THE EFFECTS OF RESIDUAL NON-BIODEGRADABLE ORGANICS ON THE TREATMENT EFFICIENCY IN THE BIOLOGICAL TOWERS

By

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DEDICATED TO MY PARENTS,

GEORGE V. AND AUDREY B. CRAVENS

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CHAPTER I

INTRODUCTION

The trickling filter process (fixed bed reactor) has been used for wastewater purification in the United States since 1889. The filter bed consists usually of crushed rock, but also uses other materials such as plastic. The word "filter" has been used to denote the process, although the process does not provide filtration in the normal sense, but in reality the filter bed is utilized by the microorganisms as a locale for biological oxidation to occur. The microorganisms present in the waste flow attach themselves to the rock surfaces and multiply by feeding on the biodegradable organic material in the waste. The removal of this biodegradable organic material from the wastewater was regarded as purification of the waste.

Several problems that are encountered with trickling filters include odors due to ventilation problems, poor distribution of the waste over the media, clogging of distribution nozzles, clogging of filter media forming ponds, filter flies in the vicinity, and ice buildup on media during cold weather.

Rock trickling filters had to be operated at rather low BOD loadings due to the clogging at the media, and nozzles. These filters were considered "low rate" operating in ranges of 2 to 14 lbs. BOD/Dy/1000-ft^3 at flow rates ranging from 45 to 140 Gpd/$ft.^2$ and this required a larger volume of media for treatment of the waste. For plastic media trickling filters the following ranges of organic loadings have been recommended for low rate filters of 5 to 25 Lbs/Dy/1000 ft^3 at flow rates ranging from 25 to 100 Gpd/ft^2, and 25 to 300 Lbs/Dy/1000 ft^3 at flow rates of 200 to 1000 Gpd/ft^2 for high rate plastic media trickling filters (1).

Biological towers employing plastic media are usually designated as "high rate" filters operating at higher organic loadings and flow rates because the filters are capable of treating greater quantities at BOD per unit volume than low rate filters because of their high specific surface areas.

The advantages of having the biological tower plastic media system over the rock trickling filter system are that the plastic media filters require less structural support than rock filters, less expensive to operate, void spaces in the plastic media are larger, and higher hydraulic and organic loadings can be applied.

During recent years at Oklahoma State University Bioenvironmental Laboratories research efforts on the biological towers waste treatment processes have proven successful. Previous investigators results of treatment efficiencies versus organic loadings in Lbs. COD (BOD)/Dy-/1000 ft^3, has produced two distinctive plots (2, 3). In reviewing the work of these investigators it is interesting to observe that the plots look identical.

The work to be presented in this thesis deals with finding out the amounts and effects of residual non-biodegradable organics on the treatment efficiencies of the biological towers. This research will confirm the beliefs of others that a residual does exist and can influence the treatment efficiencies if not taken into account.

CHAPTER II

LITERATURE REVIEW

A. Introduction

Various researchers have studied the ΔCOD concept. The term "ΔCOD" is generally defined as the amount of COD removed at any time, i.e., the difference between the COD present at the time of measurement (effluent) and the COD initially present (influent):

$$COD_i - COD_e = \Delta COD$$

When the effluent is aerated in a batch unit over an extended period of time and the COD_e remaining can no longer be biologically reduced, then the ΔCOD is a measure of the amount of organic matter in the waste sample which was available to the microorganisms. The ΔCOD concept is a simple one, yet can lead to confusion unless it is understood that this is not a comparison of the COD and BOD test. The concern here is with ΔCOD and the COD test is to ΔCOD as what the DO test is to BOD (1, 4, 5).

The measurement of ΔCOD is that portion of the COD of the waste that serves as biological substrate for acclimated microorganisms, whether it be in the activated sludge or biological tower treatment systems. The residual COD, if sufficient aeration time in a batch unit has been allowed, is composed of the non-biodegradable material that the microorganisms cannot utilize. Therefore, ΔCOD can be employed to determine the amount of biochemical oxygen demanding organic matter present even in the presence of non-biodegradable COD in the waste water. As an example, a waste may contain lignin, which can be chemically oxidized but not attacked biologically. Thus, COD_e would be high yet a serious stream liability due to depletion of dissolved oxygen would not exist.

The ΔCOD relates to the purpose of treatment, that is, the removal of biochemically available organic matter which is the way in which the BOD test has been applied to design (6). The principle of the BOD test is not objectionable but it is the use of a standard technique (BOD_5) which is inadequate for the purpose for which it is needed. It is the purpose of this chapter to present the findings and conclusions of research work utilizing ΔCOD and Total BOD for the design and operational parameters of trickling filter systems.

B. Evaluation of ΔCOD for Design of Trickling Filter Systems

Several researchers have suggested the use of ΔCOD as a design parameter. An experimental investigation which should precede design calculations, consist of an acclimation period of a heterogenus microbial population by repetitive feeding cycles of that organic waste to be treated. During the acclimation period one can determine the extent of biodegradable organic matter available as a food source (COD_i - COD_e = ΔCOD).

Symons et al (7) found that the COD of the membrane filtrate of a mixed liquor sample taken at the end of the aeration period will be a measure of nearly all the soluble organic matter leaving the pilot plant. There are three ways COD may be satisfied in this type of a pilot plant. One, chemical oxidation, such as sulfite being oxidized to sulfate, may occur. Two, the waste may be blown out of solution. If these two possibilities of COD satisfaction are checked and eliminated, then the COD reduction must be due to the third alternative, biological degradation. Therefore, the change in COD through the pilot plant is the biologically treatable portion of the industrial waste. Of course, if alternatives one or two are also present they must be subtrated from the change in COD, as they are not biological processes.

Hiser and Busch (8) presented the mass culture T_bOD technique which utilized the COD determination for measuring the soluble organic concentration of substrates. The T_bOD test clarifies the COD to BOD relationships by showing that the net reduction in soluble COD of a biological mass culture substrate system is the Total Biological Oxygen Demand (T_bOD), however this test will never be fully utilized in treatment plants or streams because synthesis is requisate for metabolism. The basic concept of T_bOD (9, 10, 11, 12) test is that the available soluble organic material in an acclimated mass cultural system is completely absorbed and metabolized during the course of batch aeration. Any remaining soluble organic material (COD) in the substrate is then relatively stable. This residual COD consists of material that was non-biodegradable to the culture for metabolism, possibly end products of intermediary metabolism or residuals of lysed organisms of the microbial populations.

Gaudy and Gaudy (4) believe that ΔCOD represents the best measurement of the amount of organic matter available in a biological treatment facility. The BOD test estimates what ΔCOD actually measures. Moreover, since ultimate BOD can only approach ΔCOD as an upper limit, the latter parameter gives a more conservative estimate of the ultimate biochemical oxygen demand of a waste sample.

In 1972, Gaudy (6) reported that there is no real need to use the 5-day BOD test as a functional loading parameter in the design of a biological treatment plant. By using a simple laboratory study, determine the course of purification of the waste using the COD test as a parameter. The difference between initial and residual COD in a batch system represents the organic matter which has been removed from the waste in terms of its oxidizability (7, 8). The data obtained by this method provides a measure of the O_2 demanding substrate in the waste which was removed via biological processes in a reasonable aeration period. Since COD is a measure of chemically oxidizable material, the ΔCOD may be precisely defined as the amount of O_2 required to chemically oxidize the organic matter which has been removed biologically during the aeration period which intervened between sampling for the COD determinations. Even if the cells are separated from the waste, ΔCOD could only be equated to BOD removal if one assumes total oxidation of the organic matter in the waste.

C. Evaluation of BOD for Design of Trickling Filter Systems

For many years researchers in the water pollution control field have considered the BOD test a measure of organic material or of organic carbon in a sample. In reality, BOD of a waste is an assessment of the amount of oxygen used for respiratory functions of microorganisms which utilize organic matter in the waste for growth. As a measure of organic matter, the BOD test cannot compare with either the COD test or TOC test and should not be used for the same purposes as are COD and TOC.

Hoover, Jacewicz, and Porges (13) made a statement concerning the BOD test and it is worthy of repeating: "The BOD test is paradoxical. It is the basis of all regulatory actions and is run routinely in almost all control and research studies on sewage and industrial waste treatment. It has been the subject of a tremendous amount of research, yet no one appears to consider it adequately understood or well adapted to his own work."

Sorrells and Zeller (14) studies trickling filter performance and observed that BOD removal varied with the organic load that was applied. The removal of soluble BOD was found to be dependent upon the organic loading rather than the hydraulic flow rate.

Deen (15) studied the effects of various organic and hydraulic loadings on an experimental fixed bed reactor. He showed that the substrate removal was a function of organic loading applied rather than hydraulic flow rate.

Ingrams (16) results of using settled sewage as a substrate showed that the hydraulic flow rate was not the limiting factor controlling the efficiency of the reactor, but believed that the BOD loading to be of more importance. The BOD removal was observed to be at the same efficiency with the same applied organic loading.

In 1973, Richard and Kingsbury (17) studied the treatment of milk waste using plastic media biological towers. Using Flocor media, they suggest that the two most important things to consider in tower design are the relation of organic load to performance and the irrigation rate.

Garrett and Sawyer (18) in 1952 studied the kinetics of the removal of soluble BOD in the activated sludge process. The relation between the rate of growth and the remaining soluble BOD is well represented by a discontinuous function. With high concentrations of BOD the rate of growth is constant and at low concentrations the rate of growth is directly proportional to the remaining soluble BOD.

Stack (19) in 1957, believed that for a given filter and waste, factors which influence biosorption establish the value of removable BOD and the rate of biosorption. Based upon the assumptions: (1) A trickling filter is basically a self-regenerating absorption tower. (2) Each unit depth of the filter will remove a constant fraction of the removable BOD applied to that unit depth. (3) Removable BOD is the fraction of the observed BOD which can be removed by biosorption. (4) The quantity of BOD that can be absorbed by one unit volume of a filter has a maximum limit, both Stack and Velz (20) developed their concept of trickling filtration. This concept refers to an equilibrium situation where food is available in the wastes, biosorptive transfer occurs and biological oxidation reactions take place.

In a 1967 study, Chipperfield (21) investigated the performance of plastic media in trickling filters. Performance characteristics for Flocor plastic media treating six different trade wastes were given at BOD loadings ranging from 50 to 200 lbs./dy/1000 ft.^{3}. The Flocor systems were found to attain removals of up to 95 per cent.

CHAPTER III

MATERIALS AND METHODS

A. Experimental Approach

To illustrate the effects that residual non-biodegradable organics can have upon a trickling filter system if not taken into account when predicting the treatment efficiencies.

The only variations applied to the system being the influent organic concentrations (70, 160, 300, 500 mg/l) and hydraulic flow rates of 750 and 1000 Gpd/ft^2. After the system was acclimated to experimental organic loading and flow rates, the COD and BOD tests were selected as the basis for determining the efficiency versus total organic loading (Lbs/Dy/1000 ft^3).

B. Experimental Apparatus

The fixed bed reactor in this study consisted of two plexiglas towers. The first tower consisted of four feet of support media and six feet of support media in the second tower. Figure 1 shows the experimental apparatus. Due to the height availability in the laboratory the tower had to be linked in series. The effluent from the first tower is pumped to the top of the second tower through pyrex plastic tubing.

The first plexiglas tower contained four-one cubic foot (1.0 x 1.0 x 1.0) modules of Flocor rigid polyvinyl chloride media. The

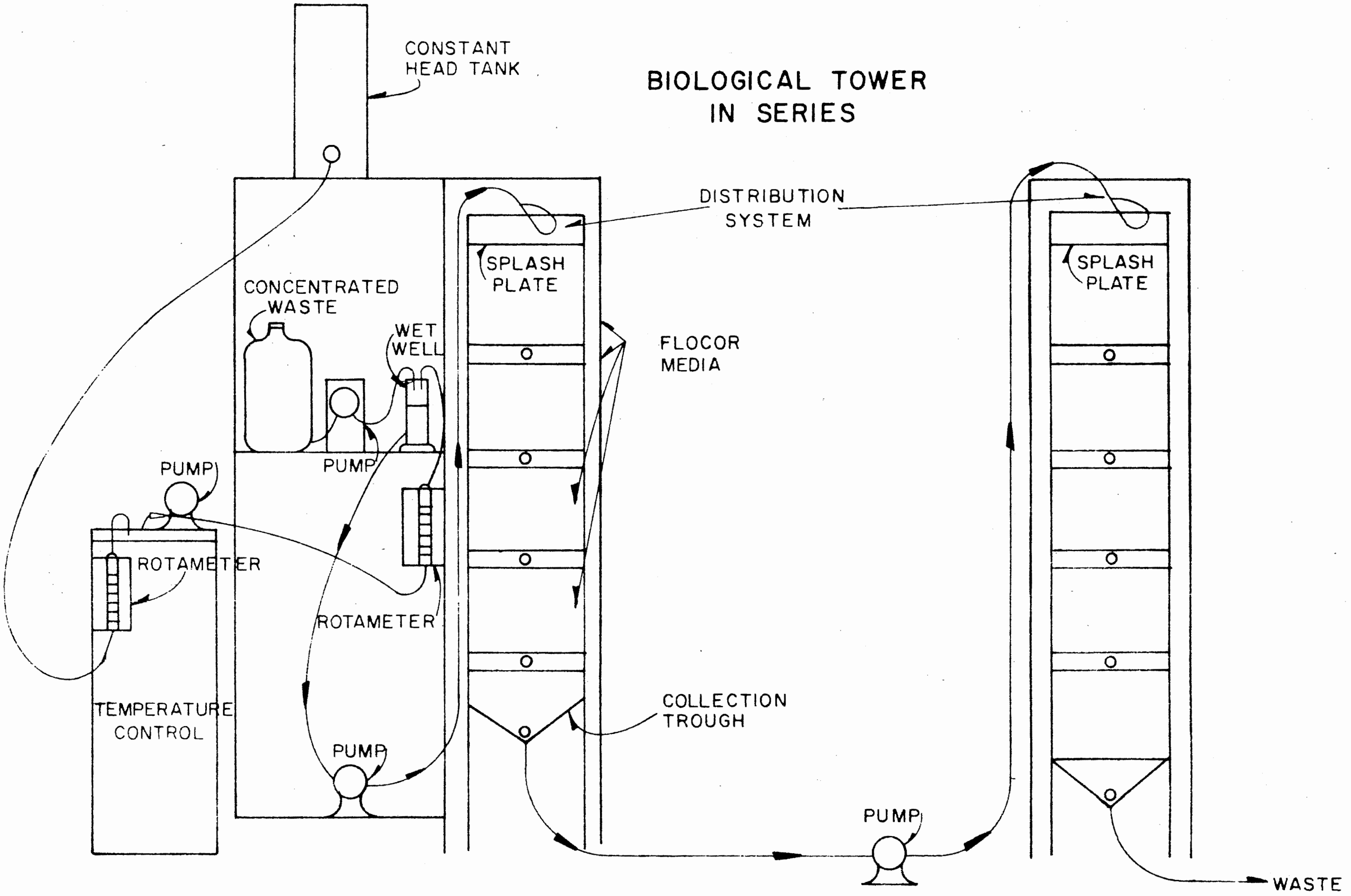

Figure 1. Experimental Apparatus

second tower contained six-one cubic foot sections of Flocor rigid PVC media. The Flocor media was first developed by the Imperial Chemical Industries, Ltd., London, England, and has previously been licensed by the Ethyl Corporation in the United States. The Flocor media has 2¼ inch triangular openings, and each cubic foot has a maximum of 24 $ft.^2/ft^3$ surface area which can be utilized for biological activity. The void ratio of 97% allows sufficient air flow for microorganisms to utilize oxygen in their chemical oxidation reactions. The air moves upward like a forced draft system. Approximately four inches of void space existed between each foot of plastic media to allow samples to be taken at various depths.

The hydraulic flow to the biological towers was maintained by means of a constant head tank which received a continuous flow of tap water from the Stillwater municipal water system. From the constant head tank the water flowed by gravity through a rotameter set during the experiment at both 750 and 1000 $gpd/ft.^2$. A temperature control device was necessary during October 1976 through January 1977 due to the cold winter that occurred. The Precision Scientific Temptrol Water Bath was used that enabled the primary reactor influent to be stabilized at 21°C ± 1.0°. The primary reactor influent was discharged into a wet well, where mixing with a concentrated synthetic waste took place.

The synthetic waste utilized sucrose ($C_{12}H_{22}O_{11}$) as the main carbon source in this experiment and levels of other chemicals were maintained such that sucrose was the growth limiting nutrient. The nitrogen was furnished by using an ammonia-nitrate fertilizer. The commercial grade fertilizer had an analysis of 33.5% nitrogen that was readily available. This nitrogen was composed of 16.25% nitrate and 16.25% was in the form of the ammonia compound. Due to the high concentrations of fertilizer involved, concentrated sulfuric acid was added to maintain the solubility of the solutions as well as prevent microbial activity from occurring in the feed bottle. The concentrated feed therefore possessed a low pH, but when mixed with the large quantities of water, pH values of the primary influent entering the biological towers were within proper ranges for biological growth to occur on the Flocor media. The concentrated waste in the feed bottle was stirred continuously by a mechanical mixer.

The desired concentration of feed was pumped to the mixing chamber by a Milroyal pump, made by Milton Roy. The Milroyal pump can be adjusted to yield the exact flow required from the feed bottle to reach a desired concentration after mixing with the hydraulic flow, from the following equation:

$$(Q_T + Q_W)\ S_i = Q_W C_W$$

Q_T = Hydraulic flow

Q_W = Waste flow

S_i = Desired influent substrate level

C_W = Concentration of waste in feed

Composition of the synthetic waste is given in Table I.

When the desired concentration by diluting with tap water in the mixing chamber is achieved the mixture is pumped to the top of the first plexiglas tower by a Teel rotary-screw pump (Model Ip610). The pump was driven by a Dayton single speed motor (Model KS55JXBJB-9B). Influent distribution at the top of the tower was accomplished by using a perforated circular section of tubing, through which the flow was transferred to a splash plate, which was a plexiglas baffle with ½ inch holes drilled uniform throughout to even out the flow over the plastic Flocor media.

Effluent from the first biological tower was pumped to the top of the second biological tower by means of a similar Teel rotary-screw pump where a similar distribution system was used to even the flow over the media.

TABLE I

COMPOSITION OF SYNTHETIC WASTE RELATIVE TO
A SUCROSE CONCENTRATION OF 100 MG/L

Constiuent	Concentration
$C_{12}H_{22}O_{11}$	100 mg/l
Ammonium-Nitrate Fertilizer	64
$MgSO_4 \cdot 7H_2O$	10
K_2HPO_4	6
$MnSO_4H_2O$	1
$CaCl_2$	0.75
$FeCl_3 \cdot 6H_2O$	0.05

C. Experimental and Analytical Procedures

Seeding the biological towers with microorganisms was not required, since it had been used by previous investigators. Original seeding was accomplished by using primary clarifier effluent from the Stillwater, Oklahoma, municipal sewage treatment plant.

The laboratory investigation covered a time span of ten and one-half months, and consisted of six experimental runs. The first four runs were at initial organic concentrations of 70, 160, 300 and 500 mg/l at the hydraulic flow rate of 750 Gpd/ft^2. The final two runs were at initial organic concentrations of 160, and 300 mg/l at a flow rate of 1000 Gpd/ft^2. Each experimental run was initiated with an acclimation period of at least two weeks for the purpose of obtaining steady state conditions. Once steady state conditions exist, nearly identical values of COD over a three day sampling period, the results of COD analysis were averaged and recorded as the values for that particular parameter for that particular run.

Prior to collecting samples for COD and BOD determinations, 100 ml. samples of the influent were collected in a 200 ml. beaker to record the temperature and pH. The temperature did not fluctuate during April 1976--September 1976, 23°C ± 1.0°C, but in October 1976--January 1977 a temperature control box was required to keep the tap water at a constant temperature of 21°C ± 1.0°C due to the unusually cold winter in Oklahoma. The pH was determined using a Beckman Expandomatic SS-2 pH meter, in order to determine if the concentrated waste was being diluted within a range of 7.5 to 8.5 due to the concentrated sulfuric acid added to the waste to help inhibit microbial growth and keep solubility high in the feed bottle.

COD samples were taken at every two foot of depth using a piece of PVC tube which had been cut along its longitudinal axis to form a trough-like sampler. The sampler was inserted into the four inch void space between each two foot section of plastic media and the sampler was then moved back and forth horizontally across the media so that a uniform sample was obtained at each two foot of depth. Exactly 50 ml. of sample was collected at each two foot sampling post, including samples of the influent and effluent. These samples were then filtered through a HA 0.45μ Millipore filter. A chemical oxygen demand (COD) of the filtrate was then determined by the procedure obtained in standard methods (22).

To determine the non-biodegradable portion of each experiment a batch unit was utilized by taking 300 ml. of effluent during the sampling period and aerating it for four to five days and taking samples in the morning and night. This sample was then filtered through a HA 0.45μ Millipore filter and COD analysis was conducted on the filtrate.

BOD samples were run according to standard methods (22). On the third day of data gathering enough sample was taken to run COD and BOD tests. Since the influent was made up of soluble BOD and no microorganisms present, the influent BOD's had to be seeded. The other sec-sections of the tower (2, 4, 6, and 10 ft) already had acclimated seed present so seeding was not necessary. Total BOD was then determined after the 5-day incubation period at 20°C was completed.

D. Method of Data Analysis

In this section, the treatment efficiency or per cent (COD) reduction and the total organic loading (Lbs/Dy/1000 ft^3) equations will be developed for application to biological fixed-bed reactors.

This treatment efficiency or per cent COD (COD, BOD) reduction can be calculated according to the following expression:

$$E = \frac{Si - Se}{Si} \times 100$$

E = efficiency of COD (ΔCOD, BOD), per cent

Si = influent substrate concentration, mg/l

Se = effluent substrate concentration, mg/l

The total organic loading (Lbs/Dy/1000 ft^3) of a biological tower can be determined by varying the hydraulic flow rates and monitoring the BOD or COD remaining at various depths. The total organic loading per 1000 ft^3 is calculated as follows:

$$L_o = \frac{F \times Si \times 8.34}{A \times D_t} \times 1000$$

L_o = organic loading, Lbs (COD, ΔCOD, BOD/Dy/1000 ft^3)

F = flow rate, MGD

A = surface cross-sectional area, ft^2

D_t = depth of tower, ft.

8.34 = converts gallons to lbs.

The following chapters will present the use of ΔCOD as a design parameter to describe the performance of an experimental fixed-bed reactor. The relationship between Total COD, ΔCOD, and Total BOD will be presented graphically and applications will be discussed.

CHAPTER IV

RESULTS

The results of this experimental investigation are presented in tabular form and various relationships are shown graphically. Data was collected at influent organic concentrations of 70, 160, 300, and 500 mg/l, and at hydraulic flow rates of 750 and 1000 Gpd/ft^2. All values are tabulated and represent an average of at least three consecutive days of sampling. The total organic loadings for each experimental run were calculated by multiplying the average influent COD by the flow rate and then converting into units of Lbs/Dy/1000 ft^3. The results are presented separately so that the individual parameters can better be evaluated.

A. Measurement of Residual COD

In this section, the results of the residual COD experiments will be given. To determine the residual non-biodegradable organics in a treatment system is accomplished within a batch unit, aerated from three to five days, and utilizing the effluent from an acclimated fixed-bed reactor.

Figure 2 shows the results of the first batch study. The initial influent organic concentration of 70 mg/l and a flow rate of 750 Gpd/ft^2 showed an effluent residual COD concentration of 33 mg/l after 70 hours of batch aeration.

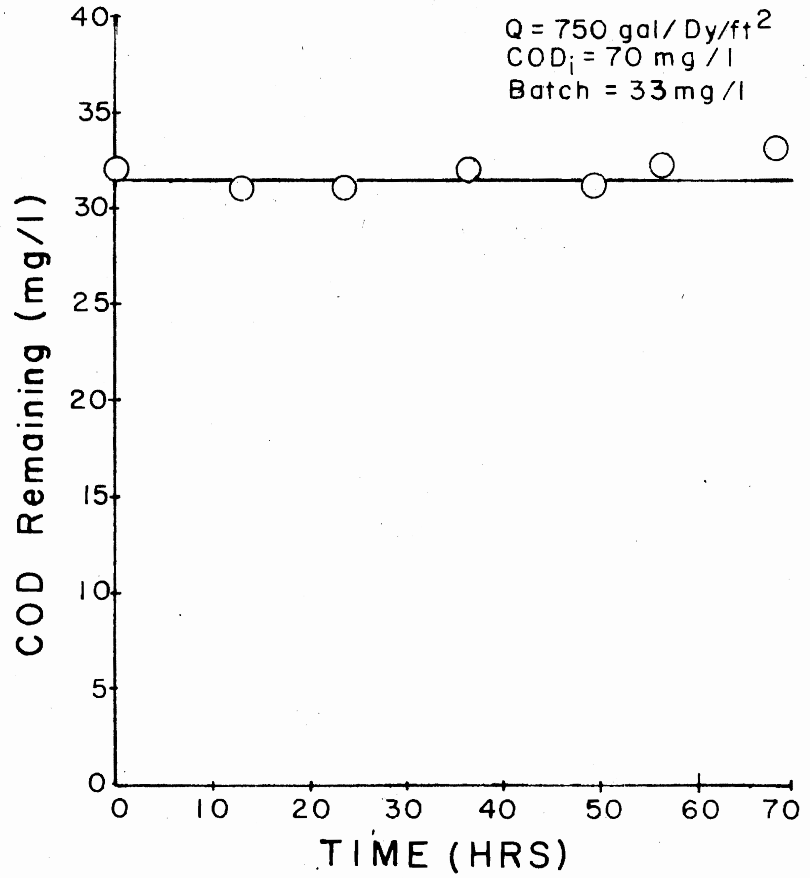

Figure 2. Residual COD in a Batch Unit Using Effluent from the Biological Towers at Influent COD of 70 mg/l and 750 Gpd/ft^2 flow rate.

In Figure 3, the initial influent COD value was 160 mg/l and a flow rate of 750 Gpd/ft^2. After 80 hours of continuous batch aeration the residual COD value was 33 mg/l.

Figure 4 expresses the batch unit for an initial influent COD of 300 mg/l and flow rate of 750 Gpd/ft^2. Over 90 hours of batch operation yielded a residual COD of 46 mg/l.

In Figure 5, at an initial influent COD of 500 mg/l and a flow rate of 750 Gpd/ft^2, the batch unit after 70 hours of aeration showed a residual COD of 60 mg/l.

Figure 6 shows a residual COD of 40 mg/l after 70 hours of batch aeration. The initial influent COD concentration is 160 mg/l and a flow rate of 1000 Gpd/ft^2.

In Figure 7, the initial influent COD is 290 mg/l and a flow rate of 1000 Gpd/ft^2. After 70 hours of continuous batch aeration of the effluent the residual COD value is 42 mg/l.

Figure 8 shows the residual COD values obtained experimentally versus their initial influent COD concentrations. A straight line relationship exist between the residual and initial COD values.

In Figure 9, the residual COD values versus total organic loadings (Lbs COD/Dy/1000 ft^3) are plotted. As in Figure 8, a straight line relationship also occurs.

B. Treatment Efficiency as Measured by ΔCOD and COD

The COD and ΔCOD data found in the appendix and also graphically represented will be analyzed.

In Figure 10, the initial COD is 70 mg/l at a flow rate of 750 Gpd/

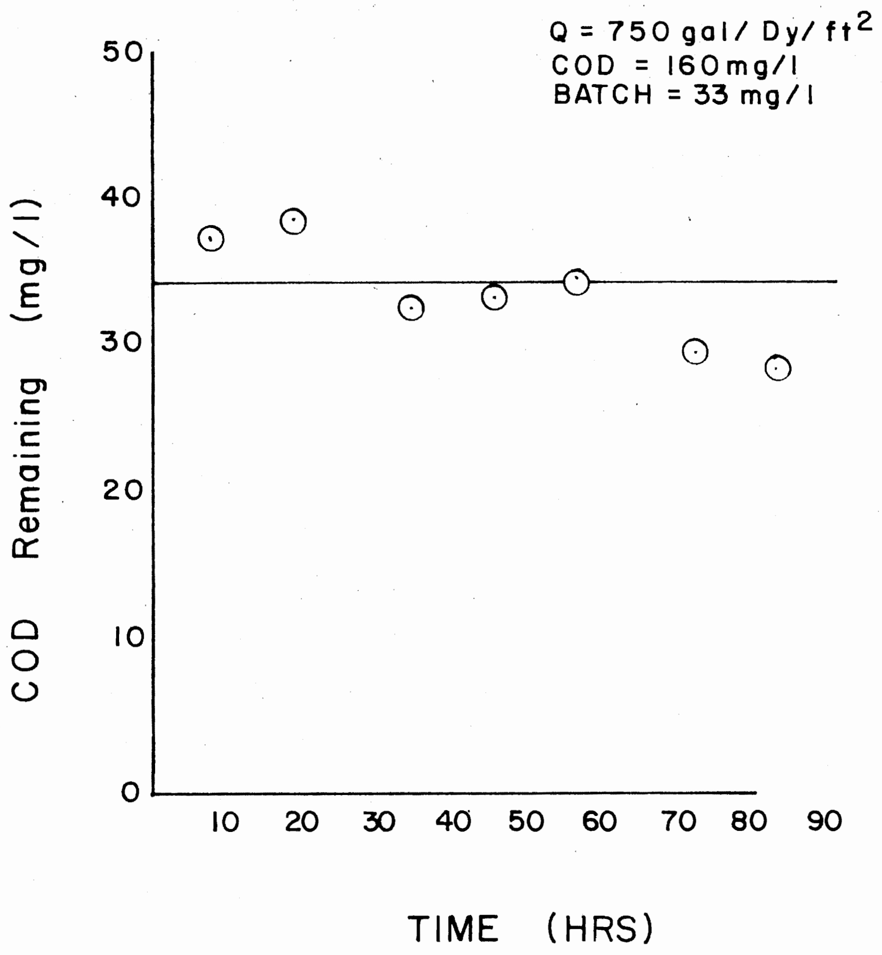

Figure 3. Residual COD in a Batch Unit Using Effluent from the Biological Towers at Influent COD of 160 mg/l and 750 Gpd/ft^2 flow rate.

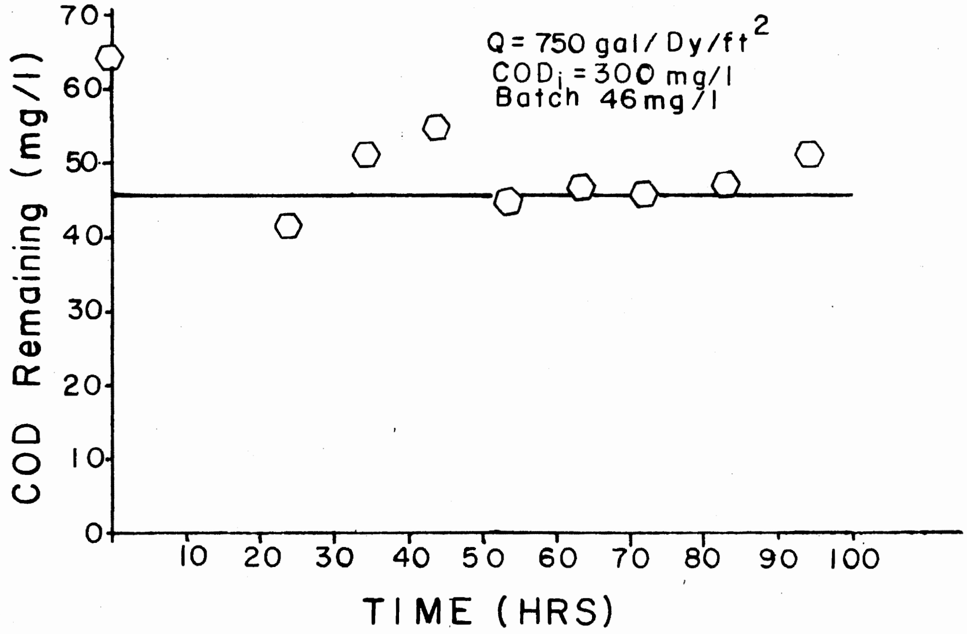

Figure 4. Residual COD in a Batch Unit Using Effluent from the Biological Towers at Influent COD of 300 mg/l and 750 Gpd/ft^2 flow rate.

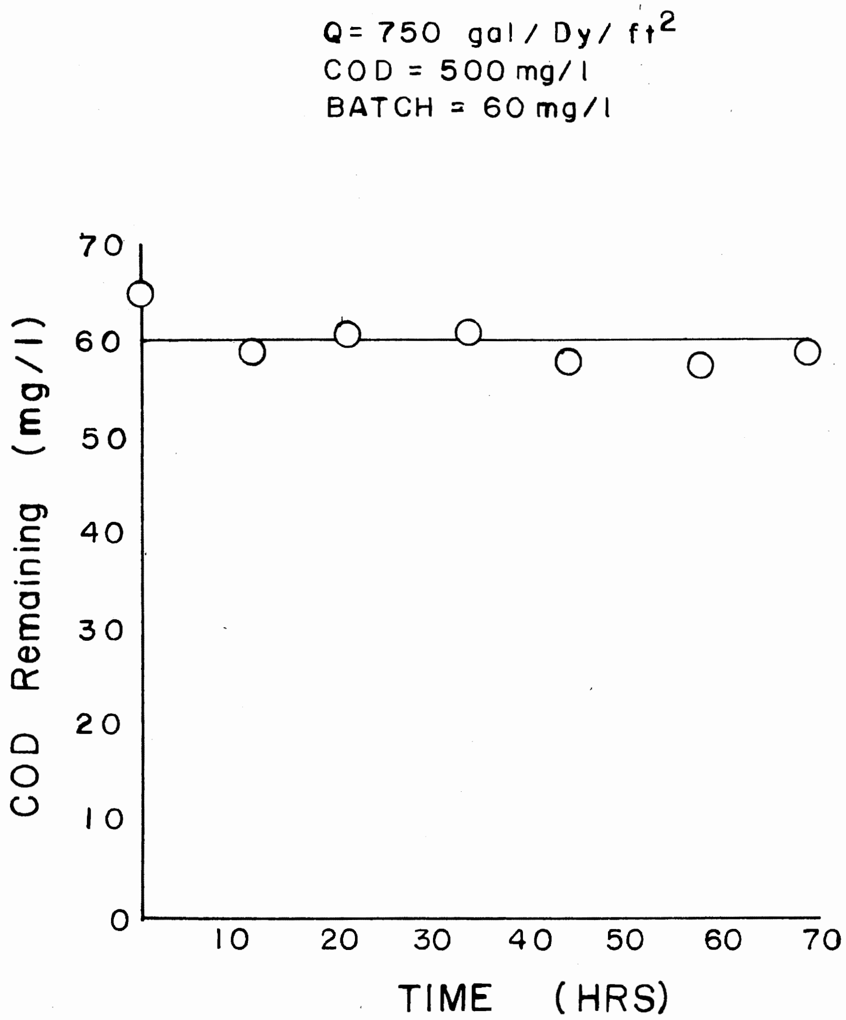

Figure 5. Residual COD in a Batch Unit Using Effluent from the Biological Towers at Influent COD of 500 mg/l and 750 Gpd/ft^2 flow rate.

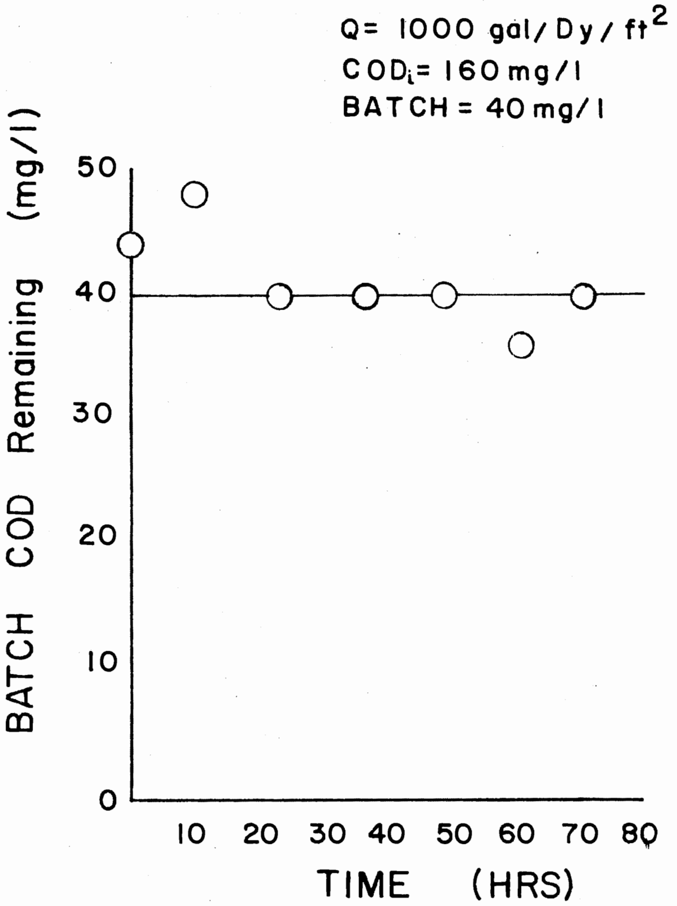

Figure 6. Residual COD in a Batch Unit Using Effluent from the Biological Towers at Influent COD of 160 mg/l and 1000 Gpd/ft^2 flow rate.

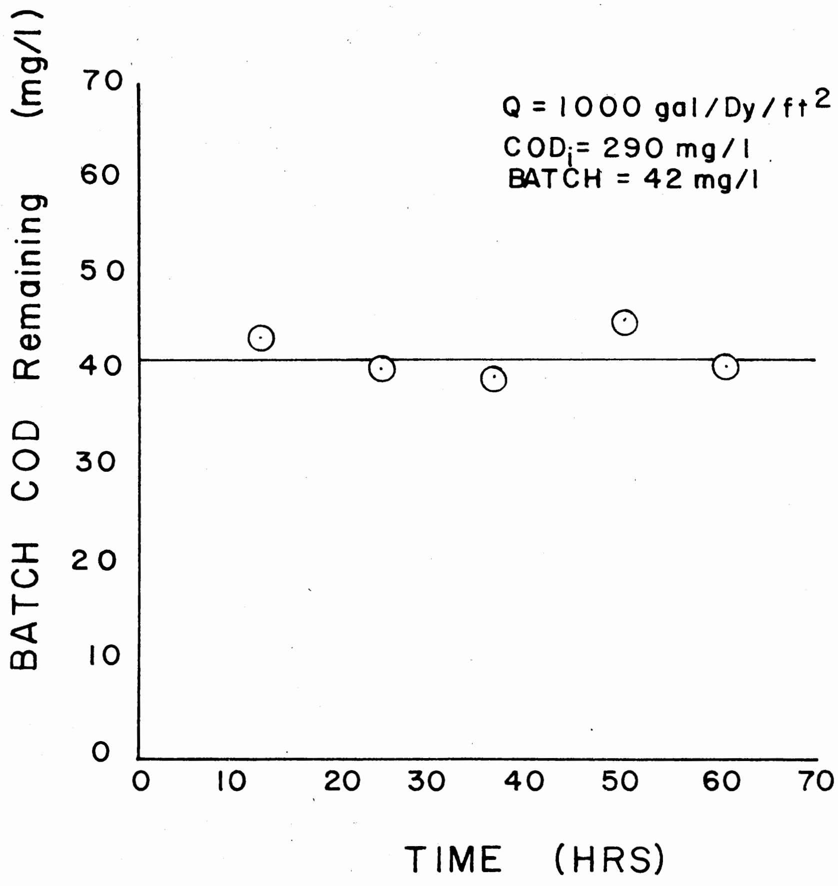

Figure 7. Residual COD in a Batch Unit Using Effluent from the Biological Towers at Influent COD of 290 mg/l and 1000 Gpd/ft^2 flow rate.

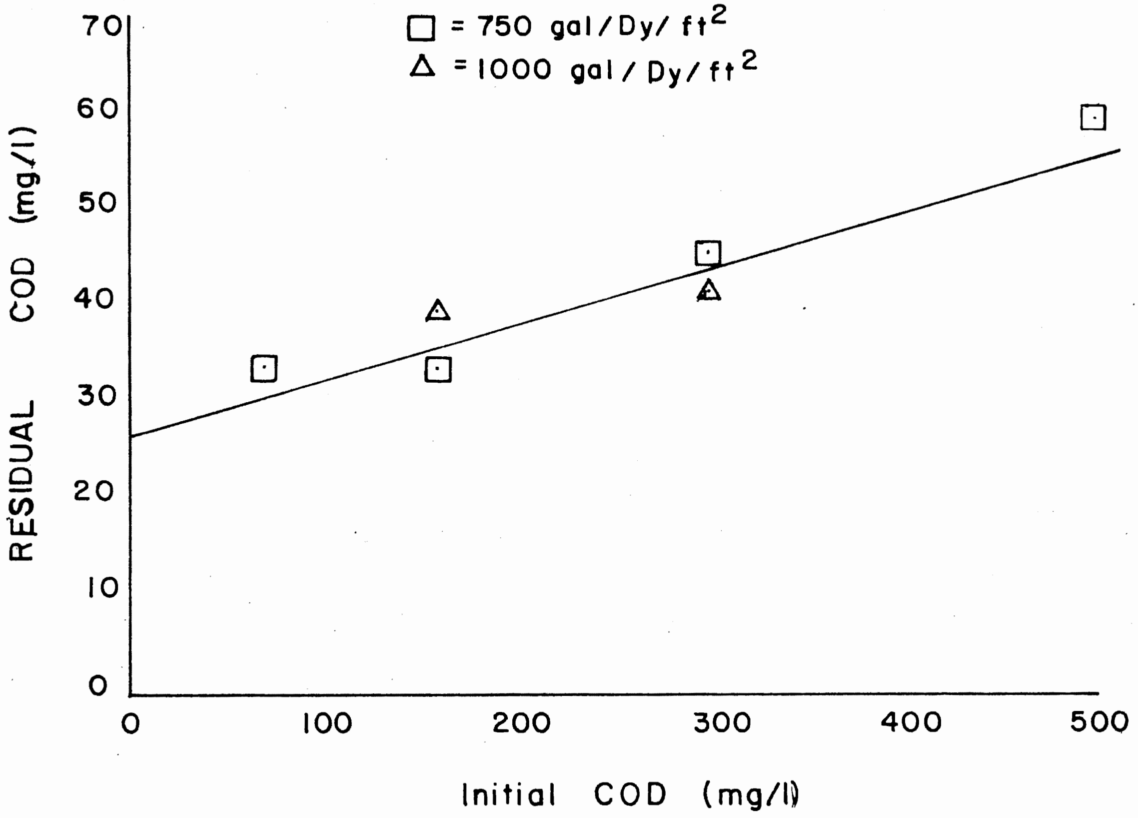

Figure 8. Residual COD Versus Initial COD

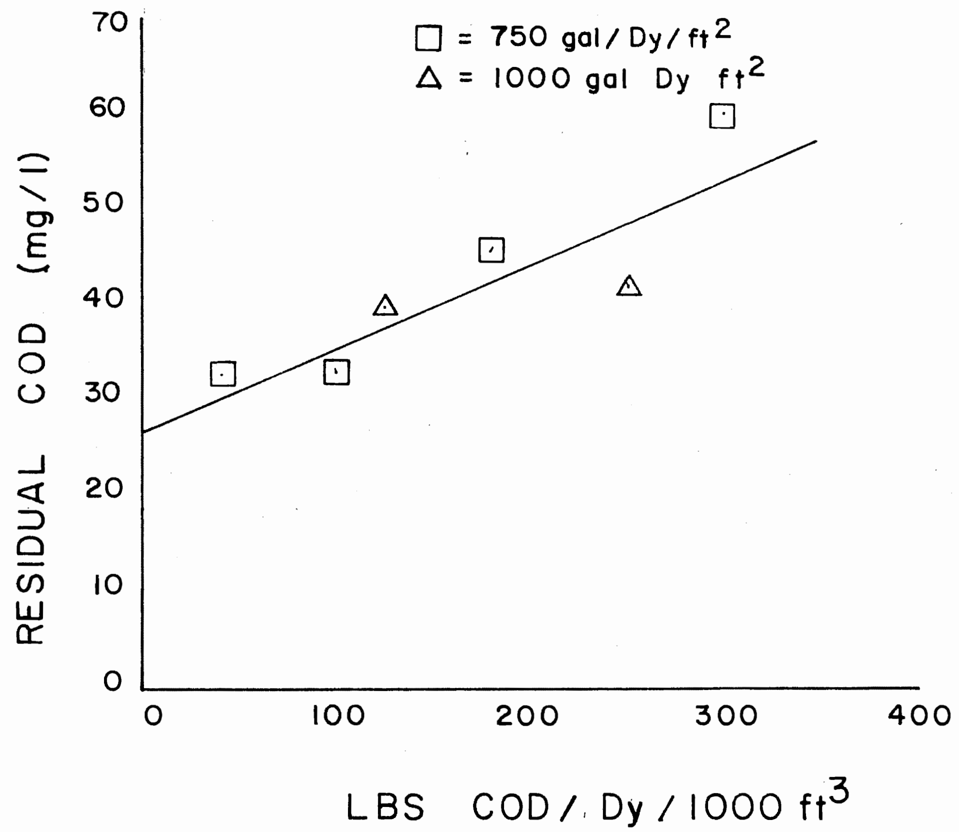

Figure 9. Residual COD Versus COD Applied
(Lbs. COD/Dy/1000 ft^3).

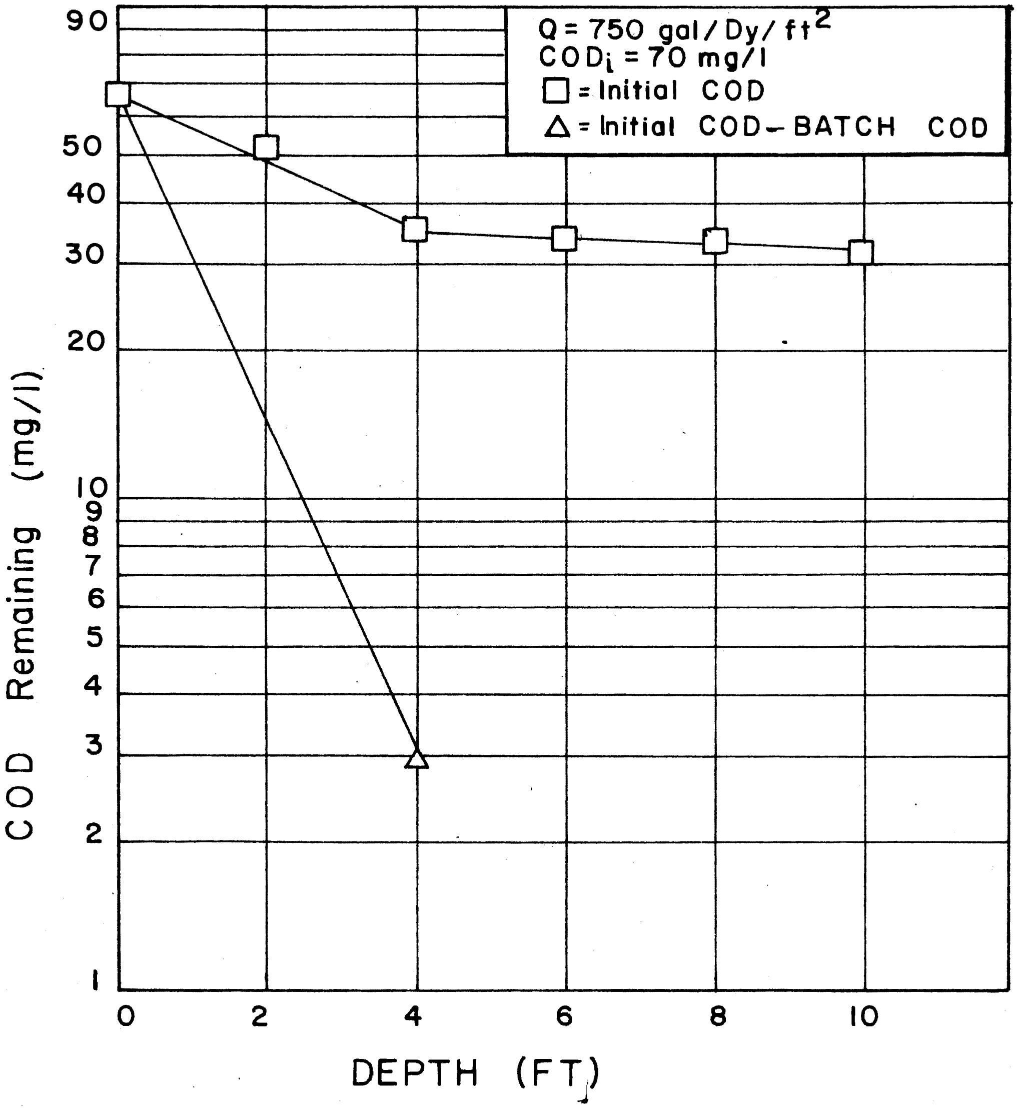

Figure 10. COD Remaining Versus Depth at Initial COD of 70 mg/l and 750 Gpd/ft^2.

ft^2. The COD removal follows first order kinetics until at the four foot depth all removal ceases. This gives only a 47% COD removal efficiency. After the residual from Figure 2 is subtracted from the four foot depth value to take into account the non-biodegradable fraction a new line is drawn from the initial COD value to the corrected ΔCOD value. The removal efficiency has now been elevated to 96%.

Figure 11 shows the graph of initial COD 160 mg/l at a flow rate of 750 Gpd/ft^2. The removal of biodegradable organics follows first order kinetics up to the six foot depth, and beyond this point no further removal occurs. The COD removal efficiency is 72.4%. The residual COD value from Figure 3 is then subtracted from the six foot depth value and a corrected ΔCOD line is drawn. The corrected removal efficiency value is 93.9%.

In Figure 12, the plotting of data for initial COD of 300 mg/l and 750 Gpd/ft^2 flow rate occurs. The removal follows first order kinetics through the ten foot depth. The COD removal efficiency is 79%. The residual COD value from Figure 4 is then subtracted out from the ten foot depth value and a corrected ΔCOD line is drawn. This corrected removal efficiency is 94.6%.

Figure 13, expresses the graph of initial COD concentration 480 mg/l and flow rate of 750 Gpd/ft^2. COD removal occurs throughout the entire ten foot tower. The COD removal efficiency is only 71%. From Figure 5, the residual COD is taken and subtracted from the ten foot depth value, and a corrected line is drawn to the initial COD value. The corrected removal efficiency value is 83.5%.

In Figure 14, the data for initial COD of 160 mg/l and 1000 Gpd/ft^2 flow rate is plotted. COD removal occurs throughout the ten foot

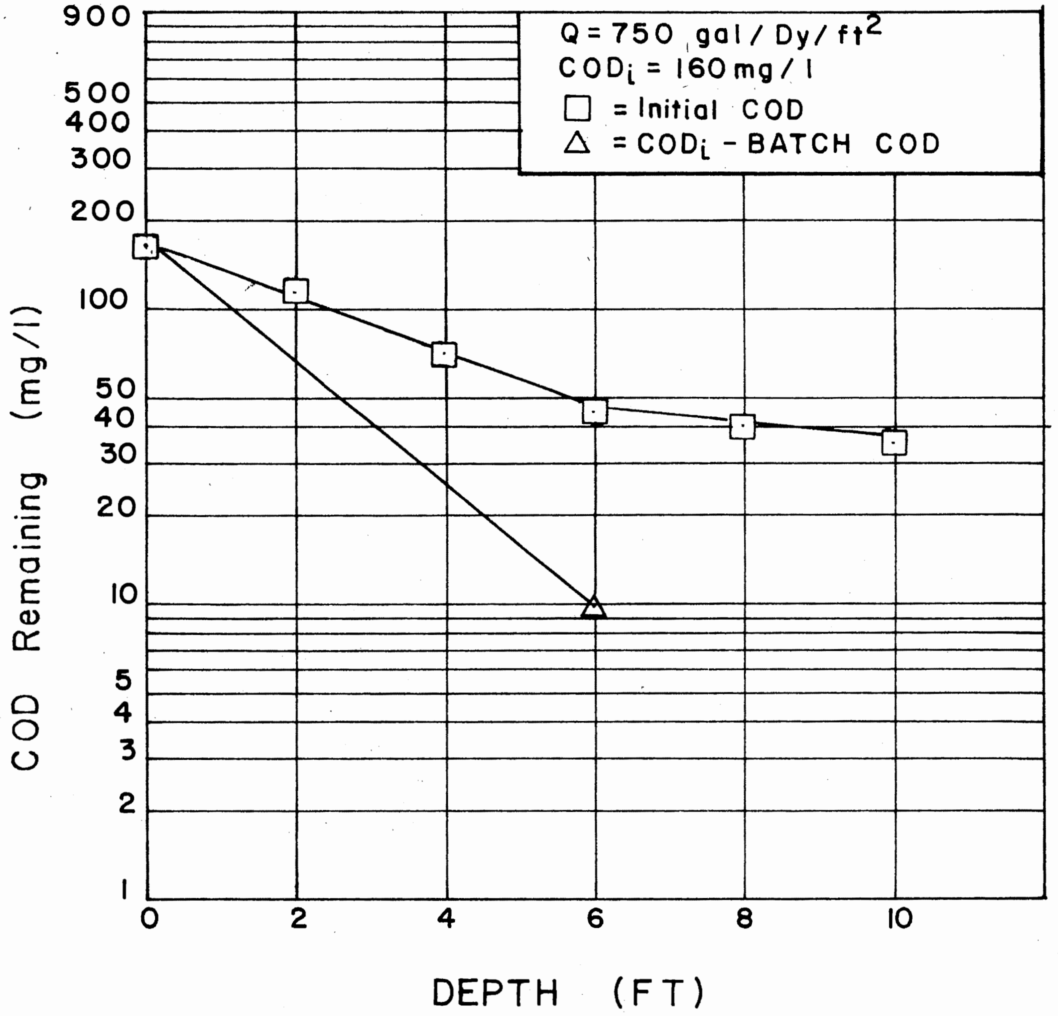

Figure 11. COD Remaining Versus Depth at Initial COD of 160 mg/l and 750 Gpd/ft^2.

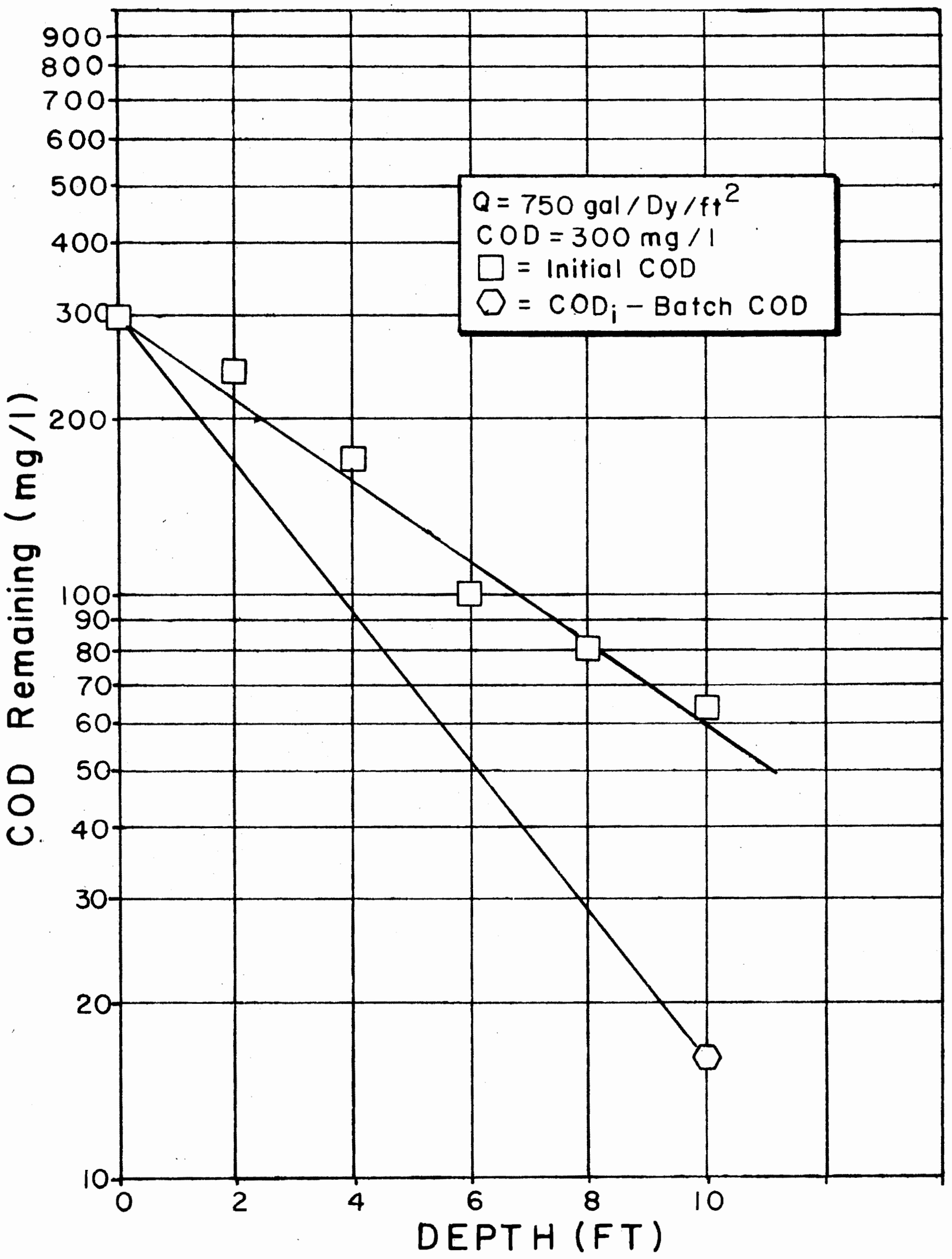

Figure 12. COD Remaining Versus Depth at Initial COD of 300 mg/l and 750 Gpd/ft^2.

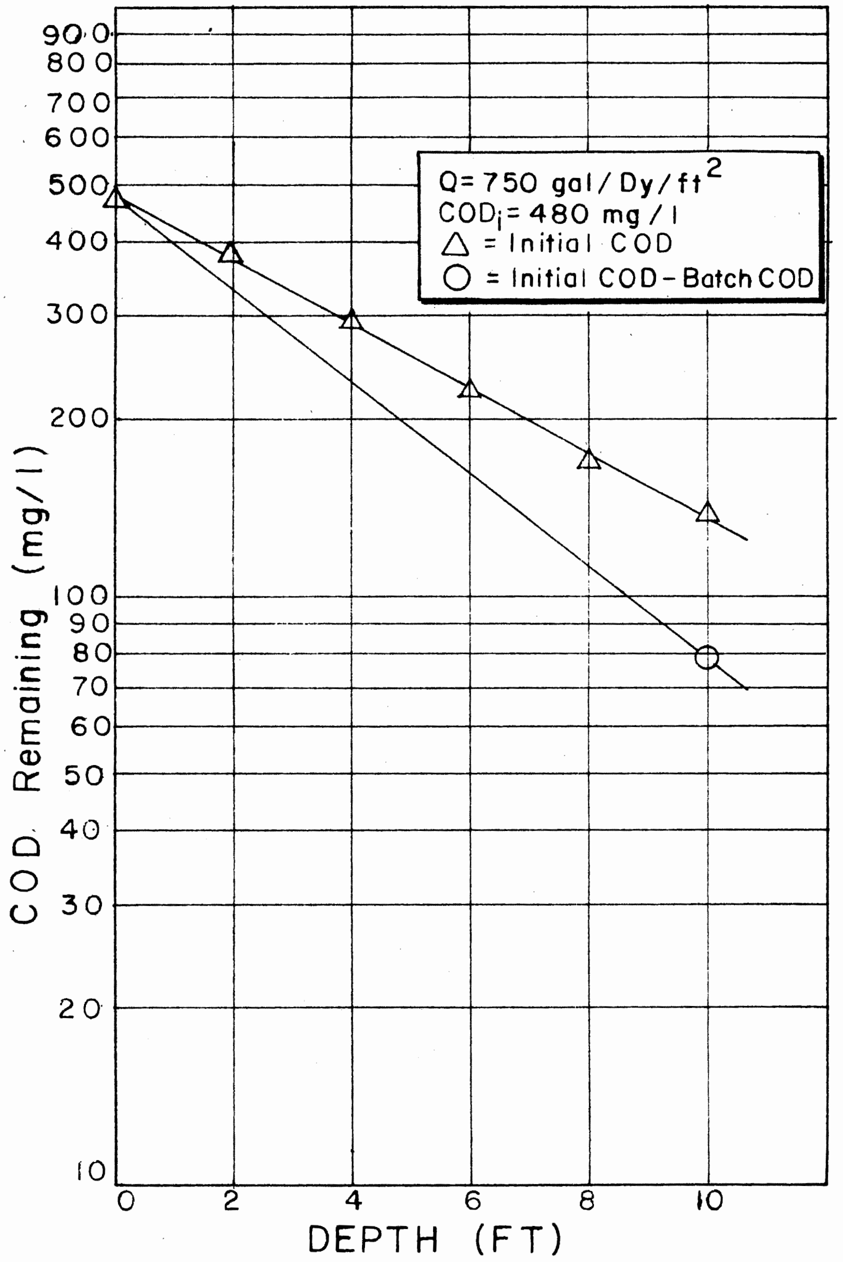

Figure 13. COD Remaining Versus Depth at Initial COD of 480 mg/l and 750 Gpd/ft^2.

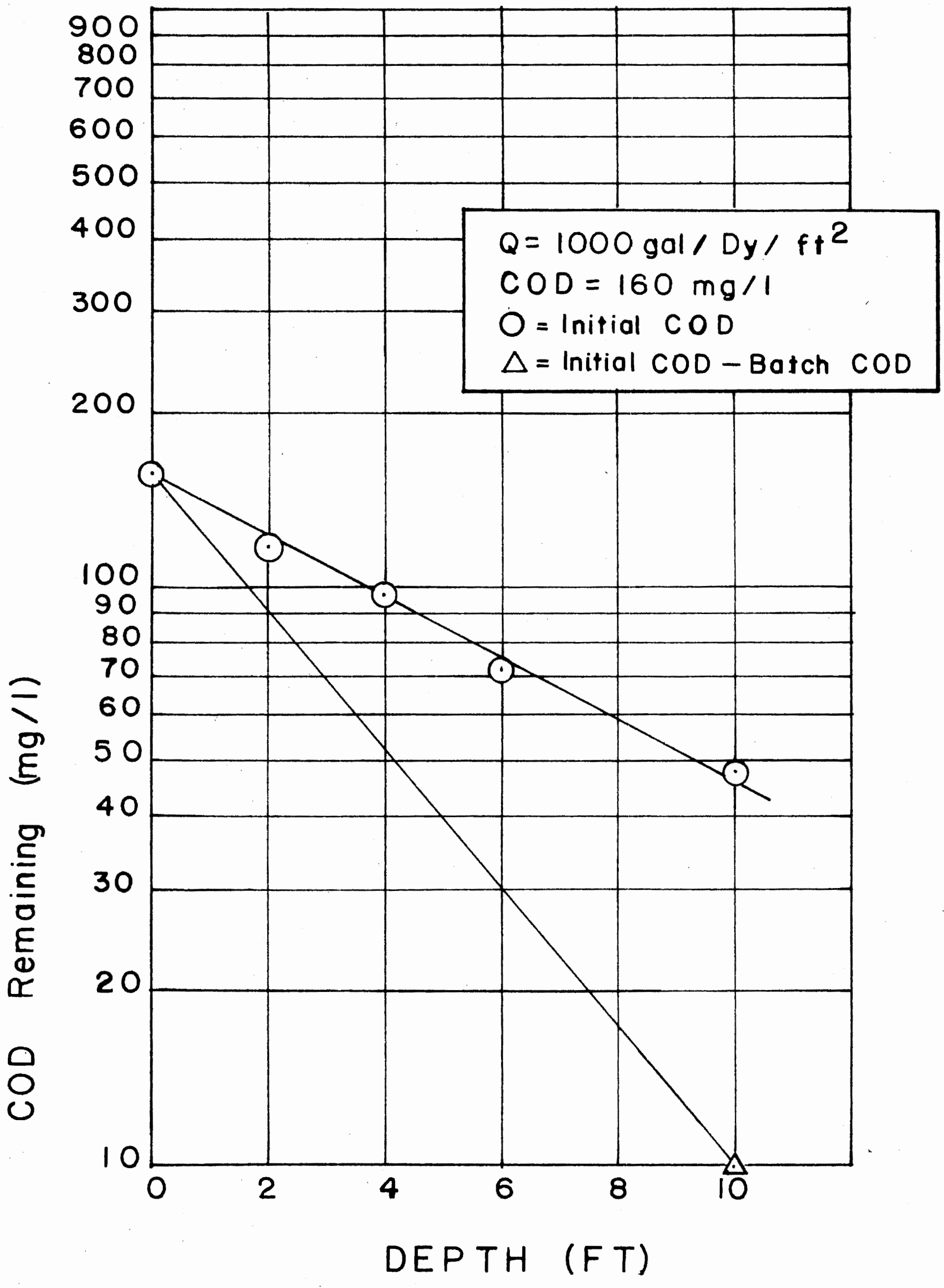

Figure 14. COD Remaining Versus Depth at Initial COD of 160 mg/l and 1000 Gpd/ft^2.

depth of the tower. The removal efficiency is 71%. The residual COD value from Figure 6 is subtracted and a new line drawn. The corrected removal efficiency is 93.7%.

Figure 15, shows the data for initial COD of 290 mg/l and flow rate of 1000 Gpd/ft^2. Removal follows first order kinetics throughout the ten foot depth. The calculated removal efficiency is 73.8%. From Figure 7, the residual COD value is taken and subtracted from the ten foot depth. A new line is drawn to the initial COD concentration of 290 mg/l. The corrected removal efficiency is 88.5%.

Removal efficiencies (COD, ΔCOD) versus total organic loadings (Lbs COD, ΔCOD/Dy/1000 ft^3) data are presented in the Appendix and Figures 16, and 17.

In Figure 16, the graph of per cent COD removed versus organic loading (Total COD) shows that at low organic loadings poor COD removal occurs. These findings correspond with other researchers (2, 3) at the Oklahoma State University Bioenvironmental Engineering Laboratories. This is due to the fact that the non-biodegradable or residual COD has not been taken into account. Even at higher organic loadings (150-250 Lbs COD/Dy/1000 ft^3) only up to 80% removals can be expected.

Figure 17, takes into account the residual COD in the system which is being produced by the microorganisms. Compared to Figure 16, the ΔCOD removal efficiencies at lower organic loadings approach 100%. Even at higher organic loadings up to 250 Lbs COD/Dy/1000 ft^3, 85% efficiencies can be obtained.

Recognizing that a residual COD does occur in either a biological tower or activated sludge process can be very helpful in determining the purification efficiency or operational parameters. Since no non-

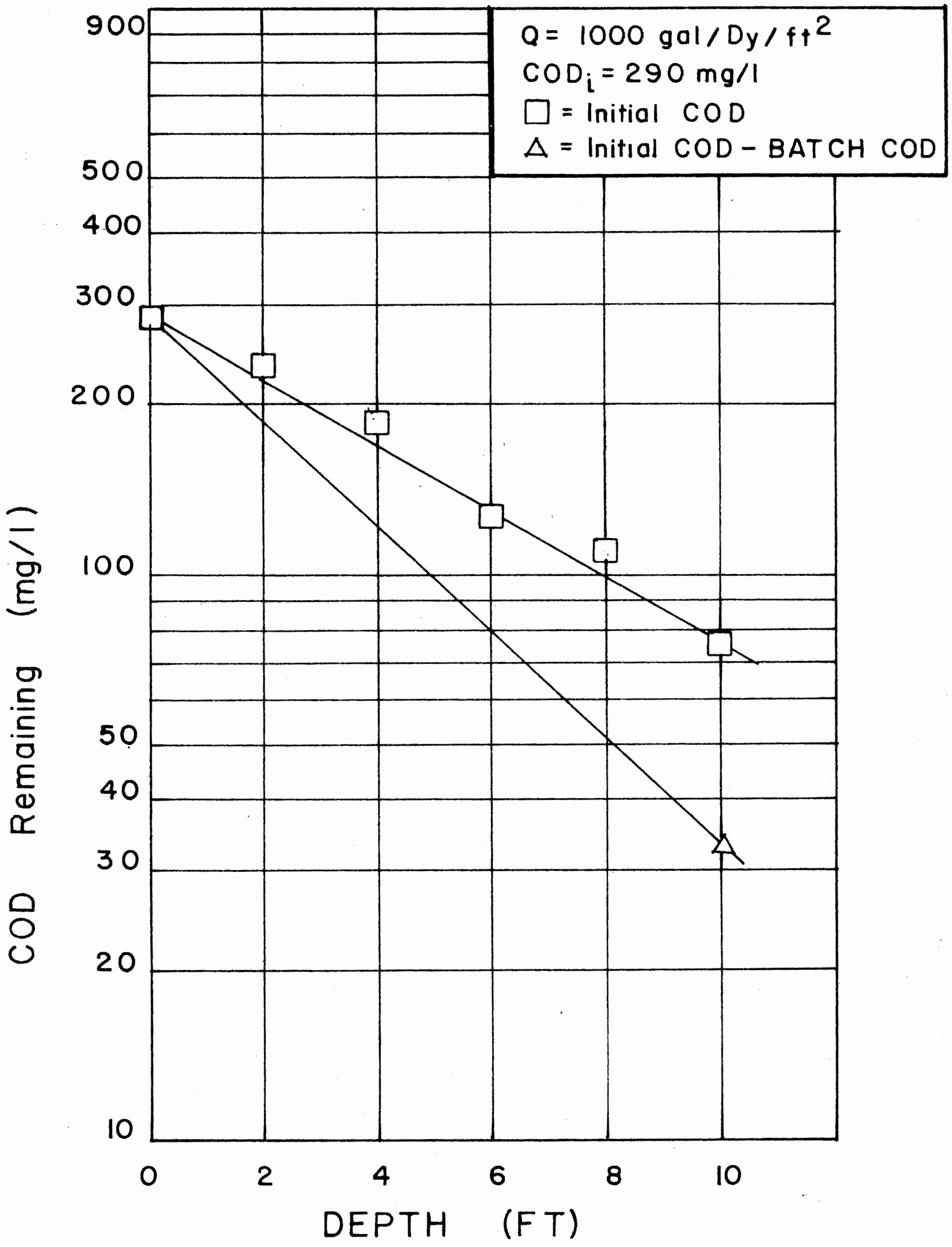

Figure 15. COD Remaining Versus Depth at Initial COD of 300 mg/l and 1000 Gpd/ft^2.

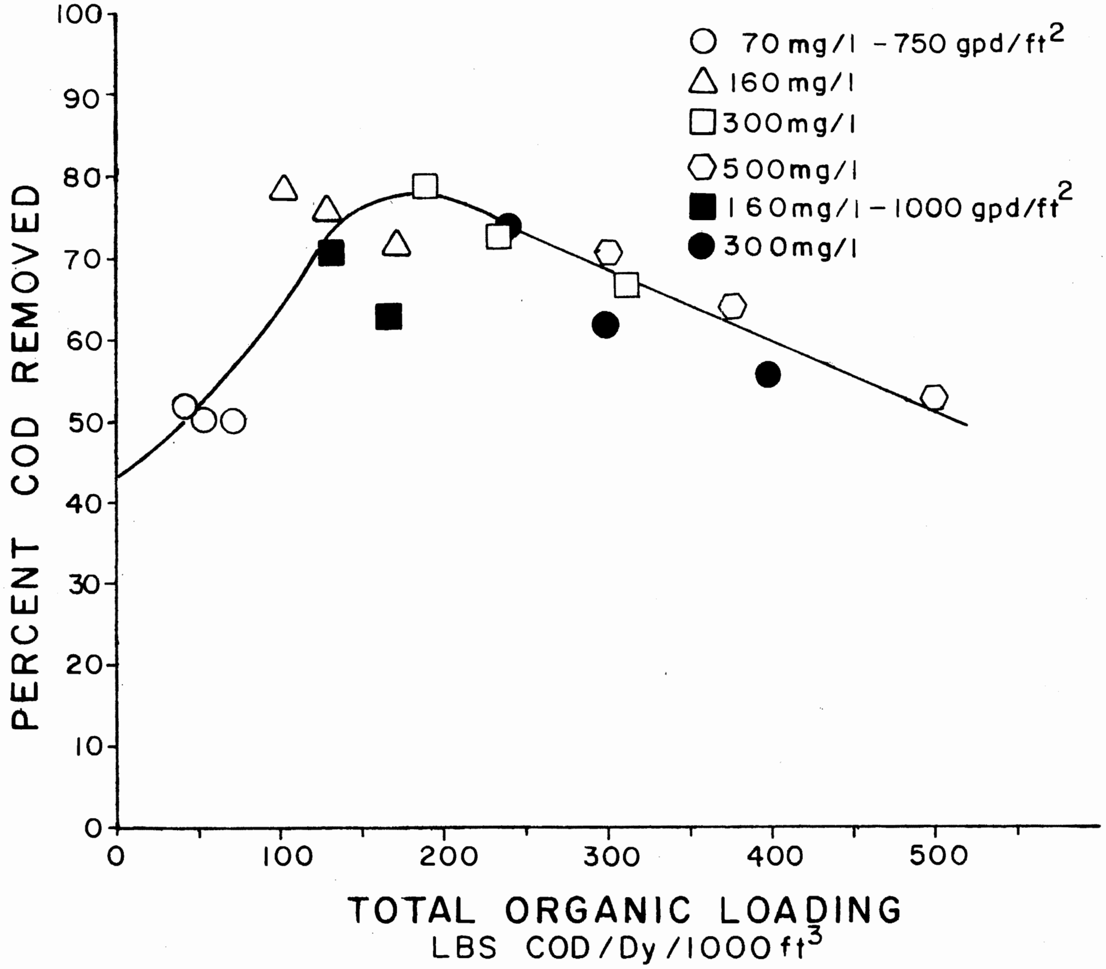

Figure 16. Per Cent COD Removed Versus Total Organic Loading (Lbs. COD/Dy/1000 ft^3).

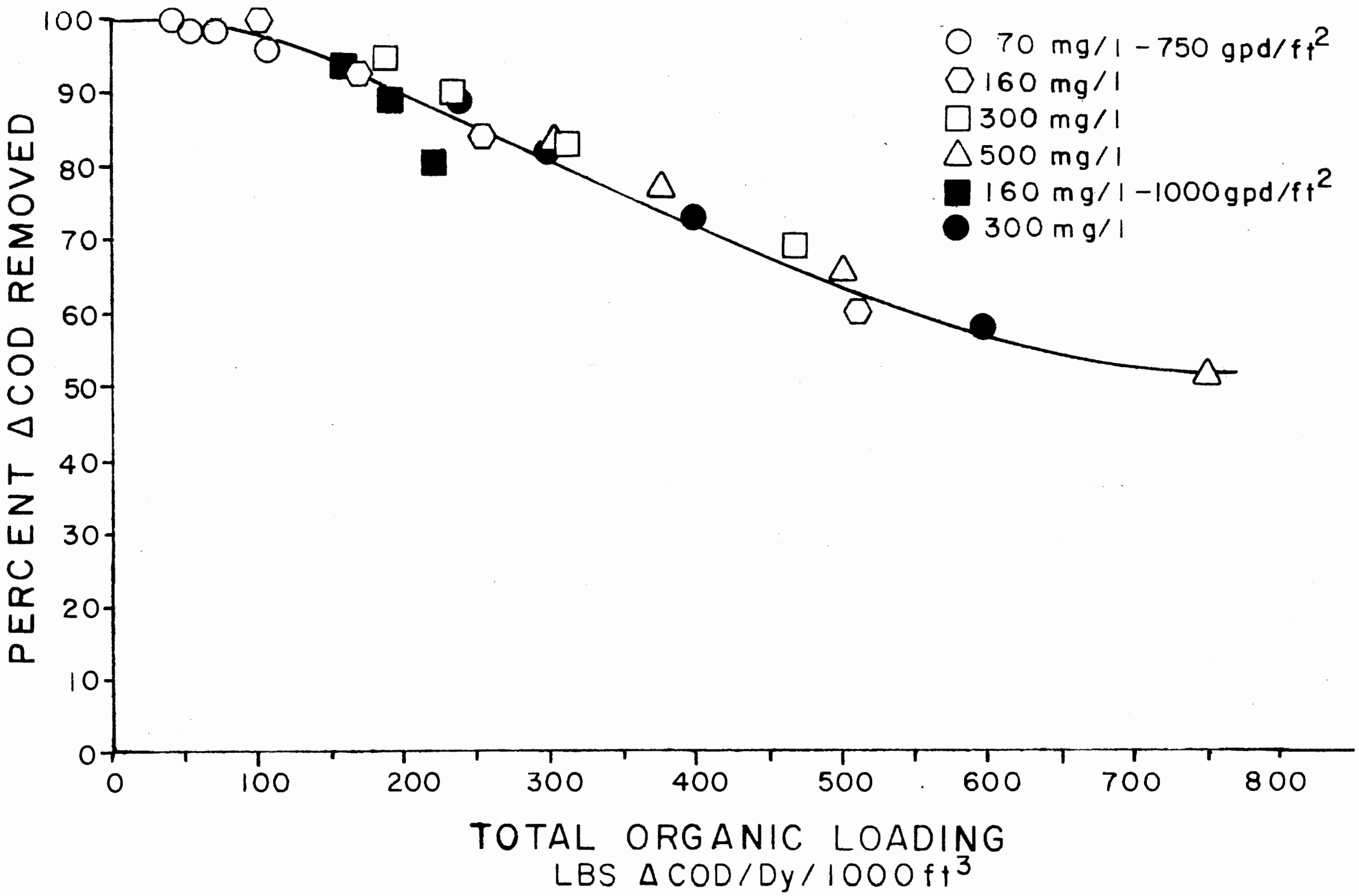

Figure 17. Per Cent ΔCOD Removed Versus Total Organic Loading (Lbs. ΔCOD/Dy/1000 ft^3).

biodegradable organics occurred in the synthetic waste, or tap water, there is only one source left and that is the microorganisms themselves.

C. Treatment Efficiency as Measured by BOD

The BOD test was used to show that as a parameter of pollutional potential or a measure of purification efficiency can no longer be justified. In every biological tower or activated sludge system there is going to be a residual or non-biodegradable portion that cannot be biologically oxidized. This non-biodegradable portion is therefore not taken into account when the BOD_5 test is used as a measure of the pollutional strength or purification efficiency of the waste.

In Figure 18, the total BOD data is plotted for an initial influent COD of 70 mg/l and flow rate of 750 Gpd/ft^2. Both Figures 10 (COD remaining) and 18 (BOD) show that removal ceases at the four foot depth. It is important to note that the total COD (35 mg/l), BOD (10 mg/l), and ΔCOD (3 mg/l) values vary. The reason this occurs is because the ΔCOD value takes into account the soluble COD plus the non-biodegradable portion that cannot be biologically oxidized, while the BOD value consists of the soluble BOD plus a solids concentration which is capable of exerting a BOD on a receiving stream after the soluble portion is gone. The total COD takes into account that the COD test can chemically oxidize certain organic compounds that microorganisms cannot.

Figure 19 shows the BOD data for initial COD of 160 mg/l and 750 Gpd/ft^2 flow rate. The BOD removal when compared to Figure 11 (COD remaining) also shows a total BOD value at the six foot depth higher (28 mg/l) than that of the ΔCOD value (10 mg/l). This is due to the

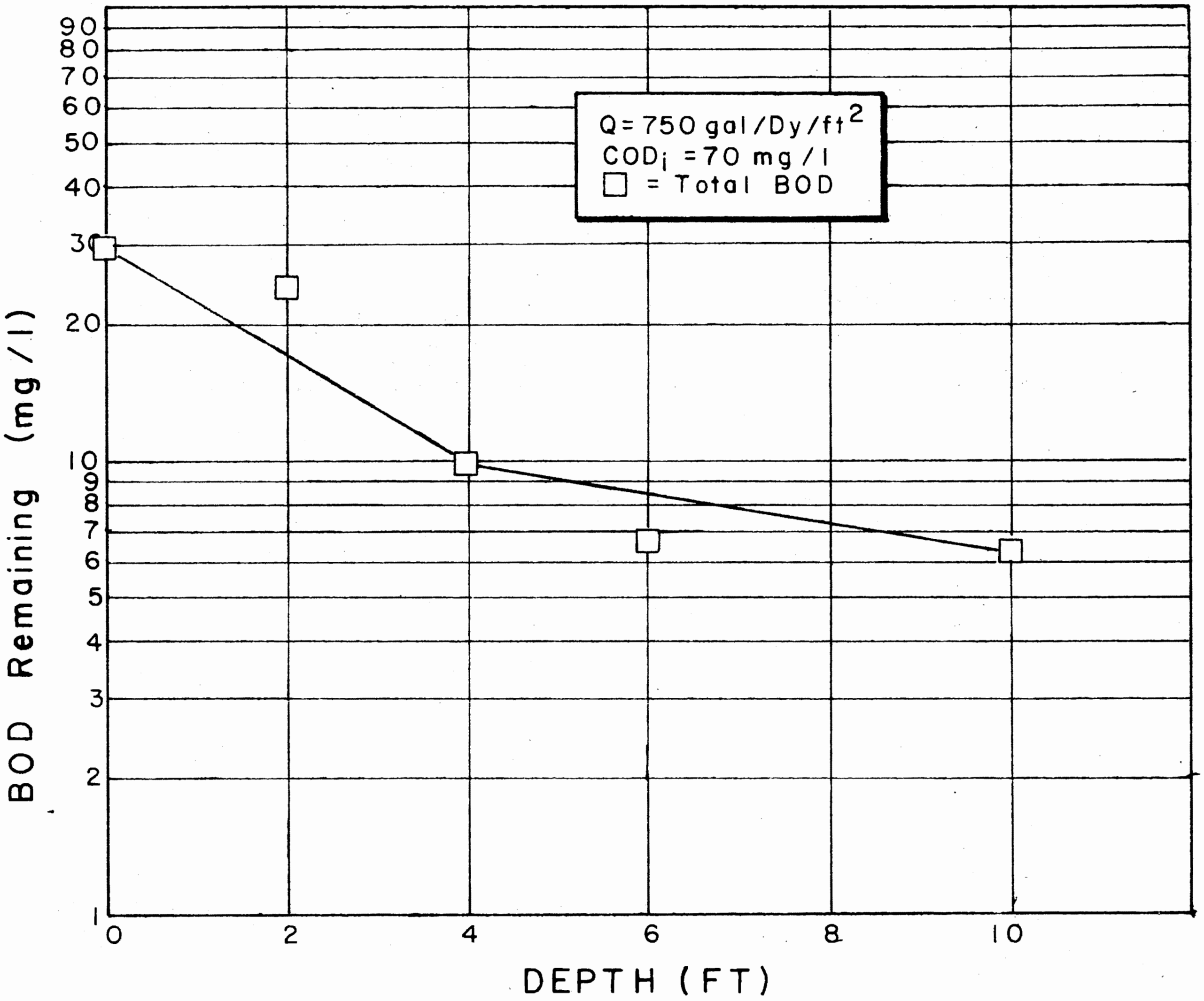

Figure 18. BOD Remaining Versus Depth at Initial COD of 70 mg/l and 750 Gpd/ft^2.

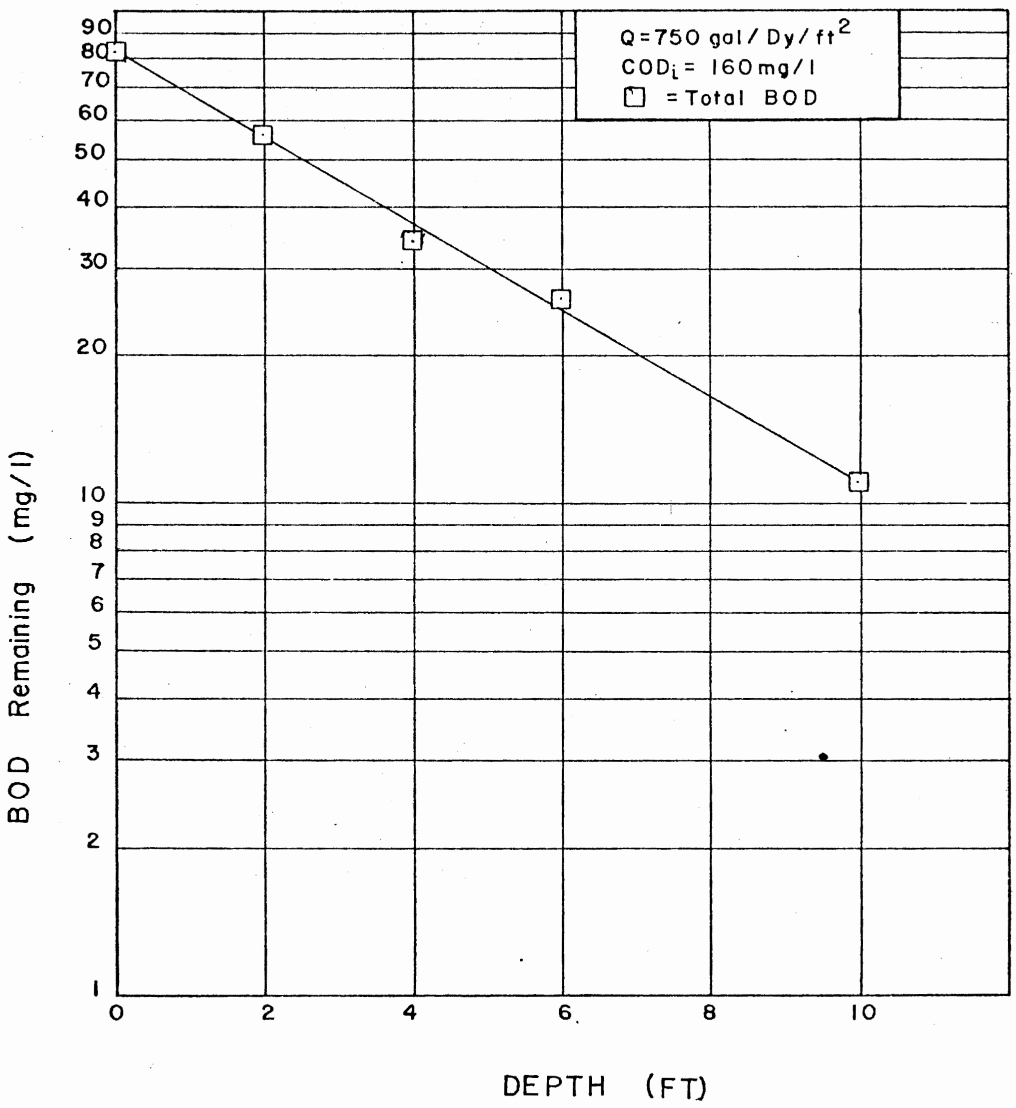

Figure 19. BOD Remaining Versus Depth at Initial COD of 160 mg/l and 750 Gpd/ft^2.

solids concentration of the BOD sample that are able to utilize the soluble organic matter first and then use themselves as a food source to carry on O_2 uptake.

In Figure 20, the data for initial COD of 300 mg/l and 750 Gpd/ft^2 flow rate is plotted. It can be seen that very little BOD was removed through the first two feet of the biological tower. This is because the influent sample is only soluble BOD that had to be seeded with a 1 ml. acclimated sample. At the two foot depth, the sample consisted of both solids and soluble BOD. Due to more solids present in the two foot depth sample the O_2 uptake kept increasing, thus after the 5-day incubation period all the soluble BOD had been utilized and the cells were into the endogenous phase. From Figure 12 it can be seen the ΔCOD value is 17 mg/l, while in Figure 20, the total BOD value at the ten foot depth is 52 mg/l. This reflects the effects of the solids concentration in the BOD sample.

Figure 21, shows the BOD remaining versus depth for initial COD of 480 mg/l and 750 Gpd/ft^2 flow rate. As in Figure 20, the same type of graph is encountered. The influent BOD gives a correct value for the soluble BOD portion, while the two foot depth value is higher because the solids concentration is greater. Comparing Figures 13 and 20, it can be seen that the total COD and total BOD ten foot depth values are extremely close. This is caused by the higher organic loadings applied to the biological tower. Even when the ΔCOD and BOD values are compared the non-biodegradable portion does not show up as being a significant amount as it does in the lower organic loadings.

In Figure 22, the BOD data found in the appendix is plotted for an initial COD of 160 mg/l and flow rate of 1000 Gpd/ft^2. At the ten

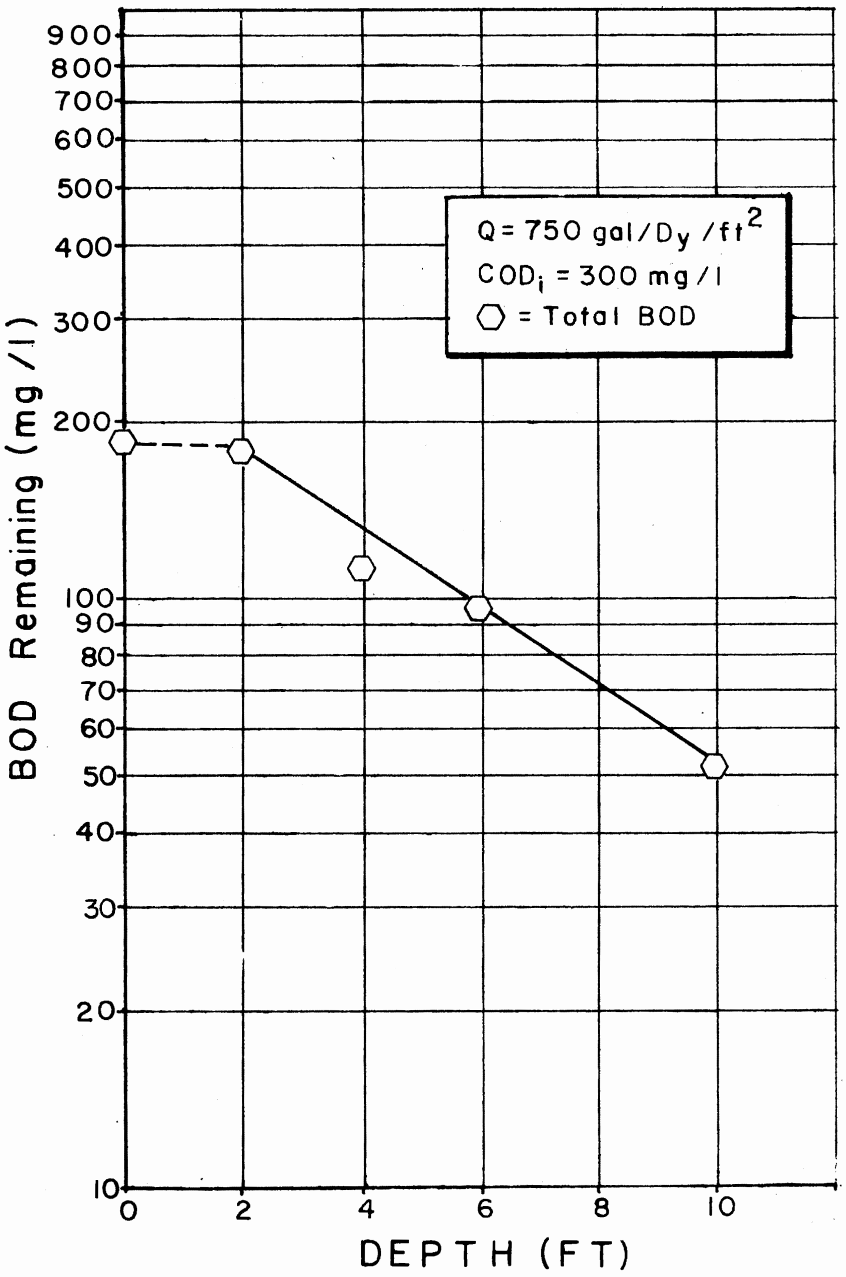

Figure 20. BOD Remaining Versus Depth of Initial COD of 300 mg/l and 750 Gpd/ft^2.

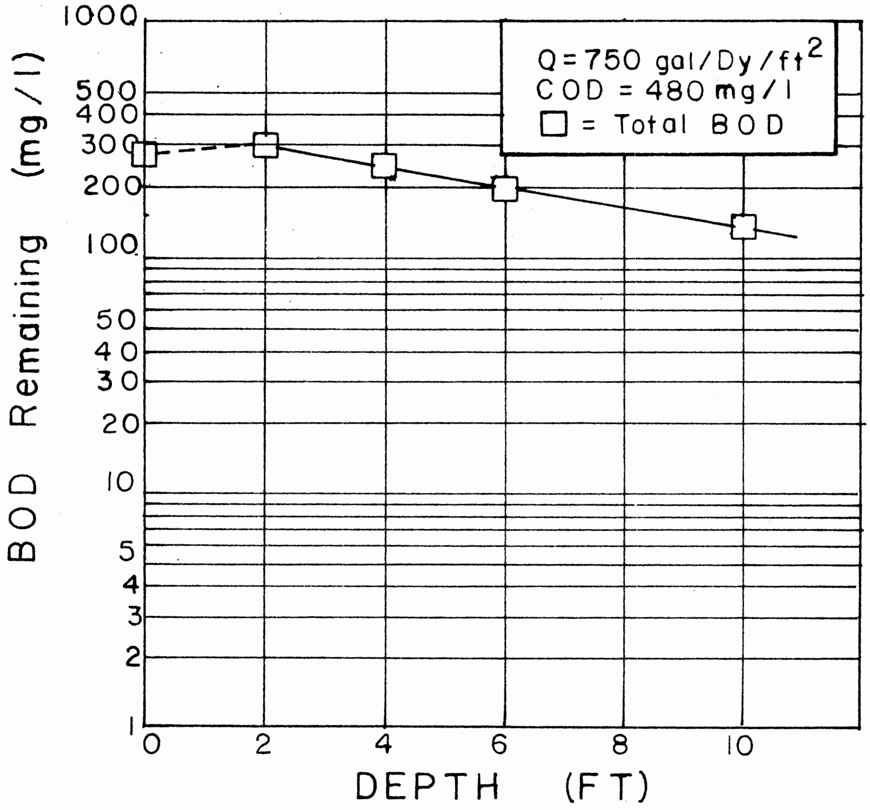

Figure 21. BOD Remaining Versus Depth at Initial COD of 480 mg/l and 750 Gpd/ft^2.

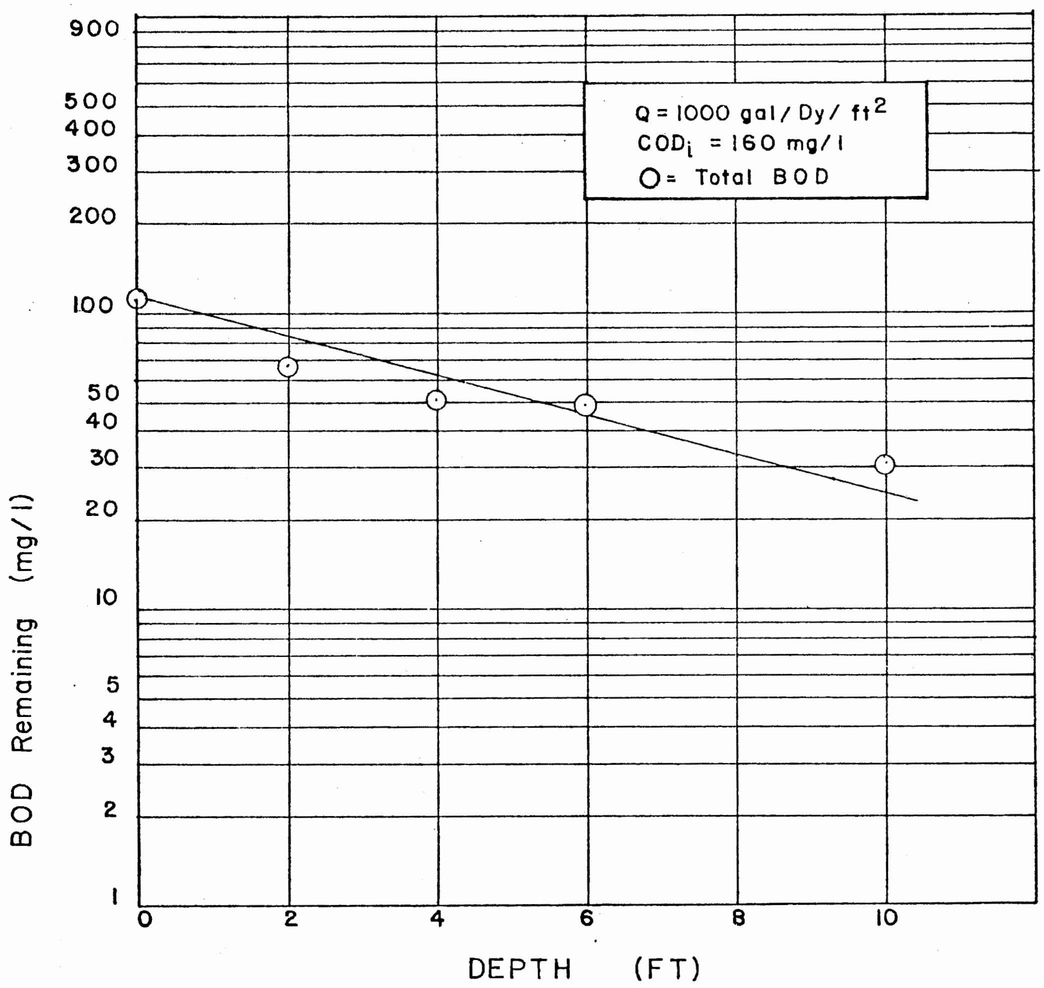

Figure 22. BOD Remaining Versus Depth at Initial COD at 160 mg/l and 1000 Gpd/ft^2.

foot depth the BOD value is 30 mg/l. When compared to the ΔCOD value of 10 mg/l in Figure 14, it is evident that at lower organic loadings the non-biodegradable portion has a significant impact on the results.

Figure 23, shows the BOD remaining versus depth for initial COD of 290 mg/l and 1000 Gpd/ft^2 flow rate. The total BOD at the ten foot depth is 80 mg/l. When compared to the ΔCOD value of 33 mg/l in Figure 15, the difference due to the non-biodegradable organics being produced by the microorganisms and the solids concentration in the BOD samples.

In Figure 24, the per cent BOD removed versus total organic loading (Lbs Total BOD/Dy/1000 ft^3) is expressed. When using total BOD as an efficiency parameter it can be seen that 90% removal can never be achieved. This is due to the non-biodegradable organics that are produced by the microorganisms in either activated sludge or biological tower treatment system. If compared to Figure 17 (% ΔCOD removed versus organic loading) which takes into account the non-biodegradable portion, efficiencies over 90% can be achieved at organic loadings up to 250 Lbs COD/Dy/1000 ft^3. If the soluble BOD portion was examined without solids interference this would give a better understanding of what is available for microbial utilization.

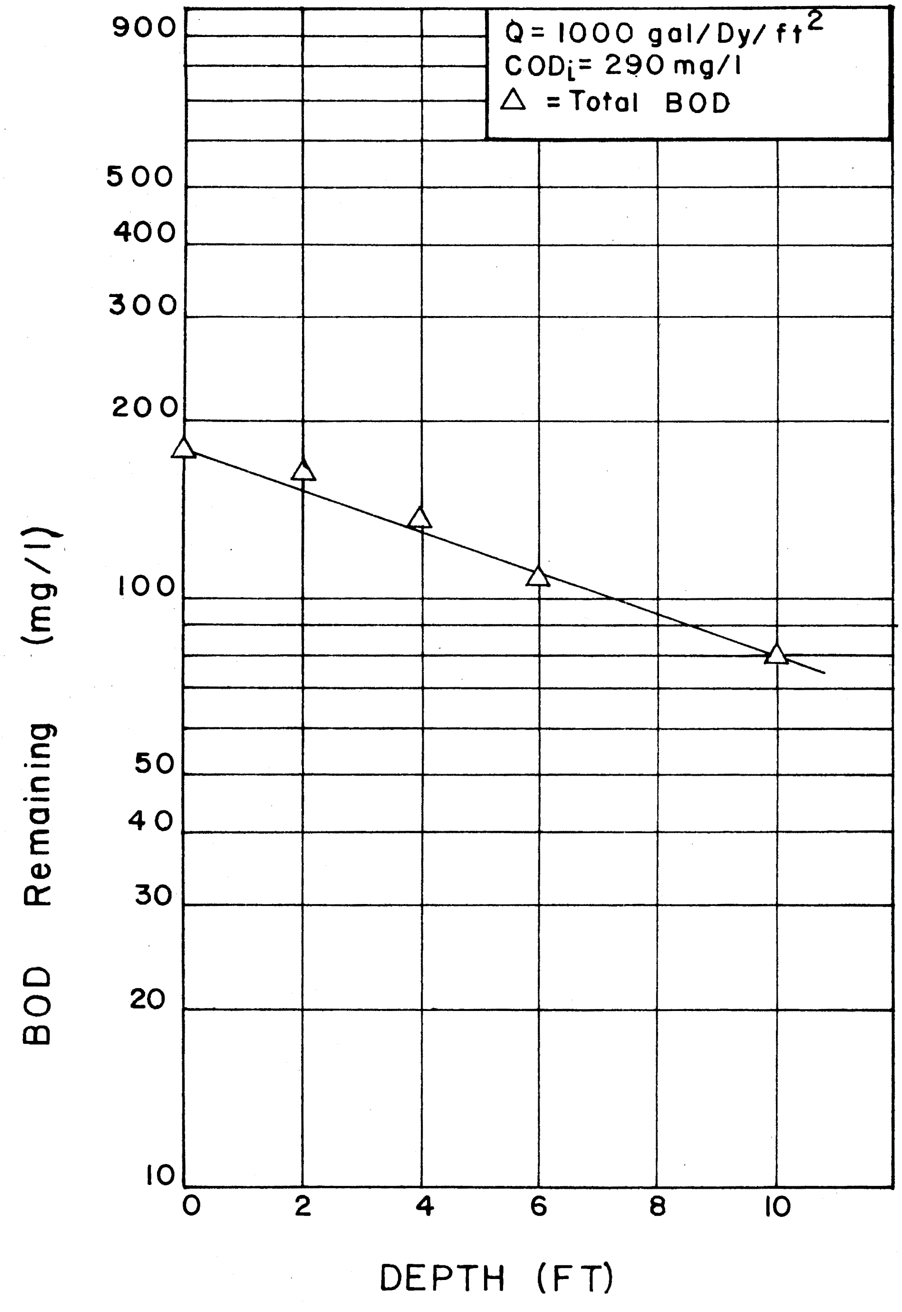

Figure 23. BOD Remaining Versus Depth at Initial COD of 300 mg/l and 1000 Gpd/ft^2.

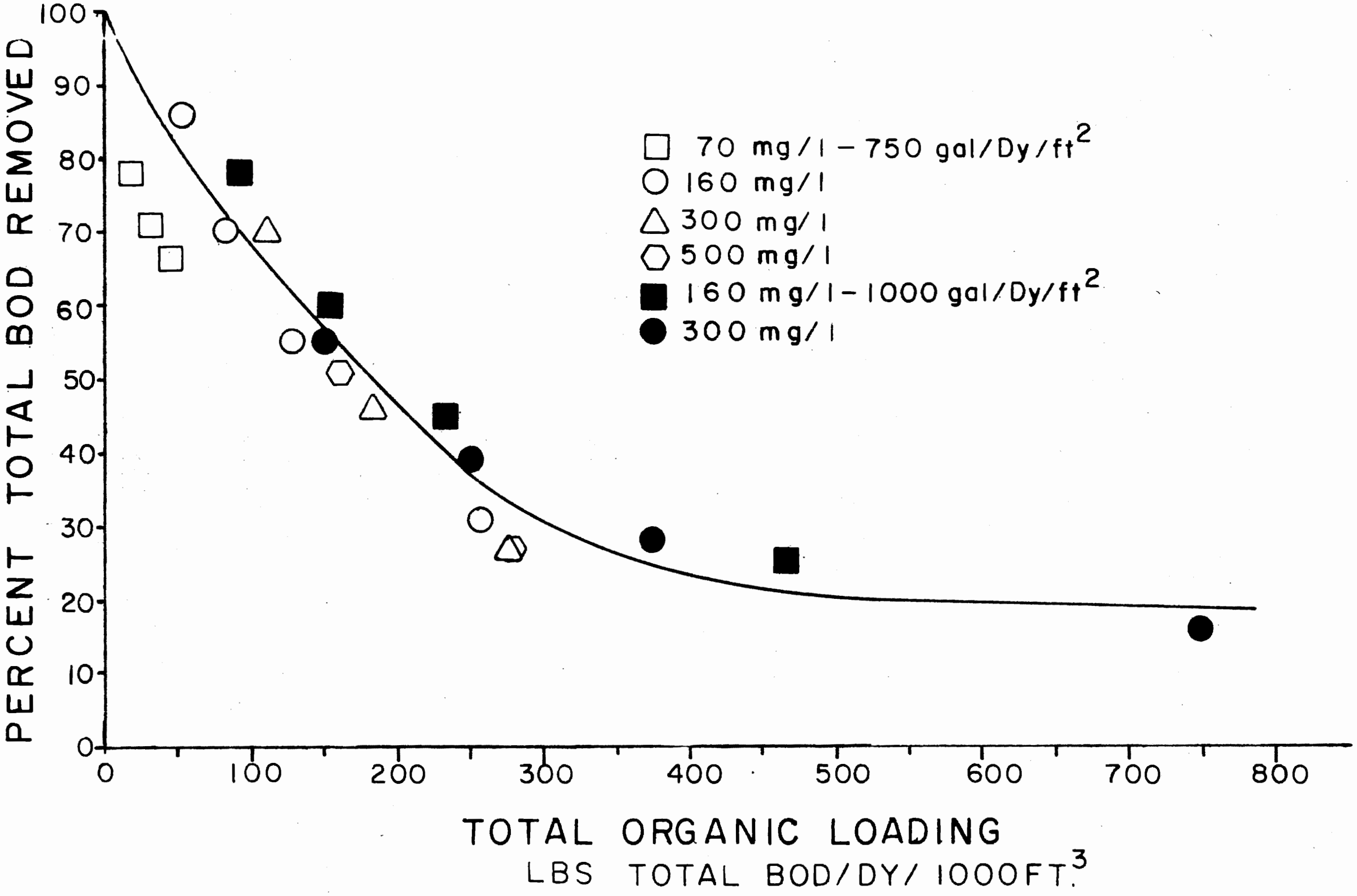

Figure 24. Per Cent BOD Removed Versus Total Organic Loading (Lbs. Total BOD/Dy/1000 ft^3).

CHAPTER V

DISCUSSION

The primary purpose of this investigation was to determine the point source of non-biodegradable organics. Various researchers (2, 3, 23) found that a residual did exist, but could not pinpoint the exact source. Possibilities for non-biodegradable organics include the synthetic waste, tap water, or microbial by-products. COD analysis were conducted on the synthetic waste minus the carbon source (sucrose) and tap water. Neither the synthetic waste nor tap water COD's proved to be significant, therefore microbial by-products exist as the source of non-biodegradable organics.

Figures 8 and 9 show that as a function of initial COD or total organic loadings (Lbs COD/Dy/1000 ft^3) the production of non-biodegradable organics increase as initial COD and organic loadings increase.

To prove that the residual COD is non-biodegradable the effluent was aerated in a batch unit for three to five days, and the BOD_5 test was used to show that the BOD_5 was much lower than the total COD, except at the higher organic loadings because the residual does not show up as significant as it does in the lower organic loading ranges.

By determining the residual COD comes from microbial by-products this allows the designer to predict better efficiencies at lower organic loadings ($<$ 100 Lbs COD/Dy/1000 ft^2). In Figures 16, and 17 the per cent removals versus organic loadings are plotted. Figure 16 shows that by using total COD the efficiencies at low loadings never get over 50% removal. This is because the non-biodegradable portion has not been subtracted out. In Figure 17, this residual COD has been accounted for removal efficiencies between 90-100% can be achieved up to organic loadings of 250 Lbs COD/Dy/1000 ft^3.

The use of ΔCOD over COD has been defended by several researchers (1, 4, 5, 6, 7, 8). Knowing the residual COD in a treatment system can be of great value in evaluating the DO exerted upon a receiving stream. Since the residual COD may eventually be degraded over an extended period of time, there is no immediate DO uptake that would harm the aquatic environment.

It's a well known fact that BOD_5 is used as a stream standard to estimate the amount of oxygen that will be used because of the presence of the organic matter, and not measuring the amount of metabolizable organic matter in the waste. The BOD_5 principle only deals with the potential depletion of the DO in the receiving stream, and because it measures a colligative effect of that organic matter in a waste water which is readily available as organic carbon source to microorganisms without requiring determination of either the total amount or types of that organic matter.

If soluble BOD_5 tests were run then the exact amount of soluble organic matter present can be determined. In 1952, Garrett and Sawyer (18) studied the removal of soluble BOD and reported that at high BOD concentrations the rate of growth is constant and at low concentrations the rate of growth is directly proportional to the remaining soluble BOD.

Using total BOD_5 measures not only the soluble BOD but the settled solids. The soluble BOD cannot be determined because the solids concentrations are varying and exerting a BOD of their own.

In Figures 20, and 21 a good example of soluble influent and soluble BOD plus solids at the two foot depth show the effects that solids have on a BOD_5 test. The influent BOD_5 measures the exact amount of soluble BOD that can exert DO depletion upon a receiving stream, while at the two foot depth this value measures the soluble BOD portion plus the solids concentration can exert an O_2 uptake after all the soluble BOD has been utilized.

CHAPTER VI

CONCLUSIONS

Based upon the results of this investigation, the following conclusions are made.

1. Non-biodegradable organics are produced by the microorganisms as the waste water organics are being utilized for microbial systems.

2. Residual COD - using the COD concept, gives improved efficiencies and a better overall view of the treatment process.

3. Total BOD_5 is not a good measure of treatment efficiencies or the pollutional potential of a waste water.

CHAPTER VII

SUGGESTIONS FOR FUTURE STUDY

Based on the findings of this study, the following suggestions are made for future studies involving single or multi-stage plastic media trickling filters.

1. Conduct soluble BOD test to determine what fraction of the sample is utilized by microorganisms as food.

2. Experimental testing to find the amount of solids being produced within the tower.

BIBLIOGRAPHY

1. Kincannon, D. F., and Gaudy, A. F. Jr., "Functional Design of Aerobic Biological Waste Water Treatment Processes." Class Notes, M-3, (Jan. 1977).

2. Bentley, T. L., "Application and Comparison of Activated Sludge Design and Operational Control Parameters to an Experimental Fixed-Bed Reactor." M.S. Thesis, Oklahoma State University (1974).

3. Marcangeli, G. E., "Study on the Performance of an Experimental Two-Stage Trickling Filter Employing a Plastic Medium." M.S. Thesis, Oklahoma State University (1973).

4. Gaudy, A. F. Jr., and Gaudy, Elizabeth T., "ΔCOD Gets Nod Over BOD Test." Industrial Water Engineering, 9, No. 5, 30-34 (1972).

5. Gaudy, A. F. Jr., and Gaudy, Elizabeth T., "Biological Concepts for Design and Operation of the Activated Sludge Process." Project Report for the Water Quality Office, Environmental Protection Agency (Sept. 1971).

6. Gaudy, A. F. Jr., "Biochemical Oxygen Demand." Water Pollution Microbiology, Chapter 13, 305-332, John Wiley & Sons (1972).

7. Symons, J. M., McKinney, R. E., and Hassis, H. H., "A Procedure for Determination of the Biological Treatability of Industrial Waste." Jour. Water Pollution Control Federation, 32, 841-852 (1960).

8. Hiser, L. L., and Busch, A. W., "An 8-Hour Biological Oxygen Demand Test Using Mass Culture Aeration and COD." Jour. Water Pollution Control Federation, 36, 505-516 (1964).

9. Grady. L. Jr., and Busch, A. W., "BOD Progression in Soluble Substances, VI, Cell Recovery Techniques in the T_bOD Test." Proceedings, 18th Industrial Waste Conference, Purdue University, Lafayette, Indiana (1963).

10. Busch, A. W., "BOD Progression in Soluble Substrates, I." Sewage and Industrial Waste, 30, 11, 1336 (Nov. 1958).

11. Myrick, N., and Busch, A. W., "BOD Progression in Soluble Substrates, II. The Selective Stimulation of Respiration in Mixed Cultures of Bacteria and Protozoa." Proceedings, 14th Industrial Waste Conference, Purdue University, Lafayette, Indiana, Ext. Ser., 104 (1960).

12. Busch, A. W., and Myrick, N., "BOD Progression in Soluble Substrates, III. Short Term BOD and Bio-Oxidation Solids Production." Proceedings, Indiana, Ext. Ser., 106, 19 (1961).

13. Hoover, S. R., Jasewicz, L., and Porges, N., "An Interpretation of the BOD Test in Terms of Endogenous Respiration of Bacteria." Jour. Water Pollution Control Federation., 23, 10, 1163 (Oct., 1953).

14. Sorrels, J. H., and Zeller, P.J.A., "Sewage Purification by Rock Filters-Removal of Oxygen Demand of Soluble Organic Material." Sewage and Industrial Wastes, 25, 779-786 (1953).

15. Deen, T. R., "Some Effects of Organic and Hydraulic Loadings on a Fixed-Bed Reactor," M.S. Thesis, Oklahoma State University, Stillwater, Oklahoma (1969).

16. Ingram, W. T., "An Investigation of the Mechanisms of Controlled Filtration." Sewage and Industrial Wastes, 31, 1147-1158 (1959).

17. Richard, J. G., and Kingsburg, R. P., "Treating Milk Waste by Biological Oxidation with Plastic Media." Proceedings, 24th Annual Oklahoma Industrial Waste and Advanced Water Conference, Oklahoma State University, Stillwater, Oklahoma (1973).

18. Garrett, M. T., and Sawyer, C. N., "Kinetics of Removal of Soluble BOD by Activated Sludge." Proceedings, 7th Industrial Waste Conference, Purdue University, Lafayette, Indiana, Ext. Ser., 79, 51-77 (1952).

19. Stack, V. T., Jr., "Theoretical Performance of the Trickling Filtration Process." Sewage and Industrial Waste, 29, 9, 987 (Sept. 1957).

20. Velz, C. J., "A Basic Law for the Performance of Biological Filters." Sewage Works Journal, 20, 4, 607 (1948).

21. Chipperfield, P.N.J., "Performance of Plastic Filter Media in Industrial and Domestic Waste Treatment." Jour. Water Pollution Control Federation, 39, 11, 1860-1873 (1967).

22. Standard Methods for the Examination of Water and Wastewater, 14th ed., American Public Health Association (New York, 1975).

23. Elrod, H. A., "The Effects of Temperature and Varying Substrate Concentrations on Biological Towers." M.S. Thesis, Oklahoma State University (1976).

24. Technical Bulletin, Ethyl Corporation, Environmental Control Div., Baton Rouge, La.

APPENDIX A

RAW DATA OF BIOLOGICAL TOWERS EXPERIMENT

TABLE II

COD REMAINING AT VARIOUS DEPTHS

Si(mg/l)	FLOW	DEPTH = 0	2	4	6	8	10
70	750 gpd/ft^2	68	52	36	34	34	32
160	750 gpd/ft^2	163	115	70	45	40	35
300	750 gpd/ft^2	299	239	167	100	80	63
480	750 gpd/ft^2	480	386	298	225	171	139
160	1000 gpd/ft^2	159	117	97	72	59	46
290	1000 gpd/ft^2	286	234	186	126	110	75

Convert to Lbs. COD/DY/1000 ft^3

TABLE III

ΔCOD REMAINING AT VARIOUS DEPTHS

Si(mg/l)	FLOW	DEPTH = 0	2	4	6	8	10
70	750 gpd/ft^2	68	35.5	3	1	1	0
160	750 gpd/ft^2	163	66	25.5	10	0	0
300	750 gpd/ft^2	299	166	93	51.5	28.5	16
480	750 gpd/ft^2	480	334	231	162	112	79
160	1000 gpd/ft^2	159	90	52	30	17.5	10
290	1000 gpd/ft^2	286	185	120	78	51	33

Convert to Lbs. ΔCOD/DY/1000 ft^3

TABLE IV

TOTAL BOD REMAINING AT VARIOUS DEPTHS

Si(mg/l)	FLOW	DEPTH = 0	2	4	6	10
70	750 gpd/ft^2	29.4	18	9.8	8.5	6.3
160	750 gpd/ft^2	82	56	36.5	24.5	11
300	750 gpd/ft^2	178	177	130	96	54
480	750 gpd/ft^2	270	297	243	198	132
160	1000 gpd/ft^2	112	84	61	45	24.5
290	1000 gpd/ft^2	180	152	130	110	80

Convert to Lbs. Total BOD/DY/1000 ft^3

APPENDIX B

DATA CONVERTED TO LBS COD (ΔCOD, BOD/DY/1000 FT^3)

TABLE V

LBS. COD/DY/1000 FT.^{3} VERSUS PER CENT COD REMOVED

Si (mg/l)	FLOW (gpd/ft.^{2})	DEPTH (ft.)	$\frac{\text{LBS. COD}}{\text{DY/1000 ft.}^3}$	% COD REMOVED
68	750	2	212.67	23.5
		4	106.34	47.0
		6	70.89	50.0
		8	53.17	50.0
		10	42.53	52.9
160	750	2	509.78	29.4
		4	254.89	57.0
		6	169.93	72.4
		8	127.45	75.5
		10	101.96	78.5
300	750	2	935.12	20.0
		4	467.56	44.1
		6	311.71	66.6
		8	233.78	73.2
		10	187.02	79.0

TABLE V (continued)

Si (mg/l)	FLOW (gpd/ft.^{2})	DEPTH (ft.)	$\frac{\text{LBS. COD}}{\text{DY/1000 ft.}^3}$	% COD REMOVED
480	750	2	1501.20	19.6
		4	750.60	37.9
		6	500.40	53.1
		8	375.30	64.0
		10	300.20	71.0
160	1000	2	663.03	26.4
		4	331.52	39.0
		6	221.01	54.7
		8	165.76	63.0
		10	132.61	71.0
290	1000	2	1192.62	18.2
		4	596.31	35.0
		6	397.54	56.0
		8	298.16	61.5
		10	238.52	73.8

TABLE VI

LBS. ΔCOD/DY/1000 FT.^{3} VERSUS PER CENT ΔCOD REMOVED

Si (mg/l)	FLOW (gpd/ft.^{2})	DEPTH (ft.)	$\frac{\text{LBS. ΔCOD}}{\text{DY/1000 ft.}^3}$	% ΔCOD REMOVED
68	750	2	212.67	48.0
		4	106.34	96.0
		6	70.89	98.5
		8	53.17	98.5
		10	42.53	100.0
160	750	2	509.78	59.6
		4	254.89	84.1
		6	169.93	93.9
		8	127.45	100.0
		10	101.96	100.0
300	750	2	935.12	44.5
		4	467.56	68.9
		6	311.71	82.8
		8	233.78	90.4
		10	187.02	94.6

TABLE VI (continued)

Si (mg/l)	FLOW (gpd/ft.^{2})	DEPTH (ft.)	$\frac{\text{LBS. }\Delta\text{COD}}{\text{DY/1000 ft.}^3}$	% ΔCOD REMOVED
480	750	2	1501.20	30.4
		4	750.50	51.9
		6	500.40	66.3
		8	375.30	76.7
		10	300.20	83.5
160	1000	2	663.03	43.4
		4	331.52	67.3
		6	221.01	81.1
		8	165.76	89.0
		10	132.61	93.7
290	1000	2	1192.62	35.3
		4	596.31	58.0
		6	392.54	72.7
		8	298.16	82.2
		10	238.52	88.5

TABLE VII

LBS. TOTAL BOD/DY/1000 FT.^{3} VERSUS PER CENT BOD REMOVED

Si (mg/l)	FLOW (gpd/ft.^{2})	DEPTH (ft.)	$\frac{\text{LBS. BOD}}{\text{DY/1000 ft.}^3}$	% BOD REMOVED
29.4	750	2	91.95	38.7
		4	45.97	66.5
		6	30.65	71.1
		10	18.39	78.6
82	750	2	256.50	31.7
		4	128.23	55.5
		6	84.41	70.1
		10	51.24	86.6
178	750	2	556.70	0.10
		4	278.35	24.9
		6	185.57	46.1
		10	111.34	69.7

TABLE VII (continued)

TABLE VII (continued)

Si (mg/l)	FLOW (gpd/ft.^{2})	DEPTH (ft.)	LBS. BOD / DY/1000 ft.^{3}	% BOD REMOVED
270	750	2	844.43	-0.10
		4	422.21	10.0
		6	281.48	26.7
		10	168.89	51.1
112	1000	2	467.04	25.1
		4	233.52	45.5
		6	155.68	59.8
		10	93.41	78.1
180	1000	2	750.60	15.5
		4	375.30	27.8
		6	250.20	38.9
		10	150.12	55.6

2

VITA

Joe Bob Cravens

Candidate for the Degree of

Master of Science

Thesis: THE EFFECTS OF RESIDUAL NON-BIODEGRADABLE ORGANICS ON THE TREATMENT EFFICIENCY IN THE BIOLOGICAL TOWERS

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