EFFECT OF OZONE ON BIOLOGICAL TREATABILITY OF 1,1,2,2 TETRACHLOROETHANE AND 1,2 DICHLOROPROPANE

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LIST OF SYMBOLS

F - Flow rate, l/day

F_w - Waste sludge flow rate, l/day

K - Maximum substrate utilization rate, day^{-1}

K_d - Cell maintance coefficient, day^{-1}

K_e' - Eckenfelder's modified costant, day^{-1}

K_s - The saturation constant, mg/l

S - Substrate concentration, mg/l

S_i - Inflowing concentration of substrate in a continuous flow system, mg/l

S_e - Effluent substrate concentration from continuous flow system, mg/l

T - Hydraulic detention time, days

U - Specific substrate utilization rate, day^{-1}

V - Volume, liters

X - Biomass concentration, mg/l

X_e - Effluent biomass concentration, mg/l

Y_t - The true cell yield

μ - Specific growth rate, day^{-1}

μ_m - Maximum specific growth rate, day^{-1}

μ_n - Net specific growth rate, day^{-1}

θ_c - Mean sludge retention time, day

CHAPTER I

INTRODUCTION

The year 1983 has been set by the Environmental Protection Agency (EPA) as the deadline for implementing the best available treatment technology, specifically aimed at difficult to oxidize pollutants, commonly referred to as bio-refroctory compounds (1). These compounds are not handled well by the biological processes and may sometimes cause operational problems resulting in exceeding the effluent limitations. Thus, it became evident that a technological breakthrough would be required in order for industry and municipalities to improve the water quality as established by the standards.

Ozone has been used for years to purify, deodorize, and disinfect drinking water in Europe and is recognized as one of the strongest and purest oxidants available. Unlike other oxidants, ozone can be generated on sites as needed. It is used primarily in industry for cleavage of carbon-carbon double bonds and has recently been applied in the industrial wastewater treatment area (2).

Ozone is a powerful oxidizing agent that has been shown to be effective in the removal of many of the organic compounds in water. In general, treatment of wastewaters

by ozone results in formation of less harmful or harmless products, and will not cause addition of toxic residue to treated effluent.

Unfortunately, the economics for complete oxidation of organic compounds in wastewater with ozone is usually prohibitive due to high energy costs. However, partial oxidation of organics with ozone usually produces oxygenated organics which are more biodegradable and less toxic than before oxidation (3). These oxidized intermediates can then be readily removed by biological treatment at lower cost.

The objectives of this study were to:

1. evaluate the feasibility of ozone pretreatment of biorefractory organics for biological processing.

2. study the variability in biological treatment performance using methods of probability.

CHAPTER II

LITERATURE REVIEW

The Development of Ozonation

The powerful oxidation and disinfection qualities of ozone gas have been known and utilized in water and wastewater purification for the last 85 years. Yet, it failed to receive any significant recognition in the United States until the mid-twentieth century (3). At present, ozone is actively being investigated for use in both water and wastewater treatment.

The presence of ozone was reported first by Van Marum who noticed its odor in 1785, during an electric discharge (4). The German chemist Schonbein was the first to discover the gas in 1839 and named it-ozone, after the Greek word: Ozein (to smell). In 1857, Siemens constructed the first ozone production machine which operated by means of electric discharge. In 1867, Soret established the chemical formula for ozone - O_3 (4, 5).

Ozone is a highly reactive allotrope of oxygen containing three oxygen atoms per molecule. It is mainly characterized by its very high oxidizing power and is extremely toxic (6). Early uses of ozone included air

purification, food preservation, bleaching of fibers and waxes, and water purification. In recent years, ozone has been applied to industrial wastewater treatment (7). Due to its powerful oxidation ability, ozone is often consided a most effective method for oxidation of many types of organics in industrial wastewater.

Properties of Ozone

Ozone, at room temperature, is a light blue gas with a characteristic smell. It has a melting point of -251°C, a boiling point of -112°C, a density of 2.14, and a solubility of 50 vol.% in 0°C water (3). In nature, ozone is produced by the photochemical reaction of solar ultraviolet light or by lightening discharges during storms. The commercial production of ozone is usually carried out by means of high voltage silent electric discharge through cleaned, cooled, and dried air (4, 8).

Ozone is a very unstable gas that decomposes rapidly in aqueous solution. It may either react directly with organics or decompose prior to reaction with organics. It is generally accepted that the decomposition of ozone leads to free radicals (7, 9, 10, 11). Hoigne and Bader (7) showed that the free radicals were the main oxidative species during ozonation. This was in agreement with the study by Peleg (9) who has reported that the dissociation products of ozone in water were more powerful oxidizing agents than

ozone itself. They also found that it might be the hydroxyl radical that was mainly responsible for the high oxidative potential of ozone in water.

Biodegradability of Ozonated Products

Recently, considerable work has been carried out on the oxidation of organic compounds by ozone. It has been proven by many authors to be an effective method of oxidizing many biorefractory compounds to a biodegradable form.

Yocum, Mayes, and Myers (1) studied the effect of ozone on the biodegradability of several biorefractory organics. Industrial wastewaters from toluene diisocyanate, ethylene glycol, styrene monomer, and ethylene dichloride processes were ozonated, and biological batch tests were performed after ozonation to determine the enhancement of ozonation on wastewater biodegradability. The results showed that the biodegradability of toluene diisocyanate, ethylene glycol, and ethylene dichloride wastewaters were greatly improved by ozonation. However, the styrene wastewater did not show significant increase in biodegradability. This was due to considerable amount of styene being stripped from the wastewater during ozonation.

Majumdar and Sproul (3) in their investigation concluded that ozone was very effective in breaking down detergents and other non-biodegradable compounds such as Alkylbenzene sulfonate, with the degree of oxidation mainly

dependent on the amount of ozone absorbed or reacted.

Kuhn et al. (8) reported that ozone treatment made humic materials more biodegradable, thereby aiding water treatment by biological processes. They also found that partial ozonation of ammonia could reduce operational problems during biological nitrification. Similar work has been done by Singer and Zilli (12), who found that ozone could readily oxidize ammonia to nitrate over the P^H range 7-9.

Three industrial wastewaters, alkybenzene sulfonate (ABS), DDT, and phenol, were studied by Hewes and Davison (11). They found that all three compounds were readily destroyed upon ozonation, and biodegradability was increased for all samples.

Several authors have shown that the biodegradability of phenolic substances are significantly increased by ozonation. Industrial wastewaters from petrochemical and coke manufacture containing various quantities of phenols were studied by Eisenhauer (13). He found that the biodegradability could be increased by increasing the ozone dose, reducing gas bubble size, increasing gas-liquid contact time, and operating at P^H 11. In a later study by Anderson (14) using high levels of phenolic wastewater, he showed that the efficiency of ozone utilization approached 100%. However, total destruction of phenol to carbon dioxide and water did not occur. The common products were

formic acid and oxalic acid.

More recently, Rice et al. (15) have done an excellent review on ozonation performance. They reported that ozonation of organic compounds usually produced oxygenated organic materials which were more readily biodegradable. They also showed that ozone was particularly reactive with unsaturated organic compounds. Unfortunately, they found these behaviors were not always true. Dieldrin, chlordane, lindane, trihalomethanes, and other highly chlorinated organics were not oxidized at all by ozone in their studies.

Kuo and Wen (16) in their investigation concluded that the reactions between ozone and formic acid, methanol, and formaldehyde were first order with respect to ozone concentration. Pottenger et al. (17) showed that biodegradability of aniline, cresol, and benzene sulfonic acid were improved by high ozone dosage.

In a batch study by Medley (18) on the effects of ozone on the biodegradability of acrylonitrile, 1,2 dichloropropane, and 2,4 dinitrophenol, he showed that the biodegradability of 1,2 dichloropropane and 2,4 dinitrophenol were increased by ozonation. However, he found the biodegradability of acrylonitrile was significantly decreased after ozonation.

Activated Sludge Design Models

Treatment of organic materials by the activated sludge

process was developed early in this century. Since then many advances have been made in creating a better understanding of the mechanism of biological oxidation of organic wastes.

In the early years, the design was simply based on empirical equations. Since the activated sludge process is a microbial system, it has become increasingly important that the equations used in design be based on the controlled studies of microbial behavior rather than on empirical equations (22).

The growth rate of pure cultures of microorganisms on defined substrates was originally reported by Monod to be related to the concentration of a growth limiting substrate by a hyperbolic equation.

$$\mu = \mu_{max} \frac{S}{K_s + S} \qquad (1)$$

where μ is growth rate, μ_{max} is maximum growth rate, S is substrate concentration, and K_s is substrate concentration at $\mu = \frac{1}{2}\mu_{max}$.

Several modifications of this equation have been developed and applied to heterogeneous waste treatment processes. However, some design models in present use assume a linear relation between growth rate and substrate concentration rather than the hyperbolic relation described by the Monod equation (22, 23, 24). Garrett et al. (23) have shown

that the Monod equation could be approximated by two separate functions. In the first phase for the lower range of substrate concentration the growth rate is assumed to increase linearly (first order) with substrate concentration. In the second phase, at higher range of substrate concentration the growth rate is assumed to be constant.

The mathematical relationship between microbial growth and substrate removal may be divided into two classes. The first class of activated sludge design models assumes that the substrate utilization follows first order Kinetics. In 1961, Eckenfelder (25, 26, 27) from his investigation on continuous flow activated sludge processes, developed a mathematical model for complete-mix activated sludge systems. This model assums a first order, decreasing rate of substrate removal. The relationship is described as follows:

$$\frac{S_i - S_e}{Xt} = K_e S_e \qquad (2)$$

Recently, Eckenfelder (28) has presented a modification of his original model. This modified approach assumes a multiple zero order concept of substrate removal as follows:

$$\frac{S_i (S_i - S_e)}{Xt} = K_e' S_e \qquad (3)$$

In 1965, Schulze (29, 30) developed another mathematical relationship based on the linear equation proposed

by Teissier. He reported that the effluent quality was dependent on hydraulic detention time and independent of biological solids concentration. In all of the other models (except the McKinney model), the effluent quality is a function of both hydraulic detention time and sludge concentration (22, 23, 28).

The second class of activated sludge design models assumes that substrate utilization follows Monod relationship. Lawrence and McCarty (31) developed a mean cell residence time model, based on the Monod equation, which states

$$\frac{1}{\theta_c} = Y_t U - K_d \tag{4}$$

and

$$U = K \frac{S_e}{K_s + S_e} \tag{5}$$

Y_t and K_d are shared by all of the activated sludge models. Generally, the sludge age of microorganisms is maintained by controlled wastage. Thus, it allows the mean cell residence time to be independent of hydraulic retention time.

In 1969, Peil and Gaudy (22) in their investigation concluded that the growth of heterogenous populations in various substrates including concentrated municipal sewage could be described by the Monod equation. This was in

agreement with the earlier study by Ramanathan (32) who had reported that the relationship between specific growth rate and substrate concentration was represented better by the Monod equation.

In 1977, Gaudy and Kincannon (33) proposed a mathematical model and design procedure based on Monod Kinetics. In the simplest form

$$\mu = \mu_{max} \frac{S_e}{K_s + S_e} \tag{6}$$

and

$$\mu_n = \mu - K_d \tag{7}$$

The biological solids and substrate mass balances are drawn around the entire system for all models; execpt Gaudy's model, which is drawn around the bioreactor.

1,1,2,2 Tetrachloroethane

1,1,2,2 Tetrachloroethane has a chemical formula of $CHCl_2CHCl_2$, a molecular weight of 167.85, a density of 1.5953, and a boiling point of 146.2°C. It is made from acetylene and chlorine, and is used chiefly as a nonflammable solvent and in making trichloroethylene and tetrachloroethylene. 1,1,2,2 Tetrachloroethane is a volatile compound that forms toxic vapors with an order similar to

that of chloroform. It is an EPA priority pollutant. Stover et al. (34) have shown that 1,1,2,2 tetrachloroethane is nonbiodegradable and highly stripable.

1,2 Dichloropropane

1,2 Dichloropropane has a chemical formula of CH_2Cl-$CHClCH_3$, a molecular weight of 112.99, a density of 1.211, and a boiling point of 94°C. It is used widely as an industrial solvent and in making alcohols, amines, nitriles, and acids. It is listed as a priority pollutant by the EPA. Kincannon et al. (35) showed that 1,2 dichloropropane is completely stripped from the activated sludge system and is not biodegradable.

CHAPTER III

MATERIALS AND METHODS

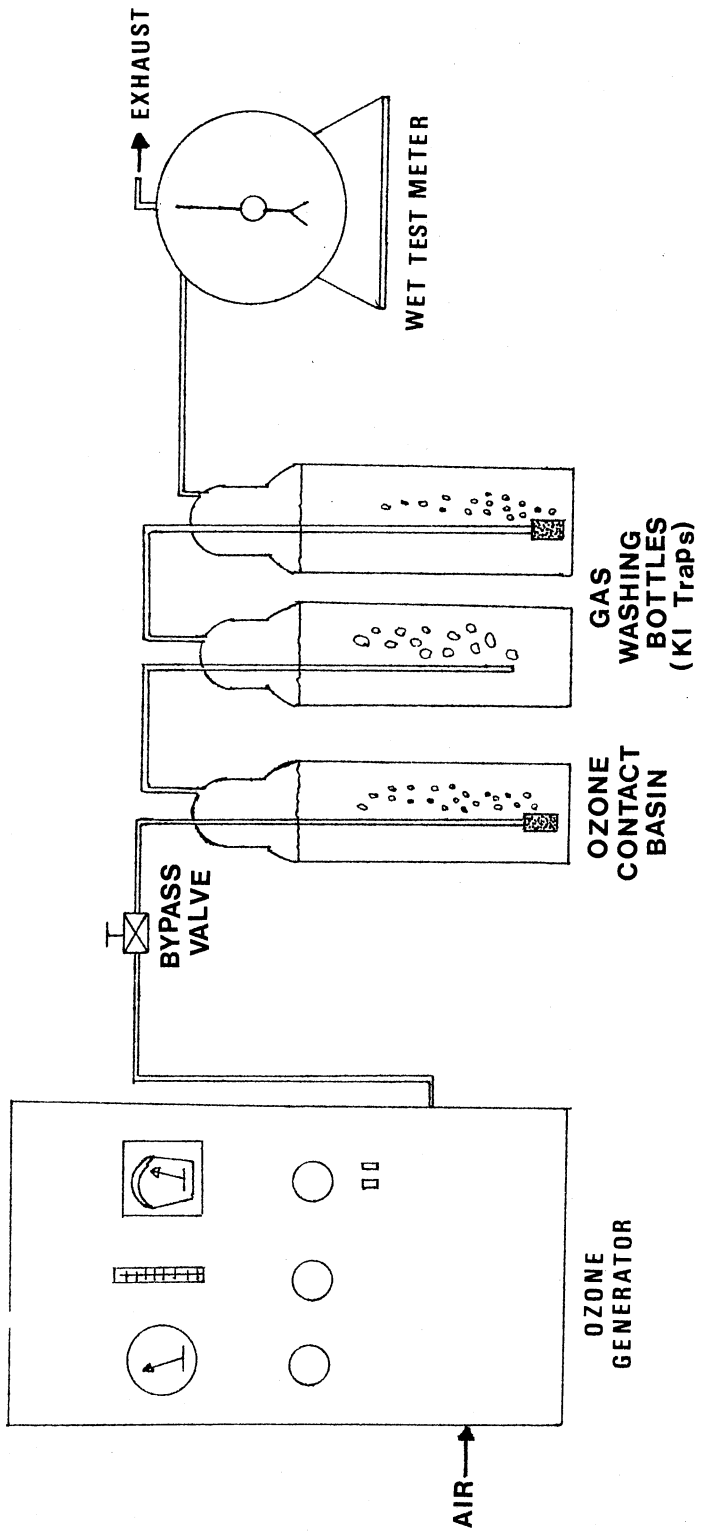
Ozonation

Experimental Apparatus

The experimental set-up used for ozonation is shown in Figure 1. Ozone gas was produced from a Welsbach Model W-20 Ozonator using air from the atmosphere. The air stream was dried initially by means of two columns of silica gel. A transformer within the cabinet increased the imput voltage to the high voltage necessary for ozone production (approximately 15,000 volts).

The ozone generated by this equipment was bubbled through a series of gas washing bottles. To avoid contamination of the ozone stream, all tubing used was made of Tygon or glass. Standard gas washing bottles which had 500 ml capacities were used. The first gas washing bottle acted as an ozone contact basin with a medium permeability porous diffuser at the bottom to optimize the gas transfer rate. The exhaust gas from this contact basin was then passed through the second gas washing bottle containing 0.05N potassium iodide solution to collect the unreacted ozone for subsequent analysis. The second gas washing

Figure 1. Schematic Diagram of Ozonation System Set Up


EXHAUST
WET TEST METER
GAS WASHING BOTTLES (KI Traps)
OZONE CONTACT BASIN
BYPASS VALVE
OZONE GENERATOR
AIR

bottle had the diffuser removed to prevent plugging, since it absorbed the bulk of the off gas ozone. Finally a back-up trap (third gas washing bottle) was employed to ensure complete absorption. The effluent gas outlet of the third gas washing bottle was connected to a wet test meter for determination of the gas sample volume. The wet test meter was a Precision Scientific Model 63111. Accuracy of this meter was rated by Precision Scientific at ±0.5% of total flow.

Sampling Method

The amount of ozone in the gas stream was measured both before and after each series of runs. The contents of the traps were titrated with standardized sodium thiosulfate using starch indicator to determine the average ozone concentration in the carrier gas. Ozone gas concentration of approximately 4.9 mg/l was maintained during all tests. The generator carrier air flow rate was maintained at a constant flow of 0.7 ft^3/min. An ozone gas flow rate of 1.0 l/min was used in the contactor since ozone absorption rate was adversely affected by higher flow rates. The absorbed ozone in the sample was determined by iodometric titration of the potassium iodide solution used to trap the off gas ozone and subtracting this value from the predetermined influent ozone concentration. Prior to gas sample collection, the gas lines were purged for at least

one minute to insure equilibrium conditions.

Analytical Techniques

The iodometric titration was performed immediately after each run. This method is based on ozone liberating free iodine from a 0.05N potassium iodide gas washing solution ($O_3+2I^-+H_2O \rightarrow O_2+I_2+2OH^-$) and subsequent titration of the liberated iodine with 0.05N sodium thiosulfate solution using starch indicator under acid conditions. This method is subject to the fewest interferences, and capable of good precision. The reagents for the iodometric analysis are listed below:

1. 2N potassium iodide stock reagent: Dissolve 332g KI in 1 liter freshly boiled and cooled distilled water. Store in a brown bottle and refrigerate.
2. 20% sulfuric acid: Add 200 ml concentrated H_2SO_4 to 800 ml distilled water in a cool water bath. Store in reagent bottle.
3. Stock 1N sodium thiosulfate solution: Dissolue 250g $Na_2S_2O_3 \cdot 5H_2O$ in 1 liter freshly boiled distilled water. Store in reagent bottle.
4. Starch indicator solution: To 5g soluble starch, add a small amount of cold distilled water and grind into a paste. Pour paste into 1 liter boiling distilled water. Preserve with 1 ml toluene after cooling.

5. Sodium thiosulfate titrant 0.05N: Add 50ml 1N $Na_2S_2O_3$ to 950ml freshly boiled distilled water. Standardize this solution daily against potassium biniodate or potassium dichromate primary standard.
6. 0.05N Potassium iodide gas washing solution: Add 25ml 2N KI to 1 liter freshly boiled and cooled distilled water.
7. 0.100N Potassium biniodate: Dissolue 3.249g $KH(IO_3)_2$ in distilled water and dilute to 1 liter.

The method employed for standardization is given below:

To 80ml distilled water, add, with constant stirring, 1 ml concentrated H_2SO_4, 10ml 0.100N $KH(IO_3)_2$ and 1g KI. Titrate immediately with 0.100N $Na_2S_2O_3$ titrant until the yellow color of the liberated iodide is almost discharged. Add 1 ml starch indicator solution and continue until the blue color disappears.

$$\text{Normality } Na_2S_2O_3 = \frac{1}{\text{ml } Na_2S_2O_3}$$

The procedure for titration is described as follows:

Transfer the solution from the gas washing bottles to a 1 liter beaker; rinse the bottles with distilled water and add 10ml 20% H_2SO_4 to produce a P^H below 2. Titrate with 0.05N $Na_2S_2O_3$ titrant until the yellow color of the liberated iodine is almost discharged. Add 5ml starch indicator solution to impart a blue color and continue the titration until the blue color just disappears.

Ozone concentration may be determined as followed:

$$mg/l\ O_3 = \frac{\text{ml of titrant X Normality of titrant X 24,000}}{\text{Volume of gas sample in ml}}$$

Applied ozone dose was calculated by:

$$D = Y_1 \left(\frac{V_g}{V_S}\right)$$

where

D = applied ozone dose, mg O_3/L sample

Y_1 = concentration of ozone in the carrier gas, mg O_3/L gas

V_g = volume of gas flow, L

V_s = volume of sample, L

Absorbed ozone dose was calculated by:

$$A = \frac{V_g}{V_s} (Y_1 - Y_2)$$

where

A = absorbed ozone dose, mg O_3/L sample

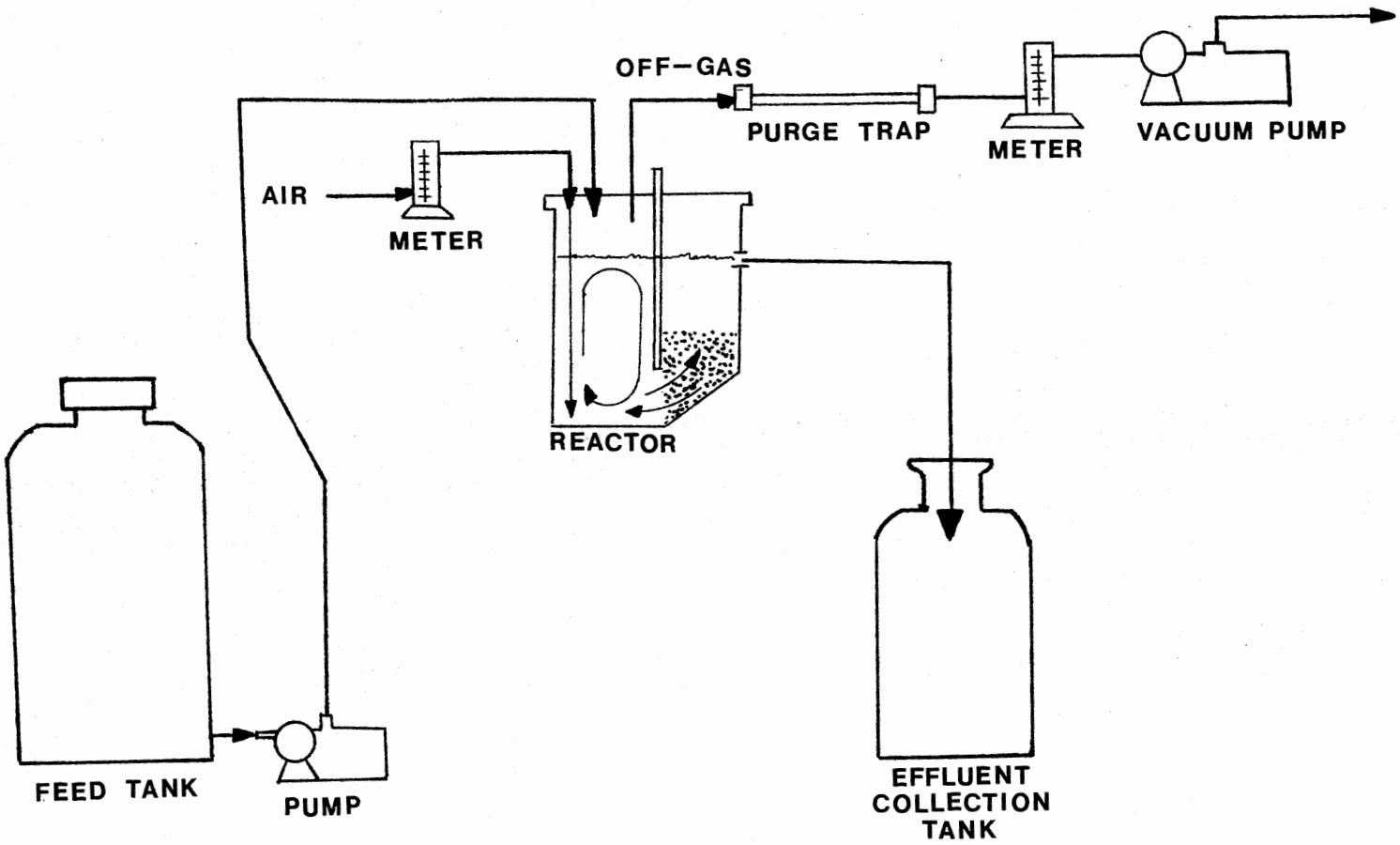
Y_2 = concentration of ozone in the gas leaving the contactor, mg O_3/L gas

Biological Treatment

Laboratory Apparatus

The complete-mix, bench-scale, continuous flow activated sludge reactor used in this study is shown in Figure 2. This pilot plant is made of stainless steel and is capable of being completely sealed. The system is composed of aeration and sedimentation compartments with internal

Figure 2. Schematic Diagram of Laboratory Scale Activated Sludge Unit with Off-Gas Sampling Device


OFF-GAS
PURGE TRAP
METER
VACUUM PUMP
AIR
METER
REACTOR
FEED TANK
PUMP
EFFLUENT
COLLECTION
TANK

recycle. A baffle between these two compartments was employed for adjusting the sludge recycling. The aeration compartment has a liquid volume of 3.01 liters. The settling compartment has a volume of 3.18 liters. The effluents from the settling compartments flowed by gravity to the collection tank.

The ozonated wastewater was pumped from a sealed 30 liter tank by a Milton Roy D pump. A continuous feed rate of approximately 6.25 ml/min was maintained to provide a hydraulic detention time of eight hours. Air was supplied to the aeration tank through two porous carborundum diffusers. The air flow rate was monitored and adjusted by a Bendix air flow meter. The P^H of the system was monitored daily with a calibrated P^H meter, and maintained at approximately 7.5.

The apparatus employed for off-gas sampling is also shown in Figure 2. The influent air and off-gas were measured and controlled with air flow meters. The off-gas was pulled by a vacuum pump through purge traps containing six inches of Tenax and four inches of silica gel for gas chromatograph analysis.

Feed Solution

The specific organic compounds to be investigated were ozonated in concentrated solutions. These ozonated organic compounds were mixed individually with a synthetic wastewater (base mix) and tap water in order to form the desired

feed concentration. The constituents of the synthetic wastewater are listed in table I.

Both 1,1,2,2 tetrachloroethane and 1,2 dichloropropane were ozonated at 2000 mg/l, and then diluted to theoretical concentrations of 300 mg/l and 200 mg/l, respectively, in the feed mixture.

Experimental and Analytical Procedures

The biological seed was taken from the activated sludge plant at Ponca City, Oklahoma. Three sludge ages, 2, 6 and 10 days, were operated for this study. The selected sludge age was maintained by wasting MLSS daily from the continuous flow reactor. This was accomplished by using the Lawrence and McCarty's mean cell residence time model as the means of operational control.

$$F_w = \frac{\frac{VX}{\theta_c} - FX_e}{X - X_e} \tag{8}$$

where

F_w = waste sludge flow rate, l/day

θ_c = sludge age, days

V = volume of reactor, liters

F = influent flow rate, l/day

X_e = effluent volatile suspended solids, mg/l

X = mixed liquor volatile suspended solids, mg/l

The X and X_e were measured by the membrane filter technique.

The system was first fed with full strength base mix.

TABLE I

CONSTINUENTS OF BASE MIX

Ethylene glycol	113.0 mg/l
Ethyl alcohol	113.0 mg/l
Glucose	113.0 mg/l
Glutamic acid	113.0 mg/l
Acetic acid	113.0 mg/l
Phenol	22.6 mg/l
Ammonium sulfate	100.0 mg/l
Phosphoric acid	15.74 mg/l
Salts	
$CaCl_2$	8.0 mg/l
$MnSO_4$	8.0 mg/l
$FeCl_3.6H_2O$	0.4 mg/l
$MgSO_4.7H_2O$	80.0 mg/l

After one week of acclimation, the ozonated priority pollutant was gradually added to the system. Due to the tremendous amount of ozonated specific compounds needed to make up the feed solution, the specific compounds were ozonated at high concentration and then diluted to the desired concentration in the feed bottle. All ozonated specific compounds were set at least one hour for residual ozone dissipation before being fed to the reactor.

During the study period, as steady state was reached, influent and effluent substrate concentrations were measured by means of the BOD_5, TOC, COD, and specific organic compound analysis.

Biochemical Oxygen Demand (BOD)

The biochemical oxygen demand was measured according to the modified BOD test procedure suggested by Stover et al. (28). The modified procedure consisted of setting up a dilution water blank and several dilutions of the seed material in the dilution water without any samples. From this method an accurate amount of dissolved oxygen depletion due to the dilution water and the seed demand during BOD testing was determined. The initial and final dissolved oxygen values were determined using a calibrated dissolved oxygen meter. The ultimate BOD was employed to determine the biodegradability of ozonated specific compounds, since this procedure would minimize the impact of possible lag

periods during BOD exertion.

Chemical Oxygen Demand (COD)

The COD was determined by use of the Hach Reactor Digestion Colorimetric Method. This method requires digestion of 2 ml sample in a Hach reactor (using Hach reagents) for two hours at 150 °C followed by colorimetric measurement using a Hach DR/2 Spectrophotometer.

Total Organic Carbon (TOC)

The influent and soluble effluent total organic carbon concentrations were measured using a Backman 915 TOC Analyzer.

Gas Chromatograph Analysis

The specific compound analyses were performed by using an F & M Model 810 Gas Chromatograph. The Gas Chromatograph had a flame ionization detector with nitrogen as the carrier gas. The liquid samples were concentrated into a Tekmar Liquid Sample Concentrator Model LSC-1. For desorbing the compound absorbed in the purge trap, the heating elements around the trap were turned up to a temperature higher than the boiling point of the compound to be investigated. The off-gas traps were connected directly onto the purge-and--trap line for GC analysis. A computerized integrater was employed to give the detention time and area corresponding to the compound analyzed.

Data Analysis

A mass balance around the activated sludge system can be written as:

$$\left(\frac{ds}{dt}\right)_R V = FS_i - FS_e - \left(\frac{ds}{dt}\right)_G V - \left(\frac{ds}{dt}\right)_S V - \left(\frac{ds}{dt}\right)_A V$$

where

$\left(\frac{ds}{dt}\right)_R$ = rate of change of specific compound in reactor

S_i = specific compound in influent

S_e = specific compound in effluent

$\left(\frac{ds}{dt}\right)_G$ = specific compound removed by biodegradation

$\left(\frac{ds}{dt}\right)_S$ = specific compound removed by stripping

$\left(\frac{ds}{dt}\right)_A$ = specific compound removed by adsorption. Due to the volatile nature of the compounds, adsorption was assumed not to be a factor.

The biological constants Y_t, K_d, K_e', K, K_s, and μ_{max} were determined in terms of BOD_5, TOC, and COD by graphical methods. The plotting and calculation technique will be given in the result section of this thesis.

The characteristics of the wastewaters and the results obtained from the pilot plant studies were variable. Statistical analysis of this data provides the basis for reliable design. The biokinetic constants were reported in terms of frequency of occurrence, which was the constants that could be expected to be equalled or exceeded 5, 25, 50, 75, or 95 per cent of the time. The 50 per cent value was

equal to the average value.

The variability analysis was performed according to the procedure suggested by Stover et al. (36). The particular variable parameters, i.e., S_e, U, and S_iU, were each arranged in order of increasing magnitude. The total number of these variable parameters was equal to n, and m was the assigned serial number from 1 to n. The plotting position was $\frac{m}{n+1}$, which was equivalent to the per cent occurrence of the value. The actual values were then plotted against the per cent occurrences on probability paper. Thus, a line of best fit was obtained. These probability levels were then used to evaluate the variability expected in the biokinetic constants.

CHAPTER IV

RESULTS AND DISCUSSION

1,1,2,2 Tetrachloroethane

Three different concentrations, 500, 1000, and 2000 mg/l, of 1,1,2,2 tetrachloroethane were ozonated. Each set of ozonations was run at constant gas flow rate and at nine different absorbed ozone doses. Samples were collected and analyzed initially and after various periods of ozonation for specific compound, TOC, COD, and ultimate BOD.

The results of these runs are shown in Figures 3, 4, and 5. It should be noted, due to the low COD recovery, all the COD at 500 and 1000 mg/l concentrations were lower than the TOC. This is probably due to 1,1,2,2 tetrachloroethane is already partially oxidized by chlorine. Figures 3, 4, and 5 also indicated that TOC and COD followed almost linear decreasing relationships with absorbed ozone dose. Specific compound analysis by gas chromatograph also gave similar results, which showed only decrease in 1,1,2,2 tetrachloroethane concentration rather than oxidation. As was mentioned in the literature review, Stover and Kincannon (34) have shown that 1,1,2,2 tetrachloroethane is a highly strippable compound with more than 93% of the compound stripped

Figure 3. TOC, COD, and Ultimate BOD vs. Absorbed Ozone Dose for 1,1,2,2 Tetrachloroethane. 1,1,2,2 Tetrachloroethane Concentration - 2000 mg/l

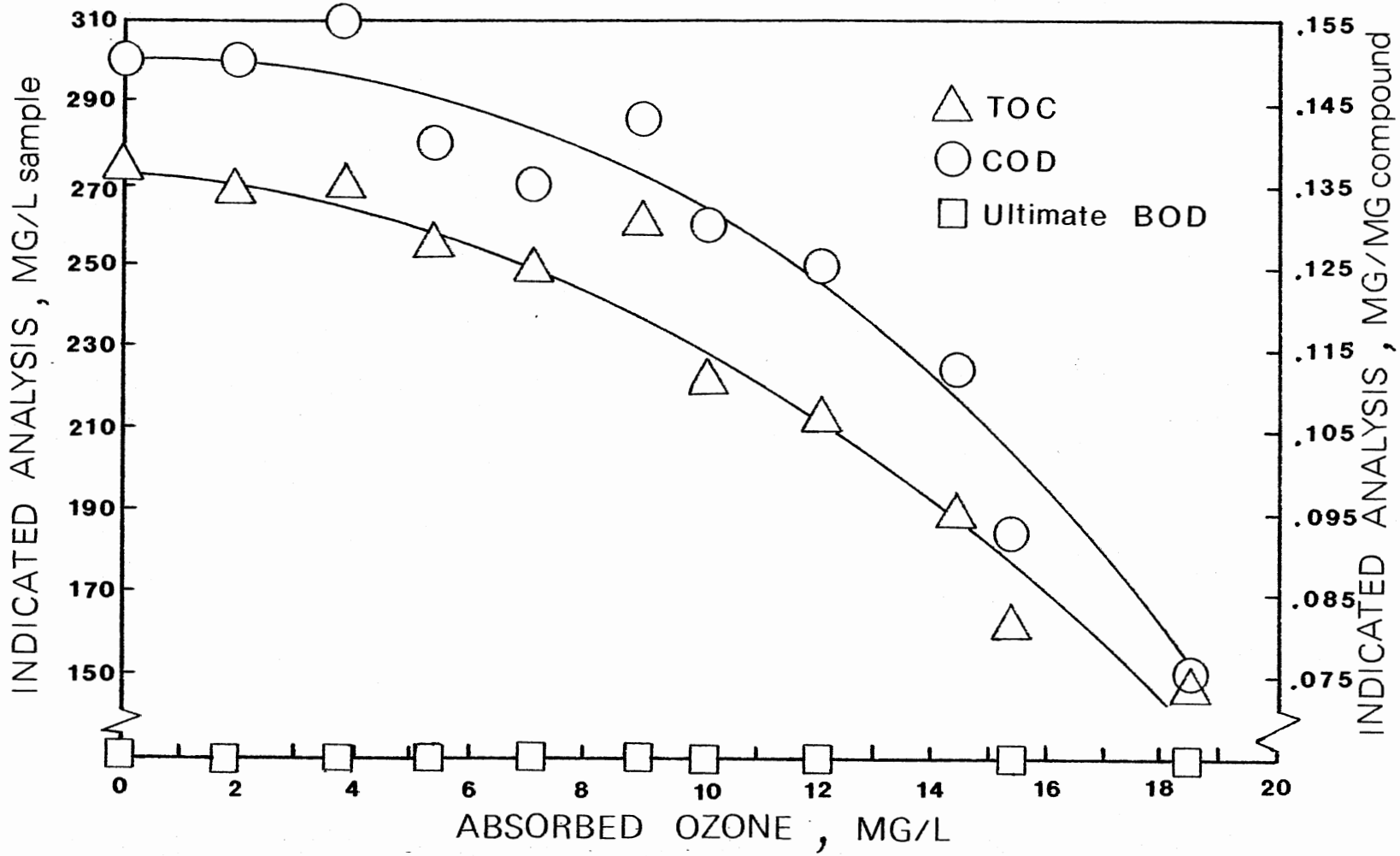

INDICATED ANALYSIS, MG/L sample
310
290
270
250
230
210
190
170
150
INDICATED ANALYSIS, MG/MG compound
.155
.145
.135
.125
.115
.105
.095
.085
.075
TOC
COD
Ultimate BOD
0
2
4
6
8
10
12
14
16
18
20
ABSORBED OZONE, MG/L

Figure 4. TOC, COD, and Ultimate BOD vs. Absorbed Ozone Dose for 1,1,2,2 Tetrachloroethane. 1,1,2,2 Tetrachloroethane Concentration - 1000 mg/l

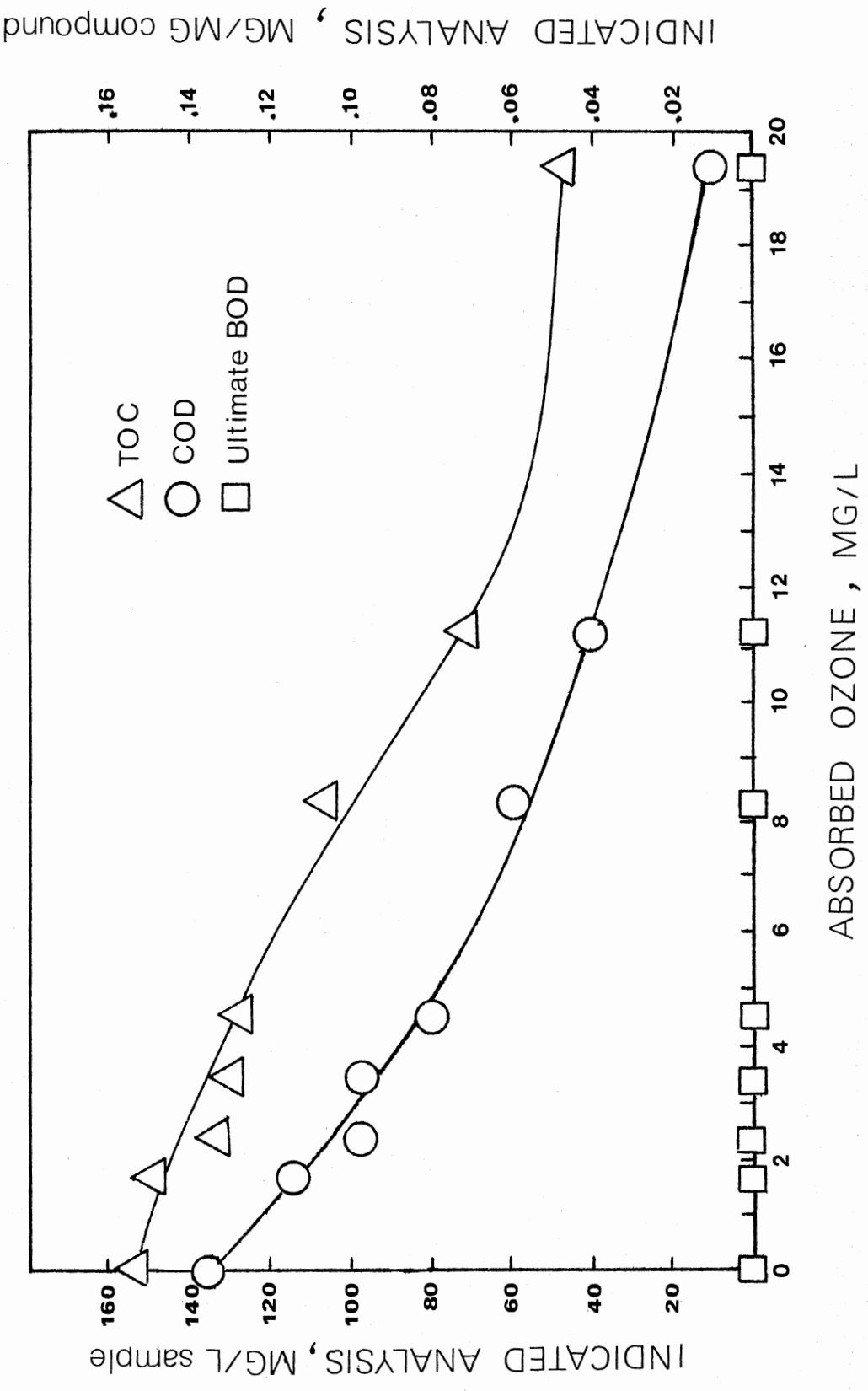
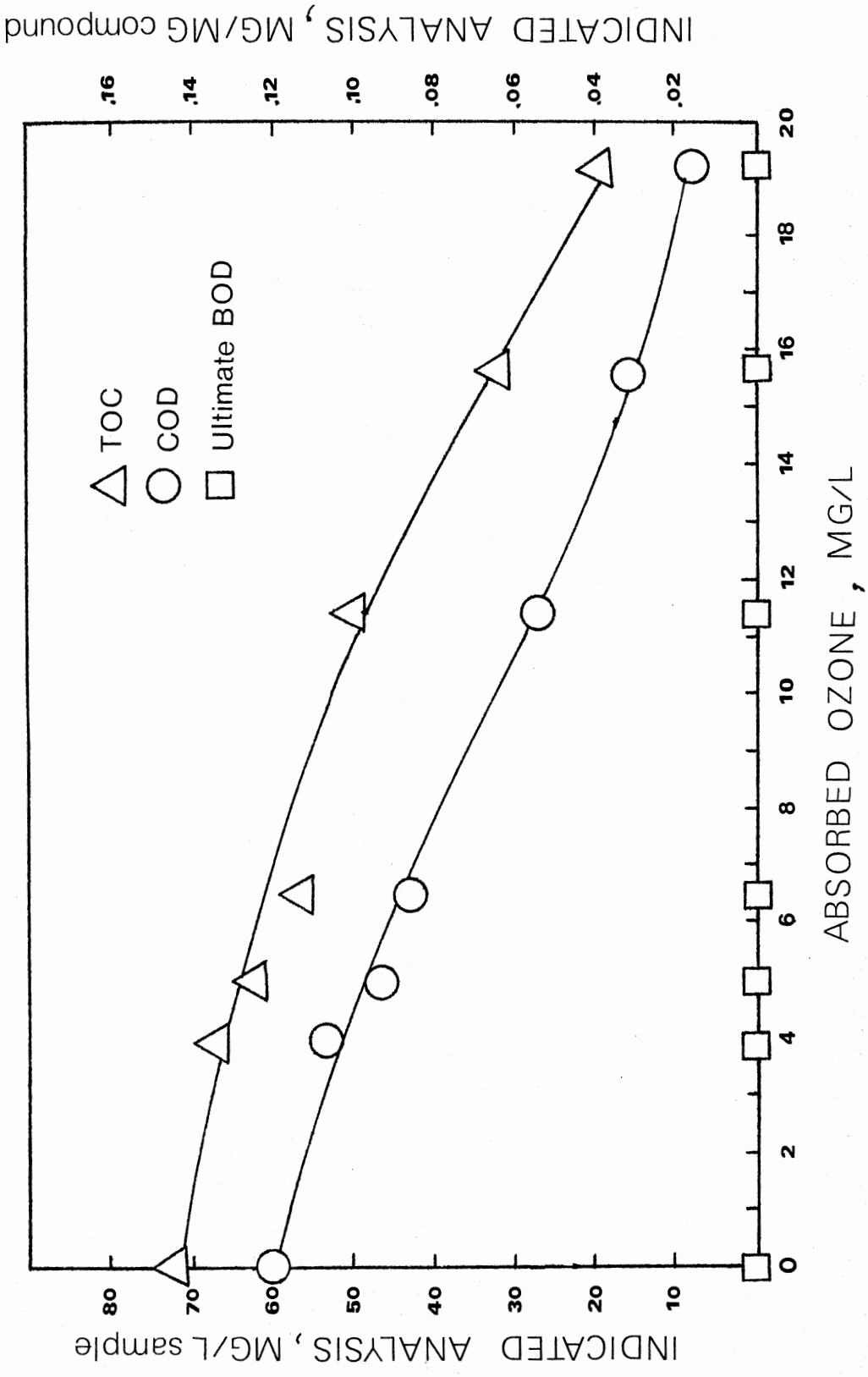

INDICATED ANALYSIS, MG/L sample
INDICATED ANALYSIS, MG/MG compound
ABSORBED OZONE, MG/L
TOC
COD
Ultimate BOD
160
140
120
100
80
60
40
20
.16
.14
.12
.10
.08
.06
.04
.02
0
2
4
6
8
10
12
14
16
18
20

Figure 5. TOC, COD, and Ultimate BOD vs. Absorbed Ozone Dose for 1,1,2,2 Tetrachloroethane. 1,1,2,2 Tetrachloroethane Concentration - 500 mg/l


INDICATED ANALYSIS, MG/L sample
INDICATED ANALYSIS, MG/MG compound
ABSORBED OZONE, MG/L
TOC
COD
Ultimate BOD
80
70
60
50
40
30
20
10
.16
.14
.12
.10
.08
.06
.04
.02
0
2
4
6
8
10
12
14
16
18
20

during biological treatment. Furthermore, the corresponding biodegradability parameters showed zero ultimate BOD with acclimated seed, Figures 3, 4, 5. This indicated ozonated 1,1,2,2 tetrachloroethane was totally resistant to biodegradation at the doses investigated. Therefore, the GC analysis and the corresponding measurements of ultimate BOD confirmed that 1,1,2,2 tetrachloroethane removal was a result only of air stripping and was not due to oxidation by ozone. This may have been due to the limited ozone output dosage (4.9 mg O_3/l_{air}) which was not strong enough to oxidize this highly chlorinated volatile compound in short contact time. Figure 6 shows the per cent of TOC remaining versus absorbed ozone dose. It is clear that 2000 mg/l solution has the lowest rate of TOC removal.

Since ozonation of 1,1,2,2 tetrachloroethane did not show improvement on biodegradation, only one sludge age (6 days) of the activated sludge system was operated for biological acclimation. 1,1,2,2 tetrachloroethane concentration in the feed was 300 mg/l. Absorbed ozone dose of 0.005 mg $O_3/mg_{compound}$ was chosen for this study. At this absorbed ozone dose the TOC and COD were reduced approximately 20% and 17% respectively.

Table II gives the mean values of BOD_5, TOC, and COD obtained from the biological activated sludge process. Data on the unozonated compound columns were obtained from EPA studies at Oklahoma State University. The comparison

Figure 6. Per Cent TOC Remaining vs. Absorbed Ozone Dose for 1,1,2,2 Tetrachloroethane

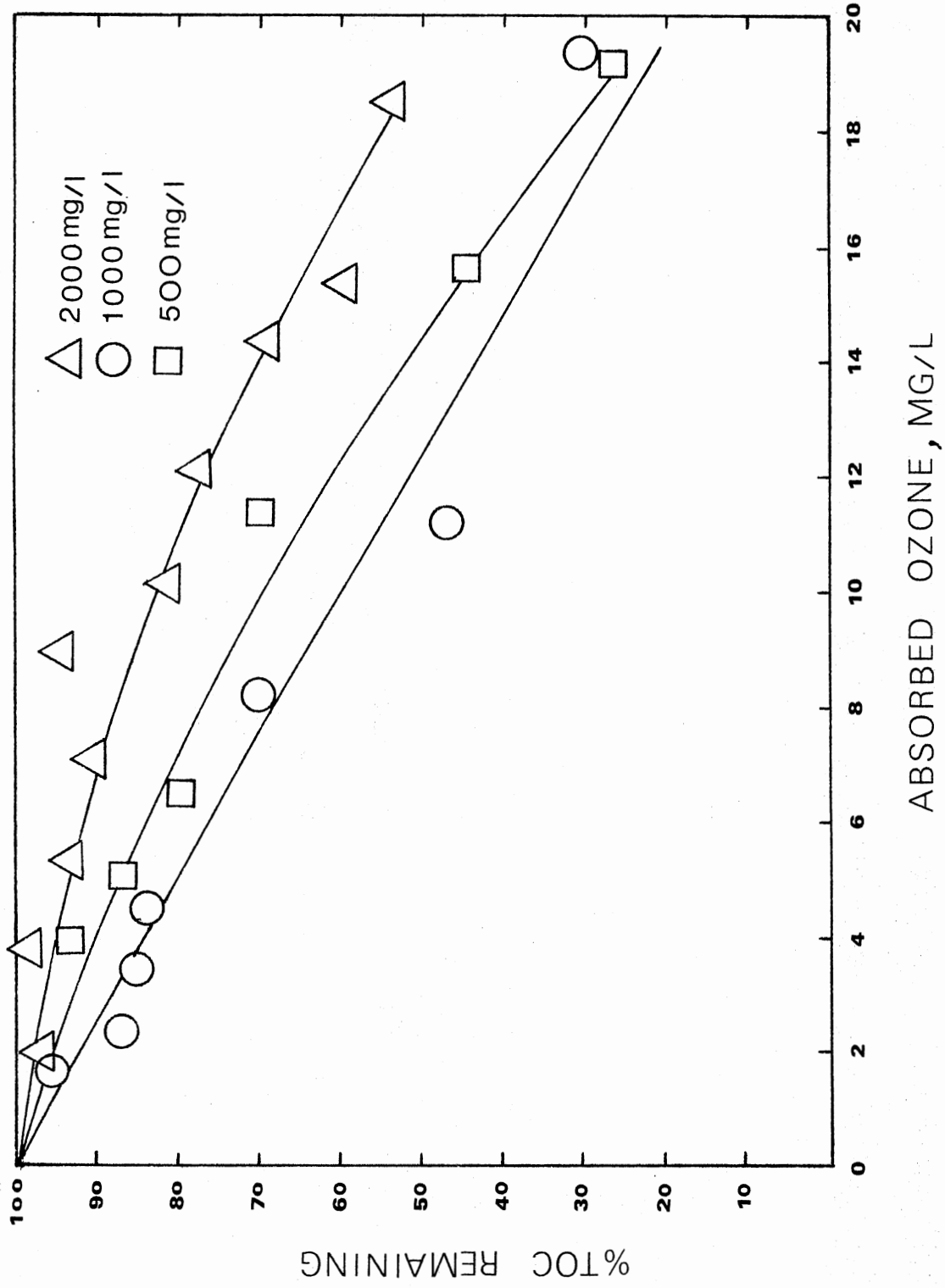

2000 mg/l
1000 mg/l
500 mg/l
% TOC REMAINING
ABSORBED OZONE, MG/L
100
90
80
70
60
50
40
30
20
10
0
2
4
6
8
10
12
14
16
18
20

TABLE II

SUMMARY DATA FOR OZONATED AND UNOZONATED
1,1,2,2 TETRACHLOROETHANE UNITS

Compound	Parameter	θ_c days	S_i mg/l	S_e mg/l	X MLVSS mg/l	X_e VSS mg/l	F/M	% Removal
Ozonated 1,1,2,2 TCE	BOD_5	5.95	260	2.3	1218	24	0.64	99.1
	TOC	5.96	183	14.1	1222	25	0.44	92.3
	COD	5.97	510	24.5	1220	25	1.30	95.2
Unozonated 1,1,2,2 TCE	BOD_5	1.6	242	2.2	614	91	1.12	99.1
		3.6	242	2.0	1140	43	0.60	99.2
		7.9	242	1.9	2338	63	0.30	99.2
	TOC	1.6	223	23.9	614	91	1.03	89.3
		3.6	223	25.1	1140	43	0.56	88.7
		7.9	223	22.9	2338	63	0.28	89.7
	COD	1.6	496	29.7	614	91	2.30	94.0
		3.6	496	28.8	1140	43	1.24	94.2
		7.9	496	27.0	2338	63	0.62	94.6

showed that X_e for the ozonated system was much lower than those for the unozonated systems. However, this was not sufficient proof that ozonation improved biological treatment. In any case, Table II indicated ozonation of 1,1,2,2 tetrachloroethane could reduce some operational problems during the biological process. In summary of the previous results, the ozone doses investigated were not high enough to make 1,1,2,2 tetrachloroethane biodegradable.

1,2 Dichloropropane

Table III shows the results of specific compound analysis with various absorbed ozone doses. Only one single peak appeard for each run throughout the experiments. The peak retention time slightly decreased with increase of absorbed ozone dose but somewhat insignificant. Moreover, attempting absorbed ozone doses greater than 0.01 $mg/mg_{compound}$ showed a sharp decrease in specific compound concentration. This was probably due to extensive stripping of the ozonated products, 1,2 dichloropropane, or both at this level of ozonation.

Figure 7 shows the BOD exertion versus time for ozonated 1,2 dichloropropane at an absorbed ozone dose of 0.0115 $mg/mg_{compound}$. As can be seen, the BOD exertion increases with time in a hyperbolic pattern. EPA studies at Oklahoma State University (34) have shown that unozonated 1,2 dichloropropane is totally resistant to biodegradation. In

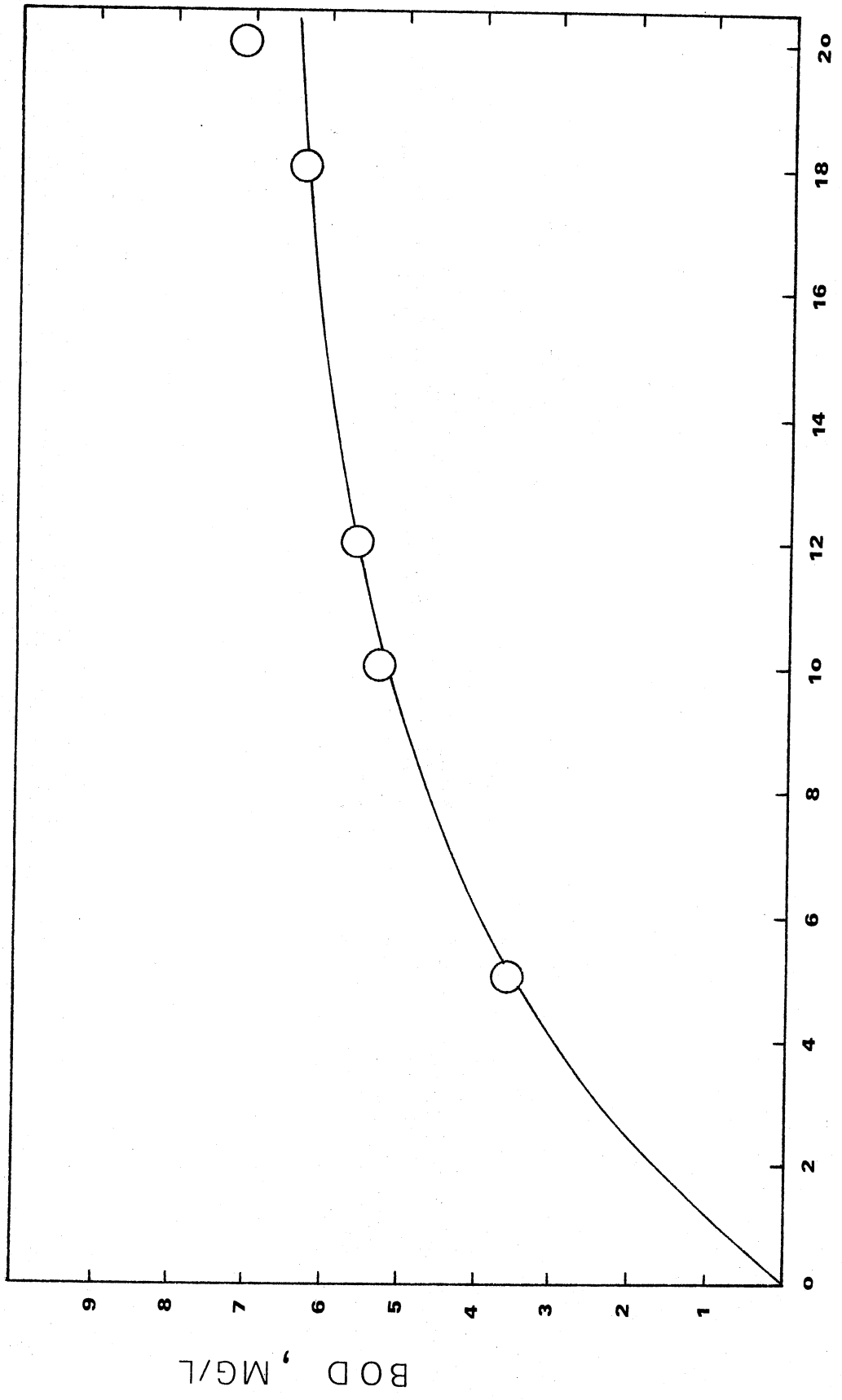
TABLE III

SPECIFIC COMPOUND ANALYSIS WITH VARIOUS ABSORBED OZONE DOSES FOR 1,2 DICHLOROPROPANE

Volume of Gas Flow	Absorbed Ozone		Peak Retention Time	Peak Area	Specific Compound Conc.
Liters	mg/l_{sample}	$mg/mg_{compound}$	Min.		mg/l
0	0.0	0.0	4.24	65,641,444	136.0
3	9.5	0.0048	4.12	34,037,927	70.3
6	11.4	0.0057	4.09	25,813,333	53.3
8	20.0	0.0100	4.10	16,359,529	34.0
15	22.5	0.0113	4.10	4,537,418	9.5
18	27.0	0.0135	4.14	793,659	1.8
20	18.0	0.0090	4.05	1,095,292	2.4
25	26.0	0.0130	4.01	514,780	1.2
27	20.0	0.0100	4.03	493,912	1.2

1,2 Dichloropropane Concentration - 2000 mg/l
All samples diluted 1/10 for GC analysis.

Figure 7. BOD Exertion vs. Time for Ozonated 1,2 Dichloropropane at Absorbed Ozone Dose of 0.0115 mg/mg compound Utilizing Biological Seed Acclimated to Ozonated 1,2 Dichloropropane. 1,2 Dichloropropane Concentration - 200 mg/l


BOD , MG/L
1
2
3
4
5
6
7
8
9
0
2
4
6
8
10
12
14
16
18
20
TIME, DAYS

other words, Figure 7 indicated that ozonation effectively increased the biodegradability of 1,2 dichloropropane. This was similar to the results found by Medley (18), that ozonated 1,2 dichloropropane showed a small, but measureable, BOD with little or no lag period.

The biological activated sludge processes were operated at three different sludge ages, 2, 6, and 10 days. The hydraulic detention time was maintained at approximately 8 hours throughout the experiments. An absorbed ozone dose of 0.01 $mg/mg_{compound}$ was chosen for this treatability study. Tables IV, V, and VI give the summaries of BOD_5, TOC, and COD characteristics for the ozonated system. The summary data for the unozonated systems are shown in Table VII. The data reported by Chung (38) and Stover and Kincannon (34, 35, 36) for the unozonated systems are presented for comparison purposes. Table VIII gives the mean values of the specific compound analysis for ozonated, unozonated, and nonbiological systems. From this comparison, it can be clearly seen that about 90% of the 1,2 dichloropropane was stripped in the biological and nonbiological system. However, upon ozonation only 43% to 58% was stripped. Moreover, it appears that the stripping efficiency for the ozonated systems was affected by θ_c. The unit with θ_c of 2.12 days had a higher stripping efficiency (58.1%), and the unit with θ_c of 10.1 days had a lower stripping efficiency (43.2%).

TABLE IV

BOD_5 SUMMARY DATA FOR ACTIVATED SLUDGE SYSTEM RECEIVING OZONATED 1,2 DICHLOROPROPANE

Parameter	S_i mg/l	S_e mg/l	X MLVSS mg/l	X_e VSS mg/l	F/M	θ_c days	% Removal
N	25	25	25	25	25	25	
$\bar{X}$	273.0	5.2	728.0	28.0	1.14	2.12	98.1
σ	33.8	1.6	118.8	12.7	0.23	0.16	
C.V.%	12.4	30.2	16.3	46.0	19.80	7.70	
N	26	26	26	26	26	26	
$\bar{X}$	270.0	3.6	1477.0	10.0	0.54	6.02	98.7
σ	20.9	2.3	132.3	7.3	0.06	0.13	
C.V.%	7.7	62.5	8.9	71.5	11.70	2.20	
N	26	26	26	26	26	26	
$\bar{X}$	277.0	3.9	2348.0	19.0	0.35	10.08	98.6
σ	25.9	1.1	111.1	13.2	0.04	0.12	
C.V.%	9.4	26.9	4.7	18.6	11.10	1.15	

TABLE V

TOC SUMMARY DATA FOR ACTIVATED SLUDGE SYSTEM
RECEIVING OZONATED 1,2 DICHLOROPROPANE

Parameter	S_i mg/l	S_e mg/l	X MLVSS mg/l	X_e VSS mg/l	F/M	θ_c days	% Removal
N	19	19	19	19	19	19	
$\bar{X}$	174.0	33.0	739.0	28.0	0.72	2.16	81.0
σ	13.2	10.0	128.7	14.7	0.12	0.17	
C.V.%	7.6	29.7	17.4	51.9	16.20	8.02	
N	25	25	25	25	25	25	
$\bar{X}$	167.0	14.0	1473.0	9.7	0.32	6.01	91.6
σ	7.0	2.7	130.7	7.1	0.03	0.18	
C.V.%	4.5	18.7	8.9	73.5	10.90	2.95	
N	20	20	20	20	20	20	
$\bar{X}$	177.0	17.0	2348.0	14.3	0.22	10.08	90.4
σ	15.2	6.7	116.7	5.0	0.02	0.12	
C.V.%	8.6	38.3	5.0	35.2	9.00	1.17	

TABLE VI

COD SUMMARY DATA FOR ACTIVATED SLUDGE SYSTEM
RECEIVING OZONATED 1,2 DICHLOROPROPANE

Parameter	S_i mg/l	S_e mg/l	X MLVSS mg/l	X_e VSS mg/l	F/M	θ_c days	% Removal
N	28	28	28	28	28	28	
$\bar{X}$	407.0	41.0	722.0	30.6	1.71	2.13	89.9
σ	45.7	13.3	116.4	15.6	0.31	0.16	
C.V.%	11.2	32.7	16.1	51.0	18.10	7.30	
N	27	27	27	27	27	27	
$\bar{X}$	444.0	29.0	1480.0	10.0	0.89	6.00	93.5
σ	48.8	8.5	130.7	7.12	0.14	0.18	
C.V.%	11.0	29.4	8.8	70.20	16.10	2.90	
N	20	20	20	20	20	20	
$\bar{X}$	403.5	27.4	2313.0	19.8	0.52	10.04	93.2
σ	38.4	11.7	105.0	20.1	0.05	0.33	
C.V.%	9.5	42.7	4.5	101.3	9.30	3.30	

TABLE VII

BOD_5, TOC, AND COD SUMMARY DATA FOR UNOZONATED 1,2 DICHLOROPROPANE UNITS

Parameter	θ_c days	S_i mg/l	S_e mg/l	X MLVSS mg/l	X_e VSS mg/l	F/M	% Removal
	1.98	247	2.9	458	21	1.47	98.8
BOD_5	3.73	247	1.1	1024	10	0.70	99.6
	6.27	247	2.1	1129	5	0.63	99.1
	2.00	197	18	490	19	1.09	90.9
TOC	3.84	199	18	1062	11	0.54	90.9
	6.01	200	24	1236	5	0.46	88.0
	1.86	480	50	477	15	2.74	89.6
COD	3.91	480	38	1040	6	1.34	92.1
	6.16	480	43	1146	5	1.20	91.0

TABLE VIII

SPECIFIC COMPOUND MASS BALANCE OF OZONATED AND UNOZONATED 1,2 DICHLOROPROPANE

Compound	θ_c days	Aeration Rate l/min	Inf. Conc. mg/l	Inf. mg/min	Eff. mg/min	Off-Gas mg/min	% Recovery from Off-Gas	Overall Removal %
Ozonated 1,2 DCP	2.12	1.5	35.0	0.218	0.00075	0.127	58.1	99.7
	6.02	1.5	30.0	0.183	0.00062	0.097	53.0	99.7
	10.1	2.0	35.1	0.217	0.00058	0.094	43.2	99.7
Unozonated 1,2 DCP	1.98	1.9	159.4	0.925	0.006	0.813	87.9	99.4
	3.73	1.5	159.4	0.922	0.008	0.813	88.2	99.1
	6.27	2.0	159.4	0.914	0.009	0.813	88.9	99.0
Unozonated 1,2 DCP (Nonbiological system)	-	2.5	141.0	0.903	0.014	0.819	92.1	98.5

In order to evaluate the performances of the biological processes, the biokinetic constants were determined. These biokinetic constants of major interest are: Y_t, K_d, K_e', K, K_s, and μ_{max}. It is recognized that variations in waste characteristics and changes in sludge condition will influence the parameters developed. Thus, these variations must be evaluated for reliable design. Figure 8 shows the probability plot of U in terms of BOD_5 at 2, 6, and 10 day sludge ages. A probability plot of S_iU for the same system is shown in Figure 9. A probability plot of S_e for the same system is also shown in Figure 10. Thus, these probability levels can then be used to evalute the variability expected in the bioknetic constants or coefficients.

The net specific growth rate is plotted against specific substrate utilization reat, $U = \frac{S_i - S_e}{Xt}$, in Figure 11. Y_t is the slope and K_d is the Y-axis intercept. All of the major design models, Eckenfelder, Lawrence and McCarty, and Gaudy, employ thses two biokinetic constants and all use a graphic method for determination of these constants similar to Figure 11.

In Figure 12, the S_iU is plotted against S_e for determination of the Eckenfelder modified constant (K_e'). The Lawrance and McCarty's constants (K and K_s) can be determined by plotting $1/U$ versus $1/S_e$, as shown in Figure 13. The maximum specific growth rate (μ_{max}) used in Gaudy's design model can be determined by plotting $1/\mu$ against

Figure 8. Observed Specific Substrate Utilization Rate (BOD_5) Variability for Activated Sludge Systems Receiving Ozonated 1,2 Dichloropropane

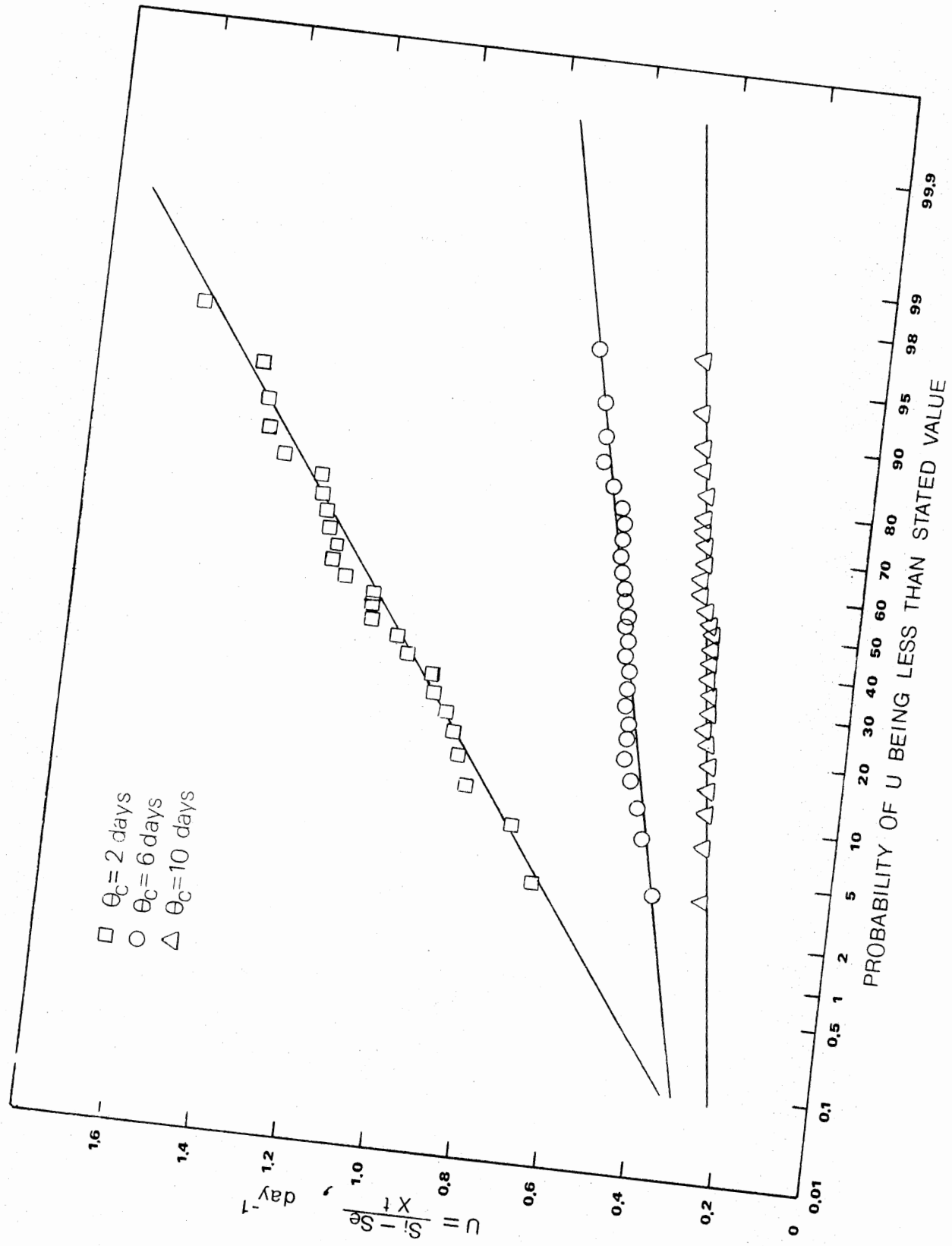

□ θc= 2 days
○ θc= 6 days
△ θc=10 days
U = (Si − Se)/Xt day⁻¹
PROBABILITY OF U BEING LESS THAN STATED VALUE
0
0,2
0,4
0,6
0,8
1,0
1,2
1,4
1,6
0,01
0,1
0,5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99,9

Figure 9. Observed $S_i(S_i-S_e)/Xt$ (BOD_5) Variability for Activated Sludge Systems Receiving Ozonated 1,2 Dichloropropane

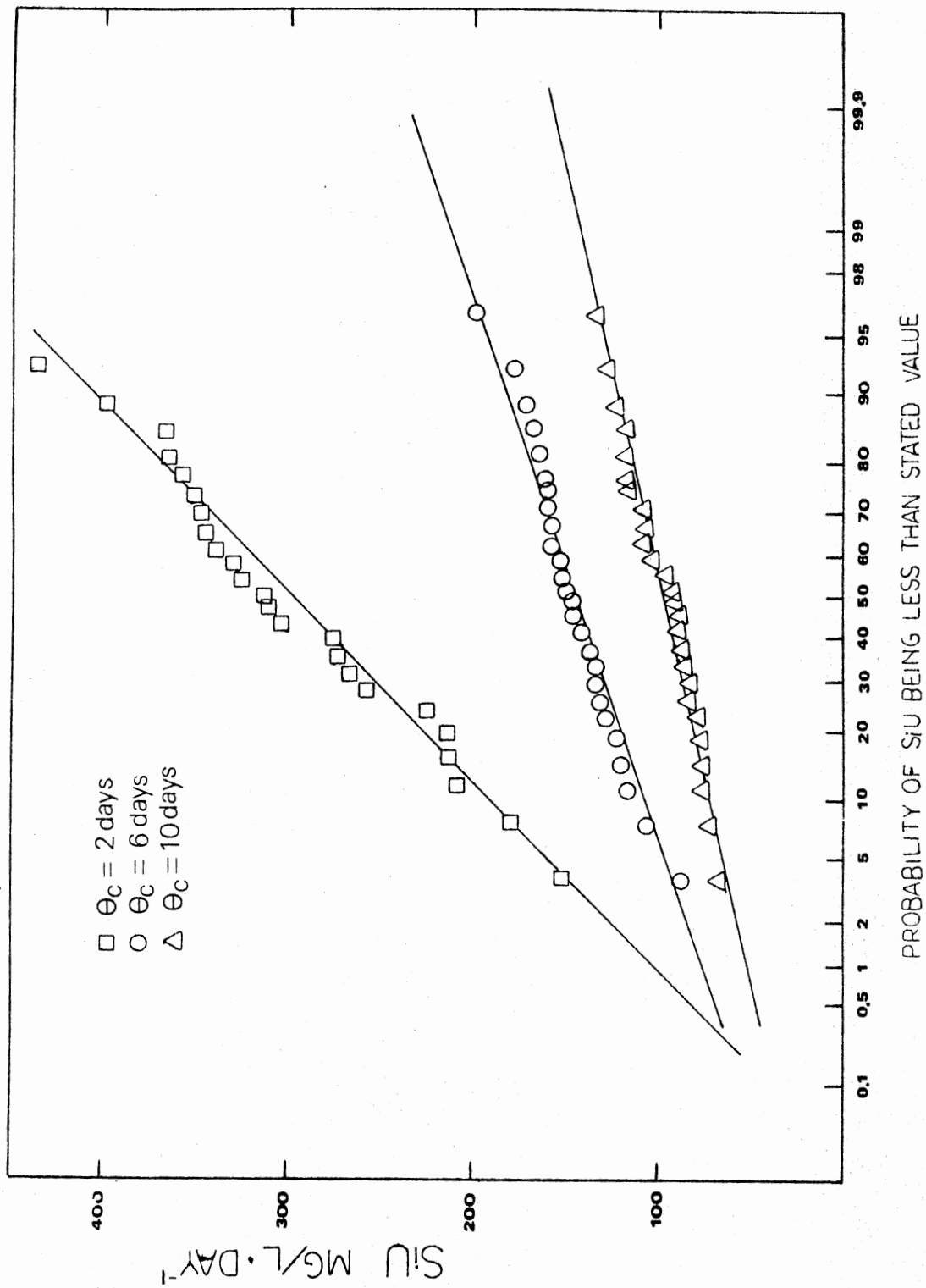

SiU MG/L·DAY⁻¹
400
300
200
100
□ θc = 2 days
○ θc = 6 days
△ θc = 10 days
0,1
0,5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99,8
PROBABILITY OF SiU BEING LESS THAN STATED VALUE

Figure 10. Observed Effluent BOD_5 Variability for Activated Sludge Systems Receiving Ozonated 1,2 Dichloropropane

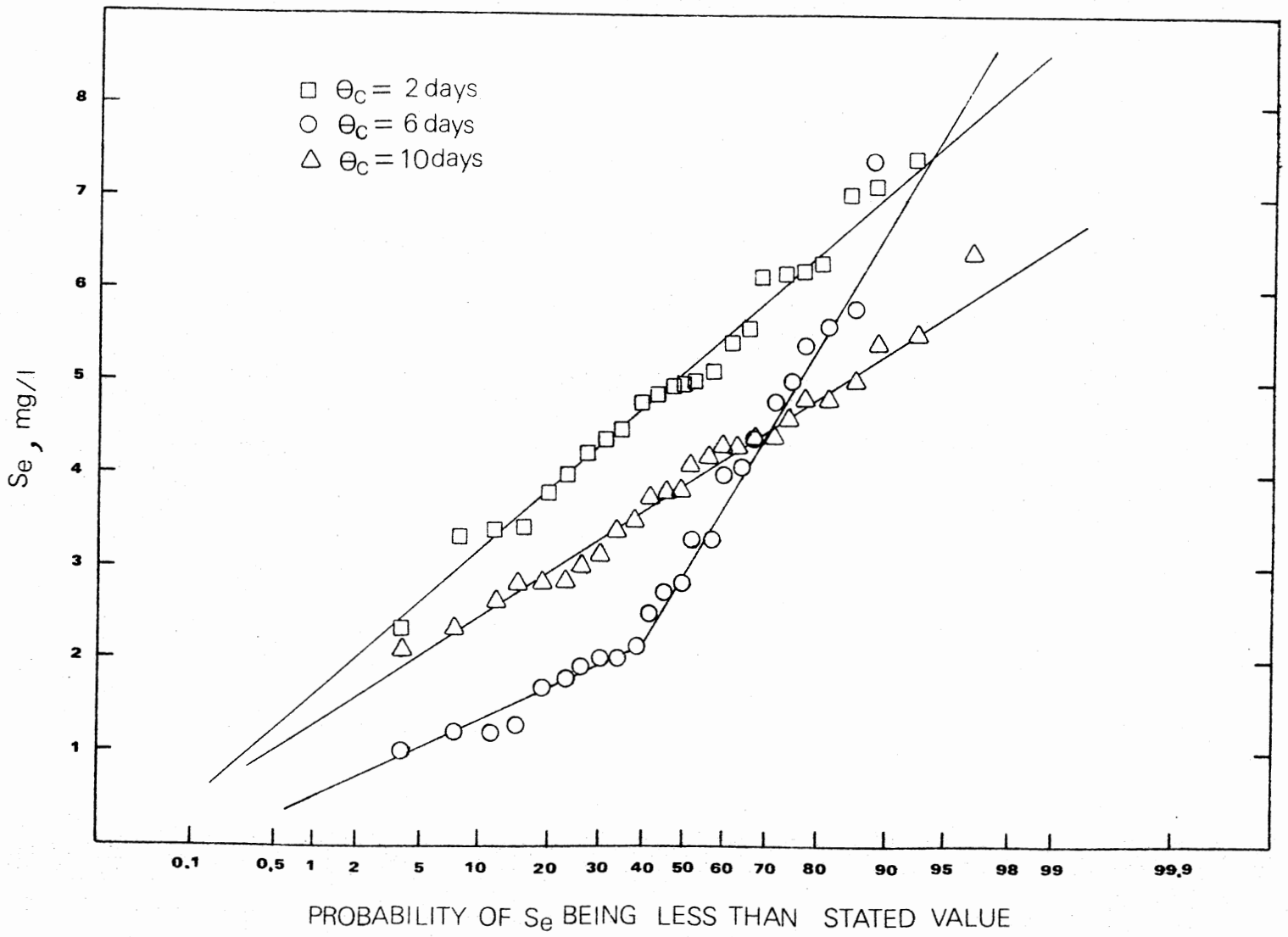

□ θc = 2 days
○ θc = 6 days
△ θc = 10 days
Se, mg/l
8
7
6
5
4
3
2
1
0.1
0,5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99,9
PROBABILITY OF Se BEING LESS THAN STATED VALUE

Figure 11. Graphical Determination of Y_t and K_d (BOD_5) at Different Probability Levels for Activated Sludge Systems Receiving Ozonated 1,2 Dichloropropane

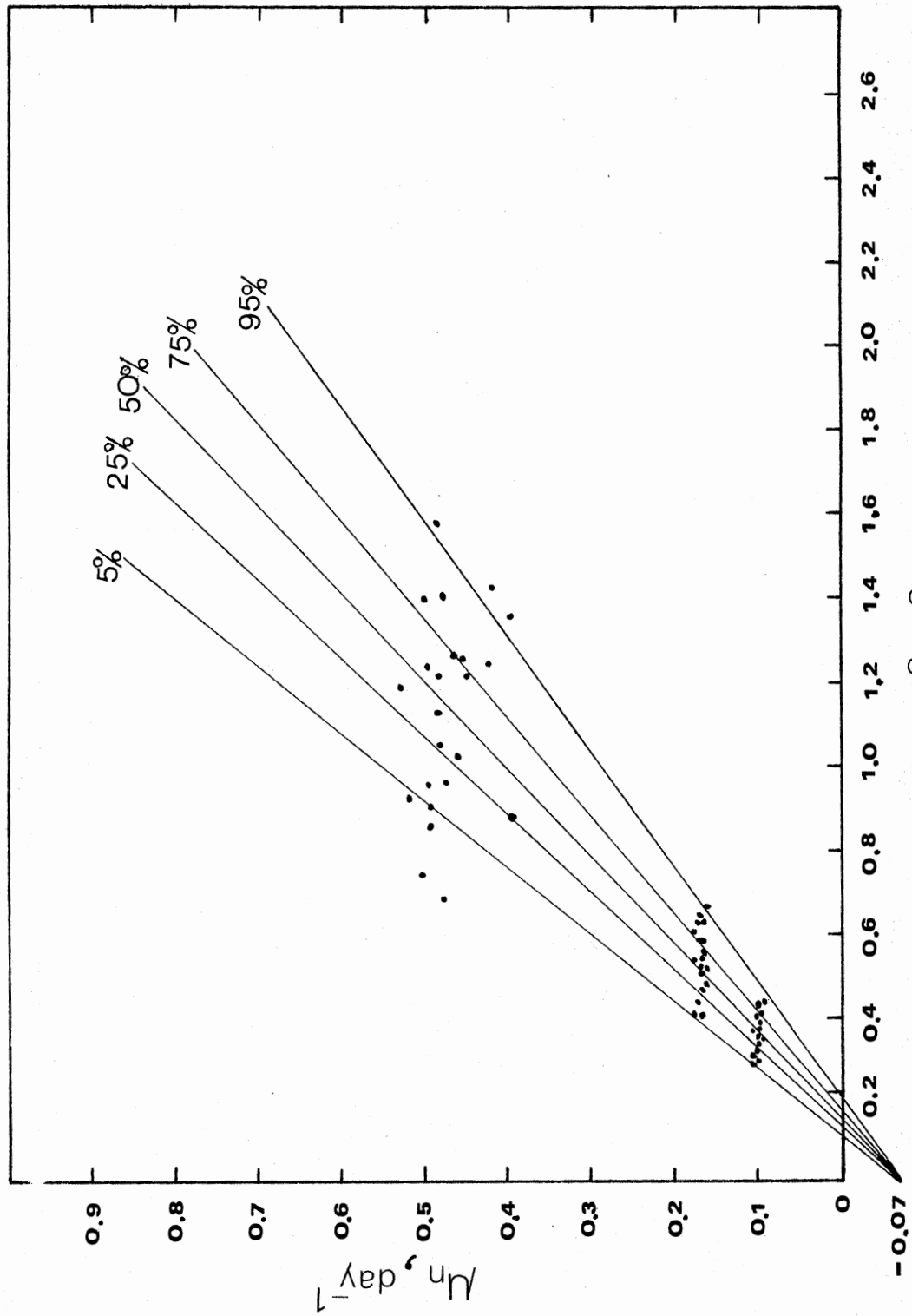

5%
25%
50%
75%
95%
μ_n, day^{-1}
$\frac{S_i - S_e}{X\,t}$, day^{-1}
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
-0.07
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6

Figure 12. Graphical Determination of K_e' (BOD_5) at Different Probability Levels for Activted Sludge Systems Receiving Ozonated 1,2 Dichloro-propane

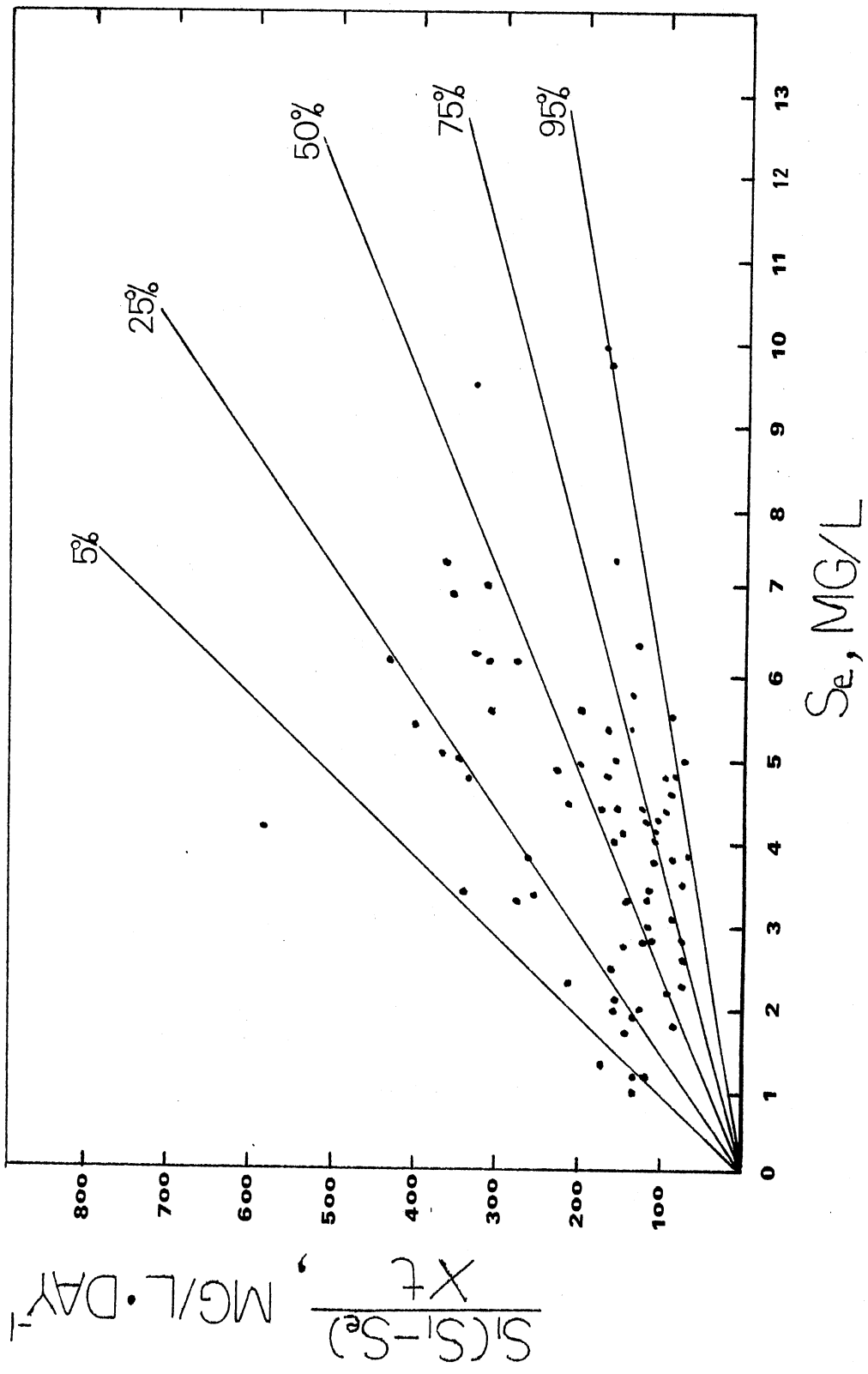

5%
25%
50%
75%
95%
$\frac{S_i(S_i-S_e)}{X_t}$, MG/L·DAY^{-1}
S_e, MG/L
0
1
2
3
4
5
6
7
8
9
10
11
12
13
100
200
300
400
500
600
700
800

Figure 13. Graphical Determination of K and K_s (BOD_5) at Different Probability Levels for Activated Sludge Systems Receiving Ozonated 1,2 Dichloropropane

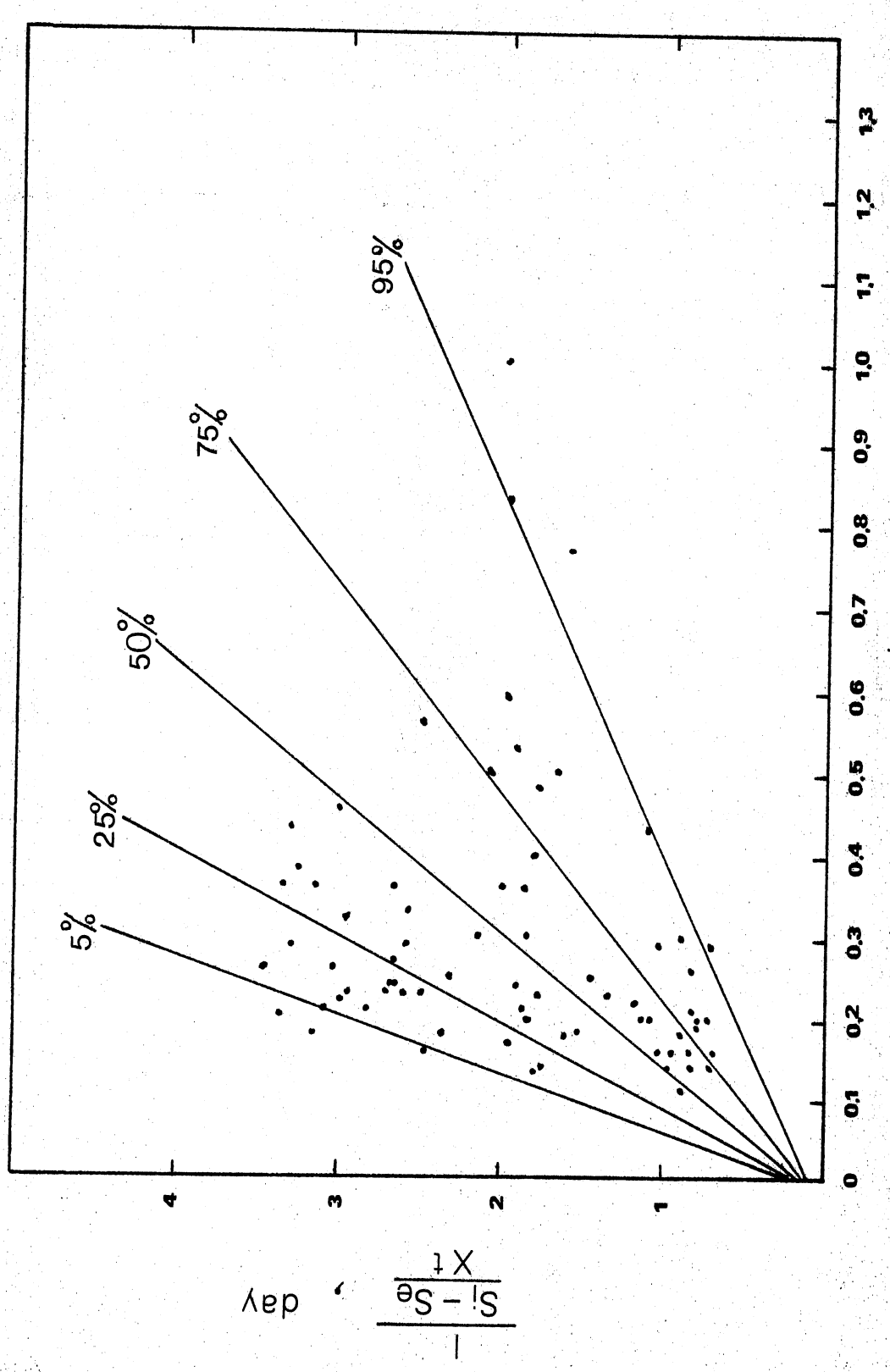
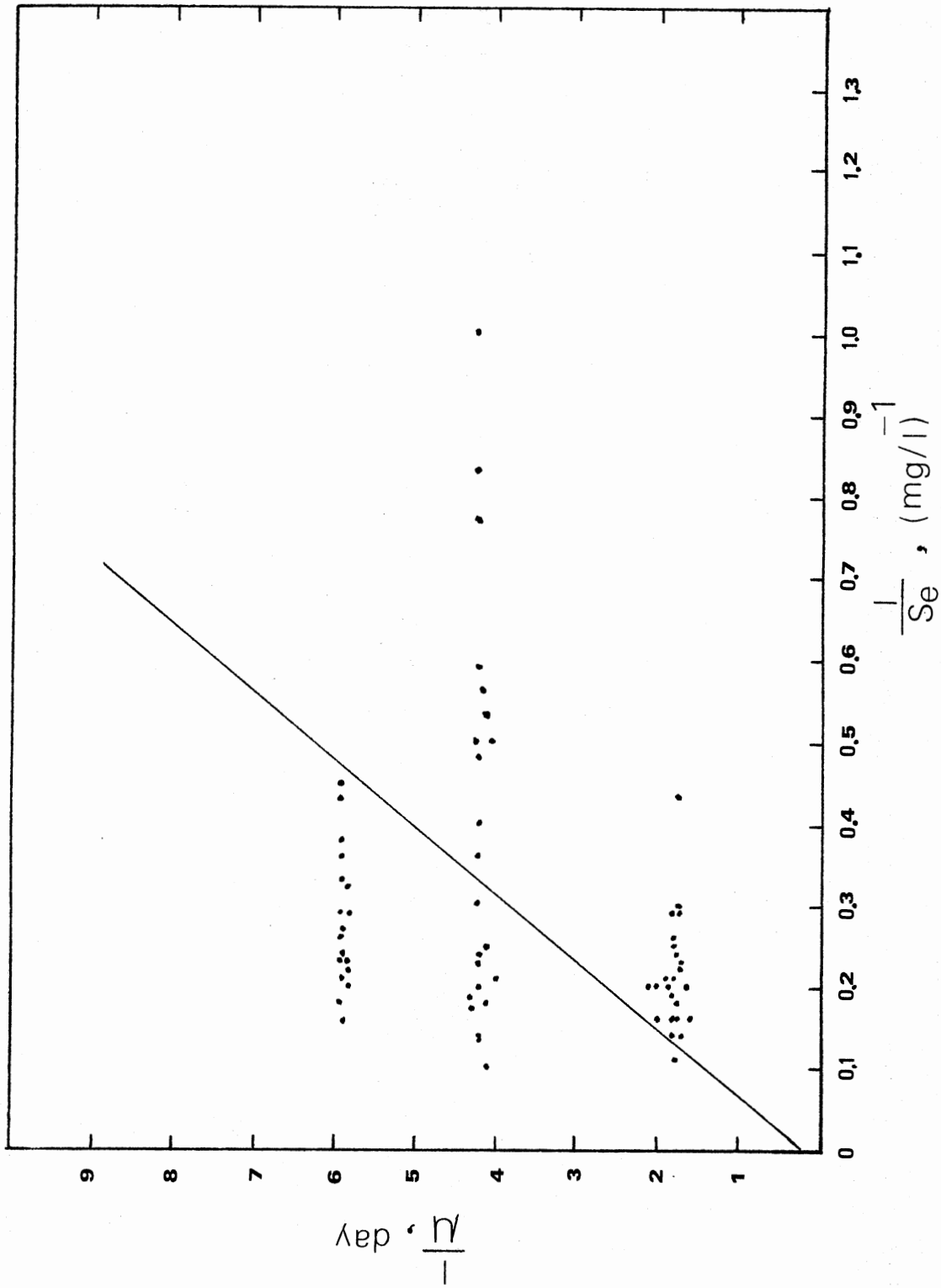

95%
75%
50%
25%
5%
0
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1,0
1,1
1,2
1,3
1
2
3
4
$\frac{1}{S_e}$, $(mg/l)^{-1}$
$\frac{1}{\frac{S_i - S_e}{X\,t}}$, day

Figure 14. Graphical Determination of μ_{max} and K_s (BOD_5) at 50% Probability Level for Activated Sludge Systems Receiving Ozonated 1,2 Dichloropropane


1/μ, day
1
2
3
4
5
6
7
8
9
0
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1,0
1,1
1,2
1,3
1/Se, (mg/l)⁻¹

$1/S_e$, Figure 14.

In Table IX, the 5, 25, 50, 75, and 95 percent probable values of the biokinetic constants obtained from Figures 11-14, in terms of BOD_5, are summarized. Similar biokinetic constants from the unozonated systems are also presented in parenthesis for comparison. As shown in Table IX, all the probable K_e' for the ozonated systems are significantly lower than those for the unozonated systems. At the 50% probability line, the K_e' for the ozonated systems is 41.8 while the K_e' for unozonated systems is 128. By using Eckenfelder's design model, $V = \frac{FS_i(S_i-S_e)}{X\ K_e'\ S_e}$, for the same design conditions the ozonated system requires a reactor volume almost three times larger than the reactor volume required by the unozonated system to meet the same effluent limitation. A possible explanation is that in the activated sludge system receiving unozonated 1,2 dichloropropane, stripping is the major removal mechanism. However, when the activated sludge process receives ozonated 1,2 dichloropropane, biological oxidation and physical stripping both become major mechanisms for removal of the compound. This agrees with the data obtained by GC analysis, which showed that in biological systems only 43% to 58% of the ozonated compound was stripped while about 90% of the unozonated 1,2 dichloropropane was stripped. Furthermore, μ_{max}, K, and K_s are all affected by ozonation. The ozonated system gives smaller μ_{max} and K but larger K_s. As stated previously,

TABLE IX

BIOKINETIC CONSTANTS IN TERMS OF BOD_5 FOR ACTIVATED SLUDGE SYSTEMS RECEIVING OZONATED 1,2 DICHLOROPROPANE

	5%	25%	50%	75%	95%
K_d (Unozonated)	0.07 (0.05)	0.07 (0.05)	0.07 (0.05)	0.07 (0.05)	0.07 (0.05)
μ_m (Unozonated)	3.3 (4.0)	3.3 (4.0)	3.3 (4.0)	3.3 (4.0)	3.3 (4.0)
Y_t (Unozonated)	0.63 (0.81)	0.54 (0.54)	0.48 (0.41)	0.43 (0.35)	0.36 (0.29)
K_e' (Unozonated)	105.3 (327)	69.3 (193)	41.8 (128)	27.3 (96)	17.5 (45)
K (Unozonated)	5.2 (4.9)	6.1 (7.4)	6.9 (9.7)	7.7 (11.4)	9.2 (13.8)
K_s (Unozonated)	73.4 (29)	58.5 (18)	42.9 (19)	30.7 (12)	21 (8)

(Unozonated) - Biokinetic Constant for Activated Sludge System Receiving Unozonated 1,2 DCP.

this is probably due to biological oxidation in the ozonated system.

Table X gives the mean values of the biokinetic constants in terms of TOC and COD. These biokinetic constants were determined from Figures 15-22. It can be clearly seen that the K_s for the ozonated systems in both TOC and COD are higher than those for the unozonated systems, and K_e' for the ozonated systems are much smaller than those for the unozonated systems. These are in agreement with the results obtained from BOD data. These results indicated that ozonated 1,2 dichloropropane, although partially stripped, was also removed by biodegradation in activated sludge processes.

TABLE X

SUMMARY OF 50% BIOKINETIC CONSTANTS IN TERMS OF TOC AND COD FOR OZONATED 1,2 DICHLOROPROPANE

Parameter	K_d	μ_m	Y_t	K_e'	K	K_s
TOC	0.07	3.3	0.82	2.7	4.0	192
(Unozonated)	(0.04)	(2.9)	(0.56)	(7.5)	(5.0)	(150)
COD	0.07	3.3	0.33	12	10	317
(Unozonated)	(0.06)	(1.0)	(0.30)	(20)	(3.3)	(73)

(Unozonated) - Biokinetic Constants for Activated Sludge System Receiving Unozonated 1,2 Dichloropropane.

Figure 15. Graphical Determination of Y_t and K_d (TOC) at 50% Probability Level for Activated Sludge Systems Receiving Ozonated 1,2 Dichloropropane

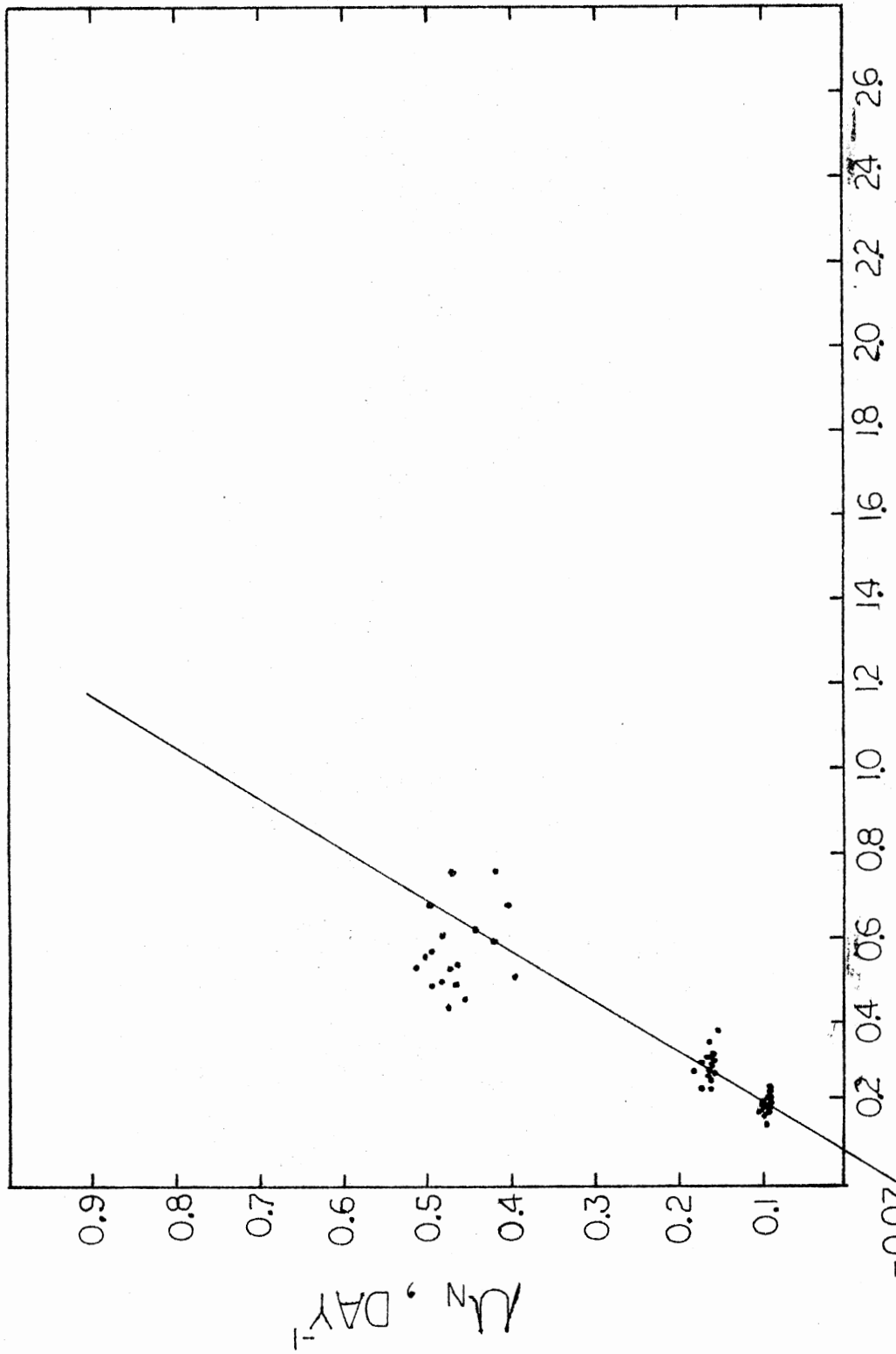

μ_N, DAY^{-1}
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
-0.07
0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6
$\frac{S_i - S_e}{Xt}$, DAY^{-1}

Figure 16. Graphical Determination of K_e' (TOC) at 50% probability Level for Activated Sludge Systems Receiving Ozonated 1,2 Dichloropropane

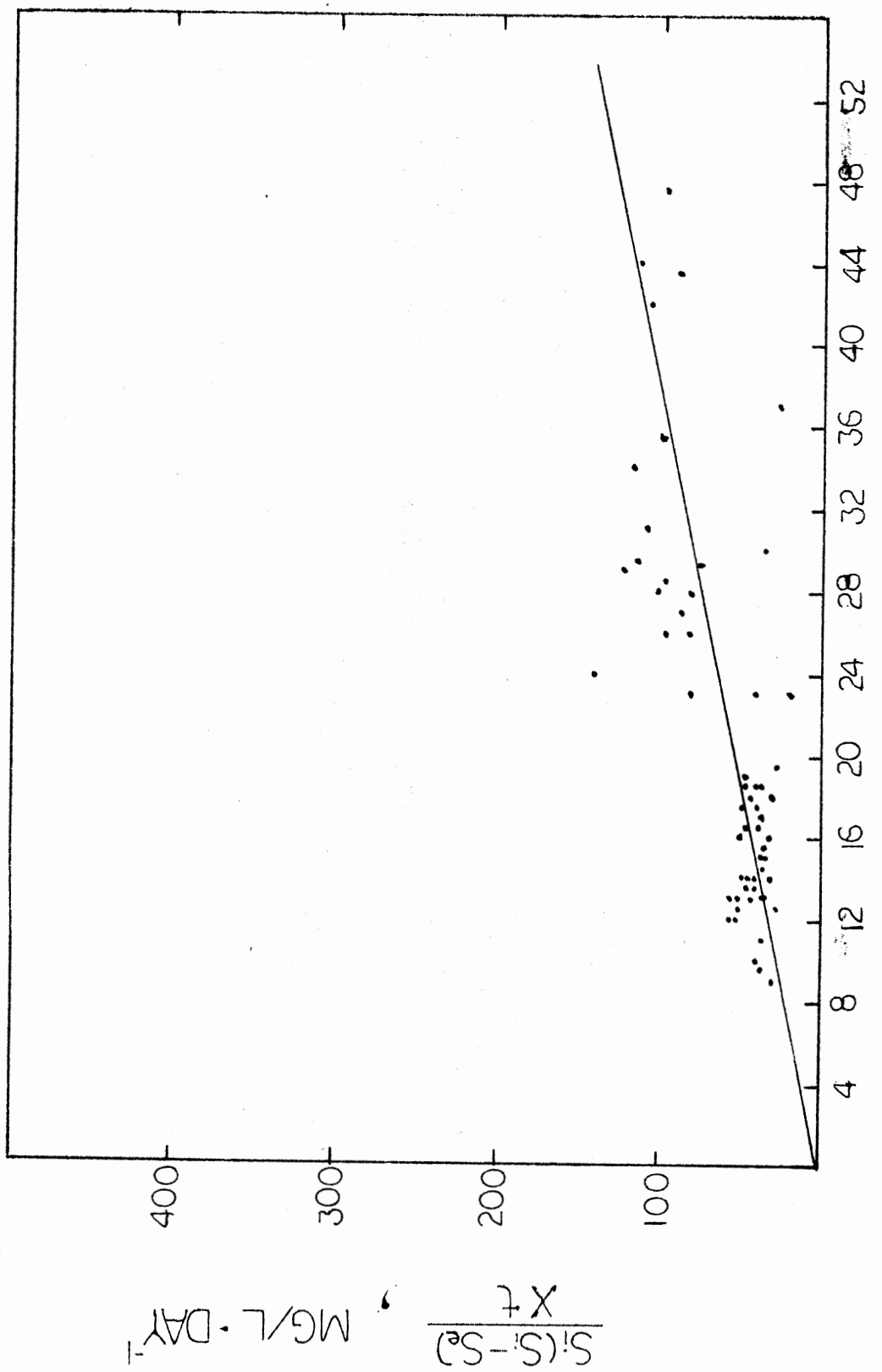

$\frac{S_i(S_i-S_e)}{X\,t}$, MG/L · DAY^{-1}
400
300
200
100
4
8
12
16
20
24
28
32
36
40
44
48
52
S_e, MG/L

Figure 17. Graphical Determination of K and K_s (TOC) at 50% Probability Level for Activated Sludge Systems Receiving Ozonated 1,2 Dichloropropane

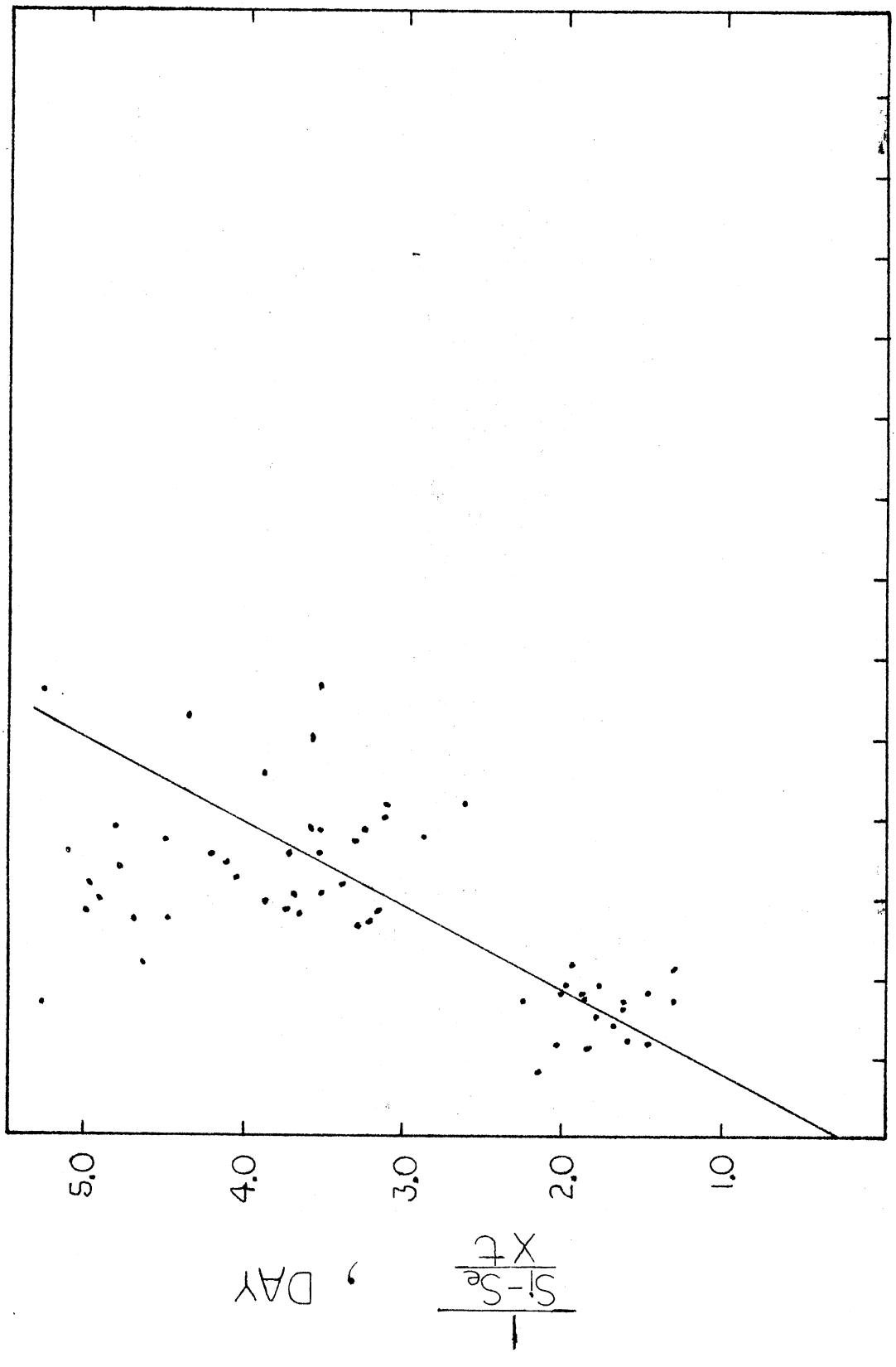

5.0
4.0
3.0
2.0
1.0
$\frac{S_i - S_e}{X\,t}$, DAY
.02 .04 .06 .08 .10 .12 .14 .16 .18 .20 .22 .24 .26
$\frac{1}{S_e}$, $(MG/L)^{-1}$

Figure 18. Graphical Determination of μ_{max} and K_s (TOC) at 50% Probability Level for Activated Sludge Systems Receiving Ozonated 1,2 Dichloropropane

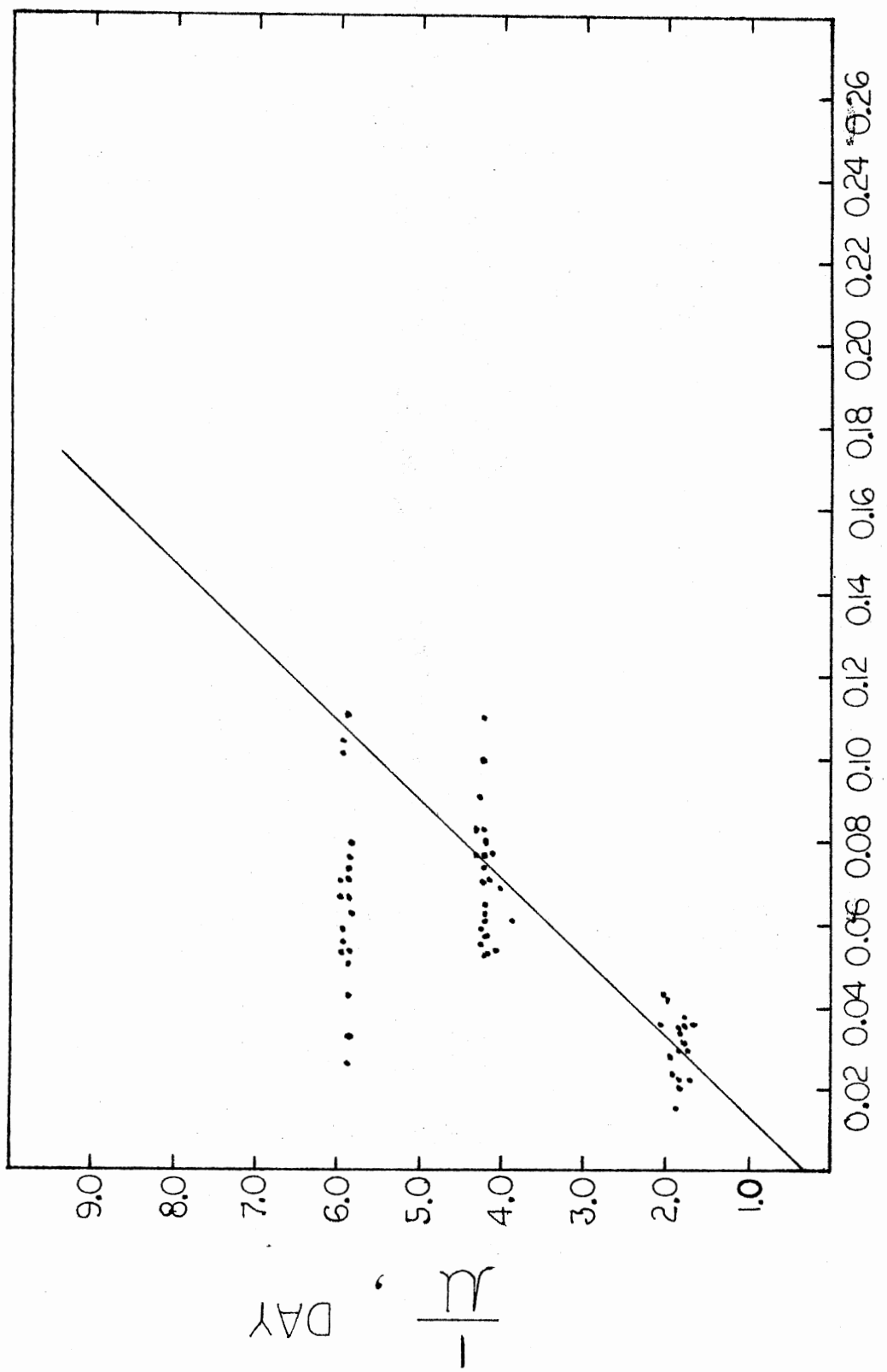

1/μ , DAY
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.02 0.04 0.06 0.08 0.10 0.12 0.14 0.16 0.18 0.20 0.22 0.24 0.26
1/Se , (MG/L)^-1

Figure 19. Graphical Determination of Y_t and K_d (COD) at 50% Probability Level for Activated Sludge Systems Receiving Ozonated 1,2 Dichloropropane

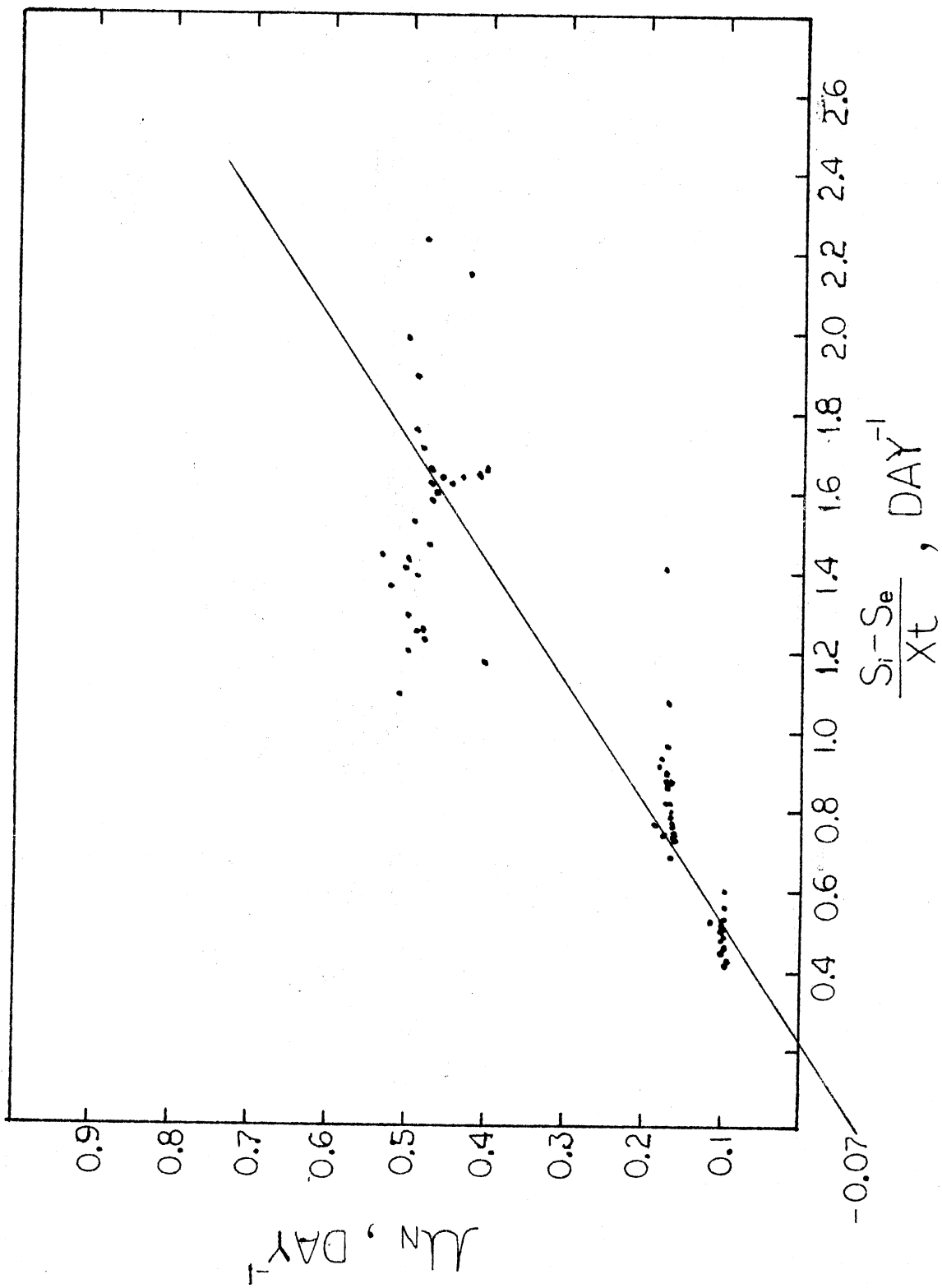

μ_N, DAY^{-1}
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
-0.07
0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6
$\frac{S_i - S_e}{Xt}$, DAY^{-1}

Figure 20. Graphical Determination of K_e' (COD) at 50% Probability Level for Activated Sludge Systems Receiving Ozonated 1,2 Dichloropropane

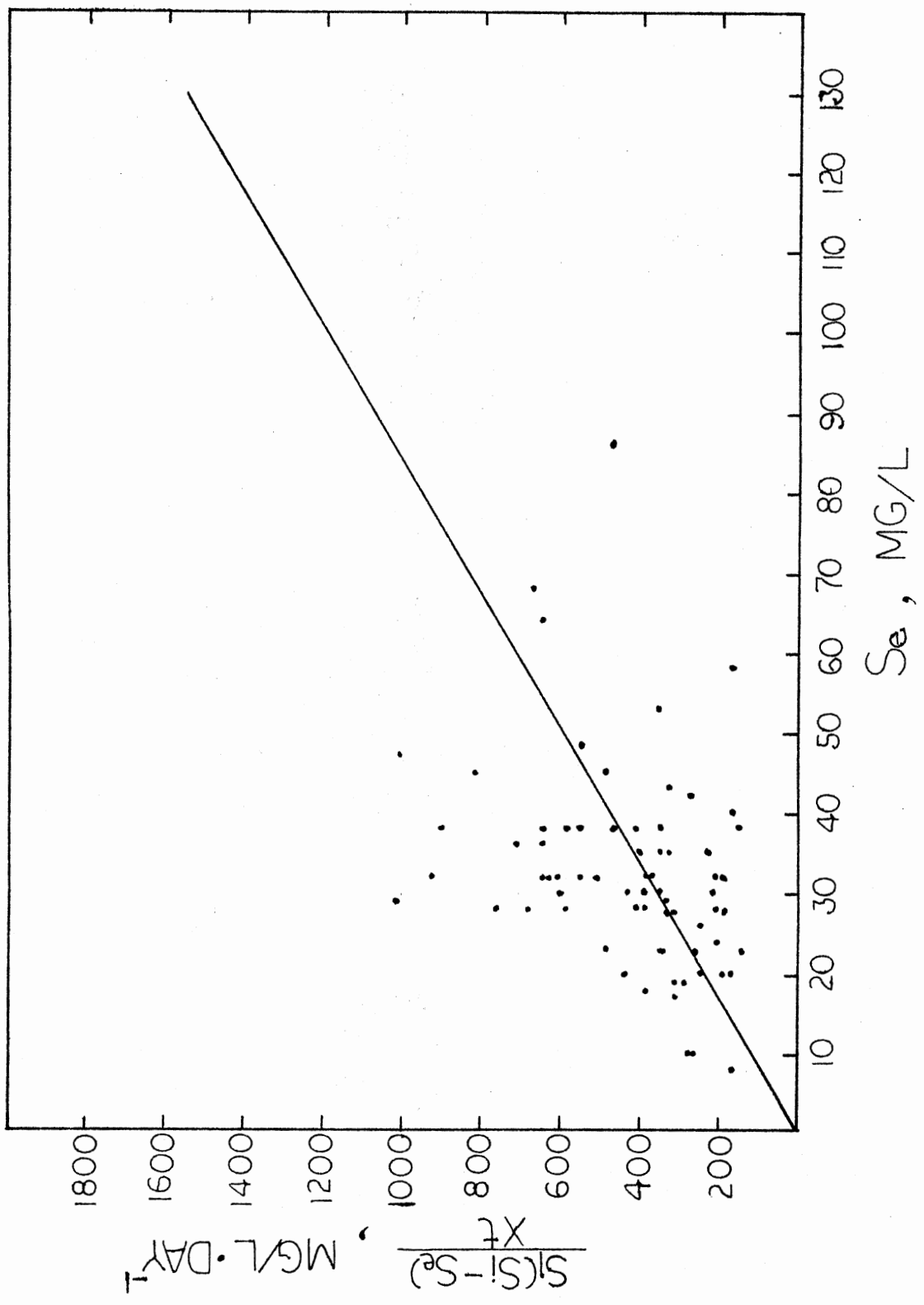

$\frac{Sl(Si-Se)}{Xt}$, MG/L·DAY^{-1}
1800
1600
1400
1200
1000
800
600
400
200
10
20
30
40
50
60
70
80
90
100
110
120
130
Se, MG/L

Figure 21. Graphical Determination of K and K_s (COD) at 50% Probability Level for Activated Sludge Systems Receiving Ozonated 1,2 Dichloropropane

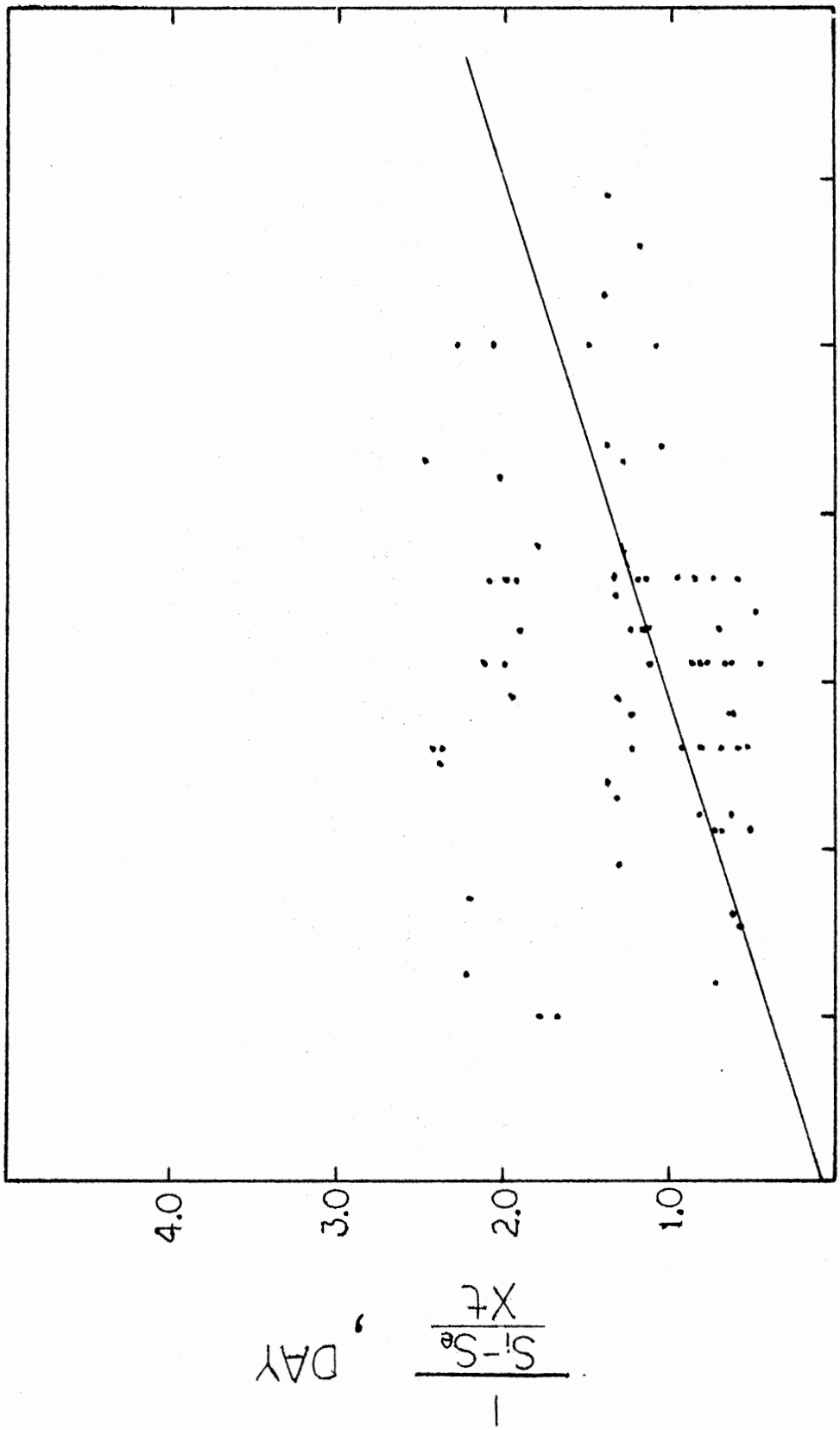
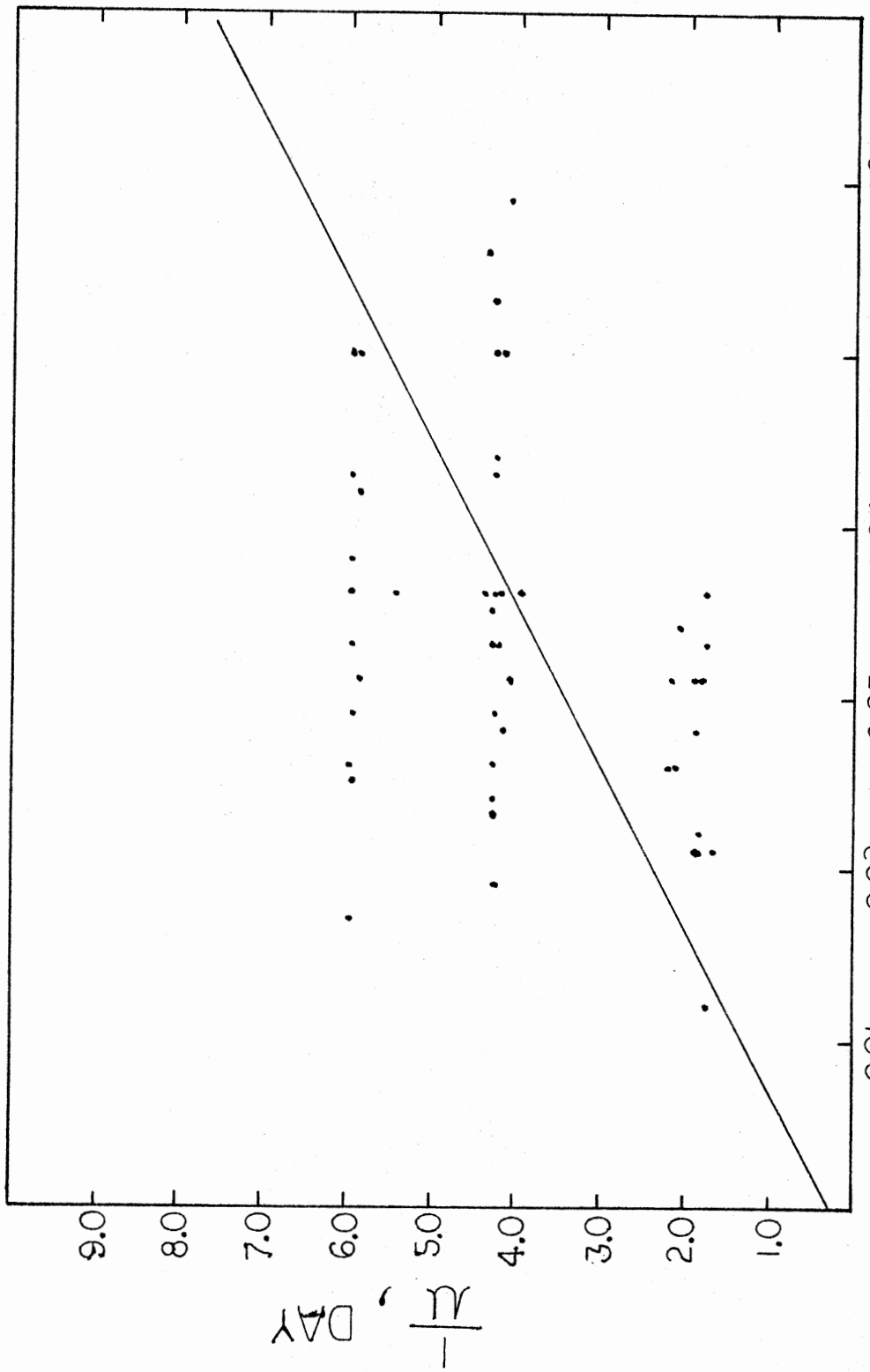

4.0
3.0
2.0
1.0
0.01
0.02
0.03
0.04
0.05
0.06
1/Se , (MG/L)^-1
1/(Si-Se)/Xt , DAY

Figure 22. Graphical Determination of μ_{max} and K_s (COD) at 50% Probability Level for Activated Sludge Systems Receiving Ozonated 1,2 Dichloropropane


9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
1/μ , DAY
0.01
0.02
0.03
0.04
0.05
0.06
1/Se , (MG/L)⁻¹

CHAPTER V

CONCLUSIONS

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

1,1,2,2 Tetrachloroethane

1. 1,1,2,2 Tetrachloroethane is not oxidized by ozone at the ozone deses investigated.

2. Ozonation of 1,1,2,2 Tetrachloroethane shows no improvement on biodegradation at doses investigated. The compound was stripped from the contact basin during ozonation.

1,2 Dichloropropane

1. Ozonation is very effective in increasing the biodegradability of 1,2 dichloropropane.

2. Ozonation has significantly decreased the physical stripping of this specific compound in the activated sludge reactor and enhanced biodegradation.

3. Ozonation may be a very practical method in biological wastewater treatment especially where 1,2 dichloropropane is present.

CHAPTER VI

SUGGESTIONS FOR FUTURE WORK

1. Study the effects of P^H and temperature on ozonation of 1,1,2,2 tetrachloroethane and 1,2 dichloropropane.

2. Investigate the operational performance of biological processes receiving higher ozonated 1,2 dichloropropane concentration.

3. Study the possibility of oxidizing highly chlorinated compounds, such as 1,1,2,2 tetrachloroethane, by high concentrations of absorbed ozone.

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