151	0.0005	0.157	99.9	13.6
	6.20	1.008	0.0	0.159	99.9+	15.8
EA	2.03	0.896	0.008	0.119	99.1	13.3
	3.86	0.896	0.004	0.286	99.6	31.9
	5.78	0.992	0.0003	0.064	99.9+	6.5
1,2DCE	2.01	1.317	0.0188	1.331	98.6	101.1
	4.07	1.320	0.0126	1.613	99.0	122.1
	5.96	1.376	0.0230	2.230	98.3	162.0
PHENOL	2.04	1.085	0.00006	0.0	99.9+	0.0
	4.11	1.058	0.00006	0.0	99.9+	0.0
	6.18	1.031	0.00006	0.0	99.9+	0.0
1,2DCB	1.99	0.602	0.0	0.125	99.9+	20.8
	4.04	0.607	0.0	0.180	99.9+	29.7
	5.86	0.605	0.0	0.131	99.9+	21.7

controlling factor, θ_c, did not affect the stripping efficiency in most cases. Only the ethyl acetate units showed the effect of θ_c on stripping efficiency. The unit with θ_c of 3.86 days had a higher stripping efficiency (31.9%) and the unit with θ_c of 5.78 days had a lower stripping efficiency (6.5 %).

Based on the stripability in activated sludge reactor priority pollutants can be categorized into three groups. These groups are (1) highly stripable compounds, (2) partially stripable compounds, and (3) not stripable compounds. Group (1) includes 1,2-dichloropropane and 1,2-dichloroethane. Group (2) includes methylene chloride, benzene, ethyl acetate, and 1,2-dichlorobenzene. Group (3) includes only phenol which also showed a nonstripable characteristics in nonbiological stripping study.

Medley(31) found that 1,2-dichloropropane was not biodegradable. Since about 88 % of 1,2-dichloropropane and about 100 % of 1,2-dichloroethane were stripped, it is concluded that when a compound is nonbiodegradable stripping then is the major removing mechanism. Therefore, these compounds were stripped immediately after they were pumped into the mixed liquor.

While compounds of group (1) showed similar behavior in biological and nonbiological studies, those of group (2) showed various degree of stripability in different systems. Table VIII summerized the stripability of each compound in nonbiological and biological systems. Contrary to the nonbiological studies, the stripability of benzene in activated sludge system were only 13.6 % to 16.7 %. This indicated that about 85 % of benzene was biologically oxidized instead of been stripped. 1,2-Dichlorobenzene and ethyl acetate were partially stripable in

TABLE VIII

STRIPABILITY OF PRIORITY POLLUTANTS IN BIOLOGICAL AND
NONBIOLOGICAL SYSTEMS BASED ON SPECIFIC
COMPOUND ANALYSIS

compound	nonbiological system		biological system	
	aeration rate l/min	% stripped	θ_c (day)	% stripped
Acrolein	2.0	62.4	-	-
Acrylonitrile	3.5	75.93	-	-
1,2-Dichloropropane	2.5	98.49	1.98 3.73 6.27	87.9 88.2 88.9
Methylene Chloride	3.0	99.42	2.05 4.22 6.08	4.6 3.2 6.8
Benzene	2.75	99.19	2.01 4.00 6.20	16.7 13.6 15.8
Ethyl Acetate	2.0	67.80	2.03 3.86 5.78	13.3 31.9 6.5
1,2-Dichloroethane	2.0	96.07	2.01 4.07 5.96	101.1 122.1 162.0
Phenol	2.0	1.93	2.04 4.11 6.18	0 0 0
1,2-Dichlorobenzene	2.0	86.11	1.99 4.04 5.86	20.8 29.7 21.7

nonbiological system. The stripping efficiency of 1,2-dichlorobenzene

and ethyl acetate in biological system were about one-fourth and

one-tenth to one-half of those of nonbiological systems respectively.

All these results indicated that these compounds, although they were

subject to stripping, were easily biodegradable. It is concluded that

biodegradation was the major mechanism and stripping was the minor

mechanism in removing these priority pollutants.

Group (3) includes two compounds which were extremely different in

stripability in nonbiological systems but had the same biodegradable

characteristics. Phenol was not stripable in both biological and

nonbiological systems and was almost 100 % biodegraded. Methylene

chloride was almost 100 % stripped immediately in nonbiological system.

However, at the presence of microorganisms only 3.2 % to 6.8 % was

stripped. In this case, stripping was negligible when compared to

biodegradation. It can be concluded that methylene chloride, even

though a favorable condition for stripping was provided, was more subject

to biodegradation than to stripping.

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Stripping Kinetic Constants and

Biokinetic Constants

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Table IX gives the stripping kinetic constants (K_a) of each

compound on two bases, TOC and specific compound analyses. The K_a value

was calculated from Eq. 8,

$$K_a = \frac{(S_i - S_e) F}{S_e V} \tag{8}$$

TABEL IX

STRIPPING KINETIC CONSTANTS BASED ON TOC
AND SPECIFIC COMPOUND ANALYSIS

compound	aeration rate 1/min	dilution rate hr^{-1}	$K_a (hr^{-1})$ TOC based	GC based
Acrolein	2.0	0.0597	0.0847	0.0992
Acrylonitrile	3.5	0.0578	0.1697	0.1824
1,2-Dichloropropane	2.5	0.0616	5.8520	4.0161
Methylene Chloroide	3.0	0.0558	2.6780	9.4860
Benzene	2.75	0.0559	5.5341	6.8875
Ethyl Acetate	2.0	0.0616	0.1890	0.1297
	1.5	0.0616	0.0874	0.2475
1,2-Dichloroethane	2.0	0.0578	0.8092	1.4139
Phenol	2.0	0.0578	0.0075	0.0014
1,2-Dichlorobenzene	2.0	0.0578	2.4854	0.3584

It was assumed that, for those compounds having effluent concentration below the TOC detection limit, the effluent concentration was 1.0 mg/l TOC.

It is very obvious that small K_a value indicates a low stripability In this study, phenol was not stripable and its stripping kinetic constant was 0.0075 hr^{-1} and 0.0014 hr^{-1} based on TOC and specific compound analyses respectively. The K_a values of those highly stripable compounds varied from 0.8092 hr^{-1} (based on TOC) of 1,2-dichloroethane to 5.8520 hr^{-1} (based on TOC) of 1,2-dichloropropane and from 0.3584 hr^{-1} (specific compound analysis based) of 1,2-dichlorobenzene to 9.4860 hr^{-1} of methylene chloride.

Referring to the results shown in Table VII, a conclusion can be made that stripping efficiency was affected by the presence of micro-organism which could either adsorb or degrade the volatile compounds. Since biological activity and physical stripping are two different types of reactions, it is assumed that they are independent of each other. Microbial particles may adsorb and then reduce the compound fed into the reactor. However, this only affects the total amount of the specific compound stripped and does not affect the stripability of that particular compound. In another words, the stripping constant will remain the same. Stripability is affected only by the aeration rate which controls the A/V ratio, and by the specific characteristics of compounds.

Considering first order stripping, a modified Mckinney's model of activated sludge process can be written as follow,

$$(\frac{dS}{dt})_R V = F S_i - F S_e - K_m S_e V - K_a S_e V$$

| change of substrate | sub-strate flow in | sub-strate flow out | substrate bio-degraded | substrate stripped |

Assuming at steady state, this expression can be rearranged as follow,

$$K_m = \frac{F\,(\,S_i - S_e\,) - K_a\,S_e\,V}{S_e\,V}$$

$$= \frac{F}{V}\,(\,\frac{S_i}{S_e} - 1\,) - K_a$$

Table X gives the biokinetic constants (K_m) calculated from the above equation. The stripping constants (TOC based and specific compound analysis based) were obtained from the nonbiological stripping studies. The dominating mechanism, either biodegradation or physical stripping, can be determined by comparing the kinetic constants of these two mechanisms.

Removal of ethyl acetate, methylene chloride, benzene, phenol and 1,2-dichlorobenzene were mainly attributed to biological degradation. As shown in Table X, biokinetic constants of these compounds were considerably larger than stripping constants. For 1,2-dichloropropane, the biokinetic constants, 6.5017 hr^{-1} (based on specific conpound analysis) and 4.4656 hr^{-1} (TOC based), were very close to the stripping constants, 4.0161 hr^{-1} (specific compound analysis based) and 5.8520 hr^{-1} (TOC based). This relationship indicated that stripping is competitive with biodegradation in removing the volatile priority pollutants.

TABLE X

BIOKINETIC CONSTANTS OF BIOLOGICAL ACTIVATED SLUDGE SYSTEMS

comp.	F_i ml/min	volume l	F/V hr^{-1}	S_i mg/l	S_e mg/l	K_a (GC) hr^{-1}	K_m hr^{-1}	K_a (TOC) hr^{-1}	K_m hr^{-1}	% strip.
ACRO	6.20	3.014	0.1234	62.4	0.867	0.0992	10.99	0.0847	11.0	–
ACRYLO	6.21	3.113	0.1197	151.8	0.05	0.1824	363	0.1697	363	–
1,2DCP	6.18	3.144	0.1179	159.4	1.767	4.0161	6.5017	5.8520	4.456	88.3
MC	6.22	3.113	0.1199	127.3	0.524	9.4860	19.5	2.6780	26.3	4.9
BENZENE	6.20	3.144	0.1183	153.1	0.155	6.8875	109.8	5.5341	111.2	15.4
EA	6.23	3.014	0.1240	167.3	0.359	0.1279	57.5	0.1890	57.5	17.2
1,2DCE	6.28	3.014	0.1250	257.5	3.865	1.4139	6.789	0.8092	7.39	128.4
PHENOL	6.13	3.113	0.1181	172.9	0.012	0.0014	1701	0.0075	1701.	0.0
1,2DCB	6.26	3.144	0.1195	55.3	0.005	0.3584	1321	2.4548	1319	24.1

Relationship Between Physical-Chemical

Properties and Stripability

Table XI gives some physical properties and stripping constants of each compound. The order of these nine compounds were arranged in accordance with descending K_a (GC based) value. It was indicated that physical properties such as boiling point, molecular weight, and density do not affect the stripability. When molecular structure was considered, it was found that compounds having chloride molecule have higher K_a(GC) value as compared to those without chloride molecule. These compounds are methylene chloride, 1,2-dichloropropane, and 1,2-dichloroethane. Also, they were less soluble compared to those partially or nonstripable compounds. Partially stripable compounds have either **double** bond (i.e., acrolein, acrylonitrile) or -CN group (i.e., acrylonitrile) or ester bondage (i.e., ethyl acetate) in their structure. This indicates that they are more soluble and subsequently less stripable. Phenol, a nonstripable compound, has an acidic hydroxyl group on its aromatic ring. This hydroxyl group can form hydrogen bond with water and make phenol nonstripable. Generally, high vapor pressure compounds having high solubility are much less stripable than high vapor pressure compounds having low solubility.

TABEL XI

PHYSICAL PROPERTIES AND STRIPPING KINETIC CONSTANTS OF EACH COMPOUND

Compound	bp	MW	density	K_a (TOC)	K_a (GC)	solubility wt per 100 part	vapor pressure mmHg ($^{\circ}$C)
Methylene Chloride	40	84.93	1.3266	2.6780	9.8640	2	5 (22) atm
Benzene	80.1	78.12	0.8787	5.5341	6.8875	0.07	100 (26.1)
1,2-Dichloropropane	96.37	112.99	1.1560	5.8520	4.0161	-	40 (19.4)
1,2-Dichloroethane	83.47	98.96	1.2351	0.8092	1.4139	0.9	1 (83.7) atm
1,2-Dichlorobenzene	180.5	147.01	1.3048	2.4854	0.3854	i	1 (20)
Ethyl Acetate	77.15	88.06	0.8945	0.1890	0.1297	8.5	100 (27)
Acrylonitrile	77.5	53.06	0.8060	0.1679	0.1824	s	100 (22.8)
Acrolein	52.5	56.07	1.4017	0.0847	0.0992	44.6	200 (17.5)
Phenol	181.75	94.11	1.0722	0.0075	0.0014	8.2	1 (40.1)

TABLE XII

MOLECULAR STRUCTURE OF PRIORITY POLLUTANTS
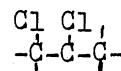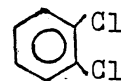

HIGHLY STRIPABLE COMPOUNDS

Methylene Chloride

$$-\overset{|}{\underset{|}{C}}-Cl$$

Benzene

1,2-Dichloropropane

$$\overset{Cl}{\underset{|}{\underset{|}{C}}}\,\overset{Cl}{\underset{|}{\underset{|}{C}}}\,-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$$

1,2-Dichloroethane

$$\overset{Cl}{\underset{|}{\underset{|}{C}}}\,\overset{Cl}{\underset{|}{\underset{|}{C}}}\,-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$$
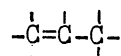
1,2-Dichlorobenzene

PARTIALLY STRIPABLE COMPOUNDS

Acrolein

$$-\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$$

Acrylonitrile

$$-\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$$

Ethyl Acetate

$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-O-\overset{\overset{O}{\|}}{C}-\overset{|}{\underset{|}{C}}-$$
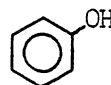
NONSTRIPABLE COMPOUND

Phenol

CHAPTER V

CONCLUSIONS

From the previous experimental data and observations, the following conclusions may be drawn:

1. The two measures employed in this study, TOC and specific compound analyses, appeared to be adequate to analyze the stripability of volatile compounds.

2. The high recovery of stripped volatile priority pollutants from off-air indicates that the off-air sampling devices employed in this study was adequate.

3. The nine priority pollutants investigated can be classified into three groups based on their stripability under the conditions employed in this study: highly stripable, partially stripable, and not stripable compounds.

4. Stripping of volatile priority pollutants cannot always be predicted by solely running separate physical stripping test because of the presence of microorganisms in the activated sludge system.

5. Among highly stripable priority pollutants (1,2-dichloropropane, methylene chloride, benzene, 1,2-dichloroethane, and 1,2-dichlorobenzene) only 1,2-dichloropropane and 1,2-dichloroethane showed high stripability in the activated sludge system.

CHAPTER VI

SUGGESTIONS FOR FUTURE WORK

Results of the present research have indicated that the following additional studies would provide useful information:

1. Although the concentration will not theoretically affect the stripping constant, the study on stripping with different initial concentration should be studied to develop a more accurate stripping constant.

2. Corelation between the presence of microorganisms (suspended solids) and the stripability of volatile priority pollutants should be investigated.

3. There is a need to study the biokinetic constant independently without the interference of stripping to prove the independency between the biokinetic and stripping constants.

BIBLIGRAPHY

1. Gaudy, A. F. Jr., and Gaudy, E. T., <u>Microbiology for Environmental Scientists and Engineers</u>. McGraw Hill Book Company, Inc., New York, N. Y. (1980).

2. Metcalf and Eddy, Inc., <u>Wastewater Engineering : Collection, Treatment, Disposal</u>. 2nd Edition. McGraw Hill Book Company, Inc., New York, N. Y. (1979).

3. Monod, J., "The Growth of Bacterial Cultures." <u>Ann. Rev. Microbiology</u>, <u>3</u>, 371-394, (1949).

4. Kincannon, D. F., and Gaudy, A. F., "Functional Design of Aerobic Biological Waste Water Treatment Processes." <u>Publication M-3 of Center for Water Research in Engineering</u>, Bioenvironmental Engineering, School of Civil Engineering, Oklahoma State University, Strillwater (1979).

5. Prather, B. V., "Will Air Flotation Remove the Chemical Oxygen Demand of Refinery Waste Water?" <u>Pertroleum Refinery</u>, <u>40</u>, (5), 177-179, (1961).

6. Prather, B. V., and Gaudy, A. F. Jr., "Combined Chemical, Physical, and Biological Process in Refinery Waste Water Purification." <u>American Petroleum Institution Proceedings</u>, <u>44</u>, 105-111, (1964).

7. Ledbetter, J. O., "Air Pollution from Aerobic Waste Treatment." <u>Water and Sewage Works</u>, <u>111</u>, 62-63, (1964).

8. Haney, P. D., "Theoretical Principles of Aeration." <u>J. American Water Workers Association</u>, <u>46</u>, 353-375, (1954).

9. Eckenfelder, W. W., Kelffman, R., and Walker, J., "Some Theoretical Aspects of Solvent Stripping and Aeration of Industrial Waste." <u>Proceedings</u>, <u>11th Industrial Waste Conference</u>, <u>Purdue University</u>, 14-25, (1956).

10. Lewis, W. K., and Whitman, W. G., "Principle of Gas Adsorption." <u>Ind. Eng. Chem.</u>, <u>16</u>, 1215-1220, (1924).

11. Engelbrecht, R. S., Gaudy, A. F., and Cederstrand, J. M., "Diffused Air Stripping of Volatile Waste Components of Petrochemical Wastes." J. Water Pollution Control Fed., 33, 127-135, (1961).

12. Gaudy, A. F., Engelbrecht, F. S., and Turner, B. F., "Stripping Kinetics of Volatile Components of Petrochemical Wastes." J. Water Pollution Control Federation, 33, (4), 382-392, (1961).

13. Gaudy, A. F., Turner, B. F., and Pusztaszeri, S., "Biological Treatment of Volatile Waste Components." J. Water Pollution Control Federation, 35, (1), 75-93, (1963).

14. Goswami, S. R., "Treatment of Stripable and Nonstripable Substrate by the Activated Sludge Process." Ph.D. Thesis, Oklahoma State University (1969).

15. Freeman, R. A., Schroy, J. M., Klieve, J. R., and Archer, S. R., "Experimental Studies on the Rate of Air Stripping of Hazardous Chemicals from Waste Treatment Systems." Presented at APCP Meeting, Montreal, Canada, June, 1980.

16. Pelizzari, E. D., and Little, L., "Collection and Analysis of Purgeable Organics Emitted from Wastewater Treatment Plants." Environmental Protection Agency, EPA-600/2-80-017, U. S. Government Printing Office, Washington, 1980.

17. Houel, N., Pearson, F. J., and Selleck, R. E., "Air Stripping of Chloroform from Water." Environmental Engineering, J. American Society of Civil Engineering, 105, 777-781, (1979).

18. Singley, J. E., Ervin. A. L., and Williamson, D. F., "Aeration (Plus Resins) Doing Job Removing TOC." Water and Sewage Worker, 124, 100-102, September, (1977).

19. Keith, L. H., and Telliard, W. A., "Priority Pollutants, Part I: Perspective View." J. Environmental Science and Technology, 13, (4), 416-423, (1979).

20. Komolrit, K., and Gaudy, A. F.Jr., "Substrate Interaction During Shockloadings to Biological Treatment Process." J. Water Pollution Control Federation, 38, 1239-1272, (1966).

21 "Guidelines Establishing Test Procedures for the Analysis of Polutants; Proposed Regulations." Federal Register, Part III, Environmental Protection Agency, 44, (233), 69464-69575, December 3, 1979.

22. Handbook of Chemistry and Physics, 62nd Edition. CRC Press, Inc. Florida, (1981).

23. Perry, R. H., and Chilton, C. H., Chemical Engineer's Handbook.
    5th Edition. McGraw Hill Book Company, Inc. New York, N. Y.
    (1973).

24. Skoog, D., and West, D. M., Fundmental of Analytical Chemistry.
    3rd Edition. Holt, Rinehart and Winston, Inc. New York, N. Y.
    (1976).

25. Thibodeaux, L J., "A Test Method for Volatile Component Stripping
    of Waste Water." Environmental Protection Technology Series,
    EPA-760/2074-044, U. S. Government Printing Office, Washington,
    1974.

26. Lingg, R. D., Melton, R. G., Kopfler, F. C., Coleman, W. E., and
    Mitchell, D. E., "Quantitative Analysis of Volatile Organics
    Compounds by GC-MS." J. American Water Workers Association,
    69, (11), 605-612, (1979).

27. Varma, M. M., Siddique, M. R., and Doty, K. T., "Purge and Trap
    Scores High With Low THM Concentrations." J. Water and Sewage
    Works, 126, 39-49, (1979).

28. Bellar, T. A., and Lechtenberg, J. J., "Determening Volatile
    Organics at Microgram-Ter-Litre Levels by Gas Chromatography."
    J. American Water Works Association, 66, (11), 739-744,
    (1974).

29. Rathbun, R. E., and Tai, D. Y., "Technique for Determin the
    Volatilization Coefficients of Priority Pollutants in Streams,"
    Water Research, 15, 243-250, (1980).

30. Cohen, U., Cocchio, W., and Mackay, D., "Laboratory Study of
    Liquid Phase Controlled Volatilization Rates in Presence of
    Wind Waves." Environmental Science and Technology, 12, (5),
    552-558, (1978).

31. Medley, D. R., "The Effects of Ozone on the Biodegradability
    of Acrylonitrile, 1,2-Dichloropropane, and 2,4-Dinitrophenol,"
    M.S. Thesis, Oklahoma State University (1981).

VITA

Yu-Ping Chung

Candidate for the Degree of

Master of Science

Thesis: STUDIES ON THE STRIPABILITY OF PRIORITY POLLUTANTS IN SEEDED AND NON-SEEDED ACTIVATED SLUDGE PROCESS

Major Field: Bioenvironmental Engineering

Biographical:

Personal Data: Born February 9, 1957, in Taipei, Taiwan, Republic of China, the son of Kuo-Tong and Chiou-Fang Chung.

Education: Graduated from the High School of National Taiwan Normal University, Taipei, Taiwan, Rep. of China, in May, 1975; received Bachelor of Science degree in Agriculture from National Taiwan University, Taipei, Taiwan, Rep. of China, in June, 1979; completed requirements for the Master of Science degree in Bioenvironmental Engineering at Oklahoma State University in December, 1981.

Professional Experience: Graduate research assistant in the Department of Bioenvironmental Engineering at Oklahoma State University from November, 1979, to December, 1981.

Membership in Professional Societies: Water pollution Control Federation, National Soceity of Professional Engineerer.