THE EFFECTS OF OZONE ON THE BIODEGRADABILITY OF ACRYLONITRILE, 1,2 DICHLOROPROPANE, AND 2,4 DINITROPHENOL

By

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1979

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the degree of
MASTER OF SCIENCE
July, 1981

Dedicated to my Parents

Cecil W. and Helen M. Medley

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ACKNOWLEDGMENTS

I would like to express my sincere thanks and appreciation to Dr. Enos L. Stover, my principal adviser, for his guidance, advice, patience, instruction, and excellent example of professionalism. I am also grateful to Dr. D. F. Kincannon and Dr. J. N. Veenstra for serving on my committee and for their instruction and inspiration. I would also like to thank Dr. M. H. Bates, Dr. R. N. DeVries and Dr. T. S. Manickam for their instruction and advice.

Thanks to all of my fellow students in the Bioenvironmental Engineering Department for your support, advice, encouragement, and demonstration that people from different parts of the world can work together productively. Thanks also to Alana Riley for her excellent typing of this manuscript.

Finally, I would like to give my sincere appreciation and thanks to my parents, Cecil W. and Helen M. Medley, my brothers Franklin, Joeseph, and Jason, and the rest of my relatives and friends for their love, encouragement, and support throughout the years of my studies.

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CHAPTER I

INTRODUCTION

Today there is a world-wide shortage of a clean, safe water supply. Contaminants are entering the receiving stream from domestic, industrial, and agricultural discharge (1) on a large and ever increasing scale. A great quantity of these pollutants are resistent to biodegradation, toxic, and or inhibitory to microbial growth. Thus these compounds are not handled well by the biological processes used principally to stabilize wastewaters and may cause operational problems resulting in exceeding the effluent requirements. These natural and synthetic organic substances which are not readily degraded by natural processes have been termed biorefractory (2) and include a variety of halogenated organics, aromatic and aliphatic hydrocarbons, and pesticides (3).

Public attention and primary concern has arisen over refractory pollutants (and appropriately so) due to known and suspected carcinogenic effects on humans. Furthermore, chlorination of organic compounds in water and wastewater treatment plants has been shown to lead to the production of chlorinated hydrocarbons (4, 5, 6), which are also suspected of being carcinogenic to humans, while the acute and long term toxicity effects of chlorinated compounds on aquatic life have been well documented (1, 2, 3, 4, 5, 7, 8).

These recent findings demonstrate the need for an innovative method for dealing with biorefractory pollutants. Ozone being one of the most powerful oxidants known to man is certainly a possible alternative (ozone's oxidation potential is exceeded only by fluorine and chlorine trifluoride (9)).

Application of ozone in water treatment is not a modern idea. Ozone was first applied in 1905 in Nice, France, where the original plant is still operating (10). Its role has steadily increased since that time and is used extensively in Europe for disinfection as well as color, taste, and odor removal. One definite advantage of ozone over other chemicals is that no combined by products are formed (ozone is pure oxidant), which as stated earlier is a major concern with chlorine.

Ozone has recently been applied to the treatment of industrial wastewaters. A significant amount of plants use the process in treating cyanide, photoprocessing, and paint stripping wastewaters (11). It has been shown by many authors to be effective in oxidizing various organics, inorganics, and wastewaters containing same (12).

Unfortunately, it is currently economically unfeasible to oxidize many compounds completely (to CO_2 and H_2O) by ozonation due to the high energy cost. There is a ray of hope, however. Partial oxidation of organics by ozone has been noticed to form biodegradable end products by several authors (11, 12, 13, 14, 15, 16, 17). The by products from the ozonized compounds can thereby, hopefully, be oxidized cheaply and effectively by biological processes.

Thus it is the purpose of this study to ascertain ozone's effect on biodegradibility of biorefractory pollutants and subsequently determine its possible use in removing problem pollutants from our water supplies.

CHAPTER II

LITERATURE REVIEW

The literature regarding ozonation and biodegradability is somewhat moderate, since attention has been drawn to the subject only of late. Methodology is to some extent questionable in the literature found, since the primary parameter used for biodegradation was the five day BOD. (The limitations of the five day BOD for determination of biological oxidation of organic chemicals have been well noted by Mills and Stack (18) and Stover et al. (19).) These were also the findings of Stephenson et al. (17) in their literature review in a late publication. With these thoughts in mind, it is the purpose of this review to examine the available studies and assemble the various methods, results, and conclusions that were established.

Biodegradabilities of Ozonized Products

The effect of ozone on increasing the biodegradability of several biorefractory pollutants has been shown to be substantial. Gilbert (13) ozonized aqueous solutions of various chlorinated phenols in which he found that the biodegradabilities of the ozonized products were higher with increasing degree of oxidation and with decreasing chlorophenol concentration. He also ozonated naphthalene-2, 7-disulfonic acid, and 4-aminobenzoic acid in which the BOD-5/COD ratio was increased from 0 to 0.8 and 0 to 0.4, respectfully. Common products formed were formic acid and oxalic acid, with chloride ion being formed also in the case of chlorinated phenols.

Yocum (14) showed that ozonation increased the biodegradability of styrene significantly. The BOD-5/TOC ratio was increased from 0.47 to 2.69 by 150 minutes of ozonation. Products formed were benzaldehyde, formaldehyde, benzoic acid, and CO_2.

Industrial wastewaters from toluene diisocyanate (TDI), ethylene glycol, styrene monomer, and ethylene dichloride processes were studied by Yocum, Mayes, and Myers (11). The TDI wastewater was ozonated to an increased biodegradable form with BOD-5 reductions of 30% and TOC reductions of up to four times greater than the unozonated waste. The ethylene glycol wastewater showed even higher increases in biodegradability. TOC reductions were only 25% but the BOD-5 showed an increase of 671%, making this type of waste highly feasible for pretreatment to biooxidation. The styrene and ethylene dichloride wastewaters also showed increased biodegradability but on a much smaller scale than the other two wastewaters.

Stephenson et al. (12) determined that ozonation is effective in increasing the biodegradability of water sources containing a high quantity of humic substances. Three water sources were examined in which the biodegradability was increased for all samples. Considerable variation was shown, however, depending on the particular source examined.

Lignin containing, kraft mill waste liquors have been shown to be better metabolized after ozonation by Stern and Gasner (20). These results were confirmed by Smith and Ferguson (21), who performed oxygen uptake studies on ozonated kraft mill wastewaters. It was observed, however, that ozonation of diluted samples produced little change in biodegradability. Therefore, they concluded that the increase in biodegradability was due to destruction of inhibitory components of the wastewater which were destroyed upon ozonation.

Bauch and Burchard (22) studied the treatment of textile wastewaters with ozone. These wastewaters contained organic dye stuffs, inorganic and organic sizing agents, organic acids, surface active agents, and inorganic acid salts. The BOD-5 was shown to increase by 77% by low dosages of ozone.

Several authors have shown that the biodegradability of dye wastewaters are significantly increased by moderate ozone doses. Stauber (23) studied the ozonation of dye wastewaters after secondary biological treatment. The BOD-5 was shown to increase 150% at low ozone doses of 8 to 15 mg/ℓ, but higher dosages above 25 mg/ℓ left the BOD-5 relatively unchanged. He concluded, therefore that biorefractory organics were being converted into biodegradable organics during early stages of ozonation. This was later confirmed by Nebel and Stauber (24) who showed that the BOD-5 increased from 21 to 53 mg/ℓ as the ozone dosages increased from 0 to 136 mg/ℓ, then decreased to 21 mg/ℓ at an ozone dosage of 34 mg/ℓ. Comparative work was conducted by Davis et al. (25), who ozonized a biologically treated effluent from a chemical plant producing organic dyes and resins. Ozone doses of up to 200 mg/ℓ produced only marginal changes in TOC content, but amazingly, approximately linear increases of BOD-5 were found of up to 2,900%.

Ozone has been shown to destroy the biological inertness of Alkylbenzene sulfonate (ABS), a non-biodegradable synthetic detergent, by Evans and Ryckman (26). The BOD-5 was shown to increase with increasing ozonation until ABS no longer was detected, at which point it decreased sharply. Kandzas and Mokina (27) varified this with their work on sewage containing ABS and sodium dodecylbenzene sulfonate. Both of these compounds were observed to be readily oxidized upon application of ozone.

Chen and Okey (28) ozonated wastewaters from a synthetic rubber plant. The wastewater contained butadiene, styrene, k resin soap, detergent, sodium pyrophosphate, cumene hydropcroxide, tertiary mercaptans, hydroquinone and N-phenyl-2-naphthylamine. The waste was only 20% biodegradable. Upon ozonation a significant increase in the oxygen uptake was observed.

Livke, Velushckak, and Plysynk (29) studied ozonation of wastewater from chemical plants producing caproluctum. The BOD-5 values were noticed to increase with increased ozone dose, while the COD values steadily declined. The BOD/COD ratio changed from 0.1 to 0.5 with 25 mg/ℓ absorbed ozone dose.

Suzuki et al. (30) studied the effect of ozone on the biodegradability of water soluble polymers, ie., polyethylene glycol, poly (vinyl alcohol), poly (vinylpyrrdidine), sodium polyacrylate, and polyacrylamide. Ozonization contributed to increased biodegradation except in the case of polyacrylamide, in which little improvement was noted.

Biodegradability Analysis

Analytical methods were generally consistent in determination of biodegradability of samples. BOD-5, TOC, and COD were the primary tests run, especially by the earlier works. Stephenson (17) noted the limited usefulness of the BOD-5 method for evaluating biodegradability of refractory pollutants, due to appreciable acclimation periods (lag times) and reduced rates of biodegradation. He, thusly, based his biodegradation test on the manometric electrolytic technique. Suzuki (30) also used long term biodegradation tests, measuring the TOC drop with biological activation time.

The researchers showed much variability, however, in the parameters used for biodegradation. Unfortunately, the majority of the authors used the BOD-5 value alone. This may show highly erronous results when the compounds are highly oxidized (large drop in TOC and COD) and or the BOD is increased greatly. These occurances are not unusual, even for small ozone doses, for some compounds. The authors of the later publications generally recognized this fact. Gilbert (13) used the BOD-5/COD ratio, Yocum (14) the BOD-5/TOC ratio, while Suzuki (30) used the ratio of the initial TOC to the TOC after biodegradation. Stephenson (17) defined his own parameter, which he states is indicative of the fraction of organics that ozonation has caused to be biodegradable. This parameter, based on the change in sample COD and TOC, is said to be equal to the fraction of COD partially oxidized. Its relation to biodegradability, however, has not been soundly proven.

Acrylonitrile

Acrylonitrile (the nitrile of acrylic acid or vinyl cyanide) is used extensively in the petrochemical industry for the production of nitrile rubber, various synthetic fibers, acrylonitrile-butadiene-styrene copolymers, polyacrylamide, polyelectrolytes, and a number of other products (31). It has a chemical formula of $CH_2{:}CHCN$, a molecular weight of 53.06, and a density of 0.8060 (32). It is produced in tremendous quantities of over 500 thousand tons per year in the United States alone. It has been shown to have high BOD lag periods by several authors (18, 33) and is listed as a priority pollutant by EPA.

1,2 Dichloropropane

1,2 Dichloropropane (propylene dichloride) is used widely as an industrial solvent for oils, fats, waxes, gums and resins. It has a chemical formula of $CH_3CHClCH_2Cl$, a molecular weight of 112.99, and a density of 1.1560 (32). It is used in many industries in the organic synthesis of alcohols, amines, nitriles and acids; as an ingredient in dry-cleaning fluids; as an inactive reaction medium for chlorination and sulfonation; scouring compounds, spotting agents and metal degreasing fluids; and as a fumigant (34). EPA has designated 1,2 dichloropropane as a priority pollutant.

2,4 Dinitrophenol

2,4 Dinitrophenol is used in the organic synthesis for the manufacture of dyes and other organic compounds such as amidol, and as a wood preservative (35). It has a chemical formula of $C_6H_4N_2O_5$, a molecular weight of 184.11, and a density of 1.683 (32). 2,4 Dinitrophenol was the first uncoupling agent ever to be described (uncoupling agents allow electron transport but prevent the phosphorylation of ADP to ATP (36)) and thus is somewhat of a classic compound in the biochemistry field. Phenolic compounds have been noted to affect the taste of domestic water supplies and cause disease (37). It is an EPA priority pollutant. Current government standards for phenolic compounds in terms of phenol are limited to 0.001 parts per million for public water supplies (37, 38).

Results

The results of the researchers reviewed were generally very consistent on the positive effect of ozone on increasing biodegradability. Also, considerable studies have been conducted on identifying products of reactions of organic compounds with ozone (12). These studies confirm the conclusion that biodegradive products are generally formed upon ozonation (primarily formic, glyoxylic, oxalic, and acetic acid). Not all biorefractory wastes are substantially improved to make ozonation feasible, as was noted by several authors (11, 17, 30). Stephenson (17) observed that some compounds, such as p-nitroanilane, become less biodegradable with ozone dose. Furthermore, Richard and Brener (39) concluded that under-ozonation of an organic material, such as paraoxon, can produce other organic materials that are toxic.

An extensive manual and computer literature search yielded no ozonation-biodegradability studies on acrylonitrile, 1,2 dichloropropane, or 2,4 dinitrophenol. This was not surprising since, as was shown by the literature review, only a small amount of studies have been conducted to date, with most analysis on wastewaters and not individual compounds.

CHAPTER III

MATERIALS AND METHODS

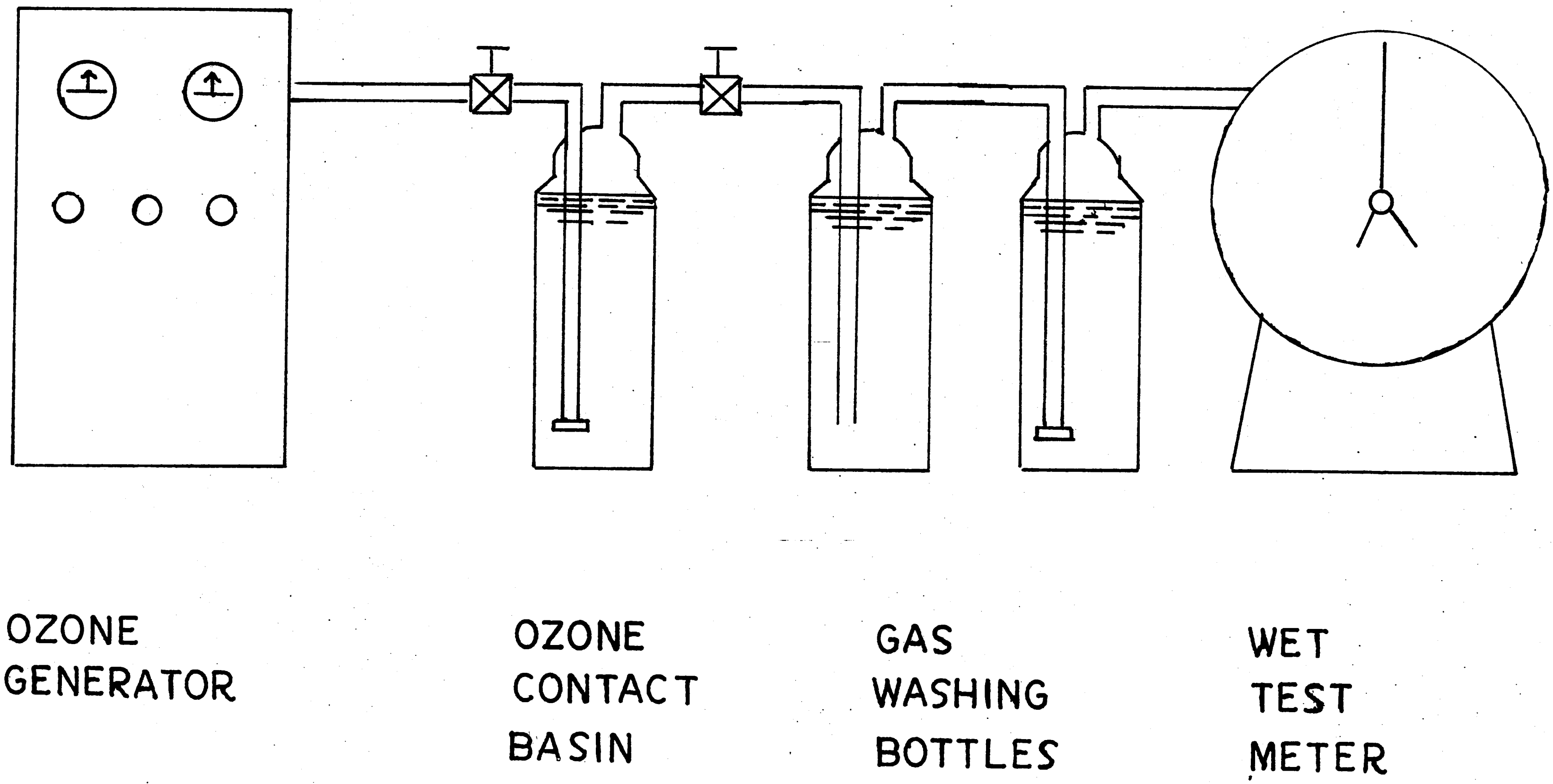
Facility Description

The ozone research facility consisted of an ozone generator connected to a series of gas washing bottles and a wet test meter. The first gas washing bottle acted as an ozone contact basin while the second and third gas washing bottles, containing .05 N potassium iodide, were used to absorb the off gas ozone. The wet test meter determined the gas volume which flowed through the sample. The facility set up is shown in Figure 1.

Experimental Apparutus

Ozone was generated from air with a Welsbach generator Model W-20. The ozone generating unit operated on 110-120 volt, 60 cycle current of 25 amperes. A transformer within the cabinet increased the primary voltage to the high voltage necessary for ozone production (approximately 15,000 volts). The ozone output was maintained by varying the voltage output of the variable transformer while the carrier gas was maintained at a constant flow of 0.9 ft^3/min. The carrier air was dried by two silica cells which operated alternately for 30 seconds at 40 psig. Pressure and flow through the unit was obtained by a 1-1/2 HP compressor Model MOT 261-8.

Figure 1. Schematic Diagram of Ozonation Facility Set Up.


OZONE
GENERATOR
OZONE
CONTACT
BASIN
GAS
WASHING
BOTTLES
WET
TEST
METER

Standard gas washing bottles were used which had 500 ml capacities with medium-permeability porous diffusers at the bottom. The second gas washing bottle had the diffuser removed to prevent plugging, since it absorbed the bulk of the off gas ozone. Ozone resistent Tygon tubing was used for all connections.

The wet test meter was a Precision Scientific Model 63111. Flow measurement is made in the device by gas displacement of water in the quandrant causing the rotor to turn. Accuracy of the meter is rated by Precision Scientific at ±1/2% of total flow. Meter leveling and water level adjustment was made before each series of runs for proper operation.

Sampling Method

Ozone concentration in the influent gas stream was determined by the Iodometric Method (also called the Wet Test Method) prior to and after each series of sample collections and the gas volume determined by the wet test meter. Ozone output of approximately 3.5 mg/ℓ was maintained during all tests. Gas flow rates of 1 liter/minute were used since ozone absorption rates were adversely affected by higher flows. Absorbed ozone dose of the samples 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. Sample volumes of 500 ml were utilized. Gas lines were purged for at least one minute prior to operation to ensure equilibrium conditions.

Analytical Techniques

The methods employed for the analysis of experimental data are given below.

Ozonation Analysis

Iodometric titration was performed on all samples immediately after collection because of the high instability of ozone. This method is quantitative and is based on ozone liberating free iodide from a potassium iodide solution and subsequent titration of the liberated iodide with sodium thiosulfate using starch as an indicator under acid conditions. It is capable of good precision and is subject to fewer interferences than other ozone determining procedures (40). Since this method is not listed in Standard Methods and thus not readily available, the methodology is given below:

Reagents:

1) 2 N Potassium iodide stock reagent: Dissolve 332 g 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 1 N Sodium thiousulfate solution: Dissolve 250 g $Na_2S_2O_3$ $5H_2O$ in 1 liter freshly boiled distilled water. Store in reagent bottle.
4) Starch indicator solution: To 5 g 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 toulene after cooling.
5) Sodium Thiousulfate titrant 0.05 N: Add 50 ml 1N $Na_2S_2O_3$ to 950 ml freshly boiled distilled water. Standardize this solution

daily against potassium biniodate or potassium dichromate primary standard. This procedure is described in Standard Methods for the Examination of Water and Wastewater. Fourteenth Edition Section 409A.2C.

6) 0.05N. Potassium iodide gas washing solution: Add 25 ml 2N KI 1 liter freshly boiled and cooled distilled water. This does not have to be exact.

7) 0.100N. Potassium Biniodate: Dissolve 3.249 g $KH(IO_3)_2$ and dilute to 1 liter in freshly boiled and cooled distilled water.

Sodium Thiosulfate Standardization Procedure:

To 80 ml distilled water, add, with constant stirring, 1 ml concentrated H_2SO_4, 10.00 ml .100N. $KH(IO_3)_2$ and 1 g KI. Titrate immediately with 0.100 N $Na_2S_2O_3$ 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.

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

Titration Procedure:

Transfer the solution from the gas washing bottles to a 1 liter beaker; rinse the bottles with distilled water and add 10 ml 20% H_2SO_4 to produce a pH below 2.0. Titrate immediately with 0.05N $Na_2S_2O_3$ titrant until the yellow color of the liberated iodine is almost discharged. Add 5 ml starch indicator solution to impart a blue color and continue the titration until the blue color just disappears.

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

Applied and absorbed ozone doses were calculated using the following equations, respectfully:

$$D = Y_1 \, (V_g/V_s)$$

where D = applied ozone dose, mg O_3/L sample

Y_1 = concentration of ozone in the carrier gas

V_g = volume of gas flow, L

V_s = volume of sample, L

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

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

Biochemical Oxygen Demand (BOD)

The biochemical oxygen tests were run according to the modified Standard Methods test suggested by Stover et al. (19). This modified procedure consisted of setting up a dilution water blank and several dilutions of the seed material in the dilution water without any samples. This allowed a more accurate determination of oxygen depletion due to the dilution water and biological seeds. Dissolved oxygen levels were read using a membrane electrode probe. Ultimate BOD and BOD-5 were determined for all samples using various biological seeds. Readings were taken at least every two days to allow for reaeration, if necessary, and determination of the oxygen uptake curve. Various sample volumes were utilized so to determine inhibition or toxicity levels and substantiate results.

Total Organic Carbon (TOC)

Organic carbon content was determined using a Beckman Combustion-

Infrared Analyzer Model 915. Both total organic carbon and inorganic carbon were tested. No inorganic carbon was detected, however. This was probably due to striping of the carbon dioxide produced. Thus total organic carbon equaled the organic carbon content.

Chemical Oxygen Demand (COD)

Chemical oxygen demands were determined using Hach Reactor Digestion-Colorimetric Method. The test requires digestion of the samples in a Hach reactor (utilizing Hach prepared reagents) for two hours at 150^{o}C followed by colorimetric measurement using a Hach DR/2 Spectrophotometer.

Biological Acclimation

The hetergenous biological population employed in this study was obtained from the activated sludge unit at the Ponca City Municipal Wastewater Treatment Facility. Biological populations were acclimated to synthetic wastes containing; a pollutant and base mix mixture, an ozonated pollutant and base mix mixture, and the base mix alone. The base mix consisted of a combination of readily biodegradable organic compounds and inorganic nutrients, as shown in Table I. Batch reactors were utilized for growth of the populations except for the unozonated 2,4 dinitrophenol acclimated population. This population was obtained from continuous flow internal recycle reactors being run in the Oklahoma State University Bioenvironmental Engineering Laboratories that were seeded from the same source and run using the same synthetic feed. Pollutant concentrations in the feed were 100 mg/ℓ for acrylonitrile and 2,4 dinitrophenol while 200 mg/ℓ was used for 1,2 dichloropropane (due to its low TOC value). Pollutants were ozonated to an approximate 15% drop in TOC then added to the base mix to comprise the ozonated pollutant-base mix feed. Feed volumes of 2/3 reactor volume were added to the reactors daily. A mean cell residence time of six days was maintained in each reactor.

Biodegradation Parameters

Long oxygen uptake lag periods prevented the BOD-5 of being an accurate estimation of biodegradation in many of the samples. Therefore, ultimate BOD/TOC ratos and ultimate BOD/COD ratios were used as the parameters for biodegradation. The highest values of these parameters is indicative of the optimum point of oxidation for biodegradability of the compounds.

TABLE I

BASE MIX CONSTITUENTS

Organic Constituents	
Ethylene Glycol	113 ml/ℓ
Ethyl Alcohol	113 ml/ℓ
Acetic Acid	113 ml/ℓ
Glutamic Acid	113 gms/ℓ
Glucose	113 gms/ℓ
Phenol	22.6 gms/ℓ
Inorganic Feed Constituents	
$(NH_4)_2\ SO_4$	100 gms/ℓ
H_3PO_4	15.7 ml/ℓ
$CaCl_2$	4 gms/ℓ
$MgSO_4 \cdot 7H_2O$	4 gms/ℓ
$FeCl_3 \cdot 6H_2O$	0.2 gms/ℓ
Fill to One Liter with Distilled Water	

Feed = 2.5 ml base mix per liter plus pollutant concentration.

CHAPTER IV

RESULTS AND DISCUSSION

For clarity of presentation, the study of each compound is presented individually.

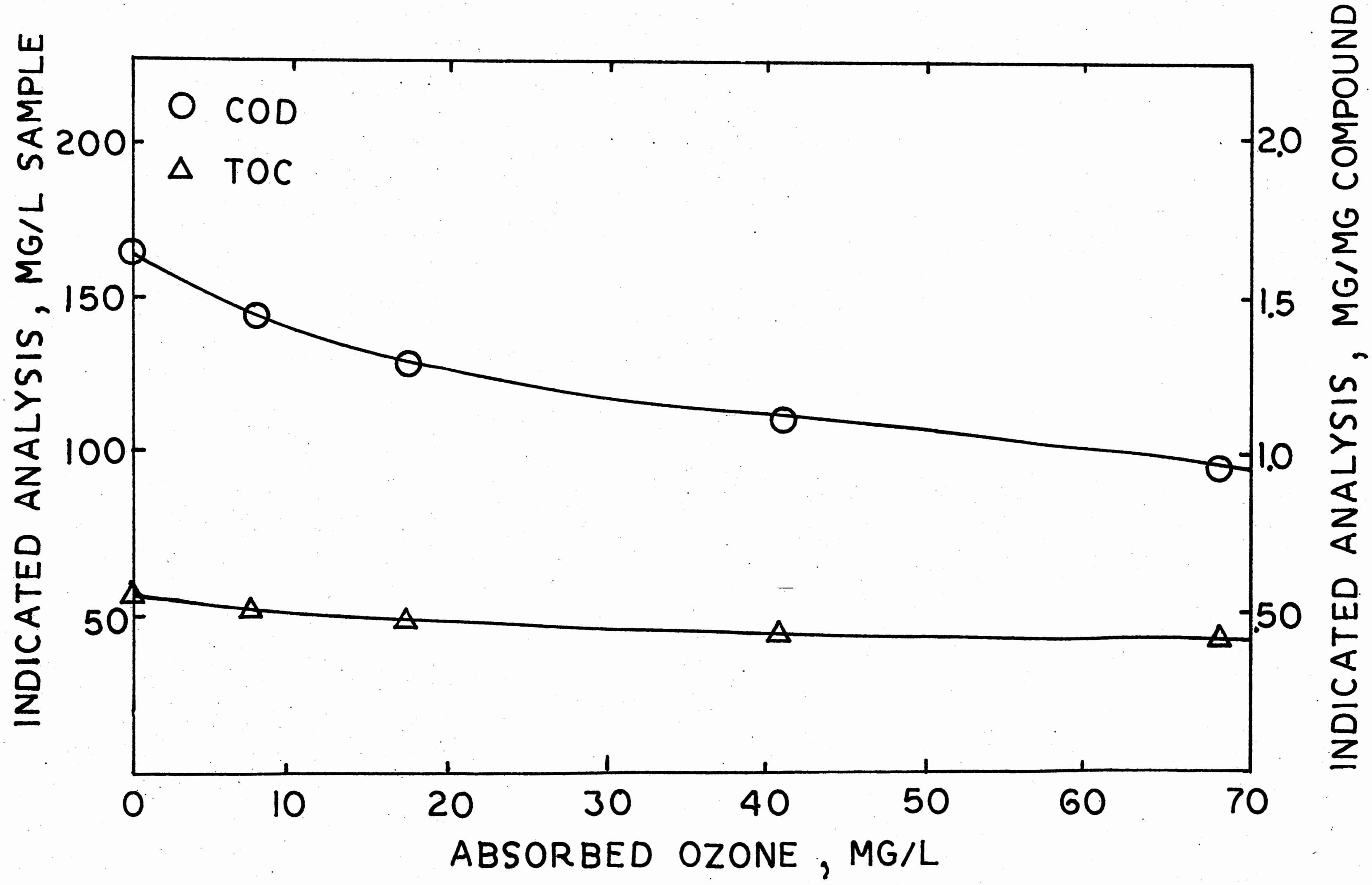
Acrylonitrile

Acrylonitrile is not oxidized readily by ozone as is shown by Figure 2. TOC and COD both leveled out at approximately 25 mg/ℓ absorbed ozone with additional ozone showing only a marginal decrease. This corresponds to a 21 and a 45 percent reduction in TOC and COD, respectfully. It should be pointed out, at this point, that the reduction in TOC is a measurement of the amount of carbon oxidized to CO_2, while the reduction in COD is a measurement of the oxygen equivalent of the portion of the compound that is oxidized. Therefore, oxidation will result in a reduction in COD but not necessarily a reduction in TOC. Evans (42) explained it thusly . . . .

> No cleavage of organic compounds is needed for a COD reduction. Only on destruction of the organic residue, when oxidation leads to formation of carbon dioxide, is there a reduction in TOC.

Thus only a small fraction of the compound is totally oxidized at considerable ozone doses. It is apparent that substantially higher levels of ozonation are required to oxidize acrylonitrile to any great extent.

Figure 2. TOC and COD vs. Absorbed Ozone Dose for Acrylonitrile. Acrylonitrile Concentration - 100 mg/ℓ.


O COD
Δ TOC
INDICATED ANALYSIS , MG/L SAMPLE
200
150
100
50
INDICATED ANALYSIS , MG/MG COMPOUND
2.0
1.5
1.0
.50
0
10
20
30
40
50
60
70
ABSORBED OZONE , MG/L

As stated earlier, acrylonitrile is well known for its high BOD lag periods. A BOD-5 inhibition plot, never the less, shows, at low sample concentrations, a substantial 5 day BOD of 90 mg/ℓ per 100 mg/ℓ sample (0.9 mg/mg of compound) can be obtained with acclimated seed, Figure 3. Since these values are somewhat higher than is reported in the literature, nitrification may be assumed to be taking place. Greater sample volumes than 20 mls showed a sharp decrease in BOD-5, giving the lags that have been previously observed by earlier authors (13, 32). Unacclimated seed shows even longer lag periods. Stover et al. (19) found somewhat comparative results of zero BOD-5 for nonacclimated seed and 0.25 BOD-5 for acclimated seed. It could be concluded, thereby, that acclimation is a neccessity for biological treatment of acrylonitrile. Furthermore, inhibition of biological activity could be observed at substantial concentrations in biological reactors. These concentrations would be expected to be considerably higher in a treatment plant since there is continuous mixing and the ratio of inhibitor to micro organisms is much smaller as compared to the BOD bottle. Stover and Kincannon (43) have confirmed this, showing no operational problems with concentrations of acrylonitrile up to 150 mg/ℓ in completely mixed, continous flow, bench scale reactors. These studies also showed that acrylonitrile was well biodegraded with less than .05 mg/ℓ in the effluent.

Ultimate BOD decreased with absorbed ozone in a flattened S type pattern, Figure 4. All BOD's were substantially lower than the initial BOD with the highest BOD recorded at 20 mg/ℓ absorbed ozone, after which the ultimate BOD decreased linearly with ozone dose with each of the biological seeds. Ozone also decreased the oxygen uptake rate, showing high lags for even small doses of ozone, Figure 5. As mentioned earlier,

Figure 3. BOD-5 Inhibition Plot for Acrylonitrile. Acrylonitrile Concentration - 100 mg/ℓ.

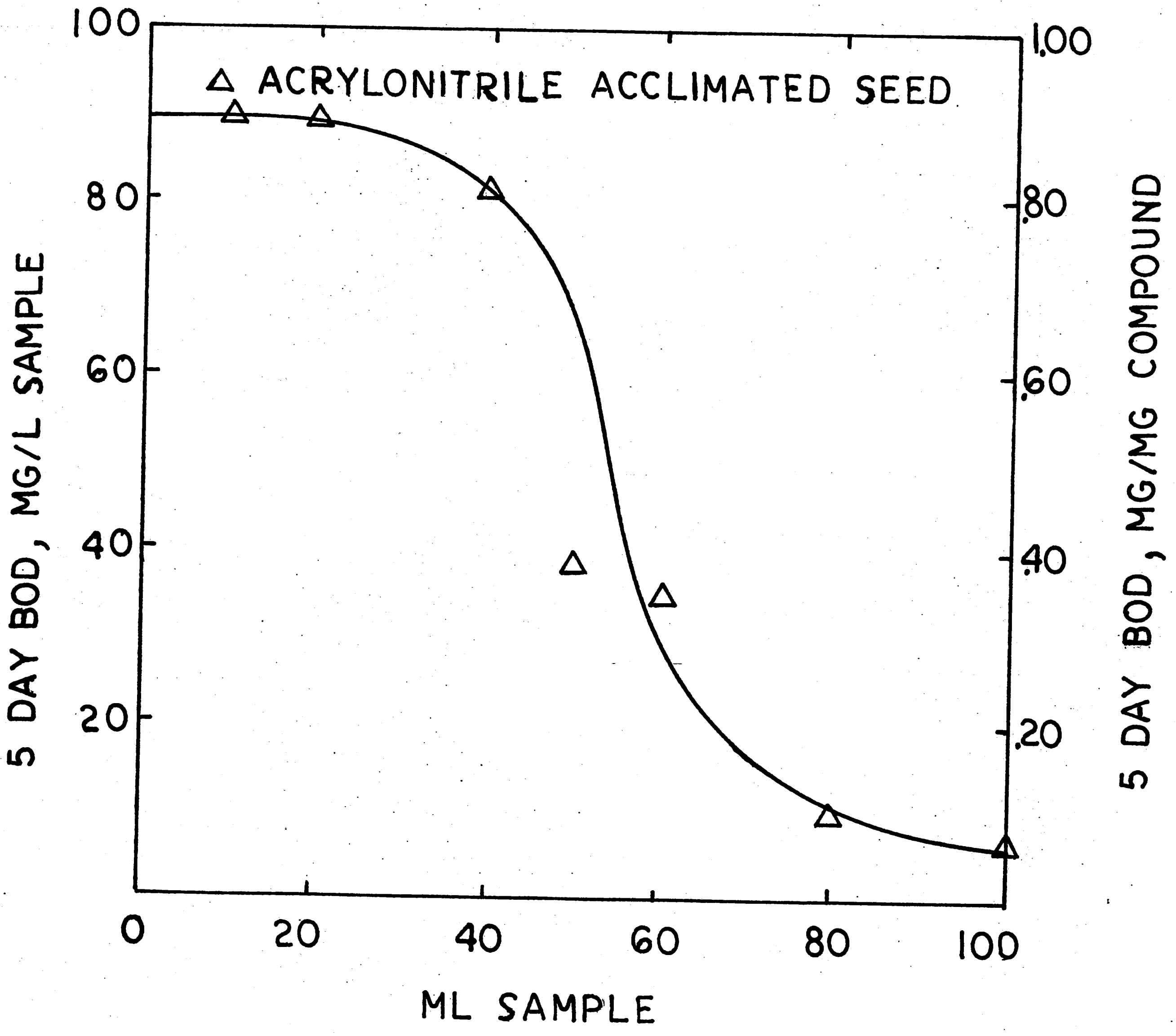

△ ACRYLONITRILE ACCLIMATED SEED
5 DAY BOD, MG/L SAMPLE
100
80
60
40
20
0
20
40
60
80
100
ML SAMPLE
5 DAY BOD, MG/MG COMPOUND
1.00
.80
.60
.40
.20

Figure 4. Ultimate BOD vs. Absorbed Ozone Dose for Acrylonitrile. Acrylonitrile Concentration - 100 mg/ℓ.

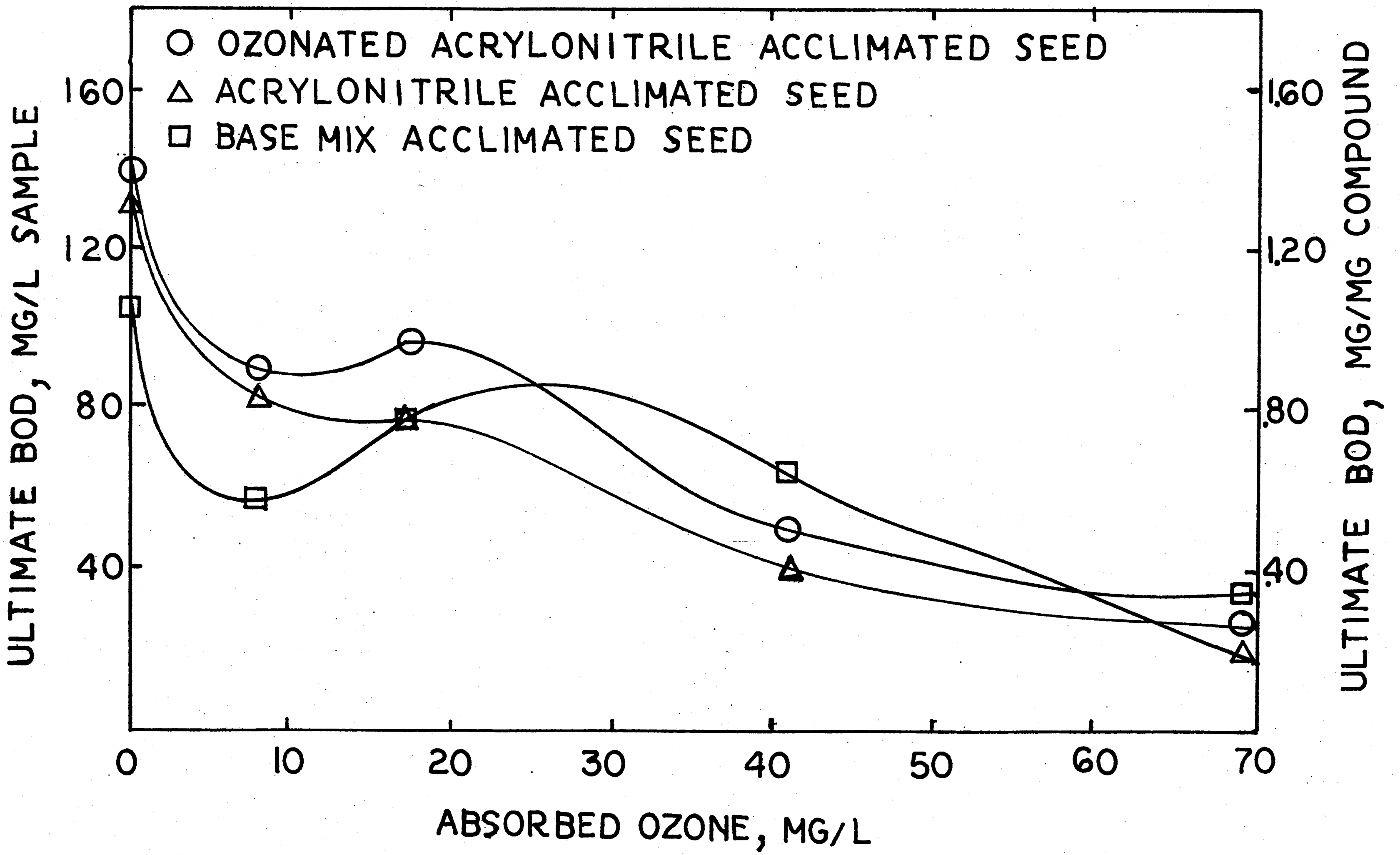
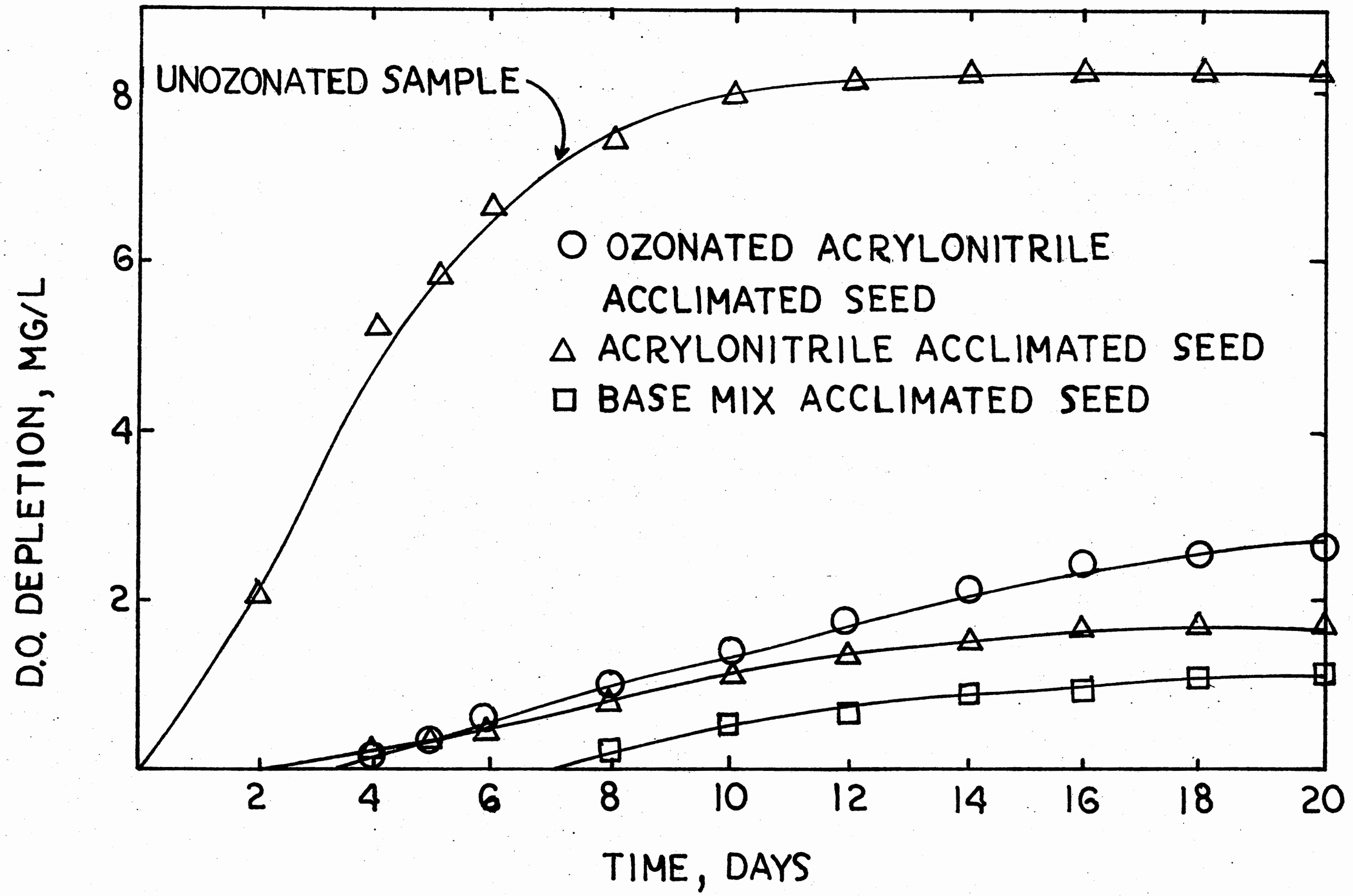

○ OZONATED ACRYLONITRILE ACCLIMATED SEED
△ ACRYLONITRILE ACCLIMATED SEED
□ BASE MIX ACCLIMATED SEED
ULTIMATE BOD, MG/L SAMPLE
160
120
80
40
ULTIMATE BOD, MG/MG COMPOUND
1.60
1.20
.80
.40
0
10
20
30
40
50
60
70
ABSORBED OZONE, MG/L

Figure 5. O_2 Uptake vs. Time for 20 ml Sample Volumes of Acrylonitrile and Ozonated Acrylonitrile at 69 mg/ℓ Absorbed Ozone Dose. Acrylonitrile Concentration - 100 mg/ℓ.


UNOZONATED SAMPLE
○ OZONATED ACRYLONITRILE ACCLIMATED SEED
△ ACRYLONITRILE ACCLIMATED SEED
□ BASE MIX ACCLIMATED SEED
D.O. DEPLETION, MG/L
8
6
4
2
2
4
6
8
10
12
14
16
18
20
TIME, DAYS

a drop in BOD does not necessarily mean a decrease in biodegradability, depending on how much of the compound is oxidized by ozone. A drop in BOD and an increase in lag periods is not a good sign however, especially for a compound like acrylonitrile, which is not oxidized to any great extent by ozone.

The ultimate BOD/TOC and ultimate BOD/COD ratios followed a similar S shaped decreasing pattern as the BOD curve, Figures 6 and 7. The highest ratios again, after ozonation, were at about 20 mg/ℓ absorbed ozone. Both biodegradation parameters showed a decrease in biodegradability with increase in ozone dose. Ozonation, therefore, had a definite adverse affect on the biodegradation of acrylonitrile with less biochemical oxygen demand per oxidized products than was originally present. All parameters showed this result and were not greatly affected by the biological populations utilized.

1,2 Dichloropropane

1,2 Dichloropropane is oxidized very readily by ozonation at very small absorbed dosages, as is shown by Figure 8. TOC and COD followed an almost linear decreasing relationship with absorbed ozone dose. Attempting absorbed doses greater than approximately 2.5 mg/ℓ ozone showed an extensive drop in absorbed ozone. This was probably due to stripping of the ozonized products. Thus precise testing beyond this point was prevented. At 2.5 mg/ℓ ozone (0.0125 mg ozone/mg compound) the TOC and COD were reduced approximately 82% and 59% respectfully. Further ozonation, though unable to be measured, showed continued reduction in TOC and COD. Complete oxidation of the compound may be, consequently, feasible with most of the compound shown to be oxidized to CO_2 at low absorbed ozone

Figure 6. Ultimate BOD/TOC Ratio vs. Absorbed Ozone Dose for Acrylonitrile. Acrylonitrile Concentration - 100 mg/ℓ.

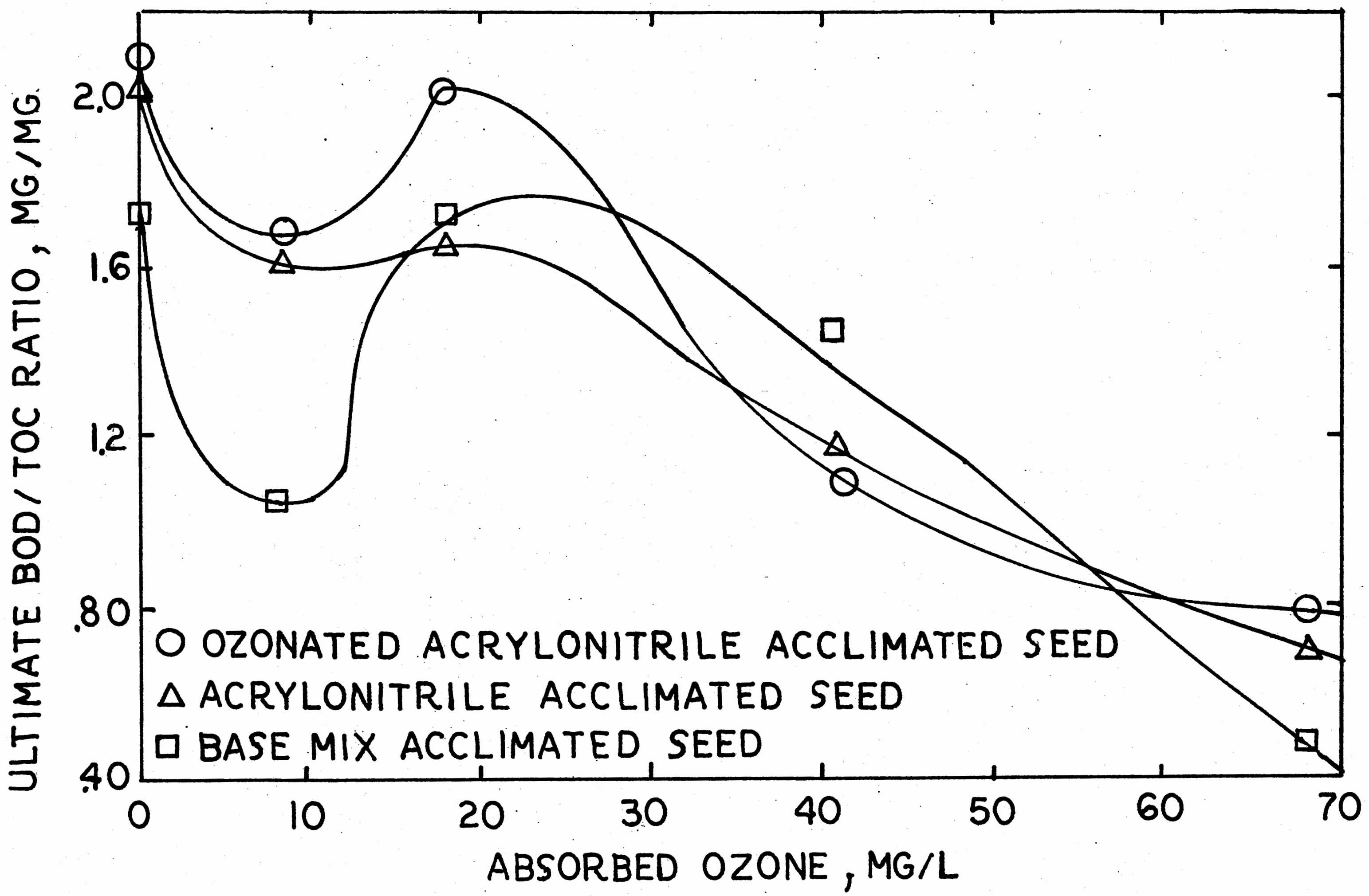
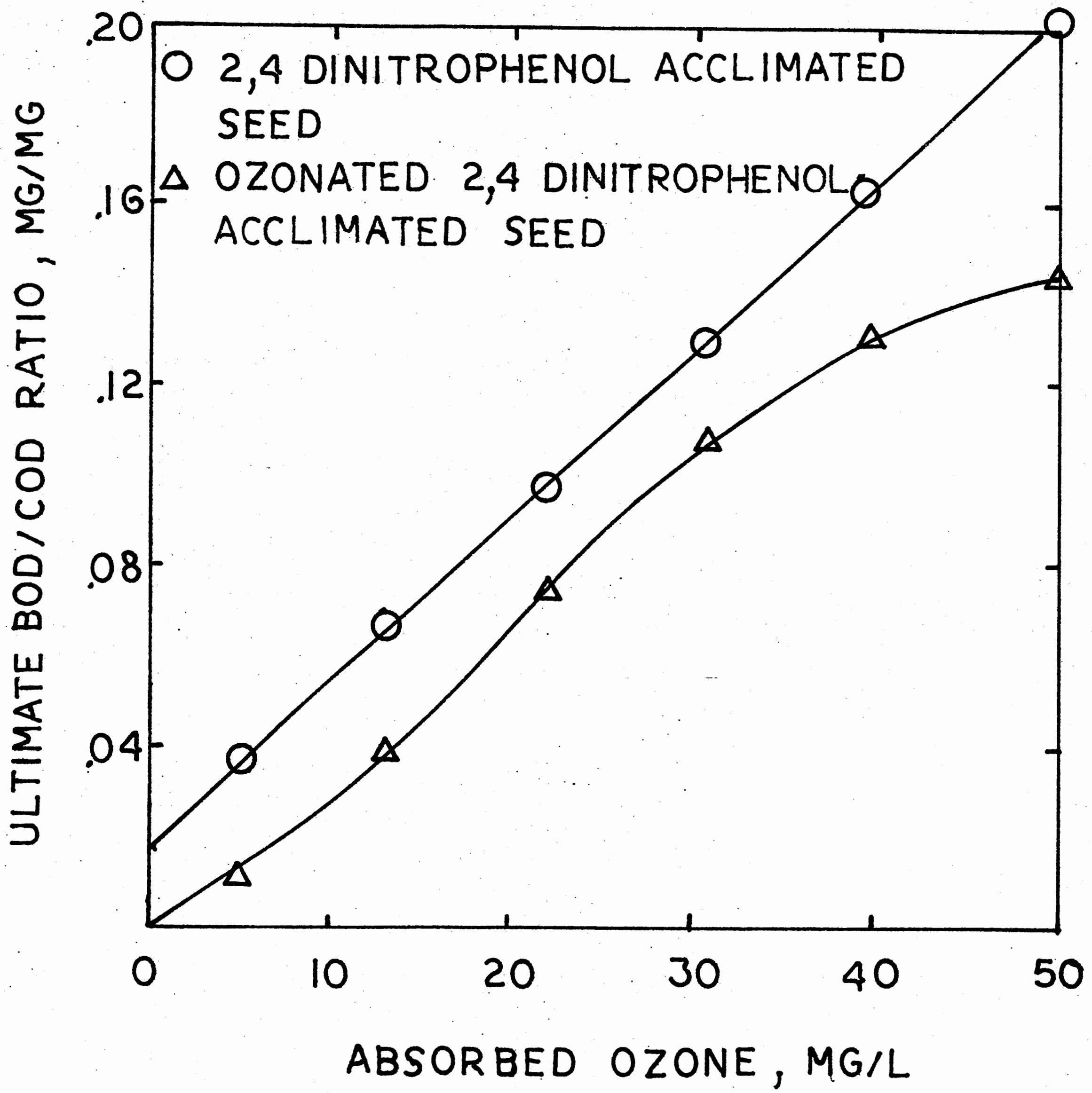
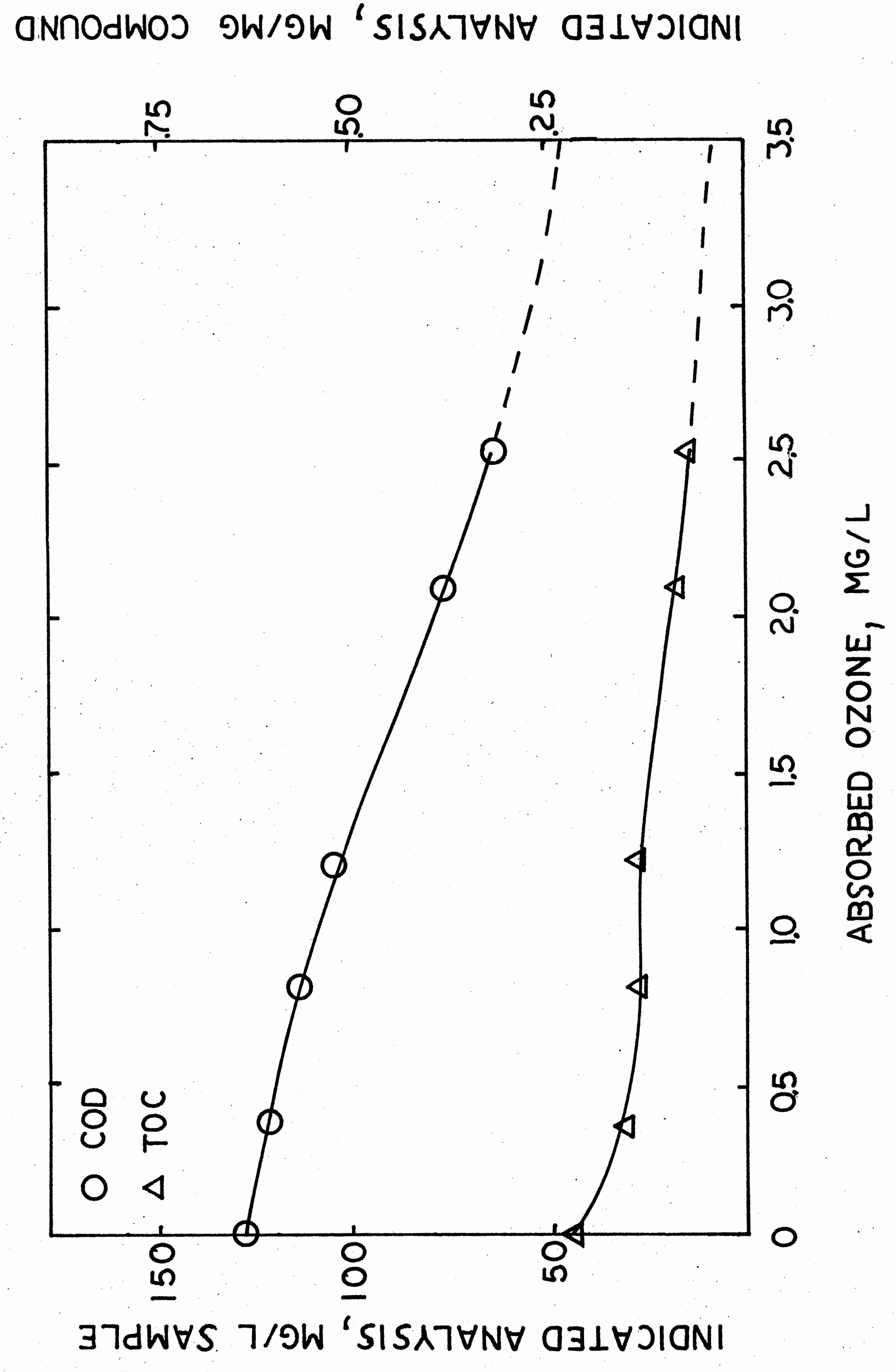

ULTIMATE BOD/TOC RATIO, MG/MG
2.0
1.6
1.2
.80
.40
0
10
20
30
40
50
60
70
ABSORBED OZONE, MG/L
○ OZONATED ACRYLONITRILE ACCLIMATED SEED
△ ACRYLONITRILE ACCLIMATED SEED
□ BASE MIX ACCLIMATED SEED

Figure 7. Ultimate BOD/COD Ratio vs. Absorbed Ozone Dose for Acrylonitrile. Acrylonitrile Concentration - 100 mg/ℓ.



○ 2,4 DINITROPHENOL ACCLIMATED SEED
△ OZONATED 2,4 DINITROPHENOL ACCLIMATED SEED
.20
.16
.12
.08
.04
ULTIMATE BOD/COD RATIO, MG/MG
0
10
20
30
40
50
ABSORBED OZONE, MG/L

Figure 8. TOC and COD vs. Absorbed Ozone Dose for 1,2 Dichloropropane.
1,2 Dichloropropane Concentration - 200 mg/ℓ.


○ COD
△ TOC
INDICATED ANALYSIS, MG/L SAMPLE
150
100
50
INDICATED ANALYSIS, MG/MG COMPOUND
.75
.50
.25
ABSORBED OZONE, MG/L
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5

doses. A review of the literature shows that complete oxidation of organic materials to CO_2 is rare, independent of the oxidant used, for aqueous solutions. In other words, a portion of the end products formed are generally resistent to chemical oxidation. Possibly, complete oxidation was not occuring here with the products oxidized past the 2.5 mg/ℓ absorbed ozone point being removed by stripping.

1,2 Dichloropropane is totally resistent to biodegradation showing zero ultimate BOD with acclimated seed. This has been confirmed in studies by Stover and Kincannon (43), where 1,2 dichloropropane was shown not to cause operational problems in activated sludge reactors at 182 mg/ℓ concentration, but was not degraded, with 99% of the compound being removed in the off gases. Upon ozonation 1,2 dichloropropane showed a small, but measureable, BOD with little or no lag period, Figure 9. Ultimate BOD increased with absorbed ozone dose in a near linear increasing pattern, Figure 10. These results were for the ozonated 1,2 dichloropropane showing less oxygen uptake nearly equaling the seed corrections so that any BOD reading could be considered negligable. The base mix acclimated seed showed oxygen uptakes less than the seed correction. These low BOD's were probably due to the low TOC of the compound (which was extensively reduced upon ozonation), lack of acclimation, or both. It should be noted, however, that oxygen uptake with unozonated 1,2 dichloropropane was substantially less than the seed corrections for all biological populations employed, due probably to inhibition. Thus, ozonation appeared to remove this inhibition.

The biodegradability parameters for 1,2 dichloropropane, using ozonated 1,2 dichloropropane acclimated seed, are shown in Figures 11 and 12. Both parameters showed an increase in biodegradation with ozone dose.

Figure 9. O_2 Uptake vs. Time for 60 ml Sample Volumes of Ozonated Acrylonitrile at Various Absorbed Ozone Doses Utilizing Biolobical Seed Acclimated to Ozonated 1,2 Dichloropropane. 1,2 Dichloropropane Concentration - 100 mg/ℓ.

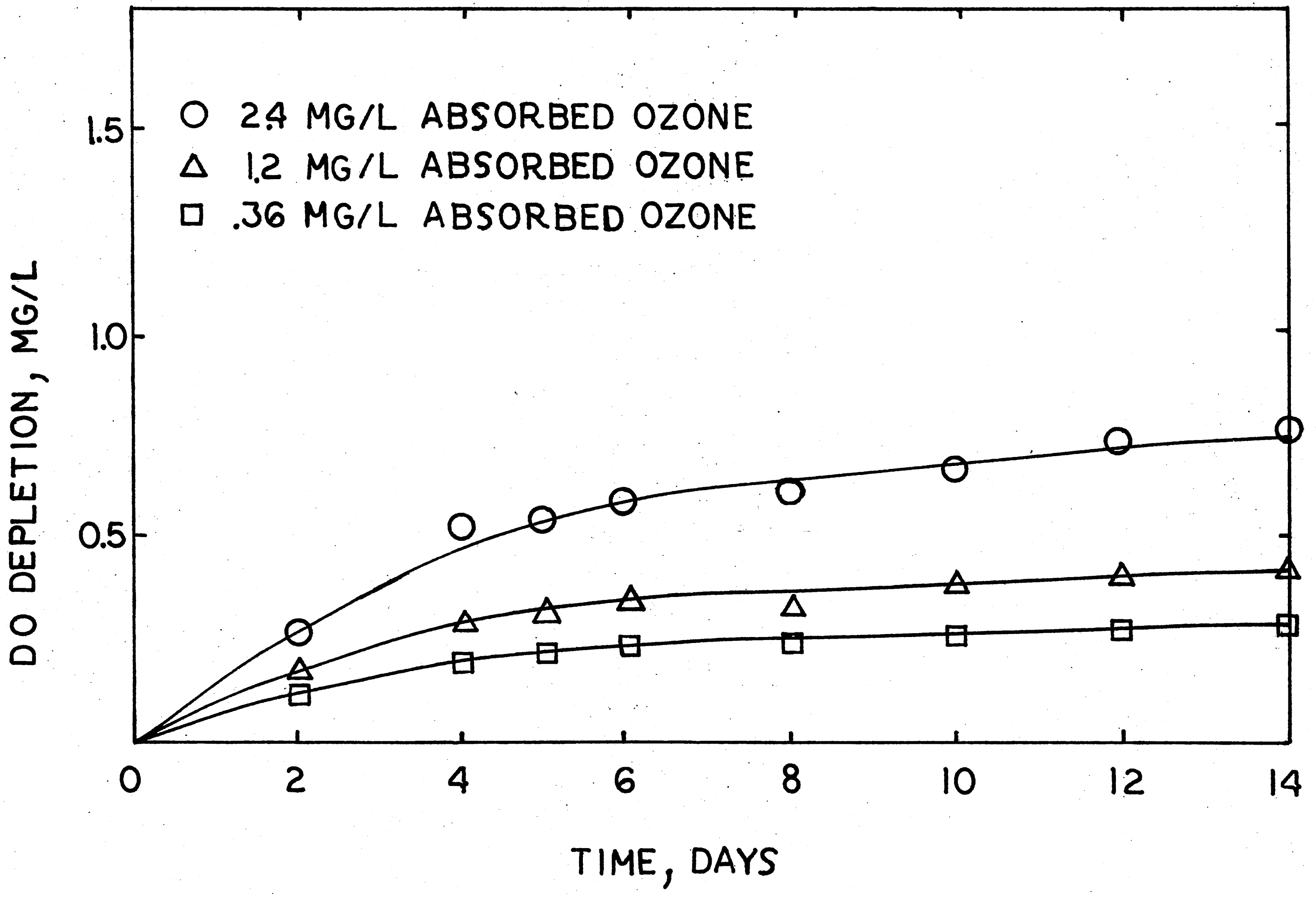

○ 2.4 MG/L ABSORBED OZONE
△ 1.2 MG/L ABSORBED OZONE
□ .36 MG/L ABSORBED OZONE
DO DEPLETION, MG/L
1.5
1.0
0.5
0
2
4
6
8
10
12
14
TIME, DAYS

Figure 10. Ultimate BOD vs. Absorbed Ozone Dose for 1,2 Dichloropropane. 1,2 Dichloropropane Concentration - 200 mg/ℓ.

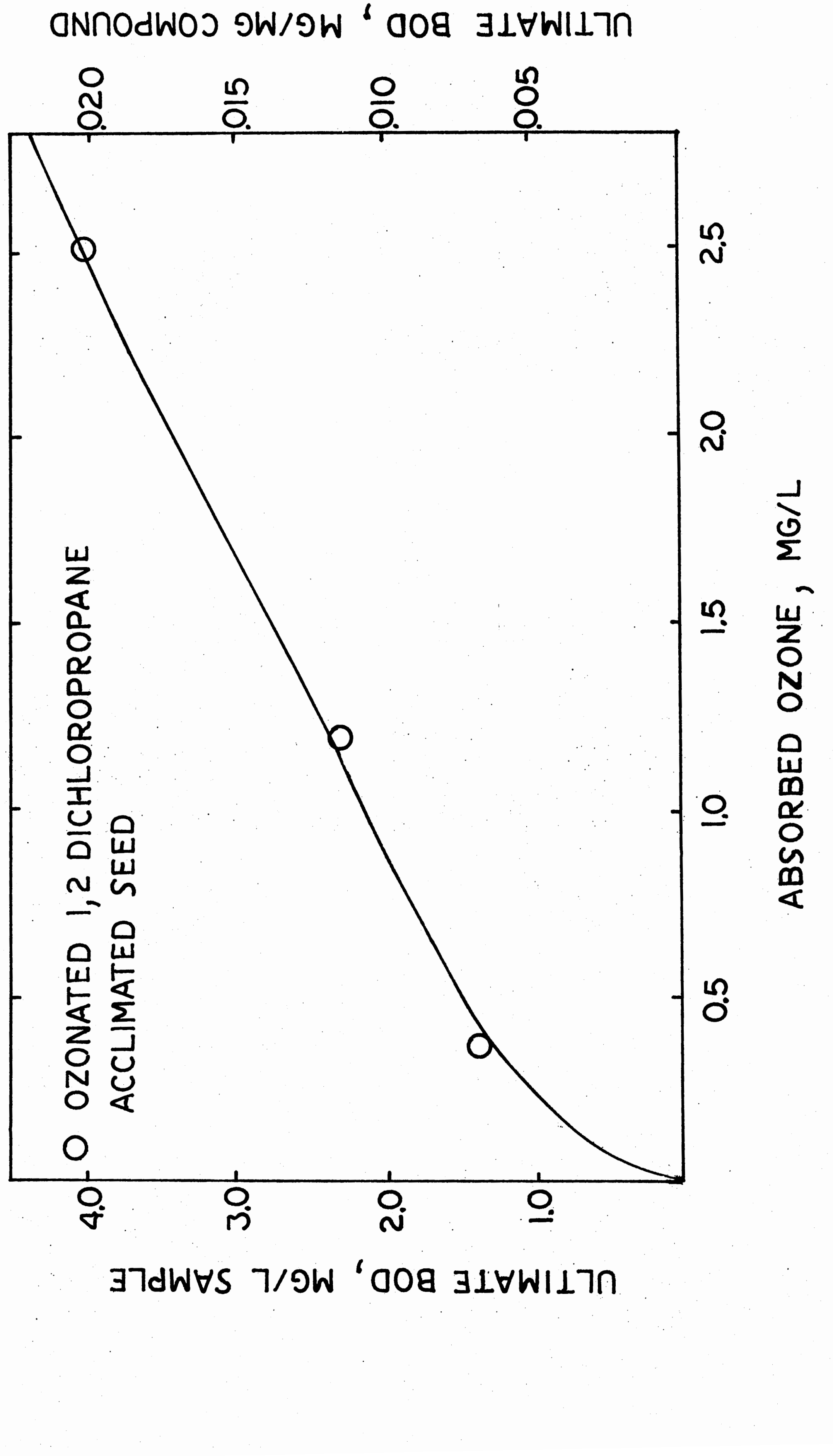

OZONATED 1,2 DICHLOROPROPANE
ACCLIMATED SEED
ABSORBED OZONE, MG/L
0.5
1.0
1.5
2.0
2.5
ULTIMATE BOD, MG/L SAMPLE
1.0
2.0
3.0
4.0
ULTIMATE BOD, MG/MG COMPOUND
.005
.010
.015
.020

Figure 11. Ultimate BOD/TOC Ratio vs. Absorbed Ozone Dose for 1,2 Dichloropropane. 1,2 Dichloropropane Concentration - 200 mg/ℓ.

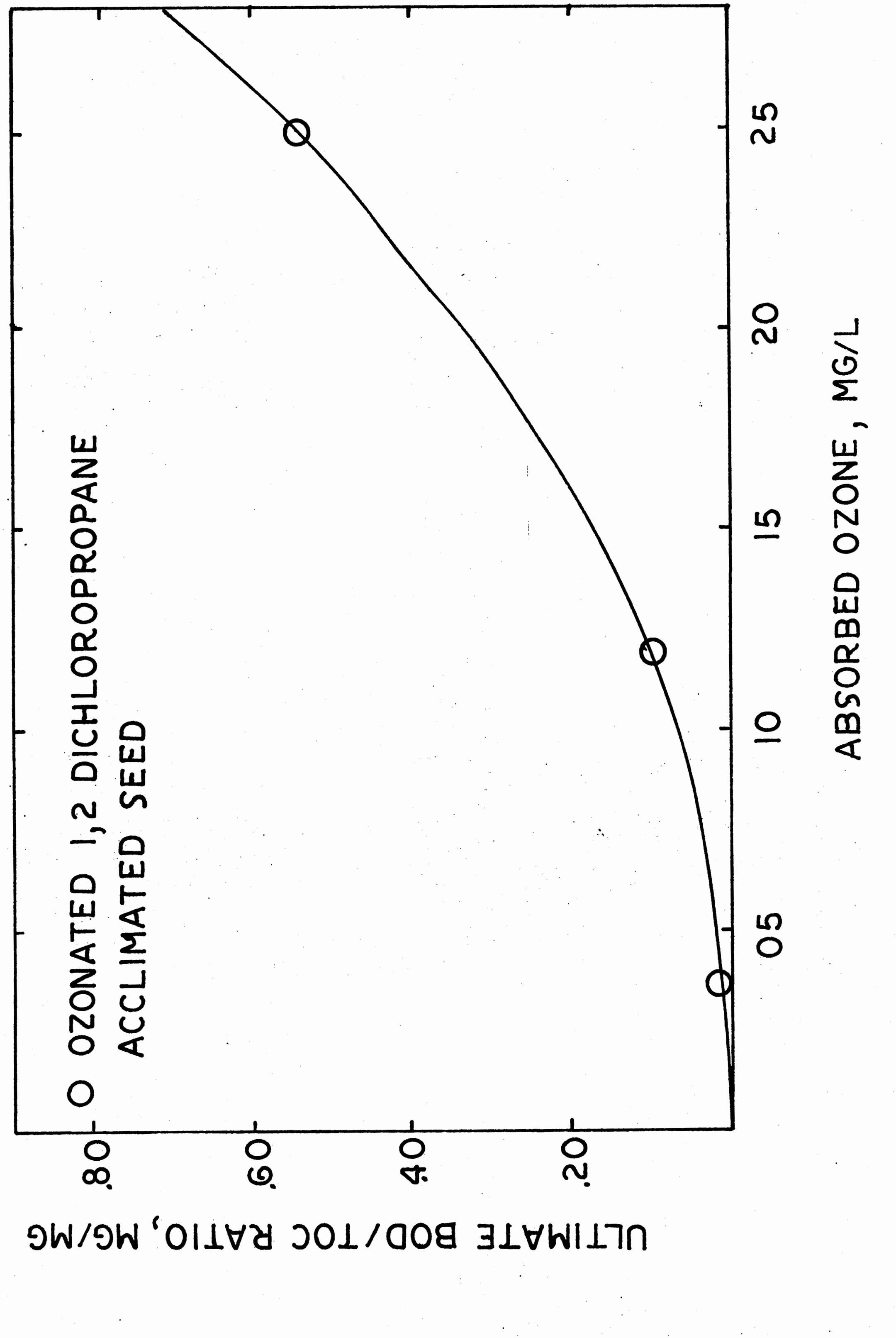
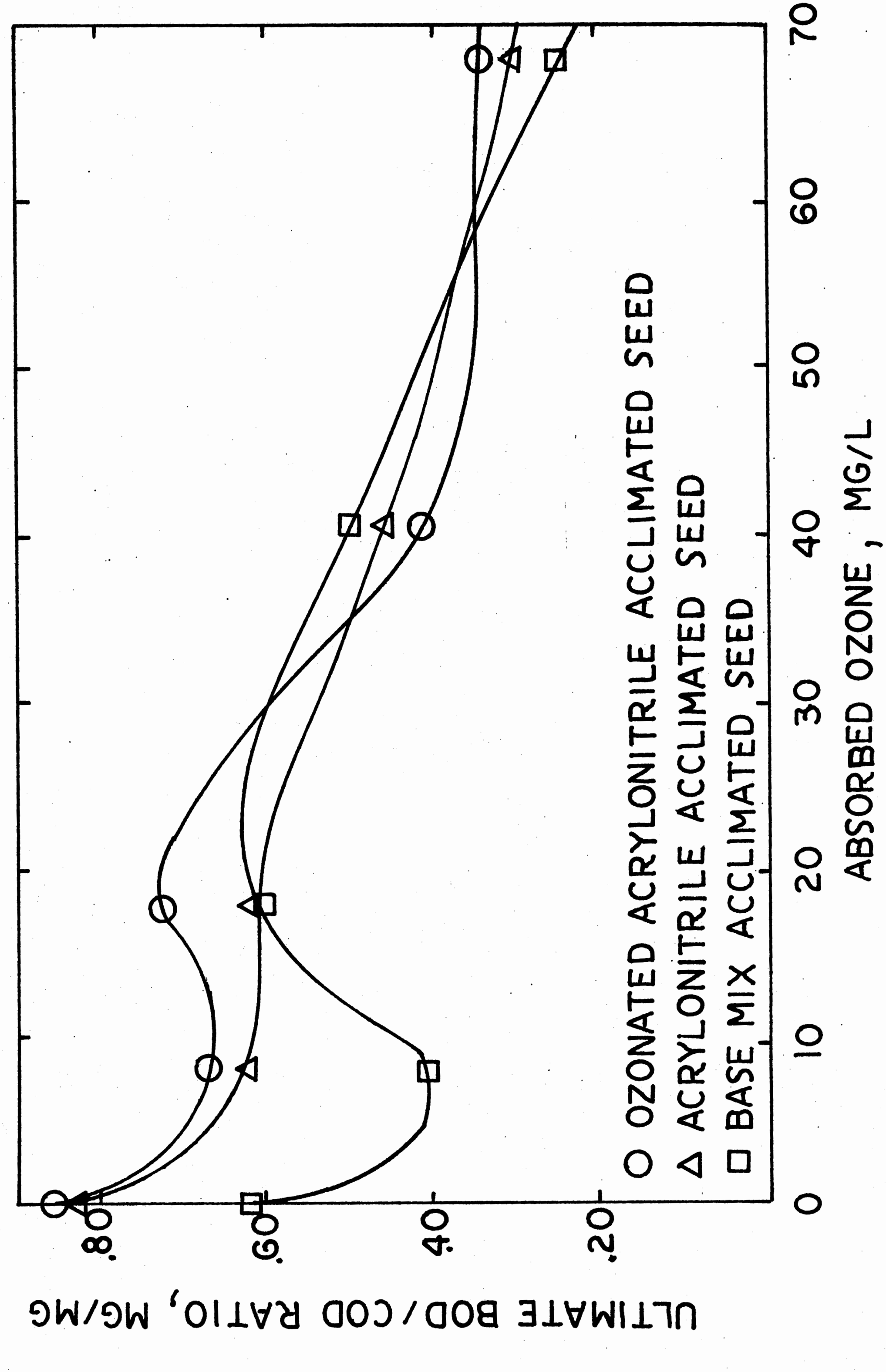

OZONATED 1,2 DICHLOROPROPANE
ACCLIMATED SEED
ULTIMATE BOD/TOC RATIO, MG/MG
.80
.60
.40
.20
ABSORBED OZONE, MG/L
05
10
15
20
25

Figure 12. Ultimate BOD/COD Ratio vs. Absorbed Ozone Dose for 1,2 Dichloropropane. 1,2 Dichloropropane Concentration - 100 mg/ℓ.


○ OZONATED ACRYLONITRILE ACCLIMATED SEED
△ ACRYLONITRILE ACCLIMATED SEED
□ BASE MIX ACCLIMATED SEED
ABSORBED OZONE, MG/L
0
10
20
30
40
50
60
70
ULTIMATE BOD/COD RATIO, MG/MG
.20
.40
.60
.80

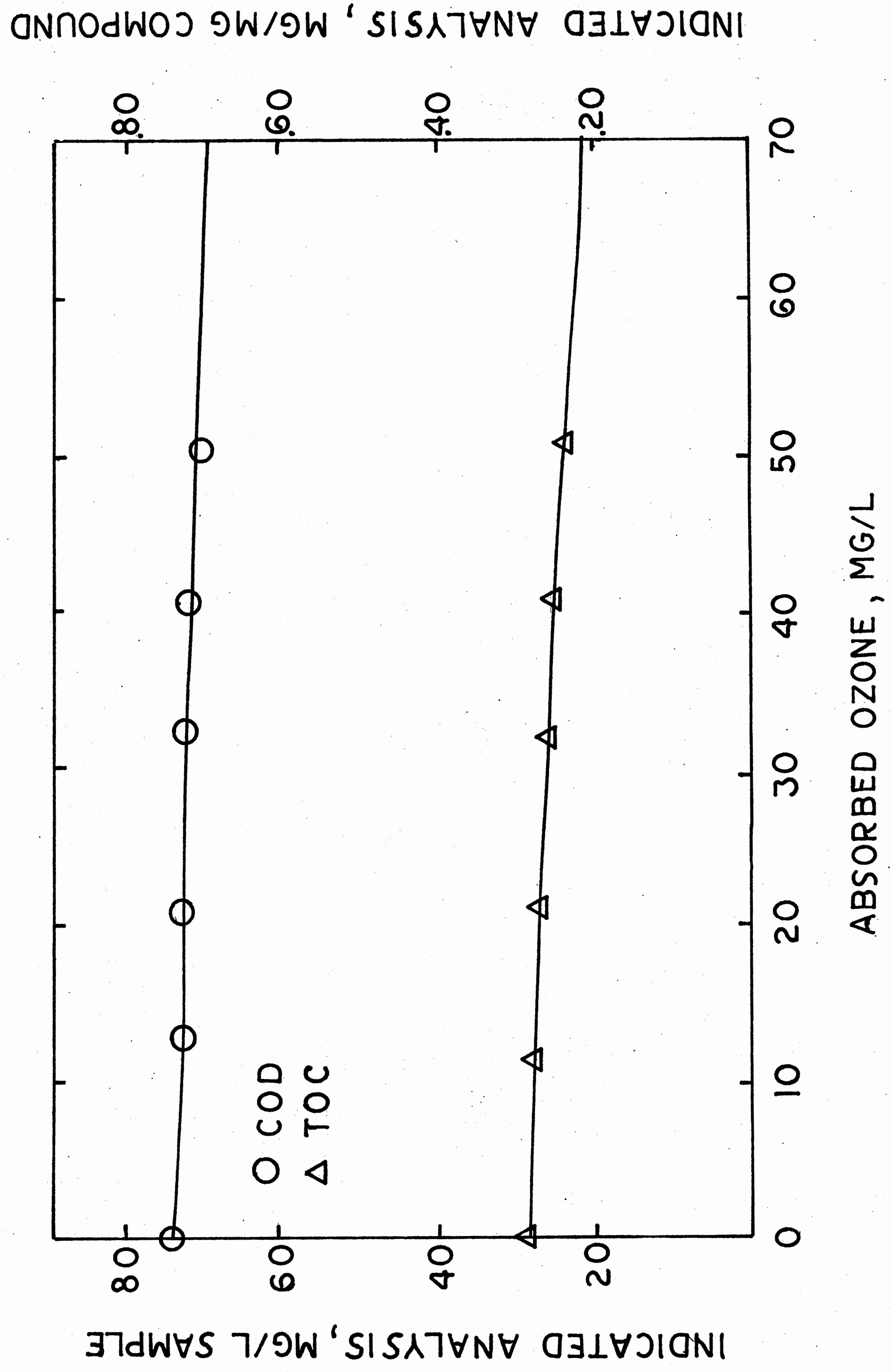
This would be expected since the BOD of the unozonated compound was zero and any increase in BOD would, thereby, show an increase in biodegradability regardless of the effect on TOC or COD. A sharp decrease in TOC or COD upon ozonation, as in this compound, would increase the values of the parameters dramatically. The ultimate BOD/TOC and ultimate BOD/COD ratios were increased to 0.64 and 0.061 respectfully, at 2.5 mg/ℓ absorbed ozone dose for ozonated 1,2 dichloropropane acclimated seed. These values are notable but somewhat insignificant compared to the degree of oxidation ozonation has upon the compound.

2,4 Dinitrophenol

2,4 Dinitrophenol is not oxidized to a great extent by low doses of ozone, Figure 13. Only a drop of 4 and 5 mg/ℓ for TOC and COD, respectfully, was obtained at an absorbed dose of 50 mg/ℓ ozone. Gabovich et al. (41) showed that it takes 5 times this amount for 2,4 dinitrophenol to be greater than 99% destroyed. Complete oxidation is obviously not a viable alternative. Previous studies on the oxidation of phenol and various other phenolic compounds have also found this result, showing that at an ozone/phenol molar ratio of 3 to 5 is required for near total destruction (12).

2,4 Dinitrophenol is not readily biodegraded and must have a well acclimated seed to achieve a BOD. Low concentrations show inhibition due to the compounds well known capacity as an ATP uncoupling agent. EPA studies at Oklahoma State University (44) have shown that concentrations of 100 mg/ℓ can be handled in complete-mix, bench-scale, continuous flow, activated sludge reactors without operational problems.

Figure 13. TOC and COD vs. Absorbed Ozone Dose for 2,4 Dintrophenol.
2,4 Dinitrophenol Concentration - 100 mg/ℓ.


INDICATED ANALYSIS, MG/MG COMPOUND
80
60
40
20
INDICATED ANALYSIS, MG/L SAMPLE
80
60
40
20
ABSORBED OZONE, MG/L
0
10
20
30
40
50
60
70
○ COD
△ TOC

Upon ozonation dissolved oxygen depletion was improved remarkably, with no lag observed, Figure 14. Ultimate BOD increased almost linearly with ozone dose for the two biological populations employed, Figure 15. The ozonated 2,4 dinitrophenol acclimated population appeared to be leveling out at this point while the 2,4 dinitrophenol acclimated population was still increasing linearly. The 2,4 dinitrophenol acclimated population showed better biodegradation than the ozonated 2,4 dinitrophenol acclimated seed throughout the tests. This may have been due to the 2,4 dinitrophenol inducing the biological population to require a higher oxygen uptake rate because of inhibition of phosphorylation during acclimation. Another possible explanation is that the 2,4 dinitrophenol acclimated seed showed nitrification and the ozonated 2,4 dinitrophenol didn't, if perhaps upon ozonation of 2,4 dinitrophenol the nitrogen is oxidized and thus no nitrifiers can be produced in this population.

The biodegradability parameters showed improved biodegradation with absorbed ozone, Figures 16 and 17. This was brought about by ozone creating biodegradable products, destroying the compounds inhibitory properties, or both. Both ultimate BOD/TOC and ultimate BOD/COD ratios, as in the ultimate BOD curve, increased linearly with ozone dose to the maximum level employed of 50 mg/ℓ absorbed ozone. This point corresponds to an increase of 0.45 and 0.19 in the BOD/TOC and BOD/COD ratios, respectfully. Thus ozone is effective in increasing the biodegradability of 2,4 dinitrophenol, with the feasibility being proportional to the economics of ozone production. As was mentioned in the literature review, this was similar to results found by previous authors on the study of products of ozonation of phenolic type compounds. These studies showed that upon ozonation, ring ruptured, aliphatic, oxidation products were formed which were biodegradable (12, 13).

Figure 14. O_2 Uptake vs. Time for 60 ml Sample Volume of Ozonated 2,4 Dinitrophenol at 50 mg/ℓ Absorbed Ozone Dose. 2,4 Dinitrophenol Concentration - 100 mg/ℓ.

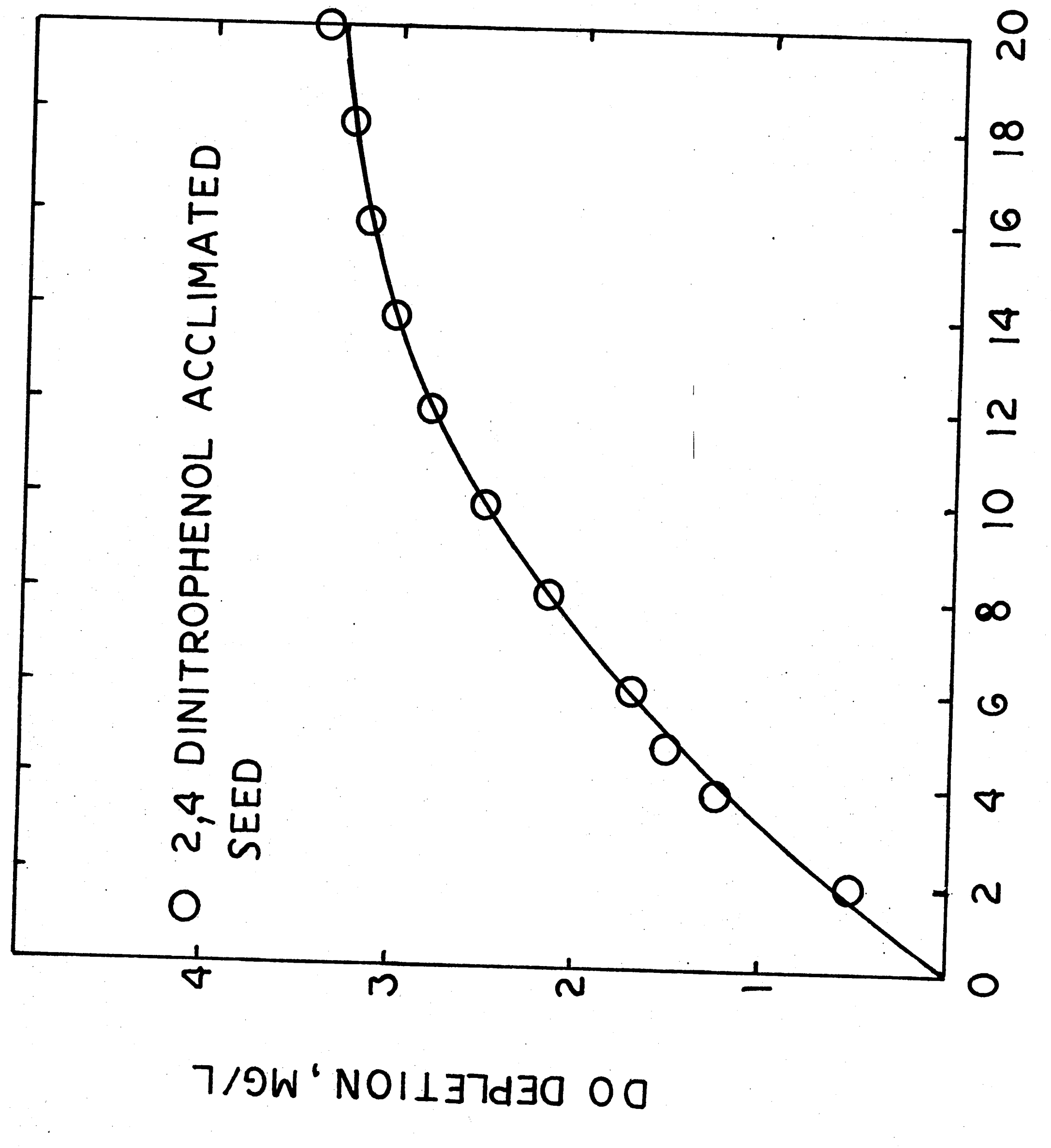

○ 2,4 DINITROPHENOL ACCLIMATED SEED
DO DEPLETION, MG/L
0
1
2
3
4
0
2
4
6
8
10
12
14
16
18
20
TIME, DAYS

Figure 15. Ultimate BOD vs. Absorbed Ozone Dose for 2,4 Dinitrophenol. 2,4 Dinitrophenol Concentration - 100 mg/ℓ.

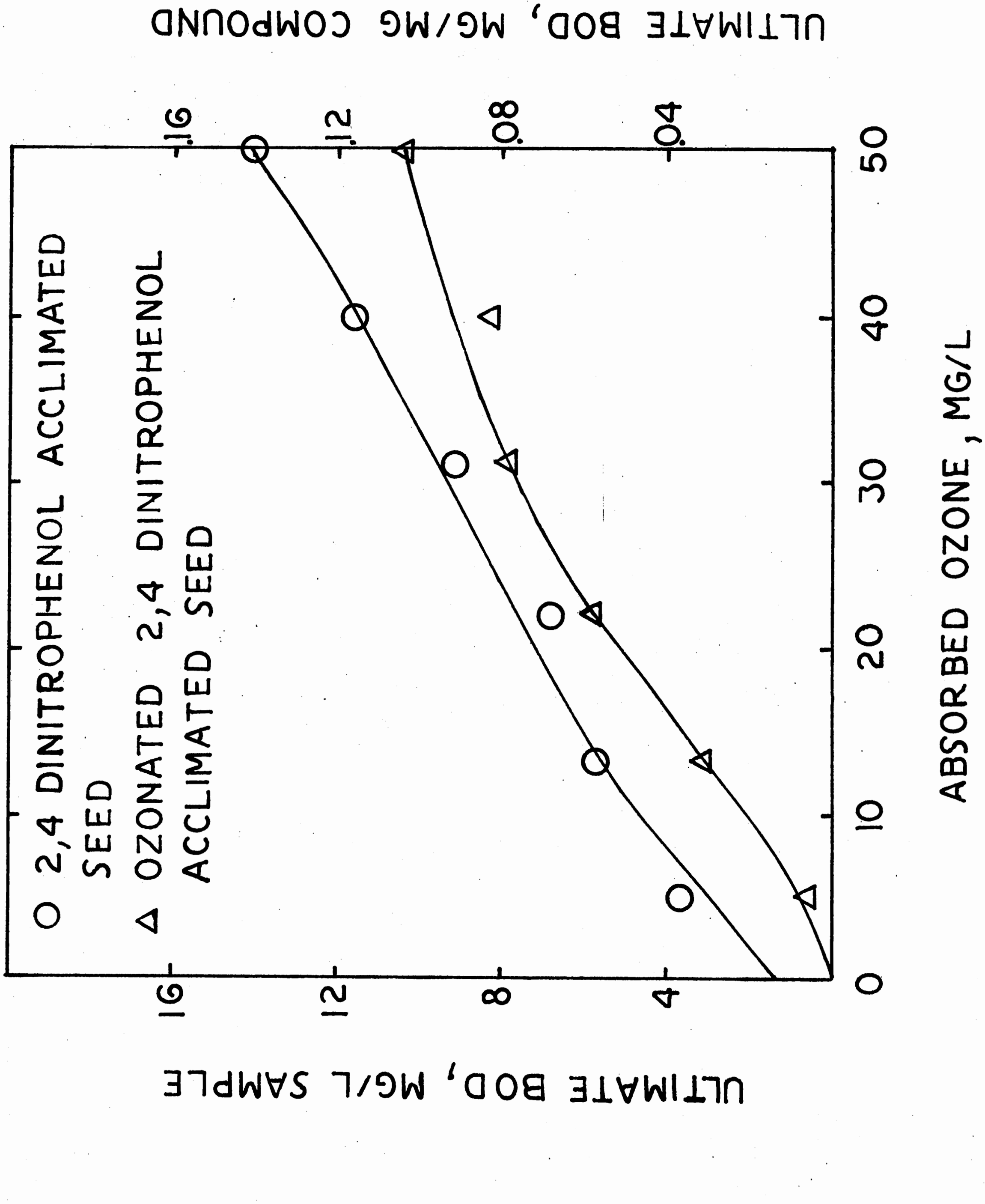

○ 2,4 DINITROPHENOL ACCLIMATED SEED
△ OZONATED 2,4 DINITROPHENOL ACCLIMATED SEED
ABSORBED OZONE, MG/L
0
10
20
30
40
50
ULTIMATE BOD, MG/L SAMPLE
4
8
12
16
ULTIMATE BOD, MG/MG COMPOUND
.04
.08
.12
.16

Figure 16. Ultimate BOD/TOC Ratio vs. Absorbed Ozone Dose for 2,4 Dinitrophenol. 2,4 Dinitrophenol Concentration - 100 mg/ℓ.

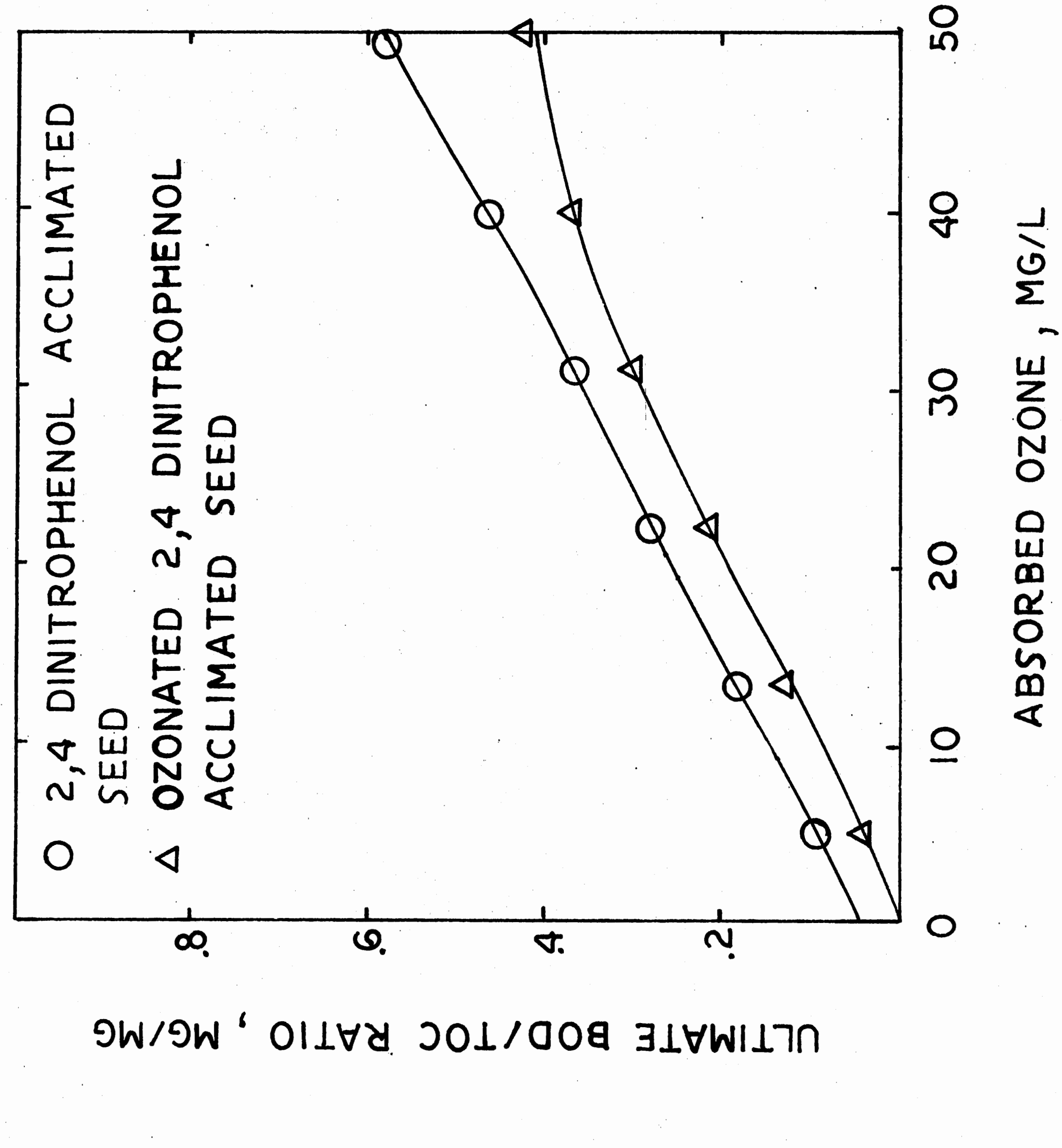
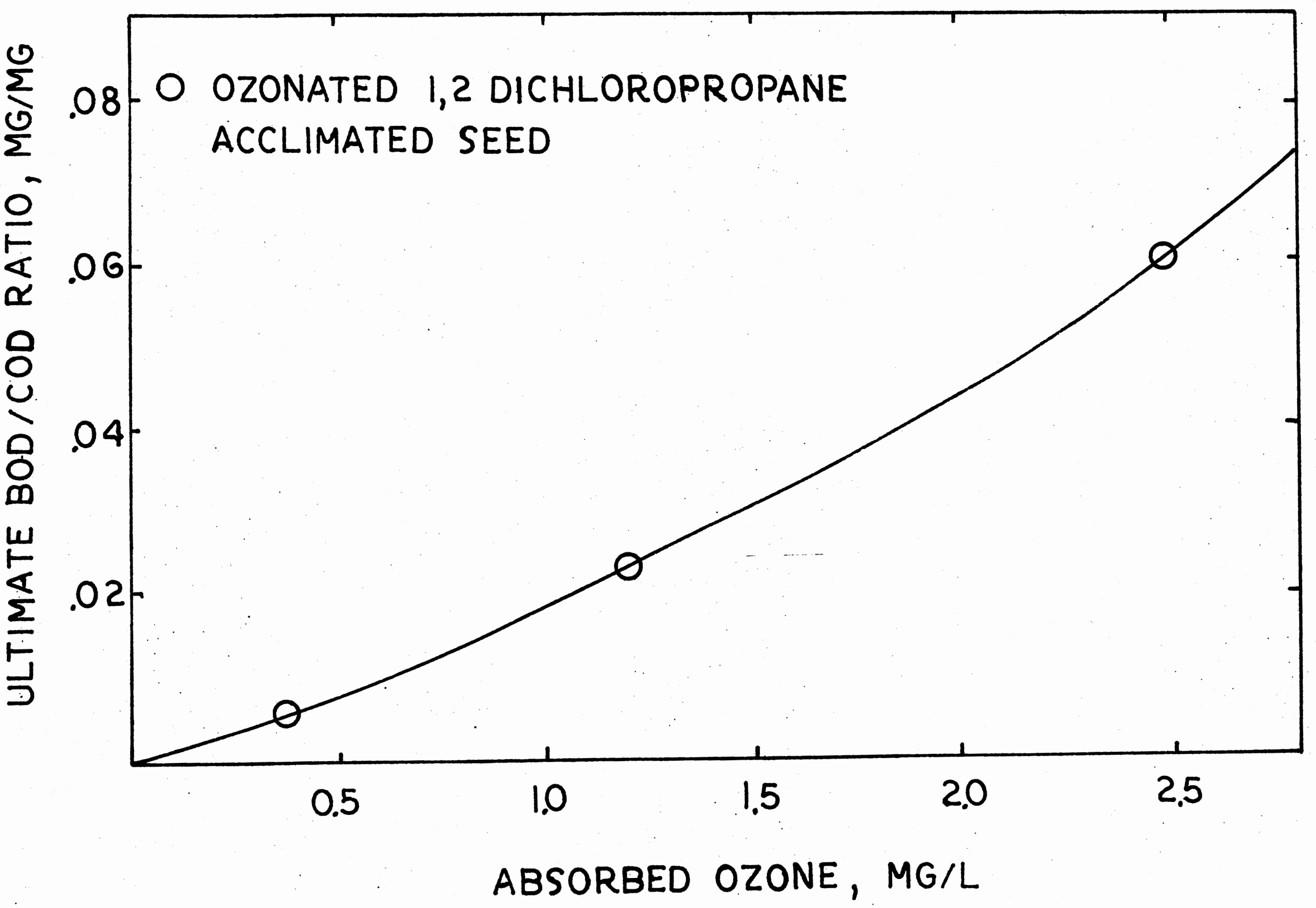

○ 2,4 DINITROPHENOL ACCLIMATED SEED
△ OZONATED 2,4 DINITROPHENOL ACCLIMATED SEED
ULTIMATE BOD/TOC RATIO , MG/MG
.2
.4
.6
.8
0
10
20
30
40
50
ABSORBED OZONE , MG/L

Figure 17. Ultimate BOD/COD Ratio vs. Absorbed Ozone Dose for 2,4 Dinitrophenol. 2,4 Dinitrophenol Concentration - 100 mg/ℓ.



○ OZONATED 1,2 DICHLOROPROPANE
ACCLIMATED SEED
.08
.06
.04
.02
ULTIMATE BOD/COD RATIO, MG/MG
0.5
1.0
1.5
2.0
2.5
ABSORBED OZONE, MG/L

CHAPTER V

CONCLUSIONS

From the previously discussed experimental data the following conclusions may be drawn:

Acrylonitrile

1. Acrylonitrile is not oxidized readily enough by ozone for it to be economically feasible to remove the compound by total oxidation.

2. Ozonation of acrylonitrile shows adverse affects on biodegradation. Therefore, ozonation of acrylonitrile wastewaters prior to biological oxidation should be avoided.

3. Treatment of acrylonitrile wastewaters by biological oxidation should be maintained at concentrations where the compound is not inhibitory. Previous studies have shown completely mixed, continuous flow, activated sludge reactors to operate at 150 mg/ℓ concentrations (43).

1,2 Dichloropropane

1. 1,2 Dichloropropane is oxidized greatly by small ozone doses making it economically feasible to totally oxidize the compound.

2. Ozonation increases the biodegradability of 1,2 dichloropropane.

3. Previous studies have shown 1,2 dichloropropane not to be degraded in completely mixed, continuous flow, activated sludge reactors but to be up to 99% stripped, while showing no operational problems (43, 44).

Thus the following treatment schemes are possible:

a. Physical stripping of the compound in biological reactors if the effluent quality can be obtained and air pollution is not a problem.

b. Ozonation prior to biological oxidation to increase biodegrability and thus increase removal efficiency. (Kincannon et al. (45) has shown that organics that are biodegraded are removed to lower effluent concentrations than those compounds that are removed by stripping alone.)

c. Ozonation following biological treatment for total oxidation of effluent 1,2 dichloropropane.

2,4 Dinitrophenol

1. 2,4 Dinitrophenol is not oxidized readily by ozone at economical doses.

2. Ozonation is very effective in increasing the biodegradation of 2,4 dinitrophenol with the increase being proportional to absorbed ozone dose.

3. Previous studies have shown 2,4 dinitrophenol to be biologically oxidized in continuous flow, completely mixed activated sludge reactors at concentrations up to 100 mg/ℓ, with zero stripping and no operational problems (45). Thus the following treatment schemes are possible:

a. Biological oxidation alone, if concentrations are below inhibitory levels.

b. Ozonation prior to biological oxidation to increase biodegradation and reduce inhibitory levels.

General

Ozone is not a "cure all" for biorefractory pollutants. Studies must be conducted on each compound to determine if it is effective and or economically feasible to use ozone for partial oxidation to increase biodegradation or to oxidize the compound completely.

CHAPTER VI

SUGGESTIONS FOR FUTURE WORK

The author found that acclimation in batch reactors limits the concentrations of many biorefractory compounds in the feed since many are stripped, toxic, and or inhibitory. The use of continuous flow reactors would allow for higher concentrations to be used and thus better acclimation.

Continuous flow reactors, which are much more representative of an actual biological treatment process, could then be used to determine the effect of ozone on the treatment efficiency of the compounds and also the effect on the biokinetics of the wastewaters. Gas chromatography and or mass spectrometry would add to and substantiate the results from the BOD, TOC, and COD tests.

Furthermore, ultimate BOD/TOC and ultimate BOD/COD should be used as the biodegradation parameters. This allows for better accuracy with less dependence on the acclimation of the biological populations utilized and also subsequent deletion of the BOD lag problem, which should always be assumed to be present in testing biorefractory pollutants.

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2

VITA

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